# Synthesis and Characterization of Tetra- and Penta-dentate Schiff Base Complexes for Application in Actinide Sensing

by

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## Abstract

The advent of the nuclear power era has the potential to provide inexpensive, plentiful electricity with reduced carbon emissions, but these benefits are offset by concerns about the potential environmental effects of a waste spill or contamination event. Further exploration into the fundamental actinide and lanthanide coordination chemistry could provide knowledge that can be applied to nuclear waste detection and remediation. A fruitful method that has been employed to sequester and identify actinides, especially in selective sequestration even in the presence of lanthanides, has been to incorporate softer nitrogen donor atoms and pair them with phenolate donors. Here, the systematic characterization by X-ray crystallography and UV-visible spectroscopy of a salphenazine ligand ($\mathbf{H_2L^I}$), containing the O-N-N-O salen type bonding motif, and corresponding metal complexes revealed the extended π-conjugation of these ligands results in differentiation of a uranyl signal as compared to these transition metal contaminants. A series of new pentadentate binding ligands ($\mathbf{H_2L^{III}}$-$\mathbf{H_2L^{VI}}$), which fully occupy the uranyl equatorial plane, removed the necessity of a coordinating solvent molecule or ligand rearrangement allowing to quickly and selectively bind uranyl in a one to one fashion. To further explore the *f*-element coordination chemistry with salen-type ligands, eleven lanthanide double decker sandwich complexes ($Ln_2[\mathbf{L^{VII}}]_3$) were synthesized and characterized and found to posses tunable solution and solid-state emission properties, with $Sm_2[\mathbf{L^{VII}}]_3$ emission at 556 nm to $Er_2[\mathbf{L^{VII}}]_3$ emission at 617 nm. Interestingly, lutetium exhibited a significant increase in fluorescent signal as compared to the other $Ln_2[\mathbf{L^{VII}}]_3$ complexes in the solid state, providing a

rare opportunity to differentiate one of the 14 lanthanides. Lastly, the double-decker thorium and cerium sandwich complexes, of the type $M[\mathbf{L}^{\mathbf{VII}}]_2$ were synthesized; the thorium analogue was observed to possess unprecedented emission characteristics, and is the first example of this behavior reported in the literature. These observations about the preferential binding of uranyl and unexpected electronic properties from thorium provide insights into the fundamental coordination chemistry of the early actinides and may be useful for the future design of selective ligands for actinide and lanthanide detection and separations.

## Acknowledgments

I would like to begin by acknowledging that I will never be able to thank all who have helped me in my journey towards this dissertation. I will make a humble attempt to mention as many as I can.

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Maddy Eddy and Kevin Wyss spent working with me as undergraduate researchers in the Gorden Lab. I would especially like to thank Charmaine Tutson and Maya West, both of whom have become great friends, ran to my side when I broke my leg and needed them, and were unconditionally supportive throughout my best and worst times at Auburn.

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## List of Abbreviations

| | |
|---|---|
| Ace | Acetone |
| Acac | Acetylacetonate |
| ACN | Acetonitrile |
| CAN | Ceric ammonium nitrate |
| CCDC | Cambridge Crystallographic Data Center |
| CIF | Crystallographic Information File |
| DCM | Dichloromethane |
| DDQ | 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone |
| DIAMEX | Diamide extraction |
| DFT | Density functional theory |
| DMF | Dimethylformamide |
| DMSO | Dimethylsulfoxide |
| En | Ethylenediamine |
| ESI | Electrospray ionization |
| $Et_2O$ | Ether |
| EtOH | Ethanol |
| GANEX | Group actinide extraction |
| HOMO | Highest occupied molecular orbital |
| LAH | Lithium aluminum hydride |

| | |
|---|---|
| LUMO | Lowest unoccupied molecular orbital |
| MeOH | Methanol |
| MOF | Metal organic framework |
| $NEt_3$ | Triethylamine |
| NIR | Near Infrared |
| OLED | Organic light emitting diodes |
| OAc | Acetate |
| PET | Positron emission topography |
| PUREX | Plutonium uranium recover by extraction |
| SMM | Single molecule magnet |
| t-bu | tert-butyl |
| TD-DFT | Time dependent density functional theory |
| TBP | Tributyl Phosphate |
| TFA | Trifluoroacetic Acid |
| TFAA | Trifluoroacetic Anhydride |
| THF | Tetrahydrofuran |
| TOF MS | Time of flight mass spectrometry |
| Tol | Toluene |
| TRUEX | Transuranium extraction process |
| UV | Ultraviolet |
| XRD | X-ray diffraction |

# Chapter 1: Introduction

## Main Objective

The main goal of this work is to describe new Schiff base and salen ligands and explore fundamental *f*-block coordination chemistry. Herein, two new salen ligand derivatives containing extended conjugation or pyridyl coordination are synthesized and characterized in terms of their ability to sense actinide ions colorimetrically. The first new compound introduces a phenazine backbone into the salen-type ligand structure; the second includes a pyridine coordination moiety in addition to the salen coordination environment. A third salen ligand derivative, "napthylsalophen", was synthesized and became a conduit to further explore f-block coordination chemistry and unusual emission properties in the presences of both lanthanides and actinides. The theme of this text is to explore *f*-block coordination chemistry in solution and the solid-state through salen-type compounds which may bring forth properties that can be applied in the areas of sensing.

## Nuclear Power and Nuclear Waste

In the twentieth century, scientists discovered new ways to utilize the actinide elements, which prompted great advances in both energy and weaponry. The advent of the nuclear power era has the potential to provide inexpensive, plentiful electricity with reduced carbon emissions, but these benefits are offset by concerns about the potential environmental effects of a waste spill or contamination event. Release events have occurred in the past and introduced radioactive

isotopes into the environment that have long-lasting effects on the environment. These types of instances have tarnished the reputation of the actinides as well as raised awareness for more fundamental research into these elements. Currently, these elements are used to generate about 20% of the United States energy and about 11% of the world's electricity.[1] Of the 30 countries that use nuclear power as an energy source, 12 use these elements to generate at least 30% of their national electricity.[1] As there are 449 operational nuclear power plants around the world, and 56 more that are currently in planning or under construction, the problem of nuclear waste generation is once again on the minds of the general public, especially given the disastrous environmental effects observed after the recent Fukushima incident.[2-4]

While the nuclear-power-related release events that have occurred were from poor design, human error, or natural disasters, the possibility of nuclear waste release still remains at the forefront of public concern. Although the waste volumes generated through nuclear power production in comparison to the energy created is much smaller than fossil fuel energy sources, residual radioactive isotopes remain after the nuclear fuel cycle, which is a once-through process in the United States.[5-7] Unfortunately, high-level waste must be stored on-site in the United States, and oftentimes the storage methods and aging containers leave room to be improved.[8] There are two main ways of approaching this problem for the long term: remediation of waste and improved storage facilities.

Research into better storage methods that would prevent these radioactive isotopes from leaching into the environment is one way engineers can help with this issue.[9-10] Another long-term solution would be to reduce the need for on-site storage by removing the most harmful nuclei, thereby reducing the volume of high-level waste. The most commonly used process to separate uranium and plutonium in this waste is the Plutonium Uranium Recover by EXtraction

(PUREX) process, which uses a tributyl phosphate (TBP) ligand and hydrocarbon solvent.[11-12] Other processes such as the diamide extraction (DIAMEX) and the transuranium extraction process (TRUEX) are also used worldwide.[11-12] Group actinide extraction (GANEX) is a proposed process currently gaining popularity in Europe to replace the PUREX process.[11] Many of these ligands shown in **Figure 1.1** use a mix of hard oxygen donor atoms and softer phosphorous or nitrogen atoms. Softer donors have been found to improve selectivity for the actinides over the lanthanides due to the more ionic character of the 4f elements and the radial extension of the 5*f* orbitals.[11]

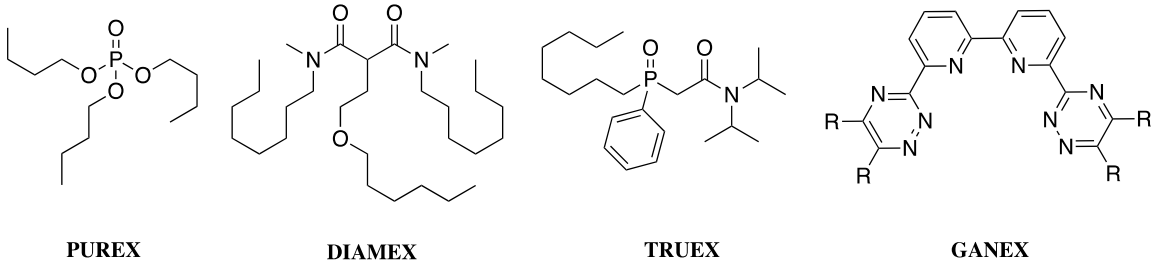


**Figure 1.1.** Ligand systems used during spent nuclear fuel remediation for each of the aforementioned separation techniques.[11]

In the immediate future, however, the need to identify when radioactive waste or material has been leaked into the environment is great. While methods to detect radioactive material are available, many of these methods cannot identify the isotope present or have high rates of misidentification.[13-14] Geiger counters are easy to use and identify radioactive material when β–particles send a charge through their wiring, but no identifying features other than the amount of β–particles present can be discerned.[13] Gamma detectors are available and can potentially identify the radioactive nuclide present, but require specialized equipment, are high cost, and need a specialist to glean any of the identifying information for a specific element.[14] A need exists for a reliable on-site sensor that can be operated by a non-specialist for these materials.

**Why Fundamental *f* -element Coordination Chemistry?**

Long-term storage, as well as the more immediate need for environmental sensors, relies on our fundamental understanding of *f*-element chemistry. To illustrate the room for fundamental chemistry left in the f-block, currently, the number of metal containing structures deposited to the Cambridge Crystallographic Data Center (CCDC) is 551,204.[15] Of these, 41,947 of them contain any *f*-block metal; only 7,666, or 1.4 %, of these structures contain an actinide metal. Of the structure containing any of the fourteen actinides, 82 % (6,295) contain uranium and 55 % (3,440) of those contain uranyl ($[UO_2]^{2+}$), the hexavalent and most stable oxidation state of uranium in an aqueous environment.[15] For comparison purposes, only 961 thorium, 215 neptunium, and 163 plutonium structures of any oxidation state can be found in the CCDC.[15] The prevalence of this particular oxidation state of uranium is due to its presence in nuclear waste as well as the robust linear dioxo uranyl unit, which provides predictable coordination geometry.

Neptunium and plutonium are also found in the –yl form in aqueous media ($[NpO_2]^+$ and $[PuO_2]$), meaning that the design and isolation of ligands designed and optimized for uranyl sensing may be useful for further study with the transactinides. Neptunium and plutonium are more difficult to work with and disproportionate at faster rates, meaning making stock solutions of a single oxidation state of these metals can be very difficult.[16-17] Highly radioactive alpha emitters also require specialized handing, which is why this text only discusses the sensing of uranyl.[18] Identifying on-site sensors that could distinguish uranyl from both transition metals and other actinides are synthetic targets of interest, with potential for further application and new knowledge about the coordination spheres of these actinide elements.

**Actinide Imine Coordination Compounds**

Many methods have been employed to coordinate actinide ions, one of the first being synthesizing ligands that contain hard oxygen donors, which capitalizes on the strong Lewis acid character and oxophilic nature of the actinides.[19] Synthetic examples and computational analyses of extraction methods for actinide cations with crown ether type compounds are common in the literature.[20-22] Another example, reported by the Raymond research group, is the 1-Hydroxypyridin-2-one (1,2-HOPO) ligand system, and derivatives thereof, containing nitrogen and oxygen donor atoms. In this case, exclusively the oxygen donors were found to bind to the actinide metal centers Th(IV), $UO_2^{2+}$(VI), and Pu(IV) when characterized in the solid-state.[23-26]

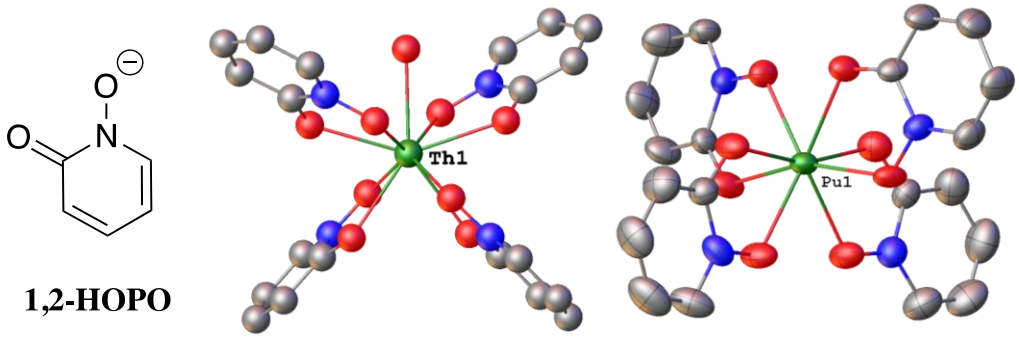


**Figure 1.2.** 1,2-HOPO ligand and projections of the 9-coordinate Th(1,2-HOPO)$_4$H$_2$O and 8-coordinate Pu(1,2-HOPO)$_4$. Carbon atoms are shown in grey, oxygen in red, nitrogen in blue and the metal center in green.[23,26]

Another fruitful method that has been employed to sequester and identify actinides, especially in selective sequestration of actinides even in the presence of lanthanides, has been to incorporate softer nitrogen donor atoms in the coordination sphere. This can be achieved through multidentate ligands, but there are also examples of successful macrocyclic systems, which can be designed to have high selectivity and large extinction coefficients. One family of macrocyclic chelators and their corresponding actinide complexes have been characterized using an expanded porphyrin framework. This area of actinide coordination chemistry has been heavily influenced

by the Sessler research group; their efforts have resulted in several unusually selective actinide coordination complexes.[27-29] One particularly interesting, recent example is a macrocyclic ligand proposed as a chemosensor that can detect uranyl in as low as parts per billion concentrations through the use of photoacoustic imaging.[29] This ligand has pyridine, pyrrole, and furan donors and is hexacoordinate; a projection of the uranyl complex of this ligand is shown below in **Figure 1.3**.[30]

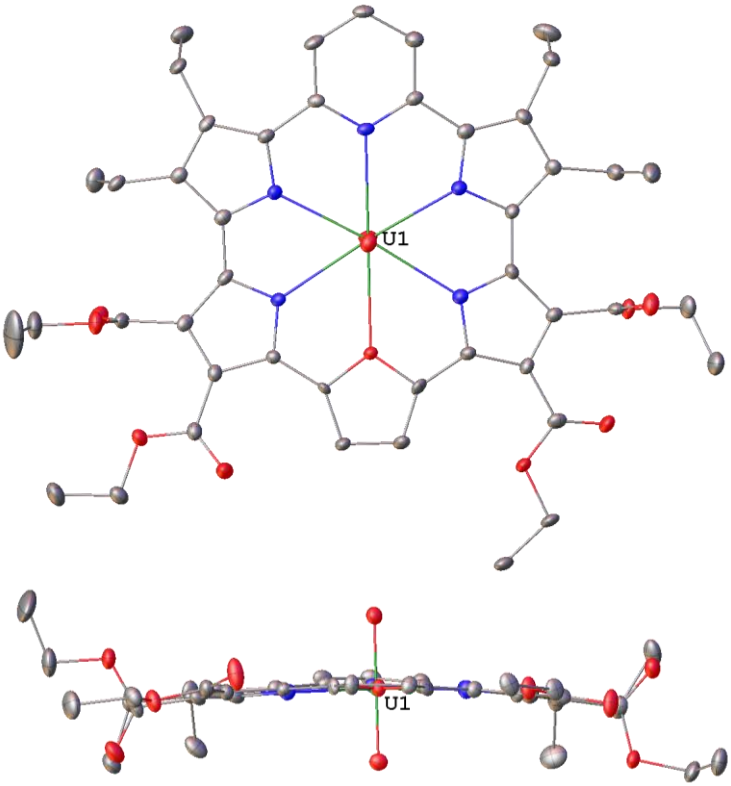


**Figure 1.3.** Projection of $UO_2$(cyclo[1]furan[1]pyridine[4]pyrrole). Carbon atoms are shown in gray, oxygen atoms shown in red, nitrogen in blue, and uranium in green.[30]

While there have been examples in the macrocyclic literature, these cryptand or porphyrin derived compounds are often quite synthetically challenging and may not scale well in mass production.[26-28] Additionally, these ligands can be difficult to manipulate as the pocket size is rigid, which both increases specificity for a particular ion and complicates synthetic efforts. An alternative sensing strategy that allows for easier modification, and perhaps decreases selectivity

of binding while broadening the capacity for use in real-time applications, is to use a non-macrocyclic ligand environment. Ligands used in this endeavor that contain N-donors such as pyridine, imine, or amine have been observed to have applications in catalysis and sensing.[31]

Specifically, salen ligand architectures, named for the salicylaldehyde and ethylenediamine starting materials, incorporate softer imine donors commonly found in the actinide sensing literature and pair them with the harder phenolate donors to yield a O-N-N-O binding pocket. These ligands have high affinities for many metals, but if differentiation can be attained in the UV-Vis signature or emission profile, more information about the contents of a waste solution can be attained. New information about the coordination chemistry of the actinides and lanthanides can be achieved through the study of these tunable compounds.

**Actinide Salen Compounds**

The first examples of $UO_2$-salen were synthesized by Pfeiffer and co-workers in 1937,[32] and the first single crystal x-ray characterization of these compounds was described in 1972 by Vigato and co-workers.[33] Since that time, actinide salen coordination chemistry has been of interest. Salen complexes of uranyl (VI), uranium (IV), thorium (IV) and neptunium (V) have been characterized in the literature.[34-37]

Salen derivatives have been applied in the development of chemosensors for uranyl. The addition of a phenolic donor in the presence of the soft imine donor, reminiscent of previously described Schiff base sensors, allows for better binding to the actinide center. A salen derivative, which includes an extended conjugated quinoxaline backbone presented in **Figure 1.4**, was synthesized in the Gorden lab and has shown promise.[38-39] The fluorescence observed from the quinoxaline and the ability to synthesize derivatives from common amino acid starting materials makes this complex unique in uranyl chemosensing.[40] The more simple salophen derivative

deposited into a film was reported in 2012 as a sensor for uranyl, although neither the solid-state characterization of the ligand nor the metal complex were reported.[41] Water soluble analogues of salen sensors have been shown to be selective in complexation of neptunyl and uranyl, with a preference for neptunyl and a very low affinity for lanthanides.[42] A few selected examples of uranyl salen complexes are shown in **Figure 1.4**.

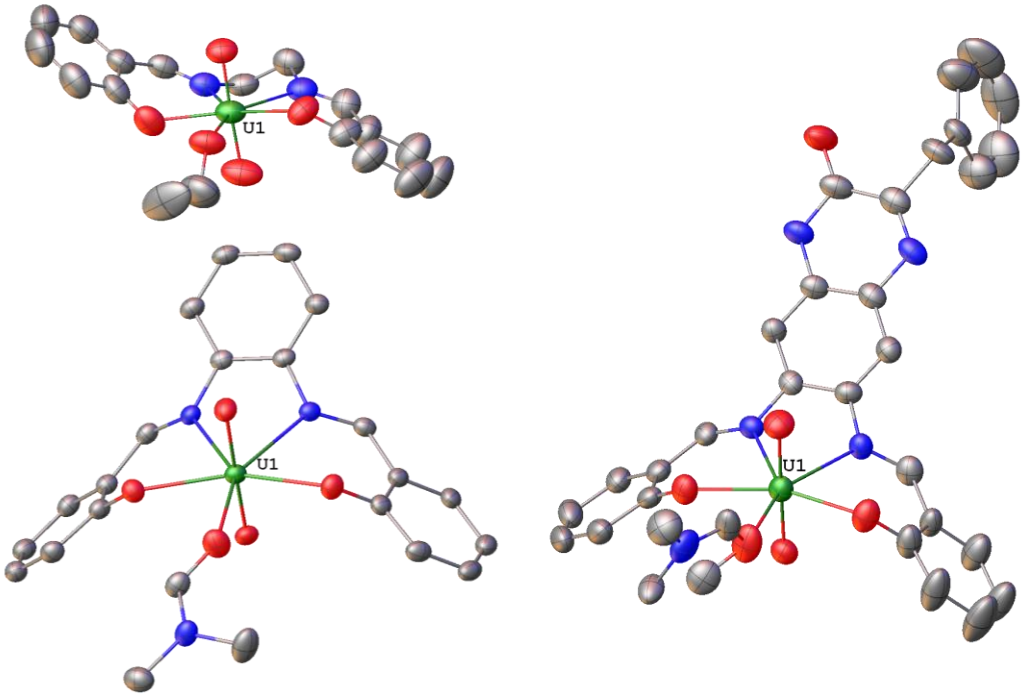


**Figure 1.4.** Projections of previously reported uranium complexes of salen, salophen, and quinoxaline salen ligands.[39,44]

Uranyl salen type species have also been used for anion recognition, capitalizing on the Lewis acidic nature of the uranyl moiety.[42-47] An early example by Reinhoudt and co-workers showed that urea and a uranyl salen complex could be co-crystallized, beginning a line of inquiry of these neutral uranyl salens applied to ion sensing.[43] Reinhoudt reported that functionalized uranyl salens were especially good receptors for phosphate ions,[44-45] and fluoride ions;[46-47] A projection of this co-crystallized complex can be found in **Figure 1.5**. Hosseini and co-workers have also shown selective recognition of the acetate anion in 2012.[48]

In addition to anion sensing, examples of cation recognition have also been observed. The Cametti and Rissanen research groups first observed recognition of quaternary ammonium halides in 2003,[49] and continued to publish many of the known examples of uranyl salens sensing quaternary ammonium salts, iminiun salts, and lithium ions.[50-52] Another interesting example of uranyl salen complexes was observed in 2012 when the metal complex was bound to a chiral cavitand, and showed enantiodiscrimination of amino acid salts.[53]

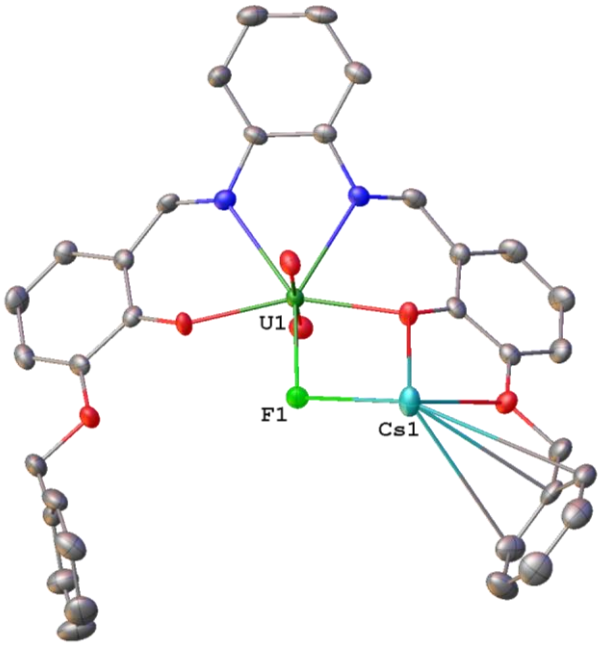


**Figure 1.5**. Projection of $UO_2$(salen) derivative and co-crystallized CsF. Carbon atoms are shown in gray, oxygen in red, nitrogen in blue, fluoride in lime green, cesium in teal, and uranium in dark green.[46]

While there have been many examples of catalysis with organometallic and low valent uranium species,[54] many of these systems contain mixed oxo and aza donor coordination environments. Uranyl salen complexes, which contain similar mixed aza and oxo donor groups, have also been characterized for their potential use in catalysis. Uranyl salens have been employed as catalysts in 1,4-thiol additions.[55-56] Through the use of asymmetric salen moieties, a chiral uranyl salen catalyst has been prepared.[57-58] One example of an asymmetric uranyl salen

was used to catalyze a Diels Alder [4+2] cylcoaddition. This catalyst functioned by stabilizing the transition state as described by Mandolini and co-workers.[59-60]

Salen type ligands have more recently been investigated for their ability to act as redox-active ligands and to store multiple electrons in the ligand scaffold for use in catalytic processes.[54,61-62] Actinide metal ions have many oxidation states readily available and they also provide opportunities for multiple electron transfer. Coupling actinide metals with redox-active ligands provides a route to synthesize new catalysts with the capability of transferring as many as 4 electrons, providing a possible pathway to complete transformations that are unattainable or extremely difficult with traditional transition metal catalysts.[54]

There are examples of this multielectron transfer and ligand non-innocence in uranium complexes with nitrogen-donating systems, although these are rare.[61-63] Salen ligands are a useful system to further explore this type of chemistry, and have been shown by Mazzanti and co-workers in 2009 to stabilize pentavalent uranyl complexes as well as polymetallic, mixed valent systems, one of which is highlighted below in **Figure 1.6**.[64] In a follow up study in 2010, salophen complexes of both uranium(III) and uranium(IV) were used to promote C-C bond formation; these compounds could then release four electrons through oxidative cleavage of that same C-C bond.[36]

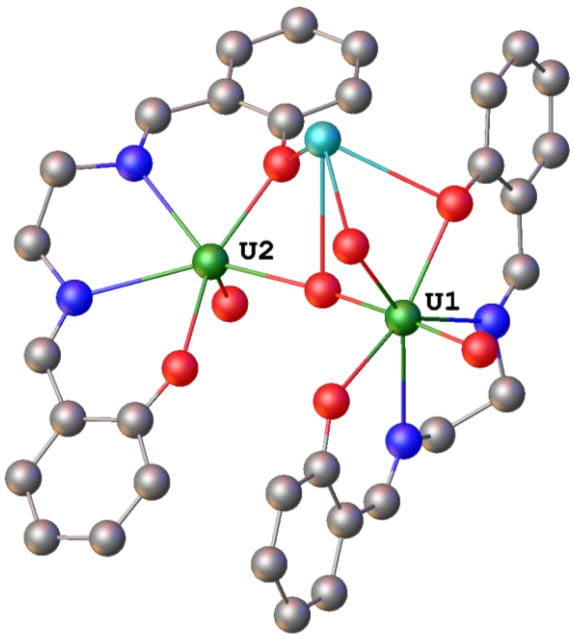


**Figure 1.6.** Projection of a mixed U(VI)/U(V) salen species, reported by Mazzanti and coworkers. Carbon atoms shown in grey, oxygen in red, nitrogen in blue, uranium in green, and potassium in teal. An interstitial pyridine, and crown ether sequestered potassium cation have been removed for clarity.[64]

**Lanthanide Salen Compounds**

Lanthanide salen compounds are less common in the literature, as lanthanides tend to be purely ionic donors and only loosely bind to the imine nitrogen donors of salen. There are, however, examples of supramolecular aggregates of salen ligands and lanthanides proposed for use in catalysis, as single molecule magnets (SMMs), and to investigate their characteristic emission properties.

Salen *f*-block complexes have the potential to be very useful in catalysis because of their varying oxidation states and large coordination spheres. While the lanthanide metals do not have the multielectron or redox potential of the actinides, they do have large, flexible coordination spheres. This can be very useful for catalysis when coupled with a redox active ligand. The first example of such a redox active salen ligand with a lanthanide was reported by Mazzanti and coworkers in 2012.[65] Karsten Meyer recently showed in 2017 that nitrogen donors in a

tetrazacyclododecane ligand framework could stabilize an air-stable mixed valent U(IV) and U(V) system.[66] A similar aryloxide derivative, with a coordinating arene unit rather than a tetraazacyclododecane, has been shown to stabilize U(II) complexes as well as Nd(II) complexes (**Figure 1.7**).[67-68] This notable example involving reduction of Ln(III) to Ln(II) complexes, which can then be used as a catalyst, was observed and further developed by Evans, Meyer, and co-workers showing tunability of overpotential depending on the lanthanide present.[68]

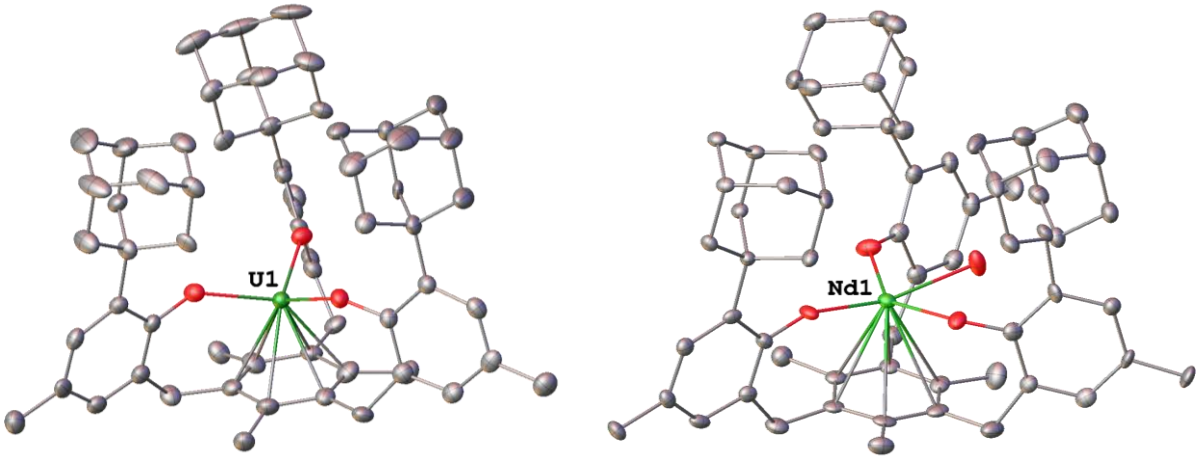


**Figure 1.7.** Projections of U(II)(arene) and Nd(II)(arene) ligands. Potassium counterions, coordinated in cryptand have been removed for clarity. Carbon atoms shown in grey, oxygen in red, nitrogen in blue, and metal ion in green.[66-67]

The tendency of the lanthanide ions is to remain trivalent may be somewhat limiting for catalysis purposes, but this stability in oxidation state with multiple unpaired *f*-electrons in these ions can be very useful in terms of synthesizing compounds with interesting magnetic properties.[69] The high number of unpaired f-electrons, seven in Gd(III), provides the potential of high magnetic moments. Multimetallic lanthanide species provide an opportunity to have multiple magnetic centers in a single complex and can be very useful for SMM applications.[69] Lanthanide chemistry varies drastically depending on the pH of solutions, the counter ions present, and equivalents used during synthesis, making multimetallic species difficult to reliably synthesize.[70-71]

In 2014, seven salophen lanthanide complexes were synthesized and characterized for potential SMM applications as the Pr, Nd, Gd, Sm, Eu, Tb, and Dy analogues.[72] Building on this work, Evangelisti and Milios reported 1-D lanthanide chains prepared from a salen derivative which demonstrated interesting magnetic cooling and relaxation of Dy and Gd analogues.[73] In 2017, Sanudo and co-workers applied the salen coordination geometry to breakthrough SMM compounds containing Tb or Dy with phthalocyanide ligands previously reported by Ishikawa (highlighted in **Figure 1.8**).[74-75] The recently reported salen multi-decker sandwich complexes of Yb and Er were described as SMMs with potential applications in quantum computing.[75-78] These compounds are also often observed to have interesting emission properties in the near infrared (NIR).[75-76]

A fair number of salen multimetallic lanthanide species have interesting emission properties lending to their use as white organic light emitting diodes (OLEDs).[79-81] One way to overcome the high cost barriers and difficulties synthesizing lanthanide coordination compounds is to use polymer-based OLEDs, as described in a recent report by Lu and coworkers.[82] Lu capitalized on the self-assembly of lanthanide salen compounds and designed metallopolymer LEDs consisting of Eu(III) or Zn(II)/Gd(III) that emitted white light.[82]

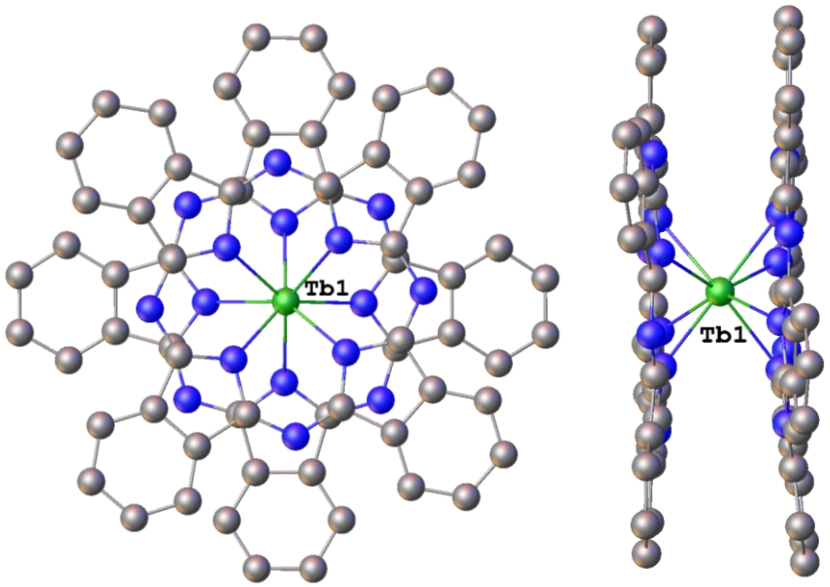


**Figure 1.8.** Projection of a Tb single molecule magnet

Finally, lanthanides have specific emission profiles and are of interest for non-invasive medical imaging. Of interest in this case, is emission in the NIR region.[83] While each lanthanide has a specific emission profile dependent on electronic transitions present in the metal center, these emissions are often low intensity as they are Laporte forbidden.[84-85] Therefore, strategies including the "antenna effect" have been employed to sensitize the lanthanide emission.[81, 86] The antenna effect (illustrated in **Figure 1.9**) couples a light-harvesting ligand species with a lanthanide metal center, and relies on ligand-to-metal electron transfer followed by emission to sensitize the lanthanide and increase the intensity of emission.[87] Salen ligands are one example of systems that have been employed as "antennas" to sensitize lanthanide emission.[85,88]

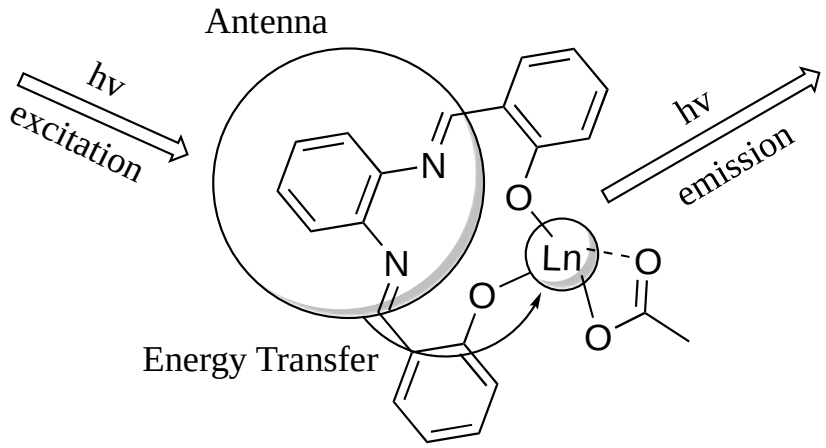


**Figure 1.9.** Cartoon of the antenna effect

One particularly useful example by Werner and co-workers incorporated a salen binding motif into a macrocyclic chelator and saw a "turn-on" emission from Eu(III) ions.[89] The tunablility of these ligands and their affinity for electron absorption makes them a perfect candidate for this type of chemistry. These types of systems often consist of mixed d and f block metal complexes and multimetallic *f*-block metal complexes.[90] Examples of these light harvesting ligands contain oxygen and nitrogen donor systems, including work by De Bettencourt-Dias and Muller, which revolves around dipicolinic acid (2,6-pyridinedicarboxylic acid) derivatives.[91-93] The Raymond research group has studied water-stable lanthanide compounds with quantum yields as high as 60% and polarized emission from a 1,2-HOPO derivative ligand that contains aza and oxo donor atoms, shown in **Figure 1.10**.[94-95]

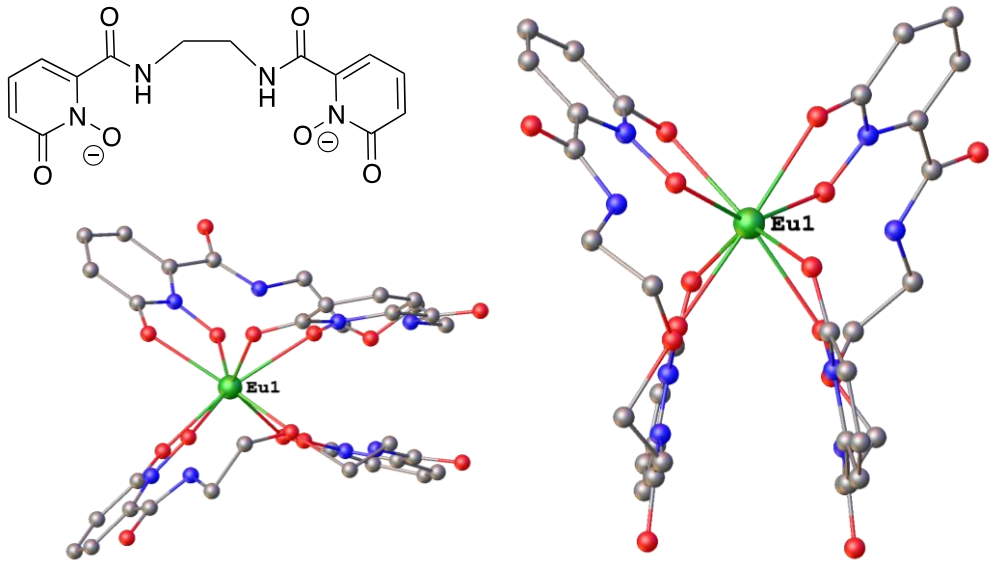


**Figure 1.10.** Schematic of a1,2-HOPO derivative and projection of the highly emissive 2:1 Eu complex reported by Raymond in 2006. Carbon atoms shown in grey, oxygen in red, nitrogen in blue, and Eu in green. Hydrogen atoms have been removed for clarity.[89]

While salen complexes are abundant in the literature, much of the potential of these complexes with lanthanides and actinides remains unexplored. In this text, Schiff base and salen ligands are described for some of the uses described in this introduction. Two new salen ligand derivatives containing extended conjugation or pyridyl coordination are synthesized and characterized in terms of their ability to sense actinide ions colorimetrically. The first new compound is the next logical progression of the previously mentioned quinoxaline salen, introducing a phenazine backbone into the salen ligand structure; the second includes the addition of a pyridine coordination moiety, which is reminiscent of the aforementioned macrocyclic ligands, and retains the flexibility of a salen system. New insights into the binding kinetics and scaffold necessary for rapid, on-site sensing were gained from these studies.

A large portion of this text is devoted to the actinide and lanthanide napthylsalophen complexes, which provide a conduit to further explore *f*-block coordination chemistry. Specifically, unexpected emission properties for thorium complexes, uncommon redox

stabilization of cerium complexes, and tunable ligand emission in self-assembled lanthanide triple-decker sandwich complexes is observed and explained herein. The overarching theme of this text is that exploring *f*-block coordination chemistry through the use of salen-type compounds may bring forth new knowledge and reveal unusual properties that can be applied in the areas of sensing, catalysis, and redox active complexes.

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## Chapter 2: Solid State π–π Stacking and Higher Order Dimensional Crystal Packing, Reactivity, Microfluidic Detection and Electrochemical Behavior of Salphenazine Actinide and Transition Metal Complexes

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### Introduction

As the population rises, so does the need for power production. The environmental ramifications of high carbon emission energy sources are well documented, and production of energy that is renewable or carbon neutral is of great importance. The application of actinides in nuclear power production is one option for the reduction of greenhouse gas emissions.[1-2] The positive attributes of nuclear power production are counterbalanced by highly publicized radioactive material release events, which subsequently raise concerns about the potential for harmful environmental and health effects.[3-5]

One way to combat these widespread environmental concerns is to apply fundamental chemical knowledge about the actinides to the creation of sensor ligands that can allow for rapid, in-the-field detection if a contamination event occurs. The rational design of ligands for actinide

selective coordination is complicated by the much higher concentrations of first row transition metals that are naturally found in environmental systems.[6-8] In particular, the highly electropositive and earth abundant copper has been found to yield a false positive result in many ligand systems designed to selectively isolate or detect uranyl ($UO_2^{2+}$), the most stable form of uranium in aqueous solution.[9]

The development of sensors that are able to selectively signal the presence of actinides in the environment is a key goal in immediate emergency response should release events occur *via* accident or incident, and such sensors could greatly improve the ease of remediation.[10-12] Schiff base-type ligands with an O-N-N-O coordination core have been investigated in numerous applications including: catalysis,[13-16] antimicrobial assays,[17-18] in organic light emitting diodes,[19-21] and as fluorescent or colorimetric sensors.[22-25] Salen metal complexes, in particular, are of interest in these and other applications due to the relative ease of introducing functionality.[23]

The O-N-N-O binding coordination pocket of salen-type ligands that can accommodate the equatorial binding geometry preferred by the uranyl dication coupled with the imine nitrogen soft donor, improves binding of actinides as compared to lanthanides, which are highly oxophilic and thus tend to form polymeric aggregates.[26-29] Our interest lies in the development of aromatic organic ligands that could be used in selective coordination of actinide ions.[30-31] It has been reported that the salen derived Salqu ligand [$\mathbf{H_2L^{II}}$] with an extended conjugated heterocycle (2-quinoxolinol) backbone can be selective for uranyl and act as a fluorescent sensor.[25] The salphenazine [$\mathbf{H_2L^{I}}$] ligand features the further extended phenazine backbone and a distinct hypsochromic shift with the coordination of uranyl dication ($UO_2^{2+}$). This is very distinct from the bathochromic shift seen in the complexes with the dicationic transition metals copper, cobalt, zinc, nickel, and the tetravalent vanadyl ($VO^{2+}$).[32-33]

Described here is the detailed characterization of salphenazine [$\mathbf{H_2L^I}$], M[$\mathbf{L^I}$] complexes, where M = $UO_2$(VI), Cu(II), VO(IV), Zn(II), Co(II), and Ni(II) and comparable salqu [$\mathbf{H_2L^{II}}$] metal complexes through x-ray crystallography, solution phase absorbance spectroscopy, and electrochemistry. A sterically constrained μ-oxo Fe(III) dimer complex was also characterized. Also described is a method of real-time microfluidic sensing *via* a microspectrophotometer on sub-nanoliter droplets. Droplet generating microfluidic devices retain many advantages of standard microfluidics, while allowing the formation of discrete, monodispersed droplets at rates up to 100 kHz.[34-37] These droplets are not strictly necessary for our proposed purposes, but they can be used to achieve statistically relevant sample sizes and provide a pathway to screen multiple ligands and metals in the same assay. A principle tenet of 5*f* chemistry is reduction of waste generation, and using these microfluidic devices can be advantageous for the aforementioned ligand screening with minimal waste production.

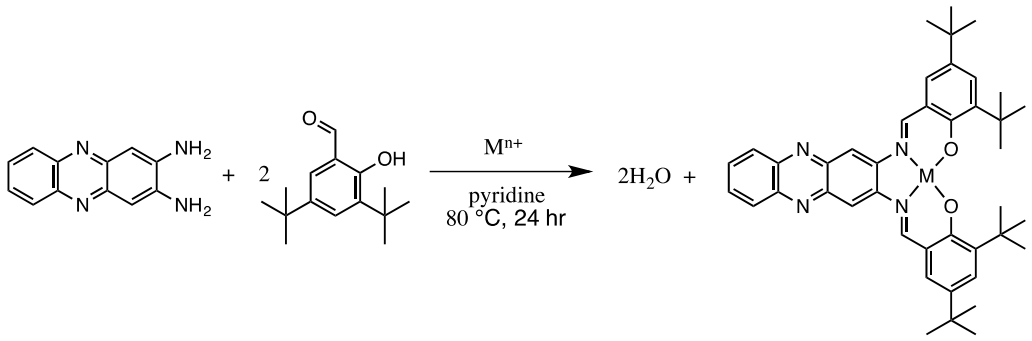
## Results and Discussion

### Synthesis

The condensation of 2,3-diaminophenazine with two equivalents of 3,5-ditertbutylsalicylaldehyde was employed to prepare a series of 1:1 metal:ligand complexes M[$\mathbf{L^I}$] in reasonable yields (20 - 36 %). The use of metal templation to prepare the metal complexes limits the formation of an imidazole 2-(1H-imidazo[4,5-b]phenazin-2-yl)phenol side product. This templation synthetic scheme (**Scheme 2.1**) was used to prepare the salphenazine M[$\mathbf{L^I}$] complexes where M = $UO_2$(VI), Cu(II), VO(IV), Zn(II), Fe(III), Co(II), and Ni(II). These compounds have been characterized in the solid state via single crystal X-ray diffraction and in

the liquid phase *via* nuclear magnetic resonance, mass spectrometry, UV spectroscopy, and electrochemistry.

The preparation of the free-base form of [$\mathbf{H_2L^I}$] in quantity both large enough and pure enough for further studies required preparing the complex in the templation reaction followed by subsequent stripping of the coordinating metal from the complex using a nitric acid wash. The free-base was dissolved in chloroform, and washed with 1 M $HNO_3$. The organic phase was then washed three times with water, and then with a saturated brine solution, followed by evaporation under reduced pressure. Finally, the free-base was separated from the monosubstitued 2-(1H-imidazo[4,5-b]phenazin-2-yl)phenol product via column chromatography.

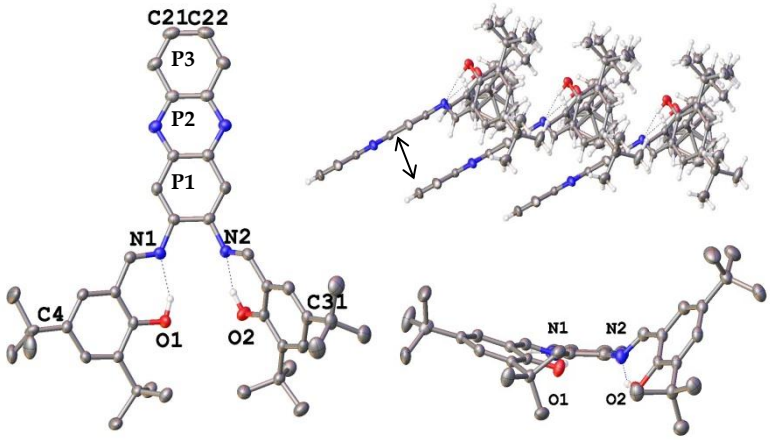



**Scheme 2.1.** Metal templated synthesis of salphenazine complexes M[$L^I$].

**X-Ray Crystallography**

The structure of the free-base form of $\mathbf{H_2L^I}$ has been characterized by single crystal X-ray diffraction. Crystallographic details of ligand and metal series are listed in **Table 2.1**. The ligand [$\mathbf{H_2L^I}$] crystallizes in the monoclinic space group $P2_1/n$. Structural representations of [$\mathbf{H_2L^I}$] are shown in **Figure 2.1**. The π–π distance between the P1-P3 rings, also depicted in **Figure 2.1**, is 3.471 Å. Of note is the non-planarity of the tetradentate binding pocket. This is counterintuitive from the highly conjugated system; however, the bond distances are such that repulsion of the

two oxygen atoms distorts the planarity of the extended π-conjugated network. One phenol oxygen atom is almost in plane with the phenazine backbone while the second distorts from planarity significantly, distances above the plane are O1-plane = 1.054(2) Å and O2-plane = 0.316(2) Å.




[$\mathbf{H_2L^I}$]

**Figure 2.1.** Salphenazine [$\mathbf{H_2L^I}$] crystal structure. Carbon atoms shown in grey, nitrogen shown in blue, oxygen shown in red, hydrogen atoms and interstitial ethyl acetate removed for clarity. Solid-state π– π interactions are highlighted in this projection.[31]

The binding of a metal to the binding pocket causes a significant change in π-overlap, which can be observed by the change in the electronic spectra of both ligands. In particular, the yellow solution of the free-base [$\mathbf{H_2L^I}$] turns red in the presence of common first row transition metals while it turns an orange color in the presence of uranyl, the coordination of which more greatly disturbs the planarity of conjugation. When a metal is bound, the electronic repulsion of the phenol oxygen atoms is eliminated.

**Table 2.1**. Crystallographic data and details of data collection for [$\mathbf{H_2L^I}$], $UO_2[\mathbf{L^I}](H_2O)$, Cu[$\mathbf{L^I}$], VO[$\mathbf{L^I}$], Zn[$\mathbf{L^I}$]($CH_3OH$), and Fe[$\mathbf{L^I}$]-O-Fe[$\mathbf{L^I}$].[31]

| | [$H_2L^I$]•0.5EtOAc | $UO_2[L^I](H_2O)$•2$H_2O$ | Cu[$L^I$] | VO[$L^I$] | Zn[$L^I$]($CH_3OH$) | Fe[$L^I$]-O-Fe[$L^I$]•1.5THF |
|---|---|---|---|---|---|---|
| **Formula** | $C_{46}H_{58}N_4O_4$ | $C_{42}H_{54}N_4O_7U$ | $C_{42}H_{48}N_4O_2Cu$ | $C_{42}H_{48}N_4O_3V$ | $C_{48}H_{53}N_4O_3Zn$ | $C_{90}H_{112}Fe_2N_8O_{6.5}$ |
| **MM (g/mol)** | 714.87 | 955.85 | 704.39 | 707.82 | 810.42 | 1529.56 |
| **Crys. size (mm)** | 0.8x0.15x0.02 | 0.1x0.4x0.2 | 0.4x0.09x0.05 | 0.6x0.08x0.08 | 0.2x0.1x0.1 | 0.1 x 0.3 x 0.6 |
| **Crystal system** | monoclinic | monoclinic | triclinic | triclinic | triclinic | monoclinic |
| **space group** | $P2_1/n$ | $P2_1/n$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $C_2/c$ |
| **volume ($Å^3$)** | 3901.1(2) | 5047.6(9) | 1836.17(7) | 2120.59(14) | 2192.78(16) | 8520.7(2) |
| **a (Å)** | 6.2422(2) | 18.0541(18) | 9.9751(2) | 10.5213(4) | 9.3102(5) | 18.9491(3) |
| **b (Å)** | 22.8992(7) | 13.4873(13) | 12.6630(3) | 12.7581(5) | 15.1537(7) | 41.3420(7) |
| **c (Å)** | 27.3841(8) | 20.820(2) | 14.8623(3) | 16.4769(8) | 16.4769(8) | 13.8422(2) |
| **α (deg)** | 90 | 90 | 93.610(1) | 77.715(1) | 105.875(2) | 90 |
| **β (deg)** | 94.7060(10) | 97.380(3) | 96.835(1) | 74.447(1) | 100.257(2) | 128.2090(10) |
| **γ (deg)** | 90 | 90 | 98.716(1) | 79.226(1) | 91.511(2) | 90 |
| **Z** | 4 | 4 | 2 | 2 | 2 | 4 |
| **ρ(calc. g $cm^{-3}$)** | 1.217 | 1.263 | 1.2658 | 1.1084 | 1.227 | 1.192 |
| **μ ($mm^{-1}$)** | 0.078 | 3.271 | 0.636 | 0.272 | 0.606 | 0.399 |
| **F(000)** | 1522 | 1892 | 737.9 | 750.9 | 864.9 | 3268 |
| **temp (K)** | 180(2) | 296(2) | 296.15 | 296.15 | 180(2) | 180(2) |
| **total no. reflec.** | 71416 | 39876 | 54883 | 35450 | 43775 | 50375 |
| **unique reflec.** | 5642 | 8274 | 15270 | 7239 | 8341 | 9764 |
| **Largest diff. peak and hole (e.$A^{-3}$)** | 0.28/-0.21 | 2.74/-1.86 | 0.76/-0.28 | 0.32/-0.33 | 0.97/-0.93 | 0.33/-0.33 |
| **Final R indices [$I > 2\sigma(I)$]** | R1 = 0.0426 | R1 = 0.0621, | R1 = 0.0375, | R1 = 0.0492, | R1 = 0.0536, | R1 = 0.0457 |
| | wR2 = 0.1013 | wR2 = 0.1816 | wR2 = 0.0952 | wR2 = 0.1321 | wR2 = 0.1260 | wR2 = 0.1374 |
| **GOF** | 1.017 | 1.134 | 1.016 | 1.059 | 1.073 | 1.122 |
| **CCDC** | 1452415 | 1019622 | 1019624 | 1452867 | 1452244 | 1018600 |

The $UO_2[\mathbf{L^I}]$ complex, which crystallizes in space group $P2_1/n$, is shown in **Figure 2.2**. Bond distances for the binding pocket can be found in **Table 2.2**. U-N distances are 2.560(7) and 2.546(8) Å. U-$O_{Ligand}$ distances are 2.242(7) and 2.265(7). For the $UO_2[\mathbf{L^I}]$ complex, the distance from a mean plane ($L_{plane}$), which is defined by atoms C22-C23-O1-O2, is 1.955 Å. Bond distances and angles for the binding pocket are found in **Table 2.2**. The Cu[$\mathbf{L^I}$] complex is shown in **Figure 2.3**; Cu-N distances are found at 1.9304(16) and 1.9477(15) Å. Cu-O ligand distances are found at 1.9091(12) and 1.8906(14) Å. For the $Cu^{2+}$ and $UO_2^{2+}$ complexes the M-O and M-N bond distances agree with previously reported data.[26,33] For the Cu[$\mathbf{L^I}$] complex, the

M-$L_{plane}$ distance is only 0.171 Å. As the XRD atomic coordinate data indicates, the Cu complex more closely resembles a planar system as compared to the uranyl complex.

**Table 2.2.** Selected bond distances (Å) and bond angles (deg) for [$\mathbf{H_2L^I}$], $UO_2$[$\mathbf{L^I}$]($H_2O$), Cu[$\mathbf{L^I}$], VO[$\mathbf{L^I}$], Zn[$\mathbf{L^I}$]($CH_3OH$), and Fe[$\mathbf{L^I}$]-O-Fe[$\mathbf{L^I}$].Images show crystals from data collection.[31]

| | [$H_2L^I$] | Cu[$L^I$] | $UO_2$[$L^I$] | VO[$L^I$] | Zn[$L^I$] | Fe[$L^I$]-O-Fe[$L^I$] |
|---|---|---|---|---|---|---|
| M-N1 | -- | 1.92 | 2.54 | 2.05 | 2.07 | 2.11 |
| M-N2 | -- | 1.94 | 2.56 | 2.05 | 2.08 | 2.10 |
| M-O1 | -- | 1.92 | 2.27 | 1.93 | 1.95 | 1.92 |
| M-O2 | -- | 1.89 | 2.24 | 1.93 | 1.97 | 1.91 |
| M-O3 | --- | | 2.45 | 1.59 | 2.11 | 1.76 |
| O1-N1 | 2.59 | 2.79 | 2.73 | 2.74 | 2.85 | 2.76 |
| N1-N2 | 2.70 | 2.58 | 2.71 | 2.59 | 2.65 | 2.62 |
| N2-O2 | 2.61 | 2.81 | 2.75 | 2.75 | 2.85 | 2.77 |
| O1-O2 | 3.41 | 2.66 | 4.42 | 2.65 | 2.89 | 2.80 |
| O1-N2 | 3.64 | 3.85 | 4.43 | 3.76 | 3.99 | 3.87 |
| O2-N1 | 4.23 | 3.81 | 4.40 | 3.83 | 3.92 | 3.85 |
| O1-M1-N1 | -- | 93.3 | 68.9 | 86.9 | 89.9 | 86.1 |
| N1-M1-N2 | -- | 83.8 | 64.1 | 78.3 | 79.5 | 76.8 |
| N2-M1-O2 | -- | 94.5 | 69.5 | 87.3 | 89.6 | 87.1 |
| O2-M1-O1 | -- | 88.7 | 157.5 | 86.9 | 94.9 | 93.9 |
| M1-O3-M1 | -- | -- | -- | -- | -- | 161.5 |
| M1-Lplane* | -- | 0.178 | 1.96 | 0.983 | 0.837 | 0.583 |

L-plane defined by C4-C21-C22-C31

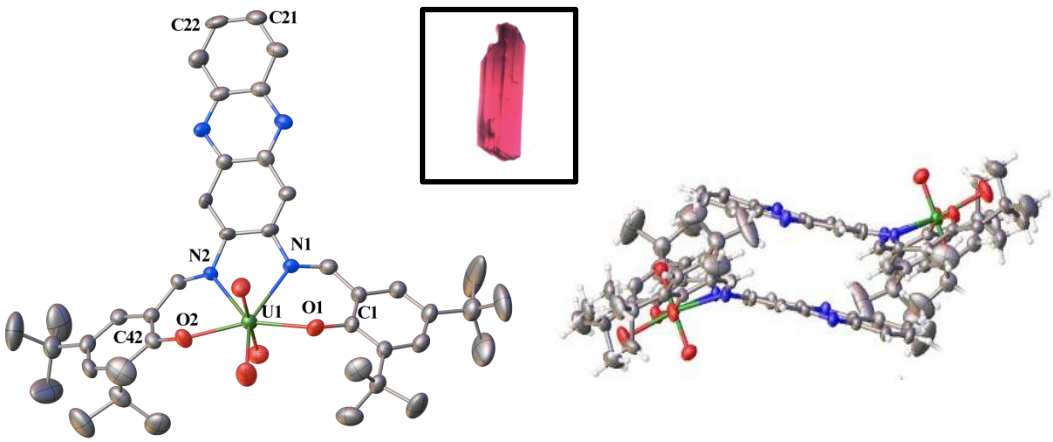



**Figure 2.2.** Projection of $UO_2[L^I]$ complex. Hydrogen atoms have been omitted for clarity. Inset image obtained on a CRAIC 20/20 PV microspectrophotometer shows the crystal employed for X-ray data collection.[30]

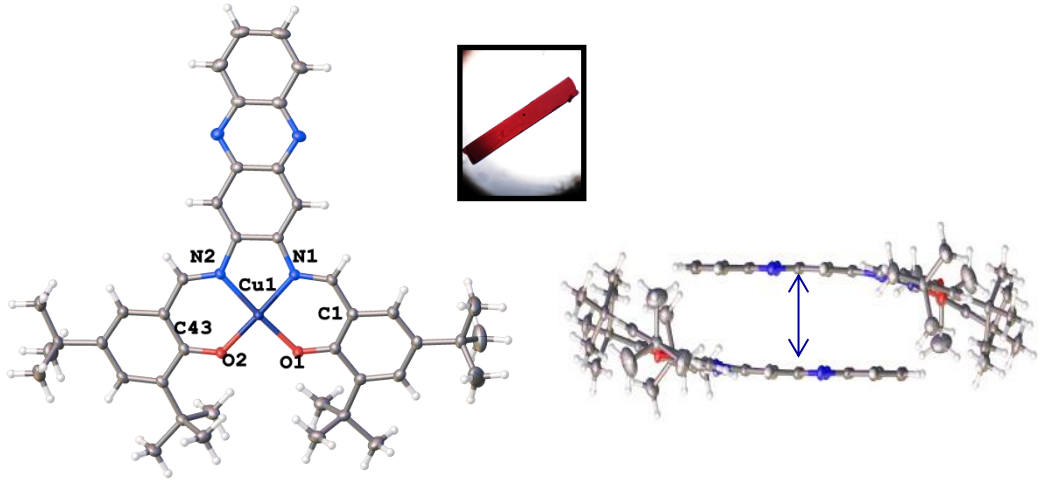



**Figure 2.3.** Projection of $Cu[L^I]$ complex. Inset image obtained on the microspectrophotometer showing the crystal used for X-ray data collection.[30]

The smaller ionic radii of transition metals allows for improved planar pi orbital overlap as compared to the distortion of the conjugated system observed upon coordination of uranyl, resulting in a bathochromic shift of the charge transfer band in the uranyl complex. Complex VO[$\mathbf{L^I}$], shown in **Figure 2.4**, crystallizes in the triclinic space group Pī . This complex has a distorted square pyramidal geometry with the axial position being an oxo group on the vanadyl cation ($VO^{2+}$). The geometry of the metal in the binding pocket is indicated by the bond angles

of O1-V-N1, N1-V-N2, N2-V-O2, O2-V-O1 of 86.94(8), 78.27(8), 87.31(8), and 86.90(7)° respectively, comparable to other vanadyl salen and salophen complexes (N1-V1-N2 77.3-78.7° and O1-V-N1, N2-V-O2, O2-V-O1 (86.3-88.8°).[38-40] The VO[$\mathbf{L^I}$] complex is skewed from square pyramidal geometry as compared to the Zn[$\mathbf{L^I}$]($CH_3OH$) and Fe[$\mathbf{L^I}$]-O-Fe[$\mathbf{L^I}$] complexes, both of which are also square pyramidal geometries. The vanadium atom V-N1 and V-N2 bond distances are 2.050(2), 2.054(2) Å, respectively. These bond lengths are comparable to others in the literature (2.05-2.07 Å) for salen type complexes, but the lack of symmetry in the angles is unusual.[38-40] The twist in $\mathbf{L^I}$ from the sterically hindered t-butyl groups causes a lack of symmetry in the binding pocket. The V-O1 and V-O2 bond distances of 1.929(2) and 1.930(2) Å respectively are comparable to literature (1.91-1.95 Å) which have greater variety than the vanadium nitrogen distances.[38-40]

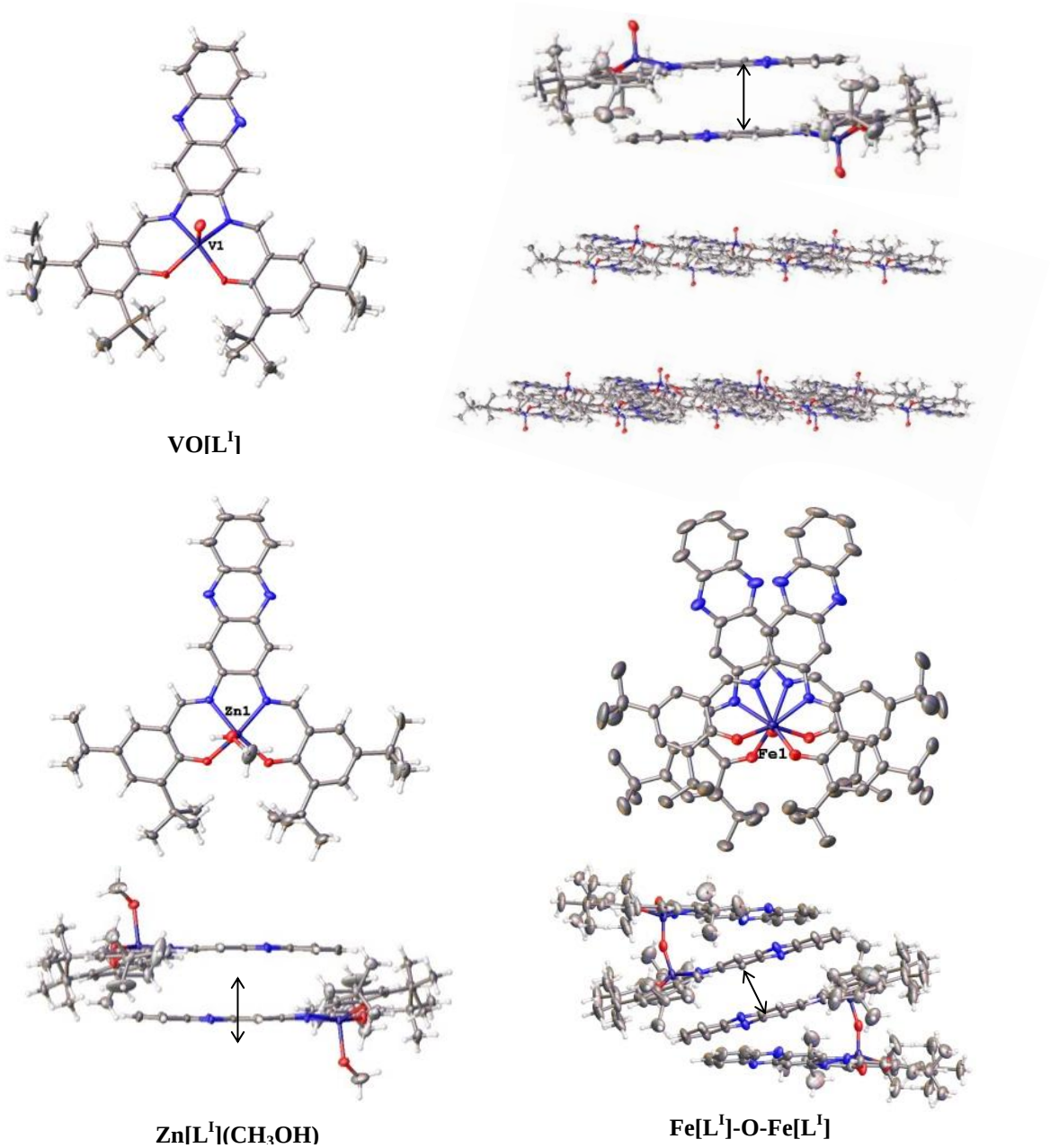



**Figure 2.4.** Projections of VO[$\mathbf{L^I}$], Zn[$\mathbf{L^I}$]($CH_3OH$), and Fe[$\mathbf{L^I}$]-O-Fe[$\mathbf{L^I}$] complexes. Solid-state dimers and pseudo 2-D sheets are also shown. Transition metal shown in purple, carbon atoms shown in grey, nitrogen shown in blue, oxygen shown in red, hydrogen (when not omitted for clarity) are shown in white. All interstitial solvents were removed for clarity.[31]

This complex forms pseudo two-dimensional sheets involving a dimer held together by π–π interactions in the solid state. These sheets are separated by 12.55 Å. The π–π distance

between the P1-P2 rings on phenazine of the dimer is 3.36 Å. These electron rich systems prefer off-center parallel π–π stacking. The M–P3 distance between the dimer phenazine rings is 3.235 Å, suggesting possible metal backbonding to the pi system of the ligand.

Complex Zn[$\mathbf{L^I}$]($CH_3OH$) crystallizes in the triclinic space group Pī and is shown in **Figure 2.4**. This complex has a square pyramidal geometry around the zinc atom with a coordinating neutral methanol molecule. This is observed by the close to 90° bond angles of the zinc to the O-N-N-O ligand donor atoms, O1-Zn-N1, N1-Zn-N2, N2-Zn-O2, O2-Zn-O1 are 89.90(11), 79.46(11), 89.55(10), 94.88(10)° respectively. These bond angles are comparable to previously reported zinc structures with coordinating methanol or pyridine solvent (79.0-95.5°).[41-42] The oxygen (O3) from the methanol is also approximately 90° from the equatorially bound ligand with O3-Zn-O1, O3-Zn-O2, O3-Zn-N1, O3-Zn-N2 angles of 101.02(11), 98.79(11), 95.01(10) and 105.18(11)° respectively. This coordination solvent is quite labile, and the zinc metal quickly dissociates from the ligand under acidic conditions. The zinc atom binds less securely than the copper in the tetradentate binding pocket with Zn-N1, Zn-N2, Zn-O1, Zn-O2 bond distances of 2.074(3), 2.076(3), 1.954(2), and 1.965(2) Å, respectively. These bond lengths are within ± 0.03 Å of the previously reported Zn(salphenzine)(DMSO) complex, [33] and within standard lengths of previously reported zinc salophen structures(Zn-O 1.93-1.97 Å and Zn-N 2.04-2.09 Å).[41-43]

Complex Fe[$\mathbf{L^I}$]-O-Fe[$\mathbf{L^I}$] crystallizes in the monoclinic space group C2/c and is shown in **Figure 2.4**. The iron(III) atom is in a square pyramidal geometry with the axial position being occupied by a bridging oxo group to a second, symmetry related, iron-ligand complex. This phenomenon is well documented in the literature, with 814 examples of mixed nitrogen and oxygen donor ligands with μ-oxo geometries, and 28 examples of salen ligands with μ –oxo

geometries reported in the Cambridge Crystallographic Data Center (CCDC).[44] The iron atom binds in the tetradentate binding pocket, but has the most distortion from square pyramidal as compared to the vanadyl and zinc structures with O1-Fe-N1, N1-Fe-N2, N2-Fe-O2, O2-Fe-O1 bond angles of 76.81(9), 87.14(10), 86.12(7), and 93.85(9)° respectively. These angles are comparable to other related examples in the literature (76.3-94.5°).[45-46] The Fe-N1, Fe-N2, Fe-O1, and Fe-O2 bond distances are also the longest of the transition metal structure in this M[$\mathbf{L^I}$] series with lengths of 2.1105(18), 2.100(3), 1.9216(17), and 1.906(2) Å, respectively. These distances are comparable to other Fe-salen dimers and elongated in comparison to some less sterically hindered complexes.[45-47] Of note is the lack of π-stacking in the dimer, and the Fe1-O3-Fe1 angle of 161.50(16)° which is comparable to other μ-oxo species[45-46] but is well below the stereotypical limits observed of 175-180°.[45-49] This can be explained by steric hindrance of the substituted aldehyde moieties. The π–π distance between the P1-P2 rings on the external dimer phenazine rings is 3.35 Å. The metal is 3.172 Å above the P3 ring.

Structurally, the uranyl metal complex $UO_2$[$\mathbf{L^I}$] is most similar to the ligand geometry. The axial positions of the uranium coordination sphere are occupied by the two oxo "-yl" groups of the uranyl subunit. The uranium atom is bound further out in the pocket than the transition metals. These bond distances are consistently 0.5 Å longer than the transition metal analogues (**Table 2.2**). This puckering of the ligand causes a shift from a planar backbone and results in the uranium atom being 1.954(9) Å above the plane of the ligand as defined by C4-C21-C22-C31. This puckering, highlighted in **Figure 2.5**, is the explanation of the spectroscopic distinction between uranyl and the transition metal analogues.

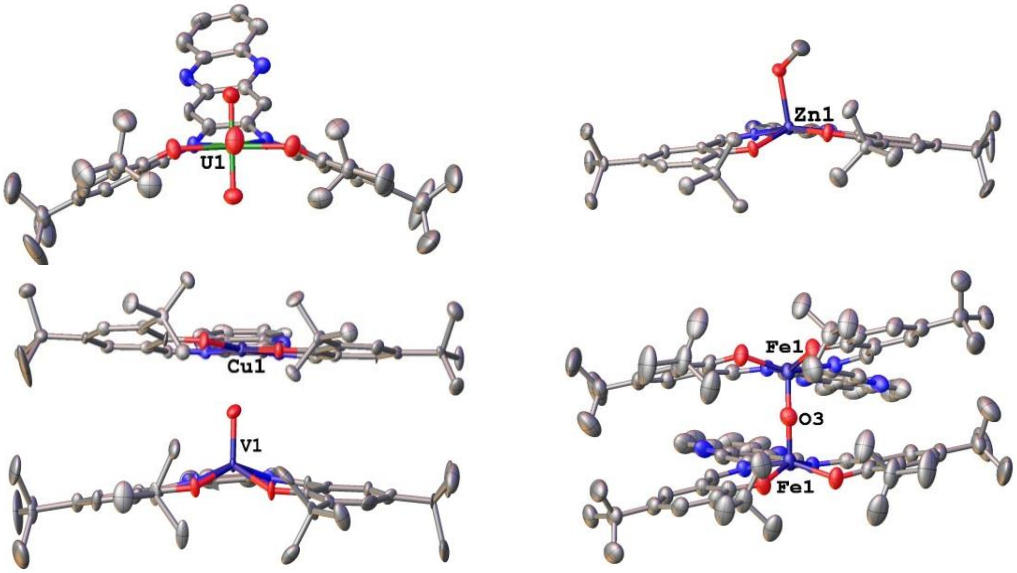



**Figure 2.5**. Projections of M[$\mathbf{L^I}$] series highlighting the pucker of the tetradentate binding pocket. Carbon atoms shown in grey, nitrogen shown in blue, oxygen shown in red, transition metals shown in purple, uranium shown in green, and hydrogen omitted for clarity.[31]

The planarity of the ligand, regardless of the steric bulk in the 3-position of the aldehyde, observed in the transition metal complexes was surprising. The planarity of the transition metal structures can be observed most distinctly by the Cu-$L_{plane}$ distance of 0.178(3) Å. The VO[$\mathbf{L^I}$] structure is second only to the uranyl structure in distance from metal to ligand plane with V-$L_{plane}$ distance of 0.967(7) Å. The Zn-$L_{plane}$ distance of 0.837(2) Å above the ligand plane is accompanied by a twist in the O-N-N-O pocket, explaining the lability observed in this metal complex as compared to the other analogues. The iron atom is closer to the plane of the ligand, however, than Zn[$\mathbf{L^I}$]($CH_3OH$) or VO[$\mathbf{L^I}$] structures, with a Fe-$L_{plane}$ distance of 0.583(2) Å. The iron atom is closer to the ligand plane than the other structures, while simultaneously having longer bond lengths suggesting that the *tert*-butyl groups in the 3 and 3' positions keep the pocket open wider than is strictly necessary for this metal centre.

**Spectroscopy**

All UV measurements were done using a Cary 50 UV-Vis spectrometer and with pyridine as a solvent due to limitations of solubility. The $\lambda_{max}$ values and molar absorptivities of the charge transfer bands for M[$\mathbf{L^I}$] complexes are listed in **Table 2.3**. Ligand [$\mathbf{H_2L^I}$] exhibits and absorption band at 420 nm. Upon 1:1 binding of $UO_2^{2+}$ a 60 nm hypsochromic shift of the π-π* excitation to 369 nm is observed. A charge transfer band with a maximum absorbance at 470 nm ($\varepsilon = 1.95 \times 10^4$ $cm^{-1}$ $M^{-1}$), a separation of 48 nm from the original ligand peak, and a shoulder at 520 nm are also observed in $UO_2$[$\mathbf{L^I}$]. By comparison, the Cu[$\mathbf{L^I}$] complex, exhibits a hypsochromic shift of the ligand peak of 24 nm and a charge transfer band at 521 nm ($\varepsilon = 1.95 \times 10^4$ $cm^{-1}$ $M^{-1}$) with a shoulder at 455 nm, a peak separation of 98 nm between absorbance maxima.

**Table 2.3**. UV-Visible data for M[$\mathbf{L^I}$]complexes and free base [$\mathbf{H_2L^I}$], 20 μM in pyridine solution.[31]

| | λ (nm) | ε (x $10^4$ $cm^{-1}$ $M^{-1}$) |
|---|---|---|
| **[$H_2L^I$]** | 420 | 1.80 |
| **$UO_2$[$L^I$]** | 369 | 2.64 |
| | 470 | 1.95 |
| **Cu[$L^I$]** | 394 | 1.62 |
| | 455 | 0.959 |
| | 521 | 1.95 |
| **VO[$L^I$]** | 375 | 1.59 |
| | 471 | 1.41 |
| **Zn[$L^I$]** | 387 | 1.79 |
| | 521 | 1.51 |
| **Fe[$L^I$]-O-Fe[$L^I$]** | 408 | 1.58 |
| | 511 | 0.926 |
| **Co[$L^I$]** | 338 | 1.88 |
| | 403 | 1.29 |
| | 509 | 1.35 |
| **Ni[$L^I$]** | 374 | 1.22 |
| | 408 | 1.08 |
| | 509 | 1.42 |

Compound [$\mathbf{H_2L^I}$] was complexed with other earth abundant transition metals $Cu^{2+}$, $Zn^{2+}$, $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, and $VO^{2+}$. **Figure 2.6** combines the complexes and free-base, highlighting the differences between these compounds. The complex Zn[$\mathbf{L^I}$] exhibits an absorbance feature at 520 nm ($\varepsilon = 1.51 \times 10^4$ $cm^{-1}$ $M^{-1}$) with a hypsochromic shift of the ligand peak by 37 nm. The Fe[$\mathbf{L^I}$]-O-Fe[$\mathbf{L^I}$] complex has a charge transfer band at 511 nm ($9.26 \times 10^3$ $cm^{-1}$ $M^{-1}$) after the templation condensation reaction, but shows no reaction when the $FeCl_3$ free metal salt is introduced. The presence of a $Co^{2+}$ ion (Co[$\mathbf{L^I}$]) induced a charge transfer band at 517 nm ($\varepsilon = 1.35 \times 10^4$ $cm^{-1}$ $M^{-1}$), a peak separation of 93 nm, and a hypsochromic shift of the ligand peak by 12 nm. Introduction of the $Ni^{2+}$ ion (Ni[$\mathbf{L^I}$]) induced a charge transfer band at 509 nm ($\varepsilon = 1.42 \times 10^4$ $cm^{-1}$ $M^{-1}$), a peak separation of 85 nm, with a shoulder at 570 nm which was not present in any of the other complexes. A hypsochromic shift of 10 nm, along with an additional high energy peak was also observed. Complex VO[$\mathbf{L^I}$], which is the least likely contaminant in waste water samples, has a maximum at 471 nm ($\varepsilon = 1.47 \times 10^4$ $cm^{-1}$ $M^{-1}$). The kinetics of binding of vanadyl was found to be much slower, over 24 hours, than the other transition metals. The $UO_2$[$\mathbf{L^I}$] complex has greater than 30 nm of separation from all the transition metals, save VO[$\mathbf{L^I}$], and 50 nm separation between the ligand and complex absorbance. The difference in the common false positive copper and uranyl is 50 nm, and can easily be seen by the naked eye (**Figure 2.7**).

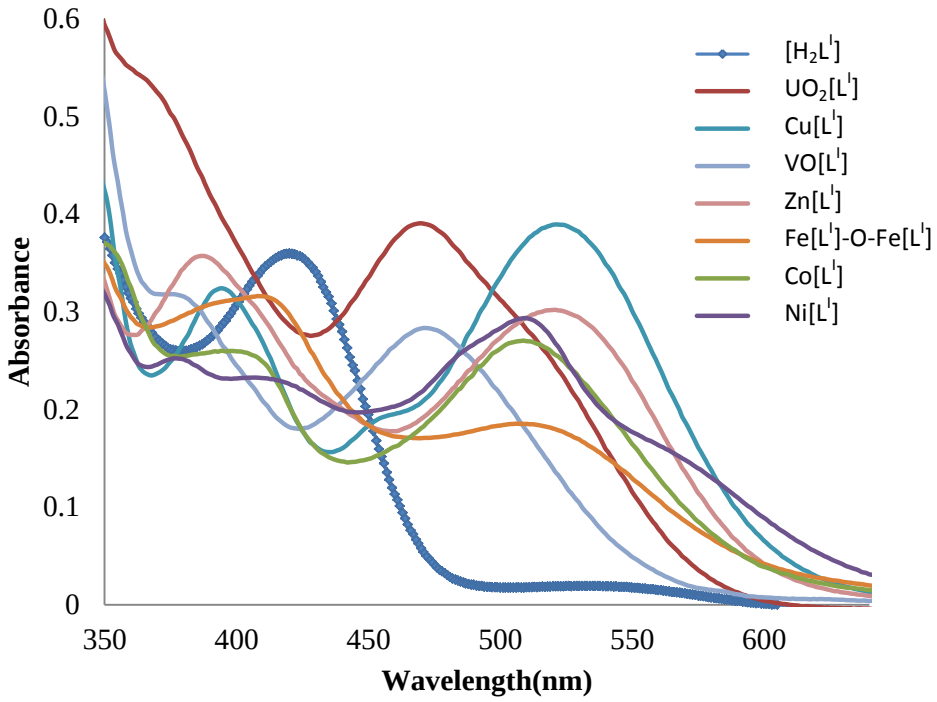



**Figure 2.6**. UV-Vis spectral changes of M[$\mathbf{L^I}$] complexes at 20 μM concentration in pyridine.[31]

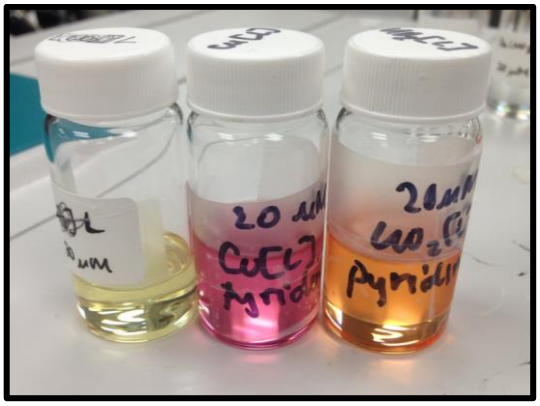


**Figure 2.7.** Vials with 20 μM solutions of $\mathbf{H_2L^I}$, Cu[$\mathbf{L^I}$] and $UO_2$[$\mathbf{L^I}$] in pyridine.

The growth of these charge transfer peaks is visualized in the metal titration spectra. Each metal salt was added to 20 μM solutions of the free base and are shown below in **Figures 2.8-2.13**. Of note are the extended mix times necessary for $UO_2^{2+}$. The rearrangement of the ligand

pocket to accommodate the larger atomic radius of uranium, coupled with the need for a fifth coordination site for a solvent molecule, requires extended periods of time.

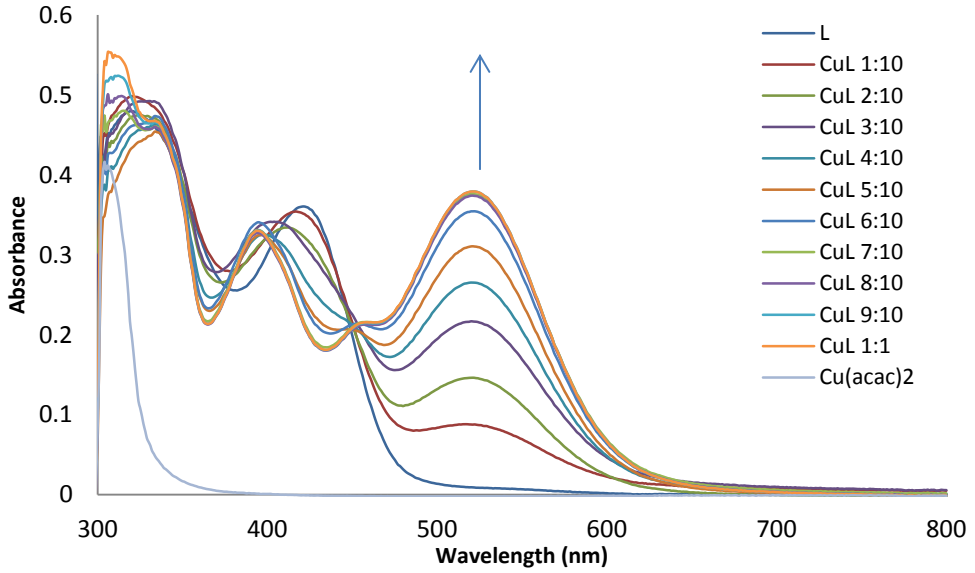



**Figure 2.8.** $Cu(acac)_2$ titration of the ligand in pyridine indicates a 1:1 $Cu^{2+}$ to $H_2L^I$. $H_2L^I$ concentration was kept at 20 μM. Spectra were obtained minutes after the solutions were made.[30]

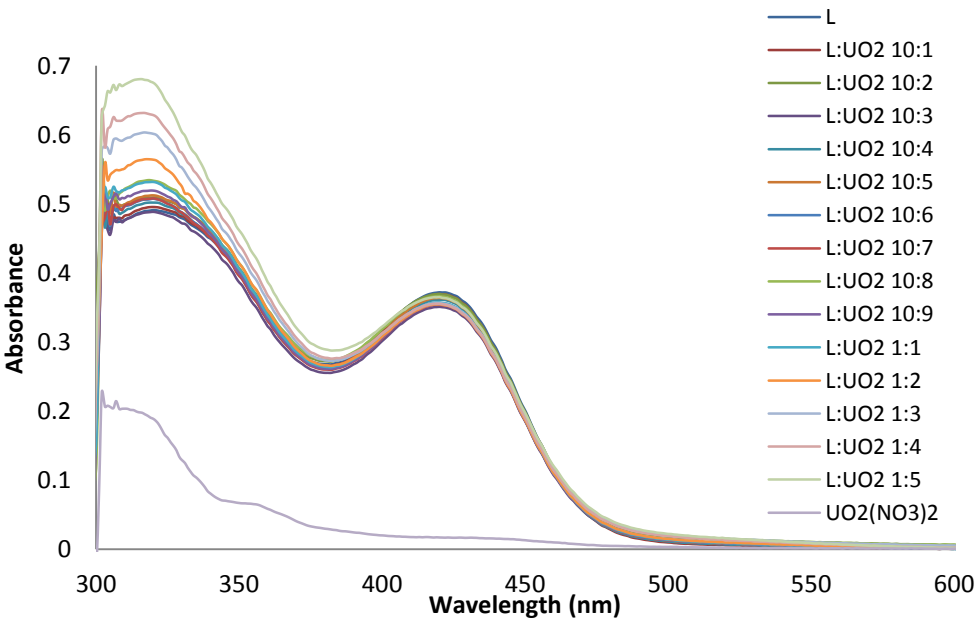



**Figure 2.9.** $UO_2(NO_3)_2$ titration of the ligand in pyridine, indicating no binding. $H_2L^I$ concentration was kept at 20 μM. Spectra were obtained minutes after the solutions were made.[30]

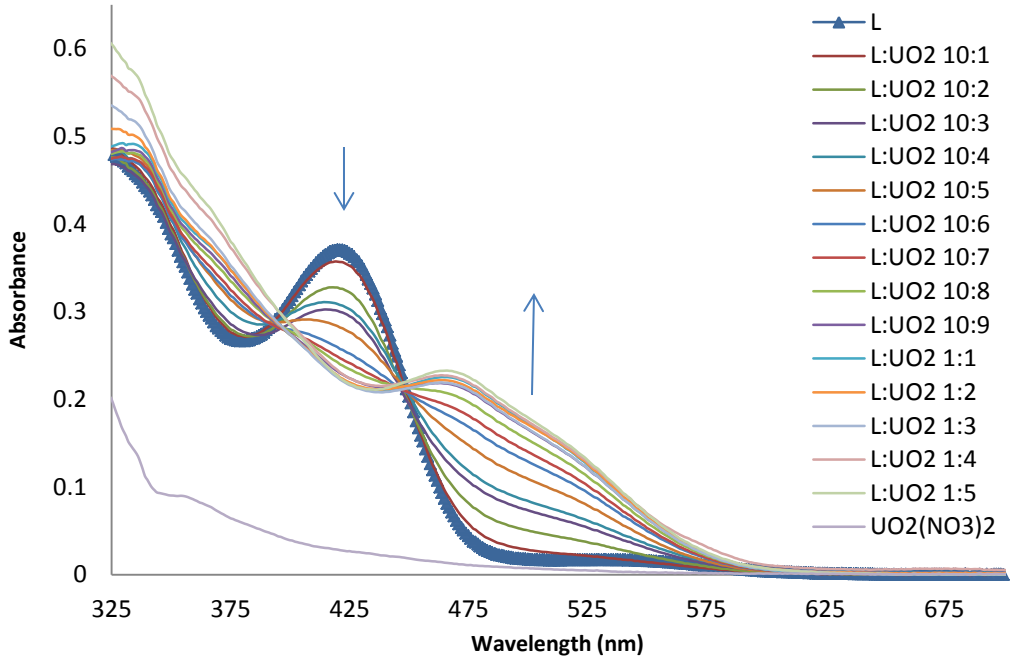



**Figure 2.10.** $UO_2(NO_3)_2$ titration of the ligand in pyridine indicates a 1:1 $UO_2^{2+}$ to $H_2L^I$ complex. $H_2L^I$ concentration was kept at 20 µM. Spectra were obtained after 3 days.[30]

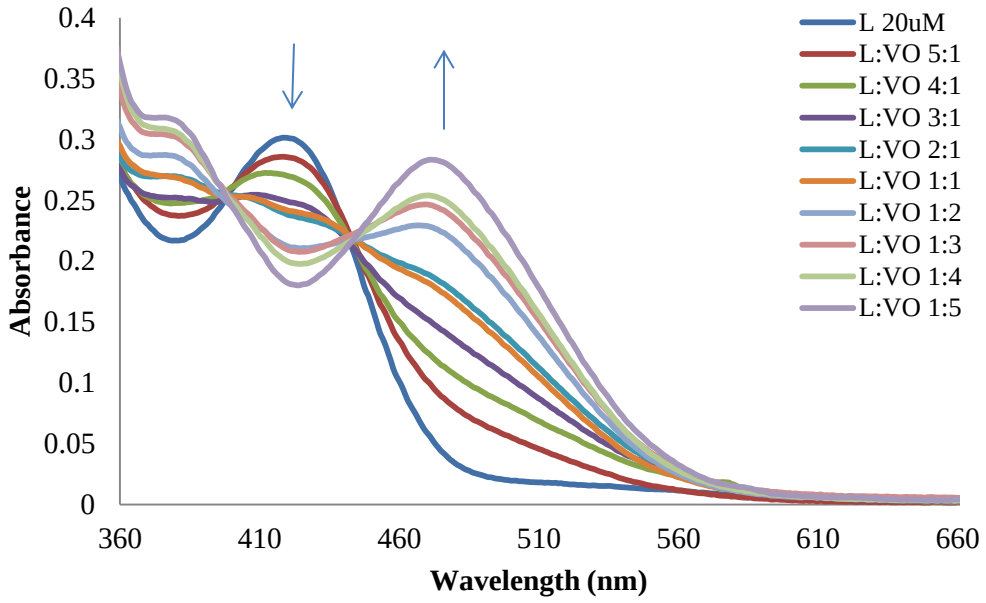



**Figure 2.11.** UV Vis spectrum of 20 µM salphenazine **[$H_2L^I$]** solution with varying $VO(acac)_2$ concentrations in pyridine after 72 hours stir time.[31]

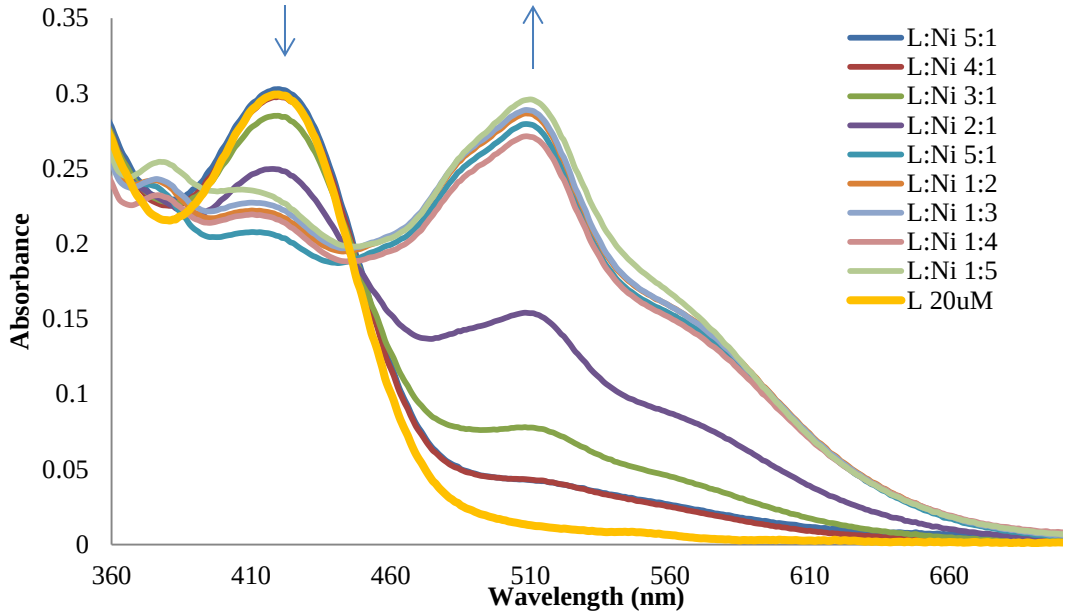



**Figure 2.12.** UV Vis spectrum of 20 µM salphenazine **[$H_2L^I$]** solution with varying Ni(acetate)$_2$ concentrations in pyridine after 15 minute stir time.[31]

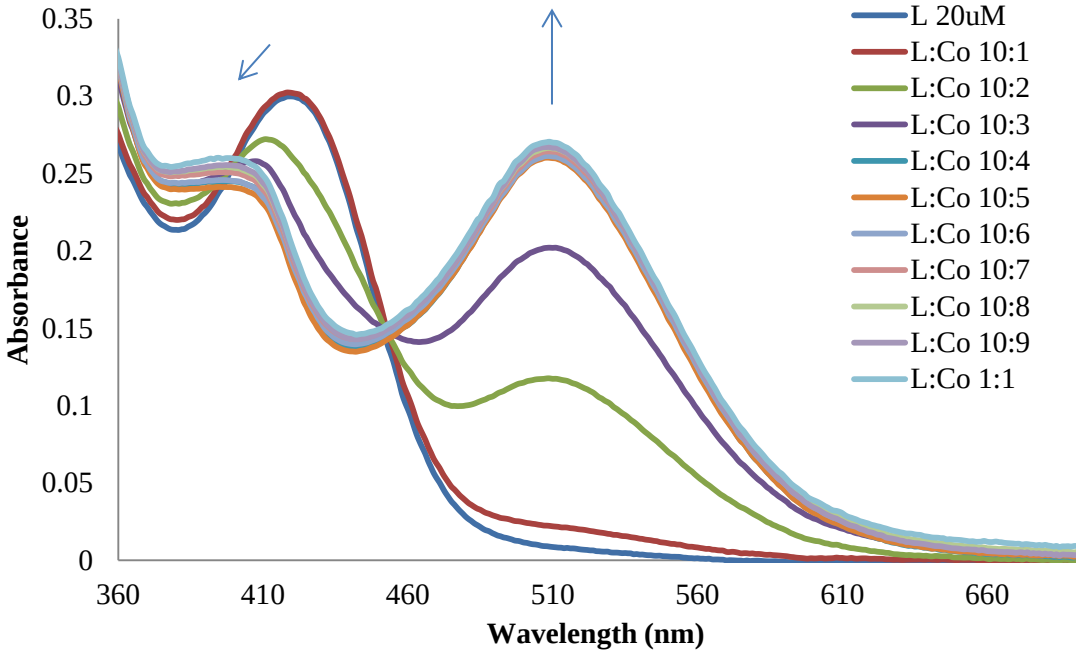
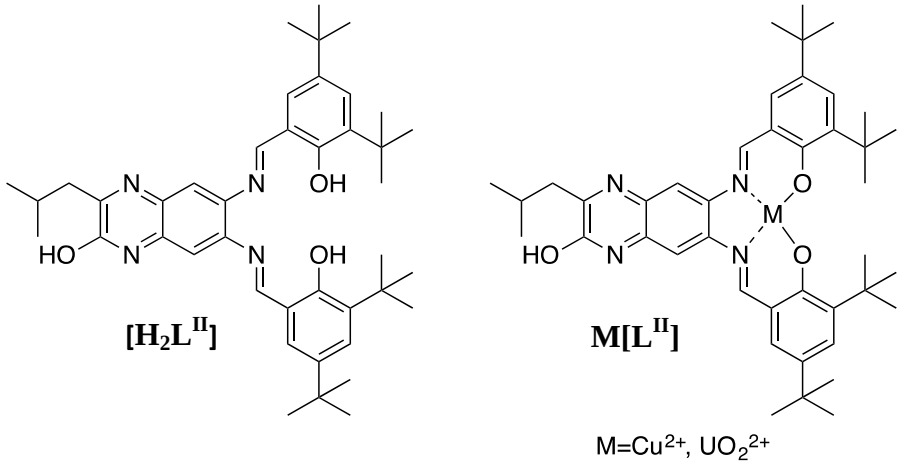



**Figure 2.13.** UV Vis spectrum of 20 µM salphenazine **[$H_2L^I$]** solution with varying Co(acetate)$_2$ concentrations in pyridine after 15 minute stir time.[31]

While extra time was necessary for the complexation of uranyl, in comparison to the other earth abundant first row transition metals, this chemistry represents a colorimetric chemosensor that can identify uranyl solutions over transition metal solutions. Further optimization of the binding geometry is necessary to create a rapid, on-site detection method.

**Electrochemistry**

Cyclic voltammagrams for the salphenazine compounds [$\mathbf{H_2L^I}$], $UO_2$[$\mathbf{L^I}$], and Cu[$\mathbf{L^I}$] are shown in **Figure 2.14**. The cyclic voltammagrams of salqu compounds (**Scheme 2.2**) [$\mathbf{H_2L^{II}}$], $UO_2$[$\mathbf{L^{II}}$], and Cu[$\mathbf{L^{II}}$] are compared in **Figure 2.15**. The change in stability of ligand oxidation was also investigated. All compounds were studied at 1.0 mM concentration in a dichloromethane solution with 0.100 M of tetra-n-butylammonium perchlorate electrolyte. Experiments were run with a scan rate of 0.10-1.50 V $s^{-1}$ on a platinum working electrode vs. a Ag/AgCl reference electrode and a platinum wire counter electrode.




**[$\mathbf{H_2L^{II}}$]** **M[$\mathbf{L^{II}}$]**

**Scheme 2.2**. Salqu [$\mathbf{H_2L^{II}}$] and salqu complexes M[$\mathbf{L^{II}}$], synthesized according to literature procedure.[31]

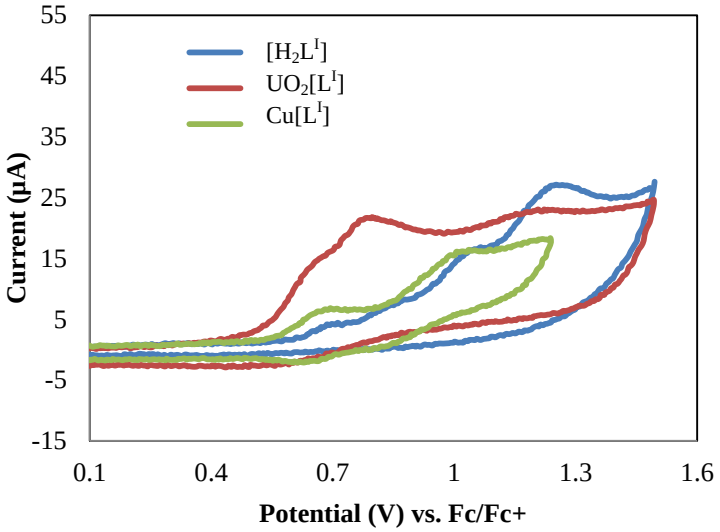



**Figure 2.14**. Cyclic voltammagram of [$\mathbf{H_2L^I}$], $UO_2$[$\mathbf{L^I}$], and Cu[$\mathbf{L^I}$]. Conditions: 0.5 mM ligand and complexes in dichloromethane, room temperature, tetra-n-butylammonium perchlorate (0.1 M) as electrolyte with a 0.10 V $s^{-1}$ scan rate.[31]

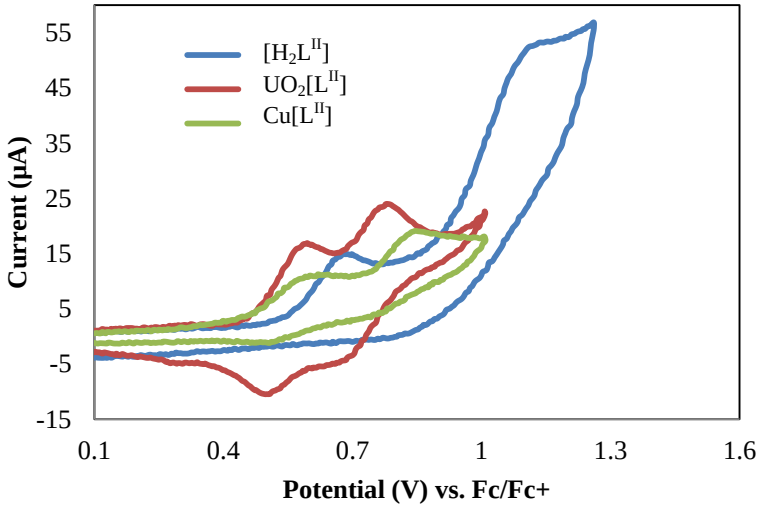



**Figure 2.15**. Cyclic voltammagram of [$\mathbf{H_2L^{II}}$], $UO_2$[$\mathbf{L^{II}}$], and Cu[$\mathbf{L^{II}}$]. Conditions: 1.0 mM ligand and complexes in dichloromethane, room temperature, tetra-n-butylammonium perchlorate (0.1 M) as electrolyte with a 0.10 V $s^{-1}$ scan rate.[31]

The salphenazine [$\mathbf{L^I}$] ligand shows four oxidation peaks, at $E_p^{ox,a}$ = 0.72 V, $E_p^{ox,b}$ = 0.89 V, $E_p^{ox,c}$ = 1.07 V, and $E_p^{ox,d}$ = 1.27 V as compared to the ferrocene ferrocenium redox couple as an internal standard, none of which are reversible. This result suggests [$\mathbf{H_2L^I}$] can stabilize not

only the cationic radical on the phenol groups, but can further oxidize. Reduction peaks were not present in [$\mathbf{H_2L^I}$]. The same is not true for salqu [$\mathbf{H_2L^{II}}$]; two oxidation peaks at $E_p^{ox,a}$ = 0.68 V and $E_p^{ox,b}$ = 1.11 V and two reduction peaks at $E_p^{red,a}$ = -0.609 V and $E_p^{red,b}$ = -1.12 V which are all not reversible are observed (shown in **Figure 2.20**). The two oxidation peaks are indicative of phenoxyl radicals formed from single electron oxidations.[50-52] The two reduction peaks are indicative of reduction of the imine nitrogen.[50-52]

One oxidation peak of [$\mathbf{H_2L^I}$] is not observed in the salphenazine complex Cu[$\mathbf{L^I}$] which has oxidation peaks at $E_p^{ox,a}$ = 0.63 V, $E_p^{ox,b}$ = 0.75 V, $E_p^{ox,c}$ = 1.16 V. The three remaining oxidation peaks do not shift in oxidation potential from the ligand by more than $E_p^{ox}$ = 0.050 V suggesting minimal stabilization of the phenoxyl radicals formed upon oxidation by the copper ion.[50] Two of the oxidation peaks from [$\mathbf{H_2L^I}$] are absent from the complex $UO_2$[$\mathbf{L^I}$] voltammagram. Two oxidation peaks at $E_p^{ox,a}$ = 0.68 V and $E_p^{ox,b}$ = 0.98 V remain and are now quasireversible, suggesting that the phenoxyl radicals are stabilized by the uranyl ion, with separation of the anodic of cathodic peaks of 60 and 100 mV respectively shown in **Figure 2.15**. A new reduction peak at $E_p^{red}$ = -0.38 V is observed in the complex $UO_2$[$\mathbf{L^I}$] that is not present in the free base, suggesting that the uranyl ion stabilizes the π–system enough to reduce the imine nitrogen that could occur in the free base [$\mathbf{H_2L^I}$] (**Figures 2.16-2.17**).

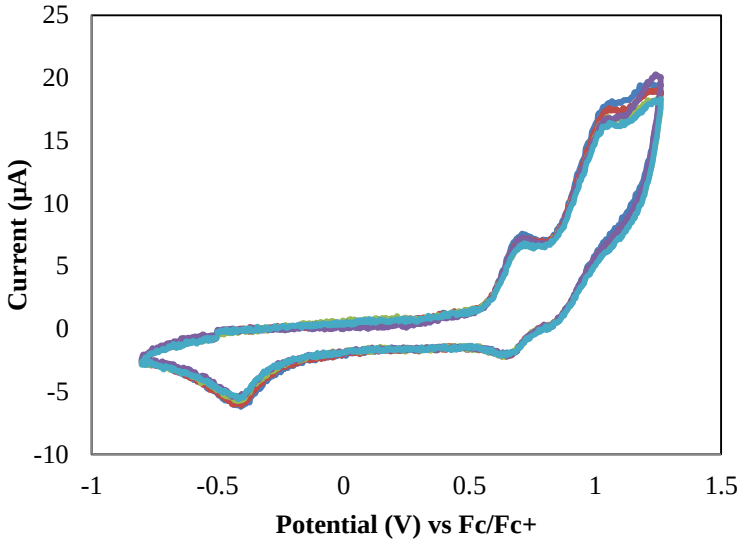



**Figure 2.16.** Cyclic voltammagram of **$UO_2[L^I]$** Conditions: 0.5 mM complex in dichloromethane, room temperature, tetra-n-butylammonium perchlorate (0.1 M) as electrolyte. Scan rate 0.100 V/s.[31]

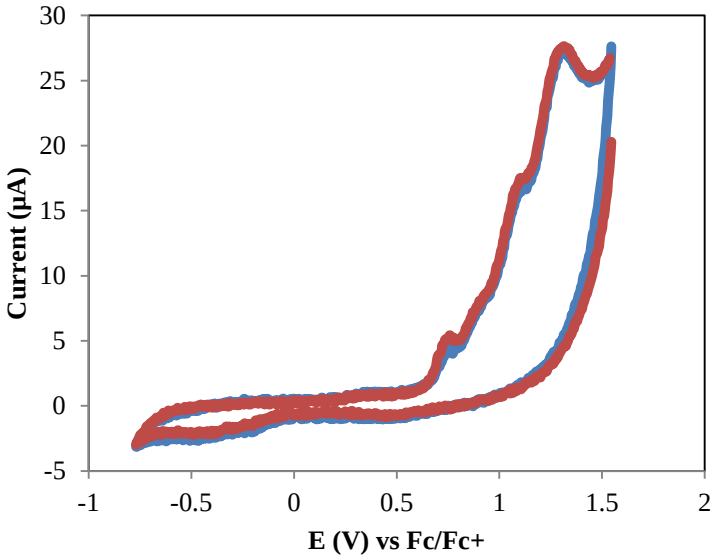



**Figure 2.17.** Cyclic voltammagram of Salphenazine **$[H_2L^I]$** Conditions: 0.5 mM ligand in dichloromethane, room temperature, tetra-n-butylammonium perchlorate (0.1 M) as electrolyte. Scan rate 0.100 V/s.[31]

The oxidation peaks in the salqu complexes $UO_2[\mathbf{L^{II}}]$ and $Cu[\mathbf{L^{II}}]$ become quasi-reversible suggesting that the phenoxyl radicals are stabilized by the metal ions.[50] Complex

Cu[$\mathbf{L^{II}}$] has two single electron oxidation peaks at $E_p^{ox,a}$ = 0.56 V $E_p^{ox,b}$ = 0.75 V with anodic and cathodic peak potential separation values in the range of 50 – 70 mV (**Figure 2.18**). Complex $UO_2$[$\mathbf{L^{II}}$] (**Figure 2.19**) has two single electron oxidation peaks at $E_p^{ox,a}$ = 0.58 V, $E_p^{ox,b}$ = 0.81 V with anodic and cathodic peak potential separation values in the range of 20 – 50 mV that seem to be quasi-reversible at best. Both metal complexes show reversible ligand oxidation peaks at $E_p^{ox,a}$ and $E_p^{ox,b}$, indicative of phenol type radical oxidation of the ligand.[50] The average shifts in the oxidation potential from the free base [$\mathbf{H_2L^{II}}$] of $E_p^{ox}$ = 0.12 and $E_p^{ox}$ = 0. 032 (**Figure 2.20**) observed in complexes $UO_2$[$\mathbf{L^{II}}$] and Cu[$\mathbf{L^{II}}$] suggest moderate stabilization of the phenoxyl radical. A third cathodic peak $E_p^{red,c}$ = 0.31 V present in complex Cu[$\mathbf{L^{II}}$] which may be attributed to a Cu(III)-phenolate species that is present simultaneously with the Cu(II)-phenoxyl radical species.

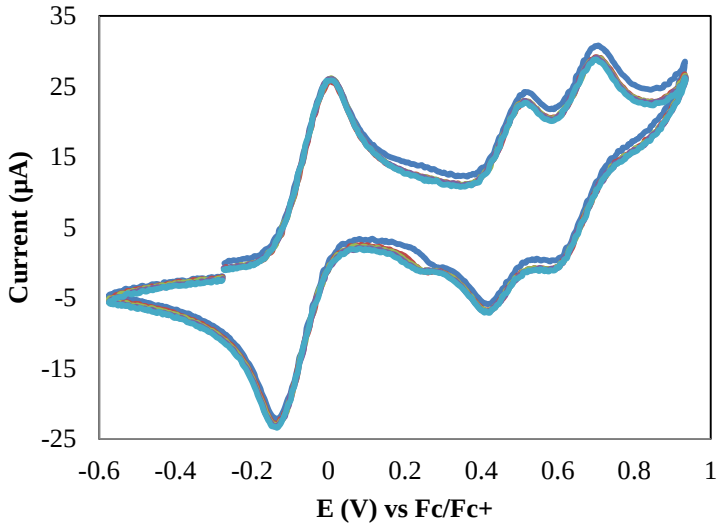



**Figure 2.18.** Cyclic voltammagram of **Cu[$\mathbf{L^{II}}$]** Conditions: 1.0 mM ligand in dichloromethane, room temperature, tetra-n-butylammonium perchlorate (0.1 M) as electrolyte. Scan rate 0.100 V/s.[31]

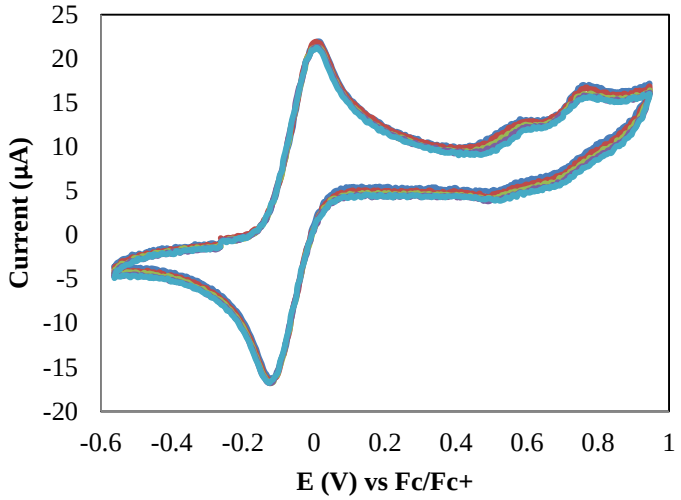



**Figure 2.19.** Cyclic Voltammagram of **$UO_2[L^{II}]$** Conditions: 1.0 mM ligand in dichloromethane, room temperature, tetra-n-butylammonium perchlorate (0.1 M) as electrolyte. Scan rate 0.100 V/s.[31]

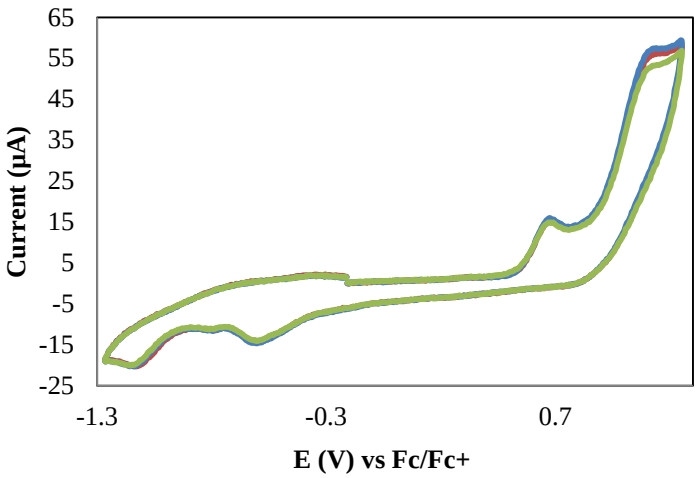



**Figure 2.20.** Cyclic Voltammagram of Salqu **$[H_2L^{II}]$** Conditions: 1.0 mM ligand in dichloromethane, room temperature, tetra-n-butylammonium perchlorate (0.1 M) as electrolyte. Scan rate 0.100 V/s.[31]

Complex $UO_2[\mathbf{L}^{I}]$ resulted in two reduction peaks, at $E_p^{red,a}$ = -1.75 V and $E_p^{red,b}$ = -2.23 V, both of which are visibly quasireversible in **Figure 2.21**. The $UO_2[\mathbf{L}^{II}]$ complex, has a reduction peak at $E_p^{red,a}$ = -1.87 V and $E_p^{red,b}$ = -2.11 V. The reduction of U(VI) to U(V) in

$UO_2$[salophen] occurs at -1.67 V in pyridine and -1.55 in DMSO.[51-52] Complex $UO_2$[$\mathbf{L^{II}}$] has an feature that is 0.20 V more negative than the reference $UO_2$[salophen] for the U(VI)/U(V) redox couple, revealing a better stabilization of the uranyl complex in the salqu ligand, even without the presence of a coordinating solvent, than in previously reported salophen complexes.[51-52]

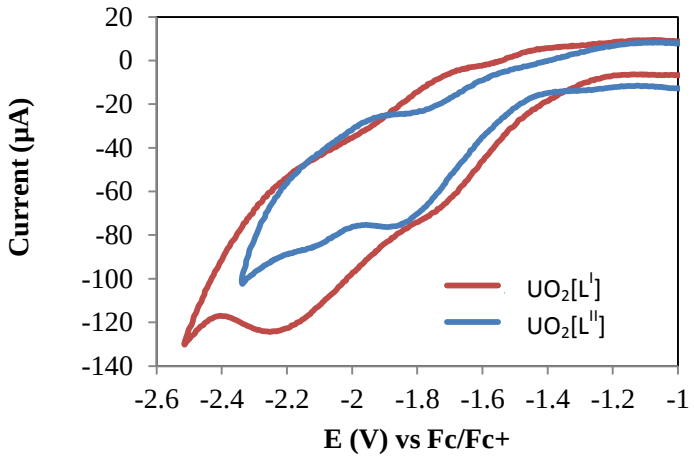



**Figure 2.21**. Cyclic Voltammagram of $UO_2$[$\mathbf{L^{I}}$] and $UO_2$[$\mathbf{L^{II}}$]. Conditions: 0.5 mM complex in dichloromethane, room temperature, tetra-n-butylammonium perchlorate (0.1 M) as electrolyte with the ferrocene redox couple as an internal standard.[31]

This stabilization is not as apparent in the $UO_2$[$\mathbf{L^{I}}$] complex which had a feature that is 0.10 V to that of the reference $UO_2$[salophen]. The second set of reduction peaks present in both $UO_2$[$\mathbf{L^{I}}$] and $UO_2$[$\mathbf{L^{II}}$] that was absent in $UO_2$[salophen] may be due to not only a reduction of uranium to the pentavalent uranyl cation, but subsequent disproportionation to U(IV) and U(VI) or a rearrangement of the uranium geometry. If a coordinating solvent is removed from the coordination sphere, an additional oxidation peak may present itself.

**Microfluidic Detection**

The electronic characterization shows that the aromatic M[$\mathbf{L^{I}}$] complexes have large molar extinction coefficients which allows these complexes to be measured at low

concentrations. Extending this fact and pairing with detection on a microspectrophotometer leads to the novel application of detection by spectral detection of metal-ligand complexes in mere picoliter volumes (4 x $10^2$ pL) on a microfluidic chip (**Figure 2.22**).

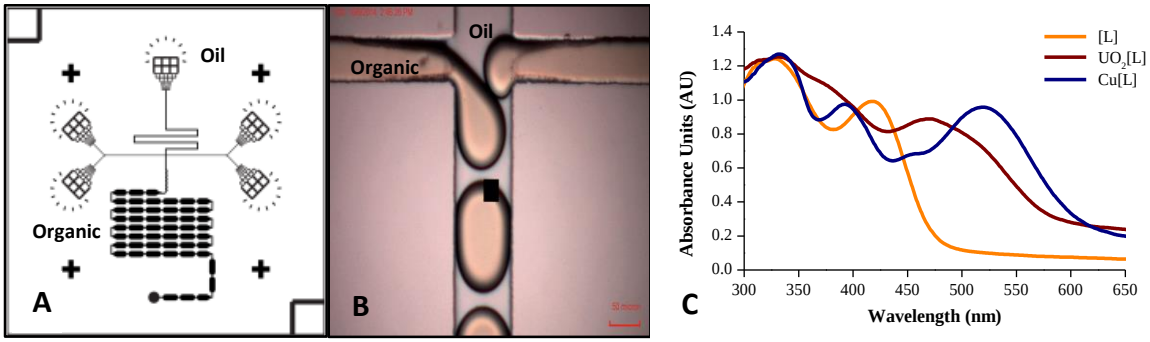



**Figure 2.22.** A. Droplet microchopper design. B. Oil and pyridine phases meet at a T-junction to form organic in oil droplets ($UO_2(NO_3)_2$ and ligand). C. CRAIC spectra of complexes collected on chip with 100 μm optical path length.[30]

Proof of concept for detection of these complexes within microfluidic droplets (pyridine droplets in perfluorocarbon oil) is shown in **Figure 2.22**. Spectra collected using the microdroplet system match well with spectra from macro-scale measurements (**Figure 2.23**). **Figure 22.24** shows an image from the microspectrophotometer showing the droplets and spectra obtained. Time consuming metal titrations can also be replicated in a fraction of the time with these methods. With a properly designed microfluidic device that includes exact mixing times, kinetics of metal binding could be determined.

Reducing sample volume by more than 6 orders of magnitude on this microchopper device[34] with concurrent spectroscopic detection (**Figure 2.22C**) could speed the ease of ligand screening within the field of environmental actinide sensing. By designing simple, easy-to-use devices, sample and waste volumes could be drastically reduced. The ability to reliably sense

actinide elements at a release event and quickly respond could play a large role in altering the current standards of immediate response in field detection procedures.

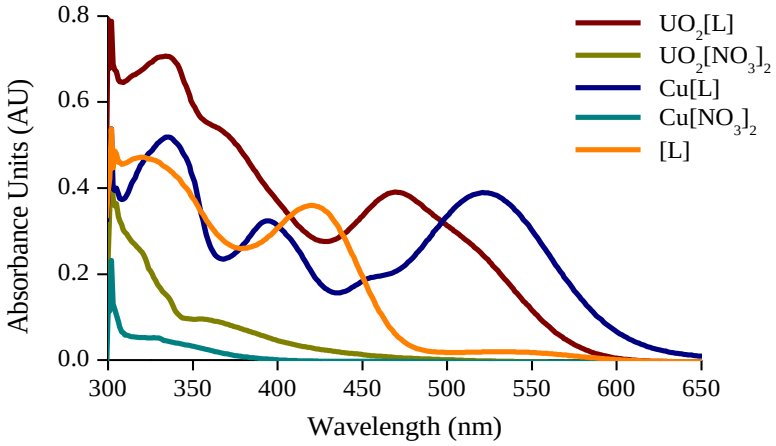



**Figure 2.23** UV-Vis spectrum of the metal starting materials [$Cu(NO_3)_2$, $UO_2(NO_3)_2$], [$H_2L^I$], $Cu[L^I]$, and $UO_2[L^I]$ complexes in pyridine at 20 μM.[30]

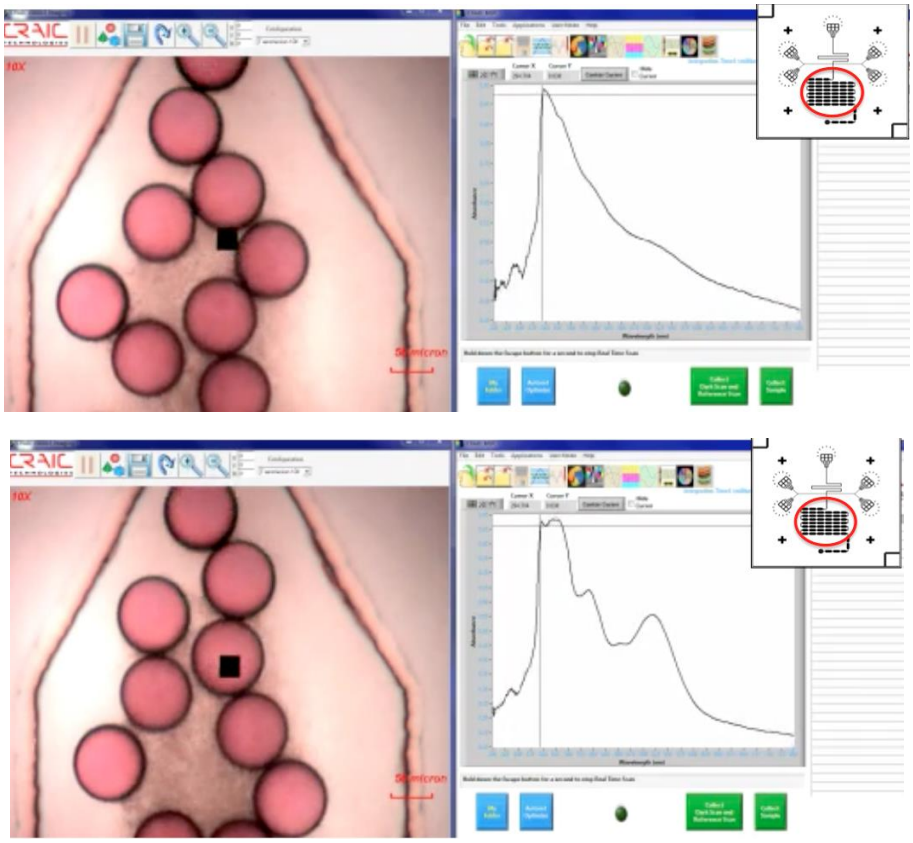


**Figure 2.24**. Images of the droplets corresponding real-time spectra showing the proof of concept that the spectra are maintained and only the droplets in the aperture are measured. Insets are the microchopper design with the position of the camera highlighted in red.

While current sensing methods for actinide elements have high selectivity and low limits of detection, they require large sample and reagent volumes and expensive instrumentation for assays that can take up to several days for the analysis to be completed.[53] By designing simple, easy-to-use devices, sample and waste volumes could be drastically reduced, opening up the potential for detection of the much more expensive and controlled neptunium or plutonium. This proof of concept requires less than 5 minutes to collect multiple spectra and determine sample composition in picoliter volumes if an adequate sensor were to be designed.

**Conclusions**

The salphenazine ligand, with the O-N-N-O salen type bonding motif, has been synthesized and characterized in the presence of various first row transition metals and uranium in the most common oxidation state in aqueous solution ($UO_2^{2+}$). Complexes have been characterized by x-ray crystallography and UV-visible spectroscopy, revealing the extended π-conjugation of these ligands results in differentiation of a uranyl signal as compared to these transition metal contaminants. The solid-state characterization of this series provides insight to the preferred coordination environment of uranyl in these conjugated systems. The π–π stacking of all the observed systems is within the confines of typical graphene stacking distance of 3.21-3.50 Å. The metal centres often are within 3.0-3.2 Å above a conjugated ring, suggesting possible metal backbonding to the ring system. These insights can guide further design for ligands with extended conjugation to be used as on-site actinide chemosensors. The free bases, compounds [$\mathbf{H_2L^I}$] and [$\mathbf{H_2L^{II}}$], along with the uranyl and copper complexes, $UO_2$[$\mathbf{L^I}$], Cu[$\mathbf{L^I}$], $UO_2$[$\mathbf{L^{II}}$], and Cu[$\mathbf{L^{II}}$], have been characterized by cyclic voltammetry. The extended π-conjugation that is deemed responsible for differentiation between metals in the spectroscopy

does not necessarily translate into a significant change in the U(V)/U(VI) redox couple, but may provide a secondary sensing method for chemosensors of this type.

## Materials and Methods

### Synthetic Details

*Caution! The uranium metal salts - $UO_2(NO_3)_2 \cdot 6H_2O$ - used in this study contained depleted uranium, standard precautions for handling radioactive materials were followed.*

The reagents 1,5-difluoro-2,4-dinitrobenzene (97%, Matrix Scientific), leucine methyl ester hydrochloride (TCI), diisopropylethylamine (Aldrich), ammonium hydroxide (BDH), ammonium formate (97%, Aldrich), palladium 5% on carbon, dry, type 87L (Alpha Aesar), 3,5-di-tert-butylsalicyaldehyde (98%, TCI), 2,3-diaminophenazine (98%, Aldrich), copper (II) acetate hydrate (>98%, MC/B), copper(II) acetylacetonate (98% STREM), vanadium(IV) bis(acetylacetonato)oxide (98%, STREM), cobalt(II) acetate tetrahydrate (Mallinckrodt), nickel(II) acetate tetrahydrate (Aldrich), zinc acetate hydrate (Aldrich) and tetra-n-butylammonium perchlorate (Alfa Aesar, electrochemical grade) were used as received without further purification. $UO_2(NO_3)_2 \cdot 6H_2O$ (98%, J. T. Baker) was recrystallized from an aqueous nitric acid solution, stored under hexanes and washed and dried before use. THF (BDH), chloroform (BDH), ethyl acetate (BDH), hexanes (BDH), acetone (BDH) and pyridine (anhydrous, Aldrich) were used as received with no further purification.

**Cu[$L^I$]**: 50 ml of pyridine was placed in a round bottom flask charged with a stir bar and heated at 80 ºC. A 0.2204 gram (0.9406 mmol) addition of 3,5-ditertbutyl salicyaldehyde was added to dissolve in the warmed solution. A 0.1253 gram (0.4787 mmol) addition of copper (II) acetylacetonate was dissolved in the warmed solution. In a separate beaker 0.0982 gram (0.4671

mmol) of 2,3-diaminophenazine was dissolved in about 25 ml of pyridine. The pyridine solution was added slowly with the aid of a syringe pump set to deliver 4 mL/hr. The reaction was allowed to proceed for 24 hours, and then the reaction mixture was allowed to come to room temperature and subsequently rotovapped to dryness. Column chromatography was performed with a mobile phase of 3:4 acetone to hexanes. This was set up in an attempt to isolate the red/maroon/violet spot seen on the TLC plate. Single crystals of X-ray diffraction quality were obtained after 2 days of slow evaporation. A THF solution containing ~50 mg was placed in several test tubes and then put in secondary containers for slow diffusion crystallization containing secondary solvents. Crystals were observed in the MeOH and EtOH slow evaporation chambers. CCDC: 1019624. HRMS (EI) m/z (M+H) calcd 703.3073, found 703.1739.

**$UO_2[L^I]$**: 50 ml of pyridine was placed in a round bottom flask charged with a stir bar and heated at 80 ºC. A 0.2219 gram (0.9500 mmol) addition of 3,5-di-tert-butylsalicyaldehyde was added to dissolve in the warmed solution. A 0.2381 gram (0.4740 mmol) addition of $UO_2(NO_3)_2 \bullet 6H_2O$ was then added to the flask and allowed to dissolve in the warmed solution. Several increments totaling 0.0996 g (0.474 mmol) of 2,3 diaminophenazine was then added to the flask in equal increments over the course of 1 hour. The reaction was then allowed to heat for 24 hours. This mixture was purified by column chromatography using a 1:1 ratio of ethyl acetate to hexanes as the mobile phase. A THF solution containing ~50 mg was placed in several test tubes and then put in secondary containers for slow diffusion crystallization containing secondary solvents. Crystals were observed in the MeOH and EtOH slow evaporation chambers. CCDC: 1019622. HRMS (EI) m/z (M+H) calcd 911.4183 found 911.4117.

**$[H_2L^I]$:** $UO_2[L^I]$ (100 mg) was dissolved in 20 mL of THF and added to 60 mL of chloroform. Nitric acid (80 mL, 1 M) was added to the red organic phase in a separatory funnel. The organic layer was washed a second time with deionized water (80 mL). The yellow organic layer was evaporated under reduced pressure and the ligand was separated from the monosubstitued side product via column chromatography (2:1 hexanes:ethyl acetate). Yield: 40%; orange crystals were grown from slow evaporation of the mobile phase. Products were confirmed via mass spec analysis HRMS (EI) m/z: (M+H) calcd 643.3934, found 643.3942. CCDC: 1452415.

**$VO[L^I]$:** 2,3-diaminophenazine (231 mg, 1.10 mmol) was dissolved in 35 mL of pyridine and added slowly to a round bottom flask containing 3,5-ditertbutylsalicylaldehyde (507 mg, 2.17 mmol), vanadium(IV) bis(acetylacetonato)oxide (281 mg, 1.06 mmol), 20 mL of pyridine, and a stir bar. The reaction vessel was heated to 80 °C for 24 hours. The solvent was removed using a rotary evaporator, and the remaining solid dried in a vacuum oven at 60 °C overnight. This crude solid was purified using column chromatography (2:1 hexanes:ethyl acetate). Yield: 27.4 %; red crystals were grown from slow diffusion of methanol into a saturated solution in THF. CCDC: 1452867. HRMS (EI) m/z (M+H) calcd 708.3166, found 708.3269.

**$Zn[L^I]$:** 2,3-diaminophenazine (197 mg, 0.940 mmol) was dissolved in 35 mL of pyridine and subsequently added slowly to a round bottom flask containing 3,5-ditertbutylsalicylaldehyde (505 mg, 2.18 mmol), zinc acetate dihydrate (237 mg, 1.04 mmol), 20 mL of pyridine, and a stir bar. The reaction vessel was heated to 80 °C for 24 hours. The solvent was removed using a rotary evaporator, and the remaining solid was dried in a vacuum oven at 60 °C overnight. This crude solid was purified using column chromatography (2:1 hexanes:ethyl acetate). Yield: 24.2 %; red crystals were grown from slow diffusion of methanol into a saturated

solution in THF. CCDC: 1452244. Metal complex formation was confirmed via UV spectroscopy, $\lambda_{max}$ = 387 nm ($\varepsilon$ = 1.79 x $10^4$ $cm^{-1}$ $M^{-1}$) and 521 nm ($\varepsilon$ = 1.51 x $10^4$ $cm^{-1}$ $M^{-1}$). IR spectroscopy, 3417.92(m), 2955.96(m), 1612.52(s), 1595.16(s), 1432.17(m), 1383.9(m), 1164.06(m), 1128.38(m), 1026.15(w), 983.71(w), 908.49(w), 870.88(w), 755.14(m), 677.99(w) $cm^{-1}$. HRMS (EI) m/z: (M+H) calcd 705.3069, found 643.3734. The HRMS matrix was found to be acidic and stripped the zinc out of the complex. The observed ion at 643.3734 m/z indicates the presence of the protonated free base.

**Fe[$L^I$]-O-Fe[$L^I$]:** 2,3-diaminophenazine (211 mg, 1.01 mmol) was dissolved in 35 mL of pyridine and subsequently added slowly to a round bottom flask containing 3,5-ditertbutylsalicylaldehyde (540. mg, 2.31 mmol), iron(III) trichloride hexahydrate (277 mg, 1.03 mmol), 20 mL of pyridine, and a stir bar. The reaction vessel was heated to 80 °C for 24 hours. The solvent was removed using a rotary evaporator. The remaining solid was dried in a vacuum at 60 °C oven overnight. The resulting crude solid was purified using column chromatography (4:3 hexanes:acetone). Yield: 21.2 %; red crystals were grown from slow evaporation of mobile phase. CCDC: 1018600. The dimer dissociates in acidic solution to $[FeL^I]^+$. HRMS (EI) m/z: ($M^+$) calcd 696.3127, found 696.3117.

**Co[$L^I$]:** 2,3-diaminophenazine (201 mg, 0.958 mmol) dissolved in 35 mL of pyridine was added slowly to a round bottom flask containing 3,5-ditertbutylsalicylaldehyde (541 mg, 2.31 mmol), cobalt(II) acetate hydrate (220. mg, 0.885 mmol), 20 mL of pyridine, and a stir bar. The reaction vessel was heated to 80 °C for 24 hours. The solvent was removed using a rotary evaporator, and the remaining solid was dried in a vacuum oven at 60 °C overnight. The resulting crude solid was purified using column chromatography (4:3 hexanes:acetone). Yield: 20.1 % HRMS (EI) m/z: (M+H) calcd 699.3109, found 699.3079.

**Ni[$L^I$]:** 2,3-diaminophenazine (190. mg, 0.904 mmol) was dissolved in 35 mL of pyridine and added slowly to a round bottom flask containing 3,5-ditertbutylsalicylaldehyde (485 mg, 2.07 mmol), nickel(II) acetate hydrate (193 mg, 0.778 mmol), 20 mL of pyridine, and a stir bar. The reaction vessel was heated to 80 °C for 24 hours. The solvent was removed using a rotary evaporator, and the remaining solid was dried in a vacuum oven at 60 °C overnight. The crude solid was purified using column chromatography (2:1 hexanes:ethyl acetate). The mobile phase was evaporated under reduced pressure to yield a dark red solid. Yield: 36.9 %. HRMS (EI) m/z: (M+H) calcd 699.3209, found 699.3221.

Synthesis of 6,7-diamino-2-quinoxalinol and 3,5-ditertbutylsal-2-quinoxalinol (salqu) **[$H_2L^{II}$]**, **$UO_2$[$L^{II}$]**, and **Cu[$L^{II}$]** were prepared using previously reported procedures. [26, 54] Purity was confirmed by HRMS and NMR spectroscopy.

**Crystallographic Details**

Datasets were collected on a Bruker SMART APEX CCD X-ray diffractometer unit using Mo Kα radiation, from crystals mounted in Paratone-N oil on glass fibers. SMART (v 5.624) was used for preliminary determination of cell constants and data collection control. [$\mathbf{H_2L^I}$], Zn[$\mathbf{L^I}$] and Fe[$\mathbf{L^I}$]-O-Fe[$\mathbf{L^I}$] datasets were collected at 180 K, and $UO_2$[$\mathbf{L^I}$], Cu[$\mathbf{L^I}$], and VO[$\mathbf{L^I}$] datasets were collected at 296 K. Determination of integrated intensities and global cell refinement were performed with the Bruker SAINT software package using a narrow-frame integration algorithm.[55] The program suite SHELXL (v 5.1) was used for space group determination, structure solution, and refinement. Refinement was performed against $F^2$ by weighted full-matrix least squares, and empirical absorption correction (SADABS) was applied.[56] The olex2.refinement package using Gauss-Newton minimization was used for further

refinement and to generate a solvent mask to account for the 3 methanol molecules in the unit cell of VO[$\mathbf{L^I}$] and for 2 interstitial THF molecules in the unit cell of Zn[$\mathbf{L^I}$].[57] Projections were generated using the Olex2.1-1 graphics program.[57] Complete lists of bond lengths, angles, refinement information, atomic coordinates, and hydrogen bonding are in Appendix I.

**Spectroscopic Details**

UV-Vis experiments were performed on a Varian Cary 50 WinUV Spectrophotometer. Pyridine solutions for each titration were made individually and stirred for 5 minutes before data collection, unless otherwise noted. All solutions were 20 μM in ligand.

**Electrochemical Details**

Cyclic voltammetry experiments were performed using a Pine AFCBP1 bipotentiostat driven by a PC with the Aftermath software package. All experiments were completed with a Pt disk working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode (BASi MF-2052). Solutions for cyclic voltammetry experiments were 1.0 mM in the salqu metal complex or ligand (M[$\mathbf{L^{II}}$] and [$\mathbf{H_2L^{II}}$]), or 0.5 mM in the salphenazine metal complex or ligand (M[$\mathbf{L^I}$] and [$\mathbf{H_2L^I}$]). All solutions were made in dichloromethane and contained 0.1 M tetra-n-butylammonium perchlorate (TBAP). Platinum electrodes were cleaned with piranha acid ($H_2SO_4/H_2O_2$), polished in between experiments, and all electrodes were stored according to factory suggestion. All experiments were performed at room temperature.

**Microfluidic Device Fabrication**

Microdevices were fabricated using polydimethylsiloxane (PDMS) and soft lithography techniques.[58-59] The silicon wafer master design (**Figure 2.22**) was a previously established

droplet generating chip designed in house.[58] Wafers were pre-treated with 1 mL of chlorotrimethylsilane for 30 min. After mixing 10:1 base to curing agent of PDMS, the de-gassed mixture was cured on top of the wafer at 65˚C overnight. Once cured, the PDMS was carefully peeled off the wafer and designated inlet/outlets were punched for sample and outlet wells. The PDMS along with a glass microscope slide was then washed with methanol, dried with a nitrogen air gun, and cleaned with scotch tape. Once cleaned, both the PDMS chip and the microscope slide were placed in an air plasma cleaner for 45 seconds (Harrick Plasma) and immediately placed on top of each other to bond together. 1.5cm OD Tygon tubing was inserted into the outlet well, and a blunt ended needle was inserted into the opposite end of the tubing. Aquapel (Pittsburgh Glass Works) was applied to each of the inlet channels of the chip and pulled through with a mild vacuum to surface treat the channels. Methanol was washed through as well to remove any excess Aquapel. Chips were then placed back into the 65 ˚C oven to dry for at least 4 hours. Solutions were flowed through the chips passively, via a handheld, 25 mL syringe connected to the needle in the tubing. Chips were taped to the imaging stage to hold them in place. Vacuum was applied to the chip on the stage and the droplets were imaged directly on the chip. In order to form oil in organic droplets, 1.8% w/w Krytox 157 FSL surfactant (Dupont) in HFE-7500 oil (3M) droplet carrier fluid was applied to the oil well.[58]

**Microspectophotometer Imaging**

UV−Visible data were acquired from microfluidic droplets and microwells using a CRAIC Technologies 20/20 PV microspectrophotometer. 400 picoliter droplets were generated on the microfluidic chip and the data were collected from 200 to 800 nm. Microwell data was also measured using the same parameters and fixed pathlength. The exposure time was auto-optimized by the CRAIC Minerva 8.7.3.12 software.

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## Chapter 3: An Unusual Example of Pyridine Donor Schiff Base Uranyl Complexes and Zinc Enhanced Ligand Emission

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### Introduction

Nuclear power is a major contributor and integral asset to carbon neutral energy production for ever-increasing energy demands.[1] Interest in fundamental actinide research has been on the rise to illuminate their fundamental chemistry and pave the way for enhanced nuclear fuel remediation techniques.[2-5] Recently, depleted uranium has been investigated for applications in catalysis to complete difficult chemical transformations.[6-7] Researchers have also sought to characterize the degree of actinide covalency both synthetically and computationally using ligands featuring nitrogen donors.[8-9] Examples of uranium coordination have included pyrrole nitrogen donors in the ligand environment, but only a handful have included the less strongly coordinating pyridine.[10-11] Sessler and co-workers have explored changes in ligand aromatic character when a pyridine moiety is bound to an actinide, further exploring uncommon coordination geometries.[12]

Previously, we have described highly conjugated, tetradentate, mixed nitrogen and oxygen donor systems designed as chemosensors in on-site detection for uranyl, the most environmentally available oxidation state of uranium in aqueous and acidic solutions.[13-15] Other nitrogen donor systems that have been explored also involve mixed oxygen and nitrogen coordination environments.[16-19] These systems often require multiple synthetic steps to prepare and are not always easily accessed or derivatized. The synthetic ease, in particular as compared to macrocyclic uranyl chelators, and the ability to change the electronic characteristics of the ligand environment easily made these Schiff base ligands an ideal scaffold for uranyl detection. The pentadentate coordination environment of a 2,6-bis[1-[(2-hydroxyphenyl)imino] ethyl]pyridine (**$[H_2L^{III}]$**) ligand scaffold was designed to accommodate the larger atomic radius of uranium as the uranyl dioxo cation, while fully occupying its equatorial plane. Here, four new uranyl ($UO_2^{2+}$) complexes utilizing this scaffold have been synthesized from successive condensation reactions and subsequent metal complexation.

Highly increased fluorescence was observed when **$[H_2L^{III}]$** was complexed with Zn(II). Zinc has been long known to be a biologically essential trace metal, which is imperative for development, immunity, and endocrine function.[20-21] Misregulation of zinc ions has been linked to various diseases, specifically Alzheimer's and other neurodegenerative diseases.[22-23] Designing molecules that selectively bind and sense zinc ions is therefore of great importance.[24-25] Recently, a common binding motif in many of these examples for biological imaging and ratiometric fluorescent sensing is the N-C-C-C-O binding pocket similar to that of a Salen ligand.[26-30] A few examples of pentadentate ligand systems with mixed oxo and aza donors have been reported for this purpose as well.[31-32] The characterization of solution phase

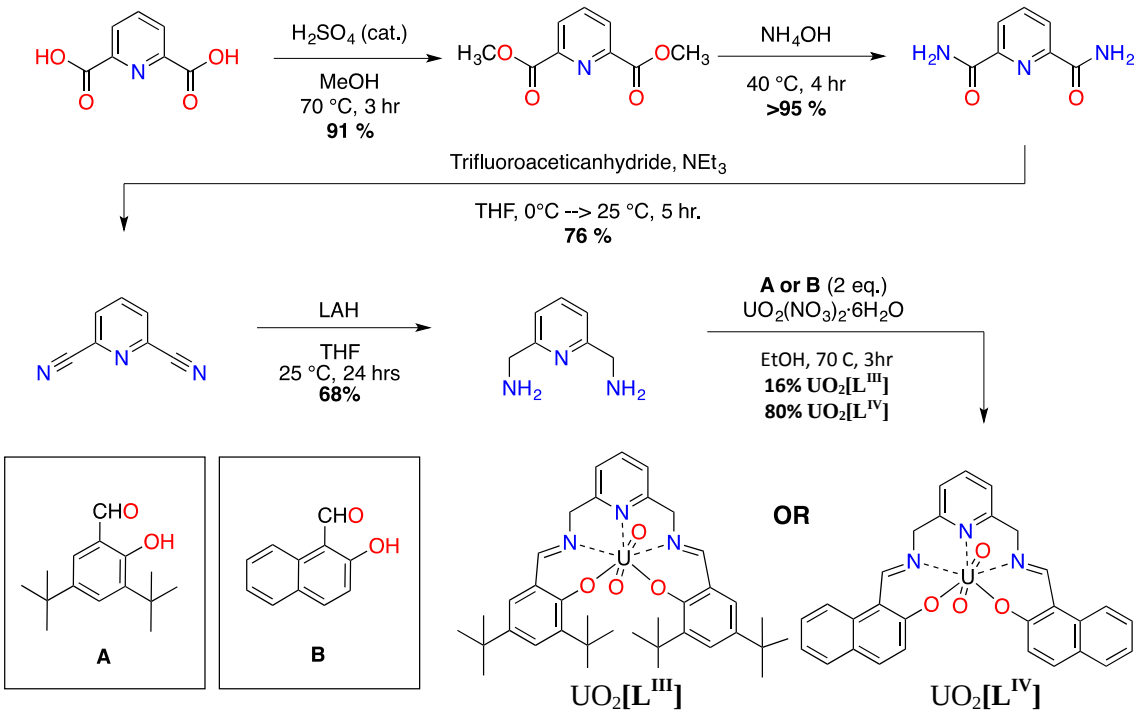
absorbance and increased emission of **Zn[$L^{III}$]**, in hopes of this system being of use for zinc sensing, is reported.

## Results and Discussion

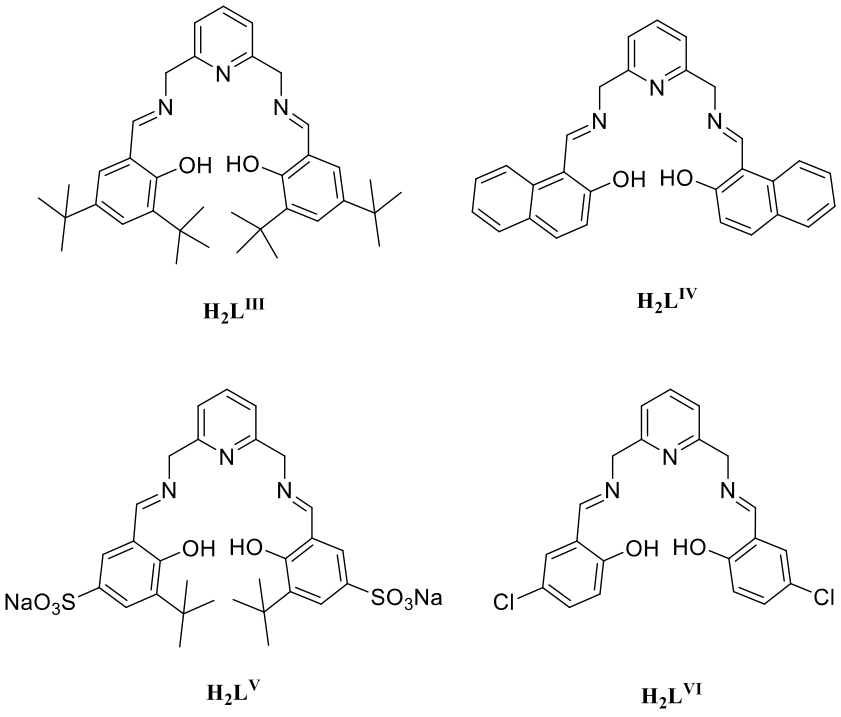
### Synthesis

The expansion and simultaneous change in π-overlap of the ligand in the tetradentate salen-type salqu and salphenazine ligands have been used to differentiate between actinide and transition metals of potential concern.[13-15] One limitation of the tetradentate binding geometry is the expansion of the binding pocket to accommodate the larger atomic radius of uranium often results in poor coordination kinetics and subsequently longer detection times. The dioxo cation uranyl has been shown to prefer a pentagonal bipyramidal binding geometry, explaining the presence of a coordinating solvent molecule in numerous reported solid-state structures. The observation of this preference led to the design of the expanded mixed oxygen and imine nitrogen coordination environment, coupled with a pyridine donor to occupy the fifth site.

As shown in **Scheme 3.1**, the 2,6-bis [1-[(2-hydroxy-3,5-ditert-butylphenyl)imino]ethyl] pyridine (**[$H_2L^{III}$]**) and 2,6-bis[1-[(2-hydroxynapthyl)imino]ethyl]pyridine ligands (**[$H_2L^{IV}$]**) and the corresponding $UO_2$(VI) complexes ($UO_2$**[$L^{III}$]**, $UO_2$**[$L^{IV}$]**) were designed and synthesized from a commercially available starting material, 2,6-pyridinedicarboxylic acid, to accommodate the larger atomic radius of uranium and fully occupy its equatorial plane.[33] Additionally 2,6-bis [1-[(2-hydroxy-3-tert-butyl-5-sulfophenyl)imino]ethyl]pyridine (**[$H_2L^{V}$]**) and 2,6-bis [1-[(2-hydroxy-5-chlorophenyl)imino]ethyl]pyridine (**[$H_2L^{VI}$]**) and uranyl complexes ($UO_2$[$L^{V}$] and $UO_2$[$L^{VI}$]) were synthesized according to the same procedure (**Scheme 3.2**).




**Scheme 3.1.** Synthetic Scheme of $UO_2$**[L$^{Iii}$]** and $UO_2$**[L$^{IV}$]**[33]




**Scheme 3.2.** Representations of ligands **[$H_2L^{III}$]**, **[$H_2L^{IV}$]**, **[$H_2L^{V}$]**, and **[$H_2L^{VI}$]**.

## X-Ray Crystallography

The complex $UO_2$**[L$^{III}$]** (**Figure 3.1**) has U1-N1, U1-N2, U1-O1, and U1-O2 bond lengths of 2.532(2), 2.508(2), 2.2548(18), and 2.2604(18) respectively. These bond lengths are comparable (±0.08 Å) to previously synthesized tetradentate salen-type uranyl complexes.[15, 34-35] The U1-N3 bond length of 2.623(2) are comparable to other U-N bonds, and average of 2.59 Å from coordinating pyridine moieties in similar ligand environments.[36-37] The bond angles O1-U1-N1, N1-U1-N3, N3-U1-N2, N2-U1-O2, O2-U1-O1 of 69.54(7), 62.09(7), 61.81(7), 70.91(7), and 96.61(7) respectively describe a beautiful pentagonal bipyramidal coordination geometry around the uranium metal centre. The O3-U1-O4 angle of 175.83(9) is within previously reported ranges.[10-12, 15, 34-38] The crystallographic information for $UO_2$**[L$^{III}$]** and $UO_2$**[L$^{IV}$]** can be found in **Table 3.1**.

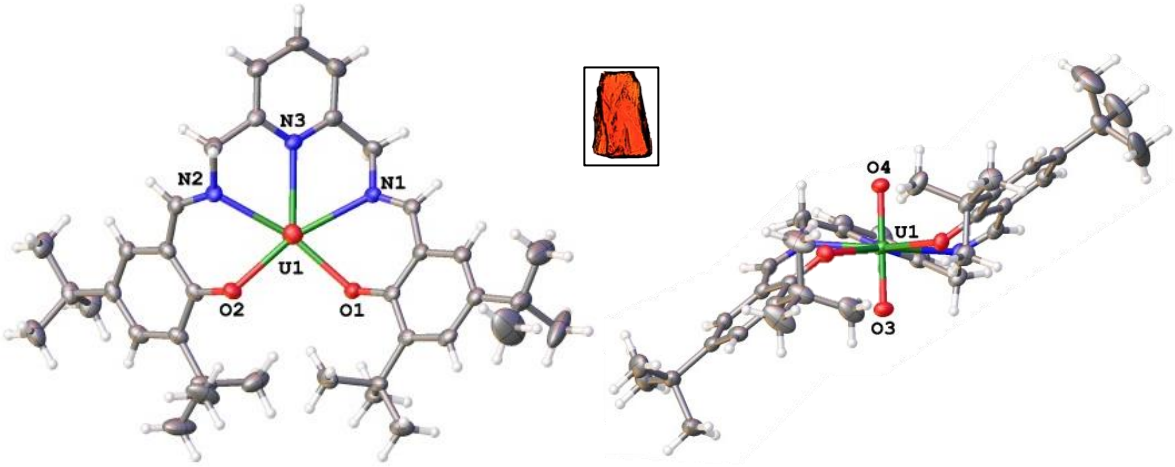



**Figure 3.1**. Projection of $UO_2$**[L$^{III}$]** is shown without the non-coordinating acetonitrile molecule. Hydrogen atoms are shown in white, nitrogen in blue, oxygen in red, and uranium in green. Inset image crystal dimensions: 0.2 x 0.09 x 0.03 mm.[33]

**Table 3.1**. Crystallographic data and details of data collection for $UO_2$**[$L^{III}$]** and $UO_2$**[$L^{IV}$]**.[33]

| | **$UO_2[L^{III}]\bullet CH_3CN$** | **$UO_2[L^{IV}]$** |
|---|---|---|
| **Empirical formula** | $C_{40}H_{52}N_4O_4U$ | $C_{29}H_{21}N_3O_4U$ |
| **Formula weight (g/mol)** | 890.88 | 713.54 |
| **Crystal size/mm$^3$** | 0.06 × 0.06 × 0.02 | 0.12 × 0.12 × 0.04 |
| **Crystal system** | orthorhombic | monoclinic |
| **Space group** | Pccn | $P2_1/c$ |
| **a/Å** | 13.9974(3) | 22.8062(10) |
| **b/Å** | 23.5111(5) | 7.2736(3) |
| **c/Å** | 23.6244(5) | 14.7805(6) |
| **α/°** | 90 | 90 |
| **β/°** | 90 | 97.3343(5) |
| **γ/°** | 90 | 90 |
| **Volume/Å$^3$** | 7774.7(3) | 2431.78(18) |
| **Z** | 8 | 4 |
| **$\rho_{calc}$mg/mm$^3$** | 1.499 | 1.9488 |
| **m/mm$^{-1}$** | 4.217 | 6.72 |
| **F(000)** | 3496 | 1320.2 |
| **Temperature/K** | 180(2) | 180.45 |
| **Radiation** | MoKα (λ = 0.71073) | Mo Kα (λ = 0.71073) |
| **Reflections collected** | 93148 | 61345 |
| **Independent reflections** | 11887 | 8098 |
| **Largest diff. peak/hole / e Å$^{-3}$** | 1.37/-0.74 | 3.18/-5.58 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0305, $wR_2$ = 0.0619 | $R_1$ = 0.0359, $wR_2$ = 0.0726 |
| **Goodness-of-fit on F$^2$** | 1.01 | 1.084 |

The complex $UO_2$**[$L^{IV}$]** (**Figure 3.2**) has U1-N1, U1-N2, U1-O1, and U1-O2 bond lengths of 2.486(3), 2.525(3), 2.264(3), and 2.267(3) respectively. These bond lengths are comparable to previously synthesized tetradentate uranyl chemosensors and to $UO_2$**[$L^{III}$]**.[15,34-35] The U1-N3 bond length of 2.566(3) is slightly shortened from the t-butyl analogue, $UO_2$**[$L^{III}$],** but only slightly shorter than the average U-N bond of 2.59 Å from other similar coordinating pyridine moieties in the literature.[36-37] The bond angles O1-U1-N1, N1-U1-N3, N3-U1-N2, N2-U1-O2, O2-U1-O1 of 69.83(10), 62.68(10), 62.99(9), 69.31(10), and 95.61(10) respectively describe a pentagonal bipyramidal coordination geometry around the uranium centre. The O3-

U1-O4 angle of 175.96(13) is also within previously reported ranges.[10-12, 15, 34-37] Dipicolinic acid (2,6-pyridinedicarboxylic acid) is a common coordination agent, and has been applied to the extraction of uranyl from acidic solutions.[39] The observed U-$N_{py}$ distance in $UO_2$**[L$^{III}$]** and $UO_2$**[L$^{IV}$]** is equivalent to, or shorter than, some examples of dipicolinic systems and their derivatives.[10,38-39]

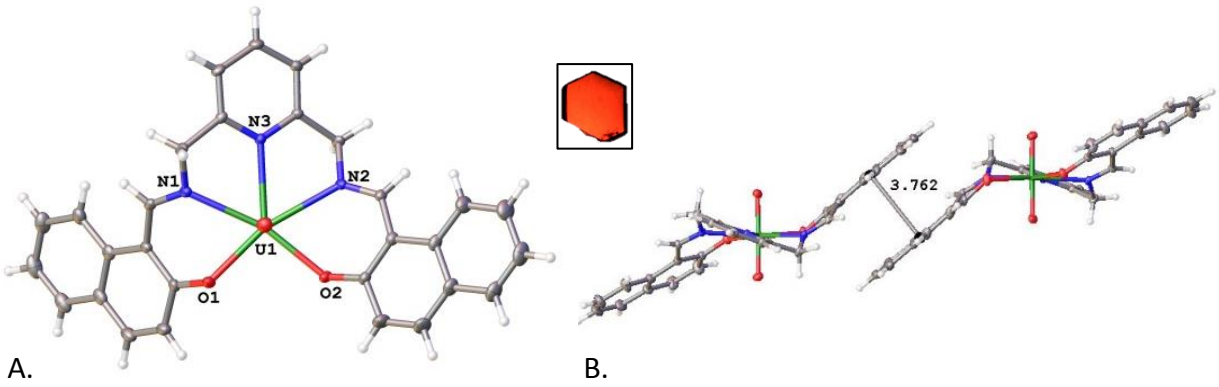



**Figure 3.2a**. Projection of $UO_2$**[L$^{IV}$]** is shown. Hydrogen atoms are shown in white, nitrogen in blue, oxygen in red, and uranium in green. Inset image is the crystal from the data collection. **Figure 3.2b.** Projections of $UO_2$**[L$^{IV}$]**, highlighting pi-pi stacking in the solid-state. Inset crystal dimenstions: 0.12 x 0.09 x 0.02 mm.[33]

The similarity of observed bond lengths and angles to tridentate and tetradentate systems discussed previously suggest that the preferred 5-coordinate binding in the equatorial plane is achieved without the necessity of significant ligand pocket expansion or solvent coordination. Thus, the improved coordination kinetics as compared to the ligand in Chapter 2, of a few seconds for $UO_2$**[L$^{III}$],** can be explained by this reduced need for ligand rearrangement. While $UO_2$**[L$^{III}$]** incorporated an interstitial acetonitrile solvent molecule, $UO_2$**[L$^{IV}$]** has π-π stacking interactions that reduced the void volume and simultaneously the need for an interstitial solvent molecule. The parallel offset π-π stacking interactions (3.76 Å) are highlighted in **Figure 3.2b** and are significantly longer than graphene (3.2-3.5 Å) and most examples of π-π interactions.[40-41]

**Spectroscopy**

Serial titrations of **[$H_2L^{III}$]** with the addition of $UO_2^{2+}$ or other common transition metals in methanol and dichloromethane were completed for comparison. In the UV-visible spectra a shift of the maximum of the free base, 334 nm (ε = 9,070 $cm^{-1}$ $M^{-1}$), to 356 nm (ε = 7,005 $cm^{-1}$ $M^{-1}$) is observed upon the addition of $UO_2$ as the nitrate salt in dichloromethane (**Figure 3.3**). This shift is accompanied by the growth of a charge transfer band at 419 nm (ε = 3,454 $cm^{-1}$ $M^{-1}$) and a large shoulder centred at 512 nm (ε = 1094 $cm^{-1}$ $M^{-1}$). These spectral changes are observed upon addition of 36 ppm of uranyl salt; modifying the ligand in future studies to include further conjugation would allow for a decrease in the limit of detection.

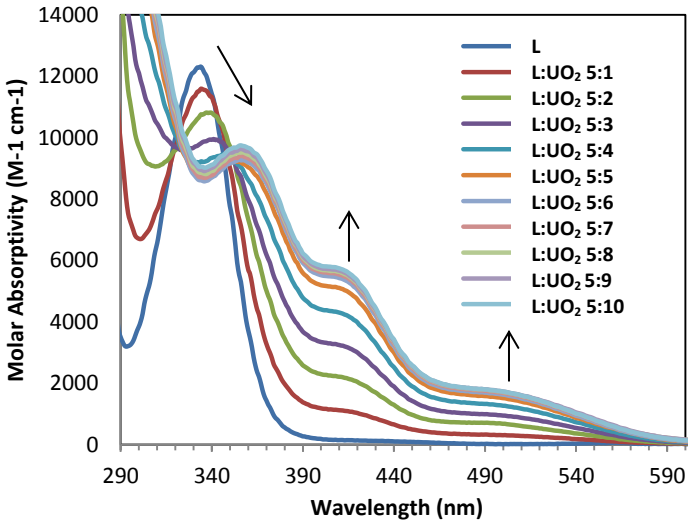



**Figure 3.3**. UV-Visible spectra of a serial titration of 0.123 mM **[$H_2L^{III}$]** in dichloromethane solution with an increasing ratios of $UO_2(NO_3)_2$, from 3:1 to 3:10 $\mathbf{L}^{III}$:$UO_2$. [33]

In an attempt to lower the limits of detection and characterize the potential effects of solvents, titrations in methanol (**Figure 3.4**) were also completed. Extinction coefficients were highest in non-coordinating solvents, but the metal salts are often not soluble in these solvents. Methanol was chosen to complete further metal titration experiments. Serial titrations of **[$H_2L^{III}$]**

were completed by introducing a known amount of various metal salts ($UO_2(NO_3)_2$, $Cu(C_2H_3O_2)_2$, etc…) to a solution of free base. Solutions consisted of 2 mL of 0.123 mM ligand, and approximately 30 µL of 1.5 mM metal salt. The actual volumes and concentrations varied depending on stock solutions, but 1/5 equivalent of metal salt was added per addition. Serial titrations were completed in DCM, EtOH and MeOH. The solutions were shaken for 3 seconds and replaced in the spectrometer followed by collection of the absorbance spectrum or fluorescence spectrum. This was repeated until an excess of metal salt was present. The absorbance at 420 nm and 500 nm increased in intensity as the absorbance at 340 nm shifted to 350 nm and reduced in intensity, until a 1:1 ratio of metal to ligand was obtained.

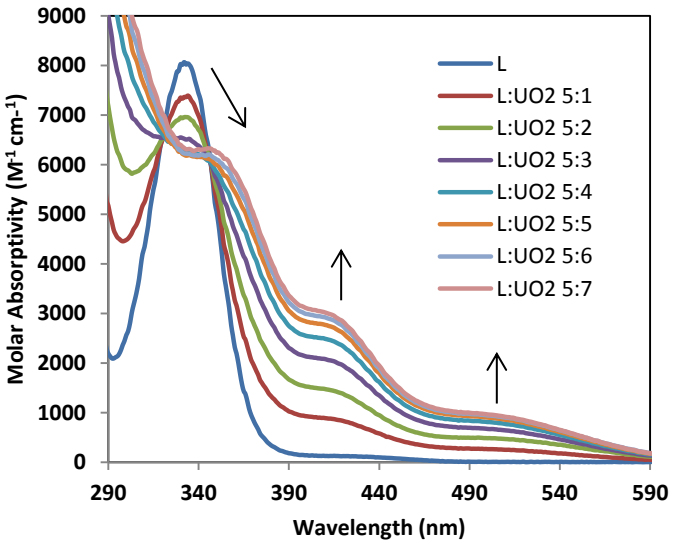



**Figure 3.4**. Absorbance spectrum of a serial titration completed via the general procedure of 0.123 mM $\mathbf{H_2L^{III}}$ in methanol solution with an increasing ratio of $UO_2(NO_3)_2$, from 5:1 to 5:7 $\mathbf{L^{III}}$:$UO_2$.[33]

Metal titration experiments from 0.2 equivalents of metal to 2 equivalents of common transition metal contaminants were completed using the same general procedure in methanol. The titration with copper(II) resulted in a decrease of the ligand peak at 384 nm and the growth

of a new charge transfer band at 399 nm ($\varepsilon$ = 5.77 x $10^3$ $cm^{-1}$ $M^{-1}$) growing charge transfer band at 600 ($\varepsilon$ = 3.47 x $10^2$ $cm^{-1}$ $M^{-1}$) nm (**Figure 3.5**). An isobestic point was observed at 360 nm. The addition of cobalt(II) resulted in the same decrease in ligand absorbance and an increase of absorbance at 415 nm ($\varepsilon$ = 5.11 x $10^3$ $cm^{-1}$ $M^{-1}$) (**Figure 3.6A**). The titrations of manganese(II), vanadyl(IV), and nickel(II) did not show significant changes in the absorbance spectra, suggesting that binding is not occurring strongly in methanol solution (**Figures 3.6B -3.6C**). Addition of zinc(II) resulted in reduction in the ligand peak and increase of a band at 386 nm ($\varepsilon$ = 7.21 x $10^3$ $cm^{-1}$ $M^{-1}$), and an isobestic point at 353 nm (**Figure 3.7**). The intensity of these absorbance features increased until a ratio of ligand to metal of 1:1.5 was reached, as shown in **Figure 3.8**.

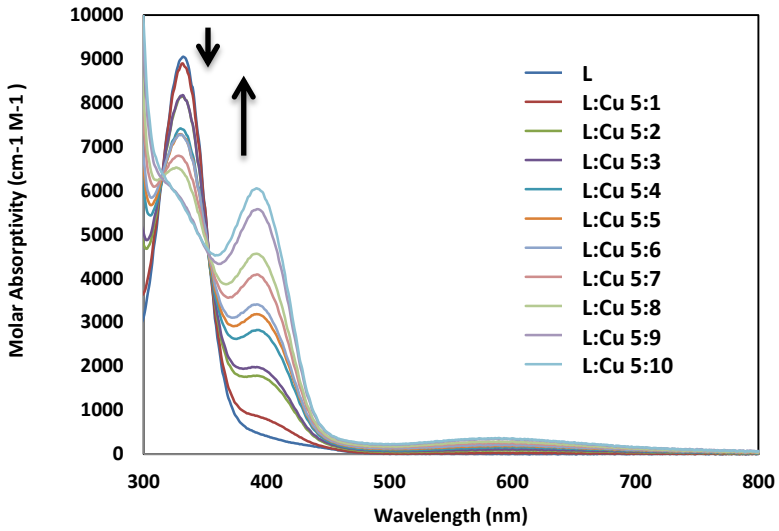



**Figure 3.5**. Absorbance spectrum of a serial titration completed via the general procedure of free base 0.123 mM $H_2\mathbf{L}^{\mathbf{III}}$ in methanol solution with an increasing ratio of $Cu(C_2H_3O_2)_2$, from 5:1 to 5:10 $\mathbf{L}^{\mathbf{III}}$:Cu.[33]

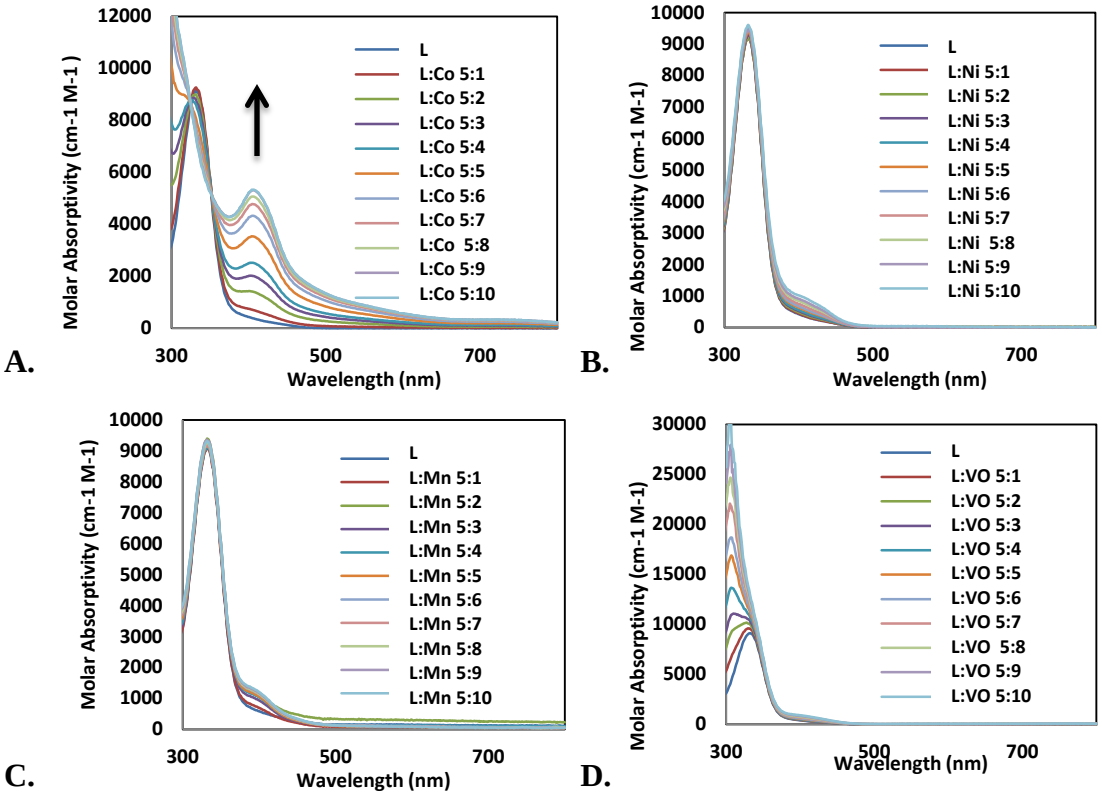



**Figure 3.6**. Absorbance spectrum of a serial titrations completed via the general procedure of free base 0.123 mM $H_2\mathbf{L}^{\mathbf{III}}$ in methanol solution with an increasing ratio of $\mathbf{L}^{\mathbf{III}}$:M 5:1 to 5:10, where M is equal to **A.** $Co(C_2H_3O_2)_2$ **B.** $Ni(C_2H_3O_2)_2$ **C.** $Mn(C_2H_3O_2)_2$ **D.** $VO(acac)_2$ .

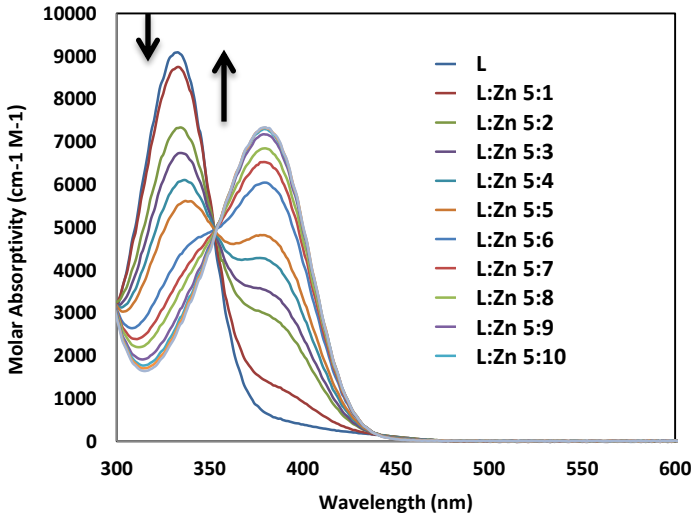



**Figure 3.7**. Absorbance spectrum of a serial titration completed via the general procedure of free base 0.123 mM $H_2\mathbf{L}^{\mathbf{III}}$ in methanol solution with an increasing ratio of $Zn(C_2H_3O_2)_2$, from 5:1 to 5:10 $\mathbf{L}^{\mathbf{III}}$:Zn.

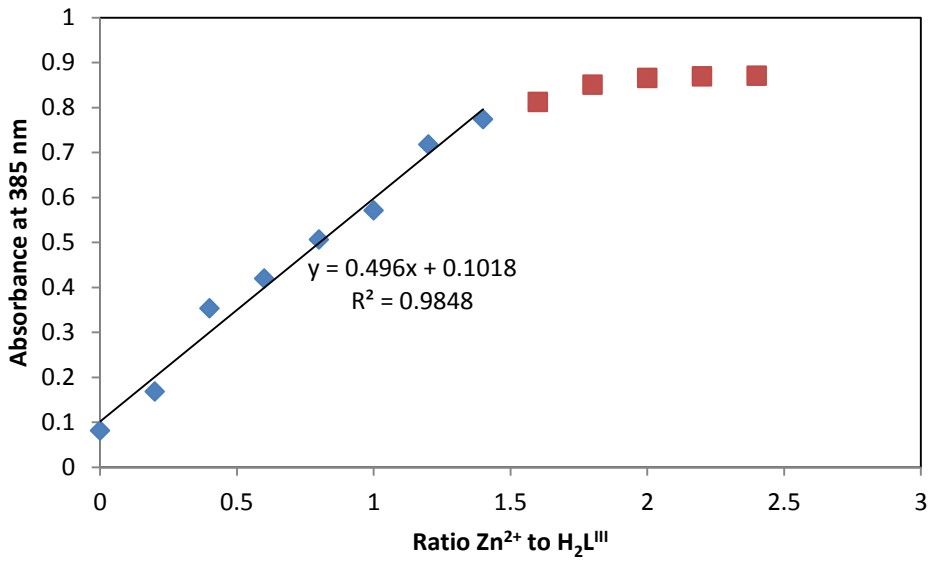



**Figure 3.8** Absorbance at 385 nm as a function of the ratio of $Zn^{2+}$ to 0.123 mM [$\mathbf{H_2L^{III}}$].

Fluorescence measurements of the metal titration experiments above were completed using the same general procedure in methanol. The titration with uranyl(VI), copper(II), cobalt(II), and nickel(II) resulted in a quenching of emission resulting from excitation at 365 nm (**Figure 3.9**). Addition of zinc(II) and vanadyl(IV) resulted in an increase of emission (**Figure 3.10**). A summation of the solution fluorescence spectra of **[$\mathbf{H_2L^{III}}$]** mixed with 1 equivalent of metal salt in methanol and images of the Zn**[$\mathbf{L^{III}}$]** emission is shown in **Figure 3.11**. The $UO_2$, Cu, Co, Mn, and Ni metals ions all quenched the ligand fluorescence induced by 365 nm excitation, while Zn, and VO increased the fluorescence. Notably, Zn increased the fluorescence by a factor of 5.

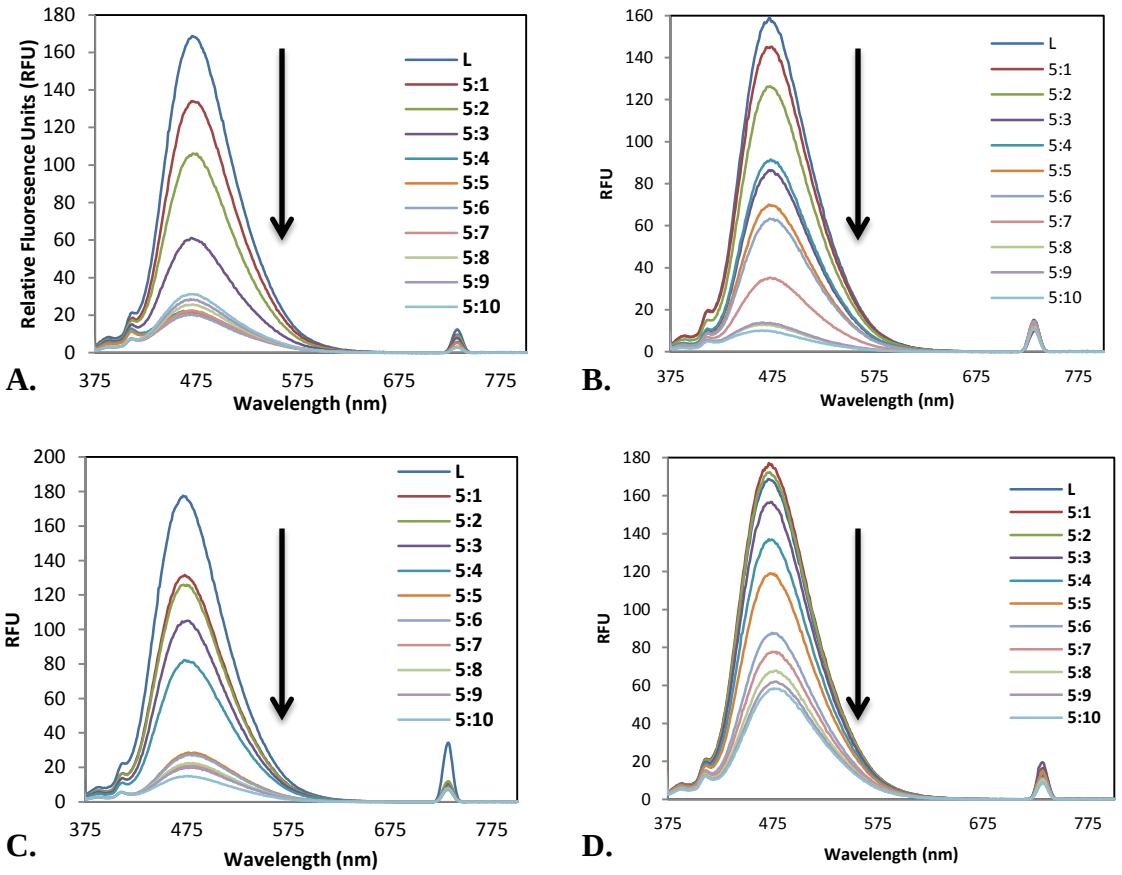



**Figure 3.9.** Emission spectrum of a serial titration completed via the general procedure of 0.123 mM $H_2\mathbf{L}^{\mathbf{III}}$ in methanol solution with an increasing ratio of $\mathbf{L}^{\mathbf{III}}$:M from 5:1 to 5:10, where M is equal to **A.** $UO_2$, **B.** Cu, **C.** Co, **D.** Ni. Excited at 365 nm.

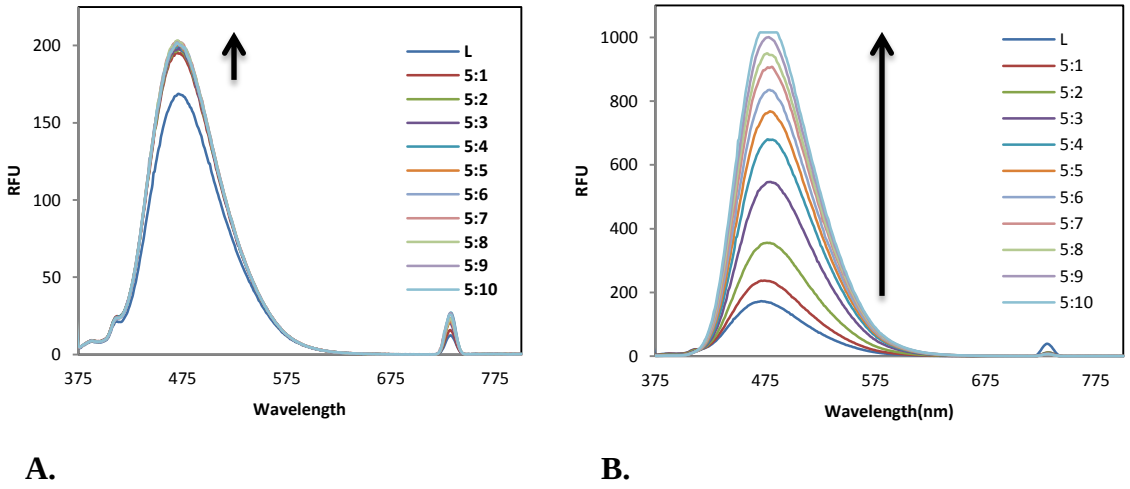



**Figure 3.10.** A. Emission spectrum of a serial titration completed via the general procedure of 0.123 mM $H_2\mathbf{L}^{\mathbf{III}}$ in methanol solution with an increasing ratio of A. $VO(acac)_2$ and B. $Zn(C_2H_3O_2)_2$ from 5:1 to 5:10 $\mathbf{L}^{\mathbf{III}}$:M. Excited at 365 nm.

After observing this increase in emission, the quantum yield of Zn**[L$^{III}$]** was calculated using **Figure 3.12** and equation 1,

$$\Phi_X = \Phi_{ST}\left(\frac{Slope_X}{Slope_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right) \qquad (1)$$

Where the subscripts ST and X denote standard and unknown respectively, Φ is the fluorescence quantum yield, Slope is the slope from the plot of fluorescence intensity vs absorbance, and $\eta$ the refractive index of the solvent. In this case the solvent was constant, and $\Phi_{ST}$ for anthracene was equal to 0.24 (24 %).[42] The quantum yield of Zn**[L$^{III}$]** was calculated to be 0.016, or 1.6 %.

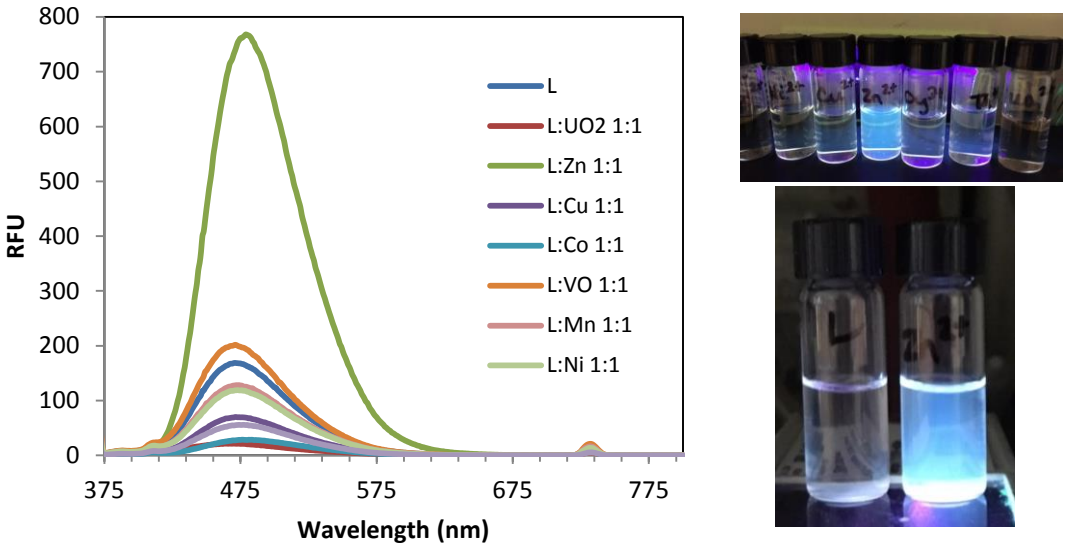



**Figure 3.11**. Solution fluorescence of a serial titration of 0.123 mM **[H$_2$L$^{III}$]** with indicated metal salts, shown is the 1:1 ratio in methanol solution at 365 nm excitation.[33]

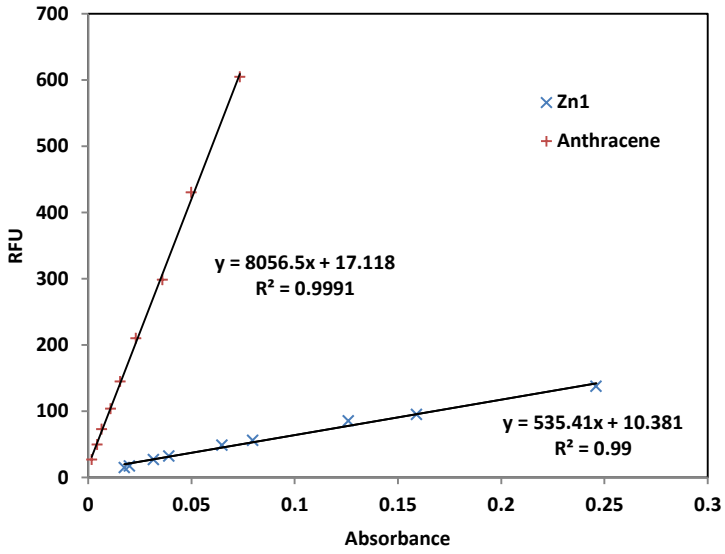



**Figure 3.12.** Zn**[$L^{III}$]** fluorescence at 473 nm after excitation at 365 nm vs. absorbance value at 365 nm of 116, 87, 58, 43.5, 29.2, 21.8, 14.5, 10.9, 7.2, 5.5, 3.6, 2.7 μM solutions in methanol and Anthracene fluorescence at 422 nm after excitation at 365 nm vs. absorbance value at 365 nm of 35.7, 23.8, 15.8, 10.6, 7.1, 4.7, 3.1, 2.0, 1.0 μM solutions in methanol.[33]

Another representation of the Zn emission, in comparison to the other transition metals investigated, are shown in **Figure 3.13**. Adding two equivalents of the zinc metal maximized the emission intensity. An image suggesting a possible 1:1 zinc binding is shown in **Scheme 3.3**, but by comparing the molar ratio of free zinc metal added to free base the emission plateaus at 1.5 equivalents of metal. A possibility is that two ligands are binding three zinc ions, including acetate counter ions, creating supramolecular aggregates that emit more intensity than the 1:1 complex.

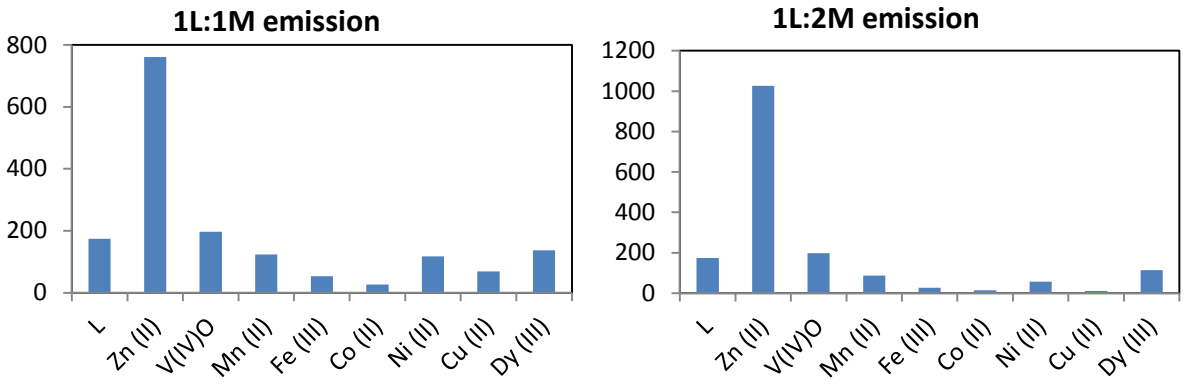
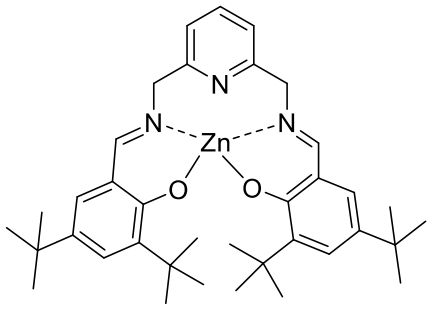



**Figure 3.13**. Zinc emission in comparison with the free base, 0.123 mM **[$H_2L^{III}$]**, and the indicated metal titrations.




**Zn[$L^{III}$]**

**Scheme 3.3.** Potential zinc binding with **[$H_2L^{III}$]**

Further studies on the selectivity of **[$H_2L^{III}$]** could ultimately lead to this ligand being tested in biological sensing of zinc ions. Additionally, the mercury and cadmium complexes of this system may be of interest. Both mercury and cadmium are common environmental contaminants that would be useful to identify through a fluorescence assay.

In an attempt to increase the extinction coefficient and reduce the limit of detection of the system, the napthyl analogue ($UO_2$**[$L^{IV}$]**) was synthesized. Absorbance is observed at 220 nm (ε = 14,300 $cm^{-1}$ $M^{-1}$), at 322 nm (ε = 4,021 $cm^{-1}$ $M^{-1}$), and at 366 nm (ε = 2,710 $cm^{-1}$ $M^{-1}$), in the UV-visible spectrum of $UO_2$**[$L^{IV}$]** (**Figure 3.14**). While increasing the conjugation of organic molecules often increases their extinction coefficient, this was not observed with **[$H_2L^{IV}$]** due to

the $sp^3$ hybridized carbon present in the backbone skeleton. The conjugation was locally increased, but the entire backbone was not conjugated, which resulted in no significant increase in absorbance.

The sulfonyl analogue ($UO_2$**[$L^V$]**) was also synthesized. Such a ligand may provide a simple method for testing waste water streams. Attempts to make the free base **[$H_2L^V$]** were unsuccessful, probably due to the electron withdrawing and deactiving nature of the sulfonyl groups. When the metal is present to aid in coordination and organization, the reactions are more likely to go to completion. Crystallization of $UO_2$**[$L^V$]** was also attempted, but resulted in no crystals of quality for diffraction methods. The chloro- analogue $UO_2$**[$L^{VI}$]** was also synthesized and purified, but no increase in extinction coefficient was observed. While crystals of $UO_2$**[$L^{VI}$]** were grown several times, none were suitable for characterization by single crystal X-ray diffraction.

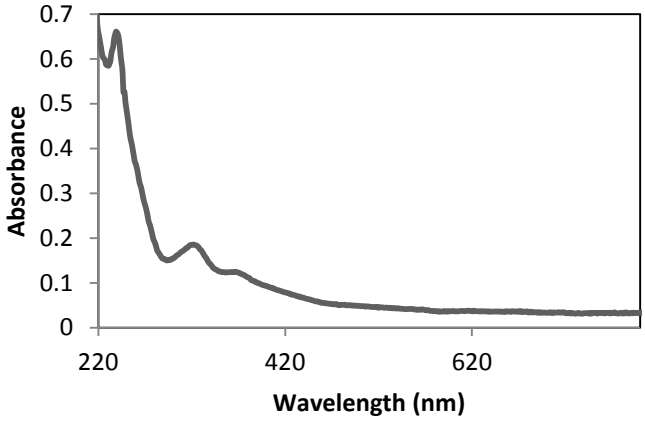



**Figure 3.14**. Absorbance spectrum of a 20 μM solution of $UO_2$**[$L^{IV}$]** in DCM.

## Conclusions

In summary, $UO_2$**[$L^{III}$]** and $UO_2$**[$L^{IV}$]** complexes with uncommon pyridine coordination have been synthesized and characterized in solution and in the solid state. This pentadentate

binding ligand fully occupies the equatorial binding environment, removing the necessity of a coordinating solvent molecule or ligand rearrangement and allowing to quickly and selectively bind uranyl in a one-to-one fashion. The $UO_2$**[$L^{V}$]** and $UO_2$**[$L^{VI}$]** complexes were also synthesized, but their molar extinction coefficients were low. These complexes do have a distinct response for uranyl over common first-row transition metals in the UV, meaning synthetic addition of a chromophore may lead to this system being a useful, in-the-field sensor. The ligand **[$H_2L^{III}$]** showed a significant increase in fluorescence in the presence of zinc, inspiring interest in use as a zinc fluorescent sensor.[25, 43]

## Materials and Methods

### Experimental

*Caution! The $UO_2(NO_3)_2$•$6H_2O$ used in this study contained depleted uranium, standard precautions for handling radioactive materials or heavy metals were followed.*

All solvents not specifically mentioned were ACS grade from EMD and used as received with no further purification. Reagents methanol (HPLC grade, EMD), ethanol (200 proof, ACS grade, Pharmco-aaper), 2,6-pyridinedicarboxylic acid (99%, Acros), sulfuric acid (95-98%, Sigma Aldrich), sodium bicarbonate (EMD), sodium chloride (Macron), ammonium hydroxide (BDH), trifluoroacetic anhydride (>99%, Sigma Aldrich), palladium 5% on carbon, dry, type 87L (Alpha Aesar), Celite (Alpha Aesar), 3,5-di-tert-butylsalicyaldehyde (98%, TCI), 2-hydroxynapthaldehyde (98%, Alpha Aesar), hydrochloric acid (ACS grade, Fischer Scientific), sodium hydroxide (ACS grade, EMD), copper(II) acetate hydrate (>98%, MC/B), zinc (II) acetate dihydrate (Sigma Aldrich), vanadium(IV) bis(acetylacetonato)oxide (98%, STREM),

cobalt(II) acetate tetrahydrate (Mallinckrodt), and nickel(II) acetate tetrahydrate (Sigma Aldrich) were used as received without further purification. Anhydrous dichloromethane (BDH) and tetrahydrofuran (Macron) were purchased, stored under argon, and dispensed from a solvent purification system. Triethylamine (99%, Alpha Aesar) was distilled and stored under argon until use. $UO_2(NO_3)_2 \cdot 6H_2O$ (98%, J. T. Baker) was recrystallized from a nitric acid solution and stored under hexanes until use.

**Dimethyl-2,6-pyridinedicarboxylate**

Methanol (320 mL) and 2,6-pyridinedicarboxylic acid (8.195 g, 49.03 mmol) were added to a round bottom flask, charged with a stir bar and gently warmed to 30 °C to aid in dissolution. Sulfuric acid (10 mL) was added slowly, followed by heating the flask to reflux for 4 hours. The reaction solution was quenched with $NaHCO_3$ until a neutral pH was attained, followed by the extraction of the ester into dichloromethane (DCM). The ester was washed twice with brine solution and remaining solvent was removed under reduced pressure yielding a white powder (8.681 g, 44.48 mmol, 91 %). $^1$H NMR (400 MHz, $CDCl_3$) δ 4.37 (s, 6H), 8.041 (t, 1H, $J$ = 7.8 Hz), 8.332 (d, 2H, $J$ = 7.6 Hz); TOF MS (ESI) m/z ($M^+$ + 1) Cald 196.0532, Found 196.0597.

**2,6-pyridinedicarboxamide**

Ammonium hydroxide (50 mL) and dimethyl-2,6-pyridinedicarboxylate (3.053 g, 15.64 mmol) were added to a round bottom flask, charged with a stir bar and heated to 40 °C for 8 hours. Resulting white powder was filtered using cold deionized water. Product was dried at 60 °C overnight in a vacuum oven, yielding a matte white solid in quantitative yield (2.583g, 15.64 mmol). $^1$H NMR (400 MHz, $D_6$-DMSO) δ 7.717 (s, 2NH) 8.117-8.198 (m, 3H) 8.881 (s, 2NH); MS (ESI) m/z ($M^+$ + 1) Cald 166.0538, Found 166.0642.

**2,6-pyridinedicarbonitrile**

Dry THF (25 mL), 2,6-pyridinedicarboxamide (3.517 g, 21.29 mmol) and freshly distilled triethylamine (7 mL) were added to a round bottom flask, charged with a stir bar and cooled to 0 °C. Trifluoroacetic anhydride (8.75 mL) was added dropwise with stirring. Reaction vessel was stirred for 30 minutes in ice, and then allowed to warm to room temperature. Reaction was allowed to continue until judged complete, for 4 hours, and quenched with saturated sodium bicarbonate solution. Solution was filtered and washed with cold deionized water, yielding a shiny white solid (2.075 g, 16.08 mmol, 76 %). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.924 (d, 2H, J = 8.0 Hz), 8.067 (t, 1H, J = 7.6 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 115.41, 131.07, 135.40, 138.78; TOF MS (ESI) m/z ($M^+$ + 1) Cald 130.0327, Found 130.0420.

**2,6-(dimethylamino)pyridine**

2,6-pyridinedicarbonitrile (0.989 g, 7.67 mmol) and dry tetrahydrofuran (100 mL) were added to a flame dried round bottom flask charged with a stir bar and allowed to dissolve. Lithium aluminum hydride (3.5 eq., 1.034 g, 27.2 mmol) was added to the reaction vessel slowly and allowed to stir at room temperature for 22 hours. The resulting solution was quenched slowly using cold isopropanol (60 mL), while stirring in an ice bath. The solution was stirred at room temperature for 2 additional hours and then filtered over Celite to remove excess aluminum salts, and solvent was removed from resulting filtrate under reduced pressure to yield a thick yellow oil (0.7239 g, 5.284 mmol, 69%). $^{1}$H NMR (600 MHz, $CDCl_3$) δ 1.676 (s, 4H), 3.967 (s, 4H), 7.145 (d, 2H, J = 7.8 Hz), 7.613 (t, 1H, J = 7.5Hz); $^{13}$C NMR (151 MHz, $CDCl_3$) δ 47.96, 119.48, 137.31, 161.56; TOF MS (ESI) m/z ($M^+$ + 1) Cald 138.0953, Found 138.0748.

**2,6-bis[1-[(2-hydroxy-3,5-ditert-butylphenyl)imino]ethyl]pyridine ($[H_2L^{III}]$)**

Ethanol (60 mL), 3,5-ditertbutylsalicylaldehyde (1.948 g, 8.325 mmol), 2,6-(dimethylamino)pyridine (0.5766 g, 4.209 mmol), trifluoroacetic acid (1 drop), and magnesium sulfate (1 g) were added to round bottom flask charged with a stir bar. The reaction vessel was heated to reflux for 18 hours until it was judged complete by TLC. Magnesium sulfate was removed via hot filtration, and the solvent was removed from the resulting filtrate under reduced pressure to yield a crude yellow oil. Crude product was purified with column chromatography with a gradient of 5% ethyl acetate in hexanes solution, followed by a 10% ethyl acetate in hexanes solution. The product was collected and concentrated under reduced pressure to yield a bright yellow solid (0.3404 g, 0.5982 mmol, 14.42%) $^1$H NMR (400 MHz, $CDCl_3$) δ 1.312 (s, 18H), 1.449 (s, 18H), 4.930 (s, 4H), 7.146 (s, 2H), 7.285 (d, 2H, *J* = 7.2 Hz), 7.408 (s, 2H), 7.686 (t, 1H, *J* = 7.5 Hz), 8.549 (s, 2H), 13.657 (s, 2OH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 29.604, 31.684, 34.314, 35.219, 65.204, 118.077, 120.587, 126.376, 127.413, 136.896, 137.850, 140.381, 158.164, 158.232, 168.179; TOF MS (ESI) m/z ($M^+$ + 1) Cald 570.3981, Found 570.3319.

**$UO_2$[2,6-bis[1-[(2-hydroxy-3,5-ditert-butylphenyl)imino]ethyl]pyridine] ($UO_2[L^{III}]$)**

Ethanol (50 mL) was added to 2,6-(dimethylamino)pyridine (0.3116 g, 2.258 mmol) in a round bottom flask charged with a stir bar, and stirred until dissolved with gentle warming. Magnesium sulfate and 3,5-ditert-butylsalicylaldehyde (1.949 g, 8.329 mmol) were added to the reaction vessel and heated to reflux for 18 hours. The resulting solution was filtered to remove the magnesium sulfate and transferred to a round bottom flask. Uranyl nitrate hexahydrate (1.082 g, 2.16 mmol) and trimethylamine (660 uL) were added to the reaction vessel and gently warmed to 40 °C for 3 hours, until the reaction was judged complete by TLC. The crude red solid, attained by removal of solvent through rotary evaporation, was purified using column

chromatography and DCM as eluent to produce a dark red solid (0.309g, 0.369 mmol, 16.3 %). $^{1}$H NMR (600 MHz, $CDCl_3$) δ 1.315 (s, 18H), 1.821 (s, 18H), 5.668 (s, 4H), 7.284 (s, 2H), 7.538 (d, 2H, *J* = 8.4 Hz), 7.741 (s, 2H), 7.942 (t, 1H, *J* = 7.5 Hz), 9.427 (s, 2H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 30.90, 31.74, 33.88, 35.93, 69.67, 120.19, 122.83, 127.87, 130.29, 139.29, 140.77, 160.96, 166.76, 169.75; $^{1}$H NMR (400 MHz, $CD_3CN$) δ 1.344 (s, 18H), 1.764 (s, 18H), 5.771 (s, 4H), 7.485 (d, 2H, J = 2.3 Hz), 7.681 (d, 2H, *J* = 2.8 Hz), 7.792 (s, 1H), 7.812 (s, 1H), 8.192 (t, 1H, *J* = 7.6 Hz), 9.427 (s, 2H); $^{13}$C NMR (100 MHz, $CD_3CN$) δ 31.481, 32.211, 34.877, 36.969, 70.476, 122.188, 124.503, 129.769, 131.071, 140.353, 141.418, 124.564, 162.222, 167.512, 171.399; MS (ESI) m/z ($M^+$ + 1) Cald 838.4231, Found 838.4254. Single crystals of $UO_2$**[$L^{III}$]** were grown from slow evaporation of a concentrated solution of $UO_2$**[$L^{III}$]** in acetonitrile. CCDC: 1469301.

**$UO_2$[2,6-bis[1-[(2-hydroxy-napthyl)imino]ethyl]pyridine] ($UO_2$[$L^{IV}$])**

Ethanol (50 mL) was added to 2,6-(dimethylamino)pyridine (0.143 g, 1.04 mmol) in a round bottom flask charged with a stir bar, and stirred until dissolved with gentle warming. 2-hydroxynapthaldehyde (0.385 g, 2.24 mmol) were added to the reaction vessel and heated to reflux for 9 hours. Uranyl nitrate hexahydrate (0.5126 g, 1.021 mmol) and trimethylamine (400 uL) were added to the reaction vessel and gently warmed to 40 °C for 12 hours, until the reaction was judged complete. The resulting solution was placed in ice to precipitate an orange solid was separated via vacuum filtration (0.5891 g, 0.826 mmol, 79.5 %). $^{1}$H NMR (400 MHz, $d_6$-DMSO) δ 6.154 (s, 4H), 7.305 (t, 2H, *J*= 7.3 Hz), 7.424 (d, 2H, *J*= 9.0 Hz), 7.585 (t, 2H, *J*= 7.6 Hz), 7.893 (d, 2H, *J*= 8.0 Hz), 7.990 (d, 2H, *J*= 7.8 Hz), 8.213 (d, 2H, *J*= 9.0 Hz), 8.353-8.382 (m, 3H), 10.581 (s, 2H); $^{13}$C NMR (150 MHz, $d_6$-DMSO) δ 69.074, 113.220, 121.487, 121.802, 123.255, 124.771, 127.753, 127.980, 129.102, 134.566, 136.351, 142.096, 161.565, 165.044,

170.347; TOF MS (ESI) m/z ($M^+$ + 1) Cald 714.2040, Found 714.2008 . Single crystals of $UO_2$**[$L^{IV}$]** were grown from slow diffusion of hexanes into a concentrated solution of $UO_2$**[$L^{IV}$]** in DCM. CCDC: 1497023.

**$UO_2$[2,6-bis[1-[(2-hydroxy-3-tert-butyl-5-suflophenyl)imino]ethyl]pyridine] ($UO_2[L^V]$)**

Methanol (120 mL) was added to 2,6-(dimethylamino)pyridine (0.3671 g, 2.679 mmol) in a round bottom flask charged with a stir bar. The reagent 5-sulfo-3-t-butylsalicylaldehyde (0.842 g, 3.00 mmol) was added to the reaction and stirred until dissolved with gentle warming. Uranyl acetate (0.5802 g, 1.495mmol) was then added to the reaction vessel which was heated to reflux for 18 hours. The resulting red solution was put in the freezer for three days. The yellow solid (residual starting material) was then filtered from the flask and the red solution was collected. The residual solvent was removed through rotary evaporation to produce a dark red solid.

**$UO_2$[2,6-bis[1-[(2-hydroxy-5-chlorophenyl)imino]ethyl]pyridine] ($UO_2[L^{VI}]$)**

Ethanol (80 mL) was added to 2,6-(dimethylamino)pyridine (0.4043 g, 2.951 mmol) in a round bottom flask charged with a stir bar, and stirred until dissolved with gentle warming. The reagent 5-chlorosalicylaldehyde (.4787 g, 3.057 mmol) were added to the reaction vessel and heated to reflux for 18 hours. Uranyl acetate hexahydrate (0.5788 g, 1.4917 mmol) was added to the reaction vessel and heated to reflux for 18 hours. The crude red solid, attained by filtration, was purified using column chromatography and 5% MeOH in DCM as the eluent to produce a red orange solid.

**NMR Spectroscopy**: $^1$H NMR spectra were recorded with a Bruker AC400 spectrometer at 400 or Bruker AC600 spectrometer at 600 MHz. $^{13}$C NMR spectra were recorded with a Bruker AC400 spectrometer at 100 or Bruker AC600 spectrometer 151 at MHz. NMR spectroscopic

data were collected using deuterated chloroform ($CDCl_3$), deuterated dimethylsulfoxide ($D_6$-DMSO) or deuterated acetonitrile ($CD_3CN$) and reported in parts per million relative to trimethylsilane (TMS, δ 0.00 ppm).

**X-ray Diffraction**: Suitable crystals were selected and mounted on a glass fiber using Paratone-n oil and data collection was completed on a 'Bruker APEX CCD' diffractometer. The crystal was kept at 180(2) K during unit cell and data collection. The structure was solved with the ShelXS structure solution program using Direct Methods[44-45] and refined with the ShelXL refinement package using Least Squares minimization[44-45], or refined with the olex2.refine[46] refinement package using Gauss-Newton minimisation. Projections were created on Olex2 software.[46]

**Absorbance Spectroscopy:** All absorbance spectra were collected on a VARIAN Cary 50 WinUV Spectrometer with a xenon lamp with absorbance spectra from 200 nm to 900 nm with a 1 cm width quartz cuvette.

**Fluorescence Spectroscopy:** All fluorescence spectra were collected on a Shimadzu RF-5301 PC fluorospectrophotometer with a xenon lamp and a 1 cm width quartz cuvette with an excitation of 365 nm and an emission spectrum of 375–900 nm. Slit widths were set so that the maximum emission of the ligand could be maintained throughout the titration.

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## Chapter 4: Unusual Thorium Fluorescence and Tunable Ligand Emission of Napthylsalophen Uranyl(VI), Thorium(IV), and Lanthanide(III) Sandwich Complexes

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### Introduction

Actinide and lanthanide compounds have been found to possess interesting near infrared fluorescence that have been explored for use in sensors and exploited in medicinal sensing technologies.[1-2] In particular, the distinctive properties of multi-nuclear lanthanide and actinide complexes are of interest for their use in biological imaging,[3-4] quantum computing,[5-6] single-molecule magnets (SMMs),[7-10] organic light emitting diodes (OLEDs),[11-12] and catalysis.[13] Additionally a variety of lanthanide molecular organic framework (Ln-MOF) and actinide molecular organic framework (An-MOF) structures have also been applied to separations or fluorescent sensors.[14-18]

Directed synthesis targeting multi-nuclear lanthanide and actinide species can be difficult, due to large coordination numbers, somewhat flexible coordination geometries, and high sensitivity to pH changes or counter anions.[19-20] As lanthanides have similar ionic radii and

are all typically found in the trivalent oxidation state, selective sensing or extraction of any given lanthanide is of great interest. As a host of applications have been found for the lanthanides, their purification is quite complex as they are often found together in natural ores as blends also often containing uranium and/or thorium, and hence, their separation has recently become a topic of intense study.[21] Lutetium, for example, has been studied for photodynamic breast cancer treatments and as a sensitizer for positron emission tomography (PET) scan detection.[22-23] While selective detection of many of the lanthanides have been investigated, discovery of new methodologies is still of great interest.[24-25]

Multidentate ligand systems coupled with highly absorbing organic ligands have been used to synthesize lanthanide and actinide complexes with intriguing fluorescence properties for use in some of the aforementioned applications.[26-29] Salen ligands have been employed as part of multidentate ligand systems and are attractive due to their relative ease of customization of the coordination environments.[30-31] There have been recent examples of double and triple decker sandwich complexes with salophen ligands and lanthanides, specifically Tb(III), Yb(III), and Dy(III).[19, 32-36] Concurrent to this work, triple-decker sandwich complexes with napthylsalophen and lanthanides were reported by Sanudo and co-workers, but the focus of that paper was the magnetic properties of the complexes, not structural, and no systematic discussion of this coordination environment was presented.[36] There have also been examples of actinide salophen sandwich complexes that provide interesting electronic properties.[37-40]

Previously, we have introduced ligands with a salen core but featuring a further extended conjugated backbone incorporating phenazine or quinoxalinol moities.[41-45] This addition of conjugation serves to enhance the change in π-overlap and increase visible absorption when bound to an actinide center. This also provides access to self-assembled multinuclear lanthanide

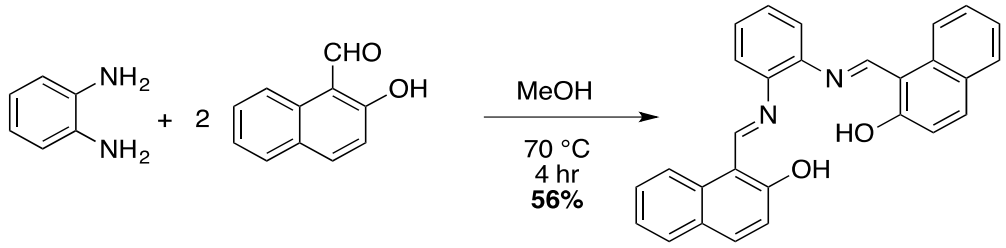
complexes. Here, we used extended conjugation on salophen ligands, in order to increase the electronic distinction between lanthanide and actinides and investigate the electronic properties of the resulting complexes. For that purpose, we have synthesized 1,1'-((1E,1'E)-(1,2-phenylenebis(azanylylidene))bis(methanylylidene))bis(naphthalen-2-ol) ([$H_2$**L**$^{\mathbf{VII}}$]), nicknamed napthylsalophen. The ligand [**H$_2$L**$^{\mathbf{VII}}$] was used to prepare lanthanide(III), cerium(IV), and thorium(IV) metal complexes. These were found to self-assemble as triple decker sandwich complexes of the type $Ln_2$[**L**$^{\mathbf{VII}}$]$_3$, where Ln = Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Yb(III), or Lu(III),[46] and double decker sandwiches of the type M[**L**$^{\mathbf{VII}}$]$_2$, where M = Ce(IV) or Th(IV).[47]

Double decker sandwiches of the type Th[**L**$^{\mathbf{VII}}$]$_2$ resulted in the first fluorescent thorium compound reported to fluoresce in both the solid-state and solution. One fluorescent thorium solid-state compound and three examples of solution phase fluorescence have been described previously; however, many more examples of thorium quenching fluorescence exist.[48-52] Additionally, the triple-decker sandwich complexes of the type $Ln_2$[**L**$^{\mathbf{VII}}$]$_3$, where Ln = Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Yb(III), or Lu(III) were synthesized and structural characterization by single crystal X-ray diffraction is described for the complexes Th[**L**$^{\mathbf{VII}}$]$_2$, Ce[**L**$^{\mathbf{VII}}$]$_2$, $Nd_2$[**L**$^{\mathbf{VII}}$]$_3$, $Gd_2$[**L**$^{\mathbf{VII}}$]$_3$, $Tb_2$[**L**$^{\mathbf{VII}}$]$_3$, $Dy_2$[**L**$^{\mathbf{VII}}$]$_3$, $Ho_2$[**L**$^{\mathbf{VII}}$]$_3$, $Yb_2$[**L**$^{\mathbf{VII}}$]$_3$, and $Lu_2$[**L**$^{\mathbf{VII}}$]$_3$. The emission properties in both solution and solid-state are discussed, where tunable ligand emission in the solid state across the $Ln_2$[**L**$^{\mathbf{VII}}$]$_3$ series with a maximum at 556 nm for the $Sm_2$[**L**$^{\mathbf{VII}}$]$_3$ complex to 617 nm for $Er_2$[**L**$^{\mathbf{VII}}$]$_3$ was observed, as well as greatly increased ligand emission selectively for the complex $Lu_2$[**L**$^{\mathbf{VII}}$]$_3$. The synthesis and interesting hydrogen bonding tetramer in the solid-state of a $UO_2$[**L**$^{\mathbf{VII}}$] complex is also discussed.

## Results and Discussion

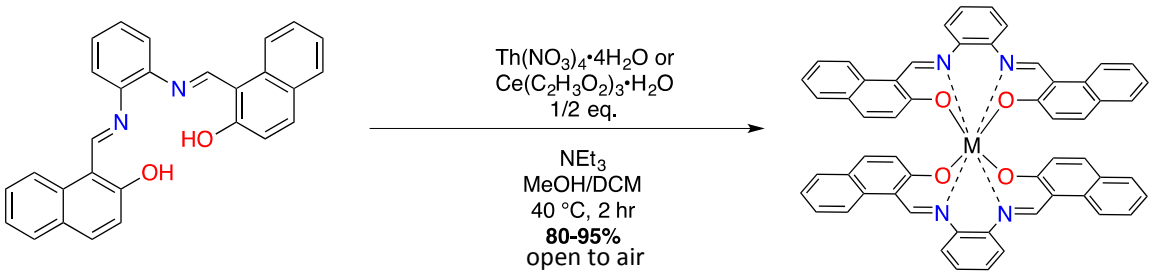
### Synthesis

The ligand [$H_2$**L**$^{VII}$] was prepared reacting two equivalents of 2-hydroxynapthaldehyde with 1,2-diaminobenzene in methanol. A precipitate formed after heating the solution to 70 °C for four hours and was isolated via vacuum filtration. The product was characterized and found to result in the desired ligand featuring a tetradentate binding pocket with two Schiff base imine donors and two phenol donors.




**Scheme 4.1**. Synthesis of $H_2$[**L**$^{VII}$].

The synthesis of Ce(IV) and Th(IV) sandwich complexes with napthylsalophen with this simple core but highly conjugated backbone is reported. Ce[**L**$^{VII}$]$_2$, and Th[**L**$^{VII}$]$_2$ were synthesized through the addition of the metal salts to a warm methanol/dichloromethane solution of ligand and triethylamine (**Scheme 4.2**).




[$H_2$**L**$^{VII}$] Th[**L**$^{VII}$]$_2$ and Ce[**L**$^{VII}$]$_2$

**Scheme 4.2.** Synthesis of Th[**L**$^{VII}$]$_2$ and Ce[**L**$^{VII}$]$_2$.[47]

The Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ complex was initially synthesized from addition of 0.5 equivalents of Ce(III) acetate salt in warm methanol/dichloromethane with triethylamine as a base. Once coordinated, oxygen oxidizes the cerium ion to Ce(IV), which is subsequently stabilized by the napthylsalophen ligands. The oxidation of Ce(III) to Ce(IV) was followed spectrophotometrically by adding 1 equivalent of Ce(III) acetate to a solution of free base in dimethylformamide under heating. The UV-visible spectra were recorded every two minutes for 36 minutes (**Figure 4.1**). A similar instance of stabilization of the Ce(IV) ion involved formation of a Ce(IV) sandwich complex in the presence of oxygen with good yields was reported by Schelter and co-workers.[53] The same Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ complex, as confirmed via a diamagnetic NMR spectrum, UV, and solid state elucidation can be synthesized using either Ce(III) salts or Ce(IV) salts in reactions with [$H_2\mathbf{L}^{\mathbf{VII}}$]. Further characterization of the stabilization of the Ce(III)/Ce(IV) redox couple by means of more detailed electrochemical analysis will be the subject of future work.

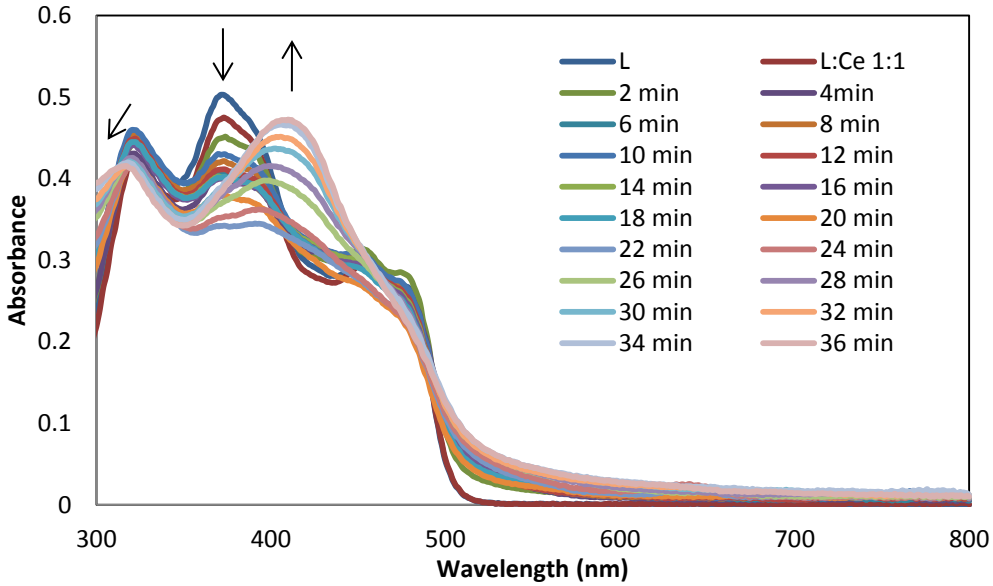
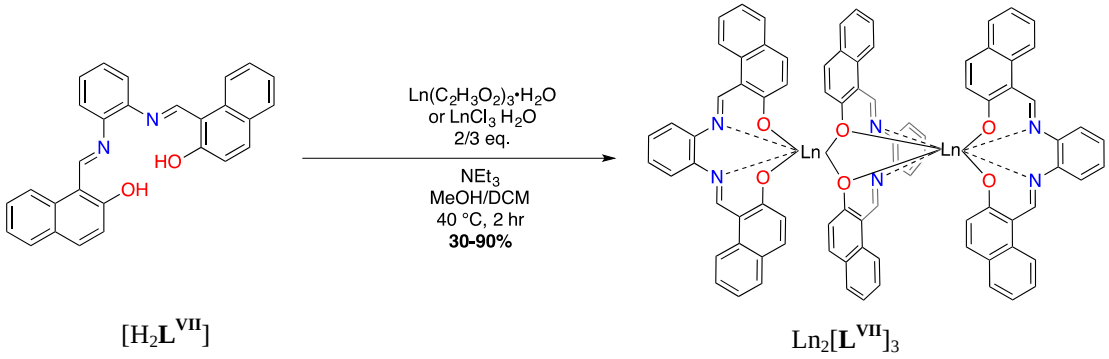


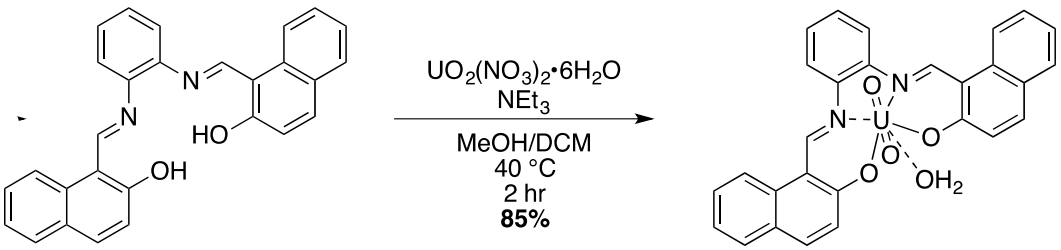

**Figure 4.1.** Solution phase absorbance of [$H_2\mathbf{L}^{\mathbf{VII}}$] ($\lambda_{max}$=324, 394, and 446 nm) and spectrophotometric observation of the formation of Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ ($\lambda_{max}$=317, and 417 nm).[47]

In addition, lanthanide salts (Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Yb(III), or Lu(III)) were added to warm solutions of [$H_2$**L**$^{VII}$] in methanol (MeOH) and dichloromethane (DCM) mixture in the presence of triethylamine ($NEt_3$) to afford $Ln_2$[**L**$^{VII}$]$_3$ complexes (**Scheme 4.3**). Lastly, the synthesis of the $UO_2$[**L**$^{VII}$] complex was preformed by addition of recrystallized uranyl nitrate hexahydrate in methanol to a warm solution of [$H_2$**L**$^{VII}$] in DCM containing triethylamine (**Scheme 4.4**).




[$H_2$**L**$^{VII}$] $Ln_2$[**L**$^{VII}$]$_3$

**Scheme 4.3.** Synthesis of $Ln_2$[**L**$^{VII}$]$_3$ complexes, where Ln = Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Yb(III), or Lu(III).[46]




**Scheme 4.4**. Synthesis of $UO_2$[**L**$^{VII}$] complex

## Crystallography

For each of the following compounds, crystals suitable for single crystal X-ray diffraction were selected and mounted on a glass fiber using Paratone-N oil and data set collection was

completed on a 'Bruker APEX CCD' diffractometer using Mo Kα radiation. A full list of tables of bond lengths and angles for all compounds characterized by single crystal X-Ray diffraction can be found in Appendix I.

Crystals of [$\mathbf{H_2L^{VII}}$] suitable for X-Ray diffraction were grown from slow evaporation of a saturated 1:1 DCM and methanol solution. [$\mathbf{H_2L^{VII}}$] crystallized in the orthorhombic space group $P2_12_12_1$ with an interstitial dichloromethane molecule in the asymmetric unit (**Figure 4.2**).The C-O1 bond length of 1.276(3) and C-O2 bond length of 1.338(3) show that the tautomerization of one phenol is the most stable form in the solid-state (**Scheme 4.5**). The longer $C_{imine}$-N1 distance of 1.319(3) in comparison to $C_{imine}$-N2 of 1.302(2) also confirms this assignment, although not as distinctly. This tautomerization has been observed and explained before for this system in solution using $^1$H NMR and IR, but this is the first crystal structure showing such phenomenon.[54] Crystallographic data for [$\mathbf{H_2L^{VII}}$], Th[$\mathbf{L^{VII}}$]$_2$, and Ce[$\mathbf{L^{VII}}$]$_2$ are shown in **Table 4.1**.

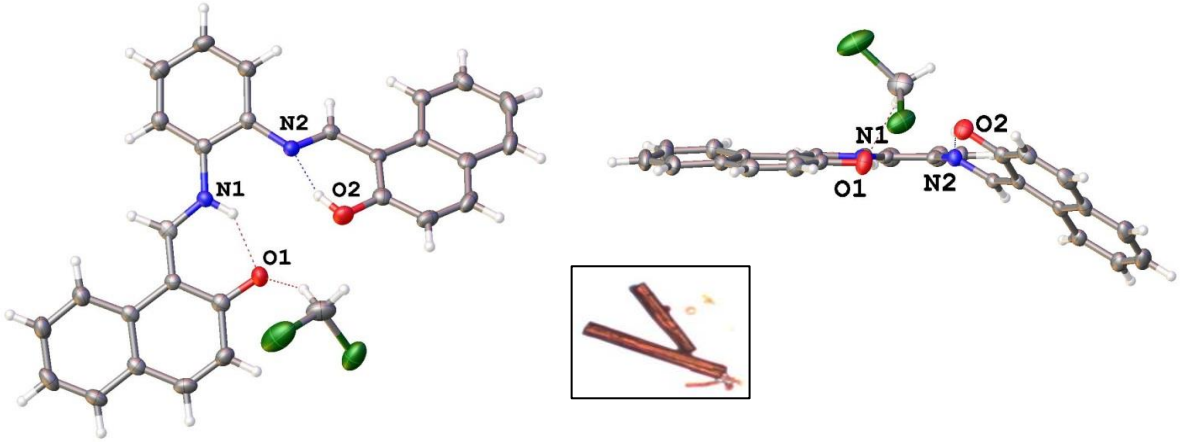
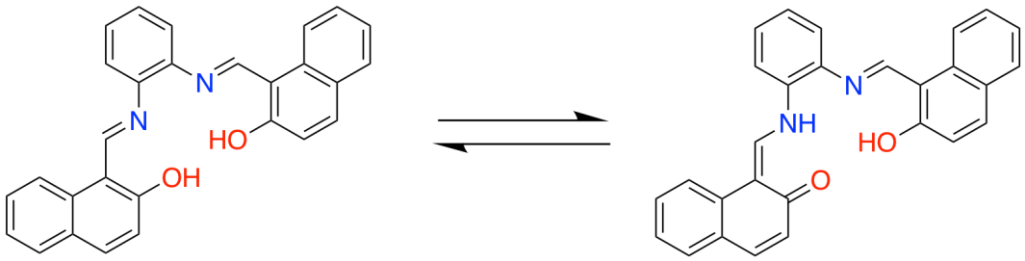



**Figure 4.2.** Projection of [$\mathbf{H_2L^{VII}}$] and interstitial DCM solvent molecule. Carbon atoms are shown in grey, nitrogen in blue, oxygen in red, and chlorine in green. Inset image of crystals.




**Scheme 4.5**. Tautomerization of [$\mathbf{H_2L^{VII}}$] observed in the solid-state and solution $^1$H NMR.

**Table 4.1**. Crystallographic data and details of data collection of [$\mathbf{H_2L^{VII}}$], Th[$\mathbf{L^{VII}}$]$_2$ and Ce[$\mathbf{L^{VII}}$]$_2$.[47]

| | [$\mathbf{H_2L^{VII}}$]•DCM | Th[$\mathbf{L^{VII}}$]$_2$•½$C_7H_8$ | Ce[$\mathbf{L^{VII}}$]$_2$•$H_2O$•½$C_6H_{14}$ |
|---|---|---|---|
| **Empirical formula** | $C_{29}H_{22}Cl_2N_2O_2$ | $C_{66.5}H_{47.5}N_4O_4Th$ | $C_{59}H_{36}CeN_4O_5$ |
| **Formula weight** | 501.42 | 1198.68 | 1021.08 |
| **Crystal size/mm$^3$** | 0.20 × 0.04 × 0.02 | 0.18 × 0.12 × 0.08 | 0.45 × 0.15 × 0.02 |
| **Crystal system** | orthorhombic | triclinic | monoclinic |
| **Space group** | $P2_12_12_1$ | P-1 | $P2_1/n$ |
| **a/Å** | 7.1378(10) | 11.4987(3) | 13.0103(8) |
| **b/Å** | 16.682(2) | 14.3613(4) | 13.9521(8) |
| **c/Å** | 20.056(3) | 16.2765(5) | 26.1970(15) |
| **α/°** | 90 | 106.2205(11) | 90 |
| **β/°** | 90 | 90.8258(11) | 99.6888(12) |
| **γ/°** | 90 | 94.1516(11) | 90 |
| **Volume/Å$^3$** | 2388.1(6) | 2572.39(13) | 4687.5(5) |
| **Z** | 4 | 2 | 4 |
| **$\rho_{calc}$mg/mm$^3$** | 1.3945 | 1.5474 | 1.4468 |
| **m/mm$^{-1}$** | 0.303 | 2.955 | 1.028 |
| **F(000)** | 1041.6 | 1180.2 | 2064.4 |
| **Temperature/K** | 180.45 | 180.45 | 180.45 |
| **Radiation** | Mo Kα (λ = 0.71073) | Mo Kα (λ = 0.71073) | Mo Kα (λ = 0.71073) |
| **Reflections collected** | 17603 | 53501 | 61172 |
| **Independent reflections** | 6177 | 8180 | 9966 |
| **Goodness-of-fit on F$^2$** | 1.036 | 1.06 | 1.068 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0557, $wR_2$ = 0.1176 | $R_1$ = 0.0242, $wR_2$ = 0.0489 | $R_1$ = 0.0292, $wR_2$ = 0.0699 |
| **Largest diff. peak/hole / e Å$^{-3}$** | 0.64/-0.64 | 0.92/-0.91 | 0.78/-0.60 |

Crystals of Th[$\mathbf{L^{VII}}$]$_2$ suitable for X-ray diffraction were grown from slow diffusion of hexanes into a saturated toluene solution. Th[$\mathbf{L^{VII}}$]$_2$ crystallized in $P\bar{1}$ with 1.5 toluene molecules per asymmetric unit, with one disordered toluene molecule lying on the mirror plane. The

resulting solid was characterized in the solid-state using single crystal diffraction and UV-Vis spectroscopy (**Figure 4.3**). The thorium atom has a distorted square antiprismatic coordination environment, with the coordinating oxygen and nitrogen on one ligand making up each square face of the coordination environment. Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ has four Th-O bonds with lengths 2.254, 2.326, 2.282, and 2.289 Å. These Th-O bonds are 0.2 Å shorter than the average observed in similar thorium sandwich complexes, suggesting stronger interactions as compared to previously reported compounds.[39,55-60]

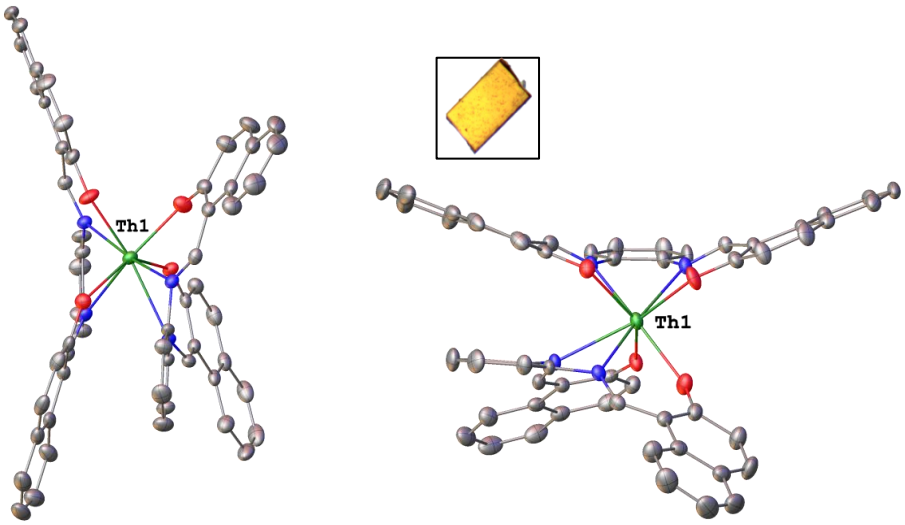



**Figure 4.3.** Projections of Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ highlighting the 8-coordinate thorium(IV) metal center. Disordered interstitial toluene solvent molecule and hydrogen atoms have been removed for clarity. Carbon atoms are shown in grey, nitrogen in blue, oxygen in red, and thorium in green. Inset image of crystal of data collection.[47]

The shortened distances do not seem to be caused by π-π overlap in the ligand systems, as there is distortion from planarity preventing π-stacking interactions. The average Th-N bond length of 2.63 Å (±0.01), is slightly longer (0.1 Å) than that in the reported porphyrin sandwich structure,[14] but comparable (within ± 0.03 Å) to many other 8 and 9 coordinate thorium sandwich complexes described previously.[39,56-58] The Th-N bond lengths are notably shorter (0.2 Å) than reported Th-N bond lengths in either tertiary amine containing ligands[59]or hydroxy

bridged species.[60] The coordination of the free base may be more properly explained as a negatively charged N donor and neutral carbonyl species, rather than a negatively charged phenol and neutral imine donor, to explain this uncommonly short Th-N bond lengths.

The Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ complex was found to be crystalline and ordered in P2$_1$/n space group, with one half of a disordered hexane molecule and one water molecule per asymmetric unit (**Figure 4.4**). The cerium(IV) atom also has a distorted square antiprismatic coordination environment. The average Ce-O bond length of 2.22 Å (±0.02) is within the standard deviation of the average Ce(IV)-O bond length in similar sandwich complexes reported in the literature.[53, 61-62] The Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ complex has Ce-N bond lengths of 2.571, 2.521, 2.580, and 2.519 Å. The Ce-O and Ce-N bond lengths in Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ are, on average, 0.2 Å shorter than reported Ce(III)-O and Ce(III)-N bond lengths, affirming the assignment as the tetrapositive $Ce^{4+}$ ion.[53, 61-63]

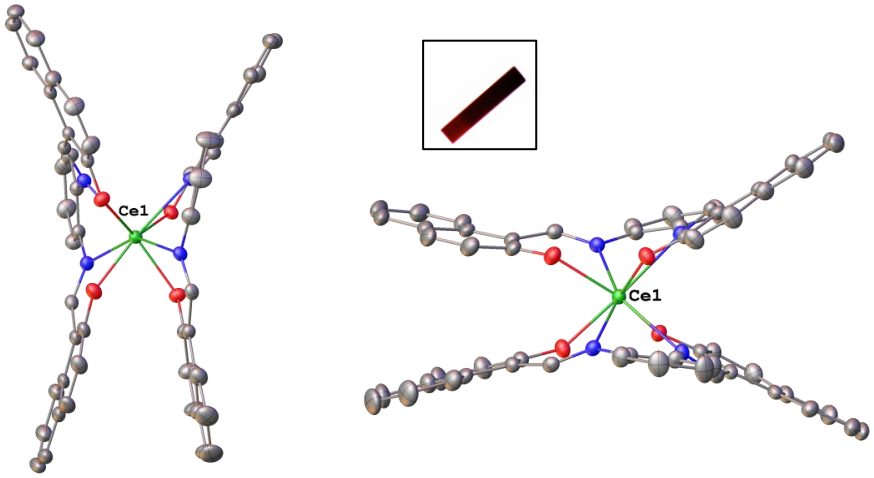



**Figure 4.4.** Projection of Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ highlighting the 8-coordinate cerium(IV) metal center. Disordered interstitial hexane and hydrogen atoms have been removed for clarity. Carbon atoms are shown in grey, nitrogen in blue, oxygen in red, and cerium in green.[47]

Nine of eleven of the Ln$_2$[$\mathbf{L}^{\mathbf{VII}}$]$_3$ complexes, Nd(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Yb(III), and Lu(III), were crystallized from slow evaporation of saturated

methanol solutions. Crystallographic data for $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$, and $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$ are reported in **Table 4.2**.

**Table 4.2.** Crystallographic data for $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$, and $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$.[46]

| **Identification code** | $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$-2MeOH | $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$-2MeOH | $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$-3MeOH | $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$-MeOH |
|---|---|---|---|---|
| **Emp. formula** | $C_{86}H_{62}N_6O_8Nd_2$ | $C_{88}H_{66}N_6O_8Gd_2Cl_4$ | $C_{87}H_{66}N_6O_9Ho_2$ | $C_{86}H_{58}N_6O_7Yb_2$ |
| **Formula weight** | 1595.96 | 1791.85 | 1669.39 | 1791.38 |
| **Crystal system** | monoclinic | triclinic | triclinic | monoclinic |
| **Space group** | $P2_1/n$ | $P\bar{1}$ | $P\bar{1}$ | $P2_1/c$ |
| **a/Å** | 10.2700(4) | 12.3985(2) | 10.3525(1) | 17.4061(8) |
| **b/Å** | 42.4242 (19) | 17.1412(3) | 17.6031(2) | 20.4222(10) |
| **c/Å** | 17.3937(8) | 17.7640(3) | 18.9169(2) | 20.6605(10) |
| **α/°** | 90 | 87.7454(8) | 82.6930(6) | 90 |
| **β/°** | 91.5379(11) | 75.9048(7) | 86.1741(6) | 96.2697 |
| **γ/°** | 90 | 85.8045(7) | 82.4147(6) | 90 |
| **Volume/Å$^3$** | 7575.6(6) | 3650.92(11) | 3385.05(6) | 7300.3(6) |
| **Z** | 4 | 2 | 2 | 4 |
| **$\rho_{calc}$ (g cm$^{-3}$)** | 1.3992 | 1.6298 | 1.6377 | 1.6298 |
| **μ (mm$^{-1}$)** | 1.415 | 2.013 | 2.39 | 2.756 |
| **Temperature/K** | 181.65 | 180.45 | 180.65 | 180.45 |
| **Radiation (Å)** | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| **collected reflns** | 66686 | 112543 | 127024 | 104807 |
| **Indpdnt reflns** | 10233 | 20486 | 20696 | 14938 |
| **GoF (on F$^2$)** | 1.073 | 1.155 | 1.154 | 1.076 |
| **$R_1$ [I=2σ (I)]** | 0.0887 | 0.0362 | 0.0271 | 0.0576 |
| **$wR_2$ [I=2σ (I)]** | 0.2250 | 0.0841 | 0.0561 | 0.1027 |
| **$(\Delta\rho)_{max}/(\Delta\rho)_{min}$ (e Å$^{-3}$)** | 2.05/-1.77 | 3.29/-2.30 | 3.23/-1.90 | 2.08/-1.79 |

While all the crystalline products were observed to form distinct 3L:2M complexes, four structures, one early, two middle, and one late lanthanide, will be discussed in detail here to highlight the key structural differences. These differences are likely due to the reduced ionic radii as caused by the lanthanide contraction (**Figure 4.5-4.8**).

The metal complex $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$, **Figure 4.5a-c**, crystallized in space group $P2_1/n$ and contains two interstitial dichloromethane (DCM) molecules. The complex was found to have two neodymium atoms that are 8-coordinate, unlike all the other structures reported here and previously reported with this ligand framework.[36,64] **Figure 4.5a** clearly shows a hydrogen

bonding interaction with a length of 1.927 Å between a coordinating methanol (O7) on Nd2 and a phenol donor (O2) that is also bound to Nd1. This interaction is maintained throughout the lanthanide series structures. As pictured in **Figure 4.5b**, Nd1 exhibits a distorted square antiprismatic binding geometry, where all eight donor atoms come from two ligand moieties. The Nd-O bond lengths range from 2.302-2.622 Å, notably the phenolic donors (2.32 on average) are shorter than the bridging oxygen (2.50 on average) indicating a stronger interaction with the phenolic oxygen. The Nd-N bond lengths range from 2.590 to 2.651 Å. The internuclear distance between Nd1 and Nd2 is 4.017 Å (**Figure 4.5b**). These bond lengths are slightly longer, ~0.05 Å, than the average of previous examples of triple-decker Nd complexes with simple salen ligands,[33,65-66] but this difference may be due to the larger pi systems of the ligand rather than notable changes in the coordination environment. The second metal ion - Nd2 is 8-coordinate, but is likewise greatly distorted from the idealized square antiprismatic ligand environment. Four donor atoms are from one ligand, two oxygen donor atoms are from a second ligand, and two are occupied by coordinating methanol solvent molecules. The two phenol donors of the internal L are μ-oxo groups. As shown in **Figure 4.5c**, the napthyl rings are not observed to have any π-stacking interactions and are, in fact, greatly distorted from planarity. This is notably different from other salen Nd salen complexes found in the literature in which π-π effects were significant reporting π-π stacking distances at 3.929 and 3.836 Å.[67]

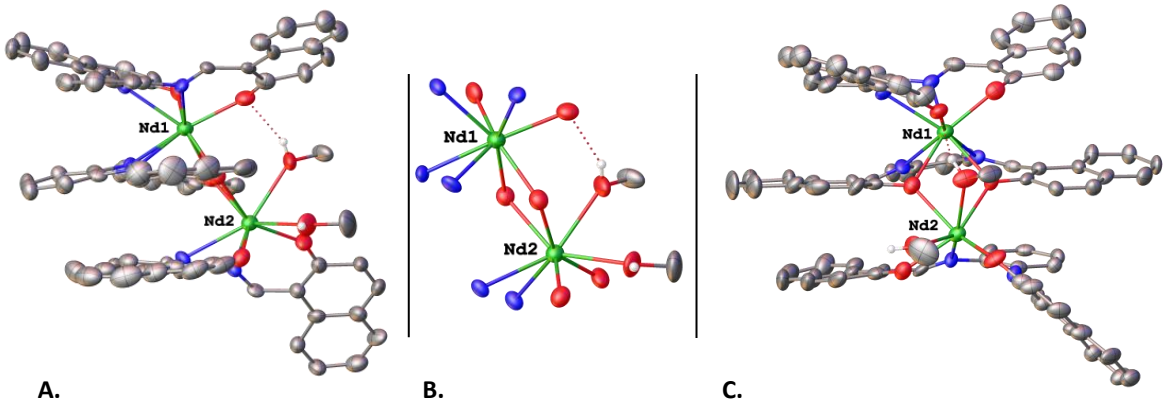



**Figure 4.5. a.** Projection of the side view of $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$ **b.** Coordination spheres of Nd1 and Nd2 **c.** Projection of the front view of $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$. Interstitial solvent and hydrogen, except those involved in hydrogen bonding have been removed for clarity. Carbon atoms are shown in grey, nitrogen in blue, oxygen in red, and neodymium in green.[46]

The lanthanide example from the middle of the series, $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$, crystallized in Pī with two interstitial DCM molecules per asymmetric unit. This structure is shown in **Figure 4.6a-c**. While the $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$ structure contains two coordinating methanol molecules, in $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$ one methanol is coordinating to the metal center and the second methanol (O8) is hydrogen bonded to the coordinating methanol (O7) and the phenol oxygen (O2). The coordination sphere of Gd1, **Figure 4.6b**, is similar to that of Nd1, and is occupied by two tetradentate ligand equivalents. The second Gd atom, however, is seven coordinate and is observed to have a monocapped trigonal prismatic geometry. Four donor atoms are from one equivalent of ligand, two donors atoms are μ-aryloxides from a second equivalent of ligand, and the final coordination site is occupied by a coordinating methanol. The Gd-O bond lengths range from 2.218-2.388 Å, with the bridged phenolic oxygen being presumably due to weaker interactions as judged by the longer lengths. The Gd-N bond lengths range from 2.487-2.562 Å. The Gd1-Gd2 distance of 3.915 Å and the Gd2-O7 distance of the coordinating methanol is 2.419 Å. While other examples of $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$ salen type sandwich complexes have been prepared and characterized,[33] this is the first example of solid-state elucidation of this coordination environment for gadolinium. As

highlighted in **Figure 4.6a** and **Figure 4.6c**, the planarity of the napthylsalophen ligand is better retained in the mid lanthanides. This planarity is greatly aided by the interaction with the additional hydrogen bonded methanol, as well as the smaller size of Gd in comparison to Nd. While the π systems of the second and third tier of the double sandwich are interacting and aligned well, the first tier ligand twists noticeably to the left as is highlighted in **Figure 4.6c**.

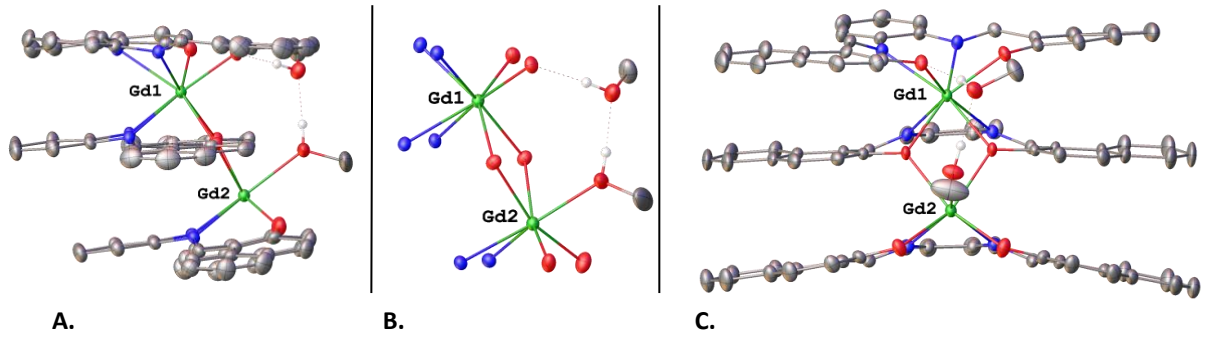



**Figure 4.6. a.** Projection of the side view of $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$ **b.** Coordination spheres of Gd1 and Gd2 **c.** Projection of the front view of $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$. Interstitial solvent and hydrogen, except those involved in hydrogen bonding have been removed for clarity. Carbon atoms are shown in grey, nitrogen in blue, oxygen in red, and gadolinium in green.[46]

The complex of $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$, with Ho, a mid-to late lanthanide, has a similar geometry as $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$, crystallized in Pī without the interstitial DCM in all the other analogues reported, but incorporates an additional methanol into the hydrogen-bonding network (**Figure 4.7a-c**). The additional methanol allows for increased planarity in the triple-decker sandwich (**Figure 4.7a**). The coordination of Ho1 is again distorted square antiprismatic, as with Gd1. Ho2 is distorted monocapped trigonal prismatic, with a coordinating methanol, a coordinating L equivalent, and two bridging oxo groups (**Figure 4.7b**). The Ho-O bond lengths range from 2.187-2.351 Å, with the longer Ho-O lengths being the bridging phenols. The Ho-N bond lengths range from 2.444-2.538 Å and the Ho1-Ho2 are separated by 3.854 Å. These bond lengths are within 0.08 Å of previously reported Ho salen structures.[67-68] As with $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$, the two bottom tiers of the

sandwich generally maintain planarity and interact through π-stacking interaction and the top tier rotates to the left (**Figure 4.7c**).

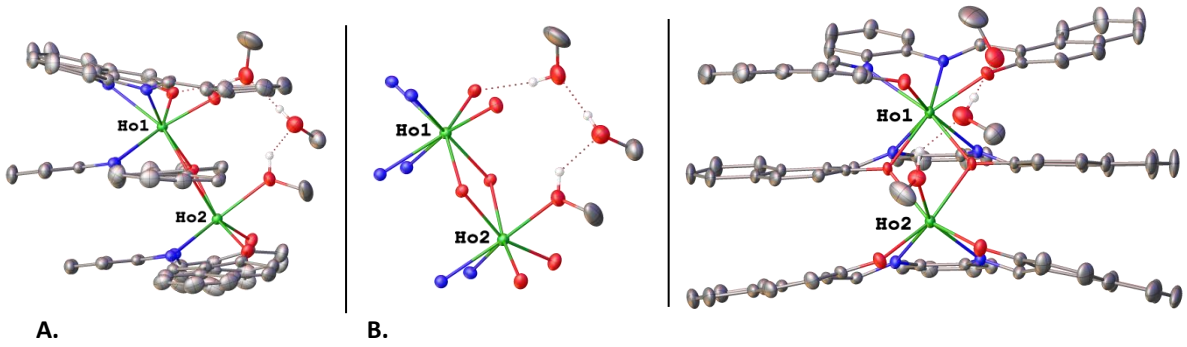



**Figure 4.7. a.** Projection of the side view of $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$ **b.** Coordination environments of Ho1 and Ho2 **c.** Projection of the front view of $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$. Interstitial DCM and hydrogen atoms, except those involved in hydrogen bonding have been removed for clarity. Carbon atoms are shown in grey, nitrogen in blue, oxygen in red, and holmium in green.[46]

$Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$, the late lanthanide example, was found to crystallize in $P2_1/c$ space group with two interstitial DCM molecules per asymmetric unit and is shown in **Figure 4.8a-c**. As highlighted in **Figure 4.8a**, the hydrogen bond between the coordinating methanol and phenol (2.159 Å) is elongated as compared to the $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$ and $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$ cases, which coordinated an additional methanol. The coordination spheres of Yb1 and Yb2 are reminiscent of $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$ and $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$. Yb1 has a distorted square antiprismatic coordination geometry, with all the donor atoms being from two equivalents of $[\mathbf{L}^{\mathbf{VII}}]^{2-}$ (**Figure 4.8b**). Yb2 has a distorted monocapped trigonal prismatic geometry, with four donor atoms coming from one equivalent of $[\mathbf{L}^{\mathbf{VII}}]^{2-}$, two donor atoms are from a second equivalent of $[\mathbf{L}^{\mathbf{VII}}]^{2-}$, and the last donor atom is from a coordinating methanol. This is similar to that observed by Sanudo and co-workers, but a coordinating water molecule completed the coordination sphere for Yb2 rather than a methanol.[36] The Yb-O bond lengths range from 2.163-2.321 Å, which is within 0.01 Å of one previously reported Yb salen complex,[36,69] but is significantly shorter (~0.1 Å) than other

examples.[19,70] The Yb-N bond lengths range from 2.400-2.501 Å, and the Yb1-Yb2 distance is 3.778 Å, which are within previously reported ranges.[19,36,70] The planarity of $[\mathbf{L}^{\mathbf{VII}}]^{2-}$ is more distorted than the Gd and Ho structures, which had additional methanol incorporation, but is generally maintained (**Figure 4.8c**). The π systems in the second and third tiers stack well, while the first tier is rotated slightly to the right due to the hydrogen bonding interaction of the methanol.

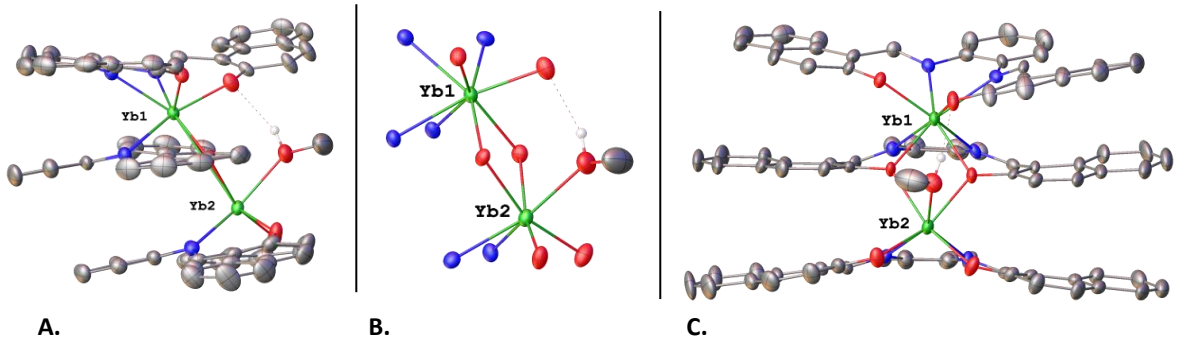



**Figure 4.8. a.** Projection of the side view of $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$ **b.** Coordination environments of Yb1 and Yb2 **c.** Projection of the front view of $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$. Interstitial solvent and hydrogen, except those involved in hydrogen bonding have been removed for clarity. Carbon atoms are shown in grey, nitrogen in blue, oxygen in red, and ytterbium in green.[46]

The metal ion coordination in the $Eu_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Tb_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Dy_2[\mathbf{L}^{\mathbf{VII}}]_3$, and $Lu_2[\mathbf{L}^{\mathbf{VII}}]_3$ complexes (**Figures 4.9-4.11 and 4.13**) are isostructural with $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$, with small variations in the unit cell (crystallographic data displayed in **Table 4.3**). $Er_2[\mathbf{L}^{\mathbf{VII}}]_3$ is isostructural with $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$, with small variations in the unit cell (**Figure 4.12**).

**Table 4.3.** Crystallographic Data for $Eu_2[\mathbf{L}^{VII}]_3$, $Tb_2[\mathbf{L}^{VII}]_3$, $Dy_2[\mathbf{L}^{VII}]_3$, $Er_2[\mathbf{L}^{VII}]_3$, and $Lu_2[\mathbf{L}^{VII}]_3$.[46]

| **Identification code** | **$Eu_2[L^{VII}]_3$-MeOH-2DCM** | **$Tb_2[L^{VII}]_3$-MeOH** | **$Dy_2[L^{VII}]_3$-MeOH** | **$Er_2[L^{VII}]_3$-3MeOH** | **$Lu_2[L^{VII}]_3$-MeOH** |
|---|---|---|---|---|---|
| **Empirical formula** | $C_{87}H_{62}Cl_4N_6O_7Eu_2$ | $C_{85}H_{58}N_6O_7Tb_2$ | $C_{85}H_{58}N_6O_7Dy_2$ | $C_{87}H_{66}N_6O_9Er_2$ | $C_{85}H_{58}N_6O_7Lu_2$ |
| **Formula weight** | 1749.24 | 1593.29 | 1600.44 | 1674.04 | 1625.38 |
| **Crystal system** | monoclinic | monoclinic | monoclinic | triclinic | monoclinic |
| **Space group** | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ | P-1 | $P2_1/c$ |
| **a/Å** | 17.512(7) | 17.4947(6) | 17.4758(9) | 10.309(2) | 17.3981(17) |
| **b/Å** | 20.500(8) | 20.5096(7) | 20.4943(11) | 17.582(4) | 20.4310(19) |
| **c/Å** | 20.517(8) | 20.6071(8) | 20.6011(11) | 18.939(4) | 20.6803(19) |
| **α/°** | 90 | 90 | 90 | 82.655(4) | 90 |
| **β/°** | 96.457(7) | 96.4934(9) | 96.445(1) | 86.443(4) | 96.1767(13) |
| **γ/°** | 90 | 90 | 90 | 82.386(4) | 90 |
| **Volume/Å$^3$** | 7319(5) | 7347.3(4) | 7331.7(7) | 3371.2(12) | 7308.4(12) |
| **Z** | 4 | 4 | 4 | 2 | 4 |
| **ρcalc (g cm$^{-3}$)** | 1.5873 | 1.4404 | 1.4498 | 1.6490 | 1.4771 |
| **m/mm-1** | 1.907 | 1.969 | 2.082 | 2.542 | 2.745 |
| **Temperature/K** | 180.45 | 180.45 | 180.45 | 180.65 | 180.45 |
| **Radiation** | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| **collected reflns** | 23881 | 107251 | 97079 | 26445 | 80420 |
| **Independent reflns** | 2833 | 16189 | 12348 | 8754 | 16055 |
| **GoF (on F2)** | 1.127 | 1.078 | 1.085 | 0.941 | 1.987 |
| **R1 [I=2σ (I)]** | 0.0682 | 0.0495 | 0.0622 | 0.0608 | 0.1491 |
| **wR2 [I=2σ (I)]** | 0.1750 | 0.0954 | 0.1037 | 0.1208 | 0.4186 |
| **(Δρ)max/(Δρ)min (e Å$^{-3}$)** | 2.67/-0.79 | 3.04/-1.35 | 2.26/-3.45 | 2.74/-2.53 | 8.78/-2.86 |

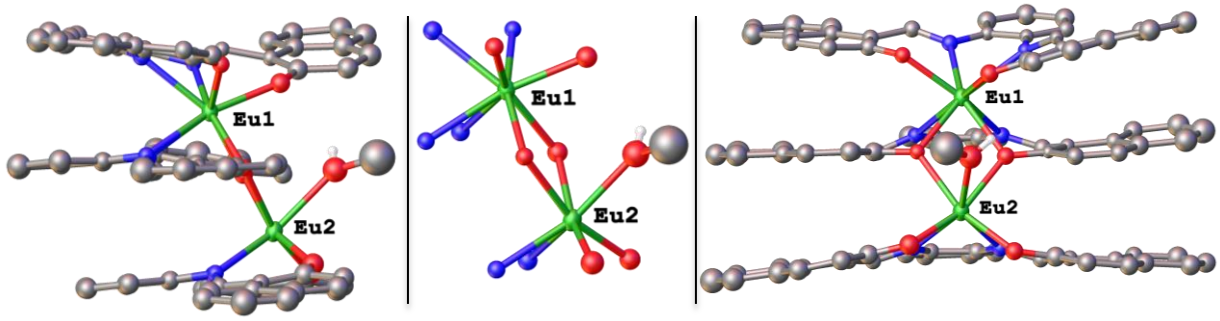



**Figure 4.9.** Projections of $Eu_2[\mathbf{L}^{VII}]_3$. Carbon atoms shown in grey, hydrogen in white, oxygen in red, nitrogen in blue, and europium in green.[46]

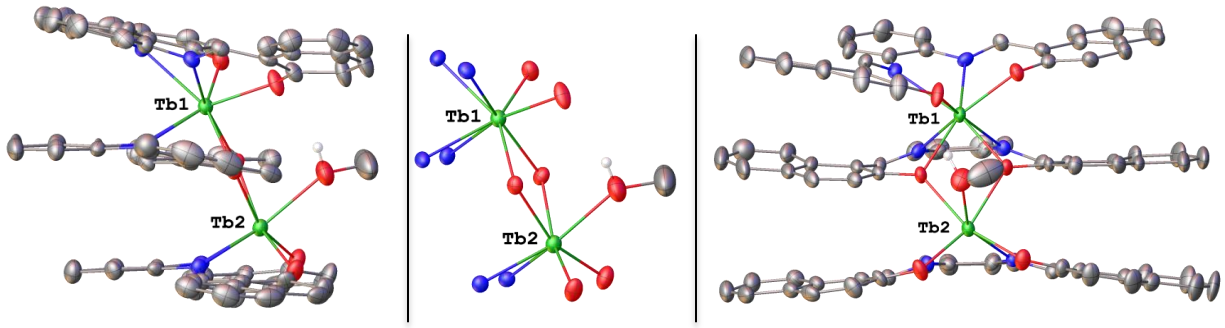



**Figure 4.10.** Projections of $Tb_2[\mathbf{L}^{\mathbf{VII}}]_3$. Carbon atoms shown in grey, hydrogen in white, oxygen in red, nitrogen in blue, and terbium in green.[46]

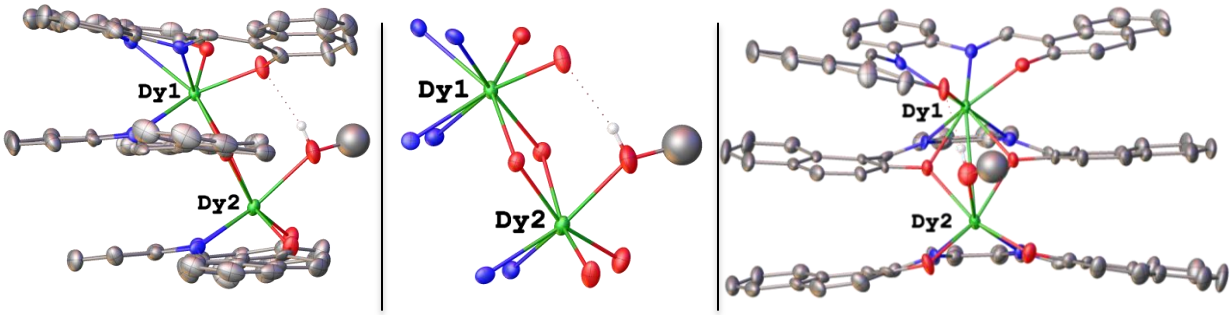



**Figure 4.11.** Projections of $Dy_2[\mathbf{L}^{\mathbf{VII}}]_3$. Carbon atoms shown in grey, hydrogen in white, oxygen in red, nitrogen in blue, and dysprosium in green.[46]

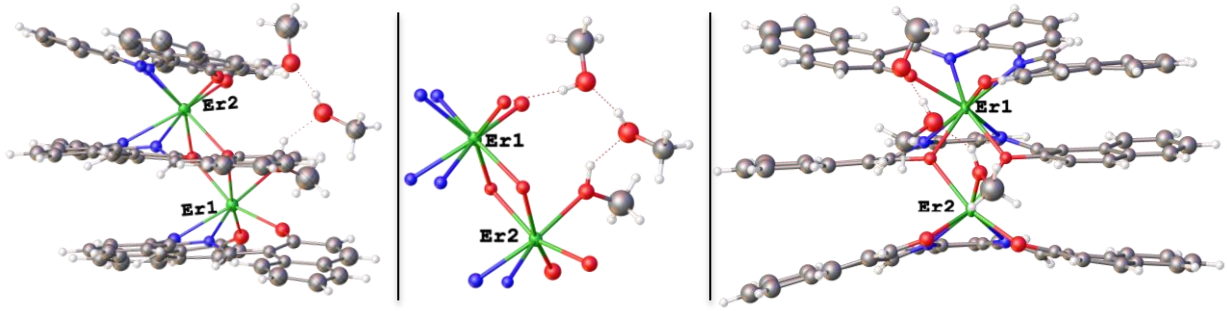



**Figure 4.12.** Projections of $Er_2[\mathbf{L}^{\mathbf{VII}}]_3$. Carbon atoms shown in grey, hydrogen in white, oxygen in red, nitrogen in blue, and erbium in green.[46]

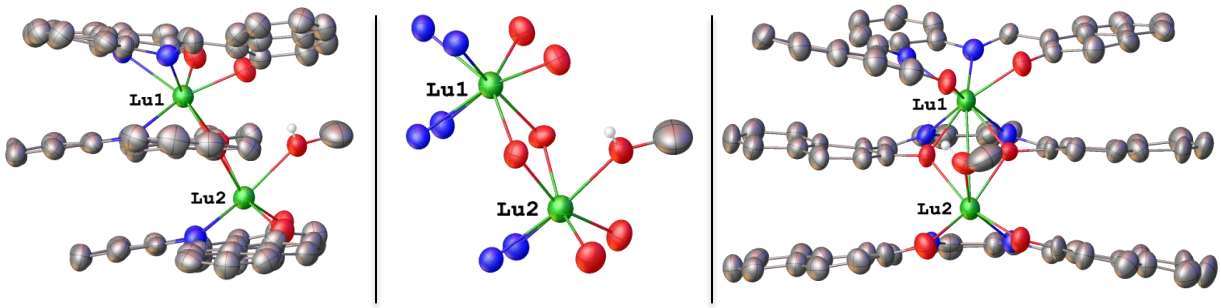



**Figure 4.13.** Projections of $Lu_2[\mathbf{L}^{\mathbf{VII}}]_3$. Carbon atoms shown in grey, hydrogen in white, oxygen in red, nitrogen in blue, and lutetium in green.[46]

As is highlighted in **Figures 4.5-4.13**, the lanthanide contraction is evident in the coordination environments of $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$, and $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$. The contraction is obvious when looking at the bond angles and lengths, which can be found in **Table 4.4** and **Table 4.5**, respectively. The bond lengths and angles of $Eu_2[\mathbf{L}^{\mathbf{VII}}]_3$ and $Dy_2[\mathbf{L}^{\mathbf{VII}}]_3$ are comparable to previously reported salen sandwich complexes.[34, 71-73] Bond angles generally widen and bond lengths shorten from early (Nd) to late (Yb) lanthanides, which is consistent with the lanthanide contraction and smaller size of the late lanthanides. In particular, these changes are most evident in the O-M-O angles, which span from 111.0° in $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$ to 90.25° in $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$. The M1-M2 distances consistently decrease from 4.017 Å to 3.778 Å, highlighting the contraction. In fact, the contraction is evident in all the bond lengths (**Table 4.5**).

**Table 4.4**. Selected bond angles (deg) of $Ln_2[\mathbf{L}^{\mathbf{VII}}]_3$ complexes[46]

| | $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$ | $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$ | $Tb_2[\mathbf{L}^{\mathbf{VII}}]_3$ | $Dy_2[\mathbf{L}^{\mathbf{VII}}]_3$ | $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$ | $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$ | $Lu_2[\mathbf{L}^{\mathbf{VII}}]_3$ |
|---|---|---|---|---|---|---|---|
| **O1-M1-N1** | 69.1 | 71.44 | 71.52 | 72.08 | 71.70 | 74.86 | 74.6 |
| **N1-M1-N2** | 64.0 | 64.54 | 65.19 | 65.37 | 66.00 | 66.04 | 65.3 |
| **N2-M1-O2** | 69.1 | 70.24 | 73.54 | 74.02 | 72.65 | 72.47 | 75.3 |
| **O2-M1-O1** | 89.2 | 80.89 | 84.48 | 83.72 | 81.74 | 81.90 | 81.4 |
| **O3-M1-N3** | 68.2 | 68.71 | 68.79 | 69.07 | 69.95 | 69.23 | 70.7 |
| **N3-M1-N4** | 61.3 | 63.02 | 63.14 | 63.23 | 63.32 | 64.55 | 63.5 |
| **N4-M1-O4** | 68.4 | 69.20 | 68.81 | 68.78 | 68.89 | 69.89 | 69.3 |
| **O4-M1-O3** | 71.3 | 69.21 | 69.84 | 69.57 | 68.85 | 68.84 | 69.1 |
| **O3-M2-O4** | 70.1 | 68.77 | 70.34 | 70.28 | 69.20 | 69.83 | 70.0 |
| **O5-M2-N5** | 67.6 | 72.81 | 73.49 | 73.97 | 73.77 | 74.64 | 75.5 |
| **N5-M2-N6** | 62.0 | 65.51 | 66.02 | 66.26 | 66.30 | 66.93 | 66.3 |
| **N6-M2-O6** | 68.0 | 72.75 | 73.47 | 73.61 | 73.03 | 75.38 | 75.0 |
| **O6-M2-O5** | 111.0 | 93.85 | 93.90 | 92.20 | 93.00 | 90.25 | 88.4 |

**Table 4.5.** Selected bond lengths (Å) of $Ln_2[\mathbf{L}^{\mathbf{VII}}]_3$ complexes[46]

| | $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$ | $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$ | $Tb_2[\mathbf{L}^{\mathbf{VII}}]_3$ | $Dy_2[\mathbf{L}^{\mathbf{VII}}]_3$ | $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$ | $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$ | $Lu_2[\mathbf{L}^{\mathbf{VII}}]_3$ |
|---|---|---|---|---|---|---|---|
| **M1-N1** | 2.590 | 2.500 | 2.489 | 2.466 | 2.477 | 2.419 | 2.37 |
| **M1-N2** | 2.600 | 2.530 | 2.472 | 2.463 | 2.445 | 2.445 | 2.37 |
| **M1-O1** | 2.302 | 2.275 | 2.271 | 2.255 | 2.241 | 2.234 | 2.22 |
| **M1-O2** | 2.373 | 2.318 | 2.281 | 2.267 | 2.232 | 2.210 | 2.22 |
| **M1-N3** | 2.609 | 2.562 | 2.559 | 2.553 | 2.538 | 2.483 | 2.48 |
| **M1-N4** | 2.651 | 2.549 | 2.537 | 2.524 | 2.533 | 2.501 | 2.46 |
| **M1-O3** | 2.458 | 2.379 | 2.350 | 2.345 | 2.351 | 2.321 | 2.31 |
| **M1-O4** | 2.440 | 2.368 | 2.379 | 2.362 | 2.338 | 2.301 | 2.32 |
| **M2-O3** | 2.514 | 2.386 | 2.357 | 2.339 | 2.330 | 2.275 | 2.28 |
| **M2-O4** | 2.455 | 2.388 | 2.343 | 2.327 | 2.339 | 2.295 | 2.30 |
| **M2-N5** | 2.637 | 2.487 | 2.461 | 2.447 | 2.448 | 2.400 | 2.39 |
| **M2-N6** | 2.631 | 2.493 | 2.463 | 2.445 | 2.444 | 2.410 | 2.37 |
| **M2-O5** | 2.280 | 2.237 | 2.211 | 2.119 | 2.187 | 2.163 | 2.20 |
| **M2-O6** | 2.331 | 2.218 | 2.218 | 2.203 | 1.196 | 2.167 | 2.18 |
| **M2-O7** | 2.594 | 2.419 | 2.467 | 2.443 | 2.383 | 2.392 | 2.37 |
| **M1-M2** | 4.017 | 3.915 | 3.858 | 3.838 | 3.854 | 3.778 | 3.77 |

Crystals of $UO_2[\mathbf{L}^{\mathbf{VII}}]$ were grown from slow diffusion of hexanes into a saturated solution of $UO_2[\mathbf{L}^{\mathbf{VII}}]$ in toluene. The compound $UO_2[\mathbf{L}^{\mathbf{VII}}]$ was observed to crystallize in the $P2_1/n$ space group with four interstitial dichloromethane molecules. Two distinct $UO_2[\mathbf{L}^{\mathbf{VII}}]$ units are found in the asymmetric unit and are shown in **Figure 4.14**. These two units are symmetrically related to two other complexes, resulting in a tetrad of $UO_2[\mathbf{L}^{\mathbf{VII}}]$ complexes held

together through hydrogen bonding interactions with a H---O distance of 1.923 and 2.032 Å (**Figure 4.15**). The average U-$O_{yl}$ bond length is 1.777 Å, which is easily within the normal range for the –yl oxo groups bound to a uranium hexavalent ion. The hydrogen bonding interactions to these –yl oxygen are reminiscent of Lewis acid interactions of -yl oxygen in compounds made by Arnold and Bart that proved to easily reduce uranyl(VI) to uranyl(V).[74-76] These compounds always showed a lengthening of the U-$O_{yl}$ bond, which unfortunately was not observed in $UO_2$[$\mathbf{L}^{\mathbf{VII}}$]. The average U-$N_{imine}$ bond lengths of 2.515 Å, U-$O_{H2O}$ bond lengths of 2.450 Å, and the U-$O_{phenol}$ bond lengths of 2.286 Å are within normal ranges. Of note is the U-$O_{phenol}$ distance of 2.311(3) Å, which is slightly lengthened and is participating in hydrogen bonding with the coordinating water molecule of the next complex.

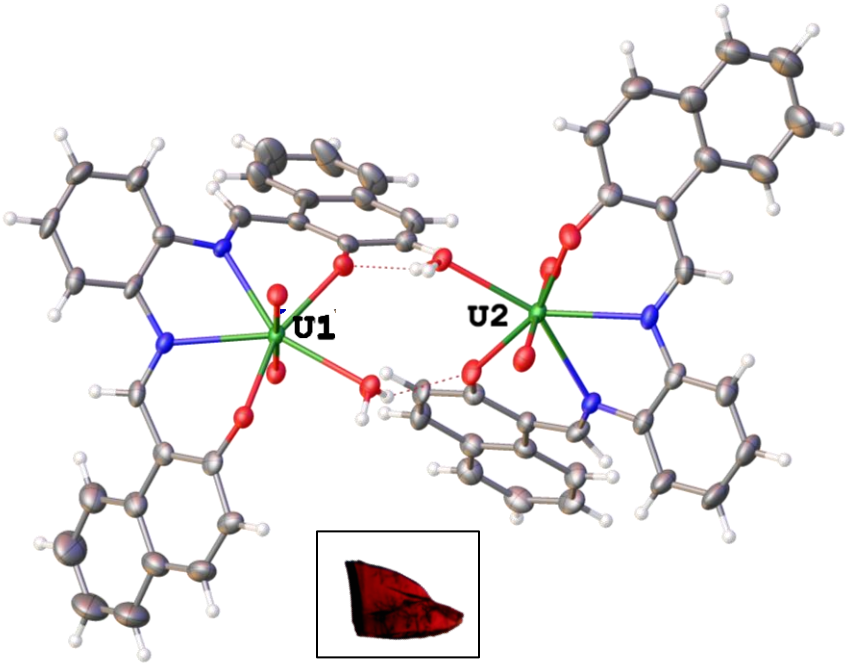



**Figure 4.14**. Projection of the asymmetric unit of $UO_2$[$\mathbf{L}^{\mathbf{VII}}$]. Carbon atoms are shown in grey, oxygen in red, nitrogen in blue, hydrogen in white, and uranium in green.

These hydrogen bonding interactions observed in the complex $UO_2$[$\mathbf{L}^{\mathbf{VII}}$], paired with pi-pi stacking of the naphthalene rings of 4.304 Å, affords an interesting supramolecular stacking

structure with void channels that are filled with interstitial DCM in the solid-state structure (**Figure 4.15**). These channels have been observed in metal organic frameworks (MOFs) and were of interest for applications in that area.[77-78] These stacking interactions are off-set, which is common in structures such as these, but is an artifact of the packing rather than an interaction that would allow this structure to maintain these tetramers in solution and therefore limits their application.

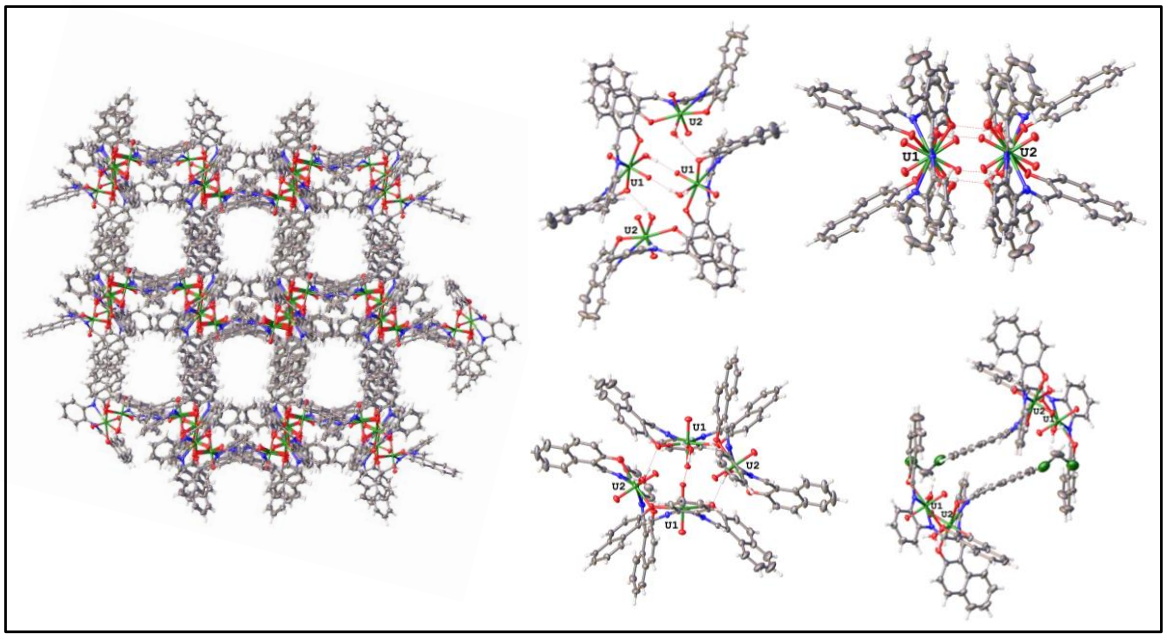



**Figure 4.15.** Projections of the $UO_2[\mathbf{L}^{\mathbf{VII}}]$ complex highlighting the hydrogen bonded tetramers and pi-pi stacking interactions resulting in an interesting supramolecular structure. Interstitial dichloromethane molecules have been removed for clarity.

**Uncharacteristic Thorium(IV) Emission**

Absorbance and fluorescence spectra for $Th[\mathbf{L}^{\mathbf{VII}}]_2$, and $Ce[\mathbf{L}^{\mathbf{VII}}]_2$ were collected both from the solutions and in the solid-state, resulting in unexpected emissive properties of the $Th[\mathbf{L}^{\mathbf{VII}}]_2$ complex. Thus far, $Th[\mathbf{L}^{\mathbf{VII}}]_2$ is the first example of a fluorescent thorium compound in both solution and solid-state. Images of $Th[\mathbf{L}^{\mathbf{VII}}]_2$ fluorescence under ambient light and with 365 nm excitation are shown in **Figure 4.16**. All fluorescence is quenched in solution and solid state

for Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ with 365 nm excitation. In solution, two absorbance peaks at 335 nm and 387 nm, with a shoulder centered on 440 nm are observed in the UV-visible spectrum (**Figure 4.17**). In dichloromethane solution the absorbance of the complex Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ features two absorbance peaks at 333 nm and 391 nm, with a shoulder centered on 440 nm, and an emission peak at 473 nm. In the solid-state, an absorbance peak centered at 488 nm, and an emission peak at 537 nm are observed. A broad emission feature is observed in solution and solid-state Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ at the same excitation wavelength. This is highly unusual for a Th(IV) complex (**Figure 4.18**).

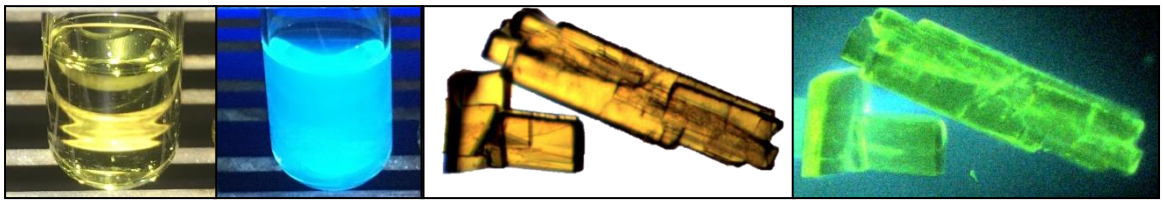
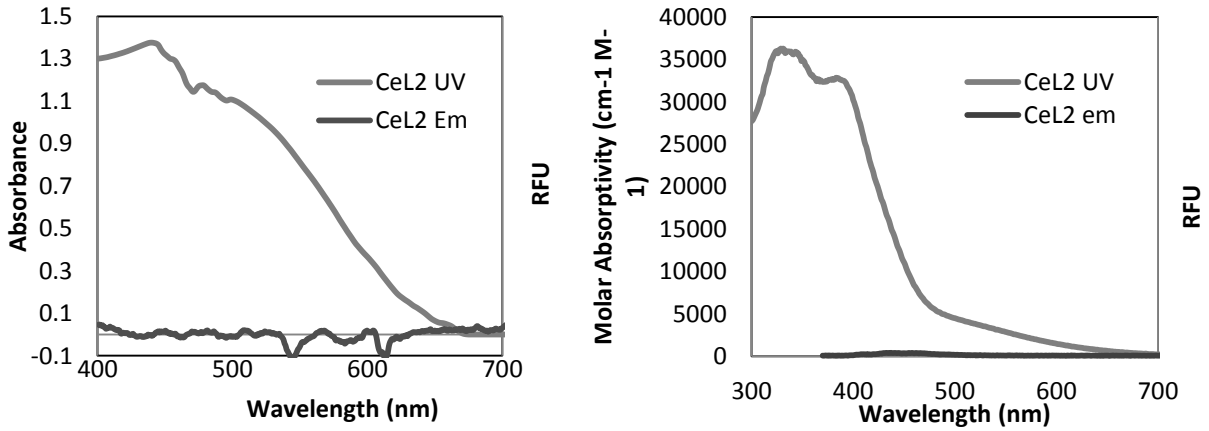
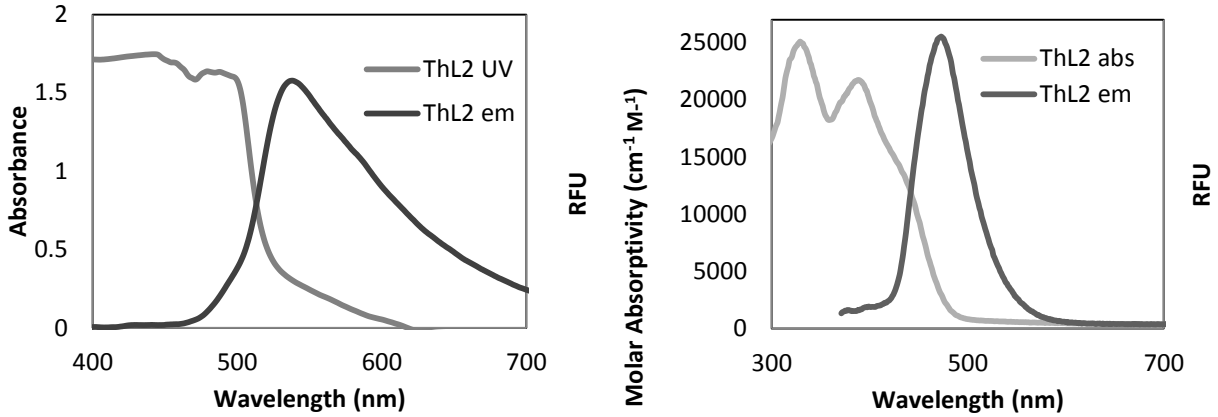


**Figure 4.16.** Absorption and emission of a 40 μM $CHCl_3$ solution of Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ and in single crystals under white light and under 365 nm excitation.[47]




**A.** **B.**

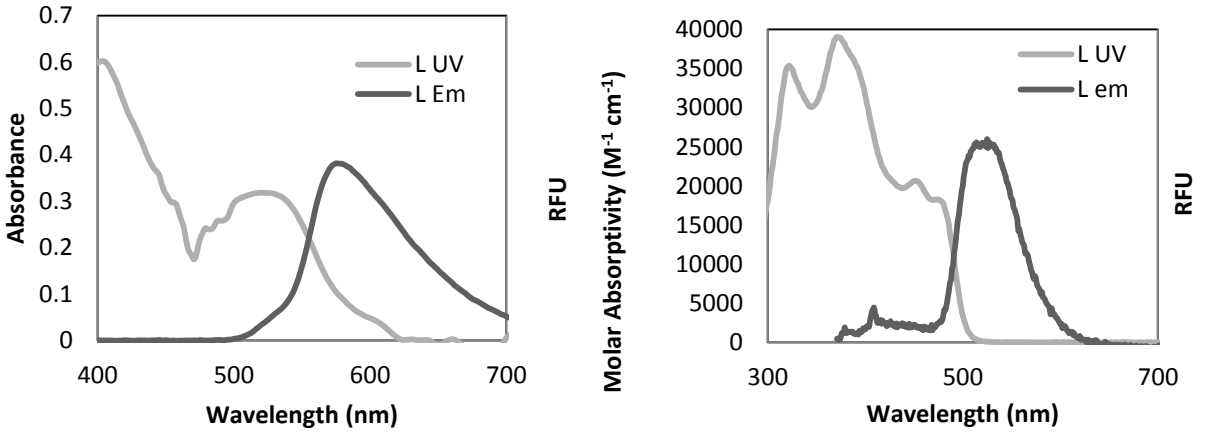
**Figure 4.17. A.** Solid-state absorbance and emission spectra with excitation at 365 nm of Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$. **B.** Solution phase absorbance and emission spectra of Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ in dichloromethane with excitation at 365 nm.[47]




**A.** **B.**

**Figure 4.18. A.** Solid-state absorbance emission spectra with excitation at 365 nm of Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$. **B.** Solution phase absorbance and emission spectra of Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ in acetonitrile with excitation at 365 nm.[47]

To compare the observed emission and quenching of the Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ and Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ complexes, the UV-visible spectrum and emission spectrum of the ligand were measured. In dichloromenthane solutions of the free base, four absorbance peaks at 326 nm, 375 nm, 456, and 476 nm are observed, with an emission peak at 517 nm. In the solid-state an absorbance peak at 520 nm and an emission peak at 575 nm are observed **(Figure 4.19)**. As the Th(IV) ion is non-emissive, the emission can be assigned to a charge transfer state within the ligand framework in agreement with our theoretical calculations described below and comparison to ligand emission in solution and solid-state**.** Most examples characterized as fluorescent sensors for thorium are "turn-off" chemosensors, due to $f^0$ ground state of Th(IV).[79-80] One fluorescent thorium solid-state compound and three examples of solution phase fluorescence have been described previously, while many more examples of thorium quenching fluorescence exist.[49-52, 80]




**A.** **B.**

**Figure 4.19. A.** Solid-state absorbance emission spectra with excitation at 365 nm of [$H_2$**L**$^{\mathbf{VII}}$]. **B.** Solution phase absorbance and emission spectra of $H_2$[**L**$^{\mathbf{VII}}$]$_2$ in acetonitrile with excitation at 365 nm.[47]

The emission from Th[**L**$^{\mathbf{VII}}$]$_2$ was characterized in a variety of solvents in solution phase, as well as two distinct solid-state crystal systems (**Figure 4.20**). The emission of Th[**L**$^{\mathbf{VII}}$]$_2$ was found to be highly solvent dependent, and is summarized in **Table 4.6**. While solvent dependent fluorescence is not uncommon,[81-82] the change in emission of Th[**L**$^{\mathbf{VII}}$]$_2$ extends from 461 nm to 502 nm in solution, to as high as 537 nm observed in the solid-state. Th[**L**$^{\mathbf{VII}}$]$_2$ in chloroform and toluene, the non-coordinating solvents, were found to have emission bands near 460 nm, while in the coordinating solvents emission closer to 500 nm was observed. The quantum yield of Th[**L**$^{\mathbf{VII}}$]$_2$ in chloroform is 2.5%, and the coordinating solvents are non-fluorescent by comparison.

We hypothesize that the distortion caused by coordinating solvents in solution causes these changes in emission to longer wavelength, and reduces the quantum yield. This claim is substantiated by the more bulky coordinating solvents causes the emission to shift the most, especially methanol which is capable of hydrogen bonding. Further, the solid-state emissions from crystals that are formally distorted by the packing structure are both at longer wavelength.

Another possibility is the equilibrium between an 8 and 9 coordinate thorium metal center occurs in solution. Crystals in coordinating solvents, acetonitrile and DMSO, were grown and collected. All species were 8 coordinate in the solid-state, but loss of symmetry in the NMR does suggest an equilibrium between the 8 and 9 coordinate species.

**Table 4.6.** Emission wavelengths and quantum yields of 45 (±0.5) μM solutions of Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ in indicated solvents and solid-state crystals.[47]

| | $\lambda_{em}$ | $\phi_f$ |
|---|---|---|
| **$CHCl_3$** | 461 | 2.50 % |
| **Tol** | 464 | 0.50 % |
| **ACN** | 473 | 0.70 % |
| **DMF** | 487 | 0 % |
| **DMSO** | 487 | 0 % |
| **MeOH** | 502 | 0 % |
| **Tol-xtal** | 523 | -- |
| **DCM-xtal** | 537 | -- |

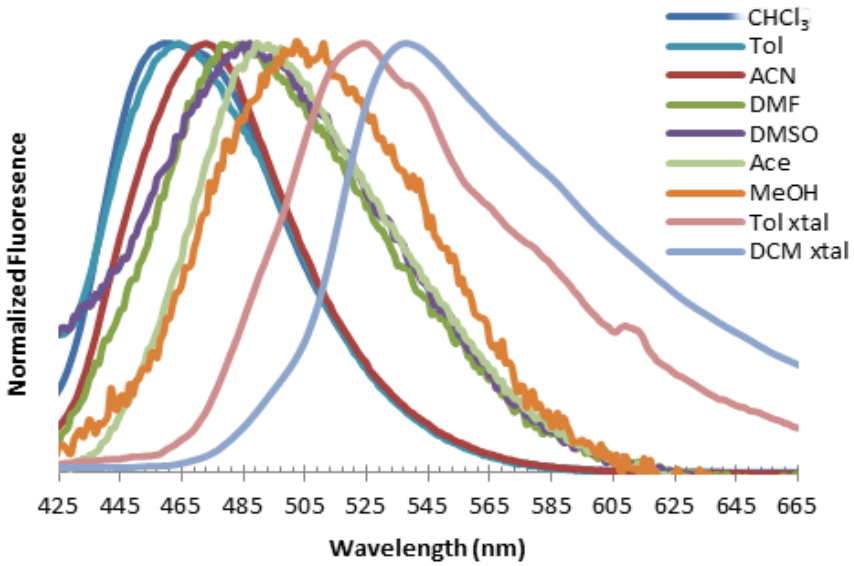



**Figure 4.20.** Normalized solution and solid-state emission of Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ with 365 nm excitation in indicated solvent.[47]

In an attempt to explain our observations, a collaborator performed density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations. The Th-O, Th-N, Ce-O, and Ce-

N bond lengths in the optimized structure range within 2.295-2.317, 2.648-2.691, 2.241-2.255, and 2.606-2.651 Å, respectively. The agreement (within ±0.05 Å) with the experimental values validates the employed methodology. The ground state of both Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ and Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ complexes were found to be closed-shell singlets with substantial Ce(IV) and Th(IV) character.

**Figure 4.21** shows the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for both complexes. Note the HOMO and LUMO for Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ are localized on the ligands. On the other hand, the HOMO of Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ is on the ligand but the LUMO is purely on cerium. The orbital resembling the LUMO of Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ is the eighth unoccupied orbital of Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$.

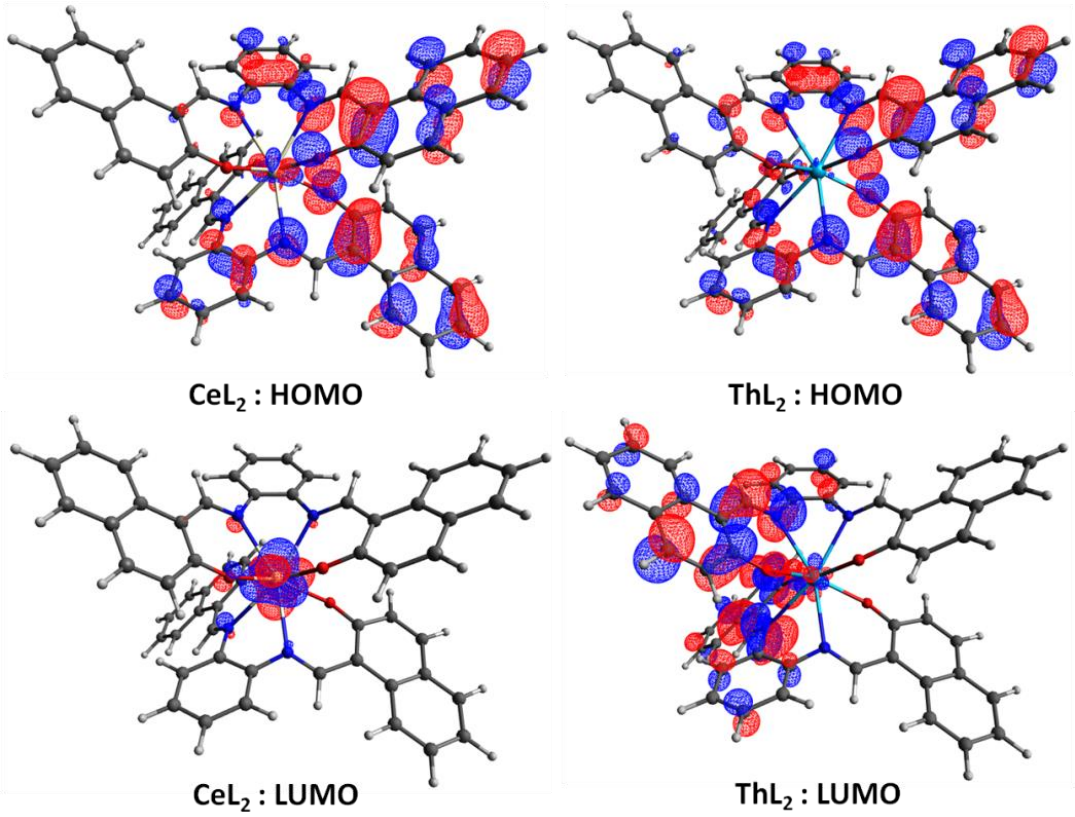



**Figure 4.21.** Ground state HOMO and LUMO of Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ and Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$.[47]

The vertical excitation energies of all electronic states of singlet spin multiplicity up to 3.5 eV are calculated at the TD-DFT level. The energy levels for the Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ and Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ complexes are compared in **Figure 4.22**. Within the present energy range all excitations of the Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ complex pertain mostly to "local" excitations within the ligands (blue lines). The electronic state with the largest transition probability is shown with a green wider line at 3.43 eV or 361 nm, which matches favorably with the experimental wavelength of 365 nm.

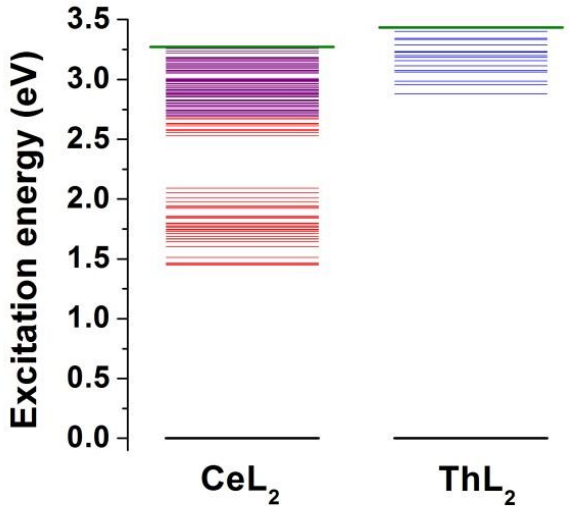



**Figure 4.22**. Vertically excited electronic levels of Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ and Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$.[47]

The Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ complex also has energy levels with a similar energy separation from the ground state (purple lines of **Figure 4.22**) that are not highly localized; the involved orbitals also have some cerium contribution. Most importantly, Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ possesses several other electronic excitations corresponding to pure intra-molecular electron transfer from the ligands to the metal (red lines of **Figure 4.22**). Access to these additional electronic states allow the slow relaxation to the lower states,[83] usually resulting from conical intersections or inter-system crossings which finally leads to fluorescence quenching.

**Tunable Ligand Emission of $Ln_2[L^{VII}]_3$**

The solution phase absorbance spectra of $Pr_2[\mathbf{L}^{VII}]_3$, $Nd_2[\mathbf{L}^{VII}]_3$, $Sm_2[\mathbf{L}^{VII}]_3$, $Eu_2[\mathbf{L}^{VII}]_3$, $Gd_2[\mathbf{L}^{VII}]_3$, $Tb_2[\mathbf{L}^{VII}]_3$, $Dy_2[\mathbf{L}^{VII}]_3$, $Ho_2[\mathbf{L}^{VII}]_3$, $Er_2[\mathbf{L}^{VII}]_3$, $Yb_2[\mathbf{L}^{VII}]_3$, and $Lu_2[\mathbf{L}^{VII}]_3$ were measured in solution phase in chloroform ($CHCl_3$) and in the solid state as crystalline solids using a microspectrophotometer. The $Ln_2[\mathbf{L}^{VII}]_3$ complexes have very similar electronic absorption spectra in solution with absorbance bands at 335 and 395 nm, and a shoulder at 440 nm. The absorption spectra of $Nd_2[\mathbf{L}^{VII}]_3$, $Gd_2[\mathbf{L}^{VII}]_3$, $Ho_2[\mathbf{L}^{VII}]_3$ and $Yb_2[\mathbf{L}^{VII}]_3$ are highlighted in **Figure 4.23**. $Gd_2[\mathbf{L}^{VII}]_3$ has a distinct third absorption feature centered at 450 nm, rather than a shoulder that is observed for the other three examples.

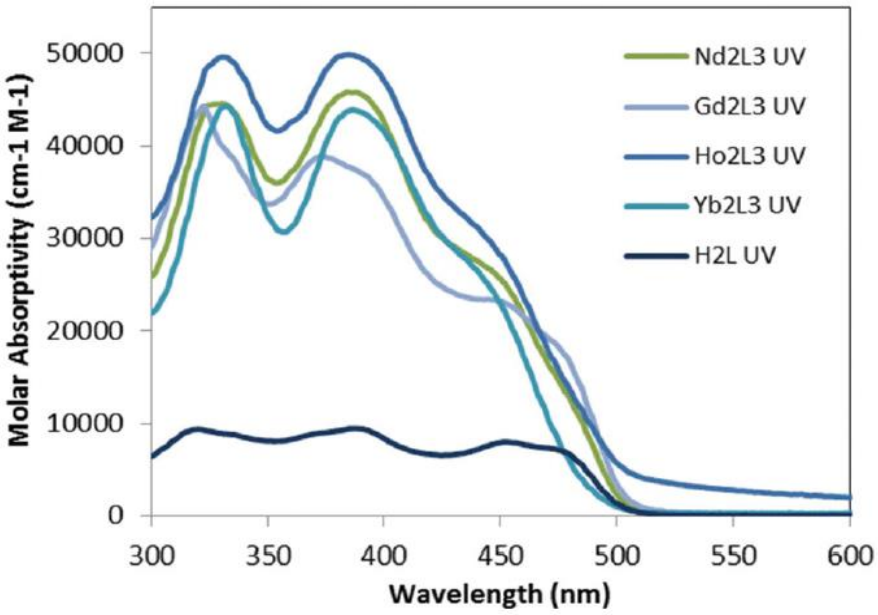



**Figure 4.23.** Absorption spectra of 15 μM solutions of $Nd_2[\mathbf{L}^{VII}]_3$, $Gd_2[\mathbf{L}^{VII}]_3$, $Ho_2[\mathbf{L}^{VII}]_3$, $Yb_2[\mathbf{L}^{VII}]_3$ and $[H_2\mathbf{L}^{VII}]$ in $CHCl_3$.[46]

The molar absorptivities of these $Ln_2[\mathbf{L}^{VII}]_3$ complexes are significant and on the order of $10^4$, which is in agreement with similar structures previously reported.[36, 64] The extinction

coefficients for the described series range from 1.5 x $10^4$ $cm^{-1}$ $M^{-1}$ for $Lu_2[\mathbf{L}^{\mathbf{VII}}]_3$ to 5.4 x $10^4$ $cm^{-1}$ $M^{-1}$ for $Sm_2[\mathbf{L}^{\mathbf{VII}}]_3$, which is consistently larger than the previously reported $[1M:1L]^+$ example.[64] The solution phase emission spectra of $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$ and $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$ are highlighted in **Figure 4.24**, with the strongest emission at 406 nm, 434 nm, 406 nm, and 460 nm respectively, attributed to a π to π* excitation. The emissions at 434 nm and 460 nm are present in all four complexes, with varying intensities, suggesting similar emission transitions. The solution phase fluorescence is dominated by ligand-to-ligand excitation and emission, which explains these similarities in the emission spectra of various lanthanides as well as the broad signal.

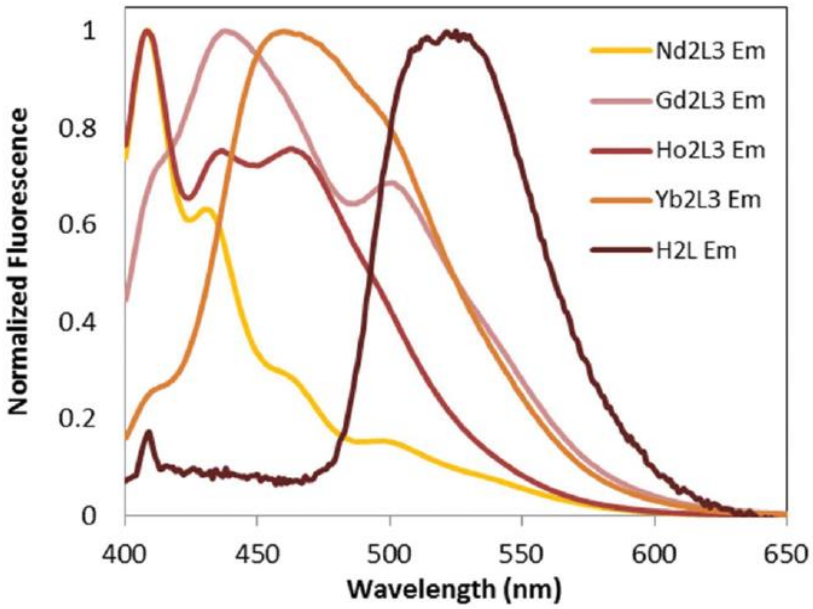



**Figure 4.24.** Normalized emission spectra of 15 μM solutions of $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$ and $[H_2\mathbf{L}^{\mathbf{VII}}]$ in $CHCl_3$ with excitation at 365 nm.[46]

The emission spectra of the $Ln_2[\mathbf{L}^{\mathbf{VII}}]_3$ complexes were sensitive to concentration, suggesting the formation of aggregates in solution. As the concentration increased, the emission was found to decrease, possibly due to self-quenching between different units in the aggregate.

Solutions with concentrations lower than 15 μM were linear with respect to concentration vs. intensity, and thus, used to calculate the quantum yields of the $Ln_2[\mathbf{L}^{\mathbf{VII}}]_3$ complexes. Experiments on solution phase fluorescence for the remaining seven complexes were conducted (**Figures 4.25-4.27**), and were dominated by ligand based emissions.

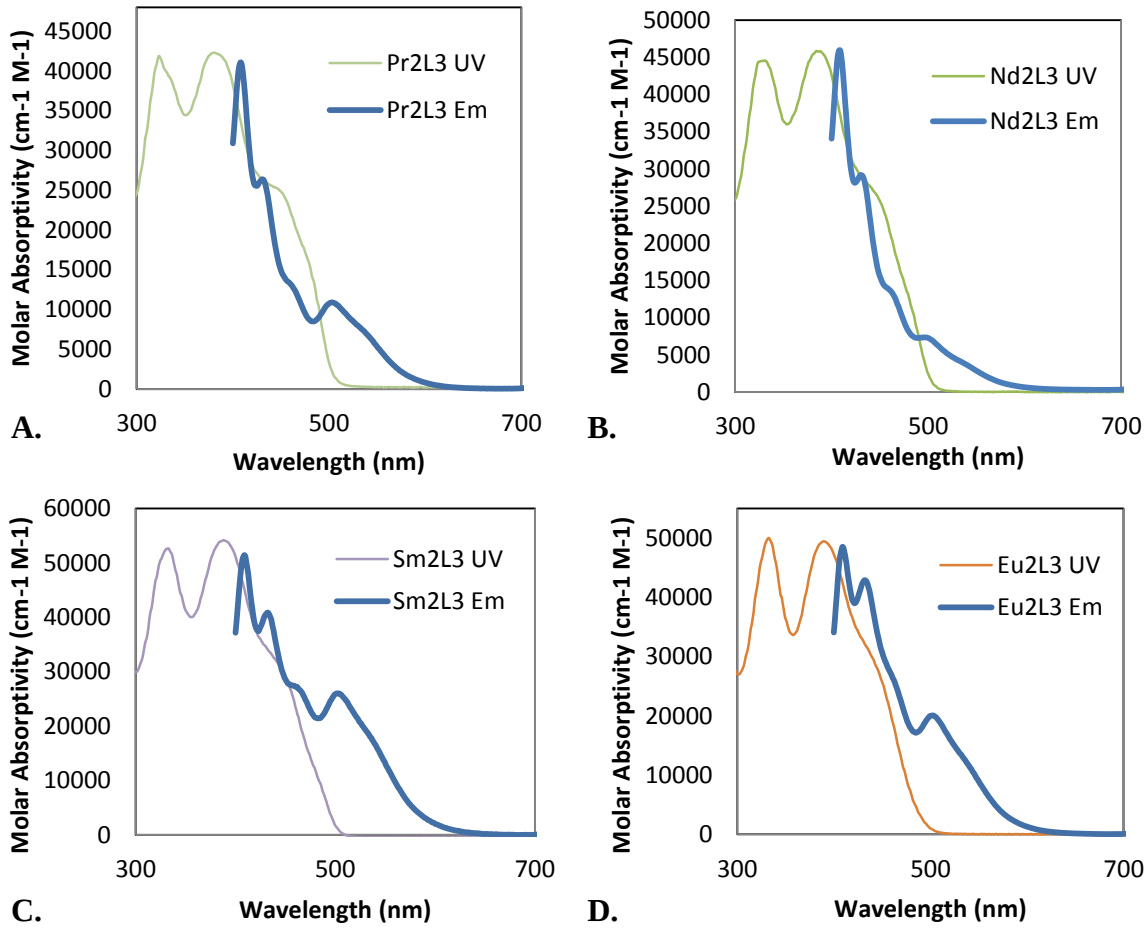



**Figure 4.25.** Solution phase absorbance and emission after 365 nm excitation of 15 μM $CHCl_3$ solutions of **A.** $Pr_2[\mathbf{L}^{\mathbf{VII}}]_3$ **B.** $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$ **C.** $Sm_2[\mathbf{L}^{\mathbf{VII}}]_3$ **D.** $Eu_2[\mathbf{L}^{\mathbf{VII}}]_3$

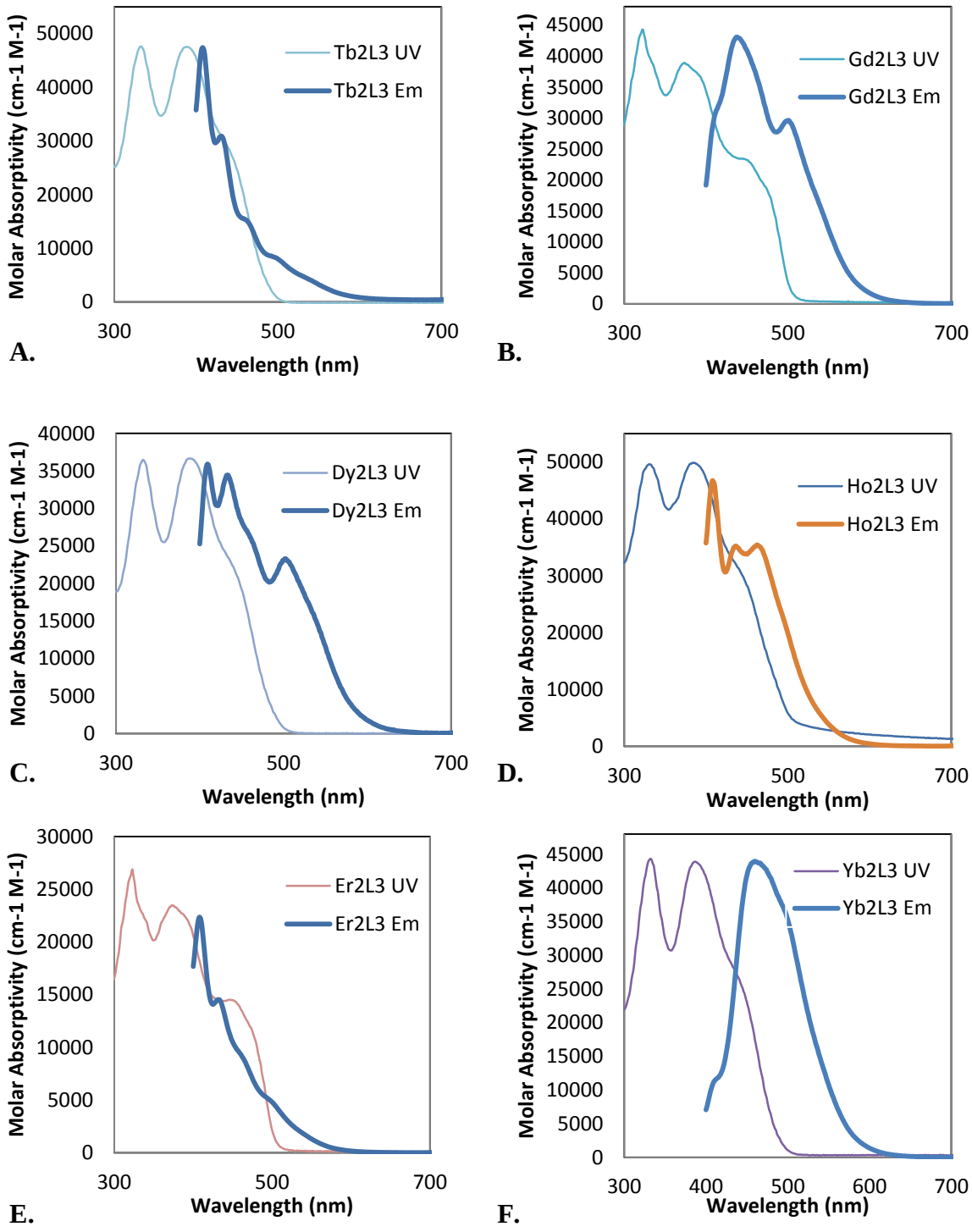



**Figure 4.26.** Solution phase absorbance and emission after 365 nm excitation of 15 μM $CHCl_3$ solutions of **A.** $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$ **B.** $Tb_2[\mathbf{L}^{\mathbf{VII}}]_3$ **C.** $Dy_2[\mathbf{L}^{\mathbf{VII}}]_3$ **D.** $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$ **E.** $Er_2[\mathbf{L}^{\mathbf{VII}}]_3$ **F.** $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$ [46]

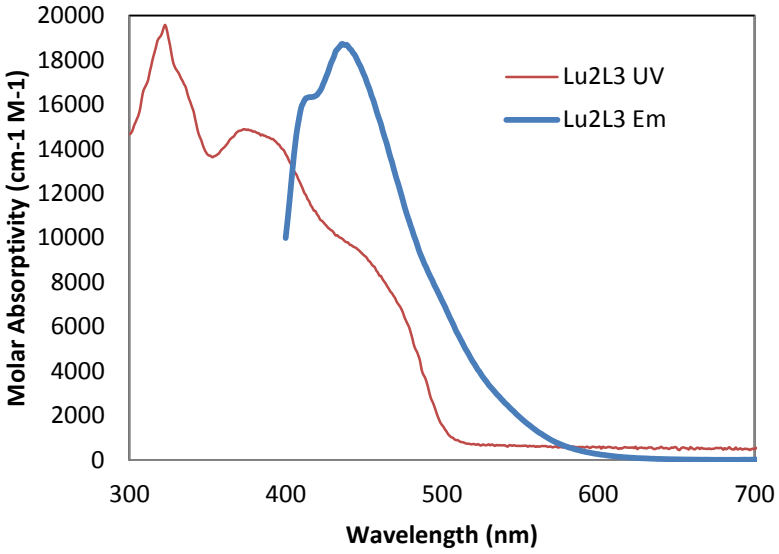



**Figure 4.27.** Solution phase absorbance and emission after 365 nm excitation of $Lu_2[\mathbf{L}^{\mathbf{VII}}]_3$ (15 μM in $CHCl_3$).[46]

The emission quantum yields in $CHCl_3$ solutions were obtained (**Table 4.6**) using **Equation 4.1**. Notably, the quantum yields for $Er_2[\mathbf{L}^{\mathbf{VII}}]_3$ and $Lu_2[\mathbf{L}^{\mathbf{VII}}]_3$ are 3.4% and 2.7 %, respectively.

$$\Phi_X = \Phi_{ST}\left(\frac{Slope_X}{Slope_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right) \qquad \textbf{(Equation 4.1)}$$

The subscripts ST and X denote standard and unknown respectively, Φ is the fluorescence quantum yield. Slope is the slope from the plot of fluorescence intensity vs absorbance, and $\eta$ the refractive index of the solvent. In this case the solvent was held constant, and $\Phi_{ST}$ was equal to 24 %.[84] The calculated quantum yields are tabulated in **Table 4.7**. The plot used to calculate quantum yield is shown in **Figure 4.28**. The intercepts of the lines of best fit are not zero, indicating there may be self-quenching or solvent effects occurring in this system.

**Table 4.7.** Quantum yields of $Ln_2[\mathbf{L}^{\mathbf{VII}}]_3$ complexes in $CHCl_3$ solution.[46]

| Metal Ion | Φ |
|---|---|
| Dy | 0.20% |
| Eu | 0.25% |
| Gd | 0.36% |
| Ho | 1.00% |
| Lu | 2.17% |
| Er | 3.40% |
| Pr | 0.33% |
| Tb | 0.22% |
| Yb | 0.38% |

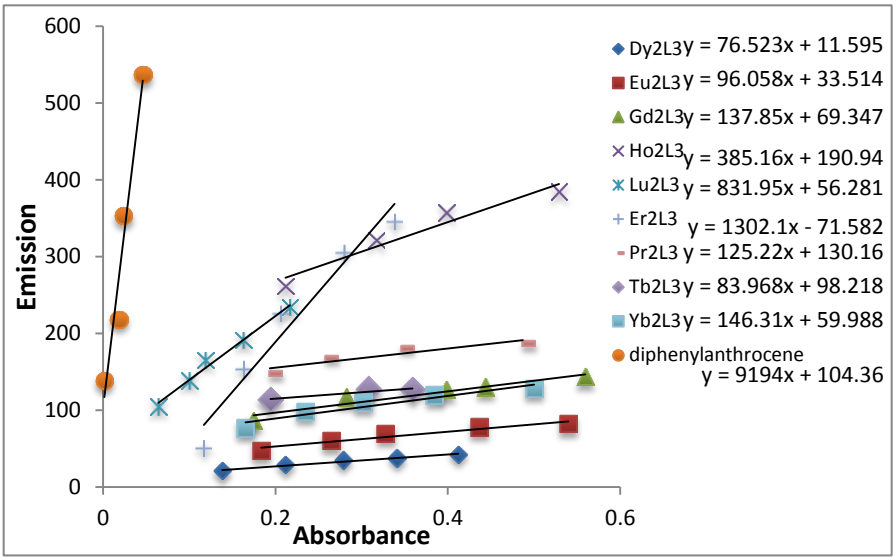



**Figure 4.28**. Quantum Yield Plot of $Ln_2[\mathbf{L}^{\mathbf{VII}}]_3$ complexes[46]

Solid-state absorbance and emission of all eleven complexes were conducted (**Figures 4.29-4.31**). The observed emission, which lacks the stereotypical sharp fluorescence of the lanthanides, is broad and can be attributed to ligand-based excitation. The small changes in coordination environment, which cause no distinct changes in absorption properties, provide tunable emission in the solid-state. The absorbance and emission of $Lu_2[\mathbf{L}^{\mathbf{VII}}]_3$ in the solid-state, as well as an inset image of $Lu_2L_3$ under ambient light and 365 nm excitation, shown in **Figure**

**4.29**. The solid-state absorbance and emission of each $Ln_2[\mathbf{L}^{\mathbf{VII}}]_3$ complex, as well as images of the crystals under ambient and 365 nm light were observed.

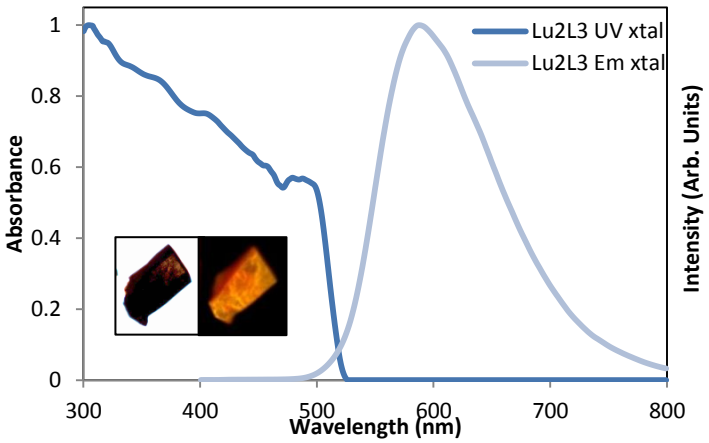



**Figure 4.29.** Solid-state absorbance and emission of a single crystal of $Lu_2[\mathbf{L}^{\mathbf{VII}}]_3$. Inset image of $Lu_2[\mathbf{L}^{\mathbf{VII}}]_3$ single crystal under ambient light and with 365 nm excitation.[46]

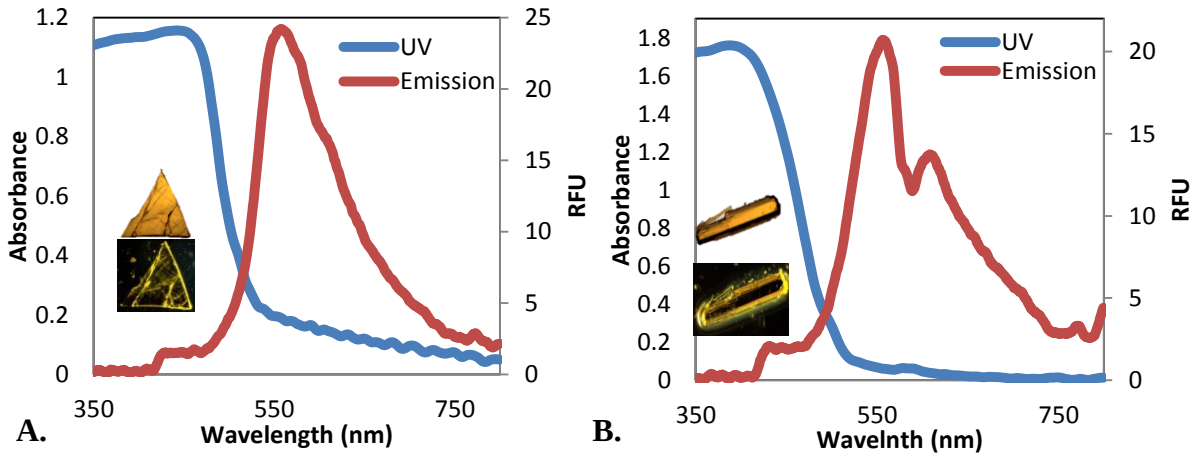



**Figure 4.30.** Solid-state absorbance and emission after 365 nm excitation of **A.** $Pr_2[\mathbf{L}^{\mathbf{VII}}]_3$. And **B.** $Nd_2[\mathbf{L}^{\mathbf{VII}}]_3$ Images of single crystals taken on a CRAIC Microspectrophotometer under ambient light and 365 nm light. [46]

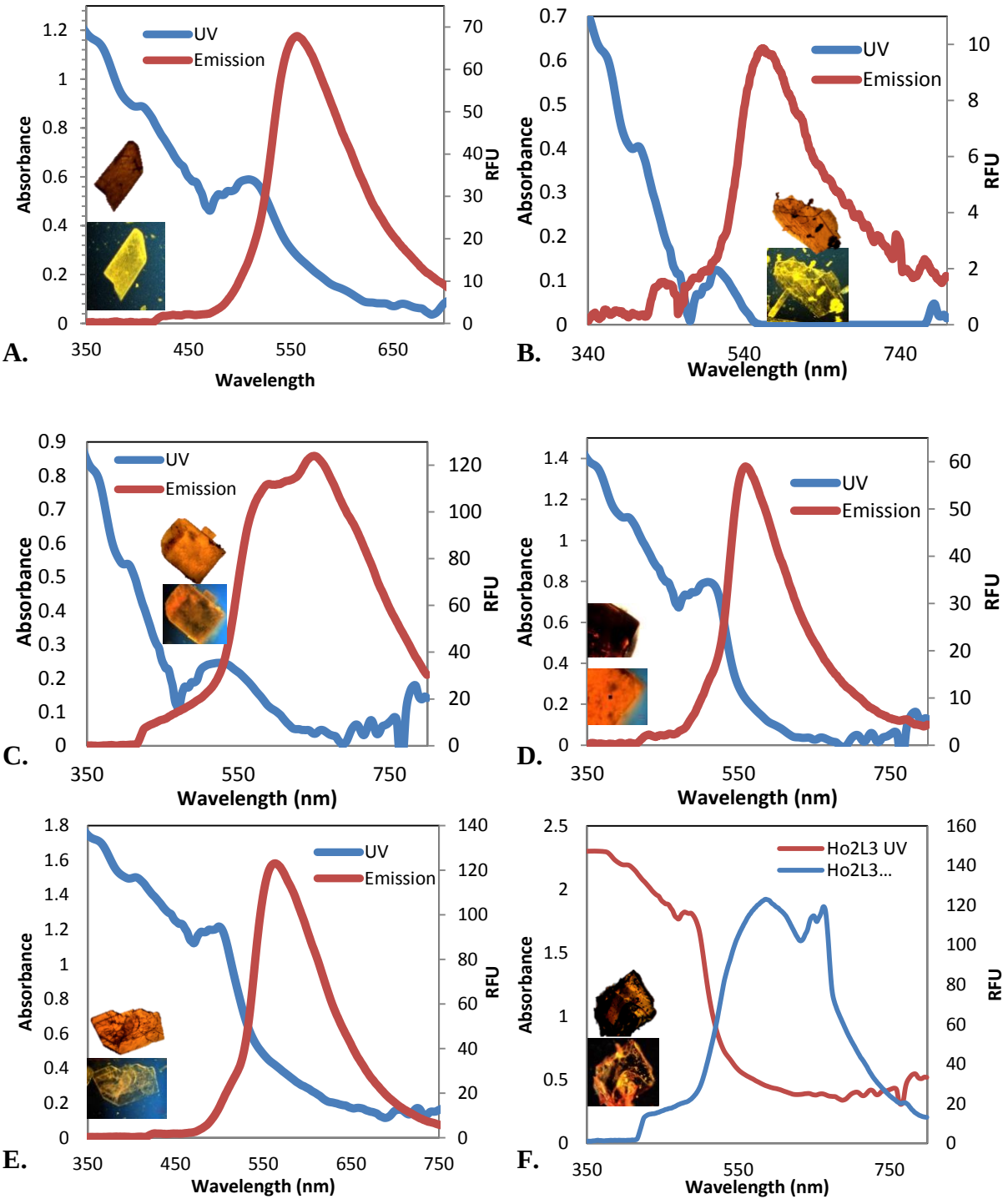



**Figure 4.31.** Solid-state absorbance and emission after 365 nm excitation of **A.** $Sm_2[\mathbf{L}^{\mathbf{VII}}]_3$ $Sm_2[\mathbf{L}^{\mathbf{VII}}]_3$ **B.** $Eu_2[\mathbf{L}^{\mathbf{VII}}]_3$ **C.** $Gd_2[\mathbf{L}^{\mathbf{VII}}]_3$ **D.**$Tb_2[\mathbf{L}^{\mathbf{VII}}]_3$ **E.** $Dy_2[\mathbf{L}^{\mathbf{VII}}]_3$ **F.** $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$. Images of single crystals of taken on a CRAIC Microspectrophotometer under ambient light and 365 nm light.[46]

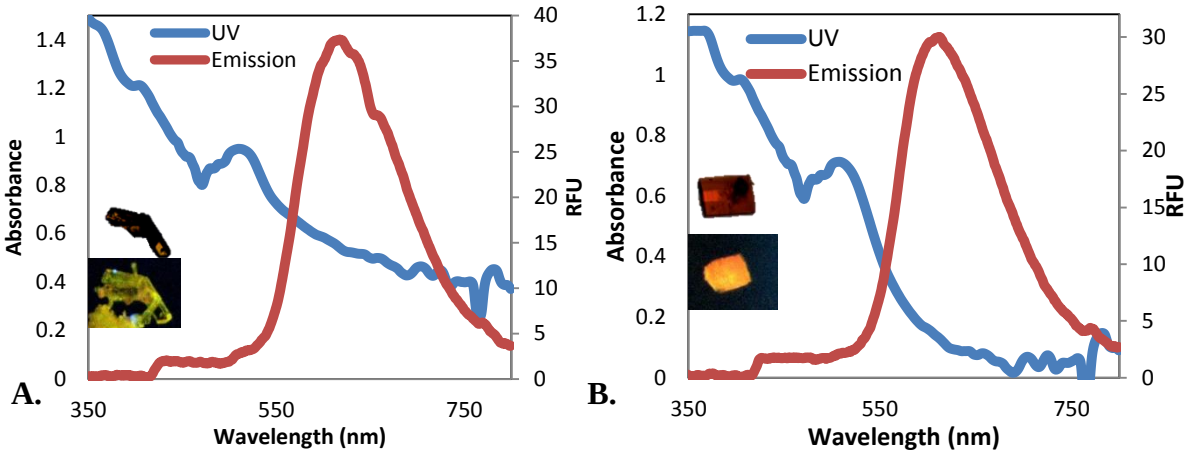



**Figure 4.32.** Solid state absorbance and emission after 365 nm excitation of A. $Er_2[\mathbf{L}^{\mathbf{VII}}]_3$ **B.** $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$. Images of single crystals taken on a CRAIC Microspectrophotometer under ambient light and 365 nm light.[46]

As highlighted in **Figure 4.33**, while all the lanthanide analogues fluoresce in the solid-state, the $Lu_2[\mathbf{L}^{\mathbf{VII}}]_3$ complex emits 1000 times more strongly than any other of the eleven $Ln_2[\mathbf{L}^{\mathbf{VII}}]_3$ complexes observed. This significant increase in fluorescence is surprising, as the changes in bond lengths from Lu to Yb, the next closest in size, are within an average of 0.02 Å. The lanthanide contraction is again evident in the change in emission, as it goes from emission at 556 nm to 617 nm from early to late lanthanides (**Table 4.8**). As the lanthanide ions get smaller, the ligands in the triple-decker sandwich are pulled closer together from early to late lanthanides, reducing the energy from the ground and excited states, until the optimum distance is achieved on reaching lutetium.

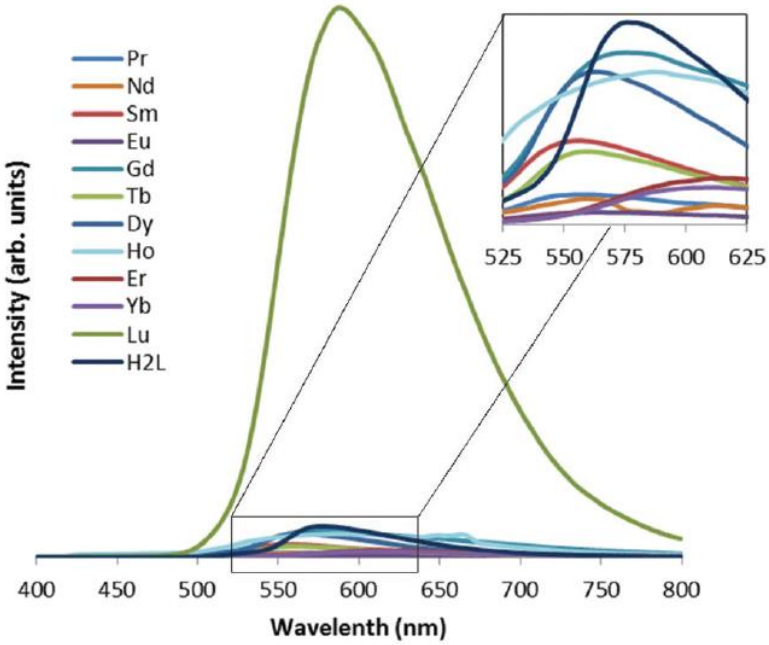



**Figure 4.33.** Solid-state emission spectra of the $Ln_2[\mathbf{L}^{\mathbf{VII}}]_3$ complexes with excitation at 365 nm.[46]

**Table 4.8.** Emission wavelengths of $Ln_2[\mathbf{L}^{\mathbf{VII}}]_3$ species in solid-state.[46]

| Metal | Max Wavelength (nm) |
|---|---|
| Sm | 556 |
| Pr | 558 |
| Nd | 559 |
| Tb | 559 |
| Eu | 563 |
| Dy | 564 |
| Gd | 575 |
| Ho | 587 |
| Lu | 588 |
| Yb | 611 |
| Er | 617 |

## Conclusions

In summary, three new mononuclear complexes $UO_2[\mathbf{L}^{\mathbf{VII}}]$, $Ce[\mathbf{L}^{\mathbf{VII}}]_2$, and $Th[\mathbf{L}^{\mathbf{VII}}]_2$ and eleven lanthanide double decker sandwich complexes ($Ln_2[\mathbf{L}^{\mathbf{VII}}]_3$), where Ln = Pr(III), Nd(III),

Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Yb(III), or Lu(III), were synthesized and characterized in the solid-state and in solution.

Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ was observed to fluoresce in both solid-state and solution phase, but Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ was not. DFT calculations indicated that this is due to fluorescence quenching in the case of cerium. Unlike Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$, Ce[$\mathbf{L}^{\mathbf{VII}}$]$_2$ was found to possess appropriate electronic states, which can facilitate a non-radiative decay from the involved excited to the lower electronic states. Solvent dependence of emission was observed and may be due to solvent coordination in the 8- and 9-coordinate equilibrium of Th[$\mathbf{L}^{\mathbf{VII}}$]$_2$ in solution. The uncommonly short M-$N_{imine}$ bond lengths may be due to a stronger imine donor than typically is observed in salen-like compounds.

The structural differences in the $Nd_2$[$\mathbf{L}^{\mathbf{VII}}$]$_3$, $Gd_2$[$\mathbf{L}^{\mathbf{VII}}$]$_3$, $Tb_2$[$\mathbf{L}^{\mathbf{VII}}$]$_3$, $Dy_2$[$\mathbf{L}^{\mathbf{VII}}$]$_3$, $Ho_2$[$\mathbf{L}^{\mathbf{VII}}$]$_3$, $Yb_2$[$\mathbf{L}^{\mathbf{VII}}$]$_3$, and $Lu_2$[$\mathbf{L}^{\mathbf{VII}}$]$_3$ analogues are minimal and can be attributed to the decreasing size of the lanthanide series. The small differences in structure afforded similar absorbance spectra, but differences in the emission properties were observed in solution. These differences were more apparent in the solid-state luminescence with $Sm_2$[$\mathbf{L}^{\mathbf{VII}}$]$_3$ emission at 556 nm to $Er_2$[$\mathbf{L}^{\mathbf{VII}}$]$_3$ emission at 617 nm. Lutetium exhibited a significant increase in fluorescent signal as compared to the other $Ln_2$[$\mathbf{L}^{\mathbf{VII}}$]$_3$ complexes in the solid state, suggesting that the late lanthanides provide a scaffold to closely hold the napthylsalophen ligands in a rigid structure to maximize ligand to ligand excitation and emission.

The complex $UO_2$[$\mathbf{L}^{\mathbf{VII}}$] was synthesized and characterized in the solid-state and may show promise as a colorimetric chemosensor similar to those species discussed in Chapters 2 and 3 in the future. Interesting hydrogen bonded tetramers of the complex ($UO_2$[$\mathbf{L}^{\mathbf{VII}}$])$_4$ were observed, but seem to be a solid-state phenomenon.

## Experimental Details

### General considerations

*Caution! Standard precautions for handling radioactive materials or heavy metals, such as $Th(NO_3)_4•6H_2O$ as used in this study, were followed.*

Any solvents not specifically identified were ACS grade, purchased from EMD, and used as received without further purification. The reagents toluene (HPLC grade, BDH), dimethylsulfoxide (99%, Macron), dimethylformamide (99.9%, EMD), acetonitrile (99.5%, BDH), chloroform (99.8%, BDH), methanol (HPLC grade, EMD), 1,2-diaminobenzene (99.5%, Aldrich), 2-hydroxynapthaldehyde (98%, Alpha Aesar), cerium(III) acetate (99.9%, STREM), samarium(III) chloride hydrate (99.9%, STREM), lutetium(III) chloride (99.9%, STREM), praseodymium(III) chloride (99.9%, STREM), terbium(III) chloride hexahydrate (99.9%, STREM), ytterbium(III) acetate hydrate (99.9%, STREM), holmium(III) chloride hydrate (99.9%, STREM) europium(III) acetate hydrate (99.9%, STREM), erbium(III) chloride hydrate (99.9%, STREM), neodymium(III) chloride hexahydrate (99.9%, STREM), dysprosium(III) acetate hydrate (99.9%, STREM), and $Th(NO_3)_4•6H_2O$ (99%, Fluka) were used as received without further purification. Anhydrous dichloromethane (BDH) was purchased, stored under argon, and dispensed from a solvent purification system. Triethylamine (99%, Alpha Aesar) was distilled and stored under argon until use. Deuterated dimethylsulfoxide (DMSO) and chloroform were purchased from Cambridge Isotope and stored in a desiccator when not in use.

### Synthetic Details

**Napthylsalophen [$H_2L^{VII}$]**: 1,2-diaminobenzene (0.433 g, 7.23 mmol) and 2-hydroxynapthaldehyde (1.32 g, 15.0 mmol) were added to 150 mL of MeOH, heated to reflux

temperature, and stirred for 6 hours. The solution was observed to change from yellow to dark orange and a precipitate formed. The solution was allowed to cool to room temperature. The resulting solid was filtered and washed with hexanes to yield a bright orange powder (2.54 g, 84%). $^{1}$H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, 2H, J = 9.2 Hz), 7.34 (t, 2H, J = 7.4 Hz), 7.44-7.39 (m, 4H), 7.51 (t, 2H, J = 8.2 Hz), 7.73 (d, 2H, J = 7.9 Hz), 7.82 (d, 2H, J = 9.2 Hz), 8.14 (d, 2H, J = 8.5 Hz), 9.46 (d, 2H, J = 3.6 Hz), 15.08 (s, 2OH); $^{13}$C NMR (151 MHz, $CDCl_3$) δ 109.40, 119.03, 119.15, 122.09, 123.63, 127.42, 127.51, 128.08, 129.41, 133.21, 136.67, 139.73, 156.17, 169.08; TOF MS (ESI) m/z ($M^+$ + 1) Calcd 417.1525, Found 417.1550. CCDC: 1523762.

**Ce[$\mathbf{L^{VII}}$]$_2$:** The napthylsalophen ligand [$H_2\mathbf{L^{VII}}$] (867 mg, 2.08 mmol) and $NEt_3$ (1.0 mL) were added to minimal amount of DCM (120 mL) and allowed to dissolve in a 250 mL round bottom flask. $Ce(OAc)_3•H_2O$ (342 mg, 1.08 mmol) was then added to the flask with minimal amount (80 mL) of MeOH to dissolve the salt after some stirring. The reaction was heated to 40 °C and stirred for 6 hours. The solution volume was reduced by half by rotary evaporation, and the precipitate, a reddish brown solid, was filtered off and collected. Crystals suitable for x-ray diffraction were grown in five days from layering a saturated toluene solution of Ce[$\mathbf{L^{VII}}$]$_2$ with hexanes. (976 mg, 94%). $^{1}$H NMR (600 MHz, $CDCl_3$) δ 6.33 (d, 4H, *J* = 9.0 Hz), 7.25-7.27 (m, 4H), 7.30-7.35 (m, 8H), 7.53 (s, 4H), 7.55 (s, 4H), 7.73 (d, 4H, *J* = 7.7 Hz), 7.97 (d, 4H, *J* = 8.4 Hz), 9.63 (s, 4H) ppm; $^{13}$C NMR (151 MHz, $CDCl_3$) δ 114.27, 118.80, 120.09, 122.55, 122.94, 127.15, 127.20, 127.83, 128.88, 133.81, 134.77, 146.74, 156.11, 168.82 ppm; TOF MS (ESI) m/z ($M^+$ + 1) Cald 969.1791, Found 969.1705. CCDC 1523760.

**$Pr_2$[$\mathbf{L^{VII}}$]$_3$:** The napthylsalophen ligand [$H_2\mathbf{L^{VII}}$] (209 mg, 0.503 mmol) and $NEt_3$ (600 μL) were added to 40 mL of DCM and 40 mL of MeOH in a 100 mL round bottom flask and allowed to stir until dissolved. $PrCl_3•7H_2O$ (141 mg, 0.378 mmol) was then added to the flask. The reaction

was heated to 40 °C, and allowed to stir for 4 hours. The solution volume was reduced by half through the use of a rotary evaporator, and the subsequent solution was allowed to evaporate slowly. Orange needles were filtered after 18 hours (230 mg, 88%). TOF MS (ESI) m/z ($M^+$ + 1) Calcd 1621.7329, Found 1621.7505 ; Elem. Anal. For $C_{87}H_{68}N_6Pr_2O_{10}$ Calcd (Found): C, 63.74 (63.61); H, 4.18 (3.83); N,5.13 (5.18).

**$Nd_2[L^{VII}]_3$:** The napthylsalophen ligand [$H_2$**L**$^{VII}$] (204 mg, 0.490 mmol) and $NEt_3$ (600 μL) were added to 40 mL of DCM and 40 mL of MeOH in a 100 mL round bottom flask and allowed to stir until dissolved. $NdCl_3$•$6H_2O$ (181 mg, 0.505 mmol) was then added to the flask. The reaction was heated to 40 °C, and allowed to stir for 4 hours. The solution volume was reduced by half through the use of a rotary evaporator, and the subsequent solution was allowed to evaporate slowly. Orange needle crystals suitable for x-ray diffraction were filtered after 18 hours (235 mg, 92%). TOF MS (ESI) m/z ($M^+$ + 1) Calcd 1531.2408, Found 1531.2390; Elem. Anal. for $C_{87}H_{64}Cl_2N_6Nd_2O_8$ Calcd % (Found %): C, 62.17 (62.02); H, 3.84 (3.88); N, 5.00 (5.11). CCDC: 1555710.

**$Sm_2[L^{VII}]_3$:** The napthylsalophen ligand [$H_2$**L**$^{VII}$] (202 mg, 0.486 mmol) and $NEt_3$ (600 μL) were added to 40 mL of DCM and 40 mL of MeOH in a 100 mL round bottom flask and allowed to stir until dissolved. $Sm(OAc)_3$•$H_2O$ (166 mg, 0.505 mmol) was then added to the flask. The reaction was heated to 40 °C, and allowed to stir for 4 hours. The solution volume was reduced by half through the use of a rotary evaporator, and the subsequent solution was allowed to evaporate slowly. Orange solid was filtered after 18 hours (74 mg, 29%). TOF MS (ESI) m/z ($M^+$ + 1) Calcd, 1545.2579 Found 1545.2465; Elem. Anal. for $C_{88}H_{68}Cl_2N_6O_9Sm_2$ Calcd % (Found %): C, 61.27 (61.11); H, 3.97 (3.80); N, 4.87 (4.88).

**$Eu_2[L^{VII}]_3$:** The napthylsalophen ligand [$H_2L^{VII}$] (208 mg, 0.500 mmol) and $NEt_3$ (600 μL) were added to 40 mL of DCM and 40 mL of MeOH in a 100 mL round bottom flask and allowed to stir until dissolved. $Eu(OAc)_3•H_2O$ (165 mg, 0.501 mmol) was then added to the flask. The reaction was heated to 40 °C, and allowed to stir for 4 hours. The solution volume was reduced by half through the use of a rotary evaporator, and the subsequent solution was allowed to evaporate slowly. Solid orange block crystals suitable for x-ray diffraction were filtered after 36 hours (121 mg, 46%). TOF MS (ESI) m/z ($M^+$ + 1) Cald 1547.2581, Found 1547.2603. Elem. Anal. for $C_{87}H_{62}Cl_4Eu_2N_6O_7$ Calcd % (Found %): C, 59.74 (59.51); H, 3.57 (3.62); N, 4.80 (4.75).

**$Gd_2[L^{VII}]_3$:** The napthylsalophen ligand [$H_2L^{VII}$] (201 mg, 0.483 mmol) and $NEt_3$ (600 μL) were added to 40 mL of DCM and 40 mL of MeOH in a 100 mL round bottom flask and allowed to stir until dissolved. $Gd(OAc)_3•H_2O$ (196 mg, 0.744 mmol) was then added to the flask. The reaction was heated to 40 °C, and allowed to stir for 4 hours. The solution volume was reduced by half through the use of a rotary evaporator, and the subsequent solution was allowed to evaporate slowly. Solid orange block crystals suitable for x-ray diffraction were filtered after 18 hours (150. mg, 59%). TOF MS (ESI) m/z ($M^+$ + 1) Calcd 1559.2695, Found 1559.2788. Elem. Anal. for $C_{86}H_{68}Gd_2N_6O_{11}$ Calcd % (Found %): C, 61.63 (61.49); H, 4.09 (4.11); N, 5.01 (5.20). CCDC: 1523761.

**$Tb_2[L^{VII}]_3$:** The napthylsalophen ligand [$H_2L^{VII}$] (202 mg, 0.486 mmol) and $NEt_3$ (600 μL) were added to 40 mL of DCM and 40 mL of MeOH in a 100 mL round bottom flask and allowed to stir until dissolved. $TbCl_3•6H_2O$ (188 mg, 0.504 mmol) was then added to the flask. The reaction was heated to 40 °C, and allowed to stir for 4 hours. The solution volume was reduced by half through the use of a rotary evaporator, and the subsequent solution was allowed to evaporate

slowly. Solid orange block crystals suitable for x-ray diffraction were filtered after 18 hours (224 mg, 85%). TOF MS (ESI) m/z ($M^+$ + 1) Cald 1562.2690, Found 1562.2859. Elem. Anal. for $C_{85}H_{58}N_6O_7Tb_2$ Calcd % (Found %): C, 64.08 (63.85); H, 3.67 (3.56); N, 5.27 (5.25). CCDC: 1555317.

**$Dy_2[L^{VII}]_3$:** The napthylsalophen ligand [$H_2L^{VII}$] (207 mg, 0.498 mmol) and $NEt_3$ (600 µL) were added to 40 mL of DCM and 40 mL of MeOH in a 100 mL round bottom flask and allowed to stir until dissolved. $Dy(OAc)_3•6H_2O$ (171 mg, 0.504 mmol) was then added to the flask. The reaction was heated to 40 °C, and allowed to stir for 4 hours. The solution volume was reduced by half through the use of a rotary evaporator, and the subsequent solution was allowed to evaporate slowly. Solid orange block crystals suitable for x-ray diffraction were filtered after 18 hours (260 mg, 98%). TOF MS (ESI) m/z ($M^+$ + 1) Calcd 1569.2799, Found 1569.2994; Elem. Anal. for $C_{85}H_{58}Dy_2N_6O_7$ Calcd % (Found %): C, 63.79 (63.32); H, 3.65 (3.72); N, 5.25 (5.30). CCDC: 1555316.

**$Ho_2[L^{VII}]_3$:** The napthylsalophen ligand [$H_2L^{VII}$] (205 mg, 0.494 mmol) and $NEt_3$ (600 µL) were added to 40 mL of DCM and 40 mL of MeOH in a 100 mL round bottom flask and allowed to stir until dissolved. $HoCl_3•6H_2O$ (189 mg, 0.4979 mmol) was then added to the flask. The reaction was heated to 40 °C, and allowed to stir for 4 hours. The solution volume was reduced by half through the use of a rotary evaporator, and the subsequent solution was allowed to evaporate slowly. A brown colored solid was filtered after 18 hours (220 mg, 83%). Dark brown crystals suitable for x-ray diffraction grew from slow evaporation of methanol. TOF MS (ESI) m/z ($M^+$ + 1) Calcd. 1572.2711, Found 1561.3846. Elem. Anal. for $C_{90}H_{76}Cl_{10}N_6O_7Ho_2$ Calcd % (Found %): C, 51.43 (51.06); H, 3.64 (3.69); N, 4.00 (4.01). CCDC:1555027.

**$Er_2[L^{VII}]_3$:** The napthylsalophen ligand [$H_2L^{VII}$] (208 mg, 0.499 mmol) and $NEt_3$ (600 μL) were added to 40 mL of DCM and 40 mL of MeOH in a 100 mL round bottom flask and allowed to stir until dissolved. $ErCl_3•H_2O$ (171 mg, 0.6264 mmol) was then added to the flask. The reaction was heated to 40 °C, and allowed to stir for 4 hours. The solution volume was reduced by half by rotary evaporation and was allowed to evaporate slowly. The resulting yellow solid was filtered (248 mg, 96%). TOF MS (ESI) m/z ($M^+$ + 1) Calcd 1577.2827, Found 1577.2870. Elem. Anal. for $C_{109}H_{125}Cl_6N_9O_{15}Er_2$ Calcd % (Found %): C, 55.06 (54.81); H, 5.45 (5.25); N, 5.45 (5.84).

**$Yb_2[L^{VII}]_3$:** The napthylsalophen ligand [$H_2L^{VII}$] (208 mg, 0.500 mmol) and $NEt_3$ (600 uL) were added to 40 mL of DCM and 40 mL of MeOH in a 100 mL round bottom flask and allowed to stir until dissolved. $Yb(OAc)_3•H_2O$ (175 mg, 0. mmol) was then added to the flask. The reaction was heated to 40 °C, and allowed to stir for 4 hours. The solution volume was reduced by half through the use of a rotary evaporator, and the subsequent solution was allowed to evaporate slowly. The reaction was heated to 40 °C, and allowed to stir for 4 hours. The solution volume was reduced by half by rotary evaporation and was allowed to evaporate slowly. Solid orange block crystals suitable for x-ray diffraction were filtered after 18 hours (141 mg, 52 %). CCDC:1555028. TOF MS (ESI) m/z ($M^+$ + 1) Calcd 1590.2974, Found 1590.2826; Elem. Anal. for $C_{85}H_{58}N_6O_7Yb_2$ Calcd % (Found %): C, 62.96 (62.14); H, 3.61 (3.65); N, 5.18 (5.25).

**$Lu_2[L^{VII}]_3$:** The napthylsalophen ligand [$H_2L^{VII}$] (210 mg, 0.506 mmol) and $NEt_3$ (600 uL) were added to 40 mL of DCM and 40 mL of MeOH in a 100 mL round bottom flask and allowed to stir until dissolved. $Lu(OAc)_3•H_2O$ (173 mg, 0.490 mmol) was then added to the flask. The reaction was heated to 40 °C, and allowed to stir for 4 hours. The solution volume was reduced by half through the use of a rotary evaporator, and the subsequent solution was allowed to evaporate slowly. Solid orange block crystals suitable for x-ray diffraction were filtered after 18

hours (279 mg, quantitative yield). TOF MS (ESI) m/z ($M^+$ + 1) Calcd 1594.3031, Found1594.3022; Elem. Anal. for $C_{85}H_{60}Lu_2N_6O_8$ Calcd % (Found %): C, 62.12 (61.69); H, 3.68 (3.64); N, 5.11 (5.18). CCDC: 1555720.

**Th[$\mathbf{L^{VII}}$]$_2$:** The napthylsalophen ligand [$H_2\mathbf{L^{VII}}$] (414 mg, 0.995 mmol) and $NEt_3$ (1.0 mL) were added to 100 mL of DCM and 50 mL of MeOH in a 250 mL round bottom flask. The mixture was stirred until all the solids were dissolved. Thorium nitrate (214 mg, 0.415 mmol) was then added to the flask. The reaction was heated to 40 °C and heated with stirring for 5.5 hours. The solution volume was reduced by half by rotary evaporation, and subsequently put in ice for 30 minutes. A yellow solid precipitated. This was filtered off and rinsed with hexanes (333 mg, 76 %). Crystals suitable for x-ray diffraction were grown in 3 days from layering a saturated toluene solution of Th[$\mathbf{L^{VII}}$]$_2$ with hexanes. $^1$H NMR (600 MHz, $CDCl_3$) δ 6.53 (d, 4H, *J* = 9.0 Hz), 7.15 (s, 4H), 7.27 (t, 4H, *J* = 7.2 Hz), 7.46 (t, 4H, *J* = 7.2 Hz), 7.56 (d, 4H, *J* = 9.0 Hz), 7.67 (d, 4H, *J* = 7.8 Hz), 7.94 (d, 4H, *J* = 8.4 Hz), 9.30 (s, 4H) ppm; $^{13}$C NMR (151 MHz, $CDCl_3$) δ 113.73, 119.62, 119.67, 122.78, 124.44, 127.43, 127.47, 127.53, 129.27, 134.54, 136.00, 145.93, 158.68, 167.15 ppm; TOF MS (ESI) m/z ($M^+$ + 1) Cald 1061.3117, Found 1061.3773. CCDC: 1548265.

$UO_2$[$\mathbf{L^{VII}}$]: The napthylsalophen ligand [$H_2\mathbf{L^{VII}}$] (970. mg, 2.33 mmol) and $NEt_3$ (1 mL) were added to 40 mL of DCM and 20 mL of MeOH in a 100 mL round bottom flask. The mixture was stirred until all the solids were dissolved. Uranyl nitrate hexahydrate (963 mg, 2.27 mmol) was then added to the flask. The reaction was heated to 40 °C and heated with stirring for 2 hours. The solution volume was reduced by half by rotary evaporation, and subsequently put in ice for 30 minutes. A yellow solid precipitated. This was filtered off and rinsed with hexanes (132 mg, 83%). Crystals suitable for x-ray diffraction were grown in 3 days from layering a saturated toluene solution of $UO_2$[$\mathbf{L^{VII}}$] with hexanes. The $^1$H NMR (600 MHz, $d_6$-DMSO) δ 7.31 (t, 2H, *J*

= 7.4 Hz), 7.38 (d, 2H, *J* = 9.1 Hz), 7.53-7.55 (m, 4H), 7.85-7.88 (m, 4H), 8.20 (d, 2H, *J* = 8.1 Hz), 8.36 (d, 2H, *J* = 8.5 Hz), 10.20 (s, 2H) ppm; $^{13}$C NMR (151 MHz, $d_6$-DMSO) δ 114.72, 120.33, 121.36, 122.92, 124.20, 127.03, 127.91, 128.49, 128.75, 134.49, 137.12, 147.38, 160.09, 171.33 ppm; TOF MS (ESI) m/z ($M^+$ + 1) Cald 685.1774, Found 685.1777, ($M(H_2O)^+$ + 1) Cald 703.1880, Found 703.1902. **Crystal Data** for $UO_2[\mathbf{L}^{\mathbf{VII}}]$: $C_{60}H_{48}Cl_8N_4O_{10}U_2$ (*M* =1744.75): monoclinic, space group $P2_1/n$ (no. 14), *a* = 15.4659(12) Å, *b* = 19.3294(14) Å, *c* = 22.2346(16) Å, *β* = 106.655(1)°, *V* = 6368.1(8) Å$^3$, *Z* = 4, *T* = 180.0 K, μ(Mo Kα) = 5.476 mm$^{-1}$, *Dcalc* = 1.8197 g/mm$^3$, 74217 reflections measured (2.84 ≤ 2Θ ≤ 51.52), 12168 unique ($R_{int}$ = 0.0706, $R_{sigma}$ = 0.0463) which were used in all calculations. The final $R_1$ was 0.0440 (I>=2u(I)) and $wR_2$ was 0.1031 (all data). CCDC: 1827293.

**Single Crystal X-ray Diffraction**

Crystals suitable for single crystal X-ray diffraction were selected and mounted on a glass fiber using Paratone-N oil and data set collection was completed on a 'Bruker APEX CCD' diffractometer using Mo Kα radiation. The crystal was kept at 180 K during unit cell and data collection. SMART (v. 5.624) was used for preliminary determination of cell constants and data collection control. Determination of integrated intensities and global cell refinement were performed with the Bruker SAINT software package, and empirical absorption correction (SADABS) was applied. The structures were solved with the ShelXS structure solution program using Direct Methods[85-86] and refined with the olex2.refine refinement package using Gauss-Newton minimisation.[87-88] Carbon atoms in coordinating methanol molecules in $Dy_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Tb_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Lu_2[\mathbf{L}^{\mathbf{VII}}]_3$ were refined isotropically, as attempts to model disorder resulted in non-convergence. A disordered interstitial toluene on an inversion center was modeled for $Th[\mathbf{L}^{\mathbf{VII}}]_2$. A half of a highly disordered interstitial hexane was modeled over two positions for $Ce[\mathbf{L}^{\mathbf{VII}}]_2$.

Solvent masks for poorly resolved and highly disordered interstitial DCM and water molecules were generated for $Yb_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Ho_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Dy_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Tb_2[\mathbf{L}^{\mathbf{VII}}]_3$, $Lu_2[\mathbf{L}^{\mathbf{VII}}]_3$ using Olex$^2$.[88] Attempts to converge the $Eu_2[\mathbf{L}^{\mathbf{VII}}]_3$ and $Er_2[\mathbf{L}^{\mathbf{VII}}]_3$ solutions with the rigor to publish in the Cambridge Crystallographic Data Center were unsuccessful, even by allowing coordinating solvent to be isotropically refined. Projections were created on Olex2.1.[87]

**NMR Spectroscopy**

$^1$H NMR spectra were recorded with a Bruker spectrometer at 600 MHz. $^{13}$C NMR spectra were recorded with a Bruker spectrometer at 151 MHz. NMR spectroscopic data were collected using deuterated chloroform ($CDCl_3$) or deuterated DMSO ($D_6$-DMSO).

**Absorbance Spectroscopy**

All solution phase absorbance spectra were collected on a VARIAN Cary 50 WinUV Spectrometer with a xenon lamp with absorbance spectra from 200 nm to 900 nm with a 1 cm width quartz cuvette. Solid-state absorbance spectra were collected on a 20/20 PV CRAIC microspectrophotometer with a xenon lamp for transmission/absorbance measurements, with optimized exposure times from single crystals of each respective complex.

**Fluorescence Spectroscopy**

All solution phase fluorescence spectra were collected on a Shimadzu RF-5301 PC fluorospectrophotometer with a xenon lamp and a 1 cm width quartz cuvette with an excitation of 365 nm and an emission spectrum of 400–900 nm. Slit widths were set so that the maximum emission of the ligand could be seen, and held constant throughout. Solid-state fluorescence spectra were collected on a 20/20 PV CRAIC microspectrophotometer with a mercury lamp for

fluorescence measurements. Samples were excited with 365 nm light with optimized exposure times from single crystals of each respective complex.

**Computational Details**

The B3LYP functional was chosen combined with the correlation consistent cc-pVDZ basis set for C, N, H, and O atoms. For Ce and Th, the Stuttgart relativistic small-core effective core potentials (RSC-ECP) and their companion basis sets were used. The inner 27 and 80 electrons are represented by the RSC-ECP for Ce and Th, respectively. A set of 5s5p4d3f/Ce and 8s7p6d4f/Th Gaussian basis functions were employed for the rest of the electrons.

The experimental geometries were used as initial structures to optimize the geometry at the B3LYP level. The Gaussian16 package was invoked for this reason. [89] No other low-lying structures (isomers) were located. The TD-DFT calculations for the excited states were done with NWChem.[90] The vertical excitation energies and transition dipole moments were obtain with TD-DFT.

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## Chapter 5: Conclusions and Future Work

### Conclusions

The systematic characterization by X-ray crystallography and UV-visible spectroscopy salphenazine ligand (**$H_2L^I$**, shown in **Figure 5.1**), containing the O-N-N-O salen type bonding motif and corresponding metal complexes was achieved. These complexes revealed the extended π-conjugation of these ligands results in differentiation of a uranyl ($UO_2^{2+}$) signal as compared to other +2 metal ions or transition metals. The solid-state characterization of this series provides insight to the preferred coordination environment of the uranyl ion in these conjugated systems. These insights can guide further design improvements in the development of ligands with extended conjugation to be used as on-site actinide chemosensors.

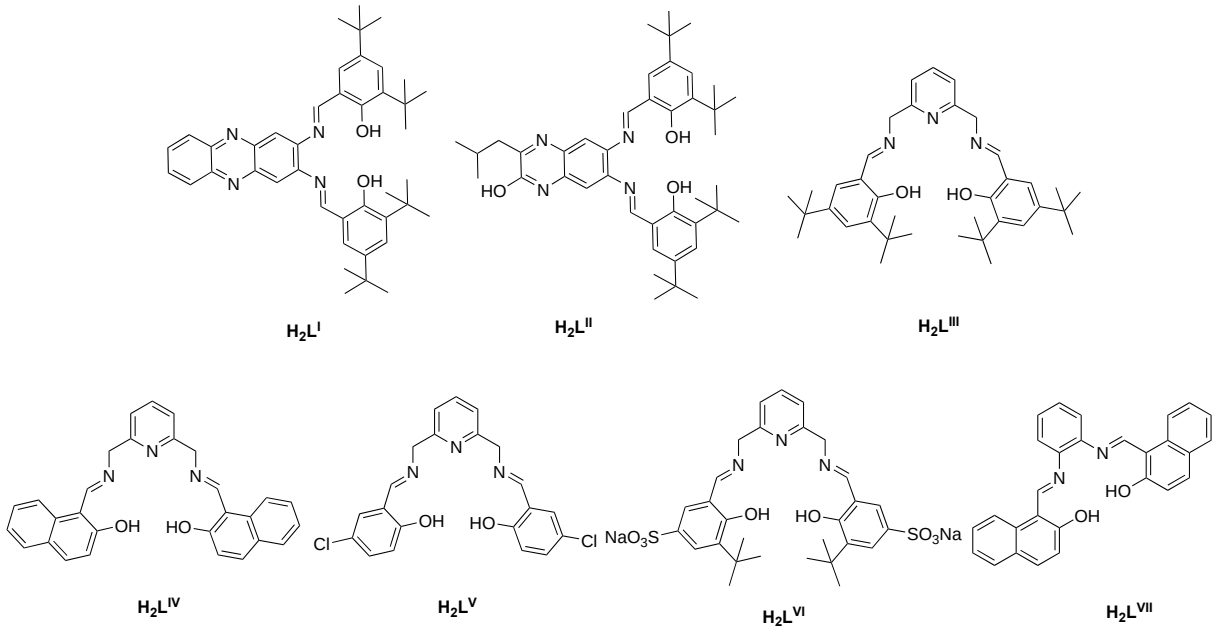



**Figure 5.1**. Projection of ligands discussed in this work

The pentadentate binding of the new ligands $\mathbf{H_2L^{III}}$-$\mathbf{H_2L^{VI}}$, which fully occupy the uranyl equatorial plane, removed the necessity of a coordinating solvent molecule or ligand rearrangement allowing to quickly and selectively bind uranyl in a one-to-one fashion. The $UO_2\mathbf{[L^{III}]}$ and $UO_2\mathbf{[L^{IV}]}$ complexes with uncommon pyridine coordination were synthesized and characterized in solution and in the solid state and found to have short U-$N_{py}$ distances as compared to the literature. These complexes have a distinct response for uranyl over common first-row transition metals in the UV and provide an example of uncommon binding for uranyl. The pyridine moiety and pentadentate coordination environment were shown to increase binding kinetics and affinity for uranyl of this system.

Eleven lanthanide double decker sandwich complexes ($Ln_2[\mathbf{L^{VII}}]_3$) were synthesized and characterized in the solid-state and in solution. The minimal structural differences in the $Nd_2[\mathbf{L^{VII}}]_3$, $Eu_2[\mathbf{L^{VII}}]_3$, $Gd_2[\mathbf{L^{VII}}]_3$, $Tb_2[\mathbf{L^{VII}}]_3$, $Dy_2[\mathbf{L^{VII}}]_3$, $Ho_2[\mathbf{L^{VII}}]_3$, $Er_2[\mathbf{L^{VII}}]_3$, $Yb_2[\mathbf{L^{VII}}]_3$, and $Lu_2[\mathbf{L^{VII}}]_3$ analogues resulted in tunable solution emission properties, but it is more apparent in the solid-state luminescence with $Sm_2[\mathbf{L^{VII}}]_3$ emission at 556 nm to $Er_2[\mathbf{L^{VII}}]_3$ emission at 617 nm. Lutetium exhibited a large increase in fluorescence as compared to the other $Ln_2[\mathbf{L^{VII}}]_3$ complexes in the solid state, providing a rare opportunity to differentiate one of the 14 lanthanides. The completeness of this solid-state series is quite uncommon in the literature, and allows for a rare example of explaining differing properties through small changes in the coordination environment.

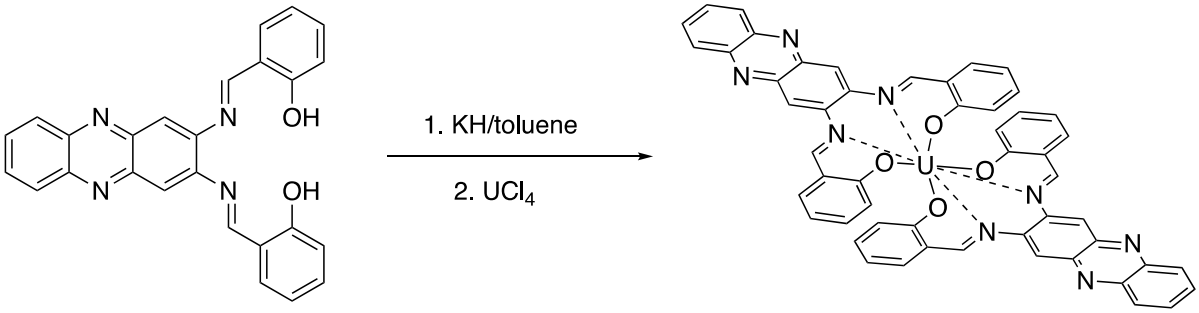
The complex $Th[\mathbf{L^{VII}}]_2$ was observed to fluoresce in both solid-state and solution phase, which at this point is unprecedented in the literature. This is the first reported example of a compound containing thorium that exhibits emission in the solid-state and solution. The quenching of the isoelectronic $Ce[\mathbf{L^{VII}}]_2$ complex was explained by the possible quenching

pathway involving the Ce(III)/(IV) redox couple, which is inaccessible in the thorium analogue. Solvent dependence of emission was observed and may be due to solvent coordination in the 8 and 9-coordinate equilibrium of Th[$\mathbf{L^{VII}}$]$_2$ in solution, and adds to the knowledge about the coordination chemistry of thorium. The $UO_2$ [$\mathbf{L^{VII}}$] complex was found to crystallize in a hydrogen bonded tetramer, with coordinated water molecules hydrogen bonding to the –yl oxygen of the symmetrically inequivalent U atom. This finding was intriguing and suggests further study of –yl activation with napthylsalophen derivatives may be of interest.

## Future Work

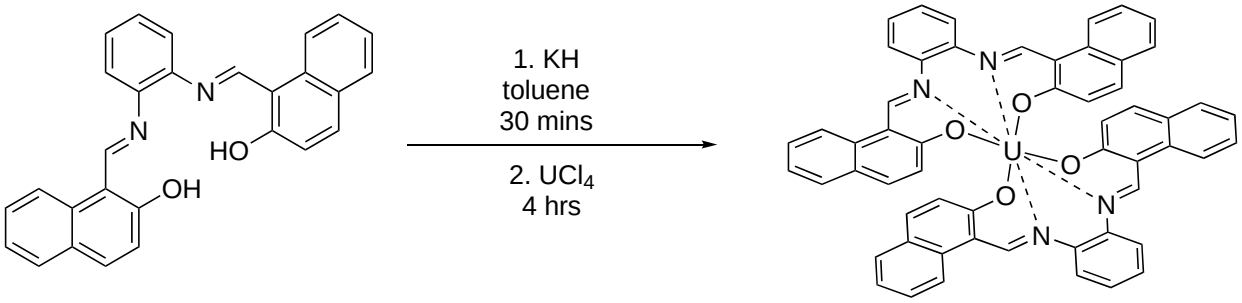
### U(IV) Complexes with Redox Active Ligands

The use of redox active ligands to stabilize low valent uranium has been of interest as the basis for new catalysts in recent years.[1-4] Such redox-active ligands would allow for electrons to be stored not only in the metal center, but also in the ligand framework for possible future use in multielectron catalysis.[5] The ligands described in Chapter 2 and Chapter 4 are prime candidates for this type of chemistry and could be explored for these purposes. A proposed synthesis for a U(IV) compound using $\mathbf{H_2L^I}$ is shown below in **Scheme 5.1**.




**Scheme 5.1**. General synthetic scheme for U(IV) salphenazine complex, U[$\mathbf{L^I}$]$_2$.

Through deprotonation of the free base ($\mathbf{H_2L^I}$) using the strong base potassium hydride, products with the more difficult to complex $UCl_4$ can be obtained. Precautions to rigorously exclude water and air from the reaction flask must be taken. Another proposed synthesis, incorporating $\mathbf{H_2L^{VII}}$, is shown in **Scheme 5.2**. Single crystals of these should be obtained for detailed characterization as a solid. Single crystals suitable for X-ray diffraction of the earlier structures were obtained through slow diffusion of hexanes into toluene for similar systems, and should be one combination attempted. Crystals of analogous systems were also grown from slow diffusion of hexanes into DCM and ether into acetonitrile.

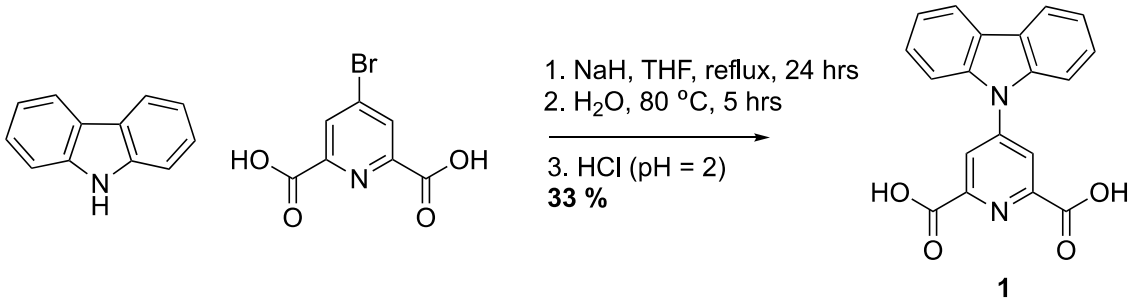



**Scheme 5.2.** General synthetic scheme for napthylsalophen U(IV) complex, $U[\mathbf{L^{VII}}]_2$.

Once these compounds and the derivatives thereof are synthesized and characterized, the electrochemical analysis of these species would also be of great interest. As mentioned in Chapter 2, the extended conjugation of the pi-system can provide stabilization of the U(V)/U(VI) redox couple. Investigation the U(III)/(IV) couple may be useful as many proposed uranium catalysts use the III/IV couple in their proposed mechanisms. Stabilization of any of these reduction potentials would be of intense interest and are similar to examples in the literature from actinide coordination chemistry research groups such as those of Polly Arnold, Marienella Mazzanti, and Suzanne Bart.[2, 4, 6] Understanding uranium chemistry at these oxidation states can also be used as model for plutonium and neptunium chemistry, which are more often found in their low valent states.[7-8]

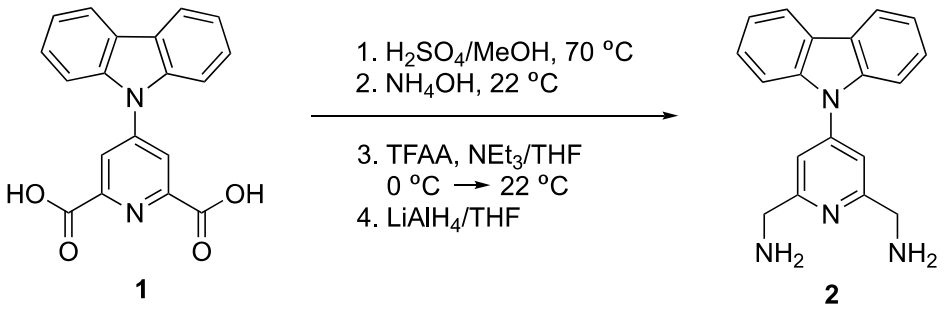
**Increasing the Extinction Coefficient of [$H_2L^{III}$]**

As was discussed in Chapter 3, the pentadentate binding environment of $\mathbf{H_2L^{III}}$ increases the binding kinetics, but there is a significant loss in extinction coefficient and consequently, signal to noise. One avenue to remedy this issue would be to add a fluorophore, or a more highly absorbing tag, into the synthetic pathway. Ana DeBettencourt-Dias and coworkers recently published a synthesis to form compound **1**, shown below as an antenna to bind lanthanide ions and absorb light in the visible spectrum.[9] The amine in **Scheme 5.3** is readily available and the brominated dipicolinic acid derivative is commercially available. This could be reacted with an acidic work-up to achieve the synthesis of **1**.



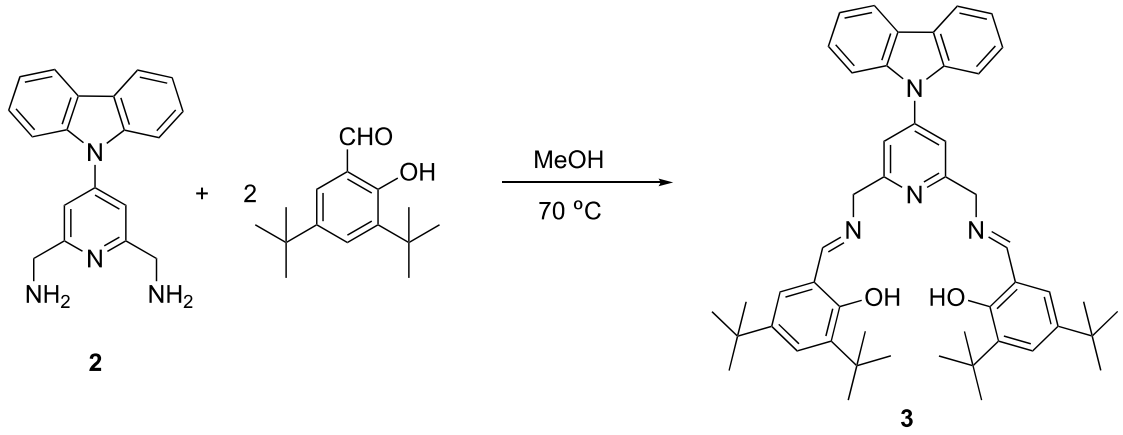

**Scheme 5.3.** Synthetic scheme for form compound **1**.[9]

Using compound **1** as a starting material in the synthetic pathway for ligands like those from Chapter 3 could yield a new ligand system with an increased extinction coefficient, without altering the binding pocket that previously resulted in such fast binding kinetics. The addition of the tertiary amine should be tolerant to the conditions listed in **Scheme 5.4** and should result in the formation of compound **2**, a diamine; however, optimization of the conditions may not be straightforward.




**Scheme 5.4.** Proposed synthetic scheme to form compound **2**

After formation of **2**, synthesizing **3** (**Scheme 5.5**) or derivatives thereof would allow ligands like those described in Chapter 3 to absorb more light, and the limit of detection for uranyl should be decreased. Compound **3** contains $sp^3$ hybridized carbon atoms that are easily oxidized and this could complicate the synthetic pathway. Due to this complexity, synthesis of compound **3** may require additional optimization, especially during purification. The salicylaldehyde shown below in **Scheme 5.5** is 3,5-ditert-butylsalicylaldehyde, but other salicylaldehyde starting materials may be chosen to change the electronic character of the ligand. These compounds would also be more soluble than the salphenazine derivatives described in Chapter 2. This could eliminate the use of pyridine as a solvent while still providing a stronger absorption on complexation. If compound **3** has a high molar extinction coefficient and can be synthesized in a reasonable yield, and also quickly bind uranyl, then it could be useful in possible applications such as color changing paints, incorporation onto solid-state supports, and in-the-field detection of uranyl.

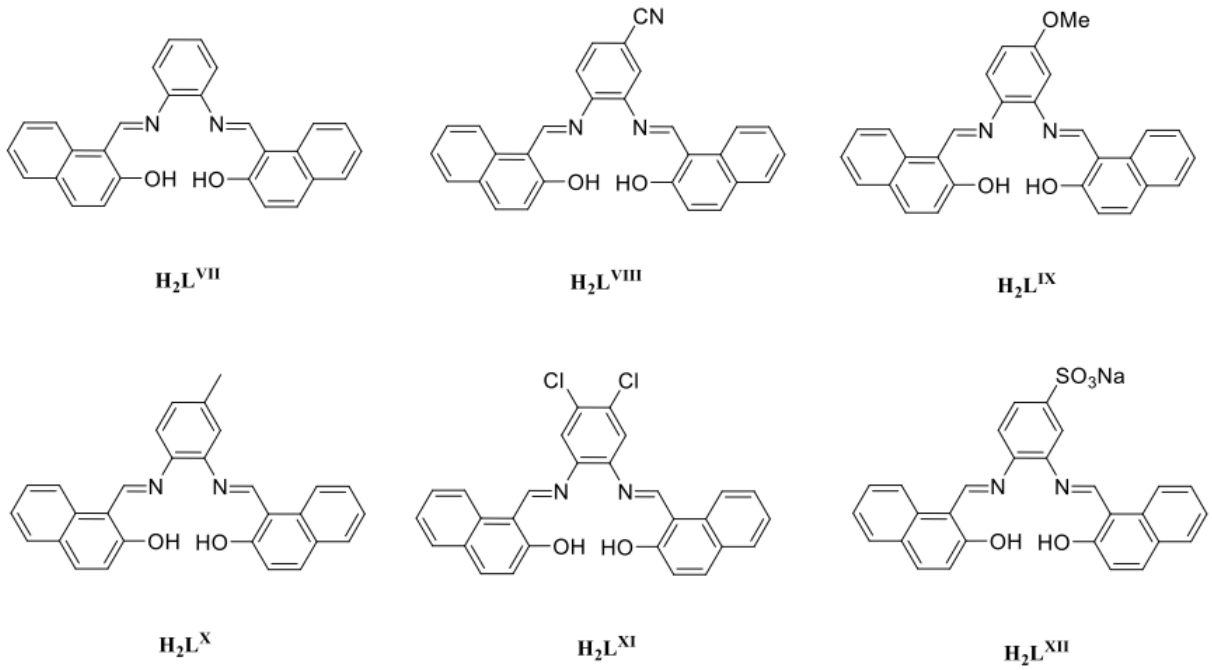



**2** **3**

**Scheme 5.5.** Synthesis for formation of **3**, a derivative of [$H_2L^{III}$].

**Napthylsalophen Derivatives**

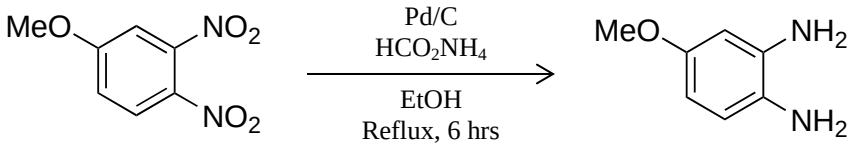
One new direction for research would be the preparation and characterization of the napthylsalophen analogues [$\mathbf{H_2L^{VIII}}$] to [$\mathbf{H_2L^{XII}}$], featuring examples of strongly and mildly electron donating or withdrawing groups, and the corresponding metal complexes. These derivatives would be of interest in probing the electronic effects of systematic modification to the ligand, and could be easily synthesized and utilized to investigate the electronic properties of thorium emission, cerium oxidation state stabilization, and lanthanide antenna effect. An example of proposed napthylsalophen derivatives can be found in **Figure 5.2**. The necessary diamines for the synthesis of [$\mathbf{H_2L^{VIII}}$], [$\mathbf{H_2L^{X}}$], and [$\mathbf{H_2L^{XI}}$] are commercially available. The diamine necessary for [$\mathbf{H_2L^{IX}}$], 1,2-diamino-4-methoxybenzene, can be synthesized by the reduction of the inexpensive and commercially available 1,2-dinitro-4-methoxybenzene via **Scheme 5.7**.




$H_2L^{VII}$ $H_2L^{VIII}$ $H_2L^{IX}$

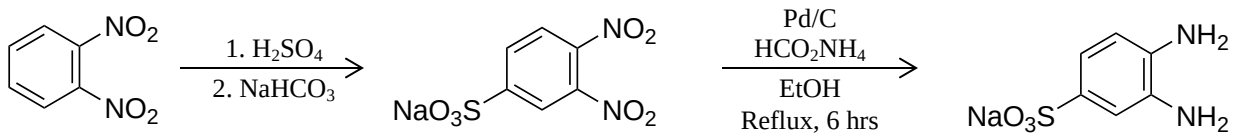
$H_2L^{X}$ $H_2L^{XI}$ $H_2L^{XII}$

**Figure 5.2.** Proposed napthylsalophen derivatives




**Scheme 5.7.** Synthetic scheme for the formation of 1,2-diamino-4-methoxybenzene.

A water-soluble analogue would be especially useful in this library of napthylsalophen ligands. The diamine necessary for [$\mathbf{H_2L^{XII}}$], 1,2-diamino-4-sulfobenzene, can be synthesized through the sulfonation and reduction of 1,2-dinitrobenzene, shown in **Scheme 5.8**. If formation of this ligand could be achieved, sensing of uranyl in contaminated ground water could be investigated.




**Scheme 5.8.** Proposed synthetic scheme for the formation of 1,2-diamino-4-sulfobenzene.

Differences in the steric hindrance of groups may also be of interest, as the multi-decker sandwiches complexes may be disrupted and could lead to interesting electronics and packing effects. The derivatives suggested in **Figure 5.2** minimize the steric influence of the additional groups, but t-butyl or isopropyl analogues may elucidate the steric factor with these systems. Once a library of napthylsalophen derivatives is synthesized and characterized, attempts to coordinate these ligands to uranyl, thorium, cerium, and lanthanides should be attempted.

The differences and ability to tune unusual emission from a thorium complex with these compounds would be of interest. The cerium(IV) analogues of these compounds would also be of interest to see if the same stabilization of the Ce(III)/Ce(IV) redox couple is observed (further explained below). If the lanthanide derivatives of these ligands were to be synthesized, particular care and urgency should be applied to the ytterbium, erbium, and neodymium complexes. These could be investigated for their possible use as near infrared (NIR) emitters and may have potential biological imaging applications. The gadolinium complexes may also be of interest, if the magnetic properties of these compounds were to be characterized using a variable temperature magnetometer. Mulitmetallic lanthanide compounds that self-assemble in a predictable fashion are uncommon and this system could be a good model to further explore f-block coordination chemistry. Compounds of this type have been used in medicinal applications as well as for molecular machines and single molecule magnets,[10-11] and would have interesting applications in addition to their interesting fundamental chemistry.

**Ceric(IV) Ammonium Nitrate (CAN) Oxidations and $Ce[L^{VII}]_2$ Derivatives**

Tangential to this, a completely new direction to be explored would be to characterize the coordination chemistry and unusual oxidation state stabilization of $Ce[L^{VII}]_2$ introduced in Chapter 4. Electrochemical analysis of $Ce[L^{VII}]_2$, as well as the cerium complexes with napthylsalophen derivatives mentioned earlier in this chapter (**Figure 5.1**), would be an interesting endeavor. Cerium is most commonly found as the Ce(III) salt and, in fact, ceric ammonium nitrate (CAN) oxidations using Ce(IV) as a single electron oxidant are prevalent in organic chemistry.[12-13] These oxidations often take place in mixed solvent systems and require stoichiometric amounts of cerium.[13] The cerium-containing compound is a single-electron oxidant, reducing the cerium metal from Ce(IV) to Ce(III) and must often be added in excess to do common oxidation transformations.[12] There are examples of catalytic CAN oxidations, but they require a co-oxidant to regenerate the reactive Ce(IV) species. The ability to use an organic scaffold that would be able to use molecular oxygen to regenerate the active cerium species would reduce the overall amounts of cerium salts required, as well as the need for mixed organic and aqueous reaction mixtures. Both of these would, in turn, reduce the overall amounts of waste generated.

Understanding the coordination chemistry of cerium compounds and producing a compound that can shift the redox potentials of this useful metal would be of great interest towards this end. Using an organic compound to stabilize the Ce(IV) oxidation state has been witnessed and explained by Eric Shelter and coworkers,[14-15] but further investigation into the compound presented here ($Ce[L^{VII}]$) may lead to another example of shifting the Ce(III)/Ce(IV) redox potential.[14] The stabilization that Shelter and coworkers found amounted to be 1.2 V; this

large stabilization is likely occurring in the Ce[$L^{VII}$] system as well, and would be of great interest as the focus of future study. If the Ce[$L^{VII}$] ligand system could be properly tuned, it could be used as a catalyst to oxidize organic materials and then be regenerated in-situ using molecular oxygen as the oxidant rather than as a sacrificial oxidant. This is a potentially greener way to carry out oxidations and as this ligand is very soluble in organic solvents, would eliminate the need for mixed solvent systems that are often necessary for CAN oxidations. This Ce(III)/Ce(IV) redox chemistry is also of great interest as a model for Pu(III)/Pu(IV) oxidation chemistry.[7]

**Macrocyclic Chemosensors**

Another way to overcome binding kinetics and overcome the need for the fifth coordinating solvent in the uranyl binding sphere would be to make a macrocycle that will eliminate the need for coordinating solvent. Many research groups have employed this stragegy but key examples are from the Sessler group.[16-17] The binding pocket of **4** has the same number of atoms that are present in the recently published macrocycle (**5**) which enabled the a parts per billion sensor of uranyl.[17] These compounds require many synthetic steps and are not trivial to isolate.[17] The size of the coordination pocket is highlighted below in **Figure 5.2**. Synthesis of this compound **4** with the inclusion of the highly fluorescent quinoxalinol backbone would be of interest spectroscopically and has a reasonable chance to bind uranyl quickly and efficiently.

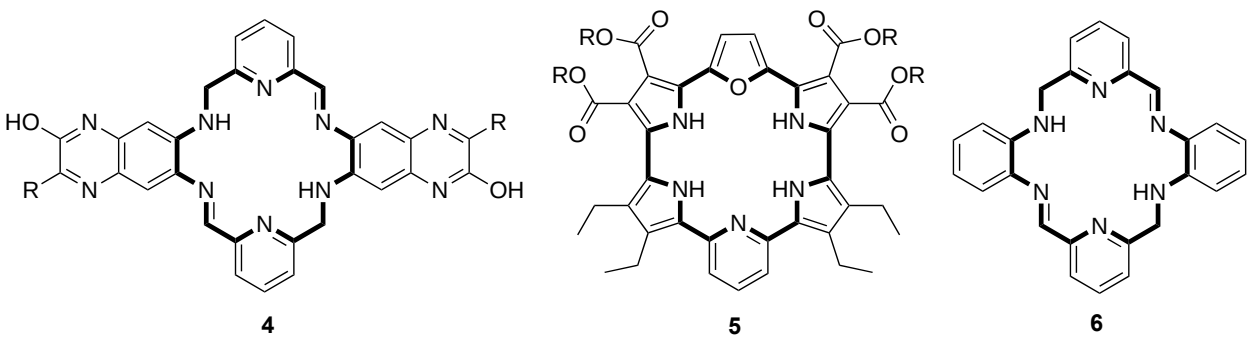
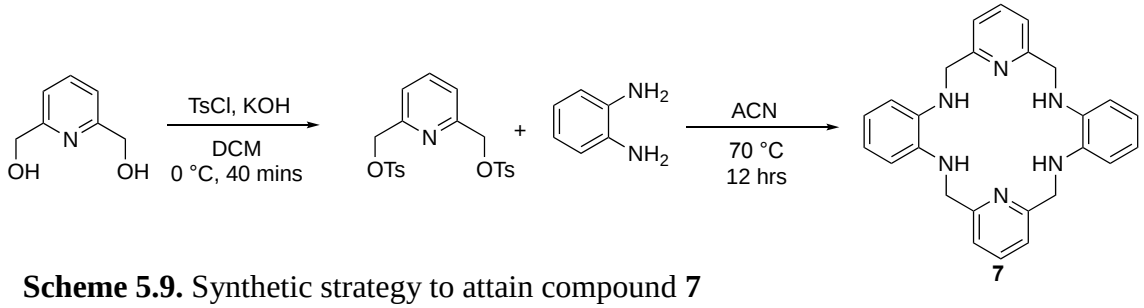



**Figure 5.3.** Proposed salqu derivatized macrocyle (compound **4**), parts per billion sensor for uranyl (compound **5**) reported by Sessler and Jokerst, and proposed benzene derivatized macrocycle (compound **6**).[17]

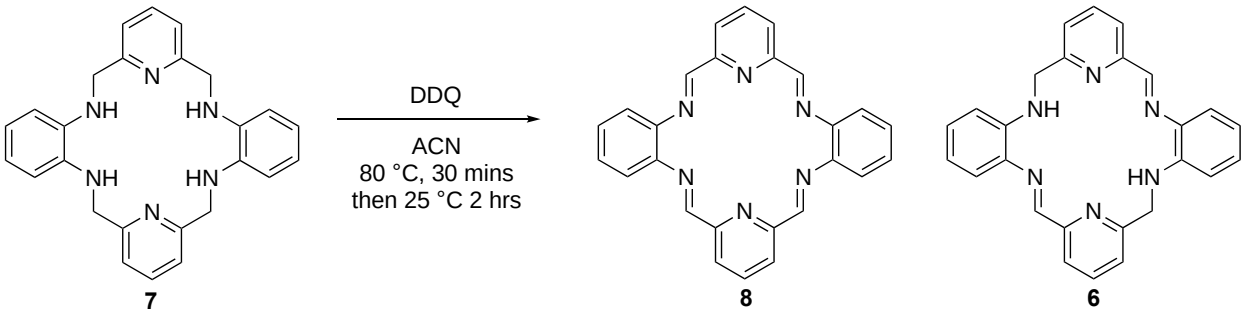
In order to attain **4** the model **6** would be useful to synthesize first, as the reagents necessary are commercially available and plentiful. Two possible synthetic routes will be described here. The synthesis of tetraamine **7** can be achieved through the synthetic pathway described in **Scheme 5.9**. First, tosyl chloride could be added to 2,6-pyridinedimethanol under basic conditions to result in a tosylated pyridine starting material. A simple $S_N2$ type reaction with a desired diamine (1,2-diaminobenzene) could then be conducted to yield **7**. These compounds will require synthetic optimization and will form many polymeric byproducts.




**Scheme 5.9.** Synthetic strategy to attain compound **7**

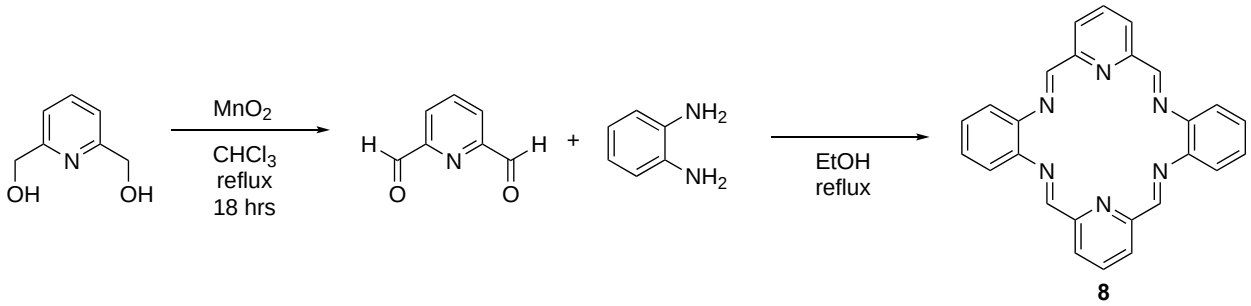
This compound may prove difficult to isolate as amines can be difficult to separate with column chromatography, but recrystallization could be attempted. These syntheses are not trivial and often require multiple columns and complexation with a metal center may aid in separation. Previous examples of metal templation with these "aza-crown" type compounds have been

achieved using strontium triflate, and may be useful here.[18-19] Further oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) of the amines may also result in a product that is more amiable to column chromatography and is shown in **Scheme 5.10**. It is likely that a mixture of products **6** and **8** will be formed and need to be isolated. These compounds will be extremely polar contain free amines, which are notoriously difficult to separate by column chromatography. The optimization for compound **6** with the commercially available starting materials listed in **Scheme 5.9** will be useful before attempts to make the quinoxalinol derivative (compound **4**) are made.




**Scheme 5.10.** Synthetic strategy to synthesize compounds **8** and **6**.

Another, more direct route to form **8** may be achieved through oxidation of the 2,6-pyridinedimethanol starting material using a soft oxidant $MnO_2$ in chloroform (**Scheme 5.11**). The resulting 2,6-pyridinedicarboxaldehyde could then be added to 1,2-diaminobenzene and after four successive condensation reactions formation of **8** could be achieved. As with any macrocycle synthesis, polymerization rather than cyclization may occur and high dilution could be used to limit the possible polymerization or side products. Regardless, the conditions for the cyclization will need to be optimized.




**Scheme 5.11.** Proposed alternate synthetic strategy to form compound **8**.

Any of the macrocyclic compounds (**6**, **7**, or **8**) would be of interest if bound to uranyl and the best synthetic route to form these compounds could then be applied using quinoxalinol diamine derivatives to yield macrocycle **4**. Similar compounds have also been used with f-block elements in recent years and have been extremely successful sequestration agents with photoacoustic medical applications.[17,20] Few crystal structures exist of these particular compounds and solid-state characterization of these compounds would be of interest in their own right, as well as the potential use in detection of actinides.

The proposed projects described here are potential avenues to learn about the fundamental coordination chemistry of actinides. The insights from the research described and proposed in this work may lead to a better understanding of environmental incorporation, selective detection, or selective extraction of these metal ions. This knowledge could potentially be applied as new waste remediation technologies or in new applications such as single molecule magnets or catalysis. New actinide properties and unexpected results are often achieved, as was reported in this work, due to the comparatively small amount of fundamental research and flexibility in both oxidation state and coordination environment of the actinides.

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## Appendix 1: Crystallographic Tables

### Data Collection: single crystal X-ray diffraction

The X-ray diffraction datasets were collected at 180K, on a Bruker SMART APEX CCD X-ray diffractometer unit using Mo Kα radiation, from crystals mounted in Paratone-N oil on glass fibers, with the exception of VO[$L^{I}$], which was mounted in epoxy on a glass fiber and collected at 273 K. SMART (v 5.624) was used for preliminary determination of cell constants and data collection control. Determination of integrated intensities and global cell refinement were performed with the Bruker SAINT software package using a narrow-frame integration algorithm for all data sets. Refinement was performed against $F^2$ by weighted full-matrix least squares, and empirical absorption correction (SADABS) was applied.[1] The program suite ShelXTL (v 5.1) was used for space group determination, and structure solution and refinement for $H_2[L^{I}]$, $UO_2[L^{I}]$, Cu[$L^{I}$], VO[$L^{I}$], Zn[$L^{I}$], Fe[$L^{I}$]-O-Fe[$L^{I}$].[2] For data sets $UO_2[L^{III}]$, $UO_2[L^{IV}]$, $H_2[L^{VII}]$, Th[$L^{VII}$]$_2$ , Ce[$L^{VII}$]$_2$, $Nd_2[L^{VII}]_3$, $Gd_2[L^{VII}]_3$, $Ho_2[L^{VII}]_3$, $Yb_2[L^{VII}]_3$, $Eu_2[L^{VII}]_3$, $Tb_2[L^{VII}]_3$, $Dy_2[L^{VII}]_3$, $Er_2[L^{VII}]_3$, $Lu_2[L^{VII}]_3$, $UO_2[L^{VII}]$ the program suite ShelXTL (v 5.1) was used for space group determination, and structure solution[2] and were refined with Olex2.refine package using Gauss-Newton minimization.[3]

An interstitial ethyl acetate molecule on an inversion center and a disorded t-butyl group were modeled for the $H_2[L^{I}]$ data set. Two interstitial THF molecules were removed using SQUEEZE for the data set Fe[$L^{I}$]-O-Fe[$L^{I}$]. Solvent masks for interstial

methanol and DCM for the data sets $VO[L^{I}]$, $Yb_2[L^{VII}]_3$, $Tb_2[L^{VII}]_3$, $Dy_2[L^{VII}]_3$ and $Lu_2[L^{VII}]_3$ were generated by Olex2.1.[3-4] A disordered toluene molecule on a mirror plane was modeled for the $Th[L^{VII}]_2$ data set. One half an equivalent of a disordered interstitial hexanes molecule was modeled for the $Ce[L^{VII}]_2$ data set. Disordered DCM molecule was modeled over two positions for the $Gd_2[L^{VII}]_3$ dataset. Only the metal atoms were refined anisotropically for the $Er_2[L^{VII}]_3$ and $Eu_2[L^{VII}]_3$ datasets due to low resolution, and resulted in the structures being useful for discussion but unpublishable. The carbon atoms on the coordinating methanol molecules on the $Yb_2[L^{VII}]_3$, $Tb_2[L^{VII}]_3$, $Dy_2[L^{VII}]_3$, and $Lu_2[L^{VII}]_3$ datasets was set as an idealized methyl group and refined isotropically to allow for data convergence. All projections were generated in the Olex2.1-1 graphics program.[4]

## $H_2[L^I]$

**Crystallographic Table 1** Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **$H_2[L^I]$**. Ueq is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| C1 | 6188(3) | 6822.0(8) | 1866.4(7) | 23.1(4) |
| N1 | 2784(2) | 6263.1(7) | 2334.9(6) | 25.3(4) |
| O1 | 5574(2) | 7089.4(6) | 2272.1(5) | 33.1(4) |
| C2 | 7814(3) | 7079.0(8) | 1609.3(7) | 21.9(4) |
| N2 | 2317(2) | 6652.3(7) | 3252.1(6) | 27.2(4) |
| O2 | 3940(2) | 7705.4(6) | 3283.5(5) | 35.8(4) |
| C3 | 8827(3) | 7669.2(8) | 1772.6(7) | 25.6(5) |
| N3 | -3479(2) | 5020.1(7) | 2404.7(6) | 27.5(4) |
| C4 | 7084(3) | 8145.7(9) | 1766.6(8) | 36.4(5) |
| N4 | -3907(2) | 5432.9(7) | 3376.4(6) | 29.6(4) |
| C5 | 9969(3) | 7613.8(9) | 2288.8(7) | 32.2(5) |
| C6 | 10500(4) | 7869.7(9) | 1431.3(8) | 42.0(6) |
| C7 | 8441(3) | 6774.7(8) | 1206.0(7) | 24.1(4) |
| C8 | 7558(3) | 6239.3(8) | 1035.4(7) | 25.3(4) |
| C13 | 5951(3) | 6007.6(8) | 1295.0(7) | 25.5(5) |
| C14 | 5231(3) | 6289.2(8) | 1705.5(7) | 22.9(4) |
| C15 | 3537(3) | 6022.5(8) | 1959.5(7) | 25.0(5) |
| C16 | 1055(3) | 6021.2(8) | 2568.9(7) | 23.1(4) |
| C17 | -403(3) | 5631.7(8) | 2359.5(7) | 25.0(5) |
| C18 | -2102(3) | 5412.5(8) | 2623.6(7) | 23.3(4) |
| C19 | -5060(3) | 4830.7(8) | 2673.2(7) | 27.0(5) |
| C20 | -6584(3) | 4417.6(9) | 2463.2(8) | 33.3(5) |
| C21 | -8210(3) | 4227.4(9) | 2724.7(8) | 37.6(6) |
| C22 | -8423(3) | 4432.7(9) | 3204.4(9) | 38.5(6) |
| C23 | -7009(3) | 4827.0(9) | 3417.7(8) | 35.4(5) |
| C24 | -5280(3) | 5037.5(8) | 3158.3(8) | 28.0(5) |
| C25 | -2323(3) | 5619.4(8) | 3110.0(7) | 25.4(5) |
| C26 | -810(3) | 6035.1(8) | 3316.8(7) | 27.9(5) |
| C27 | 831(3) | 6226.7(8) | 3060.3(7) | 24.7(4) |
| C28 | 3351(3) | 6562.8(9) | 3669.6(7) | 27.7(5) |
| C29 | 4845(3) | 6985.9(8) | 3902.0(7) | 26.5(5) |
| C30 | 6045(3) | 6825.1(9) | 4336.5(7) | 30.2(5) |
| C31 | 7510(3) | 7200.5(9) | 4574.0(7) | 29.4(5) |

| | | | | |
|---|---|---|---|---|
| C32 | 8876(3) | 7043.9(10) | 5046.6(7) | 36.4(5) |
| C33 | 8122(4) | 6479.4(11) | 5272.2(8) | 51.0(7) |
| C34 | 8729(4) | 7532.8(11) | 5427.5(8) | 46.9(6) |
| C35 | 11229(4) | 6975.6(13) | 4929.5(9) | 56.7(7) |
| C36 | 7747(3) | 7749.8(9) | 4355.2(7) | 30.3(5) |
| C37 | 6604(3) | 7940.9(9) | 3929.8(7) | 27.5(5) |
| C38 | 6956(3) | 8546.0(9) | 3708.8(7) | 31.1(5) |
| C39 | 4847(3) | 8899.1(10) | 3678.8(9) | 42.6(6) |
| C40 | 8668(4) | 8899.3(10) | 4015.9(8) | 43.7(6) |
| C41 | 7750(4) | 8477.9(10) | 3197.9(8) | 40.0(6) |
| C42 | 5107(3) | 7541.4(9) | 3699.2(7) | 26.3(5) |
| C43S | 7042(8) | 4618(2) | 4496.1(15) | 118.9(15) |
| C44S | 8738(14) | 4920(3) | 4454(2) | 84(2) |
| C45S | 8267(13) | 4726(3) | 5012(3) | 74.4(18) |
| O46S | 7458(8) | 4552.6(19) | 5368.2(17) | 90.6(14) |
| O3S | 10000 | 5000 | 5000 | 85.3(10) |
| C9 | 8373(3) | 5926.9(9) | 590.5(7) | 30.4(5) |
| C1A | 9667(12) | 5354(3) | 796(2) | 50(2) |
| C1b | 10628(9) | 5739(3) | 705.6(19) | 55(2) |
| C2A | 9950(16) | 6267(3) | 326(3) | 67(3) |
| C2b | 8347(11) | 6381(2) | 145.3(16) | 45.4(17) |
| C3A | 6512(16) | 5700(5) | 263(4) | 62(3) |
| C3b | 6953(15) | 5432(4) | 400(4) | 63(3) |

**Crystallographic Table 2** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **$H_2[L^I]$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{12}$** | **$U_{13}$** | **$U_{23}$** |
|---|---|---|---|---|---|---|
| C1 | 22.6(10) | 25.4(11) | 21.2(10) | 4.3(8) | 0.8(8) | -4.6(8) |
| N1 | 20.8(8) | 29.1(9) | 26.0(9) | -1.5(7) | 1.9(7) | 1.2(7) |
| O1 | 31.5(8) | 35.5(8) | 33.9(8) | -6.6(6) | 12.7(6) | -10.6(7) |
| C2 | 21.8(10) | 21.4(10) | 22.4(11) | 0.4(8) | 1.0(8) | -0.2(8) |
| N2 | 25.6(9) | 30.3(9) | 25.5(9) | -5.4(7) | 1.6(8) | -3.6(7) |
| O2 | 41.5(9) | 35.4(8) | 28.1(8) | -10.0(7) | -11.1(7) | 1.6(7) |
| C3 | 28.3(11) | 22(1) | 26.8(11) | -2.0(8) | 4.6(9) | -4.1(8) |
| N3 | 23.3(9) | 24.0(9) | 34.9(10) | -0.8(7) | 0.8(8) | -2.6(7) |
| C4 | 41.4(13) | 24.1(11) | 42.4(13) | 3.9(9) | -5.1(11) | -3.9(10) |
| N4 | 27.4(9) | 29.0(9) | 33.1(10) | -4.5(7) | 6.2(8) | -1.4(8) |
| C5 | 30.8(11) | 28.4(12) | 36.7(12) | 1.5(9) | -2.6(10) | -7.2(9) |
| C6 | 50.8(14) | 32.0(13) | 45.0(14) | -16.5(11) | 15.1(12) | -10.1(10) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C7 | 25.4(10) | 26.2(11) | 20.9(10) | -1.4(8) | 3.6(8) | 1.0(9) |
| C8 | 26.9(10) | 24.9(11) | 23.7(11) | -0.4(9) | 0.5(9) | -1.4(9) |
| C13 | 27.4(10) | 23.1(11) | 25.8(11) | -3.7(8) | 0.9(9) | -3.0(9) |
| C14 | 21.9(10) | 24.7(11) | 22.1(11) | 0.5(8) | 1.2(8) | 1.2(8) |
| C15 | 23.5(10) | 24.7(11) | 26.2(11) | -1.3(8) | -2.0(9) | -0.0(9) |
| C16 | 19.3(10) | 23.6(10) | 26.4(11) | 0.1(8) | 1.4(8) | 1.2(9) |
| C17 | 23.7(10) | 28.9(11) | 22.3(11) | 1.1(9) | 1.8(9) | -2.1(8) |
| C18 | 21(1) | 21.3(10) | 27.1(11) | 2.2(8) | -1.1(9) | -0.4(8) |
| C19 | 22.7(10) | 21.8(10) | 36.2(12) | 2.7(8) | 1.1(9) | 2.5(9) |
| C20 | 27.8(11) | 26.7(11) | 44.7(14) | -2.8(9) | -1.2(10) | -5.3(10) |
| C21 | 28.4(11) | 27.3(12) | 56.3(16) | -5.7(9) | -1.0(11) | 0.4(11) |
| C22 | 30.6(12) | 32.7(12) | 52.9(15) | -6(1) | 8.2(11) | 6.9(11) |
| C23 | 33.3(12) | 34.4(12) | 39.4(13) | -4.8(10) | 8.9(10) | 2.3(10) |
| C24 | 25.0(11) | 22.6(11) | 36.6(12) | -1.0(9) | 2.6(9) | 2.8(9) |
| C25 | 23.2(10) | 25.2(11) | 27.9(11) | 1.5(8) | 2.7(9) | 1.2(9) |
| C26 | 28.8(11) | 30.7(11) | 24.4(11) | -4.0(9) | 3.4(9) | -3.7(9) |
| C27 | 23.3(10) | 22.6(10) | 27.6(11) | -2.0(8) | -1.1(9) | -0.1(8) |
| C28 | 28.3(11) | 27.9(11) | 27.6(12) | -3.1(9) | 7.1(9) | 0.1(9) |
| C29 | 25.1(10) | 30.2(11) | 24.2(11) | -3.0(9) | 2.0(9) | -3.2(9) |
| C30 | 30.5(11) | 33.5(12) | 26.6(11) | 0.3(9) | 2.8(9) | 0.9(9) |
| C31 | 26.4(11) | 37.0(12) | 24.9(11) | 2.1(9) | 2.2(9) | -2.8(9) |
| C32 | 32.9(12) | 47.4(14) | 27.9(12) | 4.9(10) | -3.3(10) | -0.1(10) |
| C33 | 58.5(16) | 52.4(15) | 39.5(14) | 6.0(13) | -11.1(12) | 9.2(12) |
| C34 | 53.1(15) | 58.6(16) | 27.7(13) | -2.0(12) | -4.6(11) | 1.3(11) |
| C35 | 37.2(13) | 82(2) | 49.2(16) | 14.6(13) | -5.6(12) | 2.0(14) |
| C36 | 26.5(11) | 38.7(13) | 25.4(11) | -4.0(9) | 0.3(9) | -8.1(9) |
| C37 | 26.6(10) | 33.3(12) | 22.8(11) | -1.8(9) | 3.3(9) | -5.5(9) |
| C38 | 35.5(12) | 30.0(11) | 27.8(12) | -4.7(9) | 1.8(9) | -3.3(9) |
| C39 | 44.8(13) | 35.9(13) | 46.6(15) | 0.9(11) | 0.5(11) | -2.6(11) |
| C40 | 48.0(14) | 36.9(13) | 45.2(14) | -12.8(11) | -2.4(11) | -6.4(11) |
| C41 | 46.4(14) | 39.0(13) | 35.4(13) | -9.9(11) | 7.3(11) | 0.3(10) |
| C42 | 25.3(10) | 34.0(12) | 19.5(11) | -1.9(9) | 0.2(9) | -1.8(9) |
| C43S | 129(4) | 134(4) | 89(3) | 33(3) | -15(3) | 26(3) |
| C44S | 125(6) | 79(5) | 46(4) | -8(4) | -10(4) | 14(3) |
| C45S | 97(5) | 53(4) | 76(5) | 25(4) | 23(5) | 11(4) |
| O46S | 125(4) | 78(3) | 72(3) | 7(3) | 30(3) | 11(2) |
| O3S | 113(3) | 65(2) | 82(2) | 13(2) | 31(2) | 12.5(17) |
| C9 | 33.7(11) | 31.2(12) | 27.2(12) | -4.1(9) | 7.4(9) | -9.0(9) |
| C1A | 61(4) | 46(4) | 44(3) | 24(4) | 12(3) | -6(3) |
| C1b | 55(3) | 68(5) | 42(3) | 26(3) | 4(3) | -13(3) |
| C2A | 109(8) | 49(4) | 51(5) | -18(4) | 48(5) | -21(3) |
| C2b | 60(4) | 52(3) | 24(3) | 4(3) | 6(2) | -7(2) |
| C3A | 54(4) | 90(8) | 39(5) | 19(5) | -9(3) | -42(5) |
| C3b | 64(5) | 60(5) | 68(6) | -22(4) | 31(4) | -41(4) |

**Crystallographic Table 3** Bond Lengths for **$H_2[L^I]$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| C1 | O1 | 1.351(2) | C23 | C24 | 1.424(3) |
| C1 | C2 | 1.410(3) | C25 | C26 | 1.425(3) |
| C1 | C14 | 1.413(3) | C26 | C27 | 1.361(3) |
| N1 | C15 | 1.289(2) | C28 | C29 | 1.454(3) |
| N1 | C16 | 1.413(2) | C29 | C30 | 1.402(3) |
| C2 | C3 | 1.543(3) | C29 | C42 | 1.403(3) |
| C2 | C7 | 1.389(3) | C30 | C31 | 1.378(3) |
| N2 | C27 | 1.417(2) | C31 | C32 | 1.533(3) |
| N2 | C28 | 1.282(2) | C31 | C36 | 1.406(3) |
| O2 | C42 | 1.353(2) | C32 | C33 | 1.524(3) |
| C3 | C4 | 1.540(3) | C32 | C34 | 1.538(3) |
| C3 | C5 | 1.535(3) | C32 | C35 | 1.537(3) |
| C3 | C6 | 1.528(3) | C36 | C37 | 1.386(3) |
| N3 | C18 | 1.349(2) | C37 | C38 | 1.535(3) |
| N3 | C19 | 1.350(2) | C37 | C42 | 1.419(3) |
| N4 | C24 | 1.352(2) | C38 | C39 | 1.541(3) |
| N4 | C25 | 1.346(2) | C38 | C40 | 1.535(3) |
| C7 | C8 | 1.408(3) | C38 | C41 | 1.530(3) |
| C8 | C13 | 1.382(3) | C43S | C44S | 1.277(8) |
| C8 | C9 | 1.535(3) | C43S | C45S | 1.570(8) |
| C13 | C14 | 1.402(3) | C44S | C45S | 1.641(10) |
| C14 | C15 | 1.448(3) | C44S | O3S1 | 1.642(6) |
| C16 | C17 | 1.367(3) | C45S | O46S | 1.202(7) |
| C16 | C27 | 1.443(3) | C45S | O3S1 | 1.253(9) |
| C17 | C18 | 1.423(3) | C9 | C1A | 1.617(6) |
| C18 | C25 | 1.431(3) | C9 | C1b | 1.481(5) |
| C19 | C20 | 1.428(3) | C9 | C2A | 1.489(6) |
| C19 | C24 | 1.428(3) | C9 | C2b | 1.601(5) |
| C20 | C21 | 1.361(3) | C9 | C3A | 1.501(10) |
| C21 | C22 | 1.412(3) | C9 | C3b | 1.505(8) |
| C22 | C23 | 1.360(3) | | | |

[1]2-X,1-Y,1-Z

**Crystallographic Table 4** Bond Angles for **$H_2[L^I]$**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C2 | C1 | O1 | 119.05(16) | C29 | C28 | N2 | 122.78(18) |
| C14 | C1 | O1 | 120.42(17) | C30 | C29 | C28 | 118.37(18) |
| C14 | C1 | C2 | 120.53(17) | C42 | C29 | C28 | 121.47(17) |
| C16 | N1 | C15 | 122.43(16) | C42 | C29 | C30 | 120.16(17) |
| C3 | C2 | C1 | 121.04(16) | C31 | C30 | C29 | 121.60(19) |
| C7 | C2 | C1 | 116.66(16) | C32 | C31 | C30 | 123.63(19) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C7 | C2 | C3 | 122.31(16) | C36 | C31 | C30 | 116.47(18) |
| C28 | N2 | C27 | 119.16(16) | C36 | C31 | C32 | 119.88(17) |
| C4 | C3 | C2 | 110.19(15) | C33 | C32 | C31 | 111.82(17) |
| C5 | C3 | C2 | 110.05(15) | C34 | C32 | C31 | 110.01(17) |
| C5 | C3 | C4 | 110.04(16) | C34 | C32 | C33 | 107.76(18) |
| C6 | C3 | C2 | 111.74(16) | C35 | C32 | C31 | 108.84(17) |
| C6 | C3 | C4 | 107.37(16) | C35 | C32 | C33 | 109.3(2) |
| C6 | C3 | C5 | 107.38(16) | C35 | C32 | C34 | 109.08(19) |
| C19 | N3 | C18 | 116.06(16) | C37 | C36 | C31 | 125.15(18) |
| C25 | N4 | C24 | 116.14(17) | C38 | C37 | C36 | 122.42(17) |
| C8 | C7 | C2 | 124.93(18) | C42 | C37 | C36 | 116.44(18) |
| C13 | C8 | C7 | 116.39(17) | C42 | C37 | C38 | 121.12(17) |
| C9 | C8 | C7 | 121.53(17) | C39 | C38 | C37 | 110.22(16) |
| C9 | C8 | C13 | 122.07(17) | C40 | C38 | C37 | 112.04(16) |
| C14 | C13 | C8 | 122.00(17) | C40 | C38 | C39 | 107.82(17) |
| C13 | C14 | C1 | 119.47(17) | C41 | C38 | C37 | 109.63(16) |
| C15 | C14 | C1 | 121.42(17) | C41 | C38 | C39 | 110.13(17) |
| C15 | C14 | C13 | 119.10(17) | C41 | C38 | C40 | 106.93(17) |
| C14 | C15 | N1 | 122.11(17) | C29 | C42 | O2 | 120.83(16) |
| C17 | C16 | N1 | 124.98(17) | C37 | C42 | O2 | 119.01(17) |
| C27 | C16 | N1 | 115.55(16) | C37 | C42 | C29 | 120.16(17) |
| C27 | C16 | C17 | 119.44(17) | C45S | C43S | C44S | 69.5(5) |
| C18 | C17 | C16 | 121.04(18) | C45S | C44S | C43S | 63.7(5) |
| C17 | C18 | N3 | 118.88(17) | O3S1 | C44S | C43S | 108.5(5) |
| C25 | C18 | N3 | 121.84(17) | O3S1 | C44S | C45S | 44.9(3) |
| C25 | C18 | C17 | 119.27(17) | C44S | C45S | C43S | 46.8(3) |
| C20 | C19 | N3 | 119.08(18) | O46S | C45S | C43S | 118.2(7) |
| C24 | C19 | N3 | 122.05(17) | O46S | C45S | C44S | 164.6(8) |
| C24 | C19 | C20 | 118.87(18) | O3S1 | C45S | C43S | 114.4(6) |
| C21 | C20 | C19 | 120.1(2) | O3S1 | C45S | C44S | 67.6(5) |
| C22 | C21 | C20 | 120.94(19) | O3S1 | C45S | O46S | 127.5(7) |
| C23 | C22 | C21 | 120.9(2) | C44S | O3S | C44S1 | 180 |
| C24 | C23 | C22 | 120.1(2) | C45S | O3S | C44S | 67.5(4) |
| C19 | C24 | N4 | 121.85(17) | C45S | O3S | C44S1 | 112.5(4) |
| C23 | C24 | N4 | 119.04(19) | C45S1 | O3S | C44S | 112.5(4) |
| C23 | C24 | C19 | 119.11(18) | C45S1 | O3S | C44S1 | 67.5(4) |
| C18 | C25 | N4 | 122.05(17) | C45S1 | O3S | C45S | 180 |
| C26 | C25 | N4 | 119.28(17) | C2A | C9 | C1A | 105.2(4) |
| C26 | C25 | C18 | 118.66(17) | C2b | C9 | C1b | 107.5(3) |
| C27 | C26 | C25 | 120.82(18) | C3A | C9 | C1A | 105.5(4) |
| C16 | C27 | N2 | 117.33(16) | C3A | C9 | C2A | 113.6(5) |
| C26 | C27 | N2 | 121.87(17) | C3b | C9 | C1b | 112.1(4) |
| C26 | C27 | C16 | 120.73(17) | C3b | C9 | C2b | 104.8(4) |

[1]2-X,1-Y,1-Z

**Crystallographic Table 5** Hydrogen Atom Coordinates ($Å^2×10^4$) and Isotropic Displacement Parameters ($Å^2×10^3$)for **$H_2[L^I]$**.

| Atom | x | y | z | U(eq) |
|---|---|---|---|---|
| H1 | 4640(30) | 6885(5) | 2397(5) | 49.7(5) |
| H2 | 3190(30) | 7423(3) | 3173(5) | 53.6(6) |
| H4a | 6413(14) | 8192(4) | 1432.5(12) | 54.7(8) |
| H4b | 5989(11) | 8032(3) | 1985(4) | 54.7(8) |
| H4c | 7739(5) | 8516.3(15) | 1878(4) | 54.7(8) |
| H5a | 8936(5) | 7486(5) | 2517.6(11) | 48.4(8) |
| H5b | 11131(13) | 7327(4) | 2284.7(12) | 48.4(8) |
| H5c | 10568(17) | 7993.5(15) | 2394(2) | 48.4(8) |
| H6a | 11658(12) | 7580(3) | 1434(4) | 63.0(9) |
| H6b | 9821(6) | 7911(6) | 1097.6(13) | 63.0(9) |
| H6c | 11096(17) | 8247(3) | 1544(3) | 63.0(9) |
| H7 | 9548(3) | 6940.4(8) | 1032.1(7) | 28.9(5) |
| H13 | 5315(3) | 5646.6(8) | 1192.0(7) | 30.6(6) |
| H15 | 2962(3) | 5658.4(8) | 1845.8(7) | 30.0(5) |
| H17 | -281(3) | 5505.4(8) | 2032.5(7) | 30.0(5) |
| H20 | -6461(3) | 4275.6(9) | 2140.8(8) | 40.0(6) |
| H21 | -9216(3) | 3952.5(9) | 2582.3(8) | 45.1(7) |
| H22 | -9569(3) | 4293.6(9) | 3380.7(9) | 46.2(7) |
| H23 | -7176(3) | 4962.3(9) | 3740.3(8) | 42.4(6) |
| H26 | -948(3) | 6180.3(8) | 3637.7(7) | 33.5(6) |
| H28 | 3133(3) | 6205.1(9) | 3834.0(7) | 33.2(6) |
| H30 | 5844(3) | 6448.3(9) | 4470.5(7) | 36.2(6) |
| H33a | 6600(8) | 6514(3) | 5331(5) | 76.5(10) |
| H33b | 8310(20) | 6154.0(15) | 5047(3) | 76.5(10) |
| H33c | 8971(17) | 6407(4) | 5583(3) | 76.5(10) |
| H34a | 9280(20) | 7897.6(18) | 5298(2) | 70.4(9) |
| H34b | 7227(5) | 7586(4) | 5497(4) | 70.4(9) |
| H34c | 9589(19) | 7427(3) | 5730(2) | 70.4(9) |
| H35a | 11349(6) | 6647(5) | 4704(5) | 85.0(11) |
| H35b | 11707(9) | 7335(3) | 4777(6) | 85.0(11) |
| H35c | 12132(5) | 6901(7) | 5233.1(12) | 85.0(11) |
| H36 | 8771(3) | 8010.3(9) | 4511.2(7) | 36.4(6) |
| H39a | 3723(7) | 8682(3) | 3485(4) | 63.9(9) |
| H39b | 4406(12) | 8963(5) | 4009.8(9) | 63.9(9) |
| H39c | 5073(7) | 9277(3) | 3522(5) | 63.9(9) |
| H40a | 8193(11) | 8965(6) | 4343.8(19) | 65.6(9) |
| H40b | 10026(7) | 8682(3) | 4043(5) | 65.6(9) |
| H40c | 8878(17) | 9276(3) | 3857(3) | 65.6(9) |
| H41a | 9148(11) | 8281(5) | 3224.1(9) | 60.1(8) |
| H41b | 6714(11) | 8245(5) | 2991.9(17) | 60.1(8) |
| H41c | 7900(20) | 8864.3(10) | 3050(2) | 60.1(8) |
| H1Aa | 10910(40) | 5474(3) | 1015(10) | 75(3) |
| H1Ab | 8710(20) | 5109(8) | 977(11) | 75(3) |

| | | | | |
|---|---|---|---|---|
| H1Ac | 10160(50) | 5132(9) | 521(2) | 75(3) |
| H1ba | 11517(13) | 6079(4) | 802(12) | 83(3) |
| H1bb | 10696(12) | 5456(12) | 975(8) | 83(3) |
| H1bc | 11160(20) | 5556(14) | 416(4) | 83(3) |
| H2Aa | 9320(30) | 6643(8) | 222(14) | 101(5) |
| H2Ab | 11250(30) | 6335(16) | 544(6) | 101(5) |
| H2Ac | 10320(60) | 6047(9) | 37(9) | 101(5) |
| H2ba | 6865(12) | 6505(10) | 54(7) | 68(3) |
| H2bb | 9220(40) | 6722(6) | 246(4) | 68(3) |
| H2bc | 8940(40) | 6194(4) | -136(4) | 68(3) |
| H3Aa | 5670(40) | 5430(14) | 448(5) | 93(5) |
| H3Ab | 5600(40) | 6027(5) | 144(13) | 93(5) |
| H3Ac | 7051(16) | 5495(16) | -16(8) | 93(5) |
| H3ba | 7060(50) | 5109(7) | 635(7) | 94(4) |
| H3bb | 5460(17) | 5567(5) | 355(13) | 94(4) |
| H3bc | 7410(40) | 5298(11) | 85(8) | 94(4) |

**Crystallographic Table 6** Atomic Occupancy for **$H_2[L^I]$**

| Atom | Occupancy | Atom | Occupancy | Atom | Occupancy |
|---|---|---|---|---|---|
| C44S | 0.5 | C45S | 0.5 | O46S | 0.5 |
| C1A | 0.463(9) | H1Aa | 0.463(9) | H1Ab | 0.463(9) |
| H1Ac | 0.463(9) | C1b | 0.537(9) | H1ba | 0.537(9) |
| H1bb | 0.537(9) | H1bc | 0.537(9) | C2A | 0.463(9) |
| H2Aa | 0.463(9) | H2Ab | 0.463(9) | H2Ac | 0.463(9) |
| C2b | 0.537(9) | H2ba | 0.537(9) | H2bb | 0.537(9) |
| H2bc | 0.537(9) | C3A | 0.463(9) | H3Aa | 0.463(9) |
| H3Ab | 0.463(9) | H3Ac | 0.463(9) | C3b | 0.537(9) |
| H3ba | 0.537(9) | H3bb | 0.537(9) | H3bc | 0.537(9) |

## $UO_2[L^I]$

**Crystallographic Table 7** Crystal data and structure refinement for **$UO_2[L^I]$**

| | |
|---|---|
| Empirical formula | $C_{42}H_{45}N_4O_7U$ |
| Formula weight | 955.85 |
| Temperature/K | 296(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 18.0541(18) |
| b/Å | 13.4873(13) |
| c/Å | 20.820(2) |
| α/° | 90.00 |
| β/° | 97.380(3) |
| γ/° | 90.00 |
| Volume/Å$^3$ | 5027.6(9) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.263 |
| m/mm$^{-1}$ | 3.271 |
| F(000) | 1892.0 |
| Crystal size/mm$^3$ | ? × ? × ? |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection | 2.82 to 49.1° |
| Index ranges | $-20 \le h \le 19$, $-15 \le k \le 15$, $-24 \le l \le 24$ |
| Reflections collected | 39876 |
| Independent reflections | 8274 [$R_{int}$ = 0.0770, $R_{sigma}$ = 0.0612] |
| Data/restraints/parameters | 8274/0/499 |
| Goodness-of-fit on $F^2$ | 1.134 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0610, $wR_2$ = 0.1816 |
| Final R indexes [all data] | $R_1$ = 0.0809, $wR_2$ = 0.1931 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.74/-1.86 |

**Crystallographic Table 8** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for **$UO_2[L^I]$**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| U1 | 1462.3(2) | 1585.6(3) | 1714.81(19) | 31.01(16) |
| O1S | 2118(7) | 8436(8) | 2287(9) | 121(6) |
| N1 | 352(4) | 2570(6) | 1150(4) | 28.6(18) |
| O2S | 2773(13) | 6646(17) | 1255(11) | 213(12) |

| | | | | |
|---|---|---|---|---|
| N4 | 1786(5) | 3053(6) | 1035(4) | 32.4(19) |
| O3 | 2713(4) | 1702(5) | 1702(4) | 42.9(19) |
| O4 | 1509(4) | 2443(6) | 2379(4) | 46.0(19) |
| O5 | 1414(5) | 780(6) | 1044(4) | 44.9(19) |
| C100 | -637(6) | 1324(7) | 1170(5) | 33(2) |
| N2 | -397(5) | 5993(6) | 716(4) | 36(2) |
| N3 | 1134(5) | 6502(6) | 767(4) | 37(2) |
| O11 | 1925(5) | 366(7) | 2543(4) | 62(3) |
| O10 | 385(4) | 955(5) | 1960(3) | 39.1(18) |
| C2 | -301(6) | 763(7) | 1695(5) | 33(2) |
| C3 | -310(5) | 2230(7) | 967(5) | 31(2) |
| C4 | 492(6) | 3579(7) | 992(5) | 33(2) |
| C5 | -47(5) | 4295(7) | 912(5) | 34(2) |
| C6 | 153(5) | 5303(7) | 802(5) | 31(2) |
| C7 | -184(6) | 6928(8) | 652(5) | 35(2) |
| C8 | -730(7) | 7689(9) | 547(6) | 48(3) |
| C9 | -512(8) | 8643(8) | 498(6) | 49(3) |
| C10 | 245(7) | 8907(8) | 560(6) | 44(3) |
| C11 | 774(7) | 8216(8) | 670(6) | 44(3) |
| C12 | 585(6) | 7197(7) | 702(5) | 34(2) |
| C13 | 914(6) | 5551(7) | 803(5) | 31(2) |
| C14 | 1447(6) | 4784(7) | 876(5) | 33(2) |
| C15 | 1260(6) | 3831(7) | 952(5) | 32(2) |
| C16 | 2361(6) | 3154(8) | 743(6) | 38(3) |
| C17 | 3042(6) | 2598(8) | 819(5) | 35(2) |
| C18 | 3203(6) | 1893(8) | 1301(5) | 33(2) |
| C19 | 3922(6) | 1412(8) | 1378(5) | 36(2) |
| C20 | 4398(6) | 1676(8) | 949(6) | 43(3) |
| C21 | 4257(6) | 2389(9) | 455(6) | 43(3) |
| C22 | 3572(6) | 2841(8) | 405(6) | 42(3) |
| C23 | 4838(7) | 2612(10) | -1(7) | 58(3) |
| C24 | 5002(11) | 1665(14) | -345(10) | 105(7) |
| C25 | 5578(9) | 2930(17) | 408(9) | 102(6) |
| C26 | 4590(12) | 3392(19) | -469(12) | 169(15) |
| C27 | 4114(6) | 587(9) | 1879(6) | 44(3) |
| C28 | 3595(9) | -315(9) | 1705(7) | 67(4) |
| C29 | 4919(8) | 218(12) | 1898(8) | 78(5) |
| C30 | 4021(8) | 924(11) | 2566(6) | 64(4) |

| | | | | |
|---|---|---|---|---|
| C31 | -1371(6) | 1141(8) | 884(5) | 36(2) |
| C32 | -1785(6) | 383(8) | 1102(6) | 41(3) |
| C33 | -1443(6) | -160(8) | 1637(6) | 42(3) |
| C34 | -725(6) | -20(8) | 1938(5) | 36(2) |
| C35 | -400(7) | -663(9) | 2515(6) | 53(3) |
| C36 | -183(10) | 5(13) | 3106(7) | 86(5) |
| C37 | -971(10) | -1431(12) | 2685(8) | 87(5) |
| C38 | 304(8) | -1195(11) | 2355(7) | 71(4) |
| C39 | -2578(7) | 142(10) | 788(7) | 56(3) |
| C40 | -2798(9) | 716(17) | 171(9) | 113(7) |
| C41 | -3127(8) | 419(18) | 1247(10) | 112(7) |
| C42 | -2643(10) | -953(13) | 633(13) | 142(10) |

**Crystallographic Table 9** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **$UO_2[L^I]$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{23}$** | **$U_{13}$** | **$U_{12}$** |
|---|---|---|---|---|---|---|
| U1 | 28.9(2) | 28.1(2) | 35.1(3) | 3.44(17) | 0.21(16) | 0.47(17) |
| O1S | 62(7) | 82(9) | 216(17) | 55(9) | 13(9) | 17(6) |
| N1 | 25(4) | 23(4) | 38(5) | 6(4) | 4(4) | 1(3) |
| O2S | 180(20) | 260(30) | 180(20) | -111(18) | -56(16) | 13(16) |
| N4 | 28(5) | 25(4) | 44(5) | 5(4) | 3(4) | 2(4) |
| O3 | 37(4) | 39(4) | 54(5) | 16(4) | 10(4) | 14(3) |
| O4 | 41(4) | 43(5) | 53(5) | -11(4) | 5(4) | -2(4) |
| O5 | 57(5) | 42(5) | 36(4) | -1(3) | 4(4) | 3(4) |
| C100 | 31(6) | 29(5) | 39(6) | 1(4) | 5(5) | 2(4) |
| N2 | 26(4) | 28(5) | 52(6) | 1(4) | -3(4) | 3(4) |
| N3 | 45(5) | 27(5) | 39(5) | 4(4) | 7(4) | 0(4) |
| O11 | 48(5) | 69(6) | 67(6) | 37(5) | 2(4) | 9(4) |
| O10 | 33(4) | 42(4) | 41(4) | 16(3) | -1(3) | -4(3) |
| C2 | 36(6) | 32(6) | 32(6) | -2(4) | 4(5) | -5(5) |
| C3 | 30(6) | 29(5) | 32(6) | 2(4) | 1(4) | -3(4) |
| C4 | 32(6) | 20(5) | 47(7) | 6(4) | 3(5) | 5(4) |
| C5 | 16(5) | 31(6) | 54(7) | 4(5) | 1(4) | 3(4) |
| C6 | 30(5) | 32(5) | 31(6) | 5(4) | 0(4) | 2(4) |
| C7 | 43(6) | 28(5) | 33(6) | -4(4) | -1(5) | 9(5) |
| C8 | 38(6) | 44(7) | 60(8) | 2(6) | -3(6) | 8(5) |
| C9 | 66(9) | 25(6) | 57(8) | -2(5) | 11(6) | 19(5) |
| C10 | 54(8) | 26(6) | 53(7) | 0(5) | 11(6) | 3(5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C11 | 60(8) | 27(6) | 44(7) | 2(5) | 8(6) | -2(5) |
| C12 | 44(6) | 28(6) | 30(6) | 1(4) | 0(5) | 4(5) |
| C13 | 34(6) | 33(6) | 25(5) | 7(4) | 0(4) | -1(4) |
| C14 | 35(6) | 26(5) | 38(6) | -4(5) | 4(5) | 2(4) |
| C15 | 29(5) | 24(5) | 43(6) | 1(4) | -3(5) | 7(4) |
| C16 | 42(6) | 29(6) | 42(6) | 1(5) | 8(5) | 3(5) |
| C17 | 32(6) | 33(6) | 42(6) | 6(5) | 11(5) | 2(5) |
| C18 | 34(6) | 35(6) | 34(6) | 1(5) | 11(5) | 2(4) |
| C19 | 29(5) | 37(6) | 43(6) | 0(5) | 5(5) | 0(4) |
| C20 | 36(6) | 46(7) | 47(7) | 1(5) | 7(5) | 11(5) |
| C21 | 37(6) | 48(7) | 46(7) | 2(5) | 13(5) | 5(5) |
| C22 | 40(6) | 38(6) | 48(7) | 7(5) | 11(5) | 3(5) |
| C23 | 51(8) | 66(9) | 59(8) | 7(7) | 20(6) | 4(7) |
| C24 | 96(14) | 138(18) | 95(14) | -34(12) | 59(12) | -14(12) |
| C25 | 75(11) | 152(17) | 87(13) | -12(12) | 42(10) | -47(12) |
| C26 | 118(17) | 220(30) | 190(20) | 160(20) | 117(18) | 95(18) |
| C27 | 35(6) | 48(7) | 49(7) | 10(6) | 8(5) | 10(5) |
| C28 | 94(11) | 43(8) | 64(9) | 10(7) | 10(8) | 8(7) |
| C29 | 55(9) | 90(11) | 91(11) | 38(9) | 18(8) | 39(8) |
| C30 | 79(10) | 75(10) | 34(7) | 9(7) | -1(6) | 20(8) |
| C31 | 35(6) | 33(6) | 38(6) | -5(5) | 2(5) | -1(5) |
| C32 | 29(6) | 43(6) | 51(7) | -14(5) | 3(5) | -4(5) |
| C33 | 36(6) | 41(6) | 51(7) | 1(5) | 12(5) | -14(5) |
| C34 | 40(6) | 36(6) | 34(6) | 2(5) | 6(5) | 0(5) |
| C35 | 64(8) | 49(7) | 44(7) | 13(6) | 2(6) | -13(6) |
| C36 | 109(14) | 99(13) | 46(9) | 6(8) | -5(8) | -11(10) |
| C37 | 91(12) | 93(12) | 76(11) | 34(9) | 5(9) | -35(10) |
| C38 | 76(10) | 65(9) | 70(10) | 31(8) | 6(8) | 18(8) |
| C39 | 35(7) | 62(8) | 71(9) | -2(7) | 2(6) | -5(6) |
| C40 | 57(10) | 170(20) | 99(14) | 29(14) | -25(10) | -24(12) |
| C41 | 40(9) | 180(20) | 118(16) | -3(15) | 18(9) | -7(11) |
| C42 | 59(11) | 74(13) | 270(30) | -53(16) | -44(14) | -18(9) |

**Crystallographic Table 10** Bond Lengths for **$UO_2[L^I]$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| U1 | N1 | 2.561(8) | C11 | C12 | 1.419(14) |
| U1 | N4 | 2.546(8) | C13 | C14 | 1.407(14) |
| U1 | O3 | 2.268(7) | C14 | C15 | 1.345(14) |

| | | | | | |
|---|---|---|---|---|---|
| U1 | O4 | 1.796(8) | C16 | C17 | 1.431(14) |
| U1 | O5 | 1.763(7) | C17 | C18 | 1.385(14) |
| U1 | O11 | 2.451(8) | C17 | C22 | 1.407(14) |
| U1 | O10 | 2.241(7) | C18 | C19 | 1.442(15) |
| N1 | C3 | 1.291(12) | C19 | C20 | 1.364(15) |
| N1 | C4 | 1.430(12) | C19 | C27 | 1.533(15) |
| N4 | C15 | 1.410(13) | C20 | C21 | 1.407(16) |
| N4 | C16 | 1.276(13) | C21 | C22 | 1.370(15) |
| O3 | C18 | 1.317(12) | C21 | C23 | 1.534(16) |
| C100 | C2 | 1.402(14) | C23 | C24 | 1.51(2) |
| C100 | C3 | 1.444(14) | C23 | C25 | 1.55(2) |
| C100 | C31 | 1.404(14) | C23 | C26 | 1.46(2) |
| N2 | C6 | 1.356(13) | C27 | C28 | 1.550(18) |
| N2 | C7 | 1.330(14) | C27 | C29 | 1.532(16) |
| N3 | C12 | 1.358(13) | C27 | C30 | 1.530(17) |
| N3 | C13 | 1.347(13) | C31 | C32 | 1.377(15) |
| O10 | C2 | 1.316(12) | C32 | C33 | 1.409(16) |
| C2 | C34 | 1.434(14) | C32 | C39 | 1.529(15) |
| C4 | C5 | 1.365(13) | C33 | C34 | 1.378(15) |
| C4 | C15 | 1.440(14) | C34 | C35 | 1.535(15) |
| C5 | C6 | 1.433(14) | C35 | C36 | 1.534(19) |
| C6 | C13 | 1.415(14) | C35 | C37 | 1.535(18) |
| C7 | C8 | 1.421(15) | C35 | C38 | 1.533(19) |
| C7 | C12 | 1.426(15) | C39 | C40 | 1.51(2) |
| C8 | C9 | 1.353(16) | C39 | C41 | 1.51(2) |
| C9 | C10 | 1.403(17) | C39 | C42 | 1.51(2) |
| C10 | C11 | 1.333(16) | | | |

**Crystallographic Table 11** Bond Angles for **$UO_2[L^I]$**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| N4 | U1 | N1 | 64.1(3) | N3 | C13 | C6 | 121.2(9) |
| O3 | U1 | N1 | 132.9(2) | N3 | C13 | C14 | 120.2(9) |
| O3 | U1 | N4 | 68.8(3) | C14 | C13 | C6 | 118.5(9) |
| O3 | U1 | O11 | 78.8(3) | C15 | C14 | C13 | 122.5(10) |
| O4 | U1 | N1 | 88.6(3) | N4 | C15 | C4 | 117.2(9) |
| O4 | U1 | N4 | 86.3(3) | C14 | C15 | N4 | 123.4(9) |
| O4 | U1 | O3 | 90.9(3) | C14 | C15 | C4 | 119.4(9) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O4 | U1 | O11 | 85.0(4) | N4 | C16 | C17 | 129.1(10) |
| O4 | U1 | O10 | 91.4(3) | C18 | C17 | C16 | 122.6(9) |
| O5 | U1 | N1 | 89.9(3) | C18 | C17 | C22 | 120.5(10) |
| O5 | U1 | N4 | 91.7(3) | C22 | C17 | C16 | 116.9(10) |
| O5 | U1 | O3 | 88.9(3) | O3 | C18 | C17 | 119.8(9) |
| O5 | U1 | O4 | 177.9(4) | O3 | C18 | C19 | 120.6(9) |
| O5 | U1 | O11 | 97.0(3) | C17 | C18 | C19 | 119.5(9) |
| O5 | U1 | O10 | 89.5(3) | C18 | C19 | C27 | 121.6(9) |
| O11 | U1 | N1 | 147.9(3) | C20 | C19 | C18 | 116.3(10) |
| O11 | U1 | N4 | 146.3(3) | C20 | C19 | C27 | 121.9(10) |
| O10 | U1 | N1 | 69.5(2) | C19 | C20 | C21 | 126.0(10) |
| O10 | U1 | N4 | 133.6(3) | C20 | C21 | C23 | 120.9(10) |
| O10 | U1 | O3 | 157.5(2) | C22 | C21 | C20 | 115.9(10) |
| O10 | U1 | O11 | 79.2(3) | C22 | C21 | C23 | 123.2(11) |
| C3 | N1 | U1 | 126.2(6) | C21 | C22 | C17 | 121.8(10) |
| C3 | N1 | C4 | 117.0(8) | C21 | C23 | C24 | 108.6(12) |
| C4 | N1 | U1 | 116.6(6) | C21 | C23 | C25 | 108.9(11) |
| C15 | N4 | U1 | 116.5(6) | C24 | C23 | C25 | 106.7(14) |
| C16 | N4 | U1 | 127.4(7) | C26 | C23 | C21 | 112.2(11) |
| C16 | N4 | C15 | 116.1(9) | C26 | C23 | C24 | 110.7(17) |
| C18 | O3 | U1 | 140.5(7) | C26 | C23 | C25 | 109.6(17) |
| C2 | C100 | C3 | 122.2(9) | C19 | C27 | C28 | 109.4(10) |
| C31 | C100 | C2 | 121.7(10) | C29 | C27 | C19 | 112.6(10) |
| C31 | C100 | C3 | 115.1(9) | C29 | C27 | C28 | 107.1(11) |
| C7 | N2 | C6 | 116.6(9) | C29 | C27 | C30 | 106.9(11) |
| C13 | N3 | C12 | 116.5(9) | C30 | C27 | C19 | 112.2(10) |
| C2 | O10 | U1 | 141.0(6) | C30 | C27 | C28 | 108.5(11) |
| C100 | C2 | C34 | 118.4(9) | C32 | C31 | C100 | 120.9(10) |
| O10 | C2 | C100 | 120.6(9) | C31 | C32 | C33 | 116.4(10) |
| O10 | C2 | C34 | 120.9(9) | C31 | C32 | C39 | 122.3(11) |
| N1 | C3 | C100 | 127.8(9) | C33 | C32 | C39 | 121.2(10) |
| N1 | C4 | C15 | 115.9(8) | C34 | C33 | C32 | 125.4(10) |
| C5 | C4 | N1 | 123.8(9) | C2 | C34 | C35 | 121.6(10) |
| C5 | C4 | C15 | 120.3(9) | C33 | C34 | C2 | 117.0(10) |
| C4 | C5 | C6 | 120.0(9) | C33 | C34 | C35 | 121.4(10) |
| N2 | C6 | C5 | 118.5(9) | C34 | C35 | C36 | 109.2(11) |
| N2 | C6 | C13 | 122.2(9) | C34 | C35 | C38 | 109.8(10) |
| C13 | C6 | C5 | 119.3(9) | C36 | C35 | C38 | 108.4(12) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N2 | C7 | C8 | 119.7(10) | C37 | C35 | C34 | 111.2(11) |
| N2 | C7 | C12 | 121.8(9) | C37 | C35 | C36 | 108.7(12) |
| C12 | C7 | C8 | 118.5(10) | C37 | C35 | C38 | 109.5(12) |
| C9 | C8 | C7 | 119.7(11) | C40 | C39 | C32 | 112.6(11) |
| C8 | C9 | C10 | 121.6(11) | C41 | C39 | C32 | 109.4(12) |
| C11 | C10 | C9 | 120.4(11) | C41 | C39 | C40 | 106.8(14) |
| C10 | C11 | C12 | 120.9(12) | C42 | C39 | C32 | 109.9(11) |
| N3 | C12 | C7 | 121.5(9) | C42 | C39 | C40 | 108.3(16) |
| N3 | C12 | C11 | 119.7(10) | C42 | C39 | C41 | 109.8(15) |
| C11 | C12 | C7 | 118.8(10) | | | | |

**Crystallographic Table 12** Torsion Angles for **$UO_2[L^I]$**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| U1 | N1 | C3 | C100 | 17.0(15) | C3 | C100 | C31 | C32 | -170.6(10) |
| U1 | N1 | C4 | C5 | -155.6(9) | C4 | N1 | C3 | C100 | -166.7(10) |
| U1 | N1 | C4 | C15 | 21.1(12) | C4 | C5 | C6 | N2 | 179.1(10) |
| U1 | N4 | C15 | C4 | -26.8(12) | C4 | C5 | C6 | C13 | -2.4(16) |
| U1 | N4 | C15 | C14 | 149.4(9) | C5 | C4 | C15 | N4 | -179.5(10) |
| U1 | N4 | C16 | C17 | -14.4(17) | C5 | C4 | C15 | C14 | 4.1(17) |
| U1 | O3 | C18 | C17 | 36.3(16) | C5 | C6 | C13 | N3 | -173.3(10) |
| U1 | O3 | C18 | C19 | -146.9(8) | C5 | C6 | C13 | C14 | 3.5(15) |
| U1 | O10 | C2 | C100 | -27.9(16) | C6 | N2 | C7 | C8 | 178.8(10) |
| U1 | O10 | C2 | C34 | 152.4(8) | C6 | N2 | C7 | C12 | -2.8(15) |
| N1 | U1 | N4 | C15 | 26.3(7) | C6 | C13 | C14 | C15 | -0.8(15) |
| N1 | U1 | N4 | C16 | -151.4(10) | C7 | N2 | C6 | C5 | 176.4(10) |
| N1 | U1 | O3 | C18 | -37.8(12) | C7 | N2 | C6 | C13 | -2.2(15) |
| N1 | U1 | O10 | C2 | 39.1(10) | C7 | C8 | C9 | C10 | -1.2(19) |
| N1 | C4 | C5 | C6 | 175.2(10) | C8 | C7 | C12 | N3 | -176.4(10) |
| N1 | C4 | C15 | N4 | 3.6(14) | C8 | C7 | C12 | C11 | 2.3(15) |
| N1 | C4 | C15 | C14 | -172.8(10) | C8 | C9 | C10 | C11 | 0.0(19) |
| N4 | U1 | N1 | C3 | 151.9(9) | C9 | C10 | C11 | C12 | 2.4(18) |
| N4 | U1 | N1 | C4 | -24.4(7) | C10 | C11 | C12 | N3 | 175.2(11) |
| N4 | U1 | O3 | C18 | -41.0(10) | C10 | C11 | C12 | C7 | -3.6(17) |
| N4 | U1 | O10 | C2 | 40.7(12) | C12 | N3 | C13 | C6 | -2.8(14) |
| N4 | C16 | C17 | C18 | -7.1(19) | C12 | N3 | C13 | C14 | -179.5(9) |
| N4 | C16 | C17 | C22 | 176.8(11) | C12 | C7 | C8 | C9 | 0.0(17) |
| O3 | U1 | N1 | C3 | 148.5(8) | C13 | N3 | C12 | C7 | -2.1(15) |
| O3 | U1 | N1 | C4 | -27.8(8) | C13 | N3 | C12 | C11 | 179.2(10) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| O3 | U1 | N4 | C15 | -156.4(8) | C13 | C14 | C15 | N4 | -179.1(10) |
| O3 | U1 | N4 | C16 | 25.9(9) | C13 | C14 | C15 | C4 | -3.0(16) |
| O3 | U1 | O10 | C2 | -137.0(10) | C15 | N4 | C16 | C17 | 167.8(11) |
| O3 | C18 | C19 | C20 | -178.4(10) | C15 | C4 | C5 | C6 | -1.4(17) |
| O3 | C18 | C19 | C27 | 6.5(16) | C16 | N4 | C15 | C4 | 151.2(10) |
| O4 | U1 | N1 | C3 | -121.5(8) | C16 | N4 | C15 | C14 | -32.6(15) |
| O4 | U1 | N1 | C4 | 62.2(7) | C16 | C17 | C18 | O3 | 1.2(17) |
| O4 | U1 | N4 | C15 | -63.9(7) | C16 | C17 | C18 | C19 | -175.6(10) |
| O4 | U1 | N4 | C16 | 118.3(9) | C16 | C17 | C22 | C21 | 177.0(11) |
| O4 | U1 | O3 | C18 | -126.7(10) | C17 | C18 | C19 | C20 | -1.6(16) |
| O4 | U1 | O10 | C2 | 127.0(11) | C17 | C18 | C19 | C27 | -176.7(10) |
| O5 | U1 | N1 | C3 | 60.0(9) | C18 | C17 | C22 | C21 | 0.7(18) |
| O5 | U1 | N1 | C4 | -116.3(7) | C18 | C19 | C20 | C21 | 1.8(18) |
| O5 | U1 | N4 | C15 | 115.4(7) | C18 | C19 | C27 | C28 | 63.7(14) |
| O5 | U1 | N4 | C16 | -62.3(9) | C18 | C19 | C27 | C29 | -177.4(12) |
| O5 | U1 | O3 | C18 | 51.2(10) | C18 | C19 | C27 | C30 | -56.7(14) |
| O5 | U1 | O10 | C2 | -51.1(11) | C19 | C20 | C21 | C22 | -0.7(18) |
| C100 | C2 | C34 | C33 | -0.6(15) | C19 | C20 | C21 | C23 | -179.4(12) |
| C100 | C2 | C34 | C35 | -179.5(10) | C20 | C19 | C27 | C28 | -111.1(12) |
| C100 | C31 | C32 | C33 | 2.6(16) | C20 | C19 | C27 | C29 | 7.8(17) |
| C100 | C31 | C32 | C39 | -178.0(10) | C20 | C19 | C27 | C30 | 128.4(12) |
| N2 | C6 | C13 | N3 | 5.2(15) | C20 | C21 | C22 | C17 | -0.6(17) |
| N2 | C6 | C13 | C14 | -178.0(9) | C20 | C21 | C23 | C24 | 58.7(17) |
| N2 | C7 | C8 | C9 | 178.4(11) | C20 | C21 | C23 | C25 | -57.0(17) |
| N2 | C7 | C12 | N3 | 5.2(16) | C20 | C21 | C23 | C26 | -178.6(17) |
| N2 | C7 | C12 | C11 | -176.1(10) | C22 | C17 | C18 | O3 | 177.2(10) |
| N3 | C13 | C14 | C15 | 176.0(10) | C22 | C17 | C18 | C19 | 0.4(16) |
| O11 | U1 | N1 | C3 | -43.1(11) | C22 | C21 | C23 | C24 | -119.9(15) |
| O11 | U1 | N1 | C4 | 140.5(7) | C22 | C21 | C23 | C25 | 124.4(15) |
| O11 | U1 | N4 | C15 | -139.3(7) | C22 | C21 | C23 | C26 | 3(2) |
| O11 | U1 | N4 | C16 | 43.0(12) | C23 | C21 | C22 | C17 | 178.0(11) |
| O11 | U1 | O3 | C18 | 148.5(11) | C27 | C19 | C20 | C21 | 176.9(11) |
| O11 | U1 | O10 | C2 | -148.3(11) | C31 | C100 | C2 | O10 | -179.2(10) |
| O10 | U1 | N1 | C3 | -29.4(8) | C31 | C100 | C2 | C34 | 0.5(15) |
| O10 | U1 | N1 | C4 | 154.2(8) | C31 | C100 | C3 | N1 | -179.7(10) |
| O10 | U1 | N4 | C15 | 24.5(9) | C31 | C32 | C33 | C34 | -2.9(17) |
| O10 | U1 | N4 | C16 | -153.2(8) | C31 | C32 | C39 | C40 | 8.4(19) |
| O10 | U1 | O3 | C18 | 137.2(10) | C31 | C32 | C39 | C41 | -110.2(15) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| O10 | C2 | C34 | C33 | 179.0(10) | C31 | C32 | C39 | C42 | 129.2(16) |
| O10 | C2 | C34 | C35 | 0.2(16) | C32 | C33 | C34 | C2 | 1.9(17) |
| C2 | C100 | C3 | N1 | 11.4(17) | C32 | C33 | C34 | C35 | -179.2(11) |
| C2 | C100 | C31 | C32 | -1.6(16) | C33 | C32 | C39 | C40 | -172.3(14) |
| C2 | C34 | C35 | C36 | 59.0(15) | C33 | C32 | C39 | C41 | 69.1(16) |
| C2 | C34 | C35 | C37 | 178.9(12) | C33 | C32 | C39 | C42 | -51.5(19) |
| C2 | C34 | C35 | C38 | -59.7(15) | C33 | C34 | C35 | C36 | -119.9(13) |
| C3 | N1 | C4 | C5 | 27.7(15) | C33 | C34 | C35 | C37 | 0.1(17) |
| C3 | N1 | C4 | C15 | -155.6(10) | C33 | C34 | C35 | C38 | 121.4(13) |
| C3 | C100 | C2 | O10 | -11.0(16) | C39 | C32 | C33 | C34 | 177.7(11) |
| C3 | C100 | C2 | C34 | 168.7(9) | | | | | |

**Crystallographic Table 13** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **$UO_2[L^I]$**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H25 | -612 | 2614 | 668 | 37 |
| H24 | -544 | 4127 | 929 | 41 |
| H23 | -1236 | 7532 | 512 | 58 |
| H1 | -873 | 9135 | 421 | 58 |
| H22 | 379 | 9569 | 524 | 53 |
| H2 | 1274 | 8404 | 726 | 53 |
| H21 | 1948 | 4943 | 871 | 40 |
| H3 | 2334 | 3660 | 437 | 45 |
| H14 | 4858 | 1357 | 987 | 51 |
| H4 | 3455 | 3322 | 88 | 50 |
| H5 | 4598 | 1525 | -680 | 158 |
| H6 | 5055 | 1128 | -40 | 158 |
| H7 | 5457 | 1741 | -534 | 158 |
| H8 | 5956 | 3024 | 128 | 153 |
| H10 | 5735 | 2424 | 720 | 153 |
| H9 | 5502 | 3540 | 628 | 153 |
| H12 | 4951 | 3472 | -766 | 253 |
| H13 | 4539 | 4004 | -244 | 253 |
| H11 | 4117 | 3211 | -705 | 253 |
| H16 | 3697 | -592 | 1300 | 100 |
| H15 | 3083 | -104 | 1667 | 100 |
| H17 | 3684 | -807 | 2039 | 100 |
| H19 | 5258 | 755 | 2015 | 117 |

| | | | | |
|---|---|---|---|---|
| H20 | 4993 | -29 | 1478 | 117 |
| H18 | 5009 | -305 | 2211 | 117 |
| H30A | 4164 | 396 | 2865 | 95 |
| H30B | 3508 | 1096 | 2585 | 95 |
| H30C | 4331 | 1492 | 2678 | 95 |
| H45 | -1581 | 1538 | 543 | 43 |
| H35 | -1726 | -653 | 1802 | 50 |
| H26 | -614 | 368 | 3200 | 129 |
| H28 | 197 | 462 | 3014 | 129 |
| H27 | 2 | -396 | 3472 | 129 |
| H29 | -749 | -1837 | 3037 | 130 |
| H30 | -1123 | -1840 | 2314 | 130 |
| H31 | -1399 | -1096 | 2811 | 130 |
| H33 | 170 | -1662 | 2012 | 106 |
| H34 | 534 | -1539 | 2733 | 106 |
| H32 | 647 | -718 | 2222 | 106 |
| H36 | -2429 | 618 | -116 | 169 |
| H37 | -2830 | 1408 | 270 | 169 |
| H38 | -3274 | 486 | -32 | 169 |
| H41 | -3609 | 149 | 1092 | 168 |
| H40 | -3161 | 1128 | 1272 | 168 |
| H39 | -2959 | 157 | 1669 | 168 |
| H43 | -3066 | -1064 | 312 | 212 |
| H44 | -2705 | -1316 | 1019 | 212 |
| H42 | -2197 | -1173 | 469 | 212 |

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Others
Fixed Uiso: H25(0.037) H24(0.041) H23(0.058) H1(0.058) H22(0.053) H2(0.053) H21(0.04) H3(0.045) H14(0.051) H4(0.05) H5(0.158) H6(0.158) H7(0.158) H8(0.153) H10(0.153) H9(0.153) H12(0.253) H13(0.253) H11(0.253) H16(0.1) H15(0.1) H17(0.1) H19(0.117) H20(0.117) H18(0.117) H30A(0.095) H30B(0.095) H30C(0.095) H45(0.043) H35(0.05) H26(0.129) H28(0.129) H27(0.129) H29(0.13) H30(0.13) H31(0.13) H33(0.106) H34(0.106) H32(0.106) H36(0.169) H37(0.169) H38(0.169) H41(0.168) H40(0.168) H39(0.168) H43(0.212) H44(0.212) H42(0.212)

Fixed X: H25(-0.0612) H24(-0.0544) H23(-0.1236) H1(-0.0873) H22(0.0379) H2(0.1274) H21(0.1948) H3(0.2334) H14(0.4858) H4(0.3455) H5(0.4598) H6(0.5055) H7(0.5457) H8(0.5956) H10(0.5735) H9(0.5502) H12(0.4951) H13(0.4539) H11(0.4117) H16(0.3697) H15(0.3083) H17(0.3684) H19(0.5258) H20(0.4993) H18(0.5009) H30A(0.4164) H30B(0.3508) H30C(0.4331) H45(-0.1581) H35(-0.1726) H26(-0.0614) H28(0.0197) H27(0.0002) H29(-0.0749) H30(-0.1123) H31(-0.1399) H33(0.017) H34(0.0534) H32(0.0647) H36(-0.2429) H37(-0.283) H38(-0.3274) H41(-0.3609) H40(-0.3161) H39(-0.2959) H43(-0.3066) H44(-0.2705) H42(-0.2197)
Fixed Y: H25(0.2614) H24(0.4127) H23(0.7532) H1(0.9135) H22(0.9569) H2(0.8404) H21(0.4943) H3(0.366) H14(0.1357) H4(0.3322) H5(0.1525) H6(0.1128) H7(0.1741) H8(0.3024) H10(0.2424) H9(0.354) H12(0.3472) H13(0.4004) H11(0.3211) H16(-0.0592) H15(-0.0104) H17(-0.0807) H19(0.0755) H20(-0.0029) H18(-0.0305) H30A(0.0396) H30B(0.1096) H30C(0.1492) H45(0.1538) H35(-0.0653) H26(0.0368) H28(0.0462) H27(-0.0396) H29(-0.1837) H30(-0.184) H31(-0.1096) H33(-0.1662) H34(-0.1539) H32(-0.0718) H36(0.0618) H37(0.1408) H38(0.0486) H41(0.0149) H40(0.1128) H39(0.0157) H43(-0.1064) H44(-0.1316) H42(-0.1173)
Fixed Z: H25(0.0668) H24(0.0929) H23(0.0512) H1(0.0421) H22(0.0524) H2(0.0726) H21(0.0871) H3(0.0437) H14(0.0987) H4(0.0088) H5(-0.068) H6(-0.004) H7(-0.0534) H8(0.0128) H10(0.072) H9(0.0628) H12(-0.0766) H13(-0.0244) H11(-0.0705) H16(0.13) H15(0.1667) H17(0.2039) H19(0.2015) H20(0.1478) H18(0.2211) H30A(0.2865) H30B(0.2585) H30C(0.2678) H45(0.0543) H35(0.1802) H26(0.32) H28(0.3014) H27(0.3472) H29(0.3037) H30(0.2314) H31(0.2811) H33(0.2012) H34(0.2733) H32(0.2222) H36(-0.0116) H37(0.027) H38(-0.0032) H41(0.1092) H40(0.1272) H39(0.1669) H43(0.0312) H44(0.1019) H42(0.0469)

## Cu[$L^I$]

**Crystallographic Table 14** Crystal data and structure refinement for **Cu[$L^I$]**

| | |
|---|---|
| Formula | $C_{42}H_{48}CuN_4O_2$ |
| Dcalc./ g cm−3 | 1.274 |
| μ/ mm−1 | 0.636 |
| Formula Weight | 704.39 |
| Colour | Red |
| Shape | Prism |
| Size/mm3 | 0.48 × 0.11 × 0.05 |
| T/K | 180(2) |
| Crystal System | Triclinic |
| Space Group | $P\bar{1}$ |
| a/˚Å | 9.9751(2) |
| b/˚ | 12.6630(3) |
| c/˚ | 14.8623(3) |
| *α*/◦ | 93.6100(10) |
| *β*/◦ | 96.8350(10) |
| *γ*/◦ | 98.7160(10) |
| *V* / ˚3 | 1836.17(7) |
| *Z* | 2 |
| Θ*min*◦ | 1.38 |
| Θ*max*/◦ | 26.77 |
| Measured Refl. | 60413 |
| Independent Refl. | 7756 |
| Reflections Used | 6595 |
| $R_{int}$ | 0.0333 |
| Parameters | 454 |
| Restraints | 0 |
| Largest Peak | 0.925 |
| Deepest Hole | -0.422 |
| GooF | 1.062 |
| *wR*2(all data) | 0.0966 |
| *wR2* | 0.0924 |
| *R*1(all data) | 0.0465 |
| *R*1 | 0.0365 |

**Crystallographic Table 15** Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (˚$A^2$ ×$10^3$) for **Cu[$L^I$]**. $U_{eq}$ is defined as 1⁄3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | **X** | **Y** | **Z** | **U(eq)** |
|---|---|---|---|---|
| Cu1 | −34.8(2) | 9894.14(17) | 3409.36(14) | 7.76(8) |

| | | | | |
|---|---|---|---|---|
| O2 | −646.1(13) | 10812.6(10) | 2549.2(9) | 22.9(3) |
| O1 | −1372.4(13) | 8750.6(10) | 2809.7(9) | 24.1(3) |
| N1 | 588.6(15) | 9024.8(12) | 4345(1) | 18.0(3) |
| C3 | −3235.1(19) | 7306.3(16) | 1497.6(13) | 24.2(4) |
| N4 | 5471.4(16) | 11198.0(13) | 6253.3(11) | 23.1(3) |
| N3 | 4452.3(16) | 9069.5(13) | 6656.1(11) | 23.7(3) |
| N2 | 1449.6(15) | 10983.9(12) | 4003.7(10) | 17.7(3) |
| C16 | 1790.7(18) | 9523.4(14) | 4912.7(12) | 17.7(4) |
| C27 | 2288.2(18) | 10608.6(14) | 4713.9(12) | 17.5(4) |
| C28 | 1706.0(19) | 11965.6(14) | 3766.8(12) | 19.8(4) |
| C29 | 998.2(19) | 12396.8(14) | 3027.6(12) | 20.1(4) |
| C43 | −122.2(18) | 11788.1(14) | 2426.6(12) | 19.0(4) |
| C37 | −663.1(19) | 12281.2(15) | 1643.1(12) | 20.1(4) |
| C36 | −99.0(19) | 13318.1(15) | 1536.1(13) | 22.1(4) |
| C31 | 988.2(19) | 13946.8(15) | 2130.2(13) | 21.9(4) |
| C30 | 1511.9(19) | 13475.5(15) | 2864.0(13) | 22.4(4) |
| C32 | 1516(2) | 15084.3(15) | 1897.2(14) | 25.9(4) |
| C35 | 352(2) | 15754.7(17) | 1855.0(18) | 38.1(5) |
| C34 | 2026(2) | 15012.7(19) | 961.7(16) | 39.2(5) |
| C33 | 2697(2) | 15652.5(17) | 2588.3(17) | 37.7(5) |
| C38 | −1808(2) | 11645.7(15) | 945.4(13) | 22.9(4) |
| C41 | −1302(2) | 10660.0(18) | 533.4(14) | 34.4(5) |
| C40 | −3098(2) | 11297.0(18) | 1389.9(15) | 32.8(5) |
| C39 | −2209(2) | 12309.9(18) | 157.7(15) | 34.5(5) |
| C26 | 3487.7(19) | 11152.2(15) | 5171.1(12) | 20.9(4) |
| C25 | 4265.3(19) | 10661.9(15) | 5844.6(12) | 19.9(4) |
| C18 | 3756.9(19) | 9592.4(15) | 6046.1(12) | 20.2(4) |
| C19 | 5648.7(19) | 9611.1(16) | 7076.5(12) | 22.7(4) |
| C20 | 6433(2) | 9106.4(18) | 7742.6(13) | 28.6(4) |
| C21 | 7645(2) | 9636.1(19) | 8175.4(14) | 31.3(5) |
| C22 | 8161(2) | 10687.6(19) | 7974.3(14) | 31.2(5) |
| C23 | 7451(2) | 11198.4(17) | 7336.8(14) | 28.4(4) |
| C24 | 6165.1(19) | 10677.2(16) | 6873.5(12) | 22.3(4) |
| C17 | 2502.2(19) | 9047.7(15) | 5569.3(13) | 21.8(4) |
| C14 | −1085.7(19) | 7423.9(15) | 3867.0(13) | 20.7(4) |
| C1 | −1681.0(18) | 7780.3(14) | 3036.6(13) | 19.8(4) |
| C2 | −2645.7(18) | 7006.0(15) | 2436.5(13) | 21.0(4) |
| C4 | −4160(2) | 6347.5(18) | 939.3(15) | 35.6(5) |
| C6 | −2070(2) | 7673.1(18) | 939.1(14) | 30.9(5) |
| C5 | −4094(2) | 8202.1(19) | 1618.6(16) | 35.2(5) |
| C7 | −3006.8(19) | 5999.8(15) | 2728.0(13) | 22.8(4) |
| C8 | −2483.1(19) | 5651.4(15) | 3570.4(13) | 21.5(4) |
| C13 | −1523.9(19) | 6368.2(15) | 4111.4(13) | 22.3(4) |

| | | | | |
|---|---|---|---|---|
| C9 | −2928(2) | 4494.5(15) | 3793.5(14) | 25.1(4) |
| C10 | −4474(3) | 4182(2) | 3670(3) | 66.5(9) |
| C15 | 13.9(18) | 8047.6(14) | 4448.7(12) | 19.2(4) |
| C11 | −2341(4) | 3735(2) | 3154(2) | 60.1(8) |
| C12 | −2397(3) | 4299(2) | 4772.4(19) | 55.0(7) |

**Crystallographic Table 16** Anisotropic Displacement Parameters (×104) **Cu[L$^{I}$]**. The Anisotropic displacement factor exponent takes the form: −2π2[h2a ∗2 U11 + ... + 2hka × b × U12]

| Atom | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Cu1 | 22.10(13) | 15.05(12) | 14.70(12) | 3.27(8) | −2.47(8) | 1.40(8) |
| O2 | 27.3(7) | 18.9(7) | 19.8(7) | 6.2(5) | −5.0(5) | 0.0(5) |
| O1 | 28.0(7) | 18.4(7) | 22.3(7) | 4.3(5) | −7.0(6) | −0.8(5) |
| N1 | 20.5(8) | 17.6(7) | 15.0(7) | 1.5(6) | −0.5(6) | 2.4(6) |
| C3 | 23(1) | 24.7(10) | 22.5(10) | 1.0(8) | −2.8(8) | 0.7(8) |
| N4 | 23.7(8) | 23.6(8) | 20.7(8) | −1.1(6) | −0.1(6) | 2.7(7) |
| N3 | 23.9(8) | 28.2(9) | 18.6(8) | 5.8(7) | −1.1(6) | 4.7(7) |
| N2 | 21.3(8) | 16.8(7) | 14.7(7) | 2.6(6) | −0.2(6) | 3.5(6) |
| C16 | 19.2(9) | 18.1(9) | 15.2(9) | 0.6(7) | 0.8(7) | 2.6(7) |
| C27 | 22.0(9) | 17.5(9) | 13.4(8) | 1.8(7) | 1.6(7) | 5.1(7) |
| C28 | 23.5(9) | 17.3(9) | 17.5(9) | 0.9(7) | 0.2(7) | 1.9(7) |
| C29 | 24.1(9) | 18.5(9) | 18.1(9) | 3.8(7) | 2.1(7) | 4.8(7) |
| C43 | 22.5(9) | 17.9(9) | 17.6(9) | 3.2(7) | 3.6(7) | 5.2(7) |
| C37 | 22.7(9) | 21.7(9) | 17.5(9) | 4.1(7) | 3.2(7) | 6.7(7) |
| C36 | 24.3(10) | 23.6(10) | 20.8(10) | 9.0(8) | 2.6(7) | 8.7(8) |
| C31 | 24(1) | 17.9(9) | 25.3(10) | 6.4(7) | 4.1(8) | 4.9(7) |
| C30 | 23.6(10) | 18.1(9) | 24.8(10) | 3.3(7) | 0.0(8) | 2.8(7) |
| C32 | 27.4(10) | 19.8(9) | 31.4(11) | 11.0(8) | 2.3(8) | 4.2(8) |
| C35 | 35.7(12) | 24.2(11) | 56.3(15) | 12.1(10) | 4.7(11) | 8.6(9) |
| C34 | 43.2(13) | 36.3(13) | 38.7(13) | 14.5(10) | 11.2(10) | −0.5(10) |
| C33 | 40.2(13) | 23.6(11) | 45.7(14) | 12.5(10) | −5.3(10) | −2.3(9) |
| C38 | 27.2(10) | 23.4(10) | 17.7(9) | 5.1(7) | −1.3(8) | 5.0(8) |
| C41 | 46.1(13) | 33.7(12) | 21.9(11) | −3.2(9) | −5.9(9) | 12(1) |
| C40 | 24.9(10) | 39.2(12) | 31.8(12) | 6.1(9) | −1.2(9) | −0.5(9) |
| C39 | 38.6(12) | 35.1(12) | 27.1(11) | 10.6(9) | −9.1(9) | 4(1) |
| C26 | 25.8(10) | 16.5(9) | 19.8(9) | 2.9(7) | 0.6(7) | 2.6(7) |
| C25 | 21.3(9) | 21.7(9) | 16.0(9) | −1.7(7) | 0.0(7) | 4.4(7) |
| C18 | 21.6(9) | 23.5(9) | 15.5(9) | 2.5(7) | 1.2(7) | 4.4(7) |
| C19 | 22.1(9) | 31.4(11) | 15.5(9) | 0.7(8) | 2.3(7) | 7.2(8) |
| C20 | 28.3(11) | 38.6(12) | 20(1) | 4.6(8) | 0.3(8) | 10.7(9) |
| C21 | 26.9(11) | 48.9(13) | 19.4(10) | −0.2(9) | −2.1(8) | 15.9(10) |
| C22 | 22.1(10) | 47.1(13) | 22.5(10) | −8.6(9) | −3.1(8) | 8.7(9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C23 | 25.3(10) | 32.6(11) | 25.4(11) | −7.1(8) | 1.1(8) | 4.0(8) |
| C24 | 22.4(9) | 28.3(10) | 16.4(9) | −3.1(8) | 1.0(7) | 7.8(8) |
| C17 | 25.3(10) | 19.1(9) | 20.4(10) | 6.2(7) | 0.4(8) | 1.6(7) |
| C14 | 22.2(9) | 18.2(9) | 21.6(10) | 1.0(7) | 2.0(7) | 4.4(7) |
| C1 | 19.7(9) | 18.5(9) | 21.3(9) | 1.4(7) | 2.1(7) | 3.6(7) |
| C2 | 18.2(9) | 21.7(9) | 22.3(10) | 0.2(7) | 0.9(7) | 3.3(7) |
| C4 | 36.5(12) | 36.2(12) | 26.8(11) | 1.0(9) | −7.1(9) | −7.4(10) |
| C6 | 30.4(11) | 37.1(12) | 23.8(11) | 6.3(9) | 0.0(8) | 1.9(9) |
| C5 | 30.6(11) | 39.4(13) | 34.6(12) | 1.3(10) | −7.0(9) | 11.9(10) |
| C7 | 19.6(9) | 21.2(9) | 26.2(10) | −2.1(8) | 1.9(8) | 0.9(7) |
| C8 | 21.7(9) | 18.0(9) | 25.8(10) | 1.5(7) | 6.1(8) | 4.2(7) |
| C13 | 24.5(10) | 19.4(9) | 23.5(10) | 4.0(7) | 2.1(8) | 4.9(7) |
| C9 | 25.7(10) | 19.4(9) | 29.5(11) | 4.1(8) | 4.6(8) | 0.2(8) |
| C10 | 39.1(15) | 55.3(18) | 107(3) | 42.3(18) | 8.4(16) | −1.2(13) |
| C15 | 23.1(9) | 17.4(9) | 17.7(9) | 4.1(7) | 0.5(7) | 5.8(7) |
| C11 | 96(2) | 27.6(13) | 61.9(19) | 6.5(12) | 30.6(17) | 10.3(14) |
| C12 | 78(2) | 32.1(13) | 47.3(16) | 14.1(11) | −10.7(4) | −5.3(13) |

**Crystallographic Table 17** Bond Lengths in Å for **Cu[L$^{I}$]**

| Atom | Atom | Å | Atom | Atom | Å |
|---|---|---|---|---|---|
| Cu1 | O2 | 1.8909(12) | C31 | C30 | 1.364(3) |
| Cu1 | O1 | 1.9079(13) | C31 | C32 | 1.532(3) |
| Cu1 | N1 | 1.9305(15) | C32 | C33 | 1.524(3) |
| Cu1 | N2 | 1.9475(15) | C32 | C35 | 1.536(3) |
| O2 | C43 | 1.299(2) | C32 | C34 | 1.539(3) |
| O1 | C1 | 1.296(2) | C38 | C39 | 1.534(3) |
| N1 | C15 | 1.309(2) | C38 | C40 | 1.535(3) |
| N1 | C16 | 1.418(2) | C38 | C41 | 1.535(3) |
| C3 | C5 | 1.536(3) | C26 | C25 | 1.424(3) |
| C3 | C4 | 1.538(3) | C25 | C18 | 1.435(3) |
| C3 | C6 | 1.539(3) | C18 | C17 | 1.418(3) |
| C3 | C2 | 1.542(3) | C19 | C20 | 1.431(3) |
| N4 | C25 | 1.343(2) | C19 | C24 | 1.434(3) |
| N4 | C24 | 1.352(2) | C20 | C21 | 1.356(3) |
| N3 | C19 | 1.344(2) | C21 | C22 | 1.416(3) |
| N3 | C18 | 1.344(2) | C22 | C23 | 1.368(3) |
| N2 | C28 | 1.310(2) | C23 | C24 | 1.425(3) |
| N2 | C27 | 1.419(2) | C14 | C15 | 1.414(3) |
| C16 | C17 | 1.363(3) | C14 | C13 | 1.425(3) |
| C16 | C27 | 1.450(2) | C14 | C1 | 1.434(3) |
| C27 | C26 | 1.366(3) | C1 | C2 | 1.443(3) |
| C28 | C29 | 1.418(3) | C2 | C7 | 1.381(3) |

| | | | | | |
|---|---|---|---|---|---|
| C29 | C30 | 1.431(3) | C7 | C8 | 1.421(3) |
| C29 | C43 | 1.434(3) | C8 | C13 | 1.359(3) |
| C43 | C37 | 1.443(2) | C8 | C9 | 1.534(3) |
| C37 | C36 | 1.375(3) | C9 | C10 | 1.519(3) |
| C37 | C38 | 1.537(3) | C9 | C11 | 1.536(3) |
| C36 | C31 | 1.418(3) | C9 | C12 | 1.536(3) |

**Crystallographic Table 18** Bond Angles in ◦ for **Cu[L$^{I}$]**

| Atom | Atom | Atom | Angle/◦ | Atom | Atom | Atom | Angle/◦ |
|---|---|---|---|---|---|---|---|
| O2 | Cu1 | O1 | 89.19(5) | C31 | C32 | C34 | 108.48(17) |
| O2 | Cu1 | N1 | 176.50(6) | C35 | C32 | C34 | 109.18(18) |
| O1 | Cu1 | N1 | 93.26(6) | C39 | C38 | C40 | 107.49(17) |
| O2 | Cu1 | N2 | 93.50(6) | C39 | C38 | C41 | 107.14(17) |
| O1 | Cu1 | N2 | 175.04(6) | C40 | C38 | C41 | 110.14(17) |
| N1 | Cu1 | N2 | 84.24(6) | C39 | C38 | C37 | 111.88(16) |
| C43 | O2 | Cu1 | 129.18(12) | C40 | C38 | C37 | 110.92(16) |
| C1 | O1 | Cu1 | 128.99(12) | C41 | C38 | C37 | 109.19(16) |
| C15 | N1 | C16 | 121.28(15) | C27 | C26 | C25 | 120.61(17) |
| C15 | N1 | Cu1 | 124.84(12) | N4 | C25 | C26 | 119.25(17) |
| C16 | N1 | Cu1 | 113.84(11) | N4 | C25 | C18 | 121.80(17) |
| C5 | C3 | C4 | 107.91(17) | C26 | C25 | C18 | 118.92(16) |
| C5 | C3 | C6 | 110.12(17) | N3 | C18 | C17 | 118.30(17) |
| C4 | C3 | C6 | 106.81(17) | N3 | C18 | C25 | 122.19(17) |
| C5 | C3 | C2 | 109.76(16) | C17 | C18 | C25 | 119.47(16) |
| C4 | C3 | C2 | 111.93(16) | N3 | C19 | C20 | 119.00(18) |
| C6 | C3 | C2 | 110.26(15) | N3 | C19 | C24 | 121.92(17) |
| C25 | N4 | C24 | 116.07(16) | C20 | C19 | C24 | 119.08(18) |
| C19 | N3 | C18 | 116.09(17) | C21 | C20 | C19 | 120.1(2) |
| C28 | N2 | C27 | 121.75(16) | C20 | C21 | C22 | 120.96(19) |
| C28 | N2 | Cu1 | 124.57(12) | C23 | C22 | C21 | 120.98(19) |
| C27 | N2 | Cu1 | 113.63(11) | C22 | C23 | C24 | 120.0(2) |
| C17 | C16 | N1 | 125.35(17) | N4 | C24 | C23 | 119.18(18) |
| C17 | C16 | C27 | 120.23(17) | N4 | C24 | C19 | 121.92(17) |
| N1 | C16 | C27 | 114.35(15) | C23 | C24 | C19 | 118.91(17) |
| C26 | C27 | N2 | 126.27(16) | C16 | C17 | C18 | 120.60(17) |
| C26 | C27 | C16 | 120.14(16) | C15 | C14 | C13 | 116.33(16) |
| N2 | C27 | C16 | 113.53(15) | C15 | C14 | C1 | 123.08(17) |
| N2 | C28 | C29 | 126.28(17) | C13 | C14 | C1 | 120.43(17) |
| C28 | C29 | C30 | 116.47(17) | O1 | C1 | C14 | 122.68(17) |
| C28 | C29 | C43 | 123.27(17) | O1 | C1 | C2 | 119.92(16) |
| C30 | C29 | C43 | 120.15(16) | C14 | C1 | C2 | 117.39(16) |
| O2 | C43 | C29 | 122.89(16) | C7 | C2 | C1 | 118.03(17) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O2 | C43 | C37 | 119.10(16) | C7 | C2 | C3 | 121.79(17) |
| C29 | C43 | C37 | 117.99(16) | C1 | C2 | C3 | 120.18(16) |
| C36 | C37 | C43 | 117.83(17) | C2 | C7 | C8 | 125.23(18) |
| C36 | C37 | C38 | 121.80(16) | C13 | C8 | C7 | 116.32(17) |
| C43 | C37 | C38 | 120.36(16) | C13 | C8 | C9 | 123.62(17) |
| C37 | C36 | C31 | 125.35(17) | C7 | C8 | C9 | 119.89(17) |
| C30 | C31 | C36 | 116.81(17) | C8 | C13 | C14 | 122.40(17) |
| C30 | C31 | C32 | 124.63(18) | C10 | C9 | C8 | 112.12(18) |
| C36 | C31 | C32 | 118.54(16) | C10 | C9 | C11 | 108.3(2) |
| C31 | C30 | C29 | 121.82(18) | C8 | C9 | C11 | 108.79(17) |
| C33 | C32 | C31 | 112.48(16) | C10 | C9 | C12 | 107.4(2) |
| C33 | C32 | C35 | 108.61(18) | C8 | C9 | C12 | 112.64(17) |
| C31 | C32 | C35 | 109.85(16) | C11 | C9 | C12 | 107.3(2) |
| C33 | C3 | C3 | 108.18(18) | N1 | C15 | C1 | 126.45(17) |

## $VO[L^I]$

**Crystallographic Table 19** Crystal data and structure refinement for **$VO[L^I]$**

| | |
|---|---|
| Empirical formula | $C_{42}H_{48}N_4O_3V$ |
| Formula weight | 707.82 |
| Temperature/K | 296.15 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.5213(4) |
| b/Å | 12.7581(5) |
| c/Å | 16.9448(6) |
| α/° | 77.715(1) |
| β/° | 74.447(1) |
| γ/° | 79.226(1) |
| Volume/$Å^3$ | 2120.59(14) |
| Z | 2 |
| $\rho_{calc}mg/mm^3$ | 1.1084 |
| $m/mm^{-1}$ | 0.272 |
| F(000) | 750.9 |
| Crystal size/$mm^3$ | 0.6 × 0.08 × 0.08 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 3.3 to 49.42° |
| Index ranges | $-12 \leq h \leq 12$, $-15 \leq k \leq 15$, $-19 \leq l \leq 19$ |
| Reflections collected | 35450 |
| Independent reflections | 7239 [$R_{int}$ = 0.0414, $R_{sigma}$ = 0.0397] |
| Data/restraints/parameters | 7239/0/462 |
| Goodness-of-fit on $F^2$ | 2.571 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.1090, $wR_2$ = 0.3205 |
| Final R indexes [all data] | $R_1$ = 0.1280, $wR_2$ = 0.3266 |
| Largest diff. peak/hole / e $Å^{-3}$ | 3.47/-0.47 |

**Crystallographic Table 20** Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **$VO[L^I]$**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| V1 | 4939.4(11) | 5939.1(9) | 1615.2(6) | 21.8(4) |
| O2 | 4715(4) | 6483(4) | 2631(3) | 26.8(10) |
| O1 | 4101(4) | 4726(4) | 2300(3) | 28.2(11) |
| N2 | 6752(5) | 6499(4) | 1213(3) | 21.8(12) |

| | | | | |
|---|---|---|---|---|
| N1 | 6004(5) | 4884(4) | 832(3) | 22.4(12) |
| N3 | 9706(5) | 4813(5) | -1606(3) | 28.7(13) |
| N4 | 10561(5) | 6552(5) | -1166(3) | 28.6(13) |
| C1 | 5224(6) | 7265(5) | 2787(4) | 22.1(14) |
| C14 | 6401(6) | 7638(5) | 2265(4) | 25.1(14) |
| C2 | 4613(7) | 7718(5) | 3520(4) | 26.2(15) |
| C13 | 6948(7) | 8442(5) | 2470(4) | 28.9(15) |
| C8 | 6385(7) | 8885(6) | 3162(4) | 31.4(16) |
| C7 | 5208(7) | 8505(5) | 3678(4) | 30.4(16) |
| C16 | 7592(6) | 6126(5) | 494(4) | 21.3(13) |
| C27 | 7169(6) | 5253(5) | 261(4) | 21.5(14) |
| C26 | 7857(6) | 4839(5) | -437(4) | 25.2(14) |
| C17 | 8729(6) | 6538(5) | 16(4) | 24.6(14) |
| C25 | 9023(6) | 5251(5) | -929(4) | 24.1(14) |
| C18 | 9463(6) | 6115(5) | -703(4) | 24.2(14) |
| C24 | 10807(6) | 5234(6) | -2057(4) | 28.2(15) |
| C23 | 11591(7) | 4785(6) | -2760(4) | 36.8(18) |
| C20 | 12403(7) | 6530(7) | -2353(5) | 42.8(19) |
| C19 | 11228(6) | 6117(6) | -1840(4) | 29.1(16) |
| C22 | 12712(7) | 5215(7) | -3223(4) | 40.7(19) |
| C21 | 13108(8) | 6072(7) | -3028(5) | 45(2) |
| C29 | 4539(6) | 3494(5) | 1347(4) | 25.7(15) |
| C30 | 4241(7) | 2562(5) | 1139(4) | 30.1(16) |
| C28 | 5618(6) | 3987(5) | 786(4) | 25.5(15) |
| C31 | 3293(7) | 1980(5) | 1660(4) | 29.3(15) |
| O3 | 3974(5) | 6712(4) | 1082(3) | 32.1(11) |
| C15 | 7121(6) | 7208(5) | 1541(4) | 24.5(14) |
| C3 | 3322(7) | 7345(6) | 4106(4) | 36.0(18) |
| C9 | 6927(8) | 9780(6) | 3410(5) | 41.3(19) |
| C5 | 3612(8) | 6122(6) | 4466(4) | 42.3(19) |
| C4 | 2210(8) | 7549(7) | 3646(5) | 45(2) |
| C6 | 2840(10) | 7958(8) | 4850(5) | 59(3) |
| C11 | 5894(10) | 10793(6) | 3434(6) | 58(3) |
| C10 | 8216(10) | 10074(9) | 2789(7) | 80(4) |
| C12 | 7238(12) | 9385(8) | 4266(6) | 71(3) |
| C32 | 3006(7) | 920(6) | 1478(5) | 35.3(17) |
| C34 | 1527(9) | 845(8) | 1732(7) | 65(3) |
| C33 | 3476(11) | 858(8) | 564(6) | 68(3) |

| | | | | |
|---|---|---|---|---|
| C37 | 2866(7) | 3236(6) | 2669(4) | 30.9(16) |
| C36 | 2643(7) | 2336(6) | 2416(4) | 32.7(16) |
| C38 | 2154(7) | 3527(6) | 3523(4) | 36.0(17) |
| C41 | 3188(8) | 3365(7) | 4052(4) | 42.1(19) |
| C40 | 1494(8) | 4717(7) | 3451(5) | 45(2) |
| C39 | 1067(10) | 2817(8) | 3982(5) | 64(3) |
| C35 | 3727(13) | -31(7) | 1957(8) | 88(4) |
| C42 | 3841(6) | 3866(5) | 2103(4) | 26.1(15) |

**Crystallographic Table 21** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **VO[$L^I$]**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{12}$** | **$U_{13}$** | **$U_{23}$** |
|---|---|---|---|---|---|---|
| V1 | 23.3(6) | 24.1(6) | 19.8(6) | -8.2(4) | -3.0(4) | -6.2(4) |
| O2 | 30(2) | 31(3) | 22(2) | -13(2) | 0.4(19) | -10.3(19) |
| O1 | 32(3) | 31(3) | 23(2) | -16(2) | 1(2) | -8(2) |
| N2 | 25(3) | 21(3) | 18(3) | -3(2) | -3(2) | -5(2) |
| N1 | 24(3) | 26(3) | 18(3) | -10(2) | -3(2) | -3(2) |
| N3 | 30(3) | 34(3) | 20(3) | -3(3) | -4(2) | -5(2) |
| N4 | 23(3) | 34(3) | 25(3) | -8(2) | -2(2) | 1(2) |
| C1 | 23(3) | 22(3) | 22(3) | -6(3) | -5(3) | -4(3) |
| C14 | 29(4) | 23(3) | 25(3) | -6(3) | -5(3) | -6(3) |
| C2 | 34(4) | 25(4) | 20(3) | -6(3) | -6(3) | -5(3) |
| C13 | 30(4) | 29(4) | 29(4) | -11(3) | -2(3) | -8(3) |
| C8 | 36(4) | 28(4) | 33(4) | -10(3) | -5(3) | -10(3) |
| C7 | 40(4) | 27(4) | 25(4) | -9(3) | -3(3) | -9(3) |
| C16 | 23(3) | 23(3) | 19(3) | -5(3) | -4(3) | -4(3) |
| C27 | 21(3) | 22(3) | 19(3) | -6(3) | -3(3) | 0(3) |
| C26 | 29(4) | 25(4) | 22(3) | -5(3) | -5(3) | -5(3) |
| C17 | 24(3) | 25(4) | 24(3) | -8(3) | -3(3) | -4(3) |
| C25 | 24(3) | 25(4) | 21(3) | -1(3) | -3(3) | -3(3) |
| C18 | 23(3) | 25(4) | 22(3) | -5(3) | -5(3) | 2(3) |
| C24 | 24(4) | 37(4) | 18(3) | -1(3) | -4(3) | 3(3) |
| C23 | 32(4) | 47(5) | 24(4) | 7(3) | -4(3) | -4(3) |
| C20 | 32(4) | 54(5) | 35(4) | -13(4) | 1(3) | 4(4) |
| C19 | 22(3) | 39(4) | 20(3) | -2(3) | -3(3) | 4(3) |
| C22 | 27(4) | 59(5) | 24(4) | 5(4) | 1(3) | 2(4) |
| C21 | 26(4) | 66(6) | 30(4) | -3(4) | 3(3) | 3(4) |
| C29 | 27(4) | 26(4) | 25(3) | -10(3) | -4(3) | -2(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C30 | 32(4) | 28(4) | 31(4) | -9(3) | -6(3) | -7(3) |
| C28 | 28(4) | 29(4) | 21(3) | -9(3) | -3(3) | -7(3) |
| C31 | 29(4) | 25(4) | 35(4) | -10(3) | -9(3) | -1(3) |
| O3 | 32(3) | 34(3) | 31(3) | -4(2) | -8(2) | -5(2) |
| C15 | 25(3) | 20(3) | 29(4) | -8(3) | -2(3) | -6(3) |
| C3 | 40(4) | 40(4) | 27(4) | -17(3) | 7(3) | -14(3) |
| C9 | 45(5) | 44(5) | 40(4) | -24(4) | 4(4) | -21(4) |
| C5 | 56(5) | 42(5) | 29(4) | -21(4) | 0(4) | -5(3) |
| C4 | 34(4) | 45(5) | 53(5) | -10(4) | 3(4) | -15(4) |
| C6 | 68(6) | 68(6) | 40(5) | -32(5) | 21(4) | -31(4) |
| C11 | 81(7) | 31(5) | 66(6) | -20(4) | -4(5) | -22(4) |
| C10 | 70(7) | 87(8) | 97(8) | -56(6) | 21(6) | -58(7) |
| C12 | 102(8) | 66(7) | 69(6) | -31(6) | -38(6) | -24(5) |
| C32 | 37(4) | 25(4) | 46(4) | -11(3) | -14(3) | 1(3) |
| C34 | 57(6) | 62(6) | 89(7) | -32(5) | -13(5) | -29(5) |
| C33 | 79(7) | 52(6) | 85(7) | -32(5) | 1(6) | -40(5) |
| C37 | 29(4) | 36(4) | 28(4) | -13(3) | -5(3) | 1(3) |
| C36 | 33(4) | 32(4) | 35(4) | -19(3) | -7(3) | 3(3) |
| C38 | 35(4) | 45(5) | 27(4) | -20(3) | 2(3) | -3(3) |
| C41 | 52(5) | 44(5) | 26(4) | -8(4) | -6(4) | -2(3) |
| C40 | 31(4) | 65(6) | 38(4) | -4(4) | -4(3) | -17(4) |
| C39 | 65(6) | 83(7) | 44(5) | -51(6) | 20(5) | -18(5) |
| C35 | 121(10) | 26(5) | 146(11) | -16(5) | -92(9) | 3(6) |
| C42 | 27(4) | 27(4) | 28(4) | -12(3) | -7(3) | -3(3) |

**Crystallographic Table 22** Bond Lengths for **VO[$L^I$]**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| V1 | O2 | 1.931(4) | C25 | C18 | 1.429(9) |
| V1 | O1 | 1.928(4) | C24 | C23 | 1.420(9) |
| V1 | N2 | 2.054(5) | C24 | C19 | 1.432(10) |
| V1 | N1 | 2.056(5) | C23 | C22 | 1.367(10) |
| V1 | O3 | 1.600(5) | C20 | C19 | 1.426(10) |
| O2 | C1 | 1.319(7) | C20 | C21 | 1.366(11) |
| O1 | C42 | 1.307(7) | C22 | C21 | 1.372(12) |
| N2 | C16 | 1.415(8) | C29 | C30 | 1.418(9) |
| N2 | C15 | 1.319(8) | C29 | C28 | 1.422(9) |
| N1 | C27 | 1.430(8) | C29 | C42 | 1.424(9) |
| N1 | C28 | 1.308(8) | C30 | C31 | 1.362(9) |

| | | | | | |
|---|---|---|---|---|---|
| N3 | C25 | 1.352(8) | C31 | C32 | 1.548(9) |
| N3 | C24 | 1.341(8) | C31 | C36 | 1.405(10) |
| N4 | C18 | 1.353(8) | C3 | C5 | 1.555(11) |
| N4 | C19 | 1.341(9) | C3 | C4 | 1.527(11) |
| C1 | C14 | 1.413(9) | C3 | C6 | 1.545(10) |
| C1 | C2 | 1.424(9) | C9 | C11 | 1.525(12) |
| C14 | C13 | 1.408(9) | C9 | C10 | 1.532(11) |
| C14 | C15 | 1.418(9) | C9 | C12 | 1.531(12) |
| C2 | C7 | 1.382(9) | C32 | C34 | 1.515(11) |
| C2 | C3 | 1.541(9) | C32 | C33 | 1.509(12) |
| C13 | C8 | 1.353(9) | C32 | C35 | 1.508(11) |
| C8 | C7 | 1.413(10) | C37 | C36 | 1.386(10) |
| C8 | C9 | 1.544(9) | C37 | C38 | 1.529(10) |
| C16 | C27 | 1.435(8) | C37 | C42 | 1.439(9) |
| C16 | C17 | 1.378(9) | C38 | C41 | 1.545(10) |
| C27 | C26 | 1.366(9) | C38 | C40 | 1.541(11) |
| C26 | C25 | 1.408(9) | C38 | C39 | 1.531(10) |
| C17 | C18 | 1.410(9) | | | |

**Crystallographic Table 23** Bond Angles for **VO[L$^{I}$]**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| O1 | V1 | O2 | 86.81(18) | C19 | C24 | N3 | 121.7(6) |
| N2 | V1 | O2 | 87.49(19) | C19 | C24 | C23 | 118.9(6) |
| N2 | V1 | O1 | 141.4(2) | C22 | C23 | C24 | 119.6(8) |
| N1 | V1 | O2 | 147.9(2) | C21 | C20 | C19 | 119.9(8) |
| N1 | V1 | O1 | 86.81(19) | C24 | C19 | N4 | 121.9(6) |
| N1 | V1 | N2 | 78.2(2) | C20 | C19 | N4 | 119.5(7) |
| O3 | V1 | O2 | 108.7(2) | C20 | C19 | C24 | 118.6(6) |
| O3 | V1 | O1 | 111.0(2) | C21 | C22 | C23 | 121.8(7) |
| O3 | V1 | N2 | 107.0(2) | C22 | C21 | C20 | 121.2(7) |
| O3 | V1 | N1 | 102.9(2) | C28 | C29 | C30 | 116.3(6) |
| C1 | O2 | V1 | 131.3(4) | C42 | C29 | C30 | 121.2(6) |
| C42 | O1 | V1 | 130.8(4) | C42 | C29 | C28 | 122.4(6) |
| C16 | N2 | V1 | 114.9(4) | C31 | C30 | C29 | 121.3(6) |
| C15 | N2 | V1 | 124.9(4) | C29 | C28 | N1 | 126.2(6) |
| C15 | N2 | C16 | 120.1(5) | C32 | C31 | C30 | 122.5(6) |
| C27 | N1 | V1 | 114.8(4) | C36 | C31 | C30 | 116.8(6) |
| C28 | N1 | V1 | 124.4(4) | C36 | C31 | C32 | 120.4(6) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C28 | N1 | C27 | 120.6(5) | C14 | C15 | N2 | 126.4(6) |
| C24 | N3 | C25 | 116.7(6) | C5 | C3 | C2 | 108.8(6) |
| C19 | N4 | C18 | 116.4(6) | C4 | C3 | C2 | 110.9(6) |
| C14 | C1 | O2 | 121.8(5) | C4 | C3 | C5 | 110.8(6) |
| C2 | C1 | O2 | 119.6(5) | C6 | C3 | C2 | 111.1(6) |
| C2 | C1 | C14 | 118.5(5) | C6 | C3 | C5 | 107.1(6) |
| C13 | C14 | C1 | 120.3(6) | C6 | C3 | C4 | 108.0(7) |
| C15 | C14 | C1 | 123.1(6) | C11 | C9 | C8 | 109.5(6) |
| C15 | C14 | C13 | 116.6(6) | C10 | C9 | C8 | 111.3(6) |
| C7 | C2 | C1 | 117.8(6) | C10 | C9 | C11 | 108.6(7) |
| C3 | C2 | C1 | 120.5(5) | C12 | C9 | C8 | 109.9(6) |
| C3 | C2 | C7 | 121.7(6) | C12 | C9 | C11 | 109.8(7) |
| C8 | C13 | C14 | 122.3(6) | C12 | C9 | C10 | 107.7(8) |
| C7 | C8 | C13 | 116.9(6) | C34 | C32 | C31 | 111.0(6) |
| C9 | C8 | C13 | 124.5(6) | C33 | C32 | C31 | 111.4(6) |
| C9 | C8 | C7 | 118.6(6) | C33 | C32 | C34 | 107.5(7) |
| C8 | C7 | C2 | 124.2(6) | C35 | C32 | C31 | 108.9(6) |
| C27 | C16 | N2 | 114.9(5) | C35 | C32 | C34 | 109.3(8) |
| C17 | C16 | N2 | 125.7(5) | C35 | C32 | C33 | 108.8(8) |
| C17 | C16 | C27 | 119.4(5) | C38 | C37 | C36 | 121.9(6) |
| C16 | C27 | N1 | 113.1(5) | C42 | C37 | C36 | 116.9(6) |
| C26 | C27 | N1 | 125.7(6) | C42 | C37 | C38 | 121.1(6) |
| C26 | C27 | C16 | 121.2(6) | C37 | C36 | C31 | 125.8(6) |
| C25 | C26 | C27 | 119.8(6) | C41 | C38 | C37 | 108.8(6) |
| C18 | C17 | C16 | 120.3(6) | C40 | C38 | C37 | 111.4(6) |
| C26 | C25 | N3 | 118.8(6) | C40 | C38 | C41 | 108.4(6) |
| C18 | C25 | N3 | 121.5(6) | C39 | C38 | C37 | 111.9(6) |
| C18 | C25 | C26 | 119.7(6) | C39 | C38 | C41 | 108.7(6) |
| C17 | C18 | N4 | 118.7(6) | C39 | C38 | C40 | 107.6(7) |
| C25 | C18 | N4 | 121.7(6) | C29 | C42 | O1 | 121.8(6) |
| C25 | C18 | C17 | 119.5(6) | C37 | C42 | O1 | 120.3(6) |
| C23 | C24 | N3 | 119.4(6) | C37 | C42 | C29 | 117.8(6) |

**Crystallographic Table 24** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **VO[L$^I$]**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H13 | 7723(7) | 8676(5) | 2118(4) | 34.6(18) |
| H7 | 4807(7) | 8805(5) | 4155(4) | 36.4(19) |

| | | | | |
|---|---|---|---|---|
| H26 | 7555(6) | 4287(5) | -588(4) | 30.2(17) |
| H17 | 9014(6) | 7097(5) | 167(4) | 29.5(17) |
| H23 | 11344(7) | 4202(6) | -2905(4) | 44(2) |
| H20 | 12689(7) | 7109(7) | -2228(5) | 51(2) |
| H22 | 13219(7) | 4917(7) | -3684(4) | 49(2) |
| H21 | 13872(8) | 6347(7) | -3360(5) | 54(2) |
| H30 | 4703(7) | 2345(5) | 637(4) | 36.1(19) |
| H28 | 6095(6) | 3638(5) | 345(4) | 30.6(17) |
| H15 | 7934(6) | 7450(5) | 1271(4) | 29.4(17) |
| H5a | 3940(50) | 5717(8) | 4019(5) | 63(3) |
| H5b | 4270(40) | 6019(8) | 4780(30) | 63(3) |
| H5c | 2806(14) | 5876(12) | 4820(30) | 63(3) |
| H4a | 2040(40) | 8309(9) | 3440(30) | 67(3) |
| H4b | 2480(20) | 7150(30) | 3190(20) | 67(3) |
| H4c | 1416(17) | 7310(40) | 4022(10) | 67(3) |
| H6a | 3540(20) | 7860(40) | 5140(20) | 89(4) |
| H6b | 2610(60) | 8715(11) | 4652(6) | 89(4) |
| H6c | 2070(40) | 7680(40) | 5220(20) | 89(4) |
| H11a | 5710(50) | 11040(30) | 2894(12) | 87(4) |
| H11b | 5090(20) | 10626(14) | 3830(30) | 87(4) |
| H11c | 6230(30) | 11350(18) | 3590(40) | 87(4) |
| H10a | 8880(30) | 9450(20) | 2770(40) | 120(6) |
| H10b | 8050(20) | 10330(60) | 2246(13) | 120(6) |
| H10c | 8530(50) | 10630(50) | 2960(30) | 120(6) |
| H12a | 6430(15) | 9260(60) | 4677(9) | 106(5) |
| H12b | 7850(60) | 8730(30) | 4256(14) | 106(5) |
| H12c | 7630(70) | 9930(30) | 4400(20) | 106(5) |
| H34a | 1192(16) | 900(60) | 2308(12) | 97(4) |
| H34b | 1073(12) | 1420(30) | 1400(30) | 97(4) |
| H34c | 1379(11) | 160(20) | 1650(40) | 97(4) |
| H33a | 3130(60) | 1520(20) | 246(7) | 102(4) |
| H33b | 4431(10) | 770(60) | 407(11) | 102(4) |
| H33c | 3160(60) | 260(40) | 456(10) | 102(4) |
| H36 | 2008(7) | 1931(6) | 2779(4) | 39(2) |
| H41a | 3640(40) | 2636(14) | 4080(30) | 63(3) |
| H41b | 3820(30) | 3860(30) | 3800(18) | 63(3) |
| H41c | 2743(10) | 3500(40) | 4602(11) | 63(3) |
| H40a | 2171(8) | 5185(7) | 3270(30) | 67(3) |

| | | | | |
|---|---|---|---|---|
| H40b | 950(40) | 4859(13) | 3060(30) | 67(3) |
| H40c | 950(40) | 4847(13) | 3984(9) | 67(3) |
| H39a | 370(30) | 2970(40) | 3690(20) | 96(4) |
| H39b | 1441(17) | 2067(8) | 4010(40) | 96(4) |
| H39c | 710(50) | 2970(40) | 4535(15) | 96(4) |
| H35a | 4670(13) | -20(40) | 1770(40) | 131(6) |
| H35b | 3450(60) | 10(40) | 2539(10) | 131(6) |
| H35c | 3520(70) | -693(7) | 1870(40) | 131(6) |

**Crystallographic Table 25** Solvent masks information for **VO[L$^{I}$]**.

| **Number** | **X** | **Y** | **Z** | **Volume** | **Electron count** |
|---|---|---|---|---|---|
| 1 | 0.000 | 0.500 | 0.500 | 341.2 | 59.5 |
| 2 | 0.000 | 0.500 | 0.000 | 82.4 | 0.2 |

Refinement model description

Number of restraints - 0, number of constraints - 72.

Details:

1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C13(H13), C7(H7), C26(H26), C17(H17), C23(H23), C20(H20), C22(H22), C21(H21),
 C30(H30), C28(H28), C15(H15), C36(H36)
2.b Idealised Me refined as rotating group:
 C5(H5a,H5b,H5c), C4(H4a,H4b,H4c), C6(H6a,H6b,H6c), C11(H11a,H11b,H11c),
 C10(H10a,H10b,H10c), C12(H12a,H12b,H12c), C34(H34a,H34b,H34c),
C33(H33a,H33b,
 H33c), C41(H41a,H41b,H41c), C40(H40a,H40b,H40c), C39(H39a,H39b,H39c),
C35(H35a,
 H35b,H35c)

## $Zn[L^I]$

**Crystallographic Table 26** Crystal data and structure refinement for **$Zn[L^I]$**

| | |
|---|---|
| Empirical formula | $C_{43}H_{52}N_4O_3Zn$ |
| Formula weight | 738.31 |
| Temperature/K | 180.45 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 9.3102(5) |
| b/Å | 15.1537(7) |
| c/Å | 16.4769(8) |
| α/° | 105.875(2) |
| β/° | 100.257(2) |
| γ/° | 91.511(2) |
| Volume/Å$^3$ | 2193.30(19) |
| Z | 2 |
| $\rho_{calc}$mg/mm$^3$ | 1.1179 |
| m/mm$^{-1}$ | 0.599 |
| F(000) | 784.9 |
| Crystal size/mm$^3$ | 0.2 × 0.1 × 0.1 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 3.26 to 51.44° |
| Index ranges | $-11 \leq h \leq 11$, $-18 \leq k \leq 18$, $-20 \leq l \leq 20$ |
| Reflections collected | 43775 |
| Independent reflections | 8341 [$R_{int}$ = 0.0552, $R_{sigma}$ = 0.0462] |
| Data/restraints/parameters | 8341/1/476 |
| Goodness-of-fit on $F^2$ | 1.064 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0467, $wR_2$ = 0.1086 |
| Final R indexes [all data] | $R_1$ = 0.0614, $wR_2$ = 0.1186 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.59/-0.61 |

**Crystallographic Table 27** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for **$Zn[L^I]$**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Zn1 | 3184.2(3) | 3244.4(2) | 2731.92(18) | 22.58(10) |
| O1 | 3995(2) | 2082.2(12) | 2815.9(11) | 25.9(4) |
| O2 | 2306(2) | 2779.8(13) | 1514.3(11) | 29.2(4) |
| O3 | 5039(2) | 3993.9(14) | 2623.7(12) | 32.1(5) |

| | | | | |
|---|---|---|---|---|
| N1 | 3529(2) | 3706.8(13) | 4061.3(12) | 18.5(4) |
| N2 | 1606(2) | 4185.7(13) | 2895.9(12) | 19.7(4) |
| N4 | 146(2) | 6635.7(14) | 5118.6(14) | 26.5(5) |
| N3 | 2384(2) | 6225.3(14) | 6345.9(13) | 23.5(5) |
| C15 | 4360(3) | 3320.0(16) | 4568.9(15) | 20.2(5) |
| C6 | 5055(3) | 2488.3(17) | 4322.0(15) | 20.9(5) |
| C1 | 4801(3) | 1887.8(17) | 3457.0(16) | 20.5(5) |
| C2 | 5469(3) | 1018.5(17) | 3319.2(16) | 22.7(5) |
| C3 | 6379(3) | 854.5(17) | 4006.9(17) | 24.6(6) |
| C4 | 6674(3) | 1443.6(17) | 4860.3(16) | 23.9(6) |
| C5 | 5986(3) | 2242.6(18) | 4997.0(16) | 25.1(6) |
| C11 | 7718(3) | 1162.3(19) | 5564.2(18) | 30.4(6) |
| C13 | 9277(3) | 1179(2) | 5377(2) | 40.8(8) |
| C12 | 7727(4) | 1811(2) | 6458.7(18) | 45.0(8) |
| C14 | 7258(3) | 179(2) | 5568(2) | 41.2(8) |
| C7 | 5118(3) | 301.0(17) | 2426.8(16) | 25.0(6) |
| C8 | 5627(3) | 676(2) | 1734.5(18) | 33.7(7) |
| C9 | 3467(3) | 27.1(19) | 2164.3(18) | 31.3(6) |
| C10 | 5881(4) | -581.9(19) | 2436.2(19) | 38.0(7) |
| C16 | 2798(3) | 4494.4(16) | 4390.4(15) | 18.8(5) |
| C27 | 1696(3) | 4734.9(16) | 3751.0(15) | 18.0(5) |
| C28 | 579(3) | 4272.9(17) | 2277.1(16) | 22.6(5) |
| C29 | 332(3) | 3750.0(17) | 1394.1(15) | 22.3(5) |
| C30 | -860(3) | 3990.3(19) | 846.1(17) | 28.3(6) |
| C31 | -1264(3) | 3521(2) | -9.3(17) | 29.6(6) |
| C35 | -2543(3) | 3754(2) | -619.9(19) | 41.6(8) |
| C37 | -2050(4) | 3876(2) | -1419.0(19) | 46.4(8) |
| C38 | -3746(4) | 2973(4) | -885(4) | 112(2) |
| C36 | -3140(5) | 4654(4) | -195(2) | 103(2) |
| C32 | -465(3) | 2759.9(19) | -319.0(16) | 28.6(6) |
| C33 | 705(3) | 2480.5(18) | 165.6(16) | 24.8(6) |
| C39 | 1514(3) | 1638(2) | -211.6(17) | 31.1(6) |
| C42 | 786(4) | 1120(2) | -1141.2(19) | 44.4(8) |
| C41 | 1521(4) | 953(2) | 330(2) | 48.0(9) |
| C40 | 3095(3) | 1946(2) | -212.3(19) | 40.9(8) |
| C34 | 1171(3) | 3007.1(18) | 1054.1(16) | 22.8(6) |
| C26 | 858(3) | 5450.8(17) | 4011.1(16) | 23.8(6) |
| C25 | 1033(3) | 5962.8(16) | 4888.3(16) | 21.3(5) |

| | | | | |
|---|---|---|---|---|
| C24 | 353(3) | 7097.5(17) | 5961.2(18) | 26.7(6) |
| C19 | 1484(3) | 6897.7(17) | 6583.0(17) | 26.3(6) |
| C18 | 2160(3) | 5752.7(16) | 5509.2(16) | 20.2(5) |
| C17 | 3035(3) | 5016.1(16) | 5229.3(15) | 19.9(5) |
| C20 | 1630(3) | 7396.0(19) | 7462.8(18) | 33.8(7) |
| C21 | 701(3) | 8056(2) | 7705(2) | 40.9(8) |
| C22 | -396(3) | 8266(2) | 7096(2) | 42.0(8) |
| C23 | -579(3) | 7805.4(19) | 6244(2) | 36.6(7) |
| C43 | 5261(4) | 4059(3) | 1810(2) | 62.5(11) |

**Crystallographic Table 28** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **Zn[L$^I$]**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{12}$** | **$U_{13}$** | **$U_{23}$** |
|---|---|---|---|---|---|---|
| Zn1 | 26.03(18) | 22.46(17) | 17.66(16) | 6.54(12) | 3.51(12) | 3.04(12) |
| O1 | 36.7(11) | 21.2(9) | 17.7(9) | 10.2(8) | 3.2(8) | 2.7(7) |
| O2 | 32.0(11) | 32.8(11) | 17.7(9) | 10.5(8) | 1.2(8) | 0.4(8) |
| O3 | 30.8(11) | 40.0(12) | 26.1(10) | -1.9(9) | 3.1(9) | 12.5(9) |
| N1 | 21.8(11) | 15.6(10) | 17.1(10) | 4.2(8) | 4.2(8) | 2.3(8) |
| N2 | 23.0(11) | 18.0(11) | 18.3(10) | 4.3(8) | 4.2(9) | 4.6(8) |
| N4 | 25.9(12) | 17.7(11) | 34.2(13) | 4.7(9) | 9.8(10) | 1.9(10) |
| N3 | 26.3(12) | 20.3(11) | 21.4(11) | -0.6(9) | 8.7(9) | -0.5(9) |
| C15 | 24.9(13) | 18.8(13) | 14.8(12) | 1.7(10) | 4(1) | 1.4(10) |
| C6 | 24.1(13) | 19.2(13) | 21.1(13) | 4.2(10) | 6.4(10) | 6.8(10) |
| C1 | 21.0(13) | 20.4(13) | 22.5(13) | 2.5(10) | 9.3(10) | 6.8(10) |
| C2 | 25.0(14) | 21.0(13) | 23.8(13) | 3.5(11) | 10.0(11) | 5.8(11) |
| C3 | 25.1(14) | 19.5(13) | 32.0(14) | 9.2(11) | 10.3(11) | 8.0(11) |
| C4 | 23.5(14) | 23.5(14) | 26.0(14) | 5.0(11) | 4.9(11) | 8.7(11) |
| C5 | 28.8(14) | 26.0(14) | 19.1(13) | 5.7(11) | 3.2(11) | 4.6(11) |
| C11 | 29.7(15) | 29.6(15) | 33.1(15) | 10.7(12) | 2.9(12) | 12.2(12) |
| C13 | 29.0(16) | 44.4(19) | 52(2) | 8.5(14) | 3.6(14) | 21.2(16) |
| C12 | 52(2) | 50(2) | 29.0(16) | 23.8(16) | -3.5(14) | 9.3(14) |
| C14 | 43.3(19) | 44.6(19) | 40.8(18) | 4.3(15) | 1.4(14) | 24.8(15) |
| C7 | 30.7(15) | 19.9(13) | 24.8(13) | 6.7(11) | 10.0(11) | 3.7(11) |
| C8 | 42.1(17) | 32.6(16) | 27.8(15) | 3.5(13) | 17.1(13) | 4.3(12) |
| C9 | 36.5(16) | 26.1(15) | 28.1(15) | 1.0(12) | 10.4(12) | 0.1(12) |
| C10 | 50.6(19) | 25.2(15) | 35.5(16) | 12.8(14) | 12.0(14) | 0.9(13) |
| C16 | 20.0(13) | 15.0(12) | 21.2(12) | 0.9(10) | 5.5(10) | 4(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C27 | 18.8(12) | 14.8(12) | 20.1(12) | 0.4(10) | 5.6(10) | 3.7(10) |
| C28 | 24.7(14) | 21.3(13) | 23.7(13) | 6.4(11) | 6.3(11) | 7.9(11) |
| C29 | 23.0(13) | 25.7(14) | 19.1(12) | 0.2(11) | 2.8(10) | 8.6(11) |
| C30 | 26.8(14) | 35.0(16) | 26.3(14) | 8.4(12) | 7.7(11) | 11.6(12) |
| C31 | 19.4(14) | 47.2(18) | 25.0(14) | 0.9(12) | 2.9(11) | 15.8(13) |
| C35 | 27.1(16) | 73(2) | 29.7(16) | 8.5(15) | 2.8(13) | 24.2(16) |
| C37 | 47(2) | 66(2) | 28.7(16) | 12.3(17) | 1.0(14) | 22.6(16) |
| C38 | 30(2) | 179(5) | 145(5) | -37(3) | -38(3) | 114(4) |
| C36 | 105(4) | 181(5) | 36(2) | 111(4) | 13(2) | 41(3) |
| C32 | 24.8(14) | 40.0(16) | 17.6(13) | -5.8(12) | 3.5(11) | 3.9(12) |
| C33 | 21.7(13) | 32.4(15) | 19.2(13) | -4.1(11) | 4.2(10) | 6.1(11) |
| C39 | 30.5(15) | 35.7(16) | 20.3(13) | 1.1(12) | 3.6(11) | -2.1(12) |
| C42 | 41.0(18) | 50(2) | 29.7(16) | 3.7(15) | 3.4(14) | -7.3(14) |
| C41 | 71(2) | 26.8(16) | 43.0(19) | 6.4(16) | 13.6(17) | 1.7(14) |
| C40 | 31.1(16) | 53(2) | 30.6(16) | 4.9(14) | 7.3(13) | -2.1(14) |
| C34 | 20.8(13) | 26.8(14) | 21.4(13) | -3.4(11) | 4.3(10) | 8.1(11) |
| C26 | 24.1(14) | 22.3(13) | 22.0(13) | 5.5(11) | 0.7(10) | 3.6(11) |
| C25 | 20.9(13) | 13.9(12) | 28.4(14) | -0.2(10) | 7.2(11) | 3.4(10) |
| C24 | 26.4(14) | 17.7(13) | 34.4(15) | -1.0(11) | 13.9(12) | -0.1(11) |
| C19 | 26.5(14) | 18.5(13) | 32.8(15) | -3.7(11) | 16.1(12) | -0.8(11) |
| C18 | 21.8(13) | 15.1(12) | 22.1(13) | -1.3(10) | 7.5(10) | 0.5(10) |
| C17 | 19.7(13) | 20.2(13) | 18.8(12) | 2.7(10) | 3(1) | 4.2(10) |
| C20 | 38.0(17) | 30.2(15) | 29.2(15) | -1.3(13) | 14.4(13) | -2.9(12) |
| C21 | 44.1(19) | 32.9(17) | 40.0(18) | -4.9(14) | 26.4(15) | -9.8(14) |
| C22 | 35.1(17) | 29.3(16) | 57(2) | 2.3(13) | 28.0(16) | -7.7(15) |
| C23 | 30.5(16) | 24.6(15) | 52.6(19) | 5.3(12) | 18.2(14) | 0.4(13) |
| C43 | 61(2) | 91(3) | 43(2) | -19(2) | 7.3(18) | 35(2) |

**Crystallographic Table 29** Bond Lengths for **Zn[L$^{I}$]**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Zn1 | O1 | 1.9637(17) | C7 | C9 | 1.534(4) |
| Zn1 | O2 | 1.9499(17) | C7 | C10 | 1.534(4) |
| Zn1 | O3 | 2.1024(19) | C16 | C27 | 1.463(3) |
| Zn1 | N1 | 2.0713(19) | C16 | C17 | 1.367(3) |
| Zn1 | N2 | 2.075(2) | C27 | C26 | 1.371(3) |
| O1 | C1 | 1.291(3) | C28 | C29 | 1.428(3) |
| O2 | C34 | 1.299(3) | C29 | C30 | 1.423(4) |

| | | | | | |
|---|---|---|---|---|---|
| O3 | C43 | 1.421(4) | C29 | C34 | 1.431(4) |
| N1 | C15 | 1.305(3) | C30 | C31 | 1.372(4) |
| N1 | C16 | 1.415(3) | C31 | C35 | 1.532(4) |
| N2 | C27 | 1.413(3) | C31 | C32 | 1.415(4) |
| N2 | C28 | 1.306(3) | C35 | C37 | 1.524(4) |
| N4 | C25 | 1.345(3) | C35 | C38 | 1.523(5) |
| N4 | C24 | 1.349(3) | C35 | C36 | 1.521(5) |
| N3 | C19 | 1.355(3) | C32 | C33 | 1.379(4) |
| N3 | C18 | 1.344(3) | C33 | C39 | 1.538(4) |
| C15 | C6 | 1.424(3) | C33 | C34 | 1.444(3) |
| C6 | C1 | 1.440(3) | C39 | C42 | 1.538(4) |
| C6 | C5 | 1.424(3) | C39 | C41 | 1.543(4) |
| C1 | C2 | 1.450(3) | C39 | C40 | 1.532(4) |
| C2 | C3 | 1.374(4) | C26 | C25 | 1.419(3) |
| C2 | C7 | 1.545(3) | C25 | C18 | 1.436(3) |
| C3 | C4 | 1.419(4) | C24 | C19 | 1.432(4) |
| C4 | C5 | 1.367(4) | C24 | C23 | 1.429(4) |
| C4 | C11 | 1.537(4) | C19 | C20 | 1.420(4) |
| C11 | C13 | 1.538(4) | C18 | C17 | 1.422(3) |
| C11 | C12 | 1.530(4) | C20 | C21 | 1.364(4) |
| C11 | C14 | 1.542(4) | C21 | C22 | 1.406(5) |
| C7 | C8 | 1.544(4) | C22 | C23 | 1.364(4) |

**Crystallographic Table 30** Bond Angles for **Zn[L$^{I}$]**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| O2 | Zn1 | O1 | 94.93(7) | C17 | C16 | C27 | 119.7(2) |
| O3 | Zn1 | O1 | 101.34(8) | C16 | C27 | N2 | 115.0(2) |
| O3 | Zn1 | O2 | 98.66(8) | C26 | C27 | N2 | 125.7(2) |
| N1 | Zn1 | O1 | 89.46(7) | C26 | C27 | C16 | 119.4(2) |
| N1 | Zn1 | O2 | 164.37(8) | C29 | C28 | N2 | 127.0(2) |
| N1 | Zn1 | O3 | 95.17(8) | C30 | C29 | C28 | 115.8(2) |
| N2 | Zn1 | O1 | 152.16(8) | C34 | C29 | C28 | 124.2(2) |
| N2 | Zn1 | O2 | 89.89(8) | C34 | C29 | C30 | 120.0(2) |
| N2 | Zn1 | O3 | 105.01(8) | C31 | C30 | C29 | 122.2(3) |
| N2 | Zn1 | N1 | 79.46(8) | C35 | C31 | C30 | 123.8(3) |
| C1 | O1 | Zn1 | 130.08(16) | C32 | C31 | C30 | 116.6(2) |
| C34 | O2 | Zn1 | 131.72(16) | C32 | C31 | C35 | 119.5(2) |
| C43 | O3 | Zn1 | 120.97(19) | C37 | C35 | C31 | 110.7(2) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C15 | N1 | Zn1 | 123.74(16) | C38 | C35 | C31 | 108.8(3) |
| C16 | N1 | Zn1 | 114.68(15) | C38 | C35 | C37 | 109.3(3) |
| C16 | N1 | C15 | 121.6(2) | C36 | C35 | C31 | 111.2(3) |
| C27 | N2 | Zn1 | 114.74(15) | C36 | C35 | C37 | 106.8(3) |
| C28 | N2 | Zn1 | 124.29(17) | C36 | C35 | C38 | 109.9(4) |
| C28 | N2 | C27 | 121.0(2) | C33 | C32 | C31 | 125.0(2) |
| C24 | N4 | C25 | 116.9(2) | C39 | C33 | C32 | 122.2(2) |
| C18 | N3 | C19 | 117.2(2) | C34 | C33 | C32 | 118.0(2) |
| C6 | C15 | N1 | 127.0(2) | C34 | C33 | C39 | 119.8(2) |
| C1 | C6 | C15 | 123.6(2) | C42 | C39 | C33 | 112.3(2) |
| C5 | C6 | C15 | 116.0(2) | C41 | C39 | C33 | 110.0(2) |
| C5 | C6 | C1 | 120.3(2) | C41 | C39 | C42 | 107.3(2) |
| C6 | C1 | O1 | 123.1(2) | C40 | C39 | C33 | 109.8(2) |
| C2 | C1 | O1 | 119.5(2) | C40 | C39 | C42 | 108.0(2) |
| C2 | C1 | C6 | 117.4(2) | C40 | C39 | C41 | 109.3(3) |
| C3 | C2 | C1 | 117.9(2) | C29 | C34 | O2 | 122.8(2) |
| C7 | C2 | C1 | 120.0(2) | C33 | C34 | O2 | 119.1(2) |
| C7 | C2 | C3 | 122.0(2) | C33 | C34 | C29 | 118.0(2) |
| C4 | C3 | C2 | 125.7(2) | C25 | C26 | C27 | 121.4(2) |
| C5 | C4 | C3 | 116.2(2) | C26 | C25 | N4 | 119.3(2) |
| C11 | C4 | C3 | 119.6(2) | C18 | C25 | N4 | 121.6(2) |
| C11 | C4 | C5 | 124.2(2) | C18 | C25 | C26 | 119.1(2) |
| C4 | C5 | C6 | 122.4(2) | C19 | C24 | N4 | 121.8(2) |
| C13 | C11 | C4 | 108.9(2) | C23 | C24 | N4 | 119.2(3) |
| C12 | C11 | C4 | 111.9(2) | C23 | C24 | C19 | 118.9(2) |
| C12 | C11 | C13 | 108.9(2) | C24 | C19 | N3 | 121.0(2) |
| C14 | C11 | C4 | 110.3(2) | C20 | C19 | N3 | 119.8(3) |
| C14 | C11 | C13 | 108.5(2) | C20 | C19 | C24 | 119.2(2) |
| C14 | C11 | C12 | 108.2(2) | C25 | C18 | N3 | 121.5(2) |
| C8 | C7 | C2 | 111.4(2) | C17 | C18 | N3 | 119.7(2) |
| C9 | C7 | C2 | 110.2(2) | C17 | C18 | C25 | 118.9(2) |
| C9 | C7 | C8 | 109.3(2) | C18 | C17 | C16 | 121.3(2) |
| C10 | C7 | C2 | 111.3(2) | C21 | C20 | C19 | 119.9(3) |
| C10 | C7 | C8 | 107.5(2) | C22 | C21 | C20 | 121.2(3) |
| C10 | C7 | C9 | 107.0(2) | C23 | C22 | C21 | 121.0(3) |
| C27 | C16 | N1 | 114.6(2) | C22 | C23 | C24 | 119.8(3) |
| C17 | C16 | N1 | 125.7(2) | | | | |

**Crystallographic Table 31** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **Zn[L$^I$]**.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H15 | 4519(3) | 3626.1(16) | 5167.0(15) | 24.2(6) |
| H3a | 6853(3) | 298.1(17) | 3901.7(17) | 29.5(7) |
| H5 | 6135(3) | 2648.6(18) | 5562.8(16) | 30.1(7) |
| H13a | 9613(9) | 1810(3) | 5416(13) | 61.2(11) |
| H13b | 9937(5) | 956(14) | 5798(8) | 61.2(11) |
| H13c | 9275(5) | 780(11) | 4797(5) | 61.2(11) |
| H12a | 8375(19) | 1597(9) | 6891(2) | 67.5(13) |
| H12b | 8080(20) | 2434(4) | 6481(5) | 67.5(13) |
| H12c | 6732(6) | 1819(12) | 6577(6) | 67.5(13) |
| H14a | 7916(14) | 14(6) | 6029(9) | 61.8(11) |
| H14b | 6251(9) | 152(4) | 5665(13) | 61.8(11) |
| H14c | 7310(20) | -255(3) | 5013(5) | 61.8(11) |
| H8a | 6695(4) | 797(12) | 1872(7) | 50.5(10) |
| H8b | 5338(18) | 221(6) | 1171(3) | 50.5(10) |
| H8c | 5172(16) | 1249(7) | 1721(8) | 50.5(10) |
| H9a | 3265(4) | -455(9) | 1615(6) | 46.9(10) |
| H9b | 3138(5) | -204(12) | 2606(6) | 46.9(10) |
| H9c | 2944(3) | 565(4) | 2104(12) | 46.9(10) |
| H10a | 5586(17) | -835(8) | 2874(9) | 57.0(11) |
| H10b | 5600(18) | -1034(5) | 1871(4) | 57.0(11) |
| H10c | 6945(4) | -441(3) | 2569(13) | 57.0(11) |
| H28 | -75(3) | 4733.6(17) | 2430.9(16) | 27.1(7) |
| H30 | -1394(3) | 4492.1(19) | 1080.3(17) | 34.0(7) |
| H37a | -1242(16) | 4358(11) | -1248(2) | 69.6(13) |
| H37b | -1720(20) | 3296(5) | -1735(8) | 69.6(13) |
| H37c | -2870(7) | 4053(15) | -1788(7) | 69.6(13) |
| H38a | -3355(13) | 2396(7) | -1160(20) | 168(3) |
| H38b | -4100(30) | 2914(19) | -376(5) | 168(3) |
| H38c | -4560(20) | 3106(15) | -1290(20) | 168(3) |
| H36a | -3420(40) | 4617(11) | 343(13) | 155(3) |
| H36b | -2386(16) | 5161(5) | -70(20) | 155(3) |
| H36c | -4000(30) | 4762(15) | -582(11) | 155(3) |
| H32 | -756(3) | 2415.1(19) | -905.2(16) | 34.3(7) |
| H42a | 790(20) | 1531(5) | -1508(3) | 66.6(12) |
| H42b | 1328(14) | 585(9) | -1351(5) | 66.6(12) |

| | | | | |
|---|---|---|---|---|
| H42c | -227(8) | 913(13) | -1157(3) | 66.6(12) |
| H41a | 1970(20) | 397(7) | 59(8) | 72.1(13) |
| H41b | 2090(20) | 1237(6) | 910(5) | 72.1(13) |
| H41c | 513(4) | 787(12) | 363(12) | 72.1(13) |
| H40a | 3618(7) | 1405(2) | -431(13) | 61.4(12) |
| H40b | 3094(3) | 2354(12) | -582(11) | 61.4(12) |
| H40c | 3585(8) | 2274(13) | 375(3) | 61.4(12) |
| H26 | 145(3) | 5607.7(17) | 3595.2(16) | 28.5(7) |
| H17 | 3800(3) | 4884.1(16) | 5633.6(15) | 23.8(6) |
| H20 | 2374(3) | 7269.6(19) | 7881.9(18) | 40.6(8) |
| H21 | 796(3) | 8381(2) | 8296(2) | 49.0(9) |
| H22 | -1020(3) | 8735(2) | 7282(2) | 50.4(10) |
| H23 | -1324(3) | 7954.9(19) | 5839(2) | 44.0(9) |
| H43a | 5490(30) | 3459(6) | 1470(7) | 93.8(17) |
| H43b | 4370(11) | 4246(18) | 1507(7) | 93.8(17) |
| H43c | 6077(19) | 4517(14) | 1893(2) | 93.8(17) |
| H3 | 5880(30) | 3910(20) | 2960(20) | 65(12) |

**Crystallographic Table 32** Solvent masks information for **Zn[L$^{I}$]**.

| Number | X | Y | Z | Volume | Electron count | Content |
|---|---|---|---|---|---|---|
| 1 | -0.267 | -0.290 | 0.291 | 177.6 | 35.4 | 2 MeOH |
| 2 | 0.267 | 0.290 | 0.709 | 177.6 | 35.6 | 2 MeOH |
| 3 | 0.309 | 0.856 | 0.975 | 35.5 | 0.0 | ? |
| 4 | 0.691 | 0.144 | 0.025 | 35.5 | 0.0 | ? |

Refinement model description

Number of restraints - 1, number of constraints - 76.

Details:

N/A

## $Fe[L^I]$-O-$Fe[L^I]$

**Crystallographic Table 33** Crystal data and structure refinement for **$Fe[L^I]$-O-$Fe[L^I]$**

| | |
|---|---|
| Empirical formula | $C_{92}H_{112}Fe_2N_8O_7$ |
| Formula weight | 1553.60 |
| Temperature/K | 180(2) |
| Crystal system | monoclinic |
| Space group | C2/c |
| a/Å | 18.9491(3) |
| b/Å | 41.3420(7) |
| c/Å | 13.8422(2) |
| α/° | 90.00 |
| β/° | 128.2090(10) |
| γ/° | 90.00 |
| Volume/Å$^3$ | 8520.7(2) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.136 |
| m/mm$^{-1}$ | 0.399 |
| F(000) | 3088.0 |
| Crystal size/mm$^3$ | 0.1 × 0.1 × 0.08 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection | 1.98 to 55.48° |
| Index ranges | $-24 \le h \le 24$, $-52 \le k \le 53$, $-16 \le l \le 17$ |
| Reflections collected | 50375 |
| Independent reflections | 9764 [$R_{int}$ = 0.0359, $R_{sigma}$ = 0.0360] |
| Data/restraints/parameters | 9764/0/505 |
| Goodness-of-fit on $F^2$ | 1.033 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0557, $wR_2$ = 0.1510 |
| Final R indexes [all data] | $R_1$ = 0.0845, $wR_2$ = 0.1739 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.74/-0.55 |

**Crystallographic Table 34** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for **$Fe[L^I]$-O-$Fe[L^I]$**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Fe1 | 9557.1(2) | 1191.68(7) | 5962.5(3) | 34.58(13) |
| C1 | 9638.9(14) | 464.1(5) | 5967(2) | 32.5(5) |
| C2 | 9476.0(15) | 141.5(6) | 5953(2) | 36.5(5) |
| C6 | 11214(3) | -1164.5(7) | 7212(3) | 72.3(11) |

| | | | | |
|---|---|---|---|---|
| C11 | 11186.8(16) | 351.9(6) | 6804(2) | 38.2(5) |
| C12 | 10504.5(15) | 568.9(5) | 6345(2) | 33.3(5) |
| C3 | 10166.2(16) | -91.1(5) | 6375(2) | 36.5(5) |
| C4 | 10663(2) | -613.2(6) | 6786(2) | 48.4(7) |
| C10 | 11038.2(16) | 17.7(6) | 6833(2) | 37.7(5) |
| C9 | 11533.2(19) | -505.1(6) | 7230(3) | 47.3(6) |
| C5 | 10517(2) | -950.1(7) | 6802(3) | 66.0(9) |
| C8 | 12220(2) | -737.1(7) | 7634(3) | 61.9(8) |
| C7 | 12058(3) | -1057.0(8) | 7629(3) | 73.8(10) |
| N1 | 9029.3(12) | 719.6(4) | 5635.5(18) | 33.1(4) |
| N2 | 10558.7(13) | 903.1(4) | 6179.8(19) | 35.1(4) |
| C13 | 11204.7(16) | 1012.4(6) | 6182(2) | 39.8(6) |
| C14 | 11320.4(16) | 1338.5(6) | 5965(2) | 40.1(6) |
| C15 | 12086.6(16) | 1401.6(6) | 6035(3) | 43.7(6) |
| C19 | 10685.2(16) | 1587.6(6) | 5615(2) | 40.2(6) |
| C16 | 12249.7(16) | 1701.9(6) | 5799(3) | 44.8(6) |
| C18 | 10864.8(17) | 1906.2(6) | 5409(3) | 46.3(6) |
| C17 | 11630.4(17) | 1948.1(6) | 5508(3) | 48.4(7) |
| C20 | 8269.4(15) | 665.1(6) | 5426(2) | 35.8(5) |
| C22 | 7674.6(15) | 1231.4(6) | 4920(3) | 41.7(6) |
| C26 | 6863.1(16) | 786.6(6) | 5043(2) | 42.6(6) |
| C21 | 7605.6(15) | 898.8(6) | 5125(2) | 38.5(5) |
| C23 | 6998.9(16) | 1449.3(6) | 4692(3) | 50.7(7) |
| C25 | 6203.1(16) | 993.0(7) | 4788(3) | 46.5(6) |
| C24 | 6304.8(17) | 1322.5(7) | 4636(3) | 52.3(7) |
| C27 | 13058.0(18) | 1781.5(7) | 5843(3) | 51.1(7) |
| C28 | 13619(2) | 1480.2(8) | 6082(4) | 66.0(9) |
| C29 | 13650(2) | 2029.3(9) | 6865(3) | 72.1(10) |
| C30 | 12726(2) | 1927.0(8) | 4605(3) | 66.0(9) |
| C31 | 10215.8(19) | 2184.9(6) | 5091(3) | 58.9(8) |
| C32 | 10141(3) | 2230.6(8) | 6121(4) | 76.5(11) |
| C33 | 10546(2) | 2506.3(7) | 4944(4) | 82.5(13) |
| C34 | 9290(2) | 2115.2(8) | 3864(4) | 73.7(11) |
| C35 | 7071.8(19) | 1812.6(7) | 4540(4) | 74.9(12) |
| C36 | 7949(2) | 1942.7(8) | 5733(5) | 94.7(15) |
| C37 | 7050(2) | 1872.7(9) | 3435(4) | 94.6(15) |
| C38 | 6292(3) | 2004.3(8) | 4339(6) | 112.1(19) |
| C39 | 5384.9(19) | 885.4(8) | 4689(3) | 59.0(8) |

| | | | | |
|---|---|---|---|---|
| C42 | 5295(3) | 521(1) | 4637(6) | 107.3(18) |
| C40 | 5468(3) | 1018.5(12) | 5772(5) | 96.4(14) |
| C41 | 4528(2) | 1022.0(15) | 3509(5) | 116.9(19) |
| N4 | 11721.5(15) | -190.2(5) | 7261(2) | 47.1(5) |
| N3 | 9979.5(15) | -405.8(5) | 6350(2) | 45.0(5) |
| O2 | 9946.1(11) | 1530.8(4) | 5457.6(19) | 46.4(5) |
| O1 | 8330.4(11) | 1336.0(4) | 4939.3(18) | 46.7(5) |
| O3 | 10000 | 1260.2(6) | 7500 | 43.5(6) |
| O6 | 2875(3) | 458.4(15) | 6590(5) | 179(2) |
| C53 | 2753(5) | 489.7(15) | 5544(7) | 136(2) |
| C55 | 3313(7) | 247(3) | 5530(7) | 254(6) |
| C57 | 3331(5) | 108(3) | 6972(11) | 226(6) |
| C56 | 3731(12) | 71(4) | 6606(14) | 335(10) |

**Crystallographic Table 35** Anisotropic Displacement Parameters ($Å^2×10^3$) for **Fe[L$^I$]-O-Fe[L$^I$]**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{23}$** | **$U_{13}$** | **$U_{12}$** |
|---|---|---|---|---|---|---|
| Fe1 | 33.81(19) | 21.82(19) | 53.3(3) | 7.26(14) | 29.53(18) | 4.60(12) |
| C1 | 38.5(11) | 24.9(11) | 33.3(12) | 5.1(9) | 21.8(10) | 6.1(8) |
| C2 | 39.0(12) | 27.4(12) | 38.1(13) | 2.6(10) | 21.3(11) | 1.6(9) |
| C6 | 95(3) | 27.5(14) | 62(2) | 11.1(13) | 32.0(19) | 21.2(15) |
| C11 | 43.3(12) | 34.4(13) | 45.3(14) | 9.9(11) | 31.6(11) | 10.1(10) |
| C12 | 43.1(12) | 25.7(11) | 39.5(13) | 5.4(9) | 29.8(11) | 5.7(9) |
| C3 | 49.0(13) | 24.2(11) | 31.4(12) | 4.7(9) | 22.4(11) | 7.8(9) |
| C4 | 65.3(17) | 28.0(13) | 35.3(14) | 4.8(10) | 22.7(13) | 13.0(11) |
| C10 | 48.4(13) | 32.1(12) | 36.6(13) | 9.2(10) | 28.3(11) | 12.2(10) |
| C9 | 61.9(16) | 33.2(13) | 48.0(16) | 11.6(12) | 34.6(14) | 17.8(12) |
| C5 | 77(2) | 29.5(14) | 56.7(19) | 6.0(13) | 24.1(16) | 9.1(13) |
| C8 | 75(2) | 43.0(16) | 71(2) | 20.4(15) | 46.9(18) | 28.4(15) |
| C7 | 85(2) | 48.3(19) | 79(2) | 19.0(17) | 46(2) | 35.4(18) |
| N1 | 32.8(9) | 24.1(9) | 41.8(11) | 4.1(8) | 22.7(9) | 3.7(7) |
| N2 | 38.4(10) | 25.7(10) | 48.2(12) | 8.5(8) | 30.3(9) | 6.5(7) |
| C13 | 39.1(12) | 32.2(12) | 55.0(16) | 9.1(11) | 32.7(12) | 8.2(9) |
| C14 | 37.6(12) | 33.7(13) | 50.8(15) | 9.1(11) | 28.2(11) | 2.9(9) |
| C15 | 37.8(12) | 39.3(14) | 55.4(16) | 6.6(12) | 29.4(12) | 1.4(10) |
| C19 | 39.2(12) | 32.1(12) | 52.4(15) | 10.9(11) | 29.9(12) | 3.9(9) |
| C16 | 38.0(12) | 43.2(14) | 51.3(16) | 4.9(12) | 26.7(12) | -6.4(10) |
| C18 | 41.7(13) | 32.7(13) | 58.8(17) | 11.9(12) | 28.2(12) | 0.9(10) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C17 | 43.8(13) | 36.4(14) | 58.3(17) | 10.0(12) | 28.3(13) | -4.9(11) |
| C20 | 40.7(12) | 24.9(11) | 43.6(14) | 0.5(10) | 27.0(11) | -0.8(9) |
| C22 | 30.7(11) | 32.7(13) | 51.5(16) | 0.5(11) | 20.4(11) | 1.8(9) |
| C26 | 39.2(12) | 36.7(13) | 53.3(16) | -6.7(11) | 29.3(12) | -6.8(10) |
| C21 | 34.8(11) | 31.0(12) | 48.2(15) | -1(1) | 25.0(11) | -1.2(9) |
| C23 | 33.8(12) | 33.6(13) | 70.4(19) | -2.8(13) | 25.1(13) | 2(1) |
| C25 | 34.5(12) | 50.4(16) | 54.2(16) | -11.3(13) | 27.3(12) | -5.9(11) |
| C24 | 34.5(12) | 42.8(15) | 73(2) | -9.4(14) | 29.6(13) | 1.9(10) |
| C27 | 42.4(13) | 51.8(16) | 60.5(18) | 0.9(14) | 32.5(13) | -11.7(12) |
| C28 | 55.5(17) | 68(2) | 95(3) | 10.6(18) | 57.2(18) | 0.0(15) |
| C29 | 51.7(17) | 84(3) | 80(2) | -19.6(19) | 40.3(17) | -27.0(16) |
| C30 | 66.3(19) | 62(2) | 78(2) | 4.6(17) | 48.7(18) | -17.0(15) |
| C31 | 48.4(15) | 30.1(14) | 90(2) | 20.0(14) | 38.9(16) | 5.7(11) |
| C32 | 81(2) | 38.1(17) | 124(3) | 9.1(19) | 71(2) | 16.1(15) |
| C33 | 66(2) | 33.4(16) | 136(4) | 26.8(19) | 57(2) | 4.0(14) |
| C34 | 47.9(16) | 49.5(18) | 97(3) | 33.8(18) | 31.9(17) | 9.6(13) |
| C35 | 42.1(15) | 32.4(15) | 133(3) | 2.3(18) | 45.7(19) | 6.6(11) |
| C36 | 57.7(19) | 39.6(18) | 157(4) | -27(2) | 52(2) | -9.0(14) |
| C37 | 63(2) | 53(2) | 139(4) | 42(2) | 48(2) | 15.8(16) |
| C38 | 65(2) | 39.8(18) | 217(6) | -2(2) | 80(3) | 12.6(15) |
| C39 | 47.2(15) | 67(2) | 77(2) | -11.6(16) | 45.1(16) | -9.0(13) |
| C42 | 108(3) | 75(3) | 206(5) | -42(3) | 131(4) | -38(2) |
| C40 | 116(3) | 99(3) | 129(4) | -23(3) | 103(3) | -16(3) |
| C41 | 38.8(18) | 173(5) | 120(4) | 26(3) | 40(2) | -13(2) |
| N4 | 57.7(13) | 37.8(12) | 55.4(14) | 16.4(10) | 39.8(12) | 19.6(10) |
| N3 | 53.0(12) | 26.3(10) | 40.0(12) | 3.0(9) | 20.8(10) | 4.9(9) |
| O2 | 45.4(9) | 29.2(9) | 74.6(13) | 19.3(8) | 42(1) | 10.0(7) |
| O1 | 34.5(8) | 29.2(9) | 72.8(13) | 11.0(8) | 31.3(9) | 5.9(7) |
| O3 | 49.8(14) | 27.9(12) | 60.7(17) | 0 | 38.1(13) | 0 |
| O6 | 161(4) | 246(6) | 170(4) | 71(4) | 123(4) | 91(4) |
| C53 | 205(7) | 100(4) | 152(6) | 14(4) | 136(6) | 18(4) |
| C55 | 299(12) | 347(14) | 104(5) | 83(7) | 119(7) | 211(11) |
| C57 | 117(5) | 264(11) | 317(14) | 204(11) | 144(7) | 86(6) |
| C56 | 410(20) | 349(19) | 274(15) | 78(13) | 229(17) | 256(18) |

**Crystallographic Table 36** Bond Lengths for **Fe[$L^I$]-O-Fe[$L^I$]**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Fe1 | N1 | 2.1105(19) | C16 | C27 | 1.530(3) |

| | | | | | |
|---|---|---|---|---|---|
| Fe1 | N2 | 2.1000(18) | C18 | C17 | 1.381(4) |
| Fe1 | O2 | 1.9064(17) | C18 | C31 | 1.537(4) |
| Fe1 | O1 | 1.9216(16) | C20 | C21 | 1.429(3) |
| Fe1 | O3 | 1.7619(5) | C22 | C21 | 1.427(3) |
| C1 | C2 | 1.367(3) | C22 | C23 | 1.432(3) |
| C1 | C12 | 1.446(3) | C22 | O1 | 1.301(3) |
| C1 | N1 | 1.416(3) | C26 | C21 | 1.417(3) |
| C2 | C3 | 1.425(3) | C26 | C25 | 1.368(4) |
| C6 | C5 | 1.388(5) | C23 | C24 | 1.373(4) |
| C6 | C7 | 1.395(5) | C23 | C35 | 1.535(4) |
| C11 | C12 | 1.365(3) | C25 | C24 | 1.409(4) |
| C11 | C10 | 1.416(3) | C25 | C39 | 1.536(4) |
| C12 | N2 | 1.415(3) | C27 | C28 | 1.535(4) |
| C3 | C10 | 1.428(4) | C27 | C29 | 1.531(4) |
| C3 | N3 | 1.343(3) | C27 | C30 | 1.537(4) |
| C4 | C9 | 1.429(4) | C31 | C32 | 1.529(5) |
| C4 | C5 | 1.423(4) | C31 | C33 | 1.535(4) |
| C4 | N3 | 1.346(3) | C31 | C34 | 1.536(5) |
| C10 | N4 | 1.348(3) | C35 | C36 | 1.544(5) |
| C9 | C8 | 1.424(4) | C35 | C37 | 1.524(6) |
| C9 | N4 | 1.343(3) | C35 | C38 | 1.543(4) |
| C8 | C7 | 1.357(5) | C39 | C42 | 1.513(5) |
| N1 | C20 | 1.301(3) | C39 | C40 | 1.512(5) |
| N2 | C13 | 1.303(3) | C39 | C41 | 1.531(5) |
| C13 | C14 | 1.428(3) | O3 | Fe1[1] | 1.7619(5) |
| C14 | C15 | 1.418(3) | O6 | C53 | 1.324(7) |
| C14 | C19 | 1.422(3) | O6 | C57 | 1.601(10) |
| C15 | C16 | 1.367(4) | C53 | C55 | 1.471(9) |
| C19 | C18 | 1.433(3) | C55 | C56 | 1.384(13) |
| C19 | O2 | 1.299(3) | C57 | C56 | 1.153(12) |
| C16 | C17 | 1.411(4) | | | |

[1]2-X,+Y,3/2-Z

**Crystallographic Table 37** Bond Angles for **Fe[L$^{I}$]-O-Fe[L$^{I}$]**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| N2 | Fe1 | N1 | 76.81(7) | C17 | C18 | C19 | 117.4(2) |
| O2 | Fe1 | N1 | 147.22(9) | C17 | C18 | C31 | 122.7(2) |
| O2 | Fe1 | N2 | 87.14(7) | C18 | C17 | C16 | 125.1(2) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O2 | Fe1 | O1 | 93.86(7) | N1 | C20 | C21 | 127.0(2) |
| O1 | Fe1 | N1 | 86.12(7) | C21 | C22 | C23 | 118.1(2) |
| O1 | Fe1 | N2 | 148.88(9) | O1 | C22 | C21 | 121.4(2) |
| O3 | Fe1 | N1 | 102.48(9) | O1 | C22 | C23 | 120.6(2) |
| O3 | Fe1 | N2 | 101.84(7) | C25 | C26 | C21 | 121.4(2) |
| O3 | Fe1 | O2 | 108.74(9) | C22 | C21 | C20 | 122.5(2) |
| O3 | Fe1 | O1 | 107.20(7) | C26 | C21 | C20 | 117.0(2) |
| C2 | C1 | C12 | 119.6(2) | C26 | C21 | C22 | 120.5(2) |
| C2 | C1 | N1 | 126.3(2) | C22 | C23 | C35 | 120.1(2) |
| N1 | C1 | C12 | 114.17(19) | C24 | C23 | C22 | 117.8(2) |
| C1 | C2 | C3 | 120.7(2) | C24 | C23 | C35 | 122.0(2) |
| C5 | C6 | C7 | 121.6(3) | C26 | C25 | C24 | 117.0(2) |
| C12 | C11 | C10 | 120.5(2) | C26 | C25 | C39 | 123.6(3) |
| C11 | C12 | C1 | 120.5(2) | C24 | C25 | C39 | 119.3(2) |
| C11 | C12 | N2 | 125.1(2) | C23 | C24 | C25 | 125.1(2) |
| N2 | C12 | C1 | 114.44(18) | C16 | C27 | C28 | 112.2(2) |
| C2 | C3 | C10 | 119.1(2) | C16 | C27 | C29 | 108.9(3) |
| N3 | C3 | C2 | 118.9(2) | C16 | C27 | C30 | 109.3(2) |
| N3 | C3 | C10 | 122.1(2) | C28 | C27 | C30 | 108.0(3) |
| C5 | C4 | C9 | 118.9(3) | C29 | C27 | C28 | 109.3(3) |
| N3 | C4 | C9 | 121.9(2) | C29 | C27 | C30 | 109.2(3) |
| N3 | C4 | C5 | 119.2(3) | C32 | C31 | C18 | 110.2(3) |
| C11 | C10 | C3 | 119.4(2) | C32 | C31 | C33 | 107.3(3) |
| N4 | C10 | C11 | 118.8(2) | C32 | C31 | C34 | 110.7(3) |
| N4 | C10 | C3 | 121.8(2) | C33 | C31 | C18 | 111.6(2) |
| C8 | C9 | C4 | 119.3(3) | C33 | C31 | C34 | 107.2(3) |
| N4 | C9 | C4 | 122.0(2) | C34 | C31 | C18 | 109.9(3) |
| N4 | C9 | C8 | 118.7(3) | C23 | C35 | C36 | 108.8(3) |
| C6 | C5 | C4 | 119.1(3) | C23 | C35 | C38 | 111.7(3) |
| C7 | C8 | C9 | 120.4(3) | C37 | C35 | C23 | 110.4(3) |
| C8 | C7 | C6 | 120.7(3) | C37 | C35 | C36 | 111.0(3) |
| C1 | N1 | Fe1 | 115.90(14) | C37 | C35 | C38 | 107.9(3) |
| C20 | N1 | Fe1 | 121.36(15) | C38 | C35 | C36 | 106.9(3) |
| C20 | N1 | C1 | 120.8(2) | C42 | C39 | C25 | 111.8(2) |
| C12 | N2 | Fe1 | 115.37(14) | C42 | C39 | C41 | 107.6(4) |
| C13 | N2 | Fe1 | 124.60(16) | C40 | C39 | C25 | 109.1(3) |
| C13 | N2 | C12 | 120.03(19) | C40 | C39 | C42 | 110.4(4) |
| N2 | C13 | C14 | 126.4(2) | C40 | C39 | C41 | 108.3(4) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C15 | C14 | C13 | 116.3(2) | C41 | C39 | C25 | 109.5(3) |
| C15 | C14 | C19 | 120.3(2) | C9 | N4 | C10 | 116.1(2) |
| C19 | C14 | C13 | 123.2(2) | C3 | N3 | C4 | 116.1(2) |
| C16 | C15 | C14 | 121.6(2) | C19 | O2 | Fe1 | 133.86(15) |
| C14 | C19 | C18 | 118.6(2) | C22 | O1 | Fe1 | 128.09(16) |
| O2 | C19 | C14 | 121.6(2) | Fe1[1] | O3 | Fe1 | 161.51(15) |
| O2 | C19 | C18 | 119.8(2) | C53 | O6 | C57 | 98.2(6) |
| C15 | C16 | C17 | 116.9(2) | O6 | C53 | C55 | 107.9(6) |
| C15 | C16 | C27 | 123.7(2) | C56 | C55 | C53 | 106.4(7) |
| C17 | C16 | C27 | 119.4(2) | C56 | C57 | O6 | 110.0(10) |
| C19 | C18 | C31 | 120.0(2) | C57 | C56 | C55 | 108.0(11) |

[1]2-X,+Y,3/2-Z

**Crystallographic Table 38** Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for **Fe[L$^I$]-O-Fe[L$^I$]**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H2 | 8897 | 72 | 5660 | 44 |
| H6 | 11115 | -1390 | 7210 | 87 |
| H11 | 11765 | 426 | 7107 | 46 |
| H5 | 9949 | -1027 | 6535 | 79 |
| H8 | 12795 | -667 | 7909 | 74 |
| H7 | 12524 | -1209 | 7911 | 89 |
| H13 | 11642 | 860 | 6345 | 48 |
| H15 | 12497 | 1231 | 6252 | 52 |
| H17 | 11749 | 2159 | 5368 | 58 |
| H20 | 8142 | 446 | 5478 | 43 |
| H26 | 6823 | 563 | 5167 | 51 |
| H24 | 5858 | 1468 | 4484 | 63 |
| H28A | 13847 | 1385 | 6875 | 99 |
| H28B | 14126 | 1542 | 6098 | 99 |
| H28C | 13244 | 1322 | 5427 | 99 |
| H29A | 13298 | 2224 | 6703 | 108 |
| H29B | 14163 | 2085 | 6889 | 108 |
| H29C | 13867 | 1937 | 7658 | 108 |
| H30A | 12296 | 1779 | 3938 | 99 |
| H30B | 13238 | 1960 | 4603 | 99 |
| H30C | 12433 | 2135 | 4482 | 99 |
| H32A | 9920 | 2030 | 6230 | 115 |

| | | | | |
|---|---|---|---|---|
| H32B | 9722 | 2407 | 5906 | 115 |
| H32C | 10733 | 2283 | 6888 | 115 |
| H33A | 10111 | 2677 | 4722 | 124 |
| H33B | 10608 | 2485 | 4295 | 124 |
| H33C | 11129 | 2562 | 5720 | 124 |
| H34A | 9040 | 1918 | 3941 | 111 |
| H34B | 9352 | 2085 | 3217 | 111 |
| H34C | 8887 | 2298 | 3651 | 111 |
| H36A | 8464 | 1830 | 5884 | 142 |
| H36B | 7940 | 1906 | 6425 | 142 |
| H36C | 8000 | 2175 | 5647 | 142 |
| H37A | 7547 | 1756 | 3547 | 142 |
| H37B | 7112 | 2105 | 3362 | 142 |
| H37C | 6478 | 1796 | 2687 | 142 |
| H38A | 6357 | 2234 | 4237 | 168 |
| H38B | 6305 | 1976 | 5053 | 168 |
| H38C | 5719 | 1924 | 3600 | 168 |
| H42A | 5274 | 437 | 3958 | 161 |
| H42B | 4741 | 462 | 4507 | 161 |
| H42C | 5811 | 428 | 5413 | 161 |
| H40A | 6003 | 928 | 6536 | 145 |
| H40B | 4933 | 960 | 5694 | 145 |
| H40C | 5521 | 1255 | 5790 | 145 |
| H41A | 4588 | 1257 | 3484 | 175 |
| H41B | 4014 | 974 | 3493 | 175 |
| H41C | 4433 | 922 | 2794 | 175 |
| H53A | 2927 | 710 | 5481 | 163 |
| H53B | 2112 | 456 | 4838 | 163 |
| H55A | 2938 | 103 | 4806 | 304 |
| H55B | 3766 | 353 | 5497 | 304 |
| H57A | 3738 | 87 | 7878 | 272 |
| H57B | 2860 | -61 | 6628 | 272 |
| H56A | 3743 | -162 | 6444 | 402 |
| H56B | 4357 | 146 | 7222 | 402 |

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Others
Fixed U12: O3(0)
Fixed U23: O3(0)
Fixed Uiso: H2(0.044) H6(0.087) H11(0.046) H5(0.079) H8(0.074) H7(0.089)
H13(0.048) H15(0.052) H17(0.058) H20(0.043) H26(0.051) H24(0.063) H28A(0.099)
H28B(0.099) H28C(0.099) H29A(0.108) H29B(0.108) H29C(0.108) H30A(0.099)
H30B(0.099) H30C(0.099) H32A(0.115) H32B(0.115) H32C(0.115) H33A(0.124)
H33B(0.124) H33C(0.124) H34A(0.111) H34B(0.111) H34C(0.111) H36A(0.142)
H36B(0.142) H36C(0.142) H37A(0.142) H37B(0.142) H37C(0.142) H38A(0.168)
H38B(0.168) H38C(0.168) H42A(0.161) H42B(0.161) H42C(0.161) H40A(0.145)
H40B(0.145) H40C(0.145) H41A(0.175) H41B(0.175) H41C(0.175) H53A(0.163)
H53B(0.163) H55A(0.304) H55B(0.304) H57A(0.272) H57B(0.272) H56A(0.402)
H56B(0.402)
Fixed X: H2(0.8897) H6(1.1115) H11(1.1765) H5(0.9949) H8(1.2795) H7(1.2524)
H13(1.1642) H15(1.2497) H17(1.1749) H20(0.8142) H26(0.6823) H24(0.5858)
H28A(1.3847) H28B(1.4126) H28C(1.3244) H29A(1.3298) H29B(1.4163)
H29C(1.3867)
H30A(1.2296) H30B(1.3238) H30C(1.2433) H32A(0.992) H32B(0.9722) H32C(1.0733)
H33A(1.0111) H33B(1.0608) H33C(1.1129) H34A(0.904) H34B(0.9352) H34C(0.8887)
H36A(0.8464) H36B(0.794) H36C(0.8) H37A(0.7547) H37B(0.7112) H37C(0.6478)
H38A(0.6357) H38B(0.6305) H38C(0.5719) H42A(0.5274) H42B(0.4741)
H42C(0.5811)
H40A(0.6003) H40B(0.4933) H40C(0.5521) H41A(0.4588) H41B(0.4014)
H41C(0.4433)
O3(1) H53A(0.2927) H53B(0.2112) H55A(0.2938) H55B(0.3766) H57A(0.3738)
H57B(0.286) H56A(0.3743) H56B(0.4357)
Fixed Y: H2(0.0072) H6(-0.139) H11(0.0426) H5(-0.1027) H8(-0.0667) H7(-
0.1209) H13(0.086) H15(0.1231) H17(0.2159) H20(0.0446) H26(0.0563) H24(0.1468)
H28A(0.1385) H28B(0.1542) H28C(0.1322) H29A(0.2224) H29B(0.2085)
H29C(0.1937)
H30A(0.1779) H30B(0.196) H30C(0.2135) H32A(0.203) H32B(0.2407) H32C(0.2283)
H33A(0.2677) H33B(0.2485) H33C(0.2562) H34A(0.1918) H34B(0.2085)
H34C(0.2298)
H36A(0.183) H36B(0.1906) H36C(0.2175) H37A(0.1756) H37B(0.2105) H37C(0.1796)
H38A(0.2234) H38B(0.1976) H38C(0.1924) H42A(0.0437) H42B(0.0462)
H42C(0.0428)
H40A(0.0928) H40B(0.096) H40C(0.1255) H41A(0.1257) H41B(0.0974) H41C(0.0922)
H53A(0.071) H53B(0.0456) H55A(0.0103) H55B(0.0353) H57A(0.0087) H57B(-
0.0061)
H56A(-0.0162) H56B(0.0146)

Fixed Z: H2(0.566) H6(0.721) H11(0.7107) H5(0.6535) H8(0.7909) H7(0.7911)
H13(0.6345) H15(0.6252) H17(0.5368) H20(0.5478) H26(0.5167) H24(0.4484)
H28A(0.6875) H28B(0.6098) H28C(0.5427) H29A(0.6703) H29B(0.6889)
H29C(0.7658)
H30A(0.3938) H30B(0.4603) H30C(0.4482) H32A(0.623) H32B(0.5906) H32C(0.6888)
H33A(0.4722) H33B(0.4295) H33C(0.572) H34A(0.3941) H34B(0.3217) H34C(0.3651)
H36A(0.5884) H36B(0.6425) H36C(0.5647) H37A(0.3547) H37B(0.3362)
H37C(0.2687)
H38A(0.4237) H38B(0.5053) H38C(0.36) H42A(0.3958) H42B(0.4507) H42C(0.5413)
H40A(0.6536) H40B(0.5694) H40C(0.579) H41A(0.3484) H41B(0.3493) H41C(0.2794)
O3(0.75) H53A(0.5481) H53B(0.4838) H55A(0.4806) H55B(0.5497) H57A(0.7878)
H57B(0.6628) H56A(0.6444) H56B(0.7222)

## $UO_2[L^{III}]$

**Crystallographic Table 39** Crystal data and structure refinement for **$UO_2[L^{III}]$**

| | |
|---|---|
| Empirical formula | $C_{40}H_{52}N_3O_4U$ |
| Formula weight | 876.87 |
| Temperature/K | 180(2) |
| Crystal system | orthorhombic |
| Space group | Pccn |
| a/Å | 13.9974(3) |
| b/Å | 23.5111(5) |
| c/Å | 23.6244(5) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 7774.7(3) |
| Z | 8 |
| $\rho_{calc}$mg/mm$^3$ | 1.498 |
| m/mm$^{-1}$ | 4.217 |
| F(000) | 3496.0 |
| Crystal size/mm$^3$ | 0.06 × 0.06 × 0.02 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection | 3.386 to 61.054° |
| Index ranges | $-19 \le h \le 19$, $-23 \le k \le 33$, $-32 \le l \le 33$ |
| Reflections collected | 93148 |
| Independent reflections | 11882 [$R_{int}$ = 0.0538, $R_{sigma}$ = 0.0376] |
| Data/restraints/parameters | 11882/0/446 |
| Goodness-of-fit on $F^2$ | 1.010 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0305, $wR_2$ = 0.0619 |
| Final R indexes [all data] | $R_1$ = 0.0569, $wR_2$ = 0.0699 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.37/-0.74 |

**Crystallographic Table 40** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for **$UO_2[L^{III}]$**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| U1 | 6576.3(2) | 3772.4(2) | 2540.7(2) | 20.73(3) |
| O1 | 5726.4(13) | 3283.4(8) | 3189.2(7) | 25.9(4) |
| O2 | 5323.3(13) | 4029.0(8) | 1993.8(7) | 27.0(4) |
| O3 | 6737.5(13) | 3175.0(8) | 2089.2(8) | 29.4(4) |
| O4 | 6506.5(13) | 4379.8(8) | 2995.7(8) | 27.6(4) |
| N1 | 7681.9(15) | 3246.6(10) | 3208.1(9) | 25.0(5) |
| N2 | 7136.6(16) | 4464.9(9) | 1804.3(9) | 25.5(5) |
| N4 | 6545(3) | 5110(2) | 5271.0(18) | 97.0(15) |
| N3 | 8415.1(15) | 3971.3(11) | 2461.0(8) | 23.9(4) |
| C17 | 9050(2) | 3616.3(12) | 2710.9(11) | 26.8(6) |

| | | | | |
|---|---|---|---|---|
| C16 | 8620.7(19) | 3097.4(13) | 2975.2(12) | 30.0(6) |
| C15 | 7535(2) | 3152.6(12) | 3734.6(11) | 26.7(6) |
| C14 | 6639.3(19) | 3223.7(12) | 4035.3(11) | 25.5(6) |
| C13 | 6676(2) | 3201.3(12) | 4635.3(11) | 29.4(6) |
| C8 | 5863(2) | 3225.5(12) | 4959.0(11) | 29.0(6) |
| C7 | 4995(2) | 3246.4(12) | 4666.7(12) | 29.4(6) |
| C2 | 4901.5(19) | 3260.7(11) | 4080.5(11) | 24.8(5) |
| C1 | 5749.7(19) | 3263.8(11) | 3751.0(11) | 24.2(6) |
| C3 | 3917(2) | 3276.1(13) | 3797.5(12) | 30.3(6) |
| C4 | 3808(2) | 3843.7(14) | 3471.6(15) | 42.1(8) |
| C6 | 3104(2) | 3249.5(16) | 4232.8(14) | 41.7(8) |
| C5 | 3802(2) | 2771.4(13) | 3393.1(12) | 33.1(7) |
| C12 | 5871(2) | 3199.1(15) | 5611.7(12) | 39.9(8) |
| C10 | 5233(4) | 3671(2) | 5849.8(17) | 97.4(19) |
| C9 | 5508(4) | 2625(2) | 5801.8(15) | 93.2(19) |
| C11 | 6854(3) | 3303(2) | 5847.8(15) | 77.1(15) |
| C18 | 10034(2) | 3734.4(14) | 2711.6(14) | 38.3(8) |
| C19 | 10329(2) | 4239.4(17) | 2470.1(12) | 43.1(8) |
| C20 | 9688(2) | 4599.4(14) | 2222.1(12) | 36.3(7) |
| C21 | 8732(2) | 4448.1(12) | 2215.3(11) | 27.4(6) |
| C22 | 7983(2) | 4806.9(13) | 1932.6(12) | 31.5(6) |
| C23 | 6818(2) | 4486.4(12) | 1296.1(11) | 27.9(6) |
| C24 | 5961(2) | 4216.6(12) | 1082.3(11) | 26.6(6) |
| C37 | 5223(2) | 4017.3(12) | 1435.2(10) | 25.0(5) |
| C32 | 4361(2) | 3830.4(12) | 1170.9(11) | 28.6(6) |
| C31 | 4324(2) | 3823.5(12) | 582.1(11) | 30.3(6) |
| C26 | 5074(2) | 4000.5(12) | 227.4(11) | 28.7(6) |
| C27 | 4970(2) | 3960.5(13) | -418.3(12) | 33.8(7) |
| C29 | 4041(3) | 4250.5(16) | -608.0(14) | 50.4(9) |
| C28 | 5809(3) | 4240.4(16) | -725.3(12) | 46.9(9) |
| C30 | 4921(3) | 3325.3(14) | -577.9(12) | 43.3(8) |
| C25 | 5875(2) | 4205.8(12) | 489.0(11) | 28.6(6) |
| C33 | 3499(2) | 3641.5(17) | 1524.6(13) | 41.3(8) |
| C36 | 3754(3) | 3123.8(18) | 1879.7(14) | 53.9(10) |
| C34 | 2630(2) | 3482(2) | 1155.3(15) | 66.7(13) |
| C35 | 3182(2) | 4136(2) | 1907.1(16) | 61.5(12) |
| C38 | 6078(4) | 4773(2) | 4275.1(17) | 77.8(14) |
| C39 | 6357(3) | 4965.9(18) | 4832.1(18) | 57.7(10) |

**Crystallographic Table 41** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **$UO_2[L^{III}]$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{23}$** | **$U_{13}$** | **$U_{12}$** |
|---|---|---|---|---|---|---|
| U1 | 20.01(5) | 17.24(5) | 24.94(5) | -0.96(4) | -0.56(3) | -1.05(4) |
| O1 | 23.1(10) | 25.3(11) | 29.3(9) | 4.0(8) | 0.9(7) | -1.8(8) |
| O2 | 23.1(10) | 29.9(11) | 27.9(9) | -2.4(8) | -3.9(7) | -0.6(9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O3 | 31.1(11) | 24.5(11) | 32.5(10) | -6.4(8) | 3.1(8) | -2.0(9) |
| O4 | 31.7(11) | 22.3(10) | 28.8(9) | -5.0(8) | -2.7(8) | 2.5(9) |
| N1 | 21.9(12) | 19.6(12) | 33.7(11) | 4.3(9) | 1.6(9) | 0.1(9) |
| N2 | 28.4(12) | 17.6(12) | 30.4(11) | 1.1(9) | -4.7(9) | -5(1) |
| N4 | 120(4) | 96(4) | 75(3) | -20(3) | -34(3) | 14(3) |
| N3 | 24.4(11) | 21.8(11) | 25.5(10) | -3.0(8) | 0.0(9) | -4.9(9) |
| C17 | 26.0(14) | 28.2(16) | 26.2(12) | -2.9(11) | 3.1(10) | 0.1(12) |
| C16 | 23.6(15) | 26.9(16) | 39.5(15) | 2.2(12) | 3.4(11) | 5.3(12) |
| C15 | 23.7(14) | 20.7(15) | 35.7(14) | 3.1(11) | -1.9(11) | -1.7(11) |
| C14 | 25.6(14) | 19.4(14) | 31.5(13) | 4.2(11) | 1.2(11) | -2.5(12) |
| C13 | 27.6(15) | 26.9(16) | 33.7(13) | 3.7(12) | -3.0(11) | -4.1(12) |
| C8 | 31.5(15) | 24.6(15) | 31.0(13) | 2.8(12) | 2.5(11) | -6.8(13) |
| C7 | 30.1(16) | 20.4(15) | 37.7(14) | 1.9(12) | 7.7(11) | -4.3(12) |
| C2 | 24.7(14) | 13.8(13) | 35.8(13) | 1.6(11) | 2.5(11) | -0.3(11) |
| C1 | 25.7(14) | 15.3(13) | 31.5(13) | 2.5(11) | 0.9(10) | -2.3(11) |
| C3 | 21.9(14) | 25.7(16) | 43.1(15) | 5.8(13) | 0.7(12) | -0.4(12) |
| C4 | 32.4(17) | 31.4(19) | 62(2) | 9.8(16) | -8.8(15) | 2.9(14) |
| C6 | 24.7(16) | 47(2) | 53.1(19) | -2.4(16) | 3.7(14) | -0.8(15) |
| C5 | 25.7(15) | 31.9(17) | 41.8(15) | 3.2(13) | -2.7(12) | -7.8(13) |
| C12 | 39.8(18) | 50(2) | 30.2(14) | 0.3(14) | 2.4(13) | -12.6(16) |
| C10 | 106(4) | 142(5) | 44(2) | -29(3) | 5(2) | 30(4) |
| C9 | 145(5) | 93(4) | 42(2) | 27(2) | -17(2) | -73(4) |
| C11 | 69(3) | 127(4) | 35.4(18) | 4(2) | -9.8(18) | -45(3) |
| C18 | 28.6(16) | 47(2) | 39.5(15) | 2.7(14) | -5.8(12) | 2.7(16) |
| C19 | 21.8(15) | 62(2) | 45.7(17) | 5.8(17) | -0.3(13) | -11.8(15) |
| C20 | 33.9(17) | 37.3(19) | 37.8(15) | 2.1(13) | 0.4(13) | -13.2(14) |
| C21 | 31.9(15) | 23.5(15) | 26.6(12) | -3.8(11) | -0.8(11) | -8.1(12) |
| C22 | 36.5(17) | 22.5(16) | 35.6(14) | 2.5(12) | -6.3(12) | -10.9(13) |
| C23 | 32.6(15) | 21.8(15) | 29.2(13) | 2.1(11) | -1.3(11) | -1.4(12) |
| C24 | 26.2(14) | 21.3(15) | 32.2(13) | 0.1(11) | -6.5(11) | 0.4(12) |
| C37 | 26.1(14) | 20.6(14) | 28.3(12) | -3.8(11) | -3.9(11) | 4.8(12) |
| C32 | 25.0(14) | 27.4(16) | 33.4(13) | -6.0(12) | -3.8(10) | 3.6(12) |
| C31 | 28.2(15) | 27.7(16) | 35.0(14) | -8.4(12) | -7.2(11) | 2.5(12) |
| C26 | 36.6(16) | 20.3(14) | 29.2(13) | -1.4(11) | -7.8(11) | 3.8(12) |
| C27 | 46.5(19) | 26.4(16) | 28.7(13) | -2.7(12) | -9.2(12) | -3.4(14) |
| C29 | 58(2) | 47(2) | 46.9(18) | 3.2(17) | -23.4(17) | 4.9(19) |
| C28 | 63(2) | 49(2) | 28.8(14) | 0.8(15) | -5.9(15) | -13.5(19) |
| C30 | 62(2) | 34.3(19) | 33.8(15) | -7.5(14) | -1.0(15) | -5.6(17) |
| C25 | 33.0(16) | 24.2(16) | 28.6(13) | 2.1(11) | -3.5(11) | -0.9(12) |
| C33 | 23.7(15) | 63(2) | 37.3(15) | -15.5(15) | 0.9(12) | -4.0(16) |
| C36 | 48(2) | 71(3) | 43.0(18) | -4.5(18) | 9.6(16) | -26(2) |
| C34 | 31.3(19) | 117(4) | 52(2) | -21(2) | -1.1(16) | -24(2) |
| C35 | 30.4(19) | 95(4) | 59(2) | -31(2) | 3.2(16) | 17(2) |
| C38 | 119(4) | 57(3) | 57(2) | -17(2) | -9(3) | 6(3) |
| C39 | 67(3) | 48(2) | 59(2) | -8(2) | -7(2) | 6(2) |

**Crystallographic Table 42** Bond Lengths for **$UO_2[L^{III}]$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| U1 | O1 | 2.2548(18) | C3 | C4 | 1.548(4) |
| U1 | O2 | 2.2603(18) | C3 | C6 | 1.535(4) |
| U1 | O3 | 1.7780(19) | C3 | C5 | 1.532(4) |
| U1 | O4 | 1.7901(18) | C12 | C10 | 1.531(6) |
| U1 | N1 | 2.532(2) | C12 | C9 | 1.511(5) |
| U1 | N2 | 2.508(2) | C12 | C11 | 1.505(5) |
| U1 | N3 | 2.623(2) | C18 | C19 | 1.381(5) |
| O1 | C1 | 1.328(3) | C19 | C20 | 1.366(5) |
| O2 | C37 | 1.327(3) | C20 | C21 | 1.385(4) |
| N1 | C16 | 1.467(3) | C21 | C22 | 1.502(4) |
| N1 | C15 | 1.280(3) | C23 | C24 | 1.447(4) |
| N2 | C22 | 1.464(3) | C24 | C37 | 1.409(4) |
| N2 | C23 | 1.282(3) | C24 | C25 | 1.407(4) |
| N4 | C39 | 1.122(5) | C37 | C32 | 1.427(4) |
| N3 | C17 | 1.355(4) | C32 | C31 | 1.392(4) |
| N3 | C21 | 1.338(4) | C32 | C33 | 1.534(4) |
| C17 | C16 | 1.497(4) | C31 | C26 | 1.407(4) |
| C17 | C18 | 1.404(4) | C26 | C27 | 1.535(4) |
| C15 | C14 | 1.451(4) | C26 | C25 | 1.368(4) |
| C14 | C13 | 1.419(4) | C27 | C29 | 1.536(4) |
| C14 | C1 | 1.418(4) | C27 | C28 | 1.529(4) |
| C13 | C8 | 1.372(4) | C27 | C30 | 1.542(4) |
| C8 | C7 | 1.398(4) | C33 | C36 | 1.521(5) |
| C8 | C12 | 1.543(4) | C33 | C34 | 1.543(4) |
| C7 | C2 | 1.391(4) | C33 | C35 | 1.538(5) |
| C2 | C1 | 1.420(4) | C38 | C39 | 1.445(5) |
| C2 | C3 | 1.532(4) | | | |

**Crystallographic Table 43** Bond Angles for **$UO_2[L^{III}]$**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O1 | U1 | O2 | 96.61(6) | O1 | C1 | C2 | 121.8(2) |
| O1 | U1 | N1 | 69.53(7) | C14 | C1 | C2 | 118.3(2) |
| O1 | U1 | N2 | 165.27(7) | C2 | C3 | C4 | 109.0(2) |
| O1 | U1 | N3 | 131.10(7) | C2 | C3 | C6 | 111.9(2) |
| O2 | U1 | N1 | 163.87(7) | C6 | C3 | C4 | 107.2(3) |
| O2 | U1 | N2 | 70.91(7) | C5 | C3 | C2 | 110.4(2) |
| O2 | U1 | N3 | 132.29(7) | C5 | C3 | C4 | 110.3(3) |
| O3 | U1 | O1 | 94.12(8) | C5 | C3 | C6 | 108.0(2) |
| O3 | U1 | O2 | 88.07(8) | C10 | C12 | C8 | 109.5(3) |
| O3 | U1 | O4 | 175.83(9) | C9 | C12 | C8 | 109.3(3) |
| O3 | U1 | N1 | 84.86(8) | C9 | C12 | C10 | 110.1(4) |
| O3 | U1 | N2 | 93.27(8) | C11 | C12 | C8 | 111.7(3) |
| O3 | U1 | N3 | 88.47(8) | C11 | C12 | C10 | 106.2(4) |
| O4 | U1 | O1 | 88.28(8) | C11 | C12 | C9 | 110.0(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O4 | U1 | O2 | 95.05(8) | C19 | C18 | C17 | 117.6(3) |
| O4 | U1 | N1 | 92.80(8) | C20 | C19 | C18 | 120.9(3) |
| O4 | U1 | N2 | 85.16(8) | C19 | C20 | C21 | 118.7(3) |
| O4 | U1 | N3 | 87.38(8) | N3 | C21 | C20 | 122.0(3) |
| N1 | U1 | N3 | 62.09(7) | N3 | C21 | C22 | 115.6(2) |
| N2 | U1 | N1 | 123.90(7) | C20 | C21 | C22 | 122.3(3) |
| N2 | U1 | N3 | 61.81(7) | N2 | C22 | C21 | 110.4(2) |
| C1 | O1 | U1 | 133.14(17) | N2 | C23 | C24 | 126.7(3) |
| C37 | O2 | U1 | 130.17(16) | C37 | C24 | C23 | 123.2(2) |
| C16 | N1 | U1 | 115.51(16) | C25 | C24 | C23 | 115.3(3) |
| C15 | N1 | U1 | 126.26(19) | C25 | C24 | C37 | 121.4(2) |
| C15 | N1 | C16 | 117.8(2) | O2 | C37 | C24 | 120.2(2) |
| C22 | N2 | U1 | 117.78(16) | O2 | C37 | C32 | 122.1(2) |
| C23 | N2 | U1 | 124.48(19) | C24 | C37 | C32 | 117.6(2) |
| C23 | N2 | C22 | 117.0(2) | C37 | C32 | C33 | 121.0(2) |
| C17 | N3 | U1 | 120.18(18) | C31 | C32 | C37 | 118.2(3) |
| C21 | N3 | U1 | 120.37(18) | C31 | C32 | C33 | 120.8(3) |
| C21 | N3 | C17 | 119.2(2) | C32 | C31 | C26 | 124.3(3) |
| N3 | C17 | C16 | 114.9(2) | C31 | C26 | C27 | 120.2(3) |
| N3 | C17 | C18 | 121.5(3) | C25 | C26 | C31 | 116.5(2) |
| C18 | C17 | C16 | 123.7(3) | C25 | C26 | C27 | 123.3(3) |
| N1 | C16 | C17 | 108.7(2) | C26 | C27 | C29 | 110.1(3) |
| N1 | C15 | C14 | 126.5(3) | C26 | C27 | C30 | 107.9(2) |
| C13 | C14 | C15 | 117.0(2) | C29 | C27 | C30 | 108.7(3) |
| C1 | C14 | C15 | 122.3(2) | C28 | C27 | C26 | 111.8(2) |
| C1 | C14 | C13 | 120.5(2) | C28 | C27 | C29 | 108.7(3) |
| C8 | C13 | C14 | 121.7(3) | C28 | C27 | C30 | 109.6(3) |
| C13 | C8 | C7 | 116.5(2) | C26 | C25 | C24 | 121.8(3) |
| C13 | C8 | C12 | 123.3(3) | C32 | C33 | C34 | 112.5(3) |
| C7 | C8 | C12 | 120.1(3) | C32 | C33 | C35 | 109.1(3) |
| C2 | C7 | C8 | 125.0(3) | C36 | C33 | C32 | 110.3(3) |
| C7 | C2 | C1 | 117.8(2) | C36 | C33 | C34 | 107.6(3) |
| C7 | C2 | C3 | 121.3(2) | C36 | C33 | C35 | 110.4(3) |
| C1 | C2 | C3 | 120.8(2) | C35 | C33 | C34 | 106.8(3) |
| O1 | C1 | C14 | 119.8(2) | N4 | C39 | C38 | 177.7(5) |

**Crystallographic Table 44** Hydrogen Bonds for **$UO_2[L^{III}]$**.

| **D** | **H** | **A** | **d(D-H)/Å** | **d(H-A)/Å** | **d(D-A)/Å** | **D-H-A/°** |
|---|---|---|---|---|---|---|
| C23 | H23 | N4[1] | 0.95 | 2.71 | 3.642(5) | 167.5 |
| C38 | H38B | O4 | 0.98 | 2.61 | 3.217(4) | 120.4 |
| C38 | H38B | O4 | 0.98 | 2.61 | 3.217(4) | 120.4 |
| C38 | H38B | O4 | 0.98 | 2.61 | 3.217(4) | 120.4 |
| C38 | H38B | O4 | 0.98 | 2.61 | 3.217(4) | 120.4 |

[1]3/2-X,+Y,-1/2+Z

**Crystallographic Table 45** Torsion Angles for **$UO_2[L^{III}]$**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| U1 | O1 | C1 | C14 | -45.0(4) | C7 | C2 | C3 | C4 | 116.1(3) |
| U1 | O1 | C1 | C2 | 137.3(2) | C7 | C2 | C3 | C6 | -2.3(4) |
| U1 | O2 | C37 | C24 | -44.9(4) | C7 | C2 | C3 | C5 | -122.5(3) |
| U1 | O2 | C37 | C32 | 138.0(2) | C1 | C14 | C13 | C8 | -0.9(4) |
| U1 | N1 | C16 | C17 | 49.9(3) | C1 | C2 | C3 | C4 | -63.5(3) |
| U1 | N1 | C15 | C14 | 13.1(4) | C1 | C2 | C3 | C6 | 178.1(3) |
| U1 | N2 | C22 | C21 | 41.9(3) | C1 | C2 | C3 | C5 | 57.8(3) |
| U1 | N2 | C23 | C24 | 14.3(4) | C3 | C2 | C1 | O1 | 0.4(4) |
| U1 | N3 | C17 | C16 | 5.3(3) | C3 | C2 | C1 | C14 | -177.3(2) |
| U1 | N3 | C17 | C18 | -175.2(2) | C12 | C8 | C7 | C2 | -178.8(3) |
| U1 | N3 | C21 | C20 | 172.5(2) | C18 | C17 | C16 | N1 | 145.8(3) |
| U1 | N3 | C21 | C22 | -7.5(3) | C18 | C19 | C20 | C21 | -0.2(5) |
| O2 | C37 | C32 | C31 | -179.0(3) | C19 | C20 | C21 | N3 | 2.4(4) |
| O2 | C37 | C32 | C33 | 1.0(4) | C19 | C20 | C21 | C22 | -177.6(3) |
| N1 | C15 | C14 | C13 | -168.2(3) | C20 | C21 | C22 | N2 | 159.0(3) |
| N1 | C15 | C14 | C1 | 17.2(5) | C21 | N3 | C17 | C16 | 179.7(2) |
| N2 | C23 | C24 | C37 | 17.7(5) | C21 | N3 | C17 | C18 | -0.8(4) |
| N2 | C23 | C24 | C25 | -167.3(3) | C22 | N2 | C23 | C24 | -175.7(3) |
| N3 | C17 | C16 | N1 | -34.7(3) | C23 | N2 | C22 | C21 | -128.8(3) |
| N3 | C17 | C18 | C19 | 2.8(4) | C23 | C24 | C37 | O2 | -5.6(4) |
| N3 | C21 | C22 | N2 | -21.0(3) | C23 | C24 | C37 | C32 | 171.6(3) |
| C17 | N3 | C21 | C20 | -1.9(4) | C23 | C24 | C25 | C26 | -175.4(3) |
| C17 | N3 | C21 | C22 | 178.1(2) | C24 | C37 | C32 | C31 | 3.8(4) |
| C17 | C18 | C19 | C20 | -2.3(5) | C24 | C37 | C32 | C33 | -176.2(3) |
| C16 | N1 | C15 | C14 | -174.4(3) | C37 | C24 | C25 | C26 | -0.2(4) |
| C16 | C17 | C18 | C19 | -177.7(3) | C37 | C32 | C31 | C26 | -1.4(4) |
| C15 | N1 | C16 | C17 | -123.4(3) | C37 | C32 | C33 | C36 | -62.4(4) |
| C15 | C14 | C13 | C8 | -175.6(3) | C37 | C32 | C33 | C34 | 177.5(3) |
| C15 | C14 | C1 | O1 | -5.5(4) | C37 | C32 | C33 | C35 | 59.1(4) |
| C15 | C14 | C1 | C2 | 172.2(3) | C32 | C31 | C26 | C27 | 178.3(3) |
| C14 | C13 | C8 | C7 | 2.9(4) | C32 | C31 | C26 | C25 | -1.9(4) |
| C14 | C13 | C8 | C12 | 179.6(3) | C31 | C32 | C33 | C36 | 117.6(3) |
| C13 | C14 | C1 | O1 | -179.9(2) | C31 | C32 | C33 | C34 | -2.6(5) |
| C13 | C14 | C1 | C2 | -2.2(4) | C31 | C32 | C33 | C35 | -120.9(3) |
| C13 | C8 | C7 | C2 | -1.9(4) | C31 | C26 | C27 | C29 | 52.0(4) |
| C13 | C8 | C12 | C10 | 132.7(4) | C31 | C26 | C27 | C28 | 173.0(3) |
| C13 | C8 | C12 | C9 | -106.6(4) | C31 | C26 | C27 | C30 | -66.5(4) |
| C13 | C8 | C12 | C11 | 15.4(5) | C31 | C26 | C25 | C24 | 2.7(4) |
| C8 | C7 | C2 | C1 | -1.1(4) | C27 | C26 | C25 | C24 | -177.5(3) |
| C8 | C7 | C2 | C3 | 179.3(3) | C25 | C24 | C37 | O2 | 179.6(3) |
| C7 | C8 | C12 | C10 | -50.7(4) | C25 | C24 | C37 | C32 | -3.1(4) |
| C7 | C8 | C12 | C9 | 70.0(4) | C25 | C26 | C27 | C29 | -127.8(3) |
| C7 | C8 | C12 | C11 | -168.0(3) | C25 | C26 | C27 | C28 | -6.8(4) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C7 | C2 | C1 | O1 | -179.3(2) | C25 | C26 | C27 | C30 | 113.7(3) |
| C7 | C2 | C1 | C14 | 3.1(4) | C33 | C32 | C31 | C26 | 178.6(3) |

**Crystallographic Table 46** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **$UO_2[L^{III}]$**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H16A | 8551 | 2794 | 2688 | 36 |
| H16B | 9042 | 2955 | 3281 | 36 |
| H15 | 8066 | 3023 | 3950 | 32 |
| H13 | 7279 | 3169 | 4817 | 35 |
| H7 | 4425 | 3251 | 4885 | 35 |
| H4A | 3874 | 4163 | 3736 | 63 |
| H4B | 3177 | 3858 | 3292 | 63 |
| H4C | 4304 | 3870 | 3180 | 63 |
| H6A | 3151 | 2895 | 4449 | 63 |
| H6B | 2488 | 3263 | 4036 | 63 |
| H6C | 3153 | 3574 | 4491 | 63 |
| H5A | 4336 | 2766 | 3125 | 50 |
| H5B | 3200 | 2809 | 3185 | 50 |
| H5C | 3796 | 2416 | 3611 | 50 |
| H10A | 5254 | 3662 | 6264 | 146 |
| H10B | 4575 | 3613 | 5722 | 146 |
| H10C | 5463 | 4041 | 5715 | 146 |
| H9A | 5910 | 2325 | 5639 | 140 |
| H9B | 4847 | 2574 | 5674 | 140 |
| H9C | 5533 | 2602 | 6216 | 140 |
| H11A | 6825 | 3305 | 6262 | 116 |
| H11B | 7091 | 3672 | 5714 | 116 |
| H11C | 7286 | 3001 | 5721 | 116 |
| H18 | 10479 | 3476 | 2872 | 46 |
| H19 | 10987 | 4338 | 2476 | 52 |
| H20 | 9894 | 4947 | 2057 | 44 |
| H22A | 7804 | 5126 | 2185 | 38 |
| H22B | 8244 | 4969 | 1578 | 38 |
| H23 | 7181 | 4702 | 1033 | 33 |
| H31 | 3754 | 3690 | 408 | 36 |
| H29A | 3496 | 4072 | -417 | 76 |
| H29B | 3968 | 4210 | -1019 | 76 |
| H29C | 4064 | 4655 | -509 | 76 |
| H28A | 5831 | 4646 | -629 | 70 |
| H28B | 5726 | 4197 | -1135 | 70 |
| H28C | 6406 | 4058 | -608 | 70 |
| H30A | 5496 | 3132 | -441 | 65 |
| H30B | 4881 | 3288 | -990 | 65 |
| H30C | 4355 | 3153 | -404 | 65 |
| H25 | 6387 | 4345 | 264 | 34 |

| | | | | |
|---|---|---|---|---|
| H36A | 3980 | 2818 | 1632 | 81 |
| H36B | 3188 | 2995 | 2087 | 81 |
| H36C | 4259 | 3225 | 2149 | 81 |
| H34A | 2792 | 3153 | 918 | 100 |
| H34B | 2459 | 3805 | 914 | 100 |
| H34C | 2088 | 3385 | 1400 | 100 |
| H35A | 2640 | 4015 | 2140 | 92 |
| H35B | 2991 | 4460 | 1672 | 92 |
| H35C | 3714 | 4249 | 2153 | 92 |
| H38A | 5820 | 4386 | 4301 | 117 |
| H38B | 6637 | 4774 | 4025 | 117 |
| H38C | 5589 | 5028 | 4122 | 117 |

## $UO_2[L^{IV}]$

**Crystallographic Table 47** Crystal data and structure refinement for **$UO_2[L^{IV}]$**.

| | |
|---|---|
| Empirical formula | $C_{29}H_{21}N_3O_4U$ |
| Formula weight | 713.54 |
| Temperature/K | 180.45 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 22.8062(10) |
| b/Å | 7.2736(3) |
| c/Å | 14.7805(6) |
| α/° | 90 |
| β/° | 97.3343(5) |
| γ/° | 90 |
| Volume/Å$^3$ | 2431.78(18) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.9488 |
| m/mm$^{-1}$ | 6.720 |
| F(000) | 1320.2 |
| Crystal size/mm$^3$ | 0.12 × 0.12 × 0.04 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 3.6 to 63.04° |
| Index ranges | $-33 \leq h \leq 33$, $-10 \leq k \leq 10$, $-21 \leq l \leq 21$ |
| Reflections collected | 61345 |
| Independent reflections | 8098 [$R_{int}$ = 0.0473, $R_{sigma}$ = 0.0295] |
| Data/restraints/parameters | 8098/0/333 |
| Goodness-of-fit on $F^2$ | 1.084 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0359, $wR_2$ = 0.0726 |
| Final R indexes [all data] | $R_1$ = 0.0427, $wR_2$ = 0.0755 |
| Largest diff. peak/hole / e Å$^{-3}$ | 3.18/-5.58 |

**Crystallographic Table 48** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for **$UO_2[L^{IV}]$**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| U1 | 2665.70(6) | 6702.81(17) | 3444.78(8) | 11.33(4) |
| O2 | 2136.0(12) | 7009(4) | 2047.1(18) | 17.0(5) |
| N1 | 3348.1(15) | 7175(4) | 4877(2) | 15.4(6) |
| N2 | 1903.7(14) | 4179(4) | 3165(2) | 13.1(5) |

| | | | | |
|---|---|---|---|---|
| N3 | 2567.2(14) | 4501(4) | 4773(2) | 12.7(5) |
| C16 | 2222.4(16) | 1657(5) | 5326(2) | 15.1(6) |
| C12 | 3100.6(18) | 6796(5) | 5724(2) | 17.6(7) |
| C10 | 4217.0(17) | 8071(5) | 4181(3) | 15.8(7) |
| C13 | 2784.3(16) | 4964(5) | 5633(2) | 13.6(6) |
| C17 | 2290.3(16) | 2866(5) | 4620(2) | 12.5(6) |
| C15 | 2440.4(18) | 2166(6) | 6211(3) | 18.4(7) |
| C14 | 2723.0(18) | 3845(5) | 6371(2) | 16.9(7) |
| C9 | 4855.3(18) | 8040(5) | 4312(3) | 18.6(7) |
| C6 | 6105(2) | 8122(6) | 4530(4) | 31.4(10) |
| C2 | 4239(2) | 9706(6) | 2745(3) | 24.1(8) |
| C11 | 3904.7(18) | 7518(5) | 4933(3) | 16.3(7) |
| C1 | 3909.9(18) | 8868(5) | 3394(3) | 17.9(7) |
| C4 | 5168.0(19) | 8844(6) | 3631(3) | 21.7(8) |
| C3 | 4840(2) | 9677(6) | 2857(3) | 25.2(9) |
| C7 | 5804(2) | 7308(6) | 5196(4) | 29.6(10) |
| C8 | 5193.4(19) | 7258(6) | 5080(3) | 22.8(8) |
| C5 | 5795(2) | 8846(6) | 3757(3) | 28.1(9) |
| C20 | 1173.9(17) | 5694(5) | 2060(3) | 16.3(7) |
| C18 | 2084.2(18) | 2459(5) | 3636(3) | 15.9(7) |
| C19 | 1398.8(16) | 4216(5) | 2666(2) | 15.3(7) |
| C21 | 556.4(17) | 5688(6) | 1688(3) | 20.0(7) |
| C28 | 1348(2) | 8183(7) | 1038(3) | 30.9(10) |
| C29 | 1566.0(17) | 6964(5) | 1745(3) | 16.2(7) |
| C27 | 775(2) | 8159(6) | 656(3) | 30.4(10) |
| C25 | -238(2) | 6881(7) | 564(3) | 30.1(10) |
| C26 | 358.6(19) | 6932(6) | 967(3) | 23.6(8) |
| C24 | -629(2) | 5666(8) | 862(4) | 34.7(11) |
| O4 | 3167.7(12) | 5102(4) | 3040.0(18) | 17.9(5) |
| O3 | 2151.1(13) | 8170(4) | 3898(2) | 19.6(5) |
| C22 | 131.8(19) | 4501(7) | 1993(3) | 29.2(10) |
| C23 | -446(2) | 4490(8) | 1590(4) | 34.6(11) |
| O1 | 3322.6(13) | 8957(4) | 3251(2) | 20.7(6) |

**Crystallographic Table 49** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **$UO_2[L^{IV}]$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{12}$** | **$U_{13}$** | **$U_{23}$** |
|---|---|---|---|---|---|---|
| U1 | 13.96(6) | 9.98(6) | 9.63(6) | -0.66(5) | -0.14(4) | 1.18(5) |
| O2 | 14.8(12) | 21.6(14) | 13.9(12) | -1.3(10) | -0.8(9) | 5.2(10) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N1 | 21.7(16) | 12.1(13) | 12.3(13) | -3.5(11) | 1.0(12) | -0.6(10) |
| N2 | 18.3(15) | 11.1(13) | 9.9(13) | -1.6(11) | 2.0(11) | -0.4(10) |
| N3 | 14.6(14) | 12.0(13) | 11.2(13) | 0.2(11) | 0.4(10) | -0.4(10) |
| C16 | 16.2(16) | 12.8(15) | 15.9(15) | -1.1(13) | 0.1(12) | 3.0(13) |
| C12 | 24.8(18) | 17.6(16) | 10.2(15) | -2.5(15) | 0.9(13) | -1.6(13) |
| C10 | 20.0(17) | 12.3(16) | 14.8(15) | -4.3(13) | 1.5(13) | -0.2(12) |
| C13 | 14.5(15) | 14.8(15) | 11.4(14) | 2.0(13) | 1.2(12) | -0.5(12) |
| C17 | 14.0(15) | 10.6(14) | 12.8(15) | 0.8(11) | 1.4(12) | 1.2(11) |
| C15 | 21.1(18) | 20.8(17) | 14.0(16) | -0.9(14) | 4.7(14) | 5.2(13) |
| C14 | 20.3(18) | 20.6(17) | 10.0(15) | 0.9(14) | 2.4(13) | 1.0(13) |
| C9 | 21.8(18) | 12.7(16) | 21.2(18) | -2.0(13) | 1.6(14) | -5.0(13) |
| C6 | 17.2(19) | 27(2) | 50(3) | 2.3(16) | 4.9(19) | -14(2) |
| C2 | 33(2) | 22.2(19) | 17.2(17) | -9.2(17) | 1.9(16) | 2.9(15) |
| C11 | 22.4(18) | 11.0(15) | 14.4(16) | -1.8(13) | -2.2(13) | 1.1(12) |
| C1 | 19.7(18) | 15.4(16) | 17.8(17) | -6.5(14) | -1.1(14) | 1.0(13) |
| C4 | 23(2) | 16.7(17) | 26(2) | -4.9(15) | 5.9(16) | -7.5(15) |
| C3 | 31(2) | 26(2) | 20.7(19) | -10.6(17) | 8.7(16) | -2.2(16) |
| C7 | 22(2) | 22(2) | 43(3) | 5.5(16) | -4.1(19) | -6.3(19) |
| C8 | 22.8(19) | 14.8(17) | 30(2) | -1.8(14) | -1.9(16) | -1.5(15) |
| C5 | 25(2) | 24(2) | 38(2) | -5.0(17) | 11.7(19) | -10.5(18) |
| C20 | 14.9(16) | 18.1(16) | 15.5(16) | 1.0(13) | 0.1(13) | 0.3(13) |
| C18 | 24.2(19) | 8.5(15) | 14.2(16) | 0.3(13) | -0.8(13) | 1.6(12) |
| C19 | 14.1(16) | 18.1(16) | 13.3(15) | -1.5(13) | 0.5(12) | 2.0(13) |
| C21 | 14.8(17) | 25.1(19) | 19.3(18) | 4.4(15) | -1.1(14) | -1.6(15) |
| C28 | 31(2) | 32(2) | 28(2) | -1.6(19) | -5.0(18) | 14.4(19) |
| C29 | 16.6(17) | 17.5(17) | 13.5(15) | 1.6(13) | -2.1(12) | 0.3(13) |
| C27 | 29(2) | 25(2) | 34(2) | 3.9(18) | -8.6(18) | 11.2(18) |
| C25 | 22(2) | 36(3) | 30(2) | 10.3(18) | -6.7(17) | -1.4(19) |
| C26 | 18.0(18) | 26(2) | 25(2) | 6.4(15) | -4.0(15) | 0.6(16) |
| C24 | 15(2) | 49(3) | 38(3) | 7.3(19) | -3.6(18) | -8(2) |
| O4 | 15.0(12) | 22.4(13) | 15.6(12) | 1.8(11) | -0.5(9) | -0.8(11) |
| O3 | 22.9(14) | 15.6(12) | 20.6(13) | 3.0(11) | 3.7(11) | -1.1(11) |
| C22 | 17.3(19) | 41(3) | 29(2) | -3.1(18) | 1.1(16) | 5.6(19) |
| C23 | 17(2) | 47(3) | 39(3) | -2.1(19) | 3.0(18) | 1(2) |
| O1 | 21.6(14) | 20.1(13) | 19.1(13) | -6.1(11) | -3.2(11) | 7.6(11) |

**Crystallographic Table 50** Bond Lengths for **$UO_2[L^{IV}]$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| U1 | O2 | 2.267(3) | C9 | C4 | 1.430(6) |
| U1 | N1 | 2.486(3) | C9 | C8 | 1.409(6) |
| U1 | N2 | 2.525(3) | C6 | C7 | 1.401(7) |
| U1 | N3 | 2.565(3) | C6 | C5 | 1.369(8) |
| U1 | O4 | 1.789(3) | C2 | C1 | 1.428(5) |
| U1 | O3 | 1.780(3) | C2 | C3 | 1.360(6) |
| U1 | O1 | 2.264(3) | C1 | O1 | 1.331(5) |
| O2 | C29 | 1.320(5) | C4 | C3 | 1.421(6) |
| N1 | C12 | 1.464(5) | C4 | C5 | 1.419(6) |
| N1 | C11 | 1.286(5) | C7 | C8 | 1.382(6) |
| N2 | C18 | 1.465(5) | C20 | C19 | 1.450(5) |
| N2 | C19 | 1.286(5) | C20 | C21 | 1.445(5) |
| N3 | C13 | 1.348(4) | C20 | C29 | 1.406(5) |
| N3 | C17 | 1.352(4) | C21 | C26 | 1.426(6) |
| C16 | C17 | 1.388(5) | C21 | C22 | 1.414(6) |
| C16 | C15 | 1.389(5) | C28 | C29 | 1.412(6) |
| C12 | C13 | 1.513(5) | C28 | C27 | 1.356(7) |
| C10 | C9 | 1.444(6) | C27 | C26 | 1.421(7) |
| C10 | C11 | 1.451(5) | C25 | C26 | 1.415(6) |
| C10 | C1 | 1.404(5) | C25 | C24 | 1.367(8) |
| C13 | C14 | 1.382(5) | C24 | C23 | 1.396(8) |
| C17 | C18 | 1.501(5) | C22 | C23 | 1.375(6) |
| C15 | C14 | 1.387(6) | | | |

**Crystallographic Table 51** Bond Angles for **$UO_2[L^{IV}]$**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| N1 | U1 | O2 | 164.84(10) | C18 | C17 | C16 | 123.5(3) |
| N2 | U1 | O2 | 69.31(10) | C14 | C15 | C16 | 119.9(3) |
| N2 | U1 | N1 | 125.66(10) | C15 | C14 | C13 | 118.4(3) |
| N3 | U1 | O2 | 132.07(10) | C4 | C9 | C10 | 119.0(4) |
| N3 | U1 | N1 | 62.70(10) | C8 | C9 | C10 | 123.6(4) |
| N3 | U1 | N2 | 62.99(9) | C8 | C9 | C4 | 117.5(4) |
| O4 | U1 | O2 | 92.78(11) | C5 | C6 | C7 | 120.2(4) |
| O4 | U1 | N1 | 90.97(11) | C3 | C2 | C1 | 121.3(4) |
| O4 | U1 | N2 | 85.90(11) | C10 | C11 | N1 | 125.5(3) |
| O4 | U1 | N3 | 88.38(11) | C2 | C1 | C10 | 118.9(4) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O3 | U1 | O2 | 89.08(12) | O1 | C1 | C10 | 122.5(3) |
| O3 | U1 | N1 | 88.15(12) | O1 | C1 | C2 | 118.5(4) |
| O3 | U1 | N2 | 91.39(12) | C3 | C4 | C9 | 118.8(4) |
| O3 | U1 | N3 | 87.69(11) | C5 | C4 | C9 | 119.5(4) |
| O3 | U1 | O4 | 175.94(13) | C5 | C4 | C3 | 121.6(4) |
| O1 | U1 | O2 | 95.60(10) | C4 | C3 | C2 | 121.6(4) |
| O1 | U1 | N1 | 69.84(10) | C8 | C7 | C6 | 120.0(5) |
| O1 | U1 | N2 | 163.42(10) | C7 | C8 | C9 | 121.9(4) |
| O1 | U1 | N3 | 132.31(10) | C4 | C5 | C6 | 120.9(4) |
| O1 | U1 | O4 | 88.10(12) | C21 | C20 | C19 | 118.9(3) |
| O1 | U1 | O3 | 95.31(12) | C29 | C20 | C19 | 120.1(3) |
| C29 | O2 | U1 | 133.9(2) | C29 | C20 | C21 | 120.4(4) |
| C12 | N1 | U1 | 115.8(2) | C17 | C18 | N2 | 109.0(3) |
| C11 | N1 | U1 | 126.0(3) | C20 | C19 | N2 | 126.1(3) |
| C11 | N1 | C12 | 117.8(3) | C26 | C21 | C20 | 118.9(4) |
| C18 | N2 | U1 | 113.4(2) | C22 | C21 | C20 | 123.6(4) |
| C19 | N2 | U1 | 128.8(3) | C22 | C21 | C26 | 117.5(4) |
| C19 | N2 | C18 | 117.8(3) | C27 | C28 | C29 | 122.0(4) |
| C13 | N3 | U1 | 120.6(2) | C20 | C29 | O2 | 123.0(3) |
| C17 | N3 | U1 | 120.4(2) | C28 | C29 | O2 | 118.2(4) |
| C17 | N3 | C13 | 119.0(3) | C28 | C29 | C20 | 118.6(4) |
| C15 | C16 | C17 | 118.5(3) | C26 | C27 | C28 | 121.5(4) |
| C13 | C12 | N1 | 108.7(3) | C24 | C25 | C26 | 120.9(4) |
| C11 | C10 | C9 | 118.6(3) | C27 | C26 | C21 | 118.6(4) |
| C1 | C10 | C9 | 120.3(3) | C25 | C26 | C21 | 119.6(4) |
| C1 | C10 | C11 | 120.5(4) | C25 | C26 | C27 | 121.8(4) |
| C12 | C13 | N3 | 114.7(3) | C23 | C24 | C25 | 120.0(4) |
| C14 | C13 | N3 | 122.4(3) | C23 | C22 | C21 | 121.6(5) |
| C14 | C13 | C12 | 122.9(3) | C22 | C23 | C24 | 120.4(5) |
| C16 | C17 | N3 | 121.8(3) | C1 | O1 | U1 | 127.9(2) |
| C18 | C17 | N3 | 114.6(3) | | | | |

**Crystallographic Table 52** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **$UO_2[L^{IV}]$**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H16 | 2031.1(16) | 506(5) | 5206(2) | 18.2(7) |
| H12a | 3420.9(18) | 6759(5) | 6243(2) | 21.2(8) |
| H12b | 2819.9(18) | 7781(5) | 5840(2) | 21.2(8) |
| H15 | 2396.0(18) | 1366(6) | 6705(3) | 22.1(9) |

| | | | | |
|---|---|---|---|---|
| H14 | 2870.9(18) | 4217(5) | 6973(2) | 20.3(8) |
| H6 | 6525(2) | 8172(6) | 4615(4) | 37.6(12) |
| H2 | 4034(2) | 10295(6) | 2224(3) | 28.9(10) |
| H11 | 4130.7(18) | 7398(5) | 5516(3) | 19.6(8) |
| H3 | 5045(2) | 10227(6) | 2407(3) | 30.2(10) |
| H7 | 6020(2) | 6790(6) | 5727(4) | 35.5(12) |
| H8 | 4995.8(19) | 6680(6) | 5532(3) | 27.4(10) |
| H5 | 6003(2) | 9356(6) | 3299(3) | 33.7(11) |
| H18a | 1746.6(18) | 1594(5) | 3587(3) | 19.1(8) |
| H18b | 2407.7(18) | 1880(5) | 3350(3) | 19.1(8) |
| H19 | 1149.7(16) | 3177(5) | 2697(2) | 18.3(8) |
| H28 | 1611(2) | 9045(7) | 822(3) | 37.1(12) |
| H27 | 649(2) | 8980(6) | 170(3) | 36.5(12) |
| H25 | -369(2) | 7702(7) | 81(3) | 36.1(12) |
| H24 | -1026(2) | 5622(8) | 573(4) | 41.7(13) |
| H22 | 248.4(19) | 3692(7) | 2488(3) | 35.1(12) |
| H23 | -722(2) | 3678(8) | 1809(4) | 41.6(13) |

## $H_2[L^{VII}]$

**Crystallographic Table 53** Crystal data and structure refinement for **$H_2[L^{VII}]$**

| | |
|---|---|
| Empirical formula | $C_{29}H_{22}N_2O_2Cl_2$ |
| Formula weight | 501.42 |
| Temperature/K | 180.45 |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 7.1378(10) |
| b/Å | 16.682(2) |
| c/Å | 20.056(3) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2388.1(6) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.3945 |
| m/mm$^{-1}$ | 0.303 |
| F(000) | 1041.6 |
| Crystal size/mm$^3$ | 0.4 × 0.3 × 0.06 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 4.06 to 57.4° |
| Index ranges | $-9 \le h \le 9$, $-22 \le k \le 22$, $-27 \le l \le 22$ |
| Reflections collected | 17603 |
| Independent reflections | 6177 [$R_{int}$ = 0.0539, $R_{sigma}$ = 0.0733] |
| Data/restraints/parameters | 6177/0/318 |
| Goodness-of-fit on $F^2$ | 1.036 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0556, $wR_2$ = 0.1167 |
| Final R indexes [all data] | $R_1$ = 0.0869, $wR_2$ = 0.1284 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.65/-0.64 |
| Flack parameter | -0.10(7) |

**Crystallographic Table 54** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for **$H_2[L^{VII}]$**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Cl1 | 2694.3(12) | 711.1(5) | 7279.7(4) | 54.7(2) |
| Cl2 | -91.0(15) | -266.7(6) | 6613.8(5) | 76.7(3) |
| O1 | 3838(3) | 758.8(10) | 5454.9(9) | 33.6(4) |

| | | | | |
|---|---|---|---|---|
| O2 | 1504(3) | 2189.6(10) | 5876(1) | 32.6(4) |
| N1 | 3053(3) | 998.7(10) | 4218.4(10) | 21.9(4) |
| N2 | 2093(3) | 2498.5(10) | 4636.3(10) | 23.0(4) |
| C6 | 5919(4) | -2672.6(15) | 4246.2(15) | 39.4(7) |
| C5 | 6087(4) | -2349.1(14) | 4870.4(15) | 33.2(6) |
| C4 | 5436(3) | -1559.6(13) | 5008.4(13) | 26.1(5) |
| C9 | 4655(3) | -1092.2(13) | 4496.0(12) | 22.9(5) |
| C10 | 4117(3) | -267.4(13) | 4633.9(12) | 21.3(5) |
| C11 | 3519(3) | 241.4(13) | 4125.5(12) | 22.0(5) |
| C12 | 2486(3) | 1554.4(13) | 3731.9(11) | 21.1(5) |
| C17 | 1991(3) | 2330.3(13) | 3943.7(12) | 21.0(5) |
| C18 | 2578(3) | 3218.5(12) | 4818.0(12) | 22.2(5) |
| C19 | 2632(3) | 3464.1(13) | 5505.2(11) | 21.5(5) |
| C20 | 3239(3) | 4264.4(14) | 5691.5(12) | 25.0(5) |
| C25 | 3177(3) | 4491.4(14) | 6371.5(13) | 29.2(6) |
| C24 | 3724(4) | 5278.1(17) | 6556.7(15) | 39.2(7) |
| C23 | 4318(4) | 5817.7(16) | 6089.2(17) | 42.1(7) |
| C3 | 5601(4) | -1234.0(15) | 5666.9(14) | 31.3(6) |
| C2 | 5040(4) | -485.3(15) | 5807.1(14) | 31.0(6) |
| C1 | 4296(3) | 43.1(13) | 5300.7(13) | 25.8(5) |
| C8 | 4444(4) | -1455.5(14) | 3863.3(14) | 31.2(6) |
| C7 | 5067(4) | -2223.7(15) | 3746.3(15) | 37.3(6) |
| C13 | 2429(4) | 1369.6(14) | 3054.7(12) | 27.3(5) |
| C14 | 1881(4) | 1939.5(15) | 2595.4(13) | 31.5(6) |
| C15 | 1343(4) | 2700.5(15) | 2804.2(13) | 32.6(6) |
| C16 | 1387(4) | 2888.8(14) | 3474.6(13) | 28.5(6) |
| C26 | 2578(4) | 3930.1(16) | 6853.7(14) | 35.3(6) |
| C27 | 2049(3) | 3175.4(15) | 6680.7(13) | 31.6(6) |
| C28 | 2069(3) | 2938.2(14) | 6007.5(13) | 26.7(5) |
| C22 | 4395(4) | 5593.0(15) | 5419.0(14) | 32.8(6) |
| C21 | 3879(3) | 4843.3(14) | 5222.4(14) | 27.2(5) |
| C29 | 966(4) | 681(2) | 6663.7(16) | 50.0(8) |

**Crystallographic Table 55** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **$H_2[L^{VII}]$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{12}$** | **$U_{13}$** | **$U_{23}$** |
|---|---|---|---|---|---|---|
| Cl1 | 65.3(5) | 63.6(5) | 35.2(4) | -23.4(4) | 0.2(4) | -0.8(4) |
| Cl2 | 85.4(7) | 89.7(7) | 55.0(6) | -48.7(6) | -16.8(5) | 20.5(5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O1 | 51.3(11) | 23.7(8) | 25.8(10) | 0.6(8) | -0.2(8) | -2.6(7) |
| O2 | 40.7(10) | 31.1(9) | 25.8(11) | -3.0(8) | 4.3(9) | 5.7(8) |
| N1 | 24.1(9) | 20.4(9) | 21.2(11) | -1.9(7) | 0.6(8) | -0.1(8) |
| N2 | 26.1(10) | 21.2(9) | 21.6(11) | 1.9(8) | 0.2(8) | 1.2(8) |
| C6 | 45.0(16) | 20.5(12) | 53(2) | 4.5(11) | 11.6(14) | -2.7(12) |
| C5 | 35.6(14) | 22.2(12) | 41.8(18) | 3.1(10) | 2.2(12) | 8.0(11) |
| C4 | 22.6(11) | 21.5(11) | 34.2(16) | 0.4(9) | 2.6(10) | 2.1(10) |
| C9 | 20.0(11) | 19.5(10) | 29.2(15) | -1.6(8) | 3.5(10) | 4.1(10) |
| C10 | 18.9(10) | 20.4(10) | 24.7(14) | -2.0(8) | 0.4(9) | 0.1(9) |
| C11 | 21.2(10) | 19.6(10) | 25.2(14) | -3.7(8) | 1.1(10) | 0.6(10) |
| C12 | 18.6(10) | 22.2(10) | 22.4(13) | -3.3(9) | -0.1(10) | 4.0(9) |
| C17 | 20.8(11) | 22.9(11) | 19.2(13) | -4.9(9) | 1.7(9) | 0.4(9) |
| C18 | 20(1) | 22.6(11) | 23.8(13) | 2.8(9) | 4(1) | 4.2(9) |
| C19 | 17.7(10) | 23.3(10) | 23.6(13) | 5.1(9) | -0.8(9) | 1.4(9) |
| C20 | 18.3(10) | 28.3(12) | 28.4(14) | 6.9(9) | -3.5(9) | -3(1) |
| C25 | 26.3(12) | 32.6(13) | 28.6(15) | 11.2(10) | -5.5(10) | -4.4(11) |
| C24 | 37.6(14) | 43.5(16) | 36.6(17) | 9.2(12) | -8.7(13) | -16.0(14) |
| C23 | 36.4(14) | 30.1(14) | 60(2) | 2.7(11) | -10.3(14) | -15.2(14) |
| C3 | 30.2(13) | 30.7(12) | 33.1(17) | -0.5(10) | -1.0(11) | 12.6(11) |
| C2 | 34.7(13) | 34.6(13) | 23.8(14) | -1.5(11) | 0.1(11) | 1.7(11) |
| C1 | 24.9(11) | 23.4(11) | 29.3(15) | -3.4(9) | 3.4(10) | 2.2(10) |
| C8 | 37.3(14) | 26.1(12) | 30.2(15) | 1.0(11) | 0.3(11) | -2.0(11) |
| C7 | 47.8(16) | 27.5(13) | 36.5(17) | 3.2(12) | 6.2(13) | -6.4(12) |
| C13 | 29.9(12) | 24.7(11) | 27.4(14) | -1.2(10) | 2.5(11) | -0.3(10) |
| C14 | 35.5(13) | 38.4(13) | 20.8(15) | -2.4(11) | 2.2(11) | 1.9(11) |
| C15 | 39.7(14) | 32.4(13) | 25.8(15) | -1.5(11) | -3.4(12) | 9.0(11) |
| C16 | 35.5(13) | 21.5(11) | 28.6(15) | 0.3(10) | -2.5(11) | 2.8(10) |
| C26 | 33.1(13) | 49.2(16) | 23.5(15) | 10.7(12) | -2.9(12) | -7.3(12) |
| C27 | 30.9(13) | 42.1(14) | 21.9(14) | 8.1(11) | 4.2(11) | 4.5(11) |
| C28 | 21.9(11) | 28.4(12) | 29.6(15) | 4.4(9) | -1.9(10) | 1.9(10) |
| C22 | 32.1(13) | 25.1(12) | 41.1(17) | 3.3(10) | -4.3(12) | 0.5(11) |
| C21 | 22.7(11) | 26.5(11) | 32.2(15) | 3.4(9) | -3.7(10) | 1.0(11) |
| C29 | 52.2(17) | 52.3(18) | 45.6(19) | -2.4(15) | -0.7(15) | 22.2(15) |

**Crystallographic Table 56** Bond Lengths for **$H_2[L^{VII}]$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Cl1 | C29 | 1.747(3) | C17 | C16 | 1.392(3) |
| Cl2 | C29 | 1.755(3) | C18 | C19 | 1.438(3) |

| | | | | | |
|---|---|---|---|---|---|
| O1 | C1 | 1.276(3) | C19 | C20 | 1.453(3) |
| O2 | C28 | 1.338(3) | C19 | C28 | 1.395(3) |
| N1 | C11 | 1.319(3) | C20 | C25 | 1.416(3) |
| N1 | C12 | 1.405(3) | C20 | C21 | 1.423(3) |
| N2 | C17 | 1.419(3) | C25 | C24 | 1.419(4) |
| N2 | C18 | 1.302(3) | C25 | C26 | 1.412(4) |
| C6 | C5 | 1.369(4) | C24 | C23 | 1.367(4) |
| C6 | C7 | 1.392(4) | C23 | C22 | 1.396(4) |
| C5 | C4 | 1.424(3) | C3 | C2 | 1.341(4) |
| C4 | C9 | 1.405(3) | C2 | C1 | 1.446(4) |
| C4 | C3 | 1.433(4) | C8 | C7 | 1.376(3) |
| C9 | C10 | 1.455(3) | C13 | C14 | 1.380(3) |
| C9 | C8 | 1.414(4) | C14 | C15 | 1.391(4) |
| C10 | C11 | 1.394(3) | C15 | C16 | 1.381(4) |
| C10 | C1 | 1.440(4) | C26 | C27 | 1.359(4) |
| C12 | C17 | 1.407(3) | C27 | C28 | 1.407(4) |
| C12 | C13 | 1.393(3) | C22 | C21 | 1.362(3) |

**Crystallographic Table 57** Bond Angles for **$H_2[L^{VII}]$**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| C12 | N1 | C11 | 127.3(2) | C21 | C20 | C25 | 117.7(2) |
| C18 | N2 | C17 | 118.05(19) | C24 | C25 | C20 | 119.4(2) |
| C7 | C6 | C5 | 119.0(2) | C26 | C25 | C20 | 119.4(2) |
| C4 | C5 | C6 | 120.9(2) | C26 | C25 | C24 | 121.2(2) |
| C9 | C4 | C5 | 120.0(2) | C23 | C24 | C25 | 121.0(3) |
| C3 | C4 | C5 | 120.2(2) | C22 | C23 | C24 | 119.7(3) |
| C3 | C4 | C9 | 119.8(2) | C2 | C3 | C4 | 121.4(2) |
| C10 | C9 | C4 | 119.4(2) | C1 | C2 | C3 | 122.0(3) |
| C8 | C9 | C4 | 117.4(2) | C10 | C1 | O1 | 122.6(2) |
| C8 | C9 | C10 | 123.2(2) | C2 | C1 | O1 | 119.6(2) |
| C11 | C10 | C9 | 121.2(2) | C2 | C1 | C10 | 117.7(2) |
| C1 | C10 | C9 | 119.6(2) | C7 | C8 | C9 | 121.2(2) |
| C1 | C10 | C11 | 119.2(2) | C8 | C7 | C6 | 121.3(3) |
| C10 | C11 | N1 | 123.9(2) | C14 | C13 | C12 | 120.4(2) |
| C17 | C12 | N1 | 118.0(2) | C15 | C14 | C13 | 120.4(2) |
| C13 | C12 | N1 | 122.6(2) | C16 | C15 | C14 | 119.6(2) |
| C13 | C12 | C17 | 119.4(2) | C15 | C16 | C17 | 120.8(2) |
| C12 | C17 | N2 | 117.7(2) | C27 | C26 | C25 | 121.6(2) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C16 | C17 | N2 | 123.0(2) | C28 | C27 | C26 | 120.2(2) |
| C16 | C17 | C12 | 119.3(2) | C19 | C28 | O2 | 122.1(2) |
| C19 | C18 | N2 | 122.5(2) | C27 | C28 | O2 | 116.7(2) |
| C20 | C19 | C18 | 121.1(2) | C27 | C28 | C19 | 121.3(2) |
| C28 | C19 | C18 | 120.3(2) | C21 | C22 | C23 | 121.0(3) |
| C28 | C19 | C20 | 118.6(2) | C22 | C21 | C20 | 121.2(3) |
| C25 | C20 | C19 | 119.0(2) | Cl2 | C29 | Cl1 | 111.72(16) |
| C21 | C20 | C19 | 123.3(2) | | | | |

**Crystallographic Table 58** Hydrogen Bonds for **$H_2[L^{VII}]$**.

| D | H | A | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° |
|---|---|---|---|---|---|---|
| O2 | H2 | N2 | 0.80(3) | 1.82(3) | 2.574(3) | 156(3) |

**Crystallographic Table 59** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **$H_2[L^{VII}]$**.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H2 | 1570(50) | 2158(18) | 5480(17) | 48.8(7) |
| H6 | 6378(4) | -3195.9(15) | 4155.5(15) | 47.3(8) |
| H5 | 6646(4) | -2655.6(14) | 5216.5(15) | 39.9(7) |
| H11 | 3441(3) | 30.7(13) | 3686.3(12) | 26.4(6) |
| H18 | 2909(3) | 3596.3(12) | 4483.7(12) | 26.6(6) |
| H24 | 3676(4) | 5432.4(17) | 7012.4(15) | 47.1(8) |
| H23 | 4678(4) | 6343.0(16) | 6219.7(17) | 50.5(9) |
| H3 | 6118(4) | -1555.5(15) | 6011.8(14) | 37.6(7) |
| H2a | 5136(4) | -296.4(15) | 6252.6(14) | 37.2(7) |
| H8 | 3863(4) | -1164.2(14) | 3512.8(14) | 37.4(7) |
| H7 | 4911(4) | -2451.9(15) | 3315.8(15) | 44.8(8) |
| H13 | 2769(4) | 848.0(14) | 2908.2(12) | 32.8(6) |
| H14 | 1872(4) | 1811.2(15) | 2133.9(13) | 37.9(7) |
| H15 | 947(4) | 3088.6(15) | 2487.4(13) | 39.2(7) |
| H16 | 1000(4) | 3405.9(14) | 3617.5(13) | 34.2(7) |
| H26 | 2544(4) | 4083.6(16) | 7309.7(14) | 42.3(7) |
| H27 | 1665(3) | 2807.2(15) | 7015.3(13) | 38.0(7) |
| H22 | 4813(4) | 5968.5(15) | 5095.5(14) | 39.3(7) |
| H21 | 3947(3) | 4704.1(14) | 4763.7(14) | 32.6(6) |
| H29a | -2(4) | 1089(2) | 6763.5(16) | 60.0(9) |
| H29b | 1533(4) | 816(2) | 6227.3(16) | 60.0(9) |
| H1 | 3103(3) | 1175.6(10) | 4631.3(10) | 26.3(5) |

Refinement model description

Number of restraints - 0, number of constraints - 42.

Details:

1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups, All N(H) groups
 At 1.5 times of:
  All O(H) groups
2.a Secondary CH2 refined with riding coordinates:
 C29(H29a,H29b)
2.b Aromatic/amide H refined with riding coordinates:
 N1(H1), C6(H6), C5(H5), C11(H11), C18(H18), C24(H24), C23(H23), C3(H3),
 C2(H2a), C8(H8), C7(H7), C13(H13), C14(H14), C15(H15), C16(H16), C26(H26),
 C27(H27), C22(H22), C21(H21)

## $Th[L^{VII}]_2$

**Crystallographic Table 60** Crystal data and structure refinement for **$Th[L^{VII}]_2$**

| | |
|---|---|
| Empirical formula | $C_{66.5}H_{47.5}N_4O_4Th$ |
| Formula weight | 1198.68 |
| Temperature/K | 180.45 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 11.4987(3) |
| b/Å | 14.3613(4) |
| c/Å | 16.2765(5) |
| α/° | 106.2205(11) |
| β/° | 90.8258(11) |
| γ/° | 94.1516(11) |
| Volume/Å$^3$ | 2572.39(13) |
| Z | 2 |
| $\rho_{calc}$mg/mm$^3$ | 1.5474 |
| m/mm$^{-1}$ | 2.955 |
| F(000) | 1180.2 |
| Crystal size/mm$^3$ | 0.18 × 0.12 × 0.08 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 2.6 to 48.22° |
| Index ranges | $-13 \leq h \leq 13$, $-16 \leq k \leq 16$, $-18 \leq l \leq 18$ |
| Reflections collected | 53501 |
| Independent reflections | 8180 [$R_{int}$ = 0.0498, $R_{sigma}$ = 0.0396] |
| Data/restraints/parameters | 8180/3/686 |
| Goodness-of-fit on $F^2$ | 1.060 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0242, $wR_2$ = 0.0489 |
| Final R indexes [all data] | $R_1$ = 0.0330, $wR_2$ = 0.0516 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.92/-0.91 |

**Crystallographic Table 61** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for **$Th[L^{VII}]_2$**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Th1 | 105.71(10) | 5047.97(10) | 2558.78(8) | 18.78(5) |
| O1 | -621.3(17) | 5380.9(16) | 1388.0(13) | 21.4(5) |
| O3 | 207.8(18) | 5808.6(16) | 3993.1(13) | 22.8(5) |
| O4 | 1803.9(18) | 4430.9(17) | 2831.8(14) | 28.0(6) |

| | | | | |
|---|---|---|---|---|
| N3 | 399(2) | 6951(2) | 2905.6(16) | 18.6(6) |
| N4 | 1928(2) | 5814(2) | 1950.7(16) | 18.8(6) |
| N2 | -1484(2) | 4086(2) | 3193.3(16) | 18.5(6) |
| N1 | -1985(2) | 5709.5(19) | 2808.4(16) | 17.9(6) |
| O2 | -246.0(19) | 3440.0(18) | 1737.1(14) | 28.9(6) |
| C40 | 890(3) | 7271(2) | 2228(2) | 19.2(8) |
| C19 | -1227(3) | 2380(2) | 2444(2) | 22.0(8) |
| C10 | -2247(3) | 6345(2) | 1563(2) | 19.7(8) |
| C45 | 1692(3) | 6681(2) | 1726(2) | 20.6(8) |
| C48 | 4540(3) | 4377(2) | 1675.8(19) | 18.2(8) |
| C12 | -2506(3) | 5541(2) | 3549.0(19) | 17.4(8) |
| C11 | -2588(3) | 6117(2) | 2344(2) | 19.9(8) |
| C2 | -1056(3) | 6097(2) | 302(2) | 24.7(8) |
| C9 | -3009(3) | 6884(2) | 1186(2) | 20.8(8) |
| C16 | -2592(3) | 4539(3) | 4525(2) | 24.5(8) |
| C4 | -2758(3) | 7004(2) | 368(2) | 24.8(8) |
| C20 | -1533(3) | 1392(2) | 2472(2) | 24.2(8) |
| C27 | -348(3) | 1748(3) | 1072(2) | 34.8(10) |
| C29 | -178(3) | 6562(3) | 4549(2) | 22.2(8) |
| C17 | -2208(3) | 4717(2) | 3771(2) | 19.0(8) |
| C56 | 2837(3) | 4204(3) | 2534(2) | 24.0(8) |
| C13 | -3240(3) | 6165(3) | 4075(2) | 26.8(9) |
| C31 | -806(3) | 7235(3) | 5994(2) | 31.7(10) |
| C1 | -1287(3) | 5941(2) | 1111(2) | 18.7(8) |
| C53 | 5055(3) | 3642(3) | 1945(2) | 24.3(8) |
| C41 | 600(3) | 8106(3) | 2019(2) | 26.2(9) |
| C47 | 3411(3) | 4683(2) | 2000(2) | 19.7(8) |
| C3 | -1760(3) | 6609(2) | -48(2) | 28.0(9) |
| C39 | 97(3) | 7608(3) | 3584(2) | 22.5(8) |
| C50 | 6196(3) | 4433(2) | 773(2) | 25.7(9) |
| C8 | -4024(3) | 7291(2) | 1572(2) | 29.3(9) |
| C49 | 5137(3) | 4750(2) | 1062(2) | 23.6(8) |
| C54 | 4446(3) | 3211(3) | 2516(2) | 31.0(9) |
| C51 | 6724(3) | 3733(3) | 1068(2) | 29.4(9) |
| C28 | -587(3) | 2559(3) | 1769(2) | 25.4(9) |
| C44 | 2168(3) | 6944(3) | 1042(2) | 26.3(9) |
| C18 | -1714(3) | 3159(3) | 3054(2) | 20.5(8) |
| C38 | -335(3) | 7442(2) | 4361(2) | 20.2(8) |

| | | | | |
|---|---|---|---|---|
| C37 | -811(3) | 8231(3) | 4995(2) | 25.3(9) |
| C46 | 2965(3) | 5519(2) | 1817.4(19) | 19.1(8) |
| C15 | -3328(3) | 5161(3) | 5029(2) | 33.9(10) |
| C32 | -1016(3) | 8128(3) | 5827(2) | 27.4(9) |
| C52 | 6149(3) | 3336(3) | 1632(2) | 29.0(9) |
| C55 | 3384(3) | 3468(3) | 2796(2) | 28.0(9) |
| C25 | -1285(3) | 609(3) | 1763(2) | 30.7(9) |
| C35 | -1566(3) | 9826(3) | 5458(3) | 41(1) |
| C21 | -2047(3) | 1164(3) | 3174(2) | 34.7(10) |
| C30 | -424(3) | 6480(3) | 5384(2) | 27.2(9) |
| C43 | 1899(3) | 7787(3) | 855(2) | 32.5(9) |
| C24 | -1626(3) | -351(3) | 1772(3) | 40.9(11) |
| C36 | -1124(3) | 9090(3) | 4833(2) | 33.6(9) |
| C5 | -3507(3) | 7510(3) | -21(2) | 33.8(10) |
| C42 | 1106(3) | 8369(3) | 1343(2) | 30.5(9) |
| C14 | -3659(3) | 5958(3) | 4801(2) | 33.7(9) |
| C22 | -2345(3) | 217(3) | 3162(3) | 43.7(11) |
| C33 | -1448(3) | 8894(3) | 6459(2) | 40.3(11) |
| C26 | -700(3) | 826(3) | 1072(2) | 39.8(10) |
| C7 | -4732(3) | 7771(3) | 1169(3) | 35.5(10) |
| C34 | -1714(3) | 9725(3) | 6279(3) | 45.4(12) |
| C6 | -4473(3) | 7868(3) | 364(3) | 37.5(10) |
| C23 | -2153(3) | -542(3) | 2459(3) | 44.6(11) |
| C58S | 4787(4) | 8330(3) | 5026(3) | 50.8(12) |
| C59S | 3832(4) | 7670(3) | 4740(3) | 65.3(14) |
| C63S | 5255(4) | 8778(4) | 4452(3) | 64.5(14) |
| C62S | 4763(5) | 8614(4) | 3643(3) | 73.7(16) |
| C57S | 5301(5) | 8528(4) | 5915(3) | 81.7(17) |
| C60S | 3348(4) | 7486(4) | 3946(4) | 83.7(18) |
| C61S | 3809(5) | 7978(4) | 3390(3) | 77.3(16) |
| C66S | -6167(6) | 9853(5) | -21(7) | 105(3) |
| C64S | -6210(14) | 10433(9) | 1544(8) | 136(6) |
| C67S | -5552(9) | 9616(5) | -796(6) | 111(3) |
| C65S | -5610(8) | 10226(5) | 764(6) | 104(2) |

**Crystallographic Table 62** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **Th[L$^{VII}$]$_2$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{12}$** | **$U_{13}$** | **$U_{23}$** |
|---|---|---|---|---|---|---|

| | | | | | | |
|---|---|---|---|---|---|---|
| Th1 | 17.92(8) | 22.71(8) | 19.14(8) | 5.72(5) | 5.11(5) | 10.30(6) |
| O1 | 19.7(12) | 29.6(15) | 18.0(12) | 8.4(11) | 4(1) | 10.2(11) |
| O3 | 26.7(13) | 26.3(15) | 18.6(12) | 5.3(11) | 3.4(10) | 10.4(11) |
| O4 | 21.2(13) | 38.8(16) | 34.3(14) | 14.7(12) | 9.4(11) | 23.6(13) |
| N3 | 15.6(14) | 23.7(18) | 18.2(15) | 3.8(13) | 5.2(12) | 7.9(14) |
| N4 | 18.7(15) | 21.5(17) | 18.6(15) | 5.8(13) | 3.3(12) | 8.2(13) |
| N2 | 17.9(15) | 20.4(18) | 19.7(15) | 3.7(13) | 1.4(12) | 9.4(13) |
| N1 | 16.7(14) | 19.3(16) | 19.0(15) | 3.6(12) | 6.2(12) | 6.9(13) |
| O2 | 35.3(14) | 26.2(16) | 26.7(14) | 3.7(12) | 11.7(11) | 9.1(12) |
| C40 | 19.2(18) | 16(2) | 21.5(19) | 0.3(15) | 1.6(15) | 4.8(16) |
| C19 | 21.5(19) | 21(2) | 23(2) | 4.3(16) | -3.0(16) | 5.8(17) |
| C10 | 19.6(18) | 19(2) | 20.8(19) | 1.8(15) | -1.4(15) | 6.1(16) |
| C45 | 18.8(18) | 23(2) | 22.6(19) | 6.4(16) | 5.1(15) | 9.6(17) |
| C48 | 15.1(17) | 19(2) | 18.1(18) | 2.0(15) | 0.3(15) | 1.5(16) |
| C12 | 13.8(17) | 20(2) | 19.1(18) | 1.9(15) | 2.3(14) | 5.5(16) |
| C11 | 19.5(18) | 16(2) | 23.3(19) | 2.9(15) | 3.2(16) | 3.9(16) |
| C2 | 28(2) | 26(2) | 20.3(19) | 2.5(17) | 4.1(16) | 6.0(17) |
| C9 | 22.7(19) | 15(2) | 25(2) | -1.0(15) | -5.6(16) | 6.6(16) |
| C16 | 29(2) | 24(2) | 23.7(19) | 3.4(17) | 9.2(16) | 11.4(17) |
| C4 | 31(2) | 18(2) | 25(2) | -2.2(17) | -6.2(17) | 7.1(17) |
| C20 | 20.5(19) | 22(2) | 30(2) | 2.0(16) | -5.4(16) | 8.2(18) |
| C27 | 43(2) | 28(2) | 33(2) | 6.6(19) | 10.4(19) | 6.2(19) |
| C29 | 14.7(18) | 34(2) | 16.9(19) | -0.1(16) | -0.4(15) | 5.1(17) |
| C17 | 15.4(17) | 20(2) | 19.3(18) | 1.8(15) | 4.9(15) | 2.2(16) |
| C56 | 18.4(19) | 31(2) | 24(2) | 4.8(16) | -0.5(16) | 8.4(17) |
| C13 | 26(2) | 30(2) | 27(2) | 11.5(17) | 8.1(17) | 10.2(18) |
| C31 | 19.4(19) | 58(3) | 17(2) | 1.6(19) | 2.5(16) | 10(2) |
| C1 | 22.3(19) | 16.3(19) | 16.6(18) | -1.2(15) | -3.6(15) | 4.1(15) |
| C53 | 22.3(19) | 30(2) | 19.5(19) | 5.3(17) | -2.4(16) | 4.4(17) |
| C41 | 28(2) | 26(2) | 27(2) | 8.9(17) | 10.1(17) | 9.0(17) |
| C47 | 18.2(18) | 24(2) | 17.7(18) | 5.2(15) | 0.1(15) | 5.6(16) |
| C3 | 40(2) | 26(2) | 21(2) | -2.5(18) | -4.5(18) | 11.0(17) |
| C39 | 19.4(18) | 20(2) | 29(2) | 2.3(16) | 0.0(16) | 8.0(18) |
| C50 | 20.8(19) | 28(2) | 23(2) | -1.7(17) | 5.3(16) | 0.0(17) |
| C8 | 30(2) | 25(2) | 37(2) | 4.7(17) | -1.7(18) | 13.7(18) |
| C49 | 21.8(19) | 23(2) | 24.9(19) | 3.7(16) | 2.2(16) | 3.7(16) |
| C54 | 30(2) | 37(2) | 33(2) | 17.6(18) | 0.0(18) | 18.8(19) |
| C51 | 17.5(19) | 39(2) | 25(2) | 8.3(18) | 1.7(16) | -2.3(19) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C28 | 25(2) | 27(2) | 23(2) | 7.1(17) | -0.3(17) | 4.2(18) |
| C44 | 27(2) | 32(2) | 24(2) | 13.6(17) | 13.4(16) | 11.5(18) |
| C18 | 19.1(18) | 26(2) | 18.7(19) | 0.3(16) | 1.3(15) | 10.9(17) |
| C38 | 17.9(18) | 25(2) | 16.8(18) | 0.3(16) | 3.1(15) | 5.2(16) |
| C37 | 17.1(18) | 27(2) | 27(2) | -4.3(16) | 2.8(16) | 1.1(18) |
| C46 | 20.0(19) | 22(2) | 17.5(18) | 2.7(16) | 4.0(15) | 9.0(16) |
| C15 | 37(2) | 44(3) | 22(2) | 3(2) | 14.1(18) | 10.9(19) |
| C32 | 18.9(19) | 38(2) | 21(2) | -2.5(17) | 3.7(16) | 2.3(18) |
| C52 | 24(2) | 34(2) | 28(2) | 11.6(17) | -3.3(17) | 4.3(18) |
| C55 | 27(2) | 35(2) | 31(2) | 10.3(18) | 6.2(17) | 21.0(18) |
| C25 | 24(2) | 24(2) | 41(2) | 2.6(17) | -4.7(18) | 5.5(19) |
| C35 | 38(2) | 30(3) | 51(3) | 2.0(19) | 15(2) | 4(2) |
| C21 | 39(2) | 26(2) | 42(2) | 3.0(18) | 5.4(19) | 13(2) |
| C30 | 21.6(19) | 44(3) | 21(2) | 2.6(18) | 0.1(16) | 16.5(19) |
| C43 | 38(2) | 36(2) | 32(2) | 10.2(19) | 15.0(18) | 20.9(19) |
| C24 | 40(2) | 21(2) | 56(3) | 5.3(19) | -4(2) | 1(2) |
| C36 | 36(2) | 30(2) | 31(2) | -1.5(19) | 13.4(18) | 2.5(19) |
| C5 | 49(3) | 24(2) | 30(2) | 2(2) | -13(2) | 12.2(18) |
| C42 | 42(2) | 21(2) | 35(2) | 11.3(18) | 11.9(19) | 15.1(18) |
| C14 | 34(2) | 34(3) | 33(2) | 10.4(19) | 16.4(18) | 5.9(19) |
| C22 | 45(3) | 33(3) | 59(3) | 1(2) | 11(2) | 23(2) |
| C33 | 34(2) | 49(3) | 29(2) | -3(2) | 9.9(19) | -3(2) |
| C26 | 48(2) | 28(3) | 37(2) | 8(2) | 11(2) | -4(2) |
| C7 | 27(2) | 26(2) | 54(3) | 8.6(18) | -7(2) | 11(2) |
| C34 | 39(2) | 42(3) | 40(3) | 0(2) | 18(2) | -13(2) |
| C6 | 47(3) | 25(2) | 43(3) | 5(2) | -21(2) | 14(2) |
| C23 | 42(2) | 22(2) | 72(3) | 0(2) | 3(2) | 16(2) |
| C58S | 51(3) | 47(3) | 55(3) | 3(2) | 4(2) | 16(2) |
| C59S | 55(3) | 59(3) | 77(4) | -14(3) | 14(3) | 16(3) |
| C63S | 58(3) | 56(3) | 70(4) | -13(3) | 2(3) | 7(3) |
| C62S | 98(4) | 60(4) | 59(4) | -10(3) | 12(3) | 13(3) |
| C57S | 90(4) | 75(4) | 81(4) | 6(3) | -18(3) | 25(3) |
| C60S | 48(3) | 103(5) | 74(4) | -18(3) | -1(3) | -10(4) |
| C61S | 81(4) | 83(4) | 55(3) | 4(3) | -8(3) | -1(3) |
| C66S | 70(4) | 55(4) | 207(8) | -11(4) | -54(6) | 73(5) |
| C64S | 260(20) | 60(9) | 90(10) | 36(11) | 67(12) | 22(8) |
| C67S | 134(8) | 52(4) | 157(8) | -3(5) | -68(6) | 51(5) |
| C65S | 96(6) | 54(4) | 175(8) | 5(4) | -33(6) | 57(5) |

**Crystallographic Table 63** Bond Lengths for **Th[L$^{VII}$]$_2$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Th1 | O1 | 2.254(2) | C29 | C38 | 1.403(5) |
| Th1 | O3 | 2.282(2) | C29 | C30 | 1.427(4) |
| Th1 | O4 | 2.289(2) | C56 | C47 | 1.395(4) |
| Th1 | N3 | 2.627(3) | C56 | C55 | 1.427(5) |
| Th1 | N4 | 2.630(3) | C13 | C14 | 1.382(5) |
| Th1 | N2 | 2.608(3) | C31 | C32 | 1.419(5) |
| Th1 | N1 | 2.644(2) | C31 | C30 | 1.354(5) |
| Th1 | O2 | 2.326(2) | C53 | C54 | 1.420(5) |
| O1 | C1 | 1.311(4) | C53 | C52 | 1.417(4) |
| O3 | C29 | 1.312(4) | C41 | C42 | 1.382(4) |
| O4 | C56 | 1.318(4) | C47 | C46 | 1.442(4) |
| N3 | C40 | 1.417(4) | C39 | C38 | 1.440(4) |
| N3 | C39 | 1.307(4) | C50 | C49 | 1.374(4) |
| N4 | C45 | 1.434(4) | C50 | C51 | 1.400(5) |
| N4 | C46 | 1.295(4) | C8 | C7 | 1.374(5) |
| N2 | C17 | 1.433(4) | C54 | C55 | 1.349(4) |
| N2 | C18 | 1.293(4) | C51 | C52 | 1.363(5) |
| N1 | C12 | 1.426(4) | C44 | C43 | 1.382(5) |
| N1 | C11 | 1.297(4) | C38 | C37 | 1.449(5) |
| O2 | C28 | 1.313(4) | C37 | C32 | 1.424(5) |
| C40 | C45 | 1.408(4) | C37 | C36 | 1.401(5) |
| C40 | C41 | 1.395(4) | C15 | C14 | 1.374(5) |
| C19 | C20 | 1.451(5) | C32 | C33 | 1.407(5) |
| C19 | C28 | 1.403(5) | C25 | C24 | 1.410(5) |
| C19 | C18 | 1.427(5) | C25 | C26 | 1.415(5) |
| C10 | C11 | 1.451(4) | C35 | C36 | 1.380(5) |
| C10 | C9 | 1.447(4) | C35 | C34 | 1.396(5) |
| C10 | C1 | 1.405(4) | C21 | C22 | 1.372(5) |
| C45 | C44 | 1.381(4) | C43 | C42 | 1.386(5) |
| C48 | C53 | 1.414(4) | C24 | C23 | 1.364(5) |
| C48 | C47 | 1.459(4) | C5 | C6 | 1.347(5) |
| C48 | C49 | 1.421(4) | C22 | C23 | 1.375(5) |
| C12 | C17 | 1.394(4) | C33 | C34 | 1.359(6) |
| C12 | C13 | 1.396(4) | C7 | C6 | 1.389(5) |
| C2 | C1 | 1.422(4) | C58S | C59S | 1.382(6) |

| | | | | | |
|---|---|---|---|---|---|
| C2 | C3 | 1.351(5) | C58S | C63S | 1.370(6) |
| C9 | C4 | 1.421(4) | C58S | C57S | 1.498(6) |
| C9 | C8 | 1.418(5) | C59S | C60S | 1.347(7) |
| C16 | C17 | 1.393(4) | C63S | C62S | 1.376(6) |
| C16 | C15 | 1.381(5) | C62S | C61S | 1.356(7) |
| C4 | C3 | 1.414(5) | C60S | C61S | 1.385(7) |
| C4 | C5 | 1.416(5) | C66S | C67S | 1.425(8) |
| C20 | C25 | 1.416(5) | C66S | C65S | 1.369(8) |
| C20 | C21 | 1.401(5) | C64S | C65S | 1.422(10) |
| C27 | C28 | 1.427(5) | C67S | C65S[1] | 1.336(9) |
| C27 | C26 | 1.356(5) | | | |

[1]-1-X,2-Y,-Z

**Crystallographic Table 64** Bond Angles for **Th[L$^{VII}$]$_2$**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O3 | Th1 | O1 | 135.40(8) | C30 | C29 | C38 | 119.2(3) |
| O4 | Th1 | O1 | 132.65(8) | C12 | C17 | N2 | 116.6(3) |
| O4 | Th1 | O3 | 84.21(8) | C16 | C17 | N2 | 122.7(3) |
| N3 | Th1 | O1 | 75.34(8) | C16 | C17 | C12 | 120.7(3) |
| N3 | Th1 | O3 | 67.17(8) | C47 | C56 | O4 | 121.9(3) |
| N3 | Th1 | O4 | 110.38(8) | C55 | C56 | O4 | 117.9(3) |
| N4 | Th1 | O1 | 76.15(7) | C55 | C56 | C47 | 120.1(3) |
| N4 | Th1 | O3 | 104.69(8) | C14 | C13 | C12 | 119.9(3) |
| N4 | Th1 | O4 | 67.66(8) | C30 | C31 | C32 | 121.9(3) |
| N4 | Th1 | N3 | 61.61(8) | C10 | C1 | O1 | 122.3(3) |
| N2 | Th1 | O1 | 110.22(7) | C2 | C1 | O1 | 118.1(3) |
| N2 | Th1 | O3 | 75.51(8) | C2 | C1 | C10 | 119.5(3) |
| N2 | Th1 | O4 | 103.54(8) | C54 | C53 | C48 | 118.7(3) |
| N2 | Th1 | N3 | 125.47(8) | C52 | C53 | C48 | 120.0(3) |
| N2 | Th1 | N4 | 170.99(8) | C52 | C53 | C54 | 121.3(3) |
| N1 | Th1 | O1 | 68.12(8) | C42 | C41 | C40 | 121.1(3) |
| N1 | Th1 | O3 | 78.30(8) | C56 | C47 | C48 | 119.0(3) |
| N1 | Th1 | O4 | 159.18(8) | C46 | C47 | C48 | 119.1(3) |
| N1 | Th1 | N3 | 73.06(8) | C46 | C47 | C56 | 121.7(3) |
| N1 | Th1 | N4 | 127.74(8) | C4 | C3 | C2 | 121.7(3) |
| N1 | Th1 | N2 | 61.26(8) | C38 | C39 | N3 | 126.8(3) |
| O2 | Th1 | O1 | 83.66(8) | C51 | C50 | C49 | 121.5(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O2 | Th1 | O3 | 134.37(8) | C7 | C8 | C9 | 121.4(3) |
| O2 | Th1 | O4 | 79.63(8) | C50 | C49 | C48 | 120.9(3) |
| O2 | Th1 | N3 | 158.17(8) | C55 | C54 | C53 | 122.2(3) |
| O2 | Th1 | N4 | 107.86(8) | C52 | C51 | C50 | 118.8(3) |
| O2 | Th1 | N2 | 67.47(8) | C19 | C28 | O2 | 122.7(3) |
| O2 | Th1 | N1 | 104.75(8) | C27 | C28 | O2 | 119.0(3) |
| C1 | O1 | Th1 | 145.0(2) | C27 | C28 | C19 | 118.2(3) |
| C29 | O3 | Th1 | 140.23(19) | C43 | C44 | C45 | 121.3(3) |
| C56 | O4 | Th1 | 144.0(2) | C19 | C18 | N2 | 128.7(3) |
| C40 | N3 | Th1 | 113.26(19) | C39 | C38 | C29 | 120.4(3) |
| C39 | N3 | Th1 | 128.5(2) | C37 | C38 | C29 | 119.9(3) |
| C39 | N3 | C40 | 118.1(3) | C37 | C38 | C39 | 119.3(3) |
| C45 | N4 | Th1 | 112.75(19) | C32 | C37 | C38 | 119.0(3) |
| C46 | N4 | Th1 | 130.0(2) | C36 | C37 | C38 | 123.9(3) |
| C46 | N4 | C45 | 117.2(3) | C36 | C37 | C32 | 117.1(3) |
| C17 | N2 | Th1 | 112.25(19) | C47 | C46 | N4 | 127.4(3) |
| C18 | N2 | Th1 | 130.3(2) | C14 | C15 | C16 | 120.6(3) |
| C18 | N2 | C17 | 117.4(3) | C37 | C32 | C31 | 118.8(3) |
| C12 | N1 | Th1 | 112.66(18) | C33 | C32 | C31 | 121.2(3) |
| C11 | N1 | Th1 | 129.4(2) | C33 | C32 | C37 | 120.0(4) |
| C11 | N1 | C12 | 117.9(3) | C51 | C52 | C53 | 121.3(3) |
| C28 | O2 | Th1 | 143.8(2) | C54 | C55 | C56 | 120.5(3) |
| C45 | C40 | N3 | 116.8(3) | C24 | C25 | C20 | 119.1(4) |
| C41 | C40 | N3 | 124.2(3) | C26 | C25 | C20 | 118.3(3) |
| C41 | C40 | C45 | 119.0(3) | C26 | C25 | C24 | 122.5(4) |
| C28 | C19 | C20 | 120.6(3) | C34 | C35 | C36 | 119.9(4) |
| C18 | C19 | C20 | 118.5(3) | C22 | C21 | C20 | 121.2(4) |
| C18 | C19 | C28 | 120.4(3) | C31 | C30 | C29 | 121.1(4) |
| C9 | C10 | C11 | 118.7(3) | C42 | C43 | C44 | 119.9(3) |
| C1 | C10 | C11 | 121.2(3) | C23 | C24 | C25 | 121.4(4) |
| C1 | C10 | C9 | 119.5(3) | C35 | C36 | C37 | 121.9(4) |
| C40 | C45 | N4 | 116.7(3) | C6 | C5 | C4 | 121.1(4) |
| C44 | C45 | N4 | 124.1(3) | C43 | C42 | C41 | 119.6(3) |
| C44 | C45 | C40 | 119.1(3) | C15 | C14 | C13 | 120.6(3) |
| C47 | C48 | C53 | 119.4(3) | C23 | C22 | C21 | 121.2(4) |
| C49 | C48 | C53 | 117.3(3) | C34 | C33 | C32 | 120.9(4) |
| C49 | C48 | C47 | 123.2(3) | C25 | C26 | C27 | 122.5(4) |
| C17 | C12 | N1 | 116.6(3) | C6 | C7 | C8 | 120.6(4) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C13 | C12 | N1 | 124.4(3) | C33 | C34 | C35 | 120.2(4) |
| C13 | C12 | C17 | 118.9(3) | C7 | C6 | C5 | 120.2(3) |
| C10 | C11 | N1 | 127.6(3) | C22 | C23 | C24 | 119.3(4) |
| C3 | C2 | C1 | 121.0(3) | C63S | C58S | C59S | 116.7(4) |
| C4 | C9 | C10 | 118.9(3) | C57S | C58S | C59S | 121.5(5) |
| C8 | C9 | C10 | 124.2(3) | C57S | C58S | C63S | 121.8(4) |
| C8 | C9 | C4 | 116.8(3) | C60S | C59S | C58S | 122.7(5) |
| C15 | C16 | C17 | 119.2(3) | C62S | C63S | C58S | 121.6(4) |
| C3 | C4 | C9 | 119.2(3) | C61S | C62S | C63S | 120.1(5) |
| C5 | C4 | C9 | 119.9(3) | C61S | C60S | C59S | 119.4(5) |
| C5 | C4 | C3 | 120.9(3) | C60S | C61S | C62S | 119.4(5) |
| C25 | C20 | C19 | 118.9(3) | C65S | C66S | C67S | 122.3(7) |
| C21 | C20 | C19 | 123.4(3) | C65S[1] | C67S | C66S | 119.3(7) |
| C21 | C20 | C25 | 117.7(3) | C64S | C65S | C66S | 122.9(11) |
| C26 | C27 | C28 | 121.1(4) | C67S[1] | C65S | C66S | 118.4(8) |
| C38 | C29 | O3 | 122.9(3) | C67S[1] | C65S | C64S | 118.7(12) |
| C30 | C29 | O3 | 117.9(3) | | | | |

[1]-1-X,2-Y,-Z

**Crystallographic Table 65** Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for **Th[L$^{VII}$]$_2$**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H11 | -3340(3) | 6285(2) | 2538(2) | 23.9(10) |
| H2 | -396(3) | 5838(2) | 2(2) | 29.6(10) |
| H16 | -2350(3) | 3997(3) | 4690(2) | 29.4(10) |
| H27 | 64(3) | 1855(3) | 601(2) | 41.8(12) |
| H13 | -3450(3) | 6730(3) | 3934(2) | 32.2(10) |
| H31 | -936(3) | 7166(3) | 6550(2) | 38.1(12) |
| H41 | 47(3) | 8500(3) | 2347(2) | 31.4(10) |
| H3 | -1580(3) | 6706(2) | -587(2) | 33.6(11) |
| H39 | 171(3) | 8264(3) | 3563(2) | 26.9(10) |
| H50 | 6578(3) | 4695(2) | 364(2) | 30.8(10) |
| H8 | -4218(3) | 7231(2) | 2121(2) | 35.2(11) |
| H49 | 4799(3) | 5224(2) | 848(2) | 28.3(10) |
| H54 | 4796(3) | 2727(3) | 2707(2) | 37.2(11) |
| H51 | 7470(3) | 3538(3) | 879(2) | 35.2(11) |
| H44 | 2692(3) | 6537(3) | 692(2) | 31.5(10) |
| H18 | -2285(3) | 2971(3) | 3406(2) | 24.5(10) |

| | | | | |
|---|---|---|---|---|
| H46 | 3491(3) | 5897(2) | 1570.9(19) | 23.0(9) |
| H15 | -3607(3) | 5036(3) | 5537(2) | 40.7(11) |
| H52 | 6489(3) | 2843(3) | 1819(2) | 34.8(11) |
| H55 | 2998(3) | 3156(3) | 3172(2) | 33.6(11) |
| H35 | -1770(3) | 10401(3) | 5330(3) | 49.2(13) |
| H21 | -2193(3) | 1674(3) | 3668(2) | 41.7(12) |
| H30 | -319(3) | 5886(3) | 5514(2) | 32.7(11) |
| H43 | 2256(3) | 7966(3) | 393(2) | 39.0(11) |
| H24 | -1484(3) | -876(3) | 1289(3) | 49.1(13) |
| H36 | -1029(3) | 9167(3) | 4276(2) | 40.4(11) |
| H5 | -3326(3) | 7600(3) | -563(2) | 40.6(12) |
| H42 | 911(3) | 8945(3) | 1214(2) | 36.7(11) |
| H14 | -4181(3) | 6371(3) | 5147(2) | 40.5(11) |
| H22 | -2690(3) | 84(3) | 3648(3) | 52.5(13) |
| H33 | -1556(3) | 8830(3) | 7019(2) | 48.3(13) |
| H26 | -549(3) | 305(3) | 588(2) | 47.8(12) |
| H7 | -5405(3) | 8039(3) | 1442(3) | 42.7(12) |
| H34 | -2001(3) | 10238(3) | 6714(3) | 54.5(14) |
| H6 | -4979(3) | 8187(3) | 85(3) | 45.0(12) |
| H23 | -2386(3) | -1192(3) | 2452(3) | 53.5(13) |
| H59S | 3503(4) | 7333(3) | 5118(3) | 78.3(17) |
| H63S | 5935(4) | 9212(4) | 4615(3) | 77.4(17) |
| H62S | 5091(5) | 8947(4) | 3262(3) | 88.4(19) |
| H57a | 4760(14) | 8250(20) | 6261(7) | 122(3) |
| H57b | 6044(16) | 8230(20) | 5892(4) | 122(3) |
| H57c | 5430(30) | 9232(4) | 6172(9) | 122(3) |
| H60S | 2695(4) | 7023(4) | 3770(4) | 100(2) |
| H61S | 3460(5) | 7870(4) | 2835(3) | 92.7(19) |
| H66S | -6994(6) | 9749(5) | -50(7) | 126(3) |
| H64a | -6840(60) | 10850(70) | 1510(30) | 204(10) |
| H64b | -6540(80) | 9823(10) | 1640(40) | 204(10) |
| H64c | -5660(20) | 10770(70) | 2019(11) | 204(10) |
| H67S | -5963(9) | 9348(5) | -1331(6) | 133(3) |

**Crystallographic Table 66** Atomic Occupancy for **Th[L$^{VII}$]$_2$**.

| **Atom** | ***Occupancy*** | **Atom** | ***Occupancy*** | **Atom** | ***Occupancy*** |
|---|---|---|---|---|---|
| C64S | 0.500000 | H64a | 0.500000 | H64b | 0.500000 |
| H64c | 0.500000 | | | | |

Refinement model description

Number of restraints - 3, number of constraints - 94.

Details:

1. Others
Fixed Sof: C64S(0.5) H64a(0.5) H64b(0.5) H64c(0.5)

## $Ce[L^{VII}]_2$

**Crystallographic Table 67** Crystal data and structure refinement for **$Ce[L^{VII}]_2$**

| | |
|---|---|
| Empirical formula | $C_{59}H_{36}CeN_4O_5$ |
| Formula weight | 1021.08 |
| Temperature/K | 180.45 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 13.0103(8) |
| b/Å | 13.9521(8) |
| c/Å | 26.1970(15) |
| α/° | 90 |
| β/° | 99.6888(12) |
| γ/° | 90 |
| Volume/$Å^3$ | 4687.5(5) |
| Z | 4 |
| $\rho_{calc}mg/mm^3$ | 1.4468 |
| $m/mm^{-1}$ | 1.028 |
| F(000) | 2064.4 |
| Crystal size/$mm^3$ | 0.45 × 0.15 × 0.02 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 3.16 to 53.46° |
| Index ranges | $-16 \le h \le 15$, $-17 \le k \le 17$, $-33 \le l \le 32$ |
| Reflections collected | 61172 |
| Independent reflections | 9966 [$R_{int}$ = 0.0428, $R_{sigma}$ = 0.0340] |
| Data/restraints/parameters | 9966/0/621 |
| Goodness-of-fit on $F^2$ | 1.068 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0292, $wR_2$ = 0.0699 |
| Final R indexes [all data] | $R_1$ = 0.0442, $wR_2$ = 0.0769 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.78/-0.60 |

**Crystallographic Table 68** Fractional Atomic Coordinates (×$10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2$×$10^3$) for **$Ce[L^{VII}]_2$**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Ce1 | 1318.5(1) | 924.77(10) | 1757.27(5) | 16.96(5) |
| O1 | 2153.0(13) | 1636.4(12) | 2452.6(6) | 20.5(4) |
| O2 | 218.8(13) | 2157.9(13) | 1776.9(7) | 22.6(4) |
| N4 | 472.8(16) | 112.9(14) | 2439.2(8) | 19.3(4) |

| | | | | |
|---|---|---|---|---|
| C39 | 2988.5(19) | -1063.5(17) | 2130.4(10) | 19.4(5) |
| O4 | -210.9(14) | 285.7(13) | 1391.0(7) | 25.3(4) |
| N1 | 2969.9(16) | 1761.5(15) | 1562.4(8) | 19.7(5) |
| N2 | 1130.1(16) | 1872.6(15) | 927.5(8) | 19.3(4) |
| O3 | 1949.3(14) | -80.5(12) | 1234.8(7) | 22.9(4) |
| N3 | 2356.2(16) | -437.6(15) | 2274.5(8) | 18.7(4) |
| C46 | -520.0(19) | 3.7(18) | 2434.2(10) | 21.0(5) |
| C9 | 4885(2) | 2432.3(17) | 2724.8(10) | 21.6(5) |
| C11 | 3738.4(19) | 2143.0(18) | 1878.7(10) | 21.4(5) |
| C19 | -626(2) | 2491.1(18) | 912.6(10) | 21.4(5) |
| C53 | -3244(2) | 260.7(19) | 1688.0(12) | 29.4(6) |
| C29 | 2767(2) | -616.6(18) | 1203.3(10) | 20.6(5) |
| C8 | 5785(2) | 2590.0(18) | 2500.9(11) | 26.0(6) |
| C20 | -1563(2) | 2823.2(19) | 578.0(11) | 25.6(6) |
| C37 | 4149.1(19) | -1752.9(17) | 1555.7(10) | 20.0(5) |
| C12 | 2995(2) | 1815.7(19) | 1021.7(10) | 22.2(6) |
| C40 | 2174(2) | -483.5(18) | 2794.6(10) | 20.3(5) |
| C10 | 3890.0(19) | 2133.1(17) | 2432.7(9) | 19.0(5) |
| C45 | 1183.8(19) | -187.4(18) | 2881.2(10) | 20.6(5) |
| C56 | -1155(2) | 301.1(18) | 1506.0(11) | 24.7(6) |
| C47 | -1348.4(19) | 231.7(18) | 2015.1(10) | 21.7(5) |
| C17 | 2031(2) | 1838.1(18) | 685.4(10) | 21.8(6) |
| C35 | 5527(2) | -2890(2) | 1874.3(11) | 27.7(6) |
| C42 | 2694(2) | -761(2) | 3709.7(11) | 30.6(7) |
| C18 | 300.1(19) | 2305.4(18) | 696.2(10) | 21.7(5) |
| C38 | 3300.9(19) | -1118.8(17) | 1628.3(10) | 18.7(5) |
| C16 | 1999(2) | 1792(2) | 151.9(10) | 28.5(6) |
| C32 | 4439(2) | -1827.3(19) | 1058.2(10) | 25.4(6) |
| C52 | -4287(2) | 219(2) | 1780.9(14) | 36.5(7) |
| C43 | 1721(2) | -462(2) | 3797.7(11) | 31.4(7) |
| C34 | 5788(2) | -2974(2) | 1379.2(11) | 29.3(6) |
| C4 | 4988(2) | 2541.8(19) | 3272.3(11) | 24.6(6) |
| C1 | 3072.5(19) | 1889.4(17) | 2700(1) | 19.3(5) |
| C31 | 3890(2) | -1274(2) | 646.2(11) | 32.8(7) |
| C44 | 976(2) | -169.2(19) | 3387.6(10) | 26.5(6) |
| C36 | 4729(2) | -2299.6(19) | 1959.7(11) | 24.4(6) |
| C48 | -2409(2) | 231.1(18) | 2112.9(11) | 25.0(6) |
| C21 | -1670(2) | 2843(2) | 33.5(11) | 34.2(7) |

| | | | | |
|---|---|---|---|---|
| C25 | -2421(2) | 3140(2) | 806.4(12) | 32.1(7) |
| C6 | 6792(2) | 3009(2) | 3329.1(12) | 32.7(7) |
| C5 | 5945(2) | 2847(2) | 3559.7(11) | 31.1(6) |
| C30 | 3090(2) | -690(2) | 712.2(11) | 30.3(7) |
| C28 | -597(2) | 2460.2(18) | 1452(1) | 21.9(6) |
| C33 | 5257(2) | -2450(2) | 984.5(12) | 31.2(7) |
| C14 | 3874(2) | 1757(2) | 282.8(12) | 39.6(8) |
| C27 | -1472(2) | 2805(2) | 1661.4(11) | 32.1(7) |
| C41 | 2920(2) | -764.7(19) | 3211.9(11) | 26.4(6) |
| C54 | -3012(2) | 320(2) | 1178.8(12) | 35.0(7) |
| C3 | 4123(2) | 2301(2) | 3516.9(11) | 28.8(6) |
| C51 | -4502(2) | 171(2) | 2272.5(14) | 39.6(8) |
| C15 | 2917(2) | 1754(2) | -46.9(11) | 36.6(7) |
| C7 | 6715(2) | 2858(2) | 2797.4(12) | 30.1(6) |
| C50 | -3690(2) | 174(2) | 2691.6(13) | 35.6(7) |
| C23 | -3382(3) | 3541(3) | -40.3(14) | 48.5(9) |
| C26 | -2341(2) | 3119(2) | 1349.2(12) | 37.1(7) |
| C55 | -2020(2) | 344(2) | 1086.9(12) | 32.4(7) |
| C13 | 3911(2) | 1774(2) | 814.6(11) | 30.9(7) |
| C49 | -2668(2) | 203(2) | 2615.4(12) | 30.0(6) |
| C22 | -2555(3) | 3205(3) | -264.5(13) | 45.6(8) |
| C24 | -3325(2) | 3495(2) | 483.3(14) | 42.5(8) |
| C2 | 3217(2) | 1968.1(19) | 3246.4(10) | 24.6(6) |
| O5s | -207(2) | 742(2) | -412.4(11) | 76.0(9) |
| C59s | 5082(7) | 60(5) | 4725(3) | 164(6) |
| C58s | 6109(7) | 503(6) | 4711(4) | 164(4) |
| C57s | 6480(10) | 598(6) | 4228(3) | 209(6) |

**Crystallographic Table 69** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **Ce[$L^{VII}$]$_2$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{12}$** | **$U_{13}$** | **$U_{23}$** |
|---|---|---|---|---|---|---|
| Ce1 | 17.85(8) | 19.76(8) | 13.02(8) | -0.55(6) | 1.86(5) | 1.49(6) |
| O1 | 19.6(9) | 24.5(9) | 17.9(9) | -3.0(7) | 4.6(7) | -1.2(7) |
| O2 | 23.4(9) | 27.8(9) | 15.6(9) | 4.6(8) | 0.9(7) | -0.2(8) |
| N4 | 21.8(11) | 20.3(11) | 15.3(11) | -0.6(9) | 1.9(9) | 2.0(9) |
| C39 | 19.0(12) | 20.3(13) | 18.1(13) | -1.4(10) | 1.2(10) | 3.4(10) |
| O4 | 24.6(10) | 30.5(10) | 19.8(10) | -5.6(8) | 1.0(8) | 1.3(8) |
| N1 | 20.0(11) | 25.3(11) | 13.8(11) | 1.8(9) | 3.1(9) | 2.1(9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N2 | 20.6(11) | 22.5(11) | 14.7(11) | -2.4(9) | 3.0(9) | 1.5(9) |
| O3 | 26.0(9) | 25.3(9) | 17.0(9) | 4.6(8) | 2.2(8) | 0.1(8) |
| N3 | 20.1(10) | 22.8(11) | 13.3(11) | -1.1(9) | 2.6(9) | 1.0(9) |
| C46 | 23.8(13) | 20.5(13) | 19.3(14) | -1.9(10) | 5.9(11) | 0.1(10) |
| C9 | 22.1(13) | 16.9(12) | 24.5(14) | 2.8(10) | 0.1(11) | -0.7(10) |
| C11 | 20.6(13) | 22.6(13) | 21.4(14) | 0.6(11) | 5.1(11) | 2.7(11) |
| C19 | 22.1(13) | 20.7(13) | 20.0(14) | -0.1(10) | -0.4(11) | 1.7(10) |
| C53 | 23.7(14) | 20.2(13) | 41.8(18) | -2.1(11) | -2.0(13) | 0.1(12) |
| C29 | 22.5(13) | 20.1(12) | 19.3(14) | -3.2(10) | 3.9(11) | -0.4(10) |
| C8 | 25.6(14) | 24.3(14) | 27.8(16) | -2.3(11) | 3.7(12) | -2.0(12) |
| C20 | 23.7(13) | 24.0(13) | 26.7(15) | -4.7(11) | -2.7(11) | 3.0(12) |
| C37 | 19.2(12) | 20.4(12) | 20.6(14) | -4.8(10) | 3.5(11) | 1.7(11) |
| C12 | 24.0(13) | 28.3(14) | 15.0(13) | -2.0(11) | 5.3(11) | 3.9(11) |
| C40 | 23.7(13) | 20.9(13) | 15.7(13) | -0.7(10) | 2.1(11) | 1.4(10) |
| C10 | 20.7(12) | 19.2(12) | 16.4(13) | 1.7(10) | 1.2(10) | -1.6(10) |
| C45 | 22.5(13) | 20.3(12) | 18.6(14) | -1.2(10) | 2.1(11) | 2.7(10) |
| C56 | 22.4(13) | 21.5(13) | 28.2(15) | -5.5(11) | -1.2(11) | 1.3(11) |
| C47 | 20.9(13) | 18.1(12) | 24.9(15) | -4.1(10) | 0.3(11) | -0.2(11) |
| C17 | 26.2(14) | 23.6(13) | 16.5(13) | -1.3(11) | 6.0(11) | 3.8(11) |
| C35 | 22.2(13) | 28.7(14) | 31.4(16) | 1.3(11) | 2.4(12) | 4.9(12) |
| C42 | 37.6(16) | 35.7(16) | 15.5(14) | 6.4(13) | -4.3(12) | 1.6(12) |
| C18 | 25.7(13) | 22.9(13) | 15.6(13) | -3.1(11) | 1.4(11) | 3.4(11) |
| C38 | 19.6(12) | 17.6(12) | 19.0(13) | -2.9(10) | 3.6(10) | 0.2(10) |
| C16 | 30.1(15) | 37.6(16) | 17.1(14) | -0.5(12) | 2.2(12) | 3.0(12) |
| C32 | 26.5(14) | 28.3(14) | 23.0(15) | -0.5(11) | 8.9(12) | 2.0(12) |
| C52 | 22.4(14) | 24.4(14) | 59(2) | -2.3(12) | -2.2(14) | -1.0(14) |
| C43 | 42.1(17) | 37.2(16) | 15.5(14) | 5.4(14) | 6.4(13) | 3.2(12) |
| C34 | 23.1(14) | 30.3(15) | 36.5(17) | 4.1(12) | 11.3(13) | 1.7(13) |
| C4 | 24.0(13) | 24.7(14) | 22.9(15) | 3.5(11) | -2.1(11) | -1.5(11) |
| C1 | 21.0(13) | 17.3(12) | 18.6(13) | 2.2(10) | 0.4(10) | -0.6(10) |
| C31 | 38.7(17) | 41.9(16) | 20.4(15) | 6.8(14) | 13.1(13) | 4.6(13) |
| C44 | 29.5(15) | 31.3(15) | 19.9(14) | 3.3(12) | 7.7(12) | 1.7(12) |
| C36 | 22.1(13) | 28.6(14) | 23.1(15) | 0.1(11) | 5.5(11) | 1.3(12) |
| C48 | 20.9(13) | 17.3(12) | 35.7(16) | -4.7(10) | 1.5(12) | 0.4(11) |
| C21 | 32.5(16) | 39.5(17) | 28.1(16) | -3.8(13) | -2.2(13) | 4.9(14) |
| C25 | 27.1(15) | 32.1(15) | 35.2(18) | 2.8(12) | -0.4(13) | 3.1(13) |
| C6 | 23.9(14) | 27.2(15) | 41.6(19) | -0.7(12) | -10.3(13) | -2.9(13) |
| C5 | 30.0(15) | 32.4(15) | 26.6(16) | 0.4(12) | -7.2(12) | -3.0(13) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C30 | 39.3(17) | 33.9(15) | 18.5(15) | 6.5(13) | 7.0(13) | 7.5(12) |
| C28 | 23.5(13) | 20.7(13) | 20.8(14) | 1(1) | 1.6(11) | 1.0(11) |
| C33 | 29.8(15) | 38.1(16) | 29.2(16) | 2.5(13) | 15.0(13) | 1.0(13) |
| C14 | 31.2(16) | 65(2) | 25.7(16) | 4.6(15) | 14.2(13) | 11.5(15) |
| C27 | 31.9(15) | 39.7(16) | 25.5(16) | 8.9(13) | 6.9(13) | 0.4(13) |
| C41 | 26.6(14) | 30.1(15) | 21.2(15) | 4.7(11) | 0.9(12) | 1.2(11) |
| C54 | 26.0(15) | 32.6(16) | 40.7(19) | -4.9(12) | -11.4(13) | 3.5(14) |
| C3 | 32.8(15) | 36.7(16) | 15.9(14) | 4.1(13) | 1.3(12) | -0.0(12) |
| C51 | 22.6(15) | 29.0(16) | 69(2) | -3.8(12) | 12.5(16) | -6.5(16) |
| C15 | 39.1(17) | 58(2) | 15.1(15) | 3.0(15) | 10.2(13) | 4.8(14) |
| C7 | 22.2(14) | 27.8(14) | 39.5(18) | -1.2(12) | 3.3(13) | -1.9(13) |
| C50 | 30.0(16) | 28.8(15) | 51(2) | -1.9(13) | 16.0(15) | -3.3(14) |
| C23 | 33.6(18) | 58(2) | 46(2) | 7.3(16) | -16.1(16) | 11.5(18) |
| C26 | 28.0(15) | 43.4(18) | 40.6(19) | 12.2(13) | 8.4(14) | -0.1(15) |
| C55 | 33.2(16) | 34.5(16) | 26.3(16) | -7.5(13) | -4.4(13) | 4.7(13) |
| C13 | 26.0(15) | 45.2(17) | 21.9(15) | 1.2(13) | 4.8(12) | 5.1(13) |
| C49 | 25.1(14) | 27.4(15) | 37.5(18) | -3.3(12) | 5.2(13) | -2.3(13) |
| C22 | 40.5(19) | 60(2) | 31.2(19) | 0.7(16) | -10.1(15) | 10.3(16) |
| C24 | 26.4(16) | 48(2) | 50(2) | 9.8(14) | -2.4(15) | 5.6(17) |
| C2 | 24.3(13) | 30.9(15) | 18.8(14) | 1.8(12) | 4.4(11) | 1.1(11) |
| O5s | 51.6(16) | 114(3) | 55.2(18) | -22.1(16) | -12.2(14) | 2.7(17) |
| C59s | 118(5) | 76(4) | 260(13) | 55(4) | -82(8) | -97(8) |
| C58s | 134(6) | 108(6) | 225(10) | 50(5) | -43(7) | -74(7) |
| C57s | 421(18) | 101(5) | 94(5) | 148(8) | 8(8) | 9(4) |

**Crystallographic Table 70** Bond Lengths for **Ce[L$^{VII}$]$_2$**.

| **Atom** | **Atom** | **Length/Å** | **Atom** | **Atom** | **Length/Å** |
|---|---|---|---|---|---|
| Ce1 | O1 | 2.1948(17) | C12 | C13 | 1.391(4) |
| Ce1 | O2 | 2.2437(17) | C40 | C45 | 1.407(3) |
| Ce1 | N4 | 2.519(2) | C40 | C41 | 1.391(4) |
| Ce1 | O4 | 2.2433(17) | C10 | C1 | 1.410(3) |
| Ce1 | N1 | 2.571(2) | C45 | C44 | 1.398(4) |
| Ce1 | N2 | 2.521(2) | C56 | C47 | 1.402(4) |
| Ce1 | O3 | 2.2117(17) | C56 | C55 | 1.435(4) |
| Ce1 | N3 | 2.580(2) | C47 | C48 | 1.446(3) |
| Ce1 | C56 | 3.291(3) | C17 | C16 | 1.393(4) |
| Ce1 | C28 | 3.281(3) | C35 | C34 | 1.400(4) |
| O1 | C1 | 1.309(3) | C35 | C36 | 1.374(4) |

| | | | | | |
|---|---|---|---|---|---|
| O2 | C28 | 1.313(3) | C42 | C43 | 1.388(4) |
| N4 | C46 | 1.299(3) | C42 | C41 | 1.384(4) |
| N4 | C45 | 1.418(3) | C16 | C15 | 1.381(4) |
| C39 | N3 | 1.299(3) | C32 | C31 | 1.418(4) |
| C39 | C38 | 1.443(3) | C32 | C33 | 1.413(4) |
| O4 | C56 | 1.313(3) | C52 | C51 | 1.365(5) |
| N1 | C11 | 1.300(3) | C43 | C44 | 1.383(4) |
| N1 | C12 | 1.424(3) | C34 | C33 | 1.356(4) |
| N2 | C17 | 1.424(3) | C4 | C5 | 1.408(4) |
| N2 | C18 | 1.295(3) | C4 | C3 | 1.426(4) |
| O3 | C29 | 1.315(3) | C1 | C2 | 1.416(4) |
| N3 | C40 | 1.423(3) | C31 | C30 | 1.355(4) |
| C46 | C47 | 1.439(4) | C48 | C49 | 1.413(4) |
| C9 | C8 | 1.413(4) | C21 | C22 | 1.374(4) |
| C9 | C10 | 1.450(3) | C25 | C26 | 1.409(4) |
| C9 | C4 | 1.426(4) | C25 | C24 | 1.418(4) |
| C11 | C10 | 1.431(3) | C6 | C5 | 1.362(4) |
| C19 | C20 | 1.452(4) | C6 | C7 | 1.396(4) |
| C19 | C18 | 1.439(4) | C28 | C27 | 1.428(4) |
| C19 | C28 | 1.408(4) | C14 | C15 | 1.391(4) |
| C53 | C52 | 1.418(4) | C14 | C13 | 1.386(4) |
| C53 | C48 | 1.419(4) | C27 | C26 | 1.352(4) |
| C53 | C54 | 1.419(4) | C54 | C55 | 1.353(4) |
| C29 | C38 | 1.397(4) | C3 | C2 | 1.351(4) |
| C29 | C30 | 1.423(4) | C51 | C50 | 1.390(4) |
| C8 | C7 | 1.374(4) | C50 | C49 | 1.378(4) |
| C20 | C21 | 1.410(4) | C23 | C22 | 1.391(5) |
| C20 | C25 | 1.423(4) | C23 | C24 | 1.363(5) |
| C37 | C38 | 1.452(3) | C59s | C59s[1] | 1.503(19) |
| C37 | C32 | 1.420(4) | C59s | C58s | 1.479(14) |
| C37 | C36 | 1.415(4) | C58s | C57s | 1.435(13) |
| C12 | C17 | 1.407(4) | | | |

[1]1-X,-Y,1-Z

**Crystallographic Table 71** Bond Angles for **Ce[L$^{VII}$]$_2$**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| O2 | Ce1 | O1 | 82.09(6) | C36 | C37 | C32 | 117.2(2) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N4 | Ce1 | O1 | 80.15(6) | C17 | C12 | N1 | 117.2(2) |
| N4 | Ce1 | O2 | 88.41(6) | C13 | C12 | N1 | 123.4(2) |
| O4 | Ce1 | O1 | 144.50(6) | C13 | C12 | C17 | 119.3(2) |
| O4 | Ce1 | O2 | 77.96(7) | C45 | C40 | N3 | 116.5(2) |
| O4 | Ce1 | N4 | 70.29(6) | C41 | C40 | N3 | 123.9(2) |
| N1 | Ce1 | O1 | 69.28(6) | C41 | C40 | C45 | 119.5(2) |
| N1 | Ce1 | O2 | 102.34(6) | C11 | C10 | C9 | 119.4(2) |
| N1 | Ce1 | N4 | 145.52(7) | C1 | C10 | C9 | 119.2(2) |
| N1 | Ce1 | O4 | 143.74(6) | C1 | C10 | C11 | 121.3(2) |
| N2 | Ce1 | O1 | 116.18(6) | C40 | C45 | N4 | 116.3(2) |
| N2 | Ce1 | O2 | 69.37(6) | C44 | C45 | N4 | 124.4(2) |
| N2 | Ce1 | N4 | 148.94(7) | C44 | C45 | C40 | 119.2(2) |
| N2 | Ce1 | O4 | 83.64(6) | O4 | C56 | Ce1 | 29.48(11) |
| N2 | Ce1 | N1 | 63.50(6) | C47 | C56 | Ce1 | 98.86(16) |
| O3 | Ce1 | O1 | 128.11(6) | C47 | C56 | O4 | 122.8(2) |
| O3 | Ce1 | O2 | 143.59(6) | C55 | C56 | Ce1 | 139.15(19) |
| O3 | Ce1 | N4 | 113.92(7) | C55 | C56 | O4 | 117.9(2) |
| O3 | Ce1 | O4 | 83.00(7) | C55 | C56 | C47 | 119.2(2) |
| O3 | Ce1 | N1 | 75.85(7) | C56 | C47 | C46 | 120.7(2) |
| O3 | Ce1 | N2 | 77.96(7) | C48 | C47 | C46 | 118.7(2) |
| N3 | Ce1 | O1 | 75.83(6) | C48 | C47 | C56 | 119.9(2) |
| N3 | Ce1 | O2 | 146.33(6) | C12 | C17 | N2 | 115.8(2) |
| N3 | Ce1 | N4 | 63.17(6) | C16 | C17 | N2 | 124.2(2) |
| N3 | Ce1 | O4 | 106.25(6) | C16 | C17 | C12 | 120.0(2) |
| N3 | Ce1 | N1 | 93.32(6) | C36 | C35 | C34 | 120.6(3) |
| N3 | Ce1 | N2 | 143.68(6) | C41 | C42 | C43 | 120.1(3) |
| N3 | Ce1 | O3 | 69.02(6) | C19 | C18 | N2 | 125.9(2) |
| C56 | Ce1 | O1 | 128.03(6) | C29 | C38 | C39 | 121.4(2) |
| C56 | Ce1 | O2 | 66.52(6) | C37 | C38 | C39 | 119.3(2) |
| C56 | Ce1 | N4 | 59.60(7) | C37 | C38 | C29 | 119.2(2) |
| C56 | Ce1 | O4 | 16.74(7) | C15 | C16 | C17 | 119.9(3) |
| C56 | Ce1 | N1 | 154.42(7) | C31 | C32 | C37 | 118.8(2) |
| C56 | Ce1 | N2 | 90.93(7) | C33 | C32 | C37 | 119.5(2) |
| C56 | Ce1 | O3 | 99.25(7) | C33 | C32 | C31 | 121.7(2) |
| C56 | Ce1 | N3 | 108.54(6) | C51 | C52 | C53 | 121.2(3) |
| C28 | Ce1 | O1 | 98.99(6) | C44 | C43 | C42 | 120.0(3) |
| C28 | Ce1 | O2 | 17.06(6) | C33 | C34 | C35 | 119.3(3) |
| C28 | Ce1 | N4 | 93.55(6) | C5 | C4 | C9 | 119.7(2) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C28 | Ce1 | O4 | 64.70(6) | C3 | C4 | C9 | 118.6(2) |
| C28 | Ce1 | N1 | 106.32(6) | C3 | C4 | C5 | 121.7(3) |
| C28 | Ce1 | N2 | 59.18(6) | C10 | C1 | O1 | 121.5(2) |
| C28 | Ce1 | O3 | 127.50(6) | C2 | C1 | O1 | 118.4(2) |
| C28 | Ce1 | N3 | 156.60(6) | C2 | C1 | C10 | 120.0(2) |
| C28 | Ce1 | C56 | 56.43(6) | C30 | C31 | C32 | 121.9(3) |
| C1 | O1 | Ce1 | 144.66(16) | C43 | C44 | C45 | 120.6(2) |
| C28 | O2 | Ce1 | 132.87(15) | C35 | C36 | C37 | 121.6(3) |
| C46 | N4 | Ce1 | 126.73(17) | C47 | C48 | C53 | 119.3(3) |
| C45 | N4 | Ce1 | 114.15(15) | C49 | C48 | C53 | 117.4(2) |
| C45 | N4 | C46 | 119.0(2) | C49 | C48 | C47 | 123.3(2) |
| C38 | C39 | N3 | 126.2(2) | C22 | C21 | C20 | 120.9(3) |
| C56 | O4 | Ce1 | 133.78(17) | C26 | C25 | C20 | 119.2(3) |
| C11 | N1 | Ce1 | 129.64(16) | C24 | C25 | C20 | 119.2(3) |
| C12 | N1 | Ce1 | 112.42(15) | C24 | C25 | C26 | 121.5(3) |
| C12 | N1 | C11 | 117.9(2) | C7 | C6 | C5 | 119.3(3) |
| C17 | N2 | Ce1 | 113.49(15) | C6 | C5 | C4 | 121.5(3) |
| C18 | N2 | Ce1 | 126.90(16) | C31 | C30 | C29 | 120.6(3) |
| C18 | N2 | C17 | 119.4(2) | O2 | C28 | Ce1 | 30.07(11) |
| C29 | O3 | Ce1 | 142.02(16) | C19 | C28 | Ce1 | 98.96(16) |
| C39 | N3 | Ce1 | 130.07(17) | C19 | C28 | O2 | 122.9(2) |
| C40 | N3 | Ce1 | 112.28(15) | C27 | C28 | Ce1 | 138.44(18) |
| C40 | N3 | C39 | 117.6(2) | C27 | C28 | O2 | 118.0(2) |
| C47 | C46 | N4 | 126.7(2) | C27 | C28 | C19 | 119.1(2) |
| C10 | C9 | C8 | 123.7(2) | C34 | C33 | C32 | 121.8(3) |
| C4 | C9 | C8 | 117.2(2) | C13 | C14 | C15 | 120.0(3) |
| C4 | C9 | C10 | 119.1(2) | C26 | C27 | C28 | 121.1(3) |
| C10 | C11 | N1 | 127.0(2) | C42 | C41 | C40 | 120.5(3) |
| C18 | C19 | C20 | 119.5(2) | C55 | C54 | C53 | 122.0(3) |
| C28 | C19 | C20 | 119.6(2) | C2 | C3 | C4 | 122.0(2) |
| C28 | C19 | C18 | 120.5(2) | C50 | C51 | C52 | 119.7(3) |
| C48 | C53 | C52 | 119.5(3) | C14 | C15 | C16 | 120.4(3) |
| C54 | C53 | C52 | 121.7(3) | C6 | C7 | C8 | 120.9(3) |
| C54 | C53 | C48 | 118.9(3) | C49 | C50 | C51 | 120.6(3) |
| C38 | C29 | O3 | 122.3(2) | C24 | C23 | C22 | 119.6(3) |
| C30 | C29 | O3 | 117.6(2) | C27 | C26 | C25 | 122.0(3) |
| C30 | C29 | C38 | 120.1(2) | C54 | C55 | C56 | 120.8(3) |
| C7 | C8 | C9 | 121.3(3) | C14 | C13 | C12 | 120.4(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C21 | C20 | C19 | 123.2(3) | C50 | C49 | C48 | 121.5(3) |
| C25 | C20 | C19 | 118.9(2) | C23 | C22 | C21 | 121.2(3) |
| C25 | C20 | C21 | 117.9(3) | C23 | C24 | C25 | 121.1(3) |
| C32 | C37 | C38 | 119.3(2) | C3 | C2 | C1 | 120.8(2) |
| C36 | C37 | C38 | 123.5(2) | C57s | C58s | C59s | 120.0(9) |

**Crystallographic Table 72** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **Ce[L$^{VII}$]$_2$**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H39 | 3272.5(19) | -1529.1(17) | 2379.3(10) | 23.2(6) |
| H46 | -720.0(19) | -253.2(18) | 2738.7(10) | 25.2(6) |
| H11 | 4255.1(19) | 2462.9(18) | 1725.6(10) | 25.6(7) |
| H8 | 5748(2) | 2509.1(18) | 2138.2(11) | 31.2(7) |
| H35 | 5906(2) | -3245(2) | 2153.8(11) | 33.2(7) |
| H42 | 3205(2) | -964(2) | 3991.6(11) | 36.7(8) |
| H18 | 303.0(19) | 2519.8(18) | 352.3(10) | 26.0(7) |
| H16 | 1348(2) | 1787(2) | -75.1(10) | 34.2(7) |
| H52 | -4845(2) | 225(2) | 1495.9(14) | 43.8(9) |
| H43 | 1568(2) | -459(2) | 4139.7(11) | 37.7(8) |
| H34 | 6331(2) | -3393(2) | 1320.2(11) | 35.1(8) |
| H31 | 4089(2) | -1314(2) | 314.1(11) | 39.3(8) |
| H44 | 316(2) | 46.6(19) | 3450.5(10) | 31.8(7) |
| H36 | 4561(2) | -2257.2(19) | 2298.2(11) | 29.3(7) |
| H21 | -1123(2) | 2604(2) | -129.4(11) | 41.1(8) |
| H6 | 7429(2) | 3222(2) | 3528.3(12) | 39.2(8) |
| H5 | 6001(2) | 2942(2) | 3922.4(11) | 37.3(8) |
| H30 | 2742(2) | -328(2) | 428.1(11) | 36.4(8) |
| H33 | 5441(2) | -2504(2) | 649.7(12) | 37.4(8) |
| H14 | 4502(2) | 1746(2) | 143.5(12) | 47.5(9) |
| H27 | -1443(2) | 2814(2) | 2026.2(11) | 38.6(8) |
| H41 | 3591(2) | -960.8(19) | 3154.9(11) | 31.6(7) |
| H54 | -3570(2) | 344(2) | 894.0(12) | 42.1(8) |
| H3 | 4185(2) | 2378(2) | 3881.2(11) | 34.5(7) |
| H51 | -5204(2) | 135(2) | 2327.9(14) | 47.5(9) |
| H15 | 2894(2) | 1726(2) | -411.0(11) | 43.9(9) |
| H7 | 7313(2) | 2942(2) | 2638.1(12) | 36.1(8) |
| H50 | -3841(2) | 155(2) | 3033.9(13) | 42.8(9) |
| H23 | -3983(3) | 3800(3) | -251.0(14) | 58.2(11) |

| | | | | |
|---|---|---|---|---|
| H26 | -2914(2) | 3333(2) | 1500.6(12) | 44.5(9) |
| H55 | -1894(2) | 390(2) | 740.9(12) | 38.9(8) |
| H13 | 4565(2) | 1758(2) | 1038.9(11) | 37.1(8) |
| H49 | -2125(2) | 204(2) | 2907.4(12) | 36.0(8) |
| H22 | -2603(3) | 3226(3) | -630.3(13) | 54.8(10) |
| H24 | -3901(2) | 3705(2) | 634.3(14) | 51(1) |
| H2 | 2670(2) | 1784.3(19) | 3425(1) | 29.5(7) |

Refinement model description

Number of restraints - 0, number of constraints - 72.

Details:

1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C39(H39), C46(H46), C11(H11), C8(H8), C35(H35), C42(H42), C18(H18), C16(H16), C52(H52), C43(H43), C34(H34), C31(H31), C44(H44), C36(H36), C21(H21), C6(H6), C5(H5), C30(H30), C33(H33), C14(H14), C27(H27), C41(H41), C54(H54), C3(H3), C51(H51), C15(H15), C7(H7), C50(H50), C23(H23), C26(H26), C55(H55), C13(H13), C49(H49), C22(H22), C24(H24), C2(H2)

## $Nd_2[L^{VII}]_3$

**Crystallographic Table 73** Crystal data and structure refinement for $Nd_2[L^{VII}]_3$

| | |
|---|---|
| Empirical formula | $C_{88}H_{66}Cl_4N_6Nd_2O_8$ |
| Formula weight | 1765.82 |
| Temperature/K | 181.65 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 10.2688(4) |
| b/Å | 42.4193(19) |
| c/Å | 17.3908(8) |
| α/° | 90 |
| β/° | 91.5390(11) |
| γ/° | 90 |
| Volume/Å$^3$ | 7572.6(6) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.5487 |
| m/mm$^{-1}$ | 1.560 |
| F(000) | 3555.3 |
| Crystal size/mm$^3$ | 0.2 × 0.1 × 0.02 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 1.92 to 42.08° |
| Index ranges | $-10 \le h \le 10$, $-42 \le k \le 42$, $-17 \le l \le 17$ |
| Reflections collected | 56265 |
| Independent reflections | 8193 [$R_{int}$ = 0.0678, $R_{sigma}$ = 0.0459] |
| Data/restraints/parameters | 8193/6/981 |
| Goodness-of-fit on $F^2$ | 1.079 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0758, $wR_2$ = 0.1625 |
| Final R indexes [all data] | $R_1$ = 0.0852, $wR_2$ = 0.1704 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.53/-1.37 |

**Crystallographic Table 74** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for $Nd_2[L^{VII}]_3$. $U_{eq}$is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Nd1 | 1397.9(6) | 1180.33(16) | 3016.0(4) | 37.3(2) |
| Nd2 | 4770.0(6) | 1299.12(15) | 1934.3(4) | 35.0(2) |
| O3 | 2761(7) | 984.1(18) | 1936(4) | 35.1(19) |

| | | | | |
|---|---|---|---|---|
| O8 | 5712(8) | 902.7(18) | 1236(5) | 42(2) |
| N9 | 6396(8) | 1528(2) | 968(5) | 32(2) |
| O10 | 3328(7) | 1516.2(19) | 2893(4) | 40(2) |
| C11 | 30(10) | 1346(3) | 1236(6) | 29(3) |
| O12 | 594(8) | 1659(2) | 3457(5) | 43(2) |
| N14 | -461(9) | 929(2) | 2138(5) | 33(2) |
| C16 | 2545(10) | 758(3) | 1431(7) | 32(3) |
| N18 | 6597(8) | 1658(2) | 2514(5) | 32(2) |
| N19 | 3811(9) | 1853(2) | 1500(6) | 34(2) |
| O20 | 5687(7) | 1075.4(19) | 3076(5) | 43(2) |
| O21 | 400(8) | 767(2) | 3596(5) | 49(2) |
| C22 | 3683(10) | 1787(3) | 3213(7) | 34(3) |
| C23 | 5931(10) | 864(3) | 504(8) | 38(3) |
| C24 | 6368(12) | 1145(3) | 3703(7) | 41(3) |
| C25 | 7244(11) | 1655(3) | 3162(7) | 35(3) |
| C26 | 6883(10) | 1903(3) | 2002(7) | 34(3) |
| N27 | 395(8) | 1525(2) | 1890(5) | 29(2) |
| C28 | -399(10) | 1036(3) | 1358(7) | 33(3) |
| N29 | 3482(8) | 1337(2) | 624(5) | 30(2) |
| C30 | 7066(10) | 1429(3) | 3776(6) | 32(3) |
| C31 | 2892(10) | 1105(3) | 295(6) | 29(3) |
| C32 | -1372(10) | 731(3) | 2290(6) | 31(3) |
| C33 | 7190(11) | 2213(3) | 2219(8) | 44(3) |
| C34 | 6353(10) | 1110(3) | 16(7) | 34(3) |
| C37 | -573(12) | 568(3) | 3592(7) | 43(3) |
| C38 | 3611(10) | 2077(3) | 1968(7) | 38(3) |
| C39 | 3839(11) | 2064(3) | 2795(7) | 36(3) |
| C40 | 3465(10) | 1637(3) | 229(7) | 36(3) |
| C41 | 3588(10) | 1904(3) | 699(7) | 35(3) |
| C42 | -3628(11) | 307(3) | 2481(7) | 37(3) |
| C43 | 7754(12) | 1275(3) | 5106(8) | 48(3) |
| C44 | 6799(10) | 1841(3) | 1197(7) | 34(3) |
| C45 | -517(10) | 945(3) | 0(6) | 33(3) |
| C46 | -689(12) | 358(3) | 4244(7) | 45(3) |
| C47 | 7133(13) | 981(3) | 4967(7) | 50(4) |
| C48 | 8357(13) | 1334(4) | 5835(8) | 56(4) |
| C49 | 6593(11) | 1044(3) | -779(6) | 37(3) |
| C50 | 1596(12) | 10(3) | -134(8) | 48(3) |

| | | | | |
|---|---|---|---|---|
| C51 | 2601(12) | 564(3) | -692(7) | 43(3) |
| C52 | 7707(11) | 1505(3) | 4518(6) | 36(3) |
| C53 | -671(10) | 839(3) | 736(6) | 30(3) |
| C54 | -1507(11) | 551(3) | 2992(7) | 36(3) |
| C55 | 7262(12) | 2386(3) | 917(8) | 47(3) |
| C56 | 3359(11) | 1668(3) | -560(7) | 37(3) |
| C58 | 2686(10) | 795(3) | 633(7) | 33(3) |
| C59 | 6039(12) | 488(3) | -562(8) | 43(3) |
| C60 | 6490(12) | 917(3) | 4301(7) | 50(4) |
| C61 | 6991(11) | 2083(3) | 664(7) | 43(3) |
| C62 | 3493(12) | 2199(3) | 345(7) | 42(3) |
| C63 | 8911(13) | 1848(3) | 5416(7) | 54(4) |
| C64 | 258(10) | 1823(3) | 1869(7) | 37(3) |
| C65 | -98(10) | 1252(3) | -119(7) | 35(3) |
| C66 | 1922(11) | 253(3) | 396(7) | 40(3) |
| C67 | 192(11) | 1450(3) | 493(7) | 39(3) |
| C68 | 2276(12) | 323(3) | -1184(7) | 41(3) |
| C69 | 7377(13) | 2449(3) | 1701(8) | 53(4) |
| C70 | 6448(12) | 728(3) | -1049(7) | 43(3) |
| C71 | 853(13) | 2608(3) | 2861(9) | 57(4) |
| C72 | 654(11) | 1955(3) | 3242(8) | 43(3) |
| C73 | 4159(11) | 2352(3) | 3196(7) | 42(3) |
| C74 | -4595(12) | 90(3) | 2550(8) | 46(3) |
| C75 | 4318(12) | 2354(3) | 3997(8) | 50(4) |
| C76 | 3318(13) | 2229(3) | -433(8) | 52(4) |
| C77 | 4354(12) | 2642(3) | 2803(8) | 49(4) |
| C78 | -2658(12) | 119(3) | 3684(8) | 49(4) |
| C80 | 1775(11) | 220(3) | 1200(7) | 38(3) |
| C81 | -2589(11) | 327(3) | 3031(7) | 40(3) |
| C82 | 6771(13) | 656(3) | -1814(7) | 49(3) |
| C83 | 797(11) | 2494(3) | 1515(9) | 49(4) |
| C84 | 4146(12) | 2065(4) | 4399(8) | 62(4) |
| C86 | -4614(13) | -122(3) | 3158(9) | 55(4) |
| C87 | -1674(12) | 151(3) | 4279(7) | 48(3) |
| C88 | 5788(12) | 552(3) | 194(7) | 44(3) |
| C89 | -3664(12) | -107(3) | 3723(9) | 53(4) |
| C90 | 8324(12) | 1797(3) | 4693(8) | 48(3) |
| C92 | 7314(13) | 1191(3) | -2056(7) | 53(4) |

| | | | | |
|---|---|---|---|---|
| C93 | 2395(10) | 540(3) | 106(7) | 33(3) |
| C95 | 1773(12) | 42(3) | -912(7) | 41(3) |
| C96 | 2062(11) | 460(3) | 1695(7) | 35(3) |
| C97 | 807(12) | 2198(4) | 3823(8) | 59(4) |
| C99 | 983(14) | 2806(3) | 1330(10) | 68(4) |
| C101 | 574(11) | 2049(3) | 2460(8) | 41(3) |
| C103 | 4608(15) | 2916(4) | 3204(10) | 73(5) |
| C104 | 8943(14) | 1615(4) | 5977(8) | 62(4) |
| C108 | 706(11) | 2379(3) | 2276(8) | 47(4) |
| C109 | 7192(15) | 885(3) | -2312(8) | 62(4) |
| C111 | 7025(13) | 1277(3) | -1304(7) | 50(4) |
| C113 | 3845(11) | 1785(3) | 4031(7) | 45(3) |
| C120 | 1029(14) | 3023(4) | 1928(12) | 72(5) |
| C122 | 4605(15) | 2643(4) | 4386(9) | 70(5) |
| C132 | 983(15) | 2936(4) | 2671(12) | 76(5) |
| Cl4 | -1658(4) | 172.7(11) | -3334(3) | 89.3(14) |
| Cl6 | 488(5) | 610.1(13) | -3346(4) | 123(2) |
| Cl13 | 9567(7) | 3928(2) | 1334(4) | 164(3) |
| Cl35 | 7682(11) | 3689(3) | 2441(5) | 226(5) |
| O1 | 3316(8) | 861(2) | 3626(5) | 53(2) |
| O2 | 1481(9) | 1283(2) | 4504(4) | 56(3) |
| C3 | 6729(11) | 1413(3) | 313(7) | 43(3) |
| C4 | 3252(13) | 1961(3) | -887(8) | 52(4) |
| C5 | 3355(13) | 557(3) | 3953(9) | 61(4) |
| C6 | 896(13) | 2508(4) | 3643(10) | 61(4) |
| C7 | -189(14) | 291(4) | -2892(8) | 65(4) |
| C8 | 1365(18) | 1076(4) | 5146(8) | 88(6) |
| C10 | 8840(20) | 3950(8) | 2390(20) | 232(19) |
| C1 | 4731(18) | 2917(4) | 4006(10) | 83(5) |

**Crystallographic Table 75** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **$Nd_2[L^{VII}]_3$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{12}$** | **$U_{13}$** | **$U_{23}$** |
|---|---|---|---|---|---|---|
| Nd1 | 31.5(4) | 46.1(5) | 34.3(4) | -3.1(3) | -0.6(3) | -0.2(3) |
| Nd2 | 28.7(4) | 40.9(4) | 35.2(4) | -0.3(3) | -0.4(3) | -0.1(3) |
| O3 | 36(5) | 35(5) | 34(5) | -7(4) | -3(4) | -3(4) |
| O8 | 45(5) | 41(5) | 39(6) | -2(4) | -4(4) | 17(4) |
| N9 | 27(5) | 35(6) | 34(6) | -3(4) | -5(4) | 10(5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O10 | 40(5) | 42(5) | 39(5) | -5(4) | -4(4) | 1(4) |
| C11 | 34(7) | 28(7) | 25(7) | 4(5) | 0(5) | -3(6) |
| O12 | 43(5) | 49(6) | 38(5) | -11(4) | 4(4) | -3(4) |
| N14 | 33(6) | 28(5) | 37(6) | -5(5) | -9(4) | 4(5) |
| C16 | 20(6) | 23(7) | 52(9) | 0(5) | -3(5) | 1(6) |
| N18 | 25(5) | 35(6) | 35(6) | -7(4) | 3(5) | 7(5) |
| N19 | 30(6) | 27(6) | 45(7) | 10(4) | -10(5) | 0(5) |
| O20 | 29(5) | 50(5) | 51(6) | -5(4) | 0(4) | -3(4) |
| O21 | 33(5) | 74(6) | 38(5) | -12(5) | -11(4) | 11(5) |
| C22 | 19(6) | 51(9) | 34(8) | 3(6) | 3(5) | -8(7) |
| C23 | 18(6) | 40(8) | 56(9) | 2(5) | -16(6) | 9(7) |
| C24 | 42(8) | 34(8) | 47(8) | 7(6) | 2(7) | -10(6) |
| C25 | 22(6) | 48(8) | 35(7) | 6(5) | -2(6) | 9(6) |
| C26 | 26(6) | 39(8) | 37(8) | 1(5) | 3(5) | 0(6) |
| N27 | 30(5) | 21(6) | 36(6) | 0(4) | -9(4) | 3(4) |
| C28 | 27(6) | 33(7) | 38(8) | 4(5) | 5(5) | 6(6) |
| N29 | 28(5) | 44(6) | 17(5) | -2(5) | -3(4) | -1(5) |
| C30 | 23(6) | 50(8) | 23(7) | 13(6) | 1(5) | -1(6) |
| C31 | 22(6) | 48(8) | 17(6) | 8(6) | -1(5) | -1(6) |
| C32 | 25(6) | 35(7) | 32(7) | -4(6) | -11(5) | -6(6) |
| C33 | 30(7) | 55(9) | 48(8) | -5(6) | -6(6) | 6(7) |
| C34 | 24(6) | 41(8) | 37(8) | 12(5) | -8(5) | -7(6) |
| C37 | 38(8) | 57(9) | 34(8) | 8(7) | 3(6) | 9(7) |
| C38 | 24(7) | 36(8) | 54(9) | -13(6) | 3(6) | 7(7) |
| C39 | 33(7) | 35(8) | 39(8) | 4(6) | 2(6) | -12(6) |
| C40 | 26(7) | 36(8) | 44(8) | 1(5) | -1(5) | 5(6) |
| C41 | 22(6) | 36(8) | 46(8) | -5(5) | -7(5) | -5(6) |
| C42 | 38(7) | 41(8) | 33(7) | -3(6) | 1(6) | 5(6) |
| C43 | 40(8) | 48(9) | 55(9) | 1(7) | -5(7) | -1(7) |
| C44 | 19(6) | 44(8) | 38(8) | 11(5) | -5(5) | -8(6) |
| C45 | 35(7) | 36(8) | 29(7) | 2(6) | -5(5) | -8(6) |
| C46 | 31(7) | 64(9) | 39(8) | 3(7) | -1(6) | 19(7) |
| C47 | 57(9) | 62(10) | 32(8) | 15(7) | 3(7) | 19(7) |
| C48 | 60(9) | 73(11) | 35(8) | -3(8) | -9(7) | 3(7) |
| C49 | 29(7) | 54(9) | 27(7) | 11(6) | -9(5) | 3(6) |
| C50 | 45(8) | 33(8) | 66(10) | -11(6) | 3(7) | 1(7) |
| C51 | 53(8) | 34(8) | 42(8) | -8(6) | -7(6) | -6(6) |
| C52 | 36(7) | 46(8) | 28(7) | 15(6) | 9(5) | 9(6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C53 | 31(7) | 33(7) | 27(7) | -3(5) | 0(5) | 4(6) |
| C54 | 32(7) | 39(7) | 37(7) | 0(6) | -2(6) | 5(6) |
| C55 | 43(8) | 32(8) | 67(10) | -7(6) | -5(7) | 12(7) |
| C56 | 44(8) | 32(7) | 35(8) | -2(6) | -6(6) | -4(6) |
| C58 | 24(6) | 37(8) | 38(8) | 1(5) | 1(5) | -7(6) |
| C59 | 48(8) | 24(7) | 57(9) | -1(6) | -2(7) | -7(6) |
| C60 | 51(8) | 56(9) | 44(9) | -8(7) | -6(7) | 20(7) |
| C61 | 40(7) | 55(9) | 33(7) | 0(6) | 0(6) | 21(7) |
| C62 | 49(8) | 27(7) | 49(9) | 1(6) | 5(6) | 0(6) |
| C63 | 61(9) | 67(10) | 34(8) | -4(7) | -3(7) | -9(7) |
| C64 | 18(6) | 53(9) | 41(8) | -14(6) | 0(5) | -5(7) |
| C65 | 21(6) | 52(8) | 31(7) | 7(6) | 1(5) | 7(6) |
| C66 | 27(7) | 34(8) | 57(9) | -2(6) | -12(6) | 5(7) |
| C67 | 28(7) | 36(7) | 54(9) | -5(5) | -3(6) | -1(7) |
| C68 | 51(8) | 38(8) | 33(7) | -6(6) | -2(6) | -4(6) |
| C69 | 57(9) | 51(9) | 51(9) | -13(7) | -3(7) | -3(8) |
| C70 | 41(8) | 51(9) | 37(8) | 12(6) | -4(6) | -6(7) |
| C71 | 47(9) | 42(9) | 83(12) | -14(7) | 9(8) | -17(8) |
| C72 | 22(7) | 53(9) | 54(9) | 2(6) | 0(6) | -9(7) |
| C73 | 28(7) | 50(9) | 47(9) | -2(6) | -3(6) | -14(7) |
| C74 | 34(8) | 51(8) | 52(9) | -5(7) | -9(6) | 13(7) |
| C75 | 34(8) | 65(10) | 51(9) | -16(7) | 1(6) | -7(8) |
| C76 | 59(9) | 49(9) | 46(9) | -8(7) | -5(7) | 12(7) |
| C77 | 53(8) | 42(8) | 52(9) | -9(7) | 2(7) | -21(7) |
| C78 | 37(8) | 50(8) | 60(9) | 9(7) | 3(7) | 16(7) |
| C80 | 38(7) | 38(8) | 39(8) | -6(6) | 8(6) | 0(6) |
| C81 | 27(7) | 43(8) | 50(8) | 6(6) | 4(6) | 5(6) |
| C82 | 57(9) | 39(8) | 49(9) | 6(6) | -4(7) | -11(7) |
| C83 | 32(7) | 42(9) | 74(11) | -3(6) | -1(7) | -3(7) |
| C84 | 37(8) | 103(13) | 45(9) | 1(8) | 7(7) | -10(9) |
| C86 | 39(8) | 51(9) | 76(10) | -6(7) | 5(8) | 1(8) |
| C87 | 40(8) | 64(9) | 41(8) | 3(7) | 12(6) | 20(7) |
| C88 | 42(8) | 50(9) | 40(8) | 9(6) | -5(6) | 16(7) |
| C89 | 36(8) | 38(8) | 86(11) | -10(6) | 9(8) | 20(7) |
| C90 | 40(8) | 50(9) | 54(9) | -2(6) | -2(7) | -3(7) |
| C92 | 63(9) | 63(10) | 34(8) | 3(7) | 9(7) | 15(7) |
| C93 | 28(7) | 35(7) | 37(8) | 2(5) | -1(5) | -10(6) |
| C95 | 49(8) | 34(8) | 40(8) | -9(6) | -3(6) | -18(6) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C96 | 34(7) | 33(7) | 37(7) | 4(6) | 1(5) | -4(6) |
| C97 | 37(8) | 86(12) | 55(9) | -15(8) | 11(7) | -34(9) |
| C99 | 67(10) | 45(10) | 91(13) | -8(8) | -19(9) | 10(9) |
| C101 | 24(7) | 28(7) | 70(10) | -3(5) | -2(6) | -7(7) |
| C103 | 81(11) | 51(10) | 87(13) | -19(8) | 11(9) | -23(9) |
| C104 | 66(10) | 76(11) | 43(9) | -3(9) | -5(7) | -2(8) |
| C108 | 22(7) | 51(9) | 68(10) | -8(6) | 3(6) | -20(8) |
| C109 | 88(11) | 53(10) | 44(9) | -3(8) | 5(8) | 3(8) |
| C111 | 66(9) | 52(9) | 32(8) | 8(7) | 0(7) | -1(7) |
| C113 | 33(7) | 50(9) | 50(9) | -19(6) | -5(6) | -2(7) |
| C120 | 50(10) | 45(10) | 122(16) | -8(7) | 0(10) | -1(11) |
| C122 | 80(11) | 70(12) | 61(11) | -15(9) | 5(9) | -37(10) |
| C132 | 63(11) | 46(11) | 120(16) | -16(8) | 13(10) | -42(10) |
| Cl4 | 70(3) | 93(3) | 106(4) | 4(2) | 4(2) | -32(3) |
| Cl6 | 99(4) | 90(4) | 183(6) | -6(3) | 34(4) | 52(4) |
| Cl13 | 113(5) | 237(9) | 141(6) | 15(5) | -6(4) | -17(6) |
| Cl35 | 230(10) | 281(12) | 165(8) | -46(9) | -47(7) | 108(8) |
| O1 | 43(5) | 69(6) | 46(5) | -1(5) | -2(4) | 33(5) |
| O2 | 71(6) | 76(7) | 21(5) | 0(5) | 4(4) | -15(5) |
| C3 | 31(7) | 63(9) | 35(8) | 8(6) | 5(6) | 4(7) |
| C4 | 66(10) | 47(9) | 41(8) | -8(7) | -2(7) | 15(7) |
| C5 | 41(8) | 42(8) | 99(12) | 6(6) | 1(8) | 30(8) |
| C6 | 47(9) | 53(10) | 82(13) | -15(7) | 20(8) | -31(9) |
| C7 | 68(10) | 71(11) | 57(10) | -2(8) | 18(8) | 15(8) |
| C8 | 114(15) | 120(15) | 29(9) | 22(12) | 4(9) | 16(9) |
| C10 | 59(14) | 230(30) | 410(50) | -64(18) | 50(20) | -180(30) |
| C1 | 113(15) | 66(12) | 69(12) | -19(10) | -4(10) | -46(10) |

**Crystallographic Table 76** Bond Lengths for **$Nd_2[L^{VII}]_3$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Nd1 | O3 | 2.514(8) | C43 | C52 | 1.414(17) |
| Nd1 | O10 | 2.455(8) | C44 | C61 | 1.400(16) |
| Nd1 | O12 | 2.331(9) | C45 | C53 | 1.369(15) |
| Nd1 | N14 | 2.637(9) | C45 | C65 | 1.390(16) |
| Nd1 | O21 | 2.280(9) | C46 | C87 | 1.342(17) |
| Nd1 | N27 | 2.631(9) | C47 | C60 | 1.347(18) |
| Nd1 | O1 | 2.594(8) | C48 | C104 | 1.353(19) |
| Nd1 | O2 | 2.622(8) | C49 | C70 | 1.428(17) |

| | | | | | |
|---|---|---|---|---|---|
| Nd2 | O3 | 2.458(7) | C49 | C111 | 1.425(17) |
| Nd2 | O8 | 2.302(9) | C50 | C66 | 1.417(17) |
| Nd2 | N9 | 2.590(9) | C50 | C95 | 1.378(17) |
| Nd2 | O10 | 2.440(8) | C51 | C68 | 1.370(16) |
| Nd2 | N18 | 2.600(9) | C51 | C93 | 1.413(16) |
| Nd2 | N19 | 2.651(9) | C52 | C90 | 1.419(17) |
| Nd2 | O20 | 2.373(8) | C54 | C81 | 1.465(16) |
| Nd2 | C22 | 3.258(11) | C55 | C61 | 1.383(17) |
| Nd2 | N29 | 2.609(8) | C55 | C69 | 1.390(18) |
| O3 | C16 | 1.315(13) | C56 | C4 | 1.369(17) |
| O8 | C23 | 1.310(15) | C58 | C93 | 1.442(15) |
| N9 | C44 | 1.446(14) | C59 | C70 | 1.396(17) |
| N9 | C3 | 1.292(15) | C59 | C88 | 1.373(17) |
| O10 | C22 | 1.325(14) | C62 | C76 | 1.365(17) |
| C11 | N27 | 1.409(14) | C63 | C90 | 1.396(17) |
| C11 | C28 | 1.405(15) | C63 | C104 | 1.389(19) |
| C11 | C67 | 1.380(16) | C64 | C101 | 1.436(17) |
| O12 | C72 | 1.311(15) | C65 | C67 | 1.384(16) |
| N14 | C28 | 1.433(14) | C66 | C80 | 1.418(17) |
| N14 | C32 | 1.291(14) | C66 | C93 | 1.412(16) |
| C16 | C58 | 1.407(16) | C68 | C95 | 1.386(16) |
| C16 | C96 | 1.437(16) | C70 | C82 | 1.414(17) |
| N18 | C25 | 1.292(14) | C71 | C108 | 1.413(18) |
| N18 | C26 | 1.403(14) | C71 | C132 | 1.43(2) |
| N19 | C38 | 1.269(15) | C71 | C6 | 1.42(2) |
| N19 | C41 | 1.422(15) | C72 | C97 | 1.447(18) |
| O20 | C24 | 1.312(14) | C72 | C101 | 1.418(18) |
| O21 | C37 | 1.308(15) | C73 | C75 | 1.399(18) |
| C22 | C39 | 1.392(17) | C73 | C77 | 1.421(18) |
| C22 | C113 | 1.428(17) | C74 | C86 | 1.389(18) |
| C23 | C34 | 1.419(17) | C75 | C84 | 1.42(2) |
| C23 | C88 | 1.435(17) | C75 | C122 | 1.427(19) |
| C24 | C30 | 1.406(17) | C76 | C4 | 1.386(18) |
| C24 | C60 | 1.424(17) | C77 | C103 | 1.378(18) |
| C25 | C30 | 1.449(16) | C78 | C81 | 1.441(17) |
| C26 | C33 | 1.400(17) | C78 | C87 | 1.433(18) |
| C26 | C44 | 1.426(16) | C78 | C89 | 1.412(17) |
| N27 | C64 | 1.271(14) | C80 | C96 | 1.360(16) |

| | | | | | |
|---|---|---|---|---|---|
| C28 | C53 | 1.390(15) | C82 | C109 | 1.379(18) |
| N29 | C31 | 1.285(14) | C83 | C99 | 1.374(19) |
| N29 | C40 | 1.446(14) | C83 | C108 | 1.418(19) |
| C30 | C52 | 1.468(16) | C84 | C113 | 1.381(19) |
| C31 | C58 | 1.458(16) | C86 | C89 | 1.368(19) |
| C32 | C54 | 1.450(16) | C92 | C109 | 1.375(19) |
| C33 | C69 | 1.364(18) | C92 | C111 | 1.398(18) |
| C34 | C49 | 1.437(16) | C97 | C6 | 1.36(2) |
| C34 | C3 | 1.435(17) | C99 | C120 | 1.39(2) |
| C37 | C46 | 1.450(17) | C101 | C108 | 1.443(18) |
| C37 | C54 | 1.400(16) | C103 | C1 | 1.40(2) |
| C38 | C39 | 1.452(17) | C120 | C132 | 1.35(2) |
| C39 | C73 | 1.441(16) | C122 | C1 | 1.35(2) |
| C40 | C41 | 1.400(16) | Cl4 | C7 | 1.748(15) |
| C40 | C56 | 1.379(16) | Cl6 | C7 | 1.724(14) |
| C41 | C62 | 1.398(16) | Cl13 | C10 | 2.00(3) |
| C42 | C74 | 1.361(16) | Cl35 | C10 | 1.63(2) |
| C42 | C81 | 1.416(16) | O1 | C5 | 1.407(14) |
| C43 | C47 | 1.415(18) | O2 | C8 | 1.429(16) |
| C43 | C48 | 1.418(18) | | | |

**Crystallographic Table 77** Bond Angles for **$Nd_2[L^{VII}]_3$**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| O10 | Nd1 | O3 | 70.1(2) | C69 | C33 | C26 | 123.0(13) |
| O12 | Nd1 | O3 | 138.0(3) | C49 | C34 | C23 | 119.7(11) |
| O12 | Nd1 | O10 | 79.4(3) | C3 | C34 | C23 | 121.8(11) |
| N14 | Nd1 | O3 | 80.9(3) | C3 | C34 | C49 | 117.9(11) |
| N14 | Nd1 | O10 | 139.2(3) | C46 | C37 | O21 | 118.1(11) |
| N14 | Nd1 | O12 | 106.6(3) | C54 | C37 | O21 | 123.0(11) |
| O21 | Nd1 | O3 | 110.0(3) | C54 | C37 | C46 | 118.8(12) |
| O21 | Nd1 | O10 | 149.1(3) | C39 | C38 | N19 | 125.7(11) |
| O21 | Nd1 | O12 | 111.0(3) | C38 | C39 | C22 | 122.1(10) |
| O21 | Nd1 | N14 | 67.6(3) | C73 | C39 | C22 | 119.4(11) |
| N27 | Nd1 | O3 | 80.9(3) | C73 | C39 | C38 | 118.4(11) |
| N27 | Nd1 | O10 | 85.0(3) | C41 | C40 | N29 | 115.8(10) |
| N27 | Nd1 | O12 | 68.0(3) | C56 | C40 | N29 | 123.8(10) |
| N27 | Nd1 | N14 | 62.0(3) | C56 | C40 | C41 | 120.4(11) |
| N27 | Nd1 | O21 | 125.8(3) | C40 | C41 | N19 | 117.3(10) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O1 | Nd1 | O3 | 72.6(3) | C62 | C41 | N19 | 125.1(10) |
| O1 | Nd1 | O10 | 74.5(3) | C62 | C41 | C40 | 117.6(11) |
| O1 | Nd1 | O12 | 126.4(3) | C81 | C42 | C74 | 121.3(11) |
| O1 | Nd1 | N14 | 123.8(3) | C48 | C43 | C47 | 119.5(12) |
| O1 | Nd1 | O21 | 76.3(3) | C52 | C43 | C47 | 118.6(12) |
| O1 | Nd1 | N27 | 150.7(3) | C52 | C43 | C48 | 121.8(12) |
| O2 | Nd1 | O3 | 142.0(3) | C26 | C44 | N9 | 116.7(10) |
| O2 | Nd1 | O10 | 89.1(3) | C61 | C44 | N9 | 122.4(10) |
| O2 | Nd1 | O12 | 62.2(3) | C61 | C44 | C26 | 120.7(11) |
| O2 | Nd1 | N14 | 130.0(3) | C65 | C45 | C53 | 119.4(10) |
| O2 | Nd1 | O21 | 72.2(3) | C87 | C46 | C37 | 121.0(12) |
| O2 | Nd1 | N27 | 130.1(3) | C60 | C47 | C43 | 122.2(12) |
| O2 | Nd1 | O1 | 71.3(3) | C104 | C48 | C43 | 120.1(13) |
| O8 | Nd2 | O3 | 88.2(3) | C70 | C49 | C34 | 118.6(11) |
| N9 | Nd2 | O3 | 139.5(3) | C111 | C49 | C34 | 123.2(11) |
| N9 | Nd2 | O8 | 69.1(3) | C111 | C49 | C70 | 118.1(11) |
| O10 | Nd2 | O3 | 71.3(2) | C95 | C50 | C66 | 122.1(12) |
| O10 | Nd2 | O8 | 155.1(3) | C93 | C51 | C68 | 121.3(12) |
| O10 | Nd2 | N9 | 135.7(3) | C43 | C52 | C30 | 119.3(11) |
| N18 | Nd2 | O3 | 156.3(3) | C90 | C52 | C30 | 124.5(11) |
| N18 | Nd2 | O8 | 108.9(3) | C90 | C52 | C43 | 116.2(11) |
| N18 | Nd2 | N9 | 64.0(3) | C45 | C53 | C28 | 120.3(10) |
| N18 | Nd2 | O10 | 87.6(3) | C37 | C54 | C32 | 121.4(10) |
| N19 | Nd2 | O3 | 100.2(3) | C81 | C54 | C32 | 118.0(10) |
| N19 | Nd2 | O8 | 131.0(3) | C81 | C54 | C37 | 120.3(11) |
| N19 | Nd2 | N9 | 74.0(3) | C69 | C55 | C61 | 120.0(12) |
| N19 | Nd2 | O10 | 68.4(3) | C4 | C56 | C40 | 120.2(11) |
| N19 | Nd2 | N18 | 81.3(3) | C31 | C58 | C16 | 121.1(10) |
| O20 | Nd2 | O3 | 95.5(3) | C93 | C58 | C16 | 121.3(11) |
| O20 | Nd2 | O8 | 89.2(3) | C93 | C58 | C31 | 116.6(10) |
| O20 | Nd2 | N9 | 116.4(3) | C88 | C59 | C70 | 120.4(11) |
| O20 | Nd2 | O10 | 79.3(3) | C47 | C60 | C24 | 121.5(13) |
| O20 | Nd2 | N18 | 69.1(3) | C55 | C61 | C44 | 120.1(12) |
| O20 | Nd2 | N19 | 136.8(3) | C76 | C62 | C41 | 121.6(12) |
| C22 | Nd2 | O3 | 92.4(3) | C104 | C63 | C90 | 121.5(14) |
| C22 | Nd2 | O8 | 168.8(3) | C101 | C64 | N27 | 128.3(12) |
| C22 | Nd2 | N9 | 116.3(3) | C67 | C65 | C45 | 121.1(11) |
| C22 | Nd2 | O10 | 21.3(3) | C80 | C66 | C50 | 122.8(11) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C22 | Nd2 | N18 | 67.6(3) | C93 | C66 | C50 | 118.3(12) |
| C22 | Nd2 | N19 | 60.0(3) | C93 | C66 | C80 | 118.8(11) |
| C22 | Nd2 | O20 | 79.5(3) | C65 | C67 | C11 | 119.8(11) |
| N29 | Nd2 | O3 | 68.2(3) | C95 | C68 | C51 | 121.1(12) |
| N29 | Nd2 | O8 | 78.2(3) | C55 | C69 | C33 | 119.9(13) |
| N29 | Nd2 | N9 | 74.3(3) | C59 | C70 | C49 | 121.0(11) |
| N29 | Nd2 | O10 | 105.7(3) | C82 | C70 | C49 | 119.3(12) |
| N29 | Nd2 | N18 | 130.2(3) | C82 | C70 | C59 | 119.7(12) |
| N29 | Nd2 | N19 | 61.3(3) | C132 | C71 | C108 | 120.7(15) |
| N29 | Nd2 | O20 | 159.5(3) | C6 | C71 | C108 | 118.8(13) |
| N29 | Nd2 | C22 | 112.4(3) | C6 | C71 | C132 | 120.5(14) |
| Nd2 | O3 | Nd1 | 107.7(3) | C97 | C72 | O12 | 119.1(13) |
| C16 | O3 | Nd1 | 130.8(6) | C101 | C72 | O12 | 122.6(11) |
| C16 | O3 | Nd2 | 121.4(6) | C101 | C72 | C97 | 118.3(13) |
| C23 | O8 | Nd2 | 133.6(7) | C75 | C73 | C39 | 120.3(12) |
| C44 | N9 | Nd2 | 110.5(7) | C77 | C73 | C39 | 122.3(12) |
| C3 | N9 | Nd2 | 128.4(8) | C77 | C73 | C75 | 117.4(11) |
| C3 | N9 | C44 | 120.6(10) | C86 | C74 | C42 | 122.0(12) |
| Nd2 | O10 | Nd1 | 110.3(3) | C84 | C75 | C73 | 118.2(12) |
| C22 | O10 | Nd1 | 132.9(7) | C122 | C75 | C73 | 119.5(14) |
| C22 | O10 | Nd2 | 116.7(6) | C122 | C75 | C84 | 122.3(14) |
| C28 | C11 | N27 | 117.4(10) | C4 | C76 | C62 | 119.5(12) |
| C67 | C11 | N27 | 123.2(10) | C103 | C77 | C73 | 120.9(14) |
| C67 | C11 | C28 | 119.1(10) | C87 | C78 | C81 | 117.6(11) |
| C72 | O12 | Nd1 | 136.1(7) | C89 | C78 | C81 | 120.4(12) |
| C28 | N14 | Nd1 | 111.8(6) | C89 | C78 | C87 | 122.1(12) |
| C32 | N14 | Nd1 | 131.4(7) | C96 | C80 | C66 | 121.7(11) |
| C32 | N14 | C28 | 116.8(9) | C54 | C81 | C42 | 124.5(11) |
| C58 | C16 | O3 | 123.9(10) | C78 | C81 | C42 | 116.3(11) |
| C96 | C16 | O3 | 118.7(10) | C78 | C81 | C54 | 119.1(11) |
| C96 | C16 | C58 | 117.2(10) | C109 | C82 | C70 | 121.5(12) |
| C25 | N18 | Nd2 | 132.8(8) | C108 | C83 | C99 | 124.3(14) |
| C26 | N18 | Nd2 | 110.4(7) | C113 | C84 | C75 | 122.9(13) |
| C26 | N18 | C25 | 116.8(9) | C89 | C86 | C74 | 119.6(12) |
| C38 | N19 | Nd2 | 123.0(8) | C78 | C87 | C46 | 123.1(12) |
| C41 | N19 | Nd2 | 117.5(7) | C59 | C88 | C23 | 121.4(12) |
| C41 | N19 | C38 | 119.4(10) | C86 | C89 | C78 | 120.3(13) |
| C24 | O20 | Nd2 | 142.6(8) | C63 | C90 | C52 | 120.5(13) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C37 | O21 | Nd1 | 147.8(7) | C111 | C92 | C109 | 122.0(13) |
| O10 | C22 | Nd2 | 42.0(5) | C58 | C93 | C51 | 122.5(11) |
| C39 | C22 | Nd2 | 97.6(7) | C66 | C93 | C51 | 118.3(10) |
| C39 | C22 | O10 | 123.1(10) | C66 | C93 | C58 | 119.2(11) |
| C113 | C22 | Nd2 | 130.0(8) | C68 | C95 | C50 | 118.8(11) |
| C113 | C22 | O10 | 115.8(11) | C80 | C96 | C16 | 121.7(11) |
| C113 | C22 | C39 | 121.0(11) | C6 | C97 | C72 | 122.4(15) |
| C34 | C23 | O8 | 123.5(11) | C120 | C99 | C83 | 117.7(16) |
| C88 | C23 | O8 | 117.5(11) | C72 | C101 | C64 | 120.4(11) |
| C88 | C23 | C34 | 118.9(12) | C108 | C101 | C64 | 120.7(12) |
| C30 | C24 | O20 | 121.9(11) | C108 | C101 | C72 | 118.7(12) |
| C60 | C24 | O20 | 119.2(11) | C1 | C103 | C77 | 121.3(16) |
| C60 | C24 | C30 | 118.7(11) | C63 | C104 | C48 | 119.7(13) |
| C30 | C25 | N18 | 125.4(11) | C83 | C108 | C71 | 115.2(13) |
| C33 | C26 | N18 | 124.9(11) | C101 | C108 | C71 | 121.2(13) |
| C44 | C26 | N18 | 118.6(10) | C101 | C108 | C83 | 123.4(12) |
| C44 | C26 | C33 | 116.4(11) | C92 | C109 | C82 | 119.4(13) |
| C11 | N27 | Nd1 | 113.1(6) | C92 | C111 | C49 | 119.7(13) |
| C64 | N27 | Nd1 | 127.9(8) | C84 | C113 | C22 | 118.3(13) |
| C64 | N27 | C11 | 118.9(9) | C132 | C120 | C99 | 122.2(15) |
| N14 | C28 | C11 | 117.4(10) | C1 | C122 | C75 | 122.1(15) |
| C53 | C28 | C11 | 120.3(10) | C120 | C132 | C71 | 119.6(15) |
| C53 | C28 | N14 | 122.2(10) | C5 | O1 | Nd1 | 131.0(7) |
| C31 | N29 | Nd2 | 124.3(7) | C8 | O2 | Nd1 | 132.0(9) |
| C40 | N29 | Nd2 | 118.0(7) | C34 | C3 | N9 | 125.5(12) |
| C40 | N29 | C31 | 117.7(9) | C76 | C4 | C56 | 120.3(12) |
| C25 | C30 | C24 | 124.9(11) | C97 | C6 | C71 | 120.6(13) |
| C52 | C30 | C24 | 118.9(11) | Cl6 | C7 | Cl4 | 112.2(9) |
| C52 | C30 | C25 | 116.2(11) | Cl35 | C10 | Cl13 | 108.2(15) |
| C58 | C31 | N29 | 125.8(10) | C122 | C1 | C103 | 118.6(14) |
| C54 | C32 | N14 | 127.0(10) | | | | |

**Crystallographic Table 78** Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **$Nd_2[L^{VII}]_3$**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H25 | 7889(11) | 1812(3) | 3241(7) | 42(3) |
| H31 | 2560(10) | 1137(3) | -214(6) | 35(3) |
| H32 | -2023(10) | 699(3) | 1900(6) | 37(3) |

| | | | | |
|---|---|---|---|---|
| H33 | 7271(11) | 2261(3) | 2752(8) | 53(4) |
| H38 | 3284(10) | 2269(3) | 1759(7) | 46(4) |
| H42 | -3650(11) | 448(3) | 2055(7) | 45(4) |
| H45 | -694(10) | 809(3) | -425(6) | 40(3) |
| H46 | -58(12) | 367(3) | 4653(7) | 54(4) |
| H47 | 7172(13) | 825(3) | 5358(7) | 61(4) |
| H48 | 8348(13) | 1177(4) | 6224(8) | 68(5) |
| H50 | 1244(12) | -182(3) | 54(8) | 58(4) |
| H51 | 2972(12) | 751(3) | -892(7) | 52(4) |
| H53 | -965(10) | 630(3) | 821(6) | 36(3) |
| H55 | 7370(12) | 2551(3) | 555(8) | 57(4) |
| H56 | 3361(11) | 1486(3) | -877(7) | 44(4) |
| H59 | 5933(12) | 280(3) | -754(8) | 51(4) |
| H60 | 6109(12) | 715(3) | 4228(7) | 61(4) |
| H61 | 6935(11) | 2039(3) | 129(7) | 52(4) |
| H62 | 3552(12) | 2384(3) | 653(7) | 50(4) |
| H63 | 9296(13) | 2047(3) | 5527(7) | 65(4) |
| H64 | -98(10) | 1906(3) | 1402(7) | 45(4) |
| H65 | -9(10) | 1327(3) | -630(7) | 42(4) |
| H67 | 502(11) | 1658(3) | 403(7) | 47(4) |
| H68 | 2399(12) | 348(3) | -1720(7) | 49(4) |
| H69 | 7585(13) | 2655(3) | 1875(8) | 64(4) |
| H74 | -5277(12) | 84(3) | 2170(8) | 55(4) |
| H76 | 3241(13) | 2432(3) | -661(8) | 62(4) |
| H77 | 4309(12) | 2646(3) | 2257(8) | 59(4) |
| H80 | 1467(11) | 26(3) | 1399(7) | 45(4) |
| H82 | 6696(13) | 444(3) | -1990(7) | 58(4) |
| H83 | 725(11) | 2346(3) | 1105(9) | 59(4) |
| H84 | 4242(12) | 2065(4) | 4944(8) | 74(5) |
| H86 | -5283(13) | -276(3) | 3181(9) | 66(4) |
| H87 | -1721(12) | 19(3) | 4719(7) | 58(4) |
| H88 | 5514(12) | 386(3) | 519(7) | 53(4) |
| H89 | -3682(12) | -249(3) | 4145(9) | 64(5) |
| H90 | 8338(12) | 1958(3) | 4315(8) | 58(4) |
| H92 | 7604(13) | 1348(3) | -2401(7) | 64(4) |
| H95 | 1553(12) | -125(3) | -1256(7) | 49(4) |
| H96 | 1940(11) | 430(3) | 2230(7) | 42(3) |
| H97 | 848(12) | 2137(4) | 4349(8) | 71(5) |

| | | | | |
|---|---|---|---|---|
| H99 | 1076(14) | 2870(3) | 811(10) | 82(5) |
| H103 | 4700(15) | 3108(4) | 2930(10) | 87(6) |
| H104 | 9376(14) | 1652(4) | 6458(8) | 74(5) |
| H109 | 7396(15) | 832(3) | -2825(8) | 74(5) |
| H111 | 7117(13) | 1490(3) | -1144(7) | 60(4) |
| H113 | 3748(11) | 1595(3) | 4315(7) | 53(4) |
| H120 | 1095(14) | 3241(4) | 1809(12) | 87(6) |
| H122 | 4709(15) | 2642(4) | 4930(9) | 84(6) |
| H132 | 1038(15) | 3090(4) | 3068(12) | 91(6) |
| H1 | 4108(13) | 913(15) | 3500(50) | 79(4) |
| H2 | 1280(110) | 1472(6) | 4659(12) | 84(4) |
| H3 | 7268(11) | 1540(3) | 3(7) | 52(4) |
| H4 | 3133(13) | 1980(3) | -1429(8) | 62(4) |
| H5a | 3790(80) | 412(5) | 3600(20) | 91(6) |
| H5b | 3840(80) | 565(5) | 4450(30) | 91(6) |
| H5c | 2465(13) | 484(10) | 4030(50) | 91(6) |
| H6 | 987(13) | 2660(4) | 4042(10) | 73(5) |
| H7a | -344(14) | 346(4) | -2349(8) | 78(5) |
| H7b | 434(14) | 113(4) | -2895(8) | 78(5) |
| H8a | 520(50) | 970(20) | 5120(40) | 131(9) |
| H8b | 2060(70) | 917(18) | 5140(40) | 131(9) |
| H8c | 1440(120) | 1197(6) | 5624(8) | 131(9) |
| H10a | 9540(20) | 3904(8) | 2780(20) | 280(20) |
| H10b | 8500(20) | 4163(8) | 2480(20) | 280(20) |
| H1a | 4901(18) | 3108(4) | 4277(10) | 99(6) |

Refinement model description

Number of restraints - 6, number of constraints - 124.

Details:

1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups
2. Restrained distances
 O1-H1

0.87 with sigma of 0.01
O2-H2
0.87 with sigma of 0.01
C5-H1
1.885032 with sigma of 0.02
Nd1-H1
3.118054 with sigma of 0.02
C8-H2
1.895625 with sigma of 0.02
Nd1-H2
3.131953 with sigma of 0.02
3.a Secondary CH2 refined with riding coordinates:
C7(H7a,H7b), C10(H10a,H10b)
3.b Aromatic/amide H refined with riding coordinates:
C25(H25), C31(H31), C32(H32), C33(H33), C38(H38), C42(H42), C45(H45), C46(H46), C47(H47), C48(H48), C50(H50), C51(H51), C53(H53), C55(H55), C56(H56), C59(H59), C60(H60), C61(H61), C62(H62), C63(H63), C64(H64), C65(H65), C67(H67), C68(H68), C69(H69), C74(H74), C76(H76), C77(H77), C80(H80), C82(H82), C83(H83), C84(H84), C86(H86), C87(H87), C88(H88), C89(H89), C90(H90), C92(H92), C95(H95), C96(H96), C97(H97), C99(H99), C103(H103), C104(H104), C109(H109), C111(H111), C113(H113), C120(H120), C122(H122), C132(H132), C3(H3), C4(H4), C6(H6), C1(H1a)
3.c Idealised Me refined as rotating group:
C5(H5a,H5b,H5c), C8(H8a,H8b,H8c)

## $Gd_2[L^{VII}]_3$

**Crystallographic Table 79** Crystal data and structure refinement for **$Gd_2[L^{VII}]_3$**

| | |
|---|---|
| Empirical formula | $C_{88}H_{66}Cl_4Gd_2N_6O_8$ |
| Formula weight | 1791.85 |
| Temperature/K | 180.45 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 12.3985(2) |
| b/Å | 17.1412(3) |
| c/Å | 17.7640(3) |
| α/° | 87.7454(8) |
| β/° | 75.9048(7) |
| γ/° | 85.8045(7) |
| Volume/Å$^3$ | 3650.92(11) |
| Z | 2 |
| $\rho_{calc}$mg/mm$^3$ | 1.6298 |
| m/mm$^{-1}$ | 2.013 |
| F(000) | 1794.2 |
| Crystal size/mm$^3$ | 0.28 × 0.21 × 0.1 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 2.38 to 59.14° |
| Index ranges | -17 ≤ h ≤ 17, -23 ≤ k ≤ 23, -24 ≤ l ≤ 24 |
| Reflections collected | 112543 |
| Independent reflections | 20486 [$R_{int}$ = 0.0390, $R_{sigma}$ = 0.0280] |
| Data/restraints/parameters | 20486/3/1003 |
| Goodness-of-fit on $F^2$ | 1.155 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0362, $wR_2$ = 0.0841 |
| Final R indexes [all data] | $R_1$ = 0.0509, $wR_2$ = 0.1042 |
| Largest diff. peak/hole / e Å$^{-3}$ | 3.29/-2.30 |

**Crystallographic Table 80** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for **$Gd_2[L^{VII}]_3$**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Gd1 | 13714.93(13) | 13048.58(9) | -2942.27(9) | 14.34(4) |
| Gd2 | 12554.98(14) | 10973.24(10) | -2841.57(9) | 16.15(4) |
| O3 | 13469(2) | 11845.5(14) | -2226.1(14) | 17.5(5) |

| | | | | |
|---|---|---|---|---|
| O4 | 13004(2) | 12125.7(14) | -3621.9(14) | 17.8(5) |
| N3 | 12203(2) | 13212.1(17) | -1677.5(17) | 16.8(5) |
| N5 | 11084(3) | 11177.8(18) | -1621.6(17) | 18.8(6) |
| N4 | 11758(2) | 13498.8(17) | -3063.3(16) | 16.3(5) |
| N6 | 10692(2) | 11445.9(18) | -3039.1(17) | 17.9(6) |
| C29 | 13560(3) | 11748(2) | -1492.0(19) | 16.3(6) |
| N2 | 13930(3) | 14060.8(18) | -4035.4(17) | 18.3(6) |
| C68 | 10233(3) | 11761(2) | -1683(2) | 19.1(7) |
| O1 | 15008(2) | 13147.4(15) | -2241.6(15) | 20.4(5) |
| O2 | 15312(2) | 12727.8(15) | -3895.5(14) | 20.2(5) |
| N1 | 13651(3) | 14437.2(18) | -2543.4(17) | 18.3(6) |
| C48 | 11654(3) | 13128(2) | -5072(2) | 21.9(7) |
| C71 | 8610(3) | 12912(3) | -1894(3) | 28.9(8) |
| C73 | 10024(3) | 11901(2) | -2425(2) | 18.1(6) |
| C38 | 12965(3) | 12230(2) | -891.4(19) | 17.3(6) |
| C47 | 11950(3) | 12956(2) | -4340.3(19) | 17.0(6) |
| C56 | 12720(3) | 12328(2) | -4284.9(19) | 16.9(6) |
| C46 | 11368(3) | 13392(2) | -3660(2) | 18.2(6) |
| C39 | 12160(3) | 12846(2) | -1023(2) | 19.1(7) |
| C17 | 13355(3) | 14792(2) | -3802(2) | 18.7(7) |
| C66 | 11758(3) | 10217(2) | -757(2) | 21.8(7) |
| C67 | 10998(3) | 10816(2) | -955(2) | 21.6(7) |
| O6 | 12243(2) | 10281.5(16) | -3787.8(16) | 24.5(6) |
| C40 | 11352(3) | 13810(2) | -1714(2) | 19.0(7) |
| O5 | 12679(3) | 9924.6(17) | -2069.2(16) | 28.4(6) |
| C4 | 14521(3) | 13950(2) | -8(2) | 24.3(8) |
| C58 | 13171(4) | 9129(2) | -1080(2) | 29.1(9) |
| C45 | 11101(3) | 13949(2) | -2438(2) | 18.8(7) |
| C37 | 13076(3) | 12076(2) | -106(2) | 21.3(7) |
| C28 | 15483(3) | 12697(2) | -4655(2) | 18.6(7) |
| C12 | 13220(3) | 14996(2) | -3022(2) | 19.3(7) |
| C72 | 9218(3) | 12485(2) | -2519(2) | 23.2(7) |
| C75 | 10866(3) | 10956(2) | -4344(2) | 20.1(7) |
| C82 | 11765(4) | 10057(3) | -5674(2) | 30.9(9) |
| C30 | 14265(3) | 11106(2) | -1317(2) | 22.3(7) |
| C53 | 12132(3) | 12654(2) | -5716(2) | 25.3(8) |
| O7 | 14481(2) | 10551.4(17) | -3394.9(19) | 30.5(6) |
| C77 | 9626(3) | 11701(3) | -5100(2) | 26.0(8) |

| | | | | |
|---|---|---|---|---|
| C74 | 10321(3) | 11365(2) | -3655(2) | 19.7(7) |
| C44 | 10297(3) | 14540(2) | -2513(2) | 26.8(8) |
| C19 | 15005(3) | 13258(2) | -5101(2) | 19.2(7) |
| C54 | 12914(4) | 12024(3) | -5636(2) | 26.5(8) |
| C57 | 12531(3) | 9777(2) | -1327(2) | 23.2(7) |
| C32 | 13775(4) | 11425(2) | 48(2) | 25.0(8) |
| C20 | 15153(3) | 13142(2) | -5924(2) | 22.9(7) |
| C55 | 13199(3) | 11866(2) | -4949(2) | 21.9(7) |
| C1 | 14876(3) | 13451(2) | -1564(2) | 19.7(7) |
| C84 | 11773(3) | 10400(2) | -4363(2) | 21.1(7) |
| C41 | 10825(4) | 14281(3) | -1090(2) | 28.4(8) |
| C70 | 8814(4) | 12780(3) | -1168(2) | 30.1(9) |
| C76 | 10441(3) | 11100(2) | -5033(2) | 20.5(7) |
| C65 | 11682(3) | 10040(2) | 59(2) | 23.9(7) |
| C78 | 9263(4) | 11826(3) | -5768(3) | 32.0(9) |
| C31 | 14363(4) | 10956(2) | -576(2) | 27.2(8) |
| C11 | 13785(3) | 14639(2) | -1875(2) | 20.0(7) |
| C18 | 14404(3) | 13957(2) | -4763(2) | 19.9(7) |
| C13 | 12597(4) | 15689(2) | -2750(2) | 25.7(8) |
| C49 | 10903(4) | 13771(3) | -5171(3) | 32.1(9) |
| C81 | 10901(4) | 10645(2) | -5700(2) | 27.5(8) |
| C79 | 9700(5) | 11361(3) | -6413(3) | 41.0(11) |
| C69 | 9625(3) | 12212(2) | -1062(2) | 25.5(8) |
| C83 | 12180(4) | 9939(2) | -5037(2) | 26.5(8) |
| C26 | 16363(4) | 11974(3) | -5823(2) | 27.6(8) |
| C51 | 11088(5) | 13415(3) | -6505(3) | 44.7(13) |
| C59 | 13070(4) | 8946(2) | -319(3) | 31.6(9) |
| C10 | 14191(3) | 14135(2) | -1326(2) | 18.9(7) |
| C80 | 10509(5) | 10785(3) | -6377(3) | 39.0(11) |
| C60 | 12334(4) | 9394(2) | 277(2) | 27.6(8) |
| C25 | 15808(3) | 12481(2) | -6279(2) | 24.9(8) |
| C16 | 12845(3) | 15285(2) | -4285(2) | 25.1(8) |
| C5 | 14283(4) | 14161(3) | 779(2) | 33.1(9) |
| C21 | 14594(4) | 13627(3) | -6396(2) | 31.1(9) |
| C61 | 12262(4) | 9218(3) | 1071(3) | 35.4(10) |
| C15 | 12251(4) | 15972(2) | -4010(3) | 30.4(9) |
| C2 | 15477(3) | 13076(2) | -1035(2) | 24.8(8) |
| C9 | 13957(3) | 14364(2) | -522(2) | 21.7(7) |

| | | | | |
|---|---|---|---|---|
| C27 | 16215(3) | 12081(2) | -5049(2) | 25.3(8) |
| C43 | 9754(4) | 14989(3) | -1883(3) | 35.1(10) |
| C64 | 11012(4) | 10498(3) | 664(2) | 33.4(9) |
| C3 | 15314(4) | 13323(2) | -295(2) | 28.0(8) |
| C24 | 15887(4) | 12327(3) | -7067(2) | 34.7(10) |
| C36 | 12561(4) | 12569(3) | 520(2) | 33.5(9) |
| C50 | 10629(5) | 13899(3) | -5880(3) | 41.6(12) |
| C8 | 13141(4) | 14956(3) | -209(2) | 27.8(8) |
| C6 | 13495(4) | 14747(3) | 1064(2) | 35.5(10) |
| C42 | 10022(4) | 14862(3) | -1177(3) | 36.1(10) |
| C22 | 14697(5) | 13469(3) | -7162(3) | 40.9(11) |
| C14 | 12128(4) | 16172(2) | -3244(3) | 29.9(9) |
| C62 | 11570(5) | 9653(3) | 1641(3) | 40.0(11) |
| C63 | 10950(5) | 10305(3) | 1432(3) | 41.8(12) |
| C52 | 11827(4) | 12815(3) | -6431(2) | 37.3(11) |
| C33 | 13883(4) | 11272(3) | 820(3) | 37.8(11) |
| C35 | 12691(5) | 12406(3) | 1257(3) | 43.1(12) |
| C7 | 12918(4) | 15147(3) | 564(3) | 35.1(10) |
| Cl4 | 17991.9(17) | 13322.4(13) | -4091.0(9) | 78.8(6) |
| Cl3 | 17384(2) | 14758.5(11) | -3270.3(14) | 85.1(6) |
| C87 | 16923(5) | 13891(3) | -3525(3) | 46.6(13) |
| Cl2 | 17764(2) | 13102.0(16) | -9103.0(12) | 96.1(7) |
| Cl1 | 19776(2) | 12537.6(18) | -8622(2) | 114.7(9) |
| O8 | 16154(3) | 11403.4(17) | -3347.1(18) | 28.5(6) |
| C23 | 15335(5) | 12814(3) | -7502(3) | 42.7(12) |
| C34 | 13342(5) | 11743(3) | 1409(3) | 45.3(13) |
| C85 | 14893(6) | 9804(4) | -3681(6) | 77(3) |
| C88A | 19015(12) | 13414(6) | -9252(6) | 55(3) |
| C86 | 16731(5) | 11473(3) | -2763(3) | 40.6(11) |
| C88B | 18398(7) | 12422(6) | -8566(6) | 36(2) |

**Crystallographic Table 81** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **$Gd_2[L^{VII}]_3$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{12}$** | **$U_{13}$** | **$U_{23}$** |
|---|---|---|---|---|---|---|
| Gd1 | 16.29(8) | 15.25(8) | 11.39(7) | 0.34(6) | -3.48(6) | -0.91(5) |
| Gd2 | 17.06(8) | 16.72(8) | 15.22(8) | 0.13(6) | -5.30(6) | -0.57(6) |
| O3 | 24.6(13) | 17.3(12) | 11.6(10) | -1.0(9) | -6.7(9) | -0.1(9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O4 | 24.9(13) | 18.4(12) | 12.4(11) | -2.1(10) | -8.8(9) | 0.9(9) |
| N3 | 16.5(13) | 18.4(14) | 14.9(13) | 1.9(11) | -3.4(11) | -1.9(11) |
| N5 | 17.8(14) | 20.6(15) | 18.7(14) | -1.3(11) | -5.8(11) | 0.3(11) |
| N4 | 18.3(14) | 16.6(13) | 13.1(12) | 0.5(11) | -2.8(11) | 1.1(10) |
| N6 | 15.4(13) | 19.7(14) | 18.1(14) | 0.1(11) | -3.6(11) | -0.8(11) |
| C29 | 17.6(15) | 19.1(16) | 13.8(14) | -3.9(12) | -6.3(12) | 1.2(12) |
| N2 | 20.0(14) | 18.1(14) | 17.0(13) | 0.3(11) | -5.3(11) | -0.1(11) |
| C68 | 17.1(16) | 22.2(17) | 17.4(16) | -0.5(13) | -3.4(13) | 1.3(13) |
| O1 | 22.1(13) | 23.2(13) | 17.5(12) | 1.3(10) | -8(1) | -5.2(10) |
| O2 | 19.6(12) | 23.7(13) | 15.7(11) | 3.9(10) | -2.5(9) | -3.2(10) |
| N1 | 22.4(15) | 17.0(14) | 15.7(13) | 1.5(11) | -5.5(11) | -0.6(11) |
| C48 | 24.3(18) | 26.0(18) | 18.2(16) | -10.1(14) | -9.2(14) | 5.5(14) |
| C71 | 22.9(19) | 30(2) | 32(2) | 6.5(16) | -5.6(16) | -2.0(17) |
| C73 | 16.8(16) | 20.7(17) | 16.4(15) | -0.3(13) | -3.5(12) | -0.2(13) |
| C38 | 20.7(16) | 19.3(16) | 12.8(14) | -3.6(13) | -5.8(12) | 4.0(12) |
| C47 | 17.4(16) | 20.6(16) | 14.5(15) | -4.8(13) | -6.5(12) | 2.2(12) |
| C56 | 18.8(16) | 18.7(16) | 14.8(15) | -3.9(13) | -6.4(12) | 1.6(12) |
| C46 | 17.7(16) | 18.4(16) | 18.8(16) | -0.4(12) | -5.5(13) | 2.5(13) |
| C39 | 19.7(16) | 23.7(17) | 13.5(15) | -1.0(13) | -3.1(12) | -2.3(13) |
| C17 | 21.4(17) | 15.8(16) | 18.1(16) | -1.9(13) | -3.2(13) | 1.5(12) |
| C66 | 22.5(17) | 25.5(18) | 18.2(16) | -4.7(14) | -6.7(14) | 5.9(14) |
| C67 | 21.8(17) | 26.6(19) | 16.7(16) | -4.4(14) | -4.7(13) | 2.5(14) |
| O6 | 27.2(14) | 22.7(13) | 26.9(14) | 4.8(11) | -14.2(11) | -5.7(11) |
| C40 | 18.2(16) | 21.2(17) | 16.3(15) | 1.9(13) | -2.2(13) | -2.3(13) |
| O5 | 38.3(16) | 24.4(14) | 20.7(13) | 5.9(12) | -6.4(12) | 2.4(11) |
| C4 | 30(2) | 27.3(19) | 17.8(17) | -6.0(15) | -8.2(15) | -2.6(14) |
| C58 | 43(2) | 18.3(18) | 27(2) | 2.3(16) | -11.9(18) | 0.6(15) |
| C45 | 16.2(16) | 21.1(17) | 17.2(15) | 1.1(13) | -1.0(12) | 0.2(13) |
| C37 | 28.0(19) | 25.6(18) | 12.0(15) | -6.5(15) | -7.2(13) | 3.1(13) |
| C28 | 18.1(16) | 21.9(17) | 15.2(15) | -1.8(13) | -2.1(12) | -3.0(13) |
| C12 | 23.7(17) | 15.7(16) | 18.9(16) | -1.5(13) | -6.1(13) | 1.2(13) |
| C72 | 21.3(17) | 25.7(19) | 21.9(17) | 1.7(14) | -5.3(14) | -0.1(14) |
| C75 | 18.6(16) | 21.2(17) | 21.5(17) | -2.3(13) | -6.7(13) | -0.7(13) |
| C82 | 41(2) | 28(2) | 25.2(19) | 5.0(17) | -10.6(17) | -10.4(16) |
| C30 | 27.9(19) | 20.3(17) | 20.6(17) | 1.6(14) | -10.5(15) | 1.2(13) |
| C53 | 31(2) | 34(2) | 13.6(16) | -12.0(16) | -8.1(14) | 4.6(14) |
| O7 | 19.9(13) | 23.4(14) | 46.7(18) | 1.2(11) | -4.8(13) | -10.0(13) |
| C77 | 25.0(19) | 32(2) | 22.9(18) | 0.6(15) | -9.8(15) | -2.0(15) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C74 | 16.2(16) | 21.8(17) | 21.2(16) | -0.0(13) | -5.1(13) | 1.0(13) |
| C44 | 24.5(19) | 28(2) | 27.1(19) | 6.6(15) | -6.7(15) | 2.0(15) |
| C19 | 19.5(16) | 23.4(17) | 12.5(14) | -4.4(13) | 1.3(12) | -0.3(13) |
| C54 | 31(2) | 33(2) | 15.6(16) | -7.3(16) | -4.4(15) | -3.2(15) |
| C57 | 28.5(19) | 19.8(17) | 22.8(18) | -3.9(14) | -9.5(15) | 4.9(14) |
| C32 | 36(2) | 24.9(19) | 18.1(17) | -6.6(16) | -13.7(15) | 6.8(14) |
| C20 | 25.3(18) | 28.9(19) | 14.4(15) | -8.1(15) | -2.9(13) | -1.0(14) |
| C55 | 23.6(18) | 23.9(18) | 18.4(16) | -4.0(14) | -4.2(14) | -2.9(14) |
| C1 | 20.2(17) | 22.3(17) | 18.3(16) | -4.2(13) | -7.2(13) | -0.2(13) |
| C84 | 23.0(18) | 20.0(17) | 22.8(17) | -4.5(14) | -8.9(14) | -2.9(13) |
| C41 | 32(2) | 31(2) | 18.8(17) | 8.1(17) | -1.0(15) | -6.3(15) |
| C70 | 26(2) | 33(2) | 26(2) | 5.9(16) | 1.5(16) | -6.1(16) |
| C76 | 20.6(17) | 21.6(17) | 20.6(17) | -5.6(13) | -6.1(14) | -0.9(13) |
| C65 | 25.5(19) | 26.8(19) | 21.5(17) | -7.1(15) | -8.8(15) | 4.3(14) |
| C78 | 33(2) | 37(2) | 28(2) | -0.3(18) | -14.4(18) | 3.4(17) |
| C31 | 35(2) | 23.5(19) | 27.7(19) | 1.5(16) | -17.8(17) | 4.3(15) |
| C11 | 20.7(17) | 19.9(17) | 19.0(16) | 1.2(13) | -4.0(13) | -5.4(13) |
| C18 | 20.5(17) | 22.3(17) | 16.9(15) | -3.8(13) | -4.4(13) | 2.5(13) |
| C13 | 36(2) | 18.8(17) | 22.9(18) | 2.9(15) | -9.0(16) | -3.2(14) |
| C49 | 38(2) | 33(2) | 28(2) | -2.3(18) | -15.2(18) | 8.9(17) |
| C81 | 35(2) | 25.7(19) | 24.6(19) | -0.9(16) | -11.9(16) | -3.8(15) |
| C79 | 52(3) | 47(3) | 30(2) | 4(2) | -23(2) | -3(2) |
| C69 | 26.0(19) | 32(2) | 16.8(16) | 2.4(16) | -2.4(14) | -3.2(15) |
| C83 | 30(2) | 21.2(18) | 29(2) | 4.2(15) | -10.7(16) | -7.2(15) |
| C26 | 28(2) | 32(2) | 20.8(18) | -0.4(16) | -0.8(15) | -11.7(15) |
| C51 | 58(3) | 61(3) | 22(2) | -15(3) | -23(2) | 14(2) |
| C59 | 48(3) | 20.0(19) | 31(2) | 2.0(17) | -19.0(19) | 2.6(16) |
| C10 | 20.2(16) | 21.2(17) | 16.1(15) | -0.7(13) | -5.2(13) | -3.8(13) |
| C80 | 58(3) | 39(3) | 24(2) | 4(2) | -18(2) | -9.2(18) |
| C60 | 36(2) | 27(2) | 23.7(18) | -8.1(17) | -14.8(17) | 5.3(15) |
| C25 | 23.6(18) | 34(2) | 15.7(16) | -6.8(15) | 0.9(14) | -6.8(14) |
| C16 | 28.8(19) | 26.9(19) | 19.5(17) | 1.2(15) | -7.1(15) | 4.5(14) |
| C5 | 41(2) | 42(2) | 18.3(18) | -6(2) | -9.2(17) | -1.8(17) |
| C21 | 34(2) | 41(2) | 18.3(18) | -1.7(18) | -5.5(16) | -1.1(16) |
| C61 | 55(3) | 29(2) | 28(2) | -4(2) | -21(2) | 7.9(17) |
| C15 | 35(2) | 22.6(19) | 34(2) | 4.2(16) | -12.2(18) | 6.9(16) |
| C2 | 26.7(19) | 27.6(19) | 23.0(18) | 2.3(15) | -12.5(15) | -2.2(15) |
| C9 | 23.9(18) | 24.8(18) | 17.8(16) | -3.1(14) | -6.8(14) | -1.7(14) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C27 | 24.5(19) | 29(2) | 21.2(18) | 4.7(15) | -3.2(15) | -8.6(15) |
| C43 | 31(2) | 32(2) | 38(2) | 13.1(18) | -3.9(18) | -2.1(18) |
| C64 | 38(2) | 41(2) | 21.2(19) | 2.7(19) | -9.4(17) | 4.9(17) |
| C3 | 33(2) | 30(2) | 25.1(19) | 0.1(16) | -15.2(17) | -1.5(16) |
| C24 | 40(2) | 46(3) | 16.7(18) | -7(2) | -0.4(17) | -10.1(17) |
| C36 | 42(3) | 40(2) | 17.8(18) | 0(2) | -7.9(17) | 0.1(17) |
| C50 | 50(3) | 44(3) | 38(3) | -4(2) | -26(2) | 18(2) |
| C8 | 28(2) | 30(2) | 25.8(19) | -2.0(16) | -4.7(16) | -7.0(16) |
| C6 | 43(3) | 44(3) | 17.8(18) | -8(2) | -0.7(17) | -10.6(17) |
| C42 | 37(2) | 33(2) | 31(2) | 13.0(19) | 2.5(18) | -9.3(18) |
| C22 | 51(3) | 55(3) | 18.2(19) | -3(2) | -11.2(19) | 1.8(19) |
| C14 | 36(2) | 17.7(18) | 35(2) | 4.5(16) | -7.7(18) | -0.5(16) |
| C62 | 54(3) | 47(3) | 23(2) | -7(2) | -17(2) | 7.4(19) |
| C63 | 48(3) | 56(3) | 20(2) | 3(2) | -7.2(19) | 1(2) |
| C52 | 48(3) | 50(3) | 18.2(18) | -12(2) | -14.9(19) | 3.7(18) |
| C33 | 52(3) | 42(3) | 23(2) | 2(2) | -19(2) | 8.3(18) |
| C35 | 55(3) | 55(3) | 18(2) | 2(2) | -9(2) | -5(2) |
| C7 | 36(2) | 41(3) | 26(2) | -1.9(19) | -1.3(18) | -11.9(18) |
| Cl4 | 88.3(13) | 101.4(14) | 40.6(8) | 56.2(11) | -20.1(8) | -12.9(8) |
| Cl3 | 104.8(16) | 55.1(10) | 107.8(16) | -7.4(10) | -45.6(13) | -20.2(10) |
| C87 | 40(3) | 48(3) | 47(3) | -10(2) | 3(2) | -6(2) |
| Cl2 | 120.6(19) | 106.6(17) | 57.1(11) | 12.3(15) | -17.5(12) | -16.4(11) |
| Cl1 | 65.2(13) | 115(2) | 161(3) | -5.2(13) | -17.9(15) | -28.6(19) |
| O8 | 31.2(15) | 23.4(14) | 34.1(15) | 1.3(12) | -15.1(13) | -0.7(12) |
| C23 | 52(3) | 60(3) | 16.8(19) | -6(2) | -8.3(19) | -6(2) |
| C34 | 63(3) | 61(3) | 15.8(19) | 0(3) | -19(2) | 5(2) |
| C85 | 32(3) | 50(4) | 142(9) | 9(3) | -3(4) | -48(5) |
| C88A | 101(10) | 28(5) | 26(5) | -16(5) | 8(5) | -7(4) |
| C86 | 40(3) | 46(3) | 41(3) | 9(2) | -24(2) | -12(2) |
| C88B | 19(4) | 44(5) | 43(5) | -14(4) | 2(3) | -2(4) |

**Crystallographic Table 82** Bond Lengths for **$Gd_2[L^{VII}]_3$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Gd1 | O3 | 2.379(2) | C75 | C74 | 1.430(5) |
| Gd1 | O4 | 2.368(2) | C75 | C84 | 1.414(5) |
| Gd1 | N3 | 2.562(3) | C75 | C76 | 1.452(5) |
| Gd1 | N4 | 2.549(3) | C82 | C81 | 1.423(6) |
| Gd1 | N2 | 2.530(3) | C82 | C83 | 1.355(6) |

| | | | | | |
|---|---|---|---|---|---|
| Gd1 | O1 | 2.275(2) | C30 | C31 | 1.364(5) |
| Gd1 | O2 | 2.318(2) | C53 | C54 | 1.425(6) |
| Gd1 | N1 | 2.500(3) | C53 | C52 | 1.422(5) |
| Gd2 | O3 | 2.386(2) | O7 | C85 | 1.411(7) |
| Gd2 | O4 | 2.388(2) | C77 | C76 | 1.411(5) |
| Gd2 | N5 | 2.487(3) | C77 | C78 | 1.373(5) |
| Gd2 | N6 | 2.493(3) | C44 | C43 | 1.388(6) |
| Gd2 | O6 | 2.218(3) | C19 | C20 | 1.449(5) |
| Gd2 | O5 | 2.237(3) | C19 | C18 | 1.436(5) |
| Gd2 | O7 | 2.419(3) | C54 | C55 | 1.363(5) |
| O3 | C29 | 1.339(4) | C32 | C31 | 1.413(6) |
| O4 | C56 | 1.336(4) | C32 | C33 | 1.422(5) |
| N3 | C39 | 1.290(4) | C20 | C25 | 1.418(6) |
| N3 | C40 | 1.427(4) | C20 | C21 | 1.421(6) |
| N5 | C68 | 1.421(5) | C1 | C10 | 1.411(5) |
| N5 | C67 | 1.299(5) | C1 | C2 | 1.440(5) |
| N4 | C46 | 1.292(4) | C84 | C83 | 1.426(5) |
| N4 | C45 | 1.424(4) | C41 | C42 | 1.387(6) |
| N6 | C73 | 1.420(4) | C70 | C69 | 1.388(6) |
| N6 | C74 | 1.301(4) | C76 | C81 | 1.420(5) |
| C29 | C38 | 1.401(5) | C65 | C60 | 1.421(6) |
| C29 | C30 | 1.426(5) | C65 | C64 | 1.413(6) |
| N2 | C17 | 1.421(5) | C78 | C79 | 1.396(7) |
| N2 | C18 | 1.296(5) | C11 | C10 | 1.437(5) |
| C68 | C73 | 1.413(5) | C13 | C14 | 1.384(6) |
| C68 | C69 | 1.400(5) | C49 | C50 | 1.387(6) |
| O1 | C1 | 1.299(4) | C81 | C80 | 1.410(6) |
| O2 | C28 | 1.317(4) | C79 | C80 | 1.365(7) |
| N1 | C12 | 1.418(4) | C26 | C25 | 1.419(6) |
| N1 | C11 | 1.301(4) | C26 | C27 | 1.361(5) |
| C48 | C47 | 1.448(5) | C51 | C50 | 1.392(8) |
| C48 | C53 | 1.411(6) | C51 | C52 | 1.352(8) |
| C48 | C49 | 1.424(6) | C59 | C60 | 1.427(6) |
| C71 | C72 | 1.383(6) | C10 | C9 | 1.450(5) |
| C71 | C70 | 1.381(6) | C60 | C61 | 1.413(6) |
| C73 | C72 | 1.396(5) | C25 | C24 | 1.413(5) |
| C38 | C39 | 1.452(5) | C16 | C15 | 1.382(6) |
| C38 | C37 | 1.448(4) | C5 | C6 | 1.369(7) |

| | | | | | |
|---|---|---|---|---|---|
| C47 | C56 | 1.403(5) | C21 | C22 | 1.372(6) |
| C47 | C46 | 1.451(5) | C61 | C62 | 1.364(7) |
| C56 | C55 | 1.427(5) | C15 | C14 | 1.386(6) |
| C17 | C12 | 1.410(5) | C2 | C3 | 1.361(5) |
| C17 | C16 | 1.406(5) | C9 | C8 | 1.409(6) |
| C66 | C67 | 1.434(5) | C43 | C42 | 1.380(7) |
| C66 | C57 | 1.411(6) | C64 | C63 | 1.377(6) |
| C66 | C65 | 1.451(5) | C24 | C23 | 1.373(7) |
| O6 | C84 | 1.298(4) | C36 | C35 | 1.374(6) |
| C40 | C45 | 1.404(5) | C8 | C7 | 1.380(6) |
| C40 | C41 | 1.396(5) | C6 | C7 | 1.401(7) |
| O5 | C57 | 1.303(4) | C22 | C23 | 1.393(8) |
| C4 | C5 | 1.412(5) | C62 | C63 | 1.399(7) |
| C4 | C9 | 1.418(5) | C33 | C34 | 1.357(7) |
| C4 | C3 | 1.424(6) | C35 | C34 | 1.402(8) |
| C58 | C57 | 1.436(5) | Cl4 | C87 | 1.720(6) |
| C58 | C59 | 1.353(6) | Cl3 | C87 | 1.745(6) |
| C45 | C44 | 1.395(5) | Cl2 | C88A | 1.634(14) |
| C37 | C32 | 1.422(5) | Cl2 | C88B | 1.740(11) |
| C37 | C36 | 1.415(6) | Cl1 | C88A | 2.139(13) |
| C28 | C19 | 1.410(5) | Cl1 | C88B | 1.713(9) |
| C28 | C27 | 1.427(5) | O8 | C86 | 1.410(5) |
| C12 | C13 | 1.402(5) | | | |

**Crystallographic Table 83** Bond Angles for **$Gd_2[L^{VII}]_3$**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| O4 | Gd1 | O3 | 69.21(8) | C3 | C4 | C9 | 119.2(3) |
| N3 | Gd1 | O3 | 68.71(9) | C59 | C58 | C57 | 121.6(4) |
| N3 | Gd1 | O4 | 103.24(9) | C40 | C45 | N4 | 116.1(3) |
| N4 | Gd1 | O3 | 103.88(9) | C44 | C45 | N4 | 124.5(3) |
| N4 | Gd1 | O4 | 69.20(9) | C44 | C45 | C40 | 119.2(3) |
| N4 | Gd1 | N3 | 63.01(9) | C32 | C37 | C38 | 119.3(3) |
| N2 | Gd1 | O3 | 162.36(9) | C36 | C37 | C38 | 123.0(4) |
| N2 | Gd1 | O4 | 93.84(9) | C36 | C37 | C32 | 117.6(3) |
| N2 | Gd1 | N3 | 122.10(9) | C19 | C28 | O2 | 123.1(3) |
| N2 | Gd1 | N4 | 73.08(9) | C27 | C28 | O2 | 118.4(3) |
| O1 | Gd1 | O3 | 81.39(9) | C27 | C28 | C19 | 118.4(3) |
| O1 | Gd1 | O4 | 141.27(9) | C17 | C12 | N1 | 116.3(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O1 | Gd1 | N3 | 88.17(9) | C13 | C12 | N1 | 124.1(3) |
| O1 | Gd1 | N4 | 144.99(9) | C13 | C12 | C17 | 119.4(3) |
| O1 | Gd1 | N2 | 111.34(10) | C73 | C72 | C71 | 120.8(4) |
| O2 | Gd1 | O3 | 101.11(9) | C84 | C75 | C74 | 122.0(3) |
| O2 | Gd1 | O4 | 80.69(9) | C76 | C75 | C74 | 118.4(3) |
| O2 | Gd1 | N3 | 166.19(9) | C76 | C75 | C84 | 119.6(3) |
| O2 | Gd1 | N4 | 130.11(9) | C83 | C82 | C81 | 121.5(4) |
| O2 | Gd1 | N2 | 70.24(9) | C31 | C30 | C29 | 121.0(4) |
| O2 | Gd1 | O1 | 80.89(9) | C54 | C53 | C48 | 119.2(3) |
| N1 | Gd1 | O3 | 132.77(9) | C52 | C53 | C48 | 119.6(4) |
| N1 | Gd1 | O4 | 147.27(9) | C52 | C53 | C54 | 121.3(4) |
| N1 | Gd1 | N3 | 72.46(10) | C85 | O7 | Gd2 | 126.7(4) |
| N1 | Gd1 | N4 | 80.65(10) | C78 | C77 | C76 | 121.8(4) |
| N1 | Gd1 | N2 | 64.54(10) | C75 | C74 | N6 | 127.7(3) |
| N1 | Gd1 | O1 | 71.44(9) | C43 | C44 | C45 | 120.6(4) |
| N1 | Gd1 | O2 | 111.42(10) | C20 | C19 | C28 | 119.5(3) |
| O4 | Gd2 | O3 | 68.77(8) | C18 | C19 | C28 | 121.5(3) |
| N5 | Gd2 | O3 | 81.16(9) | C18 | C19 | C20 | 119.0(3) |
| N5 | Gd2 | O4 | 115.08(9) | C55 | C54 | C53 | 121.2(4) |
| N6 | Gd2 | O3 | 116.69(9) | O5 | C57 | C66 | 123.1(3) |
| N6 | Gd2 | O4 | 78.77(9) | C58 | C57 | C66 | 118.6(3) |
| N6 | Gd2 | N5 | 65.51(10) | C58 | C57 | O5 | 118.3(4) |
| O6 | Gd2 | O3 | 157.93(10) | C31 | C32 | C37 | 118.8(3) |
| O6 | Gd2 | O4 | 95.37(9) | C33 | C32 | C37 | 119.4(4) |
| O6 | Gd2 | N5 | 120.34(10) | C33 | C32 | C31 | 121.7(4) |
| O6 | Gd2 | N6 | 72.75(10) | C25 | C20 | C19 | 119.8(4) |
| O5 | Gd2 | O3 | 97.79(10) | C21 | C20 | C19 | 123.0(4) |
| O5 | Gd2 | O4 | 161.92(10) | C21 | C20 | C25 | 117.0(3) |
| O5 | Gd2 | N5 | 72.81(10) | C54 | C55 | C56 | 120.9(4) |
| O5 | Gd2 | N6 | 118.90(11) | C10 | C1 | O1 | 123.5(3) |
| O5 | Gd2 | O6 | 93.85(10) | C2 | C1 | O1 | 118.1(3) |
| O7 | Gd2 | O3 | 79.76(9) | C2 | C1 | C10 | 118.5(3) |
| O7 | Gd2 | O4 | 84.00(10) | C75 | C84 | O6 | 122.8(3) |
| O7 | Gd2 | N5 | 145.51(10) | C83 | C84 | O6 | 118.3(3) |
| O7 | Gd2 | N6 | 148.95(11) | C83 | C84 | C75 | 118.9(3) |
| O7 | Gd2 | O6 | 83.48(10) | C42 | C41 | C40 | 120.1(4) |
| O7 | Gd2 | O5 | 81.64(11) | C69 | C70 | C71 | 120.0(4) |
| Gd2 | O3 | Gd1 | 110.49(9) | C77 | C76 | C75 | 123.8(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C29 | O3 | Gd1 | 123.9(2) | C81 | C76 | C75 | 119.1(3) |
| C29 | O3 | Gd2 | 123.5(2) | C81 | C76 | C77 | 117.0(3) |
| Gd2 | O4 | Gd1 | 110.80(9) | C60 | C65 | C66 | 119.7(4) |
| C56 | O4 | Gd1 | 120.7(2) | C64 | C65 | C66 | 123.3(4) |
| C56 | O4 | Gd2 | 127.3(2) | C64 | C65 | C60 | 117.0(4) |
| C39 | N3 | Gd1 | 127.7(2) | C79 | C78 | C77 | 120.6(4) |
| C40 | N3 | Gd1 | 114.2(2) | C32 | C31 | C30 | 121.7(4) |
| C40 | N3 | C39 | 118.0(3) | C10 | C11 | N1 | 126.2(3) |
| C68 | N5 | Gd2 | 114.3(2) | C19 | C18 | N2 | 126.6(3) |
| C67 | N5 | Gd2 | 128.3(3) | C14 | C13 | C12 | 120.4(4) |
| C67 | N5 | C68 | 117.4(3) | C50 | C49 | C48 | 119.8(4) |
| C46 | N4 | Gd1 | 124.9(2) | C76 | C81 | C82 | 119.1(4) |
| C45 | N4 | Gd1 | 115.5(2) | C80 | C81 | C82 | 121.0(4) |
| C45 | N4 | C46 | 119.4(3) | C80 | C81 | C76 | 119.9(4) |
| C73 | N6 | Gd2 | 114.4(2) | C80 | C79 | C78 | 119.3(4) |
| C74 | N6 | Gd2 | 127.0(2) | C70 | C69 | C68 | 120.7(4) |
| C74 | N6 | C73 | 118.4(3) | C84 | C83 | C82 | 121.5(4) |
| C38 | C29 | O3 | 122.8(3) | C27 | C26 | C25 | 121.2(4) |
| C30 | C29 | O3 | 118.0(3) | C52 | C51 | C50 | 120.0(4) |
| C30 | C29 | C38 | 119.2(3) | C60 | C59 | C58 | 121.7(4) |
| C17 | N2 | Gd1 | 113.1(2) | C11 | C10 | C1 | 121.2(3) |
| C18 | N2 | Gd1 | 127.4(2) | C9 | C10 | C1 | 119.6(3) |
| C18 | N2 | C17 | 119.1(3) | C9 | C10 | C11 | 119.1(3) |
| C73 | C68 | N5 | 117.0(3) | C79 | C80 | C81 | 121.4(4) |
| C69 | C68 | N5 | 123.9(3) | C59 | C60 | C65 | 118.6(4) |
| C69 | C68 | C73 | 119.0(3) | C61 | C60 | C65 | 119.9(4) |
| C1 | O1 | Gd1 | 128.4(2) | C61 | C60 | C59 | 121.5(4) |
| C28 | O2 | Gd1 | 131.2(2) | C26 | C25 | C20 | 118.7(3) |
| C12 | N1 | Gd1 | 114.9(2) | C24 | C25 | C20 | 120.3(4) |
| C11 | N1 | Gd1 | 123.7(2) | C24 | C25 | C26 | 121.0(4) |
| C11 | N1 | C12 | 120.1(3) | C15 | C16 | C17 | 120.8(4) |
| C53 | C48 | C47 | 119.6(4) | C6 | C5 | C4 | 121.4(4) |
| C49 | C48 | C47 | 122.2(4) | C22 | C21 | C20 | 121.4(4) |
| C49 | C48 | C53 | 118.3(3) | C62 | C61 | C60 | 121.5(4) |
| C70 | C71 | C72 | 120.2(4) | C14 | C15 | C16 | 120.1(4) |
| C68 | C73 | N6 | 116.6(3) | C3 | C2 | C1 | 121.4(4) |
| C72 | C73 | N6 | 124.2(3) | C10 | C9 | C4 | 119.4(3) |
| C72 | C73 | C68 | 119.1(3) | C8 | C9 | C4 | 117.6(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C39 | C38 | C29 | 121.5(3) | C8 | C9 | C10 | 122.9(3) |
| C37 | C38 | C29 | 119.9(3) | C26 | C27 | C28 | 121.8(4) |
| C37 | C38 | C39 | 118.4(3) | C42 | C43 | C44 | 120.0(4) |
| C56 | C47 | C48 | 119.5(3) | C63 | C64 | C65 | 121.6(4) |
| C46 | C47 | C48 | 119.2(3) | C2 | C3 | C4 | 121.1(4) |
| C46 | C47 | C56 | 121.1(3) | C23 | C24 | C25 | 120.7(4) |
| C47 | C56 | O4 | 122.4(3) | C35 | C36 | C37 | 121.4(4) |
| C55 | C56 | O4 | 118.0(3) | C51 | C50 | C49 | 121.2(5) |
| C55 | C56 | C47 | 119.6(3) | C7 | C8 | C9 | 121.5(4) |
| C47 | C46 | N4 | 125.2(3) | C7 | C6 | C5 | 119.2(4) |
| C38 | C39 | N3 | 124.6(3) | C43 | C42 | C41 | 120.4(4) |
| C12 | C17 | N2 | 117.1(3) | C23 | C22 | C21 | 121.1(5) |
| C16 | C17 | N2 | 123.7(3) | C15 | C14 | C13 | 120.4(4) |
| C16 | C17 | C12 | 118.9(3) | C63 | C62 | C61 | 119.0(4) |
| C57 | C66 | C67 | 122.2(3) | C62 | C63 | C64 | 120.9(5) |
| C65 | C66 | C67 | 118.1(4) | C51 | C52 | C53 | 121.1(5) |
| C65 | C66 | C57 | 119.7(3) | C34 | C33 | C32 | 121.0(4) |
| C66 | C67 | N5 | 127.1(4) | C34 | C35 | C36 | 120.4(5) |
| C84 | O6 | Gd2 | 137.3(2) | C6 | C7 | C8 | 120.6(4) |
| C45 | C40 | N3 | 116.6(3) | Cl3 | C87 | Cl4 | 111.8(3) |
| C41 | C40 | N3 | 123.6(3) | C22 | C23 | C24 | 119.5(4) |
| C41 | C40 | C45 | 119.7(3) | C35 | C34 | C33 | 120.0(4) |
| C57 | O5 | Gd2 | 137.1(3) | Cl1 | C88A | Cl2 | 100.4(5) |
| C9 | C4 | C5 | 119.7(4) | Cl1 | C88B | Cl2 | 115.3(5) |
| C3 | C4 | C5 | 121.0(4) | | | | |

**Crystallographic Table 84** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **$Gd_2[L^{VII}]_3$**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H71 | 8050(3) | 13297(3) | -1964(3) | 34.7(10) |
| H46 | 10642(3) | 13616(2) | -3654(2) | 21.9(8) |
| H39 | 11558(3) | 12991(2) | -597(2) | 22.9(8) |
| H67 | 10363(3) | 10965(2) | -555(2) | 26.0(8) |
| H58 | 13677(4) | 8820(2) | -1460(2) | 34.9(10) |
| H72 | 9085(3) | 12590(2) | -3019(2) | 27.8(9) |
| H82 | 12057(4) | 9741(3) | -6114(2) | 37.0(11) |
| H30 | 14671(3) | 10778(2) | -1723(2) | 26.8(9) |
| H7 | 15040(12) | 10815(16) | -3370(30) | 45.7(10) |

| | | | | |
|---|---|---|---|---|
| H77 | 9321(3) | 12028(3) | -4670(2) | 31.2(9) |
| H74 | 9603(3) | 11607(2) | -3645(2) | 23.7(8) |
| H44 | 10119(3) | 14636(2) | -3001(2) | 32.2(10) |
| H54 | 13243(4) | 11707(3) | -6070(2) | 31.8(10) |
| H55 | 13723(3) | 11442(2) | -4912(2) | 26.3(8) |
| H41 | 11016(4) | 14204(3) | -605(2) | 34.1(10) |
| H70 | 8400(4) | 13077(3) | -740(2) | 36.1(10) |
| H78 | 8708(4) | 12233(3) | -5792(3) | 38.3(11) |
| H31 | 14840(4) | 10525(2) | -477(2) | 32.6(10) |
| H11 | 13596(3) | 15171(2) | -1738(2) | 24.0(8) |
| H18 | 14347(3) | 14388(2) | -5107(2) | 23.8(8) |
| H13 | 12497(4) | 15826(2) | -2224(2) | 30.9(9) |
| H49 | 10590(4) | 14111(3) | -4753(3) | 38.6(11) |
| H79 | 9439(5) | 11444(3) | -6872(3) | 49.2(14) |
| H69 | 9768(3) | 12129(2) | -562(2) | 30.6(9) |
| H83 | 12754(4) | 9540(2) | -5039(2) | 31.8(10) |
| H26 | 16847(4) | 11551(3) | -6063(2) | 33.1(10) |
| H51 | 10881(5) | 13507(3) | -6983(3) | 53.6(15) |
| H59 | 13500(4) | 8508(2) | -178(3) | 37.9(11) |
| H80 | 10813(5) | 10473(3) | -6818(3) | 46.8(13) |
| H16 | 12909(3) | 15144(2) | -4807(2) | 30.1(9) |
| H5 | 14677(4) | 13891(3) | 1117(2) | 39.8(11) |
| H21 | 14140(4) | 14071(3) | -6177(2) | 37.4(11) |
| H61 | 12706(4) | 8787(3) | 1211(3) | 42.5(12) |
| H15 | 11928(4) | 16307(2) | -4346(3) | 36.4(10) |
| H2 | 15998(3) | 12647(2) | -1207(2) | 29.8(9) |
| H27 | 16609(3) | 11737(2) | -4763(2) | 30.3(9) |
| H43 | 9197(4) | 15383(3) | -1937(3) | 42.1(12) |
| H64 | 10593(4) | 10949(3) | 537(2) | 40.1(11) |
| H3 | 15737(4) | 13072(2) | 37(2) | 33.6(10) |
| H24 | 16327(4) | 11882(3) | -7298(2) | 41.6(12) |
| H36 | 12118(4) | 13021(3) | 427(2) | 40.2(11) |
| H50 | 10119(5) | 14324(3) | -5940(3) | 50.0(14) |
| H8 | 12735(4) | 15231(3) | -537(2) | 33.4(10) |
| H6 | 13341(4) | 14881(3) | 1596(2) | 42.6(12) |
| H42 | 9656(4) | 15175(3) | -748(3) | 43.4(12) |
| H22 | 14328(5) | 13811(3) | -7467(3) | 49.1(14) |
| H14 | 11718(4) | 16645(2) | -3056(3) | 35.8(10) |

| | | | | |
|---|---|---|---|---|
| H62 | 11509(5) | 9516(3) | 2173(3) | 48.0(13) |
| H63 | 10480(5) | 10619(3) | 1825(3) | 50.2(14) |
| H52 | 12149(4) | 12495(3) | -6863(2) | 44.7(13) |
| H33 | 14340(4) | 10832(3) | 925(3) | 45.4(13) |
| H35 | 12336(5) | 12745(3) | 1668(3) | 51.7(14) |
| H7a | 12369(4) | 15553(3) | 758(3) | 42.2(12) |
| H87a | 16339(5) | 14018(3) | -3812(3) | 56.0(15) |
| H87b | 16587(5) | 13593(3) | -3048(3) | 56.0(15) |
| H8a | 15910(40) | 11849(4) | -3470(20) | 42.7(9) |
| H23 | 15387(5) | 12705(3) | -8030(3) | 51.2(14) |
| H34 | 13405(5) | 11623(3) | 1924(3) | 54.4(15) |
| H85a | 15130(70) | 9670(50) | -3360(50) | 60.9(17) |
| H85b | 15630(60) | 9760(40) | -3980(40) | 60.9(17) |
| H85c | 14330(60) | 9490(40) | -3690(40) | 60.9(17) |
| H86a | 16760(60) | 11010(40) | -2480(40) | 60.9(17) |
| H86b | 16490(50) | 11890(40) | -2400(40) | 60.9(17) |
| H86c | 17480(60) | 11590(40) | -2970(40) | 60.9(17) |
| H88a | 19395(12) | 13424(6) | -9811(6) | 66(4) |
| H88b | 19000(12) | 13940(6) | -9038(6) | 66(4) |
| H88c | 17984(7) | 12451(6) | -8015(6) | 43(2) |
| H88d | 18329(7) | 11892(6) | -8744(6) | 43(2) |

**Crystallographic Table 85** Atomic Occupancy for **$Gd_2[L^{VII}]_3$**.

| **Atom** | ***Occupancy*** | **Atom** | ***Occupancy*** | **Atom** | ***Occupancy*** |
|---|---|---|---|---|---|
| C88A | 0.500000 | C88B | 0.500000 | H88a | 0.500000 |
| H88b | 0.500000 | H88c | 0.500000 | H88d | 0.500000 |

Refinement model description

Number of restraints - 3, number of constraints - 126.

Details:

1. Others
Fixed Sof: C88A(0.5) C88B(0.5) H88a(0.5) H88b(0.5) H88c(0.5) H88d(0.5)

## $Ho_2[L^{VII}]_3$

**Crystallographic Table 86** Crystal data and structure refinement for **$Ho_2[L^{VII}]_3$**

| | |
|---|---|
| Empirical formula | $C_{87}H_{66}Ho_2N_6O_9$ |
| Formula weight | 1669.39 |
| Temperature/K | 180.65 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.3525(1) |
| b/Å | 17.6031(2) |
| c/Å | 18.9169(2) |
| α/° | 82.6930(6) |
| β/° | 86.1741(6) |
| γ/° | 82.4147(6) |
| Volume/Å$^3$ | 3385.05(6) |
| Z | 2 |
| $\rho_{calc}$mg/mm$^3$ | 1.6377 |
| m/mm$^{-1}$ | 2.390 |
| F(000) | 1672.6 |
| Crystal size/mm$^3$ | 0.22 × 0.21 × 0.2 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 3 to 61.1° |
| Index ranges | $-14 \le h \le 14$, $-25 \le k \le 25$, $-27 \le l \le 27$ |
| Reflections collected | 127024 |
| Independent reflections | 20696 [$R_{int}$ = 0.0361, $R_{sigma}$ = 0.0277] |
| Data/restraints/parameters | 20696/3/944 |
| Goodness-of-fit on $F^2$ | 1.154 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0271, $wR_2$ = 0.0561 |
| Final R indexes [all data] | $R_1$ = 0.0427, $wR_2$ = 0.0675 |
| Largest diff. peak/hole / e Å$^{-3}$ | 3.23/-1.90 |

**Crystallographic Table 87** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for **$Ho_2[L^{VII}]_3$**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Ho1 | 2619.07(10) | 7771.32(6) | 2630.58(6) | 14.39(3) |
| Ho2 | 6073.49(11) | 7857.42(6) | 1753.80(6) | 15.40(3) |
| O4 | 4341.5(17) | 8515.7(9) | 2378.6(9) | 16.3(3) |
| O3 | 4313.6(17) | 7143.9(9) | 1945.2(9) | 15.6(3) |

| | | | | |
|---|---|---|---|---|
| N4 | 3616(2) | 7984.6(11) | 3765.2(11) | 15.8(4) |
| N5 | 7139(2) | 6663.8(12) | 2388.1(12) | 18.3(4) |
| N3 | 3705(2) | 6581.1(11) | 3367.4(11) | 16.6(4) |
| C47 | 4130(2) | 9281.8(13) | 3346.0(13) | 15.6(5) |
| N6 | 7103(2) | 8050.6(12) | 2832.0(11) | 17.2(4) |
| C56 | 4321(2) | 9195.5(13) | 2616.3(13) | 15.6(4) |
| O2 | 1829.3(19) | 8594.2(10) | 1718.6(10) | 22.8(4) |
| C38 | 4296(2) | 5804.8(14) | 2391.8(14) | 17.3(5) |
| O1 | 1554.8(18) | 6961.6(11) | 2133.6(10) | 20.5(4) |
| C29 | 4330(2) | 6408.8(13) | 1830.9(13) | 16.2(5) |
| C55 | 4551(2) | 9846.8(14) | 2113.3(14) | 19.5(5) |
| C46 | 4045(2) | 8614.5(14) | 3873.1(13) | 16.8(5) |
| C40 | 3682(2) | 6622.9(14) | 4112.7(13) | 17.7(5) |
| N2 | 1191(2) | 8810.2(12) | 3133.9(12) | 17.9(4) |
| C81 | 7968(3) | 10747.0(15) | 2314.2(17) | 25.0(6) |
| C75 | 7600(2) | 9372.5(14) | 2498.3(14) | 18.9(5) |
| C45 | 3641(2) | 7362.6(14) | 4324.8(13) | 16.8(5) |
| N1 | 922(2) | 7316.7(12) | 3509.3(11) | 16.5(4) |
| O7 | 4913(2) | 8513.5(12) | 762.6(11) | 28.8(4) |
| C68 | 7160(2) | 6681.3(14) | 3135.2(14) | 17.8(5) |
| C84 | 7562(3) | 9378.7(15) | 1752.4(15) | 20.7(5) |
| C30 | 4419(3) | 6232.0(15) | 1115.7(14) | 21.8(5) |
| O5 | 7037(2) | 7178.6(11) | 933.4(10) | 24.4(4) |
| C37 | 4374(3) | 5015.3(14) | 2236.6(15) | 21.6(5) |
| C72 | 7049(3) | 7470.2(16) | 4104.2(14) | 22.3(5) |
| C48 | 4127(2) | 10037.3(14) | 3571.8(15) | 19.7(5) |
| C74 | 7536(2) | 8675.5(14) | 2973.8(14) | 18.4(5) |
| C67 | 7604(3) | 6022.3(15) | 2131.0(15) | 21.9(5) |
| C39 | 4221(2) | 5949.0(14) | 3129.7(14) | 18.0(5) |
| C4 | 579(3) | 4766.1(15) | 2793.3(15) | 24.4(6) |
| C66 | 7639(3) | 5869.1(15) | 1405.8(15) | 21.6(5) |
| C53 | 4374(3) | 10668.8(14) | 3060.1(16) | 21.8(5) |
| C54 | 4579(3) | 10552.5(15) | 2328.1(16) | 23.3(5) |
| C18 | 989(3) | 9529.3(15) | 2852.0(15) | 20.6(5) |
| C12 | 496(2) | 7825.8(14) | 4028.2(13) | 16.7(5) |
| C1 | 1203(2) | 6286.0(15) | 2365.1(15) | 20.3(5) |
| C17 | 662(2) | 8605.3(14) | 3833.5(13) | 17.5(5) |
| C28 | 1667(3) | 9338.2(15) | 1600.1(14) | 20.8(5) |

| | | | | |
|---|---|---|---|---|
| O6 | 7275.6(19) | 8798.7(11) | 1456.6(10) | 23.5(4) |
| C73 | 7119(2) | 7412.4(14) | 3373.6(13) | 17.0(5) |
| C9 | 448(3) | 5306.1(15) | 3298.1(15) | 21.7(5) |
| C32 | 4470(3) | 4865.0(15) | 1514.1(16) | 24.7(6) |
| C10 | 746(2) | 6085.0(14) | 3074.2(14) | 18.0(5) |
| C13 | -8(3) | 7593.8(16) | 4714.0(14) | 23.8(5) |
| C20 | 1372(3) | 10656.1(15) | 1977.8(15) | 21.3(5) |
| C76 | 7757(2) | 10076.4(15) | 2788.7(15) | 21.2(5) |
| C44 | 3579(3) | 7448.2(16) | 5052.2(14) | 24.2(5) |
| C11 | 449(2) | 6661.9(14) | 3555.1(14) | 17.9(5) |
| C65 | 7962(3) | 5075.1(16) | 1252.0(17) | 27.1(6) |
| C69 | 7149(3) | 6029.5(15) | 3643.6(15) | 24.1(5) |
| C31 | 4480(3) | 5491.6(16) | 964.5(16) | 25.3(6) |
| C57 | 7432(3) | 6465.2(16) | 838.0(15) | 22.9(5) |
| C71 | 7050(3) | 6816.9(17) | 4598.1(15) | 26.8(6) |
| C83 | 7864(3) | 10053.4(17) | 1295.1(16) | 27.4(6) |
| C41 | 3655(3) | 5987.2(16) | 4633.5(15) | 27.1(6) |
| C43 | 3589(3) | 6810.0(17) | 5559.7(15) | 29.8(6) |
| C36 | 4294(4) | 4383.5(16) | 2773.3(17) | 35.4(7) |
| C6 | -179(4) | 3781.6(18) | 3683.0(19) | 46.8(10) |
| C16 | 335(3) | 9123.8(16) | 4338.9(16) | 30.1(6) |
| C60 | 8208(3) | 4923.2(18) | 532.7(18) | 33.8(7) |
| C82 | 8060(3) | 10703.0(17) | 1566.4(17) | 28.8(6) |
| C19 | 1375(2) | 9827.5(14) | 2144.8(14) | 19.7(5) |
| C77 | 7651(3) | 10146.8(17) | 3526.8(16) | 27.4(6) |
| C70 | 7100(3) | 6097.7(17) | 4365.1(16) | 28.9(6) |
| C42 | 3624(3) | 6078.8(17) | 5350.0(16) | 32.8(7) |
| C78 | 7786(3) | 10829.4(18) | 3779.2(19) | 34.3(7) |
| C21 | 1314(3) | 11159.0(16) | 2506.2(17) | 27.9(6) |
| C52 | 4369(3) | 11408.8(16) | 3276.7(19) | 31.8(7) |
| C22 | 1369(3) | 11939.7(17) | 2332.3(18) | 33.7(7) |
| C2 | 1259(3) | 5729.5(17) | 1866.6(15) | 26.0(6) |
| C58 | 7671(3) | 6285.4(19) | 121.3(17) | 35.1(7) |
| C3 | 975(3) | 5004.6(17) | 2073.3(16) | 28.4(6) |
| C8 | 22(3) | 5043.6(17) | 4001.6(16) | 33.1(7) |
| C27 | 1728(3) | 9700.3(17) | 872.5(16) | 27.4(6) |
| C26 | 1640(3) | 10476.4(17) | 713.7(16) | 31.4(7) |
| C15 | -189(4) | 8884.8(18) | 5006.5(17) | 35.3(7) |

| | | | | |
|---|---|---|---|---|
| C25 | 1512(3) | 10979.4(16) | 1258.7(16) | 26.8(6) |
| C49 | 3841(3) | 10182.5(17) | 4288.5(16) | 29.7(6) |
| C62 | 8650(4) | 3555(2) | 905(2) | 51.9(11) |
| C5 | 280(4) | 4005.7(17) | 3004.5(18) | 36.1(7) |
| C59 | 8055(4) | 5548(2) | -16.3(18) | 41.0(8) |
| C80 | 8085(3) | 11440.8(17) | 2592(2) | 36.5(7) |
| C14 | -365(3) | 8120.8(17) | 5195.3(15) | 29.2(6) |
| C24 | 1556(3) | 11781.6(18) | 1095.5(18) | 35.3(7) |
| C33 | 4505(4) | 4095.1(17) | 1356.2(18) | 36.2(7) |
| C23 | 1485(3) | 12253.4(17) | 1617.6(19) | 36.9(7) |
| C63 | 8352(4) | 3694.0(19) | 1606(2) | 49.5(10) |
| C79 | 8004(3) | 11485.6(19) | 3312(2) | 40.6(8) |
| C7 | -318(4) | 4310.9(19) | 4184.9(18) | 43.2(9) |
| C50 | 3838(4) | 10913.5(18) | 4478.4(19) | 36.9(7) |
| C51 | 4110(3) | 11528.8(17) | 3975(2) | 38.3(8) |
| C64 | 7999(4) | 4435.7(17) | 1779(2) | 38.3(8) |
| C35 | 4332(5) | 3642.5(18) | 2597(2) | 51.9(11) |
| C85 | 5477(5) | 8943(3) | 163(2) | 57.6(12) |
| C61 | 8557(4) | 4154(2) | 381(2) | 47.5(9) |
| O9 | 1309(2) | 7347.0(14) | 698.7(12) | 38.3(5) |
| O8 | 3186(2) | 8053.6(15) | 3.0(13) | 41.1(6) |
| C86 | 3838(4) | 7628(2) | -532(2) | 46.7(9) |
| C34 | 4442(4) | 3497.9(18) | 1887(2) | 48.9(10) |
| C87 | 82(5) | 7821(3) | 659(3) | 77.6(16) |

**Crystallographic Table 88** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **$Ho_2[L^{VII}]_3$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Ho1 | 15.58(5) | 11.24(5) | 16.81(6) | -2.06(4) | -0.36(4) | -3.23(4) |
| Ho2 | 17.05(6) | 13.05(5) | 16.53(6) | -3.12(4) | 0.53(4) | -2.83(4) |
| O4 | 18.6(8) | 12.4(8) | 19.2(9) | -4.0(6) | 1.7(7) | -5.7(6) |
| O3 | 18.4(8) | 10.3(7) | 18.9(8) | -4.3(6) | 2.3(7) | -4.0(6) |
| N4 | 17.7(10) | 11.6(9) | 18(1) | -1.0(7) | -0.7(8) | -2.2(7) |
| N5 | 18.1(10) | 16(1) | 21.4(11) | -1.5(8) | -2.6(8) | -5.0(8) |
| N3 | 18.8(10) | 12.6(9) | 18.9(10) | -3.6(8) | -0.3(8) | -2.7(8) |
| C47 | 16.8(11) | 10.4(10) | 20.3(12) | -1.3(8) | -1.9(9) | -5.1(9) |
| N6 | 19.1(10) | 12.9(9) | 19.2(10) | -1.4(8) | -1.3(8) | -1.6(8) |
| C56 | 13.9(11) | 12.6(10) | 21.1(12) | -3.2(8) | -1.0(9) | -3.8(9) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O2 | 29.8(10) | 16.7(9) | 21.4(9) | 0.3(7) | -5.6(8) | -1.8(7) |
| C38 | 17.9(11) | 11.4(10) | 23.1(12) | -1.3(9) | 1.0(9) | -4.9(9) |
| O1 | 20.2(9) | 22.5(9) | 20.9(9) | -8.8(7) | 2.1(7) | -6.4(7) |
| C29 | 15.5(11) | 12.1(10) | 21.5(12) | -2.0(8) | 1.7(9) | -5.2(9) |
| C55 | 19.3(12) | 15.5(11) | 22.8(13) | -2.9(9) | 1.4(10) | 0.1(9) |
| C46 | 18.1(11) | 15.8(11) | 17.5(11) | -2.8(9) | -0.9(9) | -5.3(9) |
| C40 | 20.5(12) | 13.9(11) | 18.6(12) | -2.9(9) | 0.8(9) | -1.5(9) |
| N2 | 18.3(10) | 14.8(9) | 20.5(10) | -0.7(8) | -2.1(8) | -2.7(8) |
| C81 | 19.6(13) | 16.9(12) | 39.2(16) | -3.8(10) | -0.9(11) | -4.8(11) |
| C75 | 16.6(11) | 15.6(11) | 25.4(13) | -4.7(9) | -1.7(10) | -3.1(10) |
| C45 | 18.5(11) | 14.3(11) | 17.5(11) | -3.2(9) | -1.1(9) | -0.4(9) |
| N1 | 16.3(10) | 13.8(9) | 20.3(10) | -1.5(7) | -1.3(8) | -5.2(8) |
| O7 | 30.8(11) | 32.0(11) | 22.4(10) | -4.0(9) | -4.0(8) | 2.8(8) |
| C68 | 16.8(11) | 14.9(11) | 21.3(12) | -0.9(9) | -2.0(9) | -1.5(9) |
| C84 | 18.1(12) | 18.9(12) | 26.0(13) | -6.7(9) | -0.4(10) | -2.3(10) |
| C30 | 25.1(13) | 19.9(12) | 20.8(13) | -3.9(10) | 2.4(10) | -4.4(10) |
| O5 | 30.8(11) | 19.9(9) | 22.5(10) | -3.0(8) | 5.7(8) | -5.5(7) |
| C37 | 25.1(13) | 11.5(11) | 28.7(14) | -1.1(9) | -0.1(11) | -6.2(10) |
| C72 | 22.5(13) | 21.5(12) | 22.7(13) | -0.6(10) | -0.4(10) | -4.9(10) |
| C48 | 18.8(12) | 14.1(11) | 27.8(13) | -2.7(9) | -1.2(10) | -7.9(10) |
| C74 | 16.7(11) | 17.4(11) | 21.5(12) | -0.2(9) | -2.7(9) | -4.5(9) |
| C67 | 21.1(13) | 17.2(12) | 27.5(14) | 0.9(10) | -3.7(10) | -4.8(10) |
| C39 | 19.9(12) | 11.5(10) | 22.9(12) | -4.4(9) | -0.9(10) | -1.0(9) |
| C4 | 27.9(14) | 19.0(12) | 28.1(14) | -1.2(10) | -6.6(11) | -9.1(11) |
| C66 | 17.3(12) | 20.1(12) | 28.2(14) | 0.7(9) | -0.4(10) | -9.2(10) |
| C53 | 19.9(12) | 12.2(11) | 34.5(15) | -2.6(9) | -0.5(11) | -6.5(10) |
| C54 | 23.5(13) | 13.1(11) | 32.2(15) | -3.2(10) | 0.6(11) | 0.8(10) |
| C18 | 18.2(12) | 18.0(12) | 25.2(13) | 0.6(9) | -1.6(10) | -3.3(10) |
| C12 | 16.3(11) | 16.0(11) | 18.6(12) | -1.0(9) | -1.5(9) | -6.0(9) |
| C1 | 15.7(11) | 21.4(12) | 26.0(13) | -4.2(9) | -2(1) | -8.7(10) |
| C17 | 18.9(12) | 14.4(11) | 19.5(12) | -1.1(9) | -1.4(9) | -3.8(9) |
| C28 | 20.8(12) | 19.0(12) | 22.3(13) | -0.6(10) | -5.7(10) | -0.4(10) |
| O6 | 28.4(10) | 21.8(9) | 22.3(9) | -11.1(8) | 1.1(8) | -3.9(7) |
| C73 | 15.9(11) | 16.1(11) | 18.7(12) | -1.9(9) | -1.2(9) | -0.8(9) |
| C9 | 25.8(13) | 16.4(11) | 23.6(13) | -1.2(10) | -5.7(10) | -4.6(10) |
| C32 | 27.9(14) | 17.0(12) | 31.2(15) | -2.7(10) | 0.6(11) | -11.6(11) |
| C10 | 18.7(12) | 14.7(11) | 21.7(12) | -2.4(9) | -0.7(9) | -6.5(9) |
| C13 | 32.8(15) | 19.2(12) | 19.7(13) | -4.4(11) | 2.0(11) | -3.8(10) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C20 | 18.2(12) | 15.9(11) | 28.9(14) | -0.8(9) | -2.7(10) | 0.6(10) |
| C76 | 16.5(12) | 16.4(11) | 31.6(14) | -1.7(9) | -3.4(10) | -5.8(10) |
| C44 | 32.0(15) | 21.0(13) | 20.3(13) | -4.5(11) | 0.4(11) | -4.4(10) |
| C11 | 18.0(11) | 16.8(11) | 19.2(12) | -2.8(9) | 0.2(9) | -3.4(9) |
| C65 | 22.7(13) | 22.2(13) | 39.1(16) | 1.3(10) | -9.3(12) | -14.2(12) |
| C69 | 26.4(14) | 16.2(12) | 29.2(14) | -3.8(10) | -0.9(11) | 0.3(10) |
| C31 | 28.4(14) | 22.8(13) | 26.4(14) | -3.7(11) | 1.7(11) | -11.1(11) |
| C57 | 21.2(13) | 22.8(13) | 26.1(14) | -4.8(10) | 4.9(10) | -9.0(11) |
| C71 | 30.3(15) | 30.8(15) | 18.0(13) | -2.8(12) | -0.3(11) | 0.3(11) |
| C83 | 32.5(15) | 25.1(14) | 25.2(14) | -11.0(12) | 2.3(12) | 0.1(11) |
| C41 | 38.6(16) | 17.0(12) | 25.5(14) | -7.7(11) | 3.2(12) | -0.6(10) |
| C43 | 41.8(17) | 30.5(15) | 16.5(13) | -5.8(13) | 1.4(12) | -0.7(11) |
| C36 | 62(2) | 14.7(12) | 29.9(16) | -4.5(13) | -2.9(15) | -3.6(11) |
| C6 | 89(3) | 17.4(14) | 36.8(19) | -13.4(16) | -13.7(19) | 0.1(13) |
| C16 | 46.5(18) | 15.6(12) | 29.0(15) | -1.9(12) | -0.4(13) | -8.1(11) |
| C60 | 31.3(16) | 30.9(15) | 42.4(19) | 2.4(12) | -4.1(14) | -21.7(14) |
| C82 | 30.1(15) | 21.8(13) | 34.9(16) | -9.8(11) | -0.9(12) | 2.1(12) |
| C19 | 17.3(12) | 16.6(11) | 23.9(13) | 1.7(9) | -4.2(10) | -0.1(10) |
| C77 | 28.0(14) | 23.0(13) | 32.7(15) | -3.2(11) | -3.1(12) | -8.1(11) |
| C70 | 32.4(15) | 23.7(14) | 28.8(15) | -4.7(12) | -0.9(12) | 4.6(11) |
| C42 | 52(2) | 23.7(14) | 20.5(14) | -8.9(13) | 4.0(13) | 5.6(11) |
| C78 | 34.9(17) | 32.7(16) | 39.5(18) | -7.2(13) | -0.5(14) | -18.5(14) |
| C21 | 30.9(15) | 19.9(13) | 31.0(15) | 1.0(11) | -0.2(12) | -0.5(11) |
| C52 | 34.5(16) | 13.1(12) | 49.2(19) | -4.7(11) | -2.1(14) | -7.4(12) |
| C22 | 41.0(18) | 17.3(13) | 41.8(18) | -0.5(12) | -2.1(14) | -3.0(12) |
| C2 | 27.0(14) | 30.6(14) | 24.0(14) | -11.1(11) | 6.1(11) | -13.0(11) |
| C58 | 47.3(19) | 32.5(16) | 26.0(15) | -7.4(14) | 9.5(14) | -8.6(13) |
| C3 | 30.6(15) | 28.1(14) | 30.4(15) | -7.0(12) | 1.9(12) | -17.0(12) |
| C8 | 56(2) | 19.3(13) | 25.9(15) | -6.4(13) | -6.2(14) | -3.9(11) |
| C27 | 34.3(16) | 23.4(13) | 23.6(14) | -0.7(11) | -5.1(12) | -0.7(11) |
| C26 | 41.8(18) | 26.6(14) | 23.5(14) | -1.0(13) | -6.0(13) | 5.2(11) |
| C15 | 56(2) | 24.1(14) | 26.4(15) | -1.0(14) | 4.1(14) | -14.4(12) |
| C25 | 27.4(14) | 20.0(13) | 31.3(15) | -1.4(11) | -5.5(12) | 3.6(11) |
| C49 | 39.3(17) | 21.8(13) | 30.2(15) | -6.6(12) | 2.7(13) | -11.3(11) |
| C62 | 58(2) | 28.4(17) | 74(3) | 11.8(16) | -26(2) | -31.4(18) |
| C5 | 58(2) | 17.0(13) | 35.9(17) | -2.8(13) | -11.5(15) | -8.2(12) |
| C59 | 53(2) | 40.4(19) | 31.3(17) | -3.1(16) | 8.0(15) | -19.9(15) |
| C80 | 39.4(18) | 18.9(13) | 53(2) | -8.7(12) | 0.0(15) | -8.1(13) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C14 | 40.9(17) | 26.8(14) | 20.1(13) | -2.0(12) | 2.9(12) | -7.9(11) |
| C24 | 46.2(19) | 23.0(14) | 34.0(17) | -3.5(13) | -5.8(14) | 8.1(12) |
| C33 | 53(2) | 20.7(14) | 37.5(18) | -4.3(13) | 0.2(15) | -14.9(13) |
| C23 | 44.0(19) | 16.0(13) | 49(2) | -2.8(12) | -7.1(15) | 3.4(13) |
| C63 | 65(3) | 21.3(15) | 66(3) | 5.2(15) | -28(2) | -13.9(16) |
| C79 | 41.8(19) | 26.6(15) | 59(2) | -11.4(14) | 0.9(16) | -20.4(15) |
| C7 | 78(3) | 24.7(15) | 28.3(16) | -13.8(16) | -7.0(17) | 2.7(13) |
| C50 | 49(2) | 27.6(15) | 38.0(18) | -6.1(14) | 3.1(15) | -19.4(13) |
| C51 | 47(2) | 18.8(14) | 53(2) | -4.8(13) | -3.0(16) | -20.0(14) |
| C64 | 51(2) | 20.1(14) | 47(2) | 3.0(13) | -17.6(16) | -12.3(13) |
| C35 | 96(3) | 12.9(14) | 46(2) | -7.4(17) | -4(2) | -2.4(14) |
| C85 | 69(3) | 67(3) | 38(2) | -35(2) | -17.0(19) | 20.1(19) |
| C61 | 50(2) | 40(2) | 56(2) | 6.3(16) | -9.1(18) | -32.3(18) |
| O9 | 46.3(14) | 44.9(14) | 26.9(11) | -10.9(11) | -5.7(10) | -8.9(10) |
| O8 | 39.9(14) | 47.9(14) | 37.7(13) | -9.7(11) | -2.7(11) | -8.3(11) |
| C86 | 52(2) | 52(2) | 35.7(19) | 1.1(18) | -4.8(16) | -9.7(17) |
| C34 | 85(3) | 15.3(14) | 49(2) | -6.9(16) | 0(2) | -13.0(14) |
| C87 | 59(3) | 103(4) | 78(4) | -13(3) | -39(3) | -19(3) |

**Crystallographic Table 89** Bond Lengths for **$Ho_2[L^{VII}]_3$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O4 | C56 | 1.328(3) | C12 | C17 | 1.405(3) |
| O3 | C29 | 1.337(3) | C12 | C13 | 1.397(4) |
| N4 | C46 | 1.292(3) | C1 | C10 | 1.410(4) |
| N4 | C45 | 1.422(3) | C1 | C2 | 1.437(4) |
| N5 | C68 | 1.419(3) | C17 | C16 | 1.400(4) |
| N5 | C67 | 1.307(3) | C28 | C19 | 1.418(4) |
| N3 | C40 | 1.420(3) | C28 | C27 | 1.442(4) |
| N3 | C39 | 1.290(3) | C9 | C10 | 1.450(4) |
| C47 | C56 | 1.406(3) | C9 | C8 | 1.414(4) |
| C47 | C46 | 1.449(3) | C32 | C31 | 1.417(4) |
| C47 | C48 | 1.447(3) | C32 | C33 | 1.420(4) |
| N6 | C74 | 1.305(3) | C10 | C11 | 1.438(3) |
| N6 | C73 | 1.420(3) | C13 | C14 | 1.381(4) |
| C56 | C55 | 1.429(3) | C20 | C19 | 1.452(3) |
| O2 | C28 | 1.291(3) | C20 | C21 | 1.410(4) |
| C38 | C29 | 1.406(3) | C20 | C25 | 1.412(4) |
| C38 | C37 | 1.447(3) | C76 | C77 | 1.413(4) |

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|---|---|---|---|---|---|
| C38 | C39 | 1.445(4) | C44 | C43 | 1.381(4) |
| O1 | C1 | 1.304(3) | C65 | C60 | 1.420(4) |
| C29 | C30 | 1.421(4) | C65 | C64 | 1.404(5) |
| C55 | C54 | 1.360(4) | C69 | C70 | 1.382(4) |
| C40 | C45 | 1.405(3) | C57 | C58 | 1.429(4) |
| C40 | C41 | 1.396(4) | C71 | C70 | 1.386(4) |
| N2 | C18 | 1.305(3) | C83 | C82 | 1.355(4) |
| N2 | C17 | 1.420(3) | C41 | C42 | 1.383(4) |
| C81 | C76 | 1.421(4) | C43 | C42 | 1.390(4) |
| C81 | C82 | 1.423(4) | C36 | C35 | 1.381(4) |
| C81 | C80 | 1.412(4) | C6 | C5 | 1.367(5) |
| C75 | C84 | 1.413(4) | C6 | C7 | 1.401(5) |
| C75 | C74 | 1.433(4) | C16 | C15 | 1.378(4) |
| C75 | C76 | 1.450(3) | C60 | C59 | 1.413(5) |
| C45 | C44 | 1.400(4) | C60 | C61 | 1.415(4) |
| N1 | C12 | 1.422(3) | C77 | C78 | 1.375(4) |
| N1 | C11 | 1.302(3) | C78 | C79 | 1.396(5) |
| O7 | C85 | 1.417(4) | C21 | C22 | 1.380(4) |
| C68 | C73 | 1.411(3) | C52 | C51 | 1.368(5) |
| C68 | C69 | 1.401(4) | C22 | C23 | 1.398(5) |
| C84 | O6 | 1.300(3) | C2 | C3 | 1.351(4) |
| C84 | C83 | 1.434(4) | C58 | C59 | 1.360(4) |
| C30 | C31 | 1.362(4) | C8 | C7 | 1.377(4) |
| O5 | C57 | 1.299(3) | C27 | C26 | 1.353(4) |
| C37 | C32 | 1.420(4) | C26 | C25 | 1.431(4) |
| C37 | C36 | 1.414(4) | C15 | C14 | 1.380(4) |
| C72 | C73 | 1.395(4) | C25 | C24 | 1.413(4) |
| C72 | C71 | 1.387(4) | C49 | C50 | 1.379(4) |
| C48 | C53 | 1.416(4) | C62 | C63 | 1.386(6) |
| C48 | C49 | 1.416(4) | C62 | C61 | 1.351(6) |
| C67 | C66 | 1.428(4) | C80 | C79 | 1.371(5) |
| C4 | C9 | 1.419(4) | C24 | C23 | 1.361(5) |
| C4 | C3 | 1.423(4) | C33 | C34 | 1.363(5) |
| C4 | C5 | 1.416(4) | C63 | C64 | 1.383(4) |
| C66 | C65 | 1.455(4) | C50 | C51 | 1.393(5) |
| C66 | C57 | 1.409(4) | C35 | C34 | 1.394(5) |
| C53 | C54 | 1.423(4) | O9 | C87 | 1.426(5) |
| C53 | C52 | 1.414(4) | O8 | C86 | 1.417(4) |

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|---|---|---|---|
| C18 | C19 | 1.425(4) | |

**Crystallographic Table 90** Bond Angles for **$Ho_2[L^{VII}]_3$**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O3 | Ho1 | O4 | 68.85(6) | C5 | C4 | C3 | 120.8(3) |
| N4 | Ho1 | O4 | 68.89(6) | C65 | C66 | C67 | 118.5(3) |
| N4 | Ho1 | O3 | 106.11(6) | C57 | C66 | C67 | 122.0(2) |
| N3 | Ho1 | O4 | 101.82(6) | C57 | C66 | C65 | 119.4(3) |
| N3 | Ho1 | O3 | 69.95(6) | C54 | C53 | C48 | 119.2(2) |
| N3 | Ho1 | N4 | 63.32(6) | C52 | C53 | C48 | 119.9(3) |
| O2 | Ho1 | O4 | 79.99(7) | C52 | C53 | C54 | 120.9(3) |
| O2 | Ho1 | O3 | 95.14(7) | C53 | C54 | C55 | 121.2(2) |
| O2 | Ho1 | N4 | 131.80(6) | C19 | C18 | N2 | 126.3(2) |
| O2 | Ho1 | N3 | 162.62(7) | C17 | C12 | N1 | 116.3(2) |
| O1 | Ho1 | O4 | 140.73(6) | C13 | C12 | N1 | 124.4(2) |
| O1 | Ho1 | O3 | 78.58(6) | C13 | C12 | C17 | 119.2(2) |
| O1 | Ho1 | N4 | 144.05(7) | C10 | C1 | O1 | 123.1(2) |
| O1 | Ho1 | N3 | 86.41(7) | C2 | C1 | O1 | 118.1(2) |
| O1 | Ho1 | O2 | 81.74(7) | C2 | C1 | C10 | 118.8(2) |
| N2 | Ho1 | O4 | 93.12(6) | C12 | C17 | N2 | 117.1(2) |
| N2 | Ho1 | O3 | 160.09(6) | C16 | C17 | N2 | 124.2(2) |
| N2 | Ho1 | N4 | 73.30(7) | C16 | C17 | C12 | 118.7(2) |
| N2 | Ho1 | N3 | 124.13(7) | C19 | C28 | O2 | 123.7(2) |
| N2 | Ho1 | O2 | 72.65(7) | C27 | C28 | O2 | 118.8(2) |
| N2 | Ho1 | O1 | 114.00(7) | C27 | C28 | C19 | 117.4(2) |
| N1 | Ho1 | O4 | 147.55(6) | C68 | C73 | N6 | 115.9(2) |
| N1 | Ho1 | O3 | 133.90(6) | C72 | C73 | N6 | 124.6(2) |
| N1 | Ho1 | N4 | 80.99(7) | C72 | C73 | C68 | 119.5(2) |
| N1 | Ho1 | N3 | 73.71(7) | C10 | C9 | C4 | 119.4(2) |
| N1 | Ho1 | O2 | 113.98(7) | C8 | C9 | C4 | 117.0(2) |
| N1 | Ho1 | O1 | 71.70(7) | C8 | C9 | C10 | 123.6(2) |
| N1 | Ho1 | N2 | 66.00(7) | C31 | C32 | C37 | 119.1(2) |
| O3 | Ho2 | O4 | 69.20(6) | C33 | C32 | C37 | 119.5(3) |
| N5 | Ho2 | O4 | 116.15(7) | C33 | C32 | C31 | 121.3(3) |
| N5 | Ho2 | O3 | 80.13(7) | C9 | C10 | C1 | 119.5(2) |
| N6 | Ho2 | O4 | 78.21(6) | C11 | C10 | C1 | 120.7(2) |
| N6 | Ho2 | O3 | 115.16(6) | C11 | C10 | C9 | 119.6(2) |
| N6 | Ho2 | N5 | 66.30(7) | C14 | C13 | C12 | 121.0(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O7 | Ho2 | O4 | 81.27(7) | C21 | C20 | C19 | 123.0(3) |
| O7 | Ho2 | O3 | 84.50(7) | C25 | C20 | C19 | 119.5(2) |
| O7 | Ho2 | N5 | 150.11(7) | C25 | C20 | C21 | 117.4(2) |
| O7 | Ho2 | N6 | 143.52(7) | C75 | C76 | C81 | 119.2(3) |
| O5 | Ho2 | O4 | 157.23(7) | C77 | C76 | C81 | 117.3(2) |
| O5 | Ho2 | O3 | 93.96(7) | C77 | C76 | C75 | 123.4(2) |
| O5 | Ho2 | N5 | 73.77(7) | C43 | C44 | C45 | 120.4(3) |
| O5 | Ho2 | N6 | 123.92(7) | C10 | C11 | N1 | 126.5(2) |
| O5 | Ho2 | O7 | 81.95(7) | C60 | C65 | C66 | 119.3(3) |
| O6 | Ho2 | O4 | 99.48(6) | C64 | C65 | C66 | 123.4(3) |
| O6 | Ho2 | O3 | 162.94(7) | C64 | C65 | C60 | 117.2(3) |
| O6 | Ho2 | N5 | 116.80(7) | C70 | C69 | C68 | 120.9(3) |
| O6 | Ho2 | N6 | 73.03(7) | C32 | C31 | C30 | 121.4(3) |
| O6 | Ho2 | O7 | 81.08(7) | C66 | C57 | O5 | 123.0(2) |
| O6 | Ho2 | O5 | 93.00(7) | C58 | C57 | O5 | 117.9(3) |
| C45 | N4 | C46 | 119.1(2) | C58 | C57 | C66 | 119.1(3) |
| C67 | N5 | C68 | 118.1(2) | C70 | C71 | C72 | 119.7(3) |
| C39 | N3 | C40 | 118.5(2) | C82 | C83 | C84 | 121.2(3) |
| C46 | C47 | C56 | 120.6(2) | C42 | C41 | C40 | 120.6(3) |
| C48 | C47 | C56 | 119.2(2) | C42 | C43 | C44 | 120.0(3) |
| C48 | C47 | C46 | 120.0(2) | C35 | C36 | C37 | 120.8(3) |
| C73 | N6 | C74 | 118.4(2) | C7 | C6 | C5 | 119.1(3) |
| C47 | C56 | O4 | 121.9(2) | C15 | C16 | C17 | 121.0(3) |
| C55 | C56 | O4 | 118.4(2) | C59 | C60 | C65 | 118.7(3) |
| C55 | C56 | C47 | 119.7(2) | C61 | C60 | C65 | 119.6(3) |
| C37 | C38 | C29 | 120.0(2) | C61 | C60 | C59 | 121.7(3) |
| C39 | C38 | C29 | 121.5(2) | C83 | C82 | C81 | 121.6(3) |
| C39 | C38 | C37 | 118.5(2) | C28 | C19 | C18 | 121.2(2) |
| C38 | C29 | O3 | 122.4(2) | C20 | C19 | C18 | 118.5(2) |
| C30 | C29 | O3 | 118.6(2) | C20 | C19 | C28 | 120.2(2) |
| C30 | C29 | C38 | 119.0(2) | C78 | C77 | C76 | 121.5(3) |
| C54 | C55 | C56 | 121.0(2) | C71 | C70 | C69 | 120.3(3) |
| C47 | C46 | N4 | 125.3(2) | C43 | C42 | C41 | 120.2(3) |
| C45 | C40 | N3 | 116.5(2) | C79 | C78 | C77 | 121.0(3) |
| C41 | C40 | N3 | 124.3(2) | C22 | C21 | C20 | 121.7(3) |
| C41 | C40 | C45 | 119.2(2) | C51 | C52 | C53 | 120.9(3) |
| C17 | N2 | C18 | 118.7(2) | C23 | C22 | C21 | 120.2(3) |
| C82 | C81 | C76 | 119.1(2) | C3 | C2 | C1 | 121.6(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C80 | C81 | C76 | 119.6(3) | C59 | C58 | C57 | 120.9(3) |
| C80 | C81 | C82 | 121.3(3) | C2 | C3 | C4 | 121.2(3) |
| C74 | C75 | C84 | 121.2(2) | C7 | C8 | C9 | 121.9(3) |
| C76 | C75 | C84 | 119.6(2) | C26 | C27 | C28 | 121.7(3) |
| C76 | C75 | C74 | 119.1(2) | C25 | C26 | C27 | 121.8(3) |
| C40 | C45 | N4 | 116.0(2) | C14 | C15 | C16 | 120.3(3) |
| C44 | C45 | N4 | 124.5(2) | C26 | C25 | C20 | 118.6(3) |
| C44 | C45 | C40 | 119.5(2) | C24 | C25 | C20 | 119.7(3) |
| C11 | N1 | C12 | 118.8(2) | C24 | C25 | C26 | 121.7(3) |
| C73 | C68 | N5 | 117.0(2) | C50 | C49 | C48 | 120.5(3) |
| C69 | C68 | N5 | 124.2(2) | C61 | C62 | C63 | 119.3(3) |
| C69 | C68 | C73 | 118.7(2) | C6 | C5 | C4 | 121.5(3) |
| O6 | C84 | C75 | 123.2(2) | C58 | C59 | C60 | 122.2(3) |
| C83 | C84 | C75 | 118.7(2) | C79 | C80 | C81 | 121.6(3) |
| C83 | C84 | O6 | 118.0(2) | C15 | C14 | C13 | 119.7(3) |
| C31 | C30 | C29 | 121.4(3) | C23 | C24 | C25 | 121.5(3) |
| C32 | C37 | C38 | 119.1(2) | C34 | C33 | C32 | 121.1(3) |
| C36 | C37 | C38 | 123.0(3) | C24 | C23 | C22 | 119.5(3) |
| C36 | C37 | C32 | 117.9(2) | C64 | C63 | C62 | 121.1(4) |
| C71 | C72 | C73 | 120.8(3) | C80 | C79 | C78 | 118.9(3) |
| C53 | C48 | C47 | 119.6(2) | C8 | C7 | C6 | 120.6(3) |
| C49 | C48 | C47 | 122.5(2) | C51 | C50 | C49 | 121.3(3) |
| C49 | C48 | C53 | 117.8(2) | C50 | C51 | C52 | 119.4(3) |
| C75 | C74 | N6 | 126.4(2) | C63 | C64 | C65 | 121.1(3) |
| C66 | C67 | N5 | 127.4(3) | C34 | C35 | C36 | 120.9(3) |
| C38 | C39 | N3 | 125.5(2) | C62 | C61 | C60 | 121.5(3) |
| C3 | C4 | C9 | 119.3(2) | C35 | C34 | C33 | 119.7(3) |
| C5 | C4 | C9 | 119.9(3) | | | | |

**Crystallographic Table 91** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **$Ho_2[L^{VII}]_3$**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H55 | 4685(2) | 9786.0(14) | 1620.9(14) | 23.4(6) |
| H46 | 4328(2) | 8642.6(14) | 4335.6(13) | 20.1(6) |
| H7 | 4250(20) | 8341(16) | 608(12) | 43.2(7) |
| H30 | 4436(3) | 6638.8(15) | 734.9(14) | 26.2(6) |
| H72 | 7001(3) | 7963.3(16) | 4265.2(14) | 26.7(6) |
| H74 | 7838(2) | 8667.1(14) | 3438.4(14) | 22.1(6) |

| | | | | |
|---|---|---|---|---|
| H67 | 7959(3) | 5610.7(15) | 2464.5(15) | 26.3(6) |
| H39 | 4583(2) | 5544.3(14) | 3467.9(14) | 21.6(6) |
| H54 | 4739(3) | 10975.7(15) | 1983.3(16) | 27.9(7) |
| H18 | 541(3) | 9888.3(15) | 3146.6(15) | 24.7(6) |
| H13 | -105(3) | 7065.4(16) | 4851.1(14) | 28.6(7) |
| H44 | 3530(3) | 7948.6(16) | 5197.9(14) | 29.1(7) |
| H11 | -153(2) | 6554.4(14) | 3945.0(14) | 21.4(6) |
| H69 | 7175(3) | 5534.0(15) | 3490.4(15) | 29.0(7) |
| H31 | 4530(3) | 5393.3(16) | 480.5(16) | 30.3(7) |
| H71 | 7016(3) | 6862.0(17) | 5094.3(15) | 32.2(7) |
| H83 | 7927(3) | 10044.8(17) | 792.8(16) | 32.8(7) |
| H41 | 3658(3) | 5487.0(16) | 4494.6(15) | 32.5(7) |
| H43 | 3571(3) | 6871.0(17) | 6052.2(15) | 35.8(8) |
| H36 | 4212(4) | 4469.7(16) | 3260.8(17) | 42.5(9) |
| H6 | -401(4) | 3273.9(18) | 3812.4(19) | 56.2(12) |
| H16 | 476(3) | 9648.3(16) | 4220.1(16) | 36.1(8) |
| H82 | 8263(3) | 11139.5(17) | 1249.7(17) | 34.6(7) |
| H77 | 7484(3) | 9712.5(17) | 3856.2(16) | 32.9(7) |
| H70 | 7101(3) | 5649.5(17) | 4702.9(16) | 34.7(7) |
| H42 | 3627(3) | 5640.6(17) | 5699.7(16) | 39.4(8) |
| H78 | 7729(3) | 10854.9(18) | 4279.1(19) | 41.1(8) |
| H21 | 1234(3) | 10954.8(16) | 2994.5(17) | 33.5(7) |
| H52 | 4549(3) | 11828.5(16) | 2932.4(19) | 38.1(8) |
| H22 | 1328(3) | 12264.9(17) | 2699.4(18) | 40.4(8) |
| H2 | 1503(3) | 5874.7(17) | 1380.0(15) | 31.2(7) |
| H58 | 7561(3) | 6686.8(19) | -264.0(17) | 42.1(9) |
| H3 | 1039(3) | 4647.8(17) | 1731.8(16) | 34.1(7) |
| H8 | -31(3) | 5382.2(17) | 4358.3(16) | 39.8(8) |
| H27 | 1833(3) | 9385.8(17) | 495.0(16) | 32.8(7) |
| H26 | 1663(3) | 10693.1(17) | 227.4(16) | 37.7(8) |
| H15 | -429(4) | 9247.6(18) | 5338.1(17) | 42.4(9) |
| H49 | 3649(3) | 9772.8(17) | 4641.3(16) | 35.6(8) |
| H62 | 8916(4) | 3045(2) | 795(2) | 62.2(13) |
| H5 | 401(4) | 3643.1(17) | 2667.1(18) | 43.4(9) |
| H59 | 8227(4) | 5448(2) | -497.8(18) | 49.2(10) |
| H80 | 8223(3) | 11887.5(17) | 2272(2) | 43.8(9) |
| H14 | -731(3) | 7958.1(17) | 5654.8(15) | 35.0(7) |
| H24 | 1638(3) | 11996.7(18) | 610.4(18) | 42.4(9) |

| | | | | |
|---|---|---|---|---|
| H33 | 4572(4) | 3994.5(17) | 872.6(18) | 43.5(9) |
| H23 | 1513(3) | 12791.7(17) | 1497.0(19) | 44.3(9) |
| H63 | 8390(4) | 3272.0(19) | 1974(2) | 59.4(12) |
| H79 | 8096(3) | 11955.5(19) | 3490(2) | 48.7(10) |
| H7a | -649(4) | 4163.4(19) | 4655.8(18) | 51.9(11) |
| H50 | 3646(4) | 10999.4(18) | 4962.1(19) | 44.3(9) |
| H51 | 4115(3) | 12027.5(17) | 4116(2) | 46.0(9) |
| H64 | 7778(4) | 4513.9(17) | 2262(2) | 46.0(9) |
| H35 | 4283(5) | 3225.4(18) | 2966(2) | 62.3(13) |
| H85a | 6090(20) | 8595(4) | -103(10) | 86.4(18) |
| H85b | 4787(5) | 9199(15) | -147(9) | 86.4(18) |
| H85c | 5950(30) | 9333(12) | 324(2) | 86.4(18) |
| H61 | 8731(4) | 4056(2) | -101(2) | 57.0(11) |
| H86a | 3810(20) | 7951(6) | -994(3) | 70.1(13) |
| H86b | 4749(8) | 7470(14) | -414(8) | 70.1(13) |
| H86c | 3409(17) | 7169(9) | -557(10) | 70.1(13) |
| H34 | 4474(4) | 2985.3(18) | 1773(2) | 58.7(12) |
| H8a | 2580(30) | 7820(13) | 202(16) | 61.7(8) |
| H9 | 1500(20) | 7230(20) | 1127.9(17) | 57.5(8) |
| H87a | 78(14) | 8180(15) | 218(11) | 116(2) |
| H87b | -616(6) | 7495(4) | 660(20) | 116(2) |
| H87c | -59(18) | 8113(17) | 1071(11) | 116(2) |

Refinement model description

Number of restraints - 3, number of constraints - 125.

Details:

1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups
2. Restrained distances
 O7-H7
 0.87 with sigma of 0.01
 C85-H7
 1.863295 with sigma of 0.02
 Ho2-H7
 2.957705 with sigma of 0.02

3.a Aromatic/amide H refined with riding coordinates:
C55(H55), C46(H46), C30(H30), C72(H72), C74(H74), C67(H67), C39(H39), C54(H54), C18(H18), C13(H13), C44(H44), C11(H11), C69(H69), C31(H31), C71(H71), C83(H83), C41(H41), C43(H43), C36(H36), C6(H6), C16(H16), C82(H82), C77(H77), C70(H70), C42(H42), C78(H78), C21(H21), C52(H52), C22(H22), C2(H2), C58(H58), C3(H3), C8(H8), C27(H27), C26(H26), C15(H15), C49(H49), C62(H62), C5(H5), C59(H59), C80(H80), C14(H14), C24(H24), C33(H33), C23(H23), C63(H63), C79(H79), C7(H7a), C50(H50), C51(H51), C64(H64), C35(H35), C61(H61), C34(H34)
3.b Idealised Me refined as rotating group:
C85(H85a,H85b,H85c), C86(H86a,H86b,H86c), C87(H87a,H87b,H87c)
3.c Idealised tetrahedral OH refined as rotating group:
O9(H9), O8(H8a)

## $Yb_2[L^{VII}]_3$

**Crystallographic Table 92** Crystal data and structure refinement for **$Yb_2[L^{VII}]_3$**

| | |
|---|---|
| Empirical formula | $C_{87}H_{62}Cl_4N_6O_7Yb_2$ |
| Formula weight | 1791.38 |
| Temperature/K | 180.45 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 17.4061(8) |
| b/Å | 20.4222(10) |
| c/Å | 20.6605(10) |
| α/° | 90 |
| β/° | 96.2697(8) |
| γ/° | 90 |
| Volume/Å$^3$ | 7300.3(6) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.6298 |
| m/mm$^{-1}$ | 2.756 |
| F(000) | 3562.0 |
| Crystal size/mm$^3$ | 0.12 × 0.1 × 0.09 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 2.82 to 52.74° |
| Index ranges | $-21 \leq h \leq 21$, $-25 \leq k \leq 25$, $-25 \leq l \leq 25$ |
| Reflections collected | 104807 |
| Independent reflections | 14938 [$R_{int}$ = 0.0586, $R_{sigma}$ = 0.0431] |
| Data/restraints/parameters | 14938/3/958 |
| Goodness-of-fit on $F^2$ | 1.062 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0666, $wR_2$ = 0.1489 |
| Final R indexes [all data] | $R_1$ = 0.0772, $wR_2$ = 0.1561 |
| Largest diff. peak/hole / e Å$^{-3}$ | 5.13/-1.84 |

**Crystallographic Table 93** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for **$Yb_2[L^{VII}]_3$**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Yb1 | 7266.79(18) | 5570.08(17) | 7475.85(16) | 17.83(10) |
| Yb2 | 7078.7(2) | 3998.24(18) | 6506.85(17) | 20.58(10) |
| C45 | 8344(5) | 4876(4) | 8744(4) | 22.0(17) |
| O4 | 7843(3) | 4893(3) | 6779(3) | 19.4(11) |

| | | | | |
|---|---|---|---|---|
| O3 | 6458(3) | 4703(3) | 7125(3) | 21.4(12) |
| O2 | 8083(3) | 6270(3) | 7111(3) | 22.3(12) |
| C47 | 9185(5) | 4947(4) | 7175(4) | 22.6(17) |
| O1 | 6479(3) | 5980(3) | 6649(3) | 29.0(14) |
| N6 | 8201(4) | 3461(3) | 7054(3) | 22.4(15) |
| O6 | 7719(3) | 3662(3) | 5729(3) | 30.1(14) |
| C19 | 9007(5) | 6516(4) | 8022(4) | 23.3(17) |
| N3 | 6983(4) | 4878(3) | 8408(3) | 20.7(14) |
| N2 | 7754(4) | 6277(3) | 8386(3) | 21.3(14) |
| N4 | 8409(4) | 5005(3) | 8072(3) | 20.8(14) |
| O5 | 6094(4) | 3415(3) | 6125(3) | 31.7(15) |
| C30 | 5094(5) | 4642(4) | 6844(5) | 27.3(19) |
| C40 | 7587(5) | 4805(4) | 8919(4) | 24.8(18) |
| C39 | 6305(5) | 4631(4) | 8474(4) | 22.0(17) |
| C73 | 8152(5) | 3302(4) | 7720(4) | 24.3(18) |
| C54 | 9501(5) | 5100(5) | 5879(5) | 33(2) |
| C55 | 8747(5) | 5055(4) | 6020(4) | 24.9(18) |
| C10 | 5272(5) | 6234(4) | 7048(4) | 24.5(18) |
| C4 | 4129(5) | 6375(5) | 6242(5) | 34(2) |
| N1 | 6265(4) | 6134(3) | 7980(3) | 21.5(14) |
| C38 | 5649(4) | 4665(4) | 7984(4) | 20.0(16) |
| C46 | 9032(4) | 4845(4) | 7836(4) | 22.6(17) |
| C29 | 5748(4) | 4678(4) | 7327(4) | 19.7(16) |
| C11 | 5591(4) | 6316(4) | 7717(4) | 22.4(17) |
| C28 | 8785(5) | 6439(4) | 7350(4) | 23.4(17) |
| C8 | 3930(5) | 6340(5) | 7377(5) | 31(2) |
| C56 | 8583(5) | 4968(4) | 6669(4) | 22.3(17) |
| C75 | 9021(5) | 3436(4) | 6158(4) | 23.6(18) |
| C31 | 4372(5) | 4608(4) | 7026(5) | 29(2) |
| C9 | 4453(5) | 6328(4) | 6899(4) | 25.3(18) |
| C32 | 4243(5) | 4614(4) | 7696(5) | 31(2) |
| C67 | 6119(5) | 3072(4) | 7481(4) | 23.5(17) |
| C25 | 10363(5) | 6700(5) | 7801(5) | 31(2) |
| C18 | 8438(5) | 6532(4) | 8477(4) | 24.6(18) |
| C60 | 4020(5) | 2912(4) | 6810(5) | 31(2) |
| C65 | 4686(5) | 2967(4) | 7267(4) | 26.0(18) |
| C74 | 8849(5) | 3333(4) | 6809(4) | 23.6(18) |
| C27 | 9355(5) | 6557(5) | 6912(5) | 31(2) |

| | | | | |
|---|---|---|---|---|
| C64 | 4593(5) | 2916(5) | 7934(5) | 32(2) |
| C72 | 8787(5) | 3240(5) | 8186(4) | 30(2) |
| C66 | 5426(5) | 3102(4) | 7034(4) | 24.1(18) |
| C41 | 7487(6) | 4692(5) | 9574(4) | 33(2) |
| C81 | 10007(6) | 3392(5) | 5386(5) | 35(2) |
| O7 | 6560(4) | 4824(3) | 5763(3) | 36.5(16) |
| C12 | 6451(5) | 6265(4) | 8652(4) | 21.2(17) |
| N5 | 6786(4) | 3320(4) | 7396(3) | 22.1(15) |
| C63 | 3878(6) | 2799(5) | 8132(6) | 42(3) |
| C83 | 8653(6) | 3556(6) | 4988(5) | 41(3) |
| C51 | 11511(6) | 5129(6) | 6712(7) | 52(3) |
| C44 | 8971(6) | 4856(5) | 9222(5) | 37(2) |
| C48 | 9978(5) | 4998(4) | 7030(5) | 27.5(19) |
| C5 | 3323(5) | 6475(5) | 6085(5) | 38(2) |
| C37 | 4878(5) | 4656(4) | 8180(5) | 27.7(19) |
| C76 | 9819(5) | 3380(4) | 6033(5) | 27.3(19) |
| C71 | 8685(5) | 3109(5) | 8824(5) | 33(2) |
| C17 | 7238(5) | 6348(4) | 8868(4) | 24.2(18) |
| C13 | 5916(6) | 6295(5) | 9106(5) | 33(2) |
| C43 | 8856(6) | 4735(6) | 9858(5) | 44(3) |
| C53 | 10127(5) | 5072(4) | 6368(5) | 31(2) |
| C57 | 5467(5) | 3225(4) | 6362(4) | 27.9(19) |
| C49 | 10615(5) | 5020(5) | 7520(6) | 39(2) |
| C68 | 7407(5) | 3239(4) | 7897(4) | 23.4(17) |
| C6 | 2846(5) | 6504(5) | 6564(6) | 40(2) |
| C2 | 5389(5) | 6181(5) | 5888(5) | 35(2) |
| C1 | 5740(5) | 6124(4) | 6545(4) | 23.8(18) |
| C69 | 7315(5) | 3120(4) | 8549(4) | 29(2) |
| C33 | 3464(6) | 4600(5) | 7873(6) | 44(3) |
| C50 | 11361(6) | 5081(6) | 7347(7) | 52(3) |
| C84 | 8441(5) | 3558(5) | 5648(4) | 30(2) |
| C26 | 10107(5) | 6680(5) | 7127(5) | 34(2) |
| C24 | 11154(5) | 6774(5) | 8028(6) | 41(3) |
| C58 | 4779(5) | 3136(5) | 5926(5) | 38(2) |
| C14 | 6151(7) | 6404(6) | 9758(5) | 44(3) |
| C82 | 9392(6) | 3471(6) | 4872(5) | 45(3) |
| C59 | 4091(5) | 2983(5) | 6137(5) | 36(2) |
| C77 | 10442(6) | 3332(5) | 6527(5) | 40(2) |

| | | | | |
|---|---|---|---|---|
| C3 | 4632(6) | 6303(6) | 5742(5) | 42(3) |
| C16 | 7477(6) | 6442(5) | 9526(4) | 37(2) |
| C42 | 8116(7) | 4646(6) | 10043(5) | 45(3) |
| C20 | 9814(5) | 6618(4) | 8257(5) | 28.0(19) |
| C52 | 10915(6) | 5128(5) | 6229(6) | 44(3) |
| C61 | 3291(5) | 2779(5) | 7045(6) | 40(2) |
| C62 | 3223(6) | 2714(5) | 7688(6) | 47(3) |
| C36 | 4725(6) | 4709(5) | 8834(5) | 37(2) |
| C7 | 3147(5) | 6429(5) | 7212(5) | 36(2) |
| C70 | 7945(6) | 3052(5) | 9008(5) | 37(2) |
| C34 | 3354(6) | 4644(6) | 8516(7) | 54(3) |
| Cl1 | 5733(2) | 1928(2) | 4641.8(19) | 82.6(12) |
| Cl2 | 6420(3) | 1397(3) | 5860(2) | 110.0(18) |
| Cl4 | 9367(3) | 6302(3) | 10625(3) | 123(2) |
| Cl3 | 8650(6) | 6574(6) | 11752(4) | 201(4) |
| C21 | 10091(5) | 6624(5) | 8926(5) | 35(2) |
| C35 | 3971(7) | 4702(6) | 8990(6) | 52(3) |
| C22 | 10869(6) | 6712(5) | 9124(6) | 48(3) |
| C80 | 10785(7) | 3343(7) | 5258(6) | 55(3) |
| C79 | 11372(6) | 3296(7) | 5745(6) | 58(3) |
| C23 | 11407(6) | 6781(6) | 8681(6) | 48(3) |
| C78 | 11194(6) | 3295(6) | 6386(6) | 50(3) |
| C15 | 6938(7) | 6473(6) | 9971(5) | 47(3) |
| C85 | 6647(10) | 4978(7) | 5109(6) | 73(4) |
| C87 | 9001(10) | 6904(9) | 11056(11) | 113(8) |
| C86 | 6386(10) | 2070(8) | 5338(8) | 84(5) |

**Crystallographic Table 94** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **$Yb_2[L^{VII}]_3$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Yb1 | 13.51(16) | 22.65(18) | 17.51(17) | 0.48(13) | 2.49(12) | 1.55(13) |
| Yb2 | 17.15(18) | 25.62(19) | 19.00(18) | -4.08(14) | 2.16(13) | -0.78(14) |
| C45 | 20(4) | 25(4) | 19(4) | 4(3) | -5(3) | 2(3) |
| O4 | 12(3) | 25(3) | 21(3) | -4(2) | 3(2) | -4(2) |
| O3 | 15(3) | 29(3) | 21(3) | -2(2) | 7(2) | 0(2) |
| O2 | 19(3) | 27(3) | 22(3) | -6(2) | 4(2) | 2(2) |
| C47 | 21(4) | 18(4) | 29(4) | -1(3) | 6(3) | -7(3) |
| O1 | 20(3) | 41(4) | 27(3) | 3(3) | 8(2) | 8(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N6 | 21(3) | 23(4) | 24(4) | -5(3) | 5(3) | 1(3) |
| O6 | 22(3) | 48(4) | 20(3) | -1(3) | 2(2) | -7(3) |
| C19 | 19(4) | 20(4) | 30(4) | -2(3) | 1(3) | 2(3) |
| N3 | 17(3) | 26(4) | 19(3) | 6(3) | 4(3) | -1(3) |
| N2 | 23(4) | 22(4) | 19(3) | 2(3) | 4(3) | 1(3) |
| N4 | 16(3) | 26(4) | 20(3) | 2(3) | 0(3) | 1(3) |
| O5 | 30(3) | 43(4) | 22(3) | -17(3) | 6(3) | -2(3) |
| C30 | 22(4) | 25(4) | 34(5) | -6(4) | 3(4) | 1(4) |
| C40 | 30(5) | 18(4) | 26(4) | 7(3) | 2(4) | -1(3) |
| C39 | 26(4) | 19(4) | 22(4) | 3(3) | 11(3) | 1(3) |
| C73 | 23(4) | 27(4) | 23(4) | 4(3) | 2(3) | 0(3) |
| C54 | 31(5) | 40(5) | 30(5) | -4(4) | 16(4) | -4(4) |
| C55 | 22(4) | 28(5) | 26(4) | -6(3) | 8(3) | -2(4) |
| C10 | 23(4) | 18(4) | 33(5) | 2(3) | 6(4) | 6(3) |
| C4 | 27(5) | 36(5) | 39(5) | 3(4) | 4(4) | 15(4) |
| N1 | 25(4) | 18(3) | 22(3) | 1(3) | 7(3) | 3(3) |
| C38 | 15(4) | 18(4) | 27(4) | 1(3) | 7(3) | 5(3) |
| C46 | 11(4) | 23(4) | 34(5) | -1(3) | -3(3) | -3(4) |
| C29 | 15(4) | 12(4) | 33(5) | -2(3) | 8(3) | 2(3) |
| C11 | 11(4) | 21(4) | 35(5) | -1(3) | 5(3) | 6(3) |
| C28 | 20(4) | 23(4) | 29(4) | -5(3) | 7(3) | 1(3) |
| C8 | 23(4) | 31(5) | 41(5) | 7(4) | 6(4) | -2(4) |
| C56 | 17(4) | 15(4) | 36(5) | -1(3) | 9(3) | -7(3) |
| C75 | 24(4) | 22(4) | 26(4) | 1(3) | 8(3) | -5(3) |
| C31 | 11(4) | 24(5) | 52(6) | 0(3) | 4(4) | 3(4) |
| C9 | 21(4) | 18(4) | 38(5) | 4(3) | 6(4) | 6(4) |
| C32 | 23(5) | 21(4) | 50(6) | 3(3) | 16(4) | 7(4) |
| C67 | 29(4) | 15(4) | 28(4) | 1(3) | 7(4) | 2(3) |
| C25 | 21(4) | 28(5) | 43(5) | -2(4) | 6(4) | 5(4) |
| C18 | 22(4) | 28(5) | 23(4) | -1(3) | -3(3) | -1(3) |
| C60 | 23(4) | 23(5) | 49(6) | -3(4) | 9(4) | -2(4) |
| C65 | 26(4) | 17(4) | 37(5) | -1(3) | 9(4) | -1(4) |
| C74 | 19(4) | 21(4) | 32(5) | 1(3) | 7(3) | -2(3) |
| C27 | 35(5) | 32(5) | 28(5) | -3(4) | 8(4) | 3(4) |
| C64 | 27(5) | 28(5) | 43(6) | -4(4) | 7(4) | 3(4) |
| C72 | 27(5) | 32(5) | 32(5) | -1(4) | 7(4) | 3(4) |
| C66 | 22(4) | 12(4) | 38(5) | -3(3) | 4(4) | -2(3) |
| C41 | 42(6) | 36(5) | 22(4) | 5(4) | 4(4) | 6(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C81 | 32(5) | 33(5) | 41(6) | 4(4) | 17(4) | 0(4) |
| O7 | 43(4) | 41(4) | 26(3) | 4(3) | 2(3) | 5(3) |
| C12 | 16(4) | 24(4) | 25(4) | 2(3) | 9(3) | 0(3) |
| N5 | 15(3) | 29(4) | 23(4) | -1(3) | 4(3) | 3(3) |
| C63 | 44(6) | 41(6) | 47(6) | 4(5) | 26(5) | 7(5) |
| C83 | 37(6) | 60(7) | 27(5) | -1(5) | 7(4) | -16(5) |
| C51 | 19(5) | 55(7) | 86(9) | -2(5) | 20(5) | 2(7) |
| C44 | 33(5) | 46(6) | 31(5) | 5(4) | -2(4) | 4(4) |
| C48 | 18(4) | 20(4) | 45(5) | 3(3) | 8(4) | -3(4) |
| C5 | 25(5) | 43(6) | 44(6) | 7(4) | -7(4) | 5(5) |
| C37 | 20(4) | 24(4) | 41(5) | 2(3) | 12(4) | 7(4) |
| C76 | 23(4) | 24(4) | 38(5) | 3(3) | 15(4) | 0(4) |
| C71 | 23(5) | 43(6) | 33(5) | 3(4) | -2(4) | -1(4) |
| C17 | 32(5) | 20(4) | 22(4) | 0(3) | 8(3) | -4(3) |
| C13 | 31(5) | 35(5) | 36(5) | 6(4) | 13(4) | 7(4) |
| C43 | 37(6) | 60(7) | 33(5) | 7(5) | -11(4) | 5(5) |
| C53 | 25(5) | 25(5) | 47(6) | -7(4) | 14(4) | -3(4) |
| C57 | 24(4) | 26(5) | 34(5) | -7(4) | 4(4) | -3(4) |
| C49 | 17(4) | 46(6) | 53(6) | -3(4) | 9(4) | -6(5) |
| C68 | 23(4) | 23(4) | 25(4) | 3(3) | 4(3) | 2(3) |
| C6 | 13(4) | 41(6) | 65(7) | 5(4) | 7(4) | 3(5) |
| C2 | 25(5) | 52(6) | 29(5) | 11(4) | 6(4) | 20(4) |
| C1 | 15(4) | 28(5) | 28(4) | 4(3) | 3(3) | 11(4) |
| C69 | 26(5) | 30(5) | 31(5) | -6(4) | 2(4) | 8(4) |
| C33 | 19(5) | 39(6) | 75(8) | 0(4) | 14(5) | 9(5) |
| C50 | 13(5) | 60(8) | 81(9) | -1(5) | -1(5) | 1(6) |
| C84 | 29(5) | 31(5) | 31(5) | -3(4) | 12(4) | -10(4) |
| C26 | 24(5) | 29(5) | 52(6) | -5(4) | 17(4) | 6(4) |
| C24 | 22(5) | 27(5) | 73(8) | -4(4) | 8(5) | -1(5) |
| C58 | 29(5) | 50(6) | 33(5) | -14(4) | -1(4) | -4(5) |
| C14 | 49(6) | 55(7) | 32(5) | 8(5) | 19(5) | 4(5) |
| C82 | 50(7) | 54(7) | 32(5) | 3(5) | 16(5) | -12(5) |
| C59 | 19(4) | 43(6) | 43(6) | -12(4) | -1(4) | -3(5) |
| C77 | 27(5) | 51(6) | 43(6) | 9(5) | 10(4) | 7(5) |
| C3 | 37(6) | 56(7) | 34(5) | 12(5) | 3(4) | 20(5) |
| C16 | 32(5) | 55(7) | 25(5) | -2(5) | 4(4) | 0(4) |
| C42 | 60(7) | 49(7) | 24(5) | 9(5) | -2(5) | 7(4) |
| C20 | 24(4) | 22(4) | 37(5) | 2(3) | -1(4) | -2(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C52 | 27(5) | 36(6) | 75(8) | 1(4) | 30(5) | 2(5) |
| C61 | 18(4) | 33(5) | 68(7) | -6(4) | 7(5) | -5(5) |
| C62 | 31(6) | 39(6) | 75(8) | -1(5) | 25(5) | 0(6) |
| C36 | 31(5) | 40(6) | 45(6) | -4(4) | 22(4) | 6(5) |
| C7 | 23(5) | 39(6) | 48(6) | 3(4) | 9(4) | -1(5) |
| C70 | 51(6) | 31(5) | 29(5) | -6(4) | 6(4) | 8(4) |
| C34 | 26(6) | 57(7) | 83(9) | 8(5) | 26(6) | 11(7) |
| Cl1 | 76(2) | 116(3) | 60(2) | -6(2) | 27.6(19) | 4(2) |
| Cl2 | 64(3) | 177(5) | 91(3) | 2(3) | 15(2) | 49(3) |
| Cl4 | 91(3) | 160(5) | 115(4) | 23(3) | -8(3) | -48(4) |
| Cl3 | 216(9) | 295(12) | 104(5) | 40(8) | 68(6) | 23(6) |
| C21 | 27(5) | 44(6) | 33(5) | -1(4) | -5(4) | 4(4) |
| C35 | 45(7) | 52(7) | 67(8) | 11(5) | 43(6) | 8(6) |
| C22 | 42(6) | 43(6) | 53(7) | 2(5) | -22(5) | 3(5) |
| C80 | 48(7) | 74(9) | 50(7) | 8(6) | 33(6) | 1(6) |
| C79 | 25(5) | 92(10) | 60(8) | 17(6) | 24(5) | 18(7) |
| C23 | 22(5) | 45(6) | 75(8) | 0(4) | -7(5) | 3(6) |
| C78 | 23(5) | 70(8) | 59(7) | 5(5) | 12(5) | 14(6) |
| C15 | 54(7) | 68(8) | 22(5) | 4(6) | 15(5) | -5(5) |
| C85 | 121(13) | 55(8) | 43(7) | 11(8) | 15(8) | 5(6) |
| C87 | 76(12) | 69(11) | 180(20) | 23(9) | -25(13) | -40(13) |
| C86 | 83(11) | 73(10) | 98(12) | -16(9) | 24(9) | -30(9) |

**Crystallographic Table 95** Bond Lengths for $\mathbf{Yb_2[L^{VII}]_3}$.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Yb1 | O4 | 2.303(5) | C32 | C33 | 1.443(12) |
| Yb1 | O3 | 2.328(6) | C67 | C66 | 1.438(12) |
| Yb1 | O2 | 2.206(5) | C67 | N5 | 1.296(11) |
| Yb1 | O1 | 2.234(6) | C25 | C26 | 1.416(14) |
| Yb1 | N3 | 2.481(7) | C25 | C24 | 1.413(13) |
| Yb1 | N2 | 2.447(7) | C25 | C20 | 1.423(13) |
| Yb1 | N4 | 2.504(6) | C60 | C65 | 1.417(13) |
| Yb1 | N1 | 2.419(7) | C60 | C59 | 1.416(14) |
| Yb2 | O4 | 2.294(5) | C60 | C61 | 1.433(12) |
| Yb2 | O3 | 2.274(6) | C65 | C64 | 1.408(13) |
| Yb2 | N6 | 2.413(7) | C65 | C66 | 1.450(12) |
| Yb2 | O6 | 2.165(6) | C27 | C26 | 1.360(13) |
| Yb2 | O5 | 2.165(6) | C64 | C63 | 1.372(13) |

| | | | | | |
|---|---|---|---|---|---|
| Yb2 | O7 | 2.392(7) | C72 | C71 | 1.374(13) |
| Yb2 | N5 | 2.400(7) | C66 | C57 | 1.422(13) |
| C45 | N4 | 1.430(10) | C41 | C42 | 1.384(14) |
| C45 | C40 | 1.410(12) | C81 | C76 | 1.412(13) |
| C45 | C44 | 1.390(12) | C81 | C82 | 1.432(15) |
| O4 | C56 | 1.340(9) | C81 | C80 | 1.412(14) |
| O3 | C29 | 1.347(9) | O7 | C85 | 1.411(13) |
| O2 | C28 | 1.313(10) | C12 | C17 | 1.403(12) |
| C47 | C46 | 1.434(12) | C12 | C13 | 1.393(12) |
| C47 | C56 | 1.398(12) | N5 | C68 | 1.422(11) |
| C47 | C48 | 1.449(11) | C63 | C62 | 1.394(16) |
| O1 | C1 | 1.315(10) | C83 | C84 | 1.450(13) |
| N6 | C73 | 1.424(11) | C83 | C82 | 1.346(14) |
| N6 | C74 | 1.312(10) | C51 | C50 | 1.368(18) |
| O6 | C84 | 1.302(11) | C51 | C52 | 1.358(17) |
| C19 | C28 | 1.409(12) | C44 | C43 | 1.374(14) |
| C19 | C18 | 1.439(12) | C48 | C53 | 1.426(13) |
| C19 | C20 | 1.450(12) | C48 | C49 | 1.419(13) |
| N3 | C40 | 1.415(10) | C5 | C6 | 1.361(14) |
| N3 | C39 | 1.304(11) | C37 | C36 | 1.409(13) |
| N2 | C18 | 1.294(11) | C76 | C77 | 1.410(14) |
| N2 | C17 | 1.419(10) | C71 | C70 | 1.387(14) |
| N4 | C46 | 1.278(10) | C17 | C16 | 1.391(12) |
| O5 | C57 | 1.302(10) | C13 | C14 | 1.381(14) |
| C30 | C29 | 1.432(12) | C43 | C42 | 1.395(16) |
| C30 | C31 | 1.352(12) | C53 | C52 | 1.436(12) |
| C40 | C41 | 1.402(12) | C57 | C58 | 1.430(12) |
| C39 | C38 | 1.444(11) | C49 | C50 | 1.390(13) |
| C73 | C72 | 1.391(12) | C68 | C69 | 1.395(12) |
| C73 | C68 | 1.392(12) | C6 | C7 | 1.391(15) |
| C54 | C55 | 1.378(12) | C2 | C1 | 1.432(12) |
| C54 | C53 | 1.404(14) | C2 | C3 | 1.342(13) |
| C55 | C56 | 1.413(12) | C69 | C70 | 1.377(13) |
| C10 | C11 | 1.442(12) | C33 | C34 | 1.367(17) |
| C10 | C9 | 1.438(12) | C24 | C23 | 1.372(16) |
| C10 | C1 | 1.408(12) | C58 | C59 | 1.355(13) |
| C4 | C9 | 1.416(13) | C14 | C15 | 1.398(16) |
| C4 | C5 | 1.419(13) | C77 | C78 | 1.374(13) |

| | | | | | |
|---|---|---|---|---|---|
| C4 | C3 | 1.432(14) | C16 | C15 | 1.385(14) |
| N1 | C11 | 1.291(10) | C20 | C21 | 1.412(13) |
| N1 | C12 | 1.416(11) | C61 | C62 | 1.354(16) |
| C38 | C29 | 1.387(12) | C36 | C35 | 1.386(13) |
| C38 | C37 | 1.442(11) | C34 | C35 | 1.377(18) |
| C28 | C27 | 1.435(12) | Cl1 | C86 | 1.757(17) |
| C8 | C9 | 1.414(12) | Cl2 | C86 | 1.745(18) |
| C8 | C7 | 1.381(13) | Cl4 | C87 | 1.683(18) |
| C75 | C74 | 1.425(12) | Cl3 | C87 | 1.76(2) |
| C75 | C76 | 1.444(11) | C21 | C22 | 1.384(14) |
| C75 | C84 | 1.401(13) | C22 | C23 | 1.385(17) |
| C31 | C32 | 1.427(14) | C80 | C79 | 1.355(17) |
| C32 | C37 | 1.411(13) | C79 | C78 | 1.393(16) |

**Crystallographic Table 96** Bond Angles for **$Yb_2[L^{VII}]_3$**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| O3 | Yb1 | O4 | 68.82(18) | C55 | C56 | O4 | 118.2(8) |
| O2 | Yb1 | O4 | 80.5(2) | C55 | C56 | C47 | 120.0(7) |
| O2 | Yb1 | O3 | 140.9(2) | C76 | C75 | C74 | 117.5(8) |
| O1 | Yb1 | O4 | 91.1(2) | C84 | C75 | C74 | 121.9(8) |
| O1 | Yb1 | O3 | 75.3(2) | C84 | C75 | C76 | 120.6(8) |
| O1 | Yb1 | O2 | 81.9(2) | C32 | C31 | C30 | 121.2(9) |
| N3 | Yb1 | O4 | 106.3(2) | C4 | C9 | C10 | 119.8(8) |
| N3 | Yb1 | O3 | 69.2(2) | C8 | C9 | C10 | 123.4(8) |
| N3 | Yb1 | O2 | 145.6(2) | C8 | C9 | C4 | 116.7(8) |
| N3 | Yb1 | O1 | 130.5(2) | C37 | C32 | C31 | 119.7(8) |
| N2 | Yb1 | O4 | 134.1(2) | C33 | C32 | C31 | 119.8(9) |
| N2 | Yb1 | O3 | 146.6(2) | C33 | C32 | C37 | 120.5(9) |
| N2 | Yb1 | O2 | 72.5(2) | N5 | C67 | C66 | 126.7(8) |
| N2 | Yb1 | O1 | 119.9(2) | C24 | C25 | C26 | 121.3(9) |
| N2 | Yb1 | N3 | 79.7(2) | C20 | C25 | C26 | 119.1(8) |
| N4 | Yb1 | O4 | 69.8(2) | C20 | C25 | C24 | 119.6(9) |
| N4 | Yb1 | O3 | 103.0(2) | N2 | C18 | C19 | 125.7(8) |
| N4 | Yb1 | O2 | 87.7(2) | C59 | C60 | C65 | 119.6(8) |
| N4 | Yb1 | O1 | 159.6(2) | C61 | C60 | C65 | 118.6(9) |
| N4 | Yb1 | N3 | 64.6(2) | C61 | C60 | C59 | 121.8(9) |
| N4 | Yb1 | N2 | 72.8(2) | C64 | C65 | C60 | 118.2(8) |
| N1 | Yb1 | O4 | 159.8(2) | C66 | C65 | C60 | 119.0(8) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N1 | Yb1 | O3 | 93.2(2) | C66 | C65 | C64 | 122.7(8) |
| N1 | Yb1 | O2 | 111.1(2) | C75 | C74 | N6 | 127.8(8) |
| N1 | Yb1 | O1 | 74.9(2) | C26 | C27 | C28 | 122.1(9) |
| N1 | Yb1 | N3 | 73.9(2) | C63 | C64 | C65 | 120.7(9) |
| N1 | Yb1 | N2 | 66.0(2) | C71 | C72 | C73 | 120.4(8) |
| N1 | Yb1 | N4 | 125.4(2) | C65 | C66 | C67 | 119.5(8) |
| O3 | Yb2 | O4 | 69.91(19) | C57 | C66 | C67 | 120.4(8) |
| N6 | Yb2 | O4 | 80.2(2) | C57 | C66 | C65 | 120.0(8) |
| N6 | Yb2 | O3 | 115.8(2) | C42 | C41 | C40 | 121.0(10) |
| O6 | Yb2 | O4 | 95.9(2) | C82 | C81 | C76 | 118.2(8) |
| O6 | Yb2 | O3 | 158.8(2) | C80 | C81 | C76 | 120.1(10) |
| O6 | Yb2 | N6 | 75.3(2) | C80 | C81 | C82 | 121.7(10) |
| O5 | Yb2 | O4 | 160.5(2) | C85 | O7 | Yb2 | 134.4(7) |
| O5 | Yb2 | O3 | 98.4(2) | C17 | C12 | N1 | 116.4(7) |
| O5 | Yb2 | N6 | 119.3(2) | C13 | C12 | N1 | 124.7(8) |
| O5 | Yb2 | O6 | 90.4(2) | C13 | C12 | C17 | 118.8(8) |
| O7 | Yb2 | O4 | 76.3(2) | C67 | N5 | Yb2 | 126.7(6) |
| O7 | Yb2 | O3 | 75.2(2) | C68 | N5 | Yb2 | 114.6(5) |
| O7 | Yb2 | N6 | 148.4(2) | C68 | N5 | C67 | 118.5(7) |
| O7 | Yb2 | O6 | 86.3(2) | C62 | C63 | C64 | 121.8(10) |
| O7 | Yb2 | O5 | 85.7(2) | C82 | C83 | C84 | 121.0(10) |
| N5 | Yb2 | O4 | 116.0(2) | C52 | C51 | C50 | 119.6(9) |
| N5 | Yb2 | O3 | 77.4(2) | C43 | C44 | C45 | 119.9(9) |
| N5 | Yb2 | N6 | 66.9(2) | C53 | C48 | C47 | 118.9(8) |
| N5 | Yb2 | O6 | 123.7(2) | C49 | C48 | C47 | 122.8(9) |
| N5 | Yb2 | O5 | 74.6(2) | C49 | C48 | C53 | 118.1(8) |
| N5 | Yb2 | O7 | 143.3(2) | C6 | C5 | C4 | 120.5(9) |
| C40 | C45 | N4 | 116.4(7) | C32 | C37 | C38 | 118.8(8) |
| C44 | C45 | N4 | 123.7(8) | C36 | C37 | C38 | 123.2(9) |
| C44 | C45 | C40 | 119.9(8) | C36 | C37 | C32 | 117.9(8) |
| Yb2 | O4 | Yb1 | 110.5(2) | C81 | C76 | C75 | 119.6(9) |
| C56 | O4 | Yb1 | 122.0(5) | C77 | C76 | C75 | 123.7(8) |
| C56 | O4 | Yb2 | 126.2(5) | C77 | C76 | C81 | 116.6(8) |
| Yb2 | O3 | Yb1 | 110.4(2) | C70 | C71 | C72 | 120.1(9) |
| C29 | O3 | Yb1 | 118.4(5) | C12 | C17 | N2 | 115.8(7) |
| C29 | O3 | Yb2 | 131.2(5) | C16 | C17 | N2 | 123.8(8) |
| C28 | O2 | Yb1 | 130.4(5) | C16 | C17 | C12 | 120.2(8) |
| C56 | C47 | C46 | 121.0(7) | C14 | C13 | C12 | 121.0(9) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C48 | C47 | C46 | 119.2(8) | C42 | C43 | C44 | 121.4(9) |
| C48 | C47 | C56 | 119.8(8) | C48 | C53 | C54 | 119.0(8) |
| C1 | O1 | Yb1 | 135.8(5) | C52 | C53 | C54 | 122.3(9) |
| C73 | N6 | Yb2 | 115.1(5) | C52 | C53 | C48 | 118.6(9) |
| C74 | N6 | Yb2 | 126.6(6) | C66 | C57 | O5 | 123.6(8) |
| C74 | N6 | C73 | 118.2(7) | C58 | C57 | O5 | 118.7(8) |
| C84 | O6 | Yb2 | 136.8(6) | C58 | C57 | C66 | 117.7(8) |
| C18 | C19 | C28 | 120.8(7) | C50 | C49 | C48 | 119.9(10) |
| C20 | C19 | C28 | 119.9(8) | N5 | C68 | C73 | 116.9(7) |
| C20 | C19 | C18 | 119.3(8) | C69 | C68 | C73 | 118.7(8) |
| C40 | N3 | Yb1 | 116.4(5) | C69 | C68 | N5 | 124.4(8) |
| C39 | N3 | Yb1 | 124.1(5) | C7 | C6 | C5 | 119.9(9) |
| C39 | N3 | C40 | 119.2(7) | C3 | C2 | C1 | 122.2(9) |
| C18 | N2 | Yb1 | 125.8(6) | C10 | C1 | O1 | 123.4(8) |
| C17 | N2 | Yb1 | 114.0(5) | C2 | C1 | O1 | 118.7(8) |
| C17 | N2 | C18 | 119.9(7) | C2 | C1 | C10 | 117.8(8) |
| C45 | N4 | Yb1 | 114.8(5) | C70 | C69 | C68 | 121.1(9) |
| C46 | N4 | Yb1 | 126.2(6) | C34 | C33 | C32 | 118.7(10) |
| C46 | N4 | C45 | 119.0(7) | C49 | C50 | C51 | 122.3(11) |
| C57 | O5 | Yb2 | 133.6(6) | C75 | C84 | O6 | 123.9(8) |
| C31 | C30 | C29 | 120.2(9) | C83 | C84 | O6 | 118.0(9) |
| N3 | C40 | C45 | 115.9(7) | C83 | C84 | C75 | 118.0(8) |
| C41 | C40 | C45 | 118.8(8) | C27 | C26 | C25 | 121.0(9) |
| C41 | C40 | N3 | 125.3(8) | C23 | C24 | C25 | 121.5(10) |
| C38 | C39 | N3 | 124.3(7) | C59 | C58 | C57 | 122.4(9) |
| C72 | C73 | N6 | 124.3(8) | C15 | C14 | C13 | 119.9(9) |
| C68 | C73 | N6 | 115.6(7) | C83 | C82 | C81 | 122.2(10) |
| C68 | C73 | C72 | 120.1(8) | C58 | C59 | C60 | 121.0(9) |
| C53 | C54 | C55 | 121.8(9) | C78 | C77 | C76 | 121.7(10) |
| C56 | C55 | C54 | 120.3(8) | C2 | C3 | C4 | 121.4(9) |
| C9 | C10 | C11 | 117.4(8) | C15 | C16 | C17 | 120.3(9) |
| C1 | C10 | C11 | 122.1(8) | C43 | C42 | C41 | 118.9(9) |
| C1 | C10 | C9 | 120.2(8) | C25 | C20 | C19 | 119.4(8) |
| C5 | C4 | C9 | 120.6(9) | C21 | C20 | C19 | 122.9(9) |
| C3 | C4 | C9 | 118.2(8) | C21 | C20 | C25 | 117.6(8) |
| C3 | C4 | C5 | 121.2(9) | C53 | C52 | C51 | 121.4(11) |
| C11 | N1 | Yb1 | 128.2(6) | C62 | C61 | C60 | 121.8(10) |
| C12 | N1 | Yb1 | 114.4(5) | C61 | C62 | C63 | 118.8(9) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C12 | N1 | C11 | 117.3(7) | C35 | C36 | C37 | 120.4(11) |
| C29 | C38 | C39 | 120.9(7) | C6 | C7 | C8 | 120.7(9) |
| C37 | C38 | C39 | 119.4(8) | C69 | C70 | C71 | 119.7(9) |
| C37 | C38 | C29 | 119.7(8) | C35 | C34 | C33 | 121.1(10) |
| N4 | C46 | C47 | 125.4(8) | C22 | C21 | C20 | 120.6(10) |
| C30 | C29 | O3 | 118.1(7) | C34 | C35 | C36 | 121.3(11) |
| C38 | C29 | O3 | 121.4(7) | C23 | C22 | C21 | 121.8(10) |
| C38 | C29 | C30 | 120.4(7) | C79 | C80 | C81 | 121.8(10) |
| N1 | C11 | C10 | 127.5(8) | C78 | C79 | C80 | 118.5(10) |
| C19 | C28 | O2 | 123.0(7) | C22 | C23 | C24 | 118.8(10) |
| C27 | C28 | O2 | 119.0(8) | C79 | C78 | C77 | 121.2(11) |
| C27 | C28 | C19 | 118.0(8) | C16 | C15 | C14 | 119.8(9) |
| C7 | C8 | C9 | 121.4(9) | Cl3 | C87 | Cl4 | 109.9(11) |
| C47 | C56 | O4 | 121.7(8) | Cl2 | C86 | Cl1 | 110.5(9) |

**Crystallographic Table 97** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **$Yb_2[L^{VII}]_3$**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H30 | 5167(5) | 4642(4) | 6395(5) | 33(2) |
| H39 | 6240(5) | 4414(4) | 8871(4) | 26(2) |
| H54 | 9601(5) | 5150(5) | 5439(5) | 39(3) |
| H55 | 8336(5) | 5083(4) | 5679(4) | 30(2) |
| H46 | 9426(4) | 4642(4) | 8122(4) | 27(2) |
| H11 | 5270(4) | 6528(4) | 7996(4) | 27(2) |
| H8 | 4123(5) | 6286(5) | 7822(5) | 38(2) |
| H31 | 3942(5) | 4579(4) | 6701(5) | 35(2) |
| H67 | 6085(5) | 2846(4) | 7879(4) | 28(2) |
| H18 | 8576(5) | 6748(4) | 8880(4) | 30(2) |
| H74 | 9253(5) | 3150(4) | 7100(4) | 28(2) |
| H27 | 9201(5) | 6549(5) | 6456(5) | 38(2) |
| H64 | 5029(5) | 2962(5) | 8249(5) | 39(2) |
| H72 | 9295(5) | 3288(5) | 8064(4) | 36(2) |
| H41 | 6980(6) | 4647(5) | 9698(4) | 40(3) |
| H7 | 6440(50) | 5188(16) | 5950(10) | 55(2) |
| H63 | 3828(6) | 2775(5) | 8585(6) | 51(3) |
| H83 | 8264(6) | 3615(6) | 4633(5) | 50(3) |
| H51 | 12028(6) | 5163(6) | 6610(7) | 63(4) |
| H44 | 9479(6) | 4926(5) | 9108(5) | 44(3) |

| | | | | |
|---|---|---|---|---|
| H5 | 3116(5) | 6523(5) | 5643(5) | 46(3) |
| H71 | 9121(5) | 3057(5) | 9138(5) | 40(3) |
| H13 | 5382(6) | 6239(5) | 8966(5) | 40(3) |
| H43 | 9290(6) | 4711(6) | 10179(5) | 53(3) |
| H49 | 10531(5) | 4992(5) | 7966(6) | 46(3) |
| H6 | 2308(5) | 6576(5) | 6456(6) | 48(3) |
| H2 | 5703(5) | 6131(5) | 5542(5) | 42(3) |
| H69 | 6809(5) | 3085(4) | 8678(4) | 35(2) |
| H33 | 3036(6) | 4562(5) | 7548(6) | 52(3) |
| H50 | 11782(6) | 5089(6) | 7681(7) | 62(4) |
| H26 | 10467(5) | 6754(5) | 6820(5) | 41(3) |
| H24 | 11519(5) | 6821(5) | 7722(6) | 49(3) |
| H58 | 4805(5) | 3185(5) | 5471(5) | 45(3) |
| H14 | 5779(7) | 6433(6) | 10060(5) | 53(3) |
| H82 | 9510(6) | 3464(6) | 4434(5) | 54(3) |
| H59 | 3650(5) | 2923(5) | 5830(5) | 43(3) |
| H77 | 10339(6) | 3325(5) | 6970(5) | 48(3) |
| H3 | 4426(6) | 6342(6) | 5299(5) | 51(3) |
| H16 | 8011(6) | 6484(5) | 9671(4) | 44(3) |
| H42 | 8045(7) | 4556(6) | 10483(5) | 54(3) |
| H52 | 11022(6) | 5166(5) | 5789(6) | 53(3) |
| H61 | 2844(5) | 2735(5) | 6741(6) | 48(3) |
| H62 | 2738(6) | 2613(5) | 7834(6) | 56(3) |
| H36 | 5141(6) | 4750(5) | 9170(5) | 45(3) |
| H7a | 2810(5) | 6439(5) | 7544(5) | 43(3) |
| H70 | 7873(6) | 2966(5) | 9450(5) | 44(3) |
| H34 | 2844(6) | 4633(6) | 8639(7) | 65(4) |
| H21 | 9739(5) | 6568(5) | 9242(5) | 42(3) |
| H35 | 3878(7) | 4738(6) | 9434(6) | 62(4) |
| H22 | 11040(6) | 6724(5) | 9576(6) | 58(3) |
| H80 | 10901(7) | 3342(7) | 4820(6) | 66(4) |
| H79 | 11893(6) | 3265(7) | 5650(6) | 69(4) |
| H23 | 11940(6) | 6832(6) | 8827(6) | 58(3) |
| H78 | 11600(6) | 3268(6) | 6731(6) | 60(4) |
| H15 | 7102(7) | 6541(6) | 10420(5) | 57(3) |
| H85a | 6136(10) | 5030(50) | 4864(13) | 109(7) |
| H85b | 6940(60) | 5390(30) | 5093(7) | 109(7) |
| H85c | 6930(60) | 4620(30) | 4917(17) | 109(7) |

| | | | | |
|---|---|---|---|---|
| H87a | 9408(10) | 7231(9) | 11187(11) | 135(9) |
| H87b | 8576(10) | 7126(9) | 10783(11) | 135(9) |
| H86a | 6907(10) | 2154(8) | 5207(8) | 100(6) |
| H86b | 6223(10) | 2463(8) | 5568(8) | 100(6) |

Refinement model description

Number of restraints - 3, number of constraints - 119.

Details:

1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups
2. Restrained distances
 O7-H7
 0.87 with sigma of 0.01
 C85-H7
 1.886919 with sigma of 0.02
 Yb2-H7
 2.888526 with sigma of 0.02
3.a Secondary CH2 refined with riding coordinates:
 C87(H87a,H87b), C86(H86a,H86b)
3.b Aromatic/amide H refined with riding coordinates:
 C30(H30), C39(H39), C54(H54), C55(H55), C46(H46), C11(H11), C8(H8), C31(H31),
 C67(H67), C18(H18), C74(H74), C27(H27), C64(H64), C72(H72), C41(H41),
C63(H63),
  C83(H83), C51(H51), C44(H44), C5(H5), C71(H71), C13(H13), C43(H43), C49(H49),
 C6(H6), C2(H2), C69(H69), C33(H33), C50(H50), C26(H26), C24(H24), C58(H58),
 C14(H14), C82(H82), C59(H59), C77(H77), C3(H3), C16(H16), C42(H42), C52(H52),
 C61(H61), C62(H62), C36(H36), C7(H7a), C70(H70), C34(H34), C21(H21), C35(H35),
 C22(H22), C80(H80), C79(H79), C23(H23), C78(H78), C15(H15)
3.c Idealised Me refined as rotating group:
 C85(H85a,H85b,H85c)

## $Eu_2[L^{VII}]_3$

**Crystallographic Table 98** Crystal data and structure refinement for $Eu_2[L^{VII}]_3$

| | |
|---|---|
| Empirical formula | $C_{87}H_{62}N_6O_7Eu_2Cl_4$ |
| Formula weight | 1749.24 |
| Temperature/K | 180.45 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 17.512(7) |
| b/Å | 20.500(8) |
| c/Å | 20.517(8) |
| α/° | 90 |
| β/° | 96.457(7) |
| γ/° | 90 |
| Volume/Å$^3$ | 7319(5) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.5873 |
| m/mm$^{-1}$ | 1.907 |
| F(000) | 3507.5 |
| Crystal size/mm$^3$ | 0.12 × 0.1 × 0.08 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 2.82 to 29.5° |
| Index ranges | $-12 \le h \le 12$, $-14 \le k \le 14$, $-14 \le l \le 14$ |
| Reflections collected | 23881 |
| Independent reflections | 2833 [$R_{int}$ = 0.1459, $R_{sigma}$ = 0.0769] |
| Data/restraints/parameters | 2833/3/438 |
| Goodness-of-fit on $F^2$ | 1.129 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0647, $wR_2$ = 0.1637 |
| Final R indexes [all data] | $R_1$ = 0.0946, $wR_2$ = 0.1807 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.65/-0.83 |

**Crystallographic Table 99** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for $Eu_2[L^{VII}]_3$. $U_{eq}$is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Eu1 | 2252.8(10) | 574.8(9) | 7422.2(8) | 23.7(9) |
| Eu2 | 2103.5(10) | -1047.0(9) | 6424.3(8) | 26.2(9) |
| O4 | 2899(12) | -119(9) | 6720(9) | 23(6) |
| N6 | 3261(14) | -1590(11) | 7010(11) | 16(8) |

| | | | | |
|---|---|---|---|---|
| O3 | 1443(12) | -336(9) | 7066(9) | 27(6) |
| N1 | 1227(14) | 1146(11) | 7963(12) | 18(8) |
| C75 | 4100(20) | -1594(14) | 6109(16) | 26(10) |
| C64 | -318(19) | -2095(14) | 7964(15) | 29(10) |
| N2 | 2728(16) | 1303(12) | 8360(12) | 27(8) |
| C65 | -251(17) | -2058(13) | 7289(15) | 11(10) |
| C84 | 3500(20) | -1493(15) | 5596(17) | 34(11) |
| C66 | 470(18) | -1961(14) | 7029(15) | 17(10) |
| N5 | 1827(16) | -1751(12) | 7371(12) | 26(8) |
| C76 | 4900(20) | -1652(14) | 6049(17) | 28(11) |
| C57 | 500(20) | -1837(16) | 6340(17) | 36(11) |
| C63 | -994(19) | -2210(14) | 8219(16) | 34(11) |
| C62 | -1661(19) | -2275(14) | 7786(15) | 32(10) |
| C74 | 3934(18) | -1713(14) | 6769(15) | 21(10) |
| C67 | 1173(18) | -1981(14) | 7458(15) | 15(10) |
| O1 | 1382(12) | 970(9) | 6587(9) | 27(6) |
| O6 | 2795(12) | -1395(9) | 5649(9) | 30(7) |
| C31 | -629(19) | -423(13) | 6987(15) | 23(10) |
| O2 | 3099(12) | 1324(9) | 7086(9) | 26(7) |
| C37 | -117(18) | -371(13) | 8168(15) | 15(10) |
| C30 | 88(18) | -399(13) | 6820(15) | 24(10) |
| O5 | 1109(12) | -1675(9) | 6082(9) | 28(7) |
| C38 | 648(18) | -364(13) | 7938(15) | 15(10) |
| O7 | 1545(12) | -160(10) | 5680(10) | 43(7) |
| C60 | -930(20) | -2107(15) | 6841(17) | 33(11) |
| C61 | -1649(19) | -2227(14) | 7097(15) | 29(10) |
| C59 | -889(18) | -2047(13) | 6179(15) | 17(10) |
| C82 | 4520(20) | -1550(14) | 4830(17) | 36(11) |
| C81 | 5080(20) | -1605(16) | 5378(18) | 41(12) |
| C83 | 3770(20) | -1480(15) | 4942(16) | 37(11) |
| C29 | 760(18) | -360(13) | 7290(15) | 11(9) |
| C39 | 1288(18) | -411(14) | 8446(15) | 24(10) |
| C2 | 270(20) | 1165(14) | 5856(16) | 34(11) |
| C73 | 3193(19) | -1733(14) | 7693(15) | 16(10) |
| C28 | 3800(20) | 1457(14) | 7352(16) | 21(10) |
| C51 | 6520(20) | 98(15) | 6742(16) | 39(11) |
| C17 | 2196(18) | 1350(13) | 8850(15) | 9(9) |
| C72 | 3847(19) | -1787(14) | 8168(15) | 29(10) |

| | | | | |
|---|---|---|---|---|
| C11 | 524(18) | 1316(13) | 7712(14) | 16(10) |
| C25 | 5360(20) | 1682(14) | 7832(17) | 26(10) |
| C32 | -760(20) | -419(15) | 7662(17) | 39(11) |
| C10 | 203(19) | 1209(14) | 7045(15) | 18(10) |
| C35 | -1009(19) | -319(14) | 8979(16) | 33(11) |
| C49 | 5640(20) | -41(15) | 7570(17) | 41(11) |
| C19 | 4013(19) | 1523(14) | 8033(16) | 23(10) |
| C36 | -245(18) | -299(14) | 8829(16) | 28(10) |
| C47 | 4228(19) | -73(14) | 7176(16) | 18(10) |
| C26 | 5097(19) | 1679(14) | 7160(16) | 31(11) |
| C77 | 5503(19) | -1679(14) | 6546(16) | 30(11) |
| C33 | -1520(20) | -417(15) | 7864(17) | 46(12) |
| C52 | 5960(20) | 112(15) | 6258(17) | 41(11) |
| C55 | 3792(19) | 43(14) | 5999(16) | 33(11) |
| C1 | 650(20) | 1119(15) | 6507(17) | 34(11) |
| C48 | 5026(19) | -28(14) | 7038(16) | 18(10) |
| C20 | 4820(20) | 1625(14) | 8295(16) | 25(10) |
| C78 | 6260(19) | -1700(14) | 6434(16) | 28(10) |
| C18 | 3393(19) | 1568(14) | 8435(14) | 19(10) |
| C53 | 5162(19) | 69(15) | 6387(16) | 24(10) |
| C56 | 3660(20) | -53(15) | 6659(17) | 27(10) |
| Cl3 | 5682(9) | -1307(8) | 9358(7) | 157(6) |
| N4 | 3419(14) | -3(11) | 8069(11) | 14(8) |
| Cl4 | 6406(11) | -1628(9) | 8283(9) | 196(8) |
| N3 | 1983(14) | -143(11) | 8387(11) | 13(7) |
| C70 | 2995(19) | -1961(14) | 8996(16) | 28(10) |
| C80 | 5900(20) | -1645(15) | 5284(18) | 51(12) |
| C8 | -1109(19) | 1326(14) | 7384(16) | 28(10) |
| C5 | -1770(20) | 1449(15) | 6105(17) | 41(11) |
| C6 | -2230(20) | 1467(15) | 6601(16) | 36(11) |
| C69 | 2380(20) | -1929(14) | 8551(16) | 33(11) |
| C21 | 5040(20) | 1638(15) | 8975(17) | 41(11) |
| C23 | 6375(19) | 1740(14) | 8762(16) | 26(10) |
| C27 | 4346(19) | 1561(14) | 6913(16) | 30(11) |
| C4 | -940(20) | 1357(15) | 6221(16) | 28(10) |
| C9 | -620(20) | 1295(15) | 6898(17) | 27(10) |
| C58 | -227(19) | -1934(14) | 5925(16) | 34(11) |
| C12 | 1436(19) | 1272(14) | 8634(15) | 15(10) |

| | | | | |
|---|---|---|---|---|
| C15 | 1900(20) | 1474(15) | 9974(17) | 45(12) |
| C3 | -470(20) | 1295(14) | 5727(17) | 35(11) |
| C14 | 1130(20) | 1399(15) | 9762(16) | 44(11) |
| C50 | 6380(20) | 48(17) | 7387(19) | 66(13) |
| C24 | 6120(20) | 1730(15) | 8127(17) | 40(11) |
| C7 | -1886(19) | 1391(14) | 7246(16) | 34(11) |
| C54 | 4564(18) | 83(13) | 5872(15) | 23(10) |
| C16 | 2450(19) | 1476(14) | 9517(15) | 30(10) |
| C68 | 2450(20) | -1821(14) | 7876(16) | 25(10) |
| C34 | -1570(20) | -384(16) | 8507(18) | 57(12) |
| Cl1 | 758(6) | -1891(5) | 9618(5) | 81(4) |
| Cl2 | 1441(7) | -1370(6) | 10839(6) | 109(5) |
| C41 | 2489(19) | -301(14) | 9562(16) | 31(10) |
| C71 | 3733(19) | -1917(14) | 8814(15) | 27(10) |
| C43 | 3830(20) | -260(15) | 9859(17) | 44(12) |
| C13 | 880(20) | 1291(14) | 9081(16) | 39(11) |
| C46 | 4048(19) | -179(14) | 7832(15) | 23(10) |
| C44 | 3966(19) | -126(14) | 9237(16) | 31(11) |
| C22 | 5820(20) | 1697(15) | 9185(18) | 52(12) |
| C42 | 3120(20) | -339(15) | 10050(17) | 43(11) |
| C45 | 3342(19) | -138(14) | 8747(16) | 15(10) |
| C86 | 1430(20) | -2035(18) | 10307(17) | 84(14) |
| C85 | 5990(30) | -1980(20) | 8970(20) | 121(18) |
| C79 | 6470(20) | -1692(16) | 5777(18) | 57(12) |
| C40 | 2610(20) | -218(15) | 8910(17) | 30(11) |
| C87 | 1720(20) | 70(20) | 5032(16) | 104(16) |

**Crystallographic Table 100** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **$Eu_2[L^{VII}]_3$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Eu1 | 19.7(15) | 32.3(16) | 18.9(14) | 0.6(12) | 1.1(10) | 0.8(12) |
| Eu2 | 24.0(16) | 34.0(16) | 20.4(14) | -2.5(12) | 1.6(11) | -1.7(12) |

**Crystallographic Table 101** Bond Lengths for **$Eu_2[L^{VII}]_3$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Eu1 | O4 | 2.396(19) | C73 | C68 | 1.40(4) |
| Eu1 | O3 | 2.408(19) | C28 | C19 | 1.41(4) |
| Eu1 | N1 | 2.51(2) | C28 | C27 | 1.40(4) |

| | | | | | |
|---|---|---|---|---|---|
| Eu1 | N2 | 2.50(2) | C51 | C52 | 1.32(3) |
| Eu1 | O1 | 2.31(2) | C51 | C50 | 1.37(4) |
| Eu1 | O2 | 2.29(2) | C17 | C12 | 1.37(3) |
| Eu1 | C29 | 3.23(3) | C17 | C16 | 1.41(3) |
| Eu1 | N4 | 2.59(2) | C72 | C71 | 1.39(3) |
| Eu1 | N3 | 2.55(2) | C11 | C10 | 1.44(3) |
| Eu2 | O4 | 2.395(19) | C25 | C26 | 1.40(3) |
| Eu2 | N6 | 2.50(2) | C25 | C20 | 1.42(4) |
| Eu2 | O3 | 2.35(2) | C25 | C24 | 1.41(4) |
| Eu2 | N5 | 2.51(2) | C32 | C33 | 1.45(4) |
| Eu2 | C57 | 3.23(4) | C10 | C1 | 1.44(4) |
| Eu2 | O6 | 2.22(2) | C10 | C9 | 1.45(4) |
| Eu2 | O5 | 2.22(2) | C35 | C36 | 1.41(4) |
| Eu2 | O7 | 2.502(19) | C35 | C34 | 1.31(4) |
| O4 | C56 | 1.36(3) | C49 | C48 | 1.44(3) |
| N6 | C74 | 1.35(3) | C49 | C50 | 1.41(4) |
| N6 | C73 | 1.45(3) | C19 | C20 | 1.46(4) |
| O3 | C29 | 1.33(3) | C19 | C18 | 1.44(4) |
| N1 | C11 | 1.33(3) | C47 | C48 | 1.46(4) |
| N1 | C12 | 1.41(3) | C47 | C56 | 1.37(3) |
| C75 | C84 | 1.41(4) | C47 | C46 | 1.43(3) |
| C75 | C76 | 1.43(4) | C26 | C27 | 1.38(4) |
| C75 | C74 | 1.44(4) | C77 | C78 | 1.37(4) |
| C64 | C65 | 1.40(3) | C33 | C34 | 1.34(4) |
| C64 | C63 | 1.37(4) | C52 | C53 | 1.45(4) |
| N2 | C17 | 1.45(3) | C55 | C56 | 1.41(4) |
| N2 | C18 | 1.28(3) | C55 | C54 | 1.41(4) |
| C65 | C66 | 1.44(3) | C48 | C53 | 1.40(3) |
| C65 | C60 | 1.42(3) | C20 | C21 | 1.41(4) |
| C84 | O6 | 1.28(3) | C78 | C79 | 1.43(4) |
| C84 | C83 | 1.47(4) | C53 | C54 | 1.40(3) |
| C66 | C57 | 1.44(4) | Cl3 | C85 | 1.72(4) |
| C66 | C67 | 1.43(3) | N4 | C46 | 1.30(3) |
| N5 | C67 | 1.27(3) | N4 | C45 | 1.44(3) |
| N5 | C68 | 1.43(3) | Cl4 | C85 | 1.81(4) |
| C76 | C81 | 1.45(4) | N3 | C40 | 1.45(3) |
| C76 | C77 | 1.38(4) | C70 | C69 | 1.34(3) |
| C57 | O5 | 1.29(3) | C70 | C71 | 1.39(4) |

| | | | | | |
|---|---|---|---|---|---|
| C57 | C58 | 1.46(4) | C80 | C79 | 1.34(4) |
| C63 | C62 | 1.39(3) | C8 | C9 | 1.39(4) |
| C62 | C61 | 1.42(3) | C8 | C7 | 1.37(4) |
| O1 | C1 | 1.31(3) | C5 | C6 | 1.36(4) |
| C31 | C30 | 1.34(3) | C5 | C4 | 1.46(4) |
| C31 | C32 | 1.43(4) | C6 | C7 | 1.40(4) |
| O2 | C28 | 1.32(3) | C69 | C68 | 1.42(4) |
| C37 | C38 | 1.47(4) | C21 | C22 | 1.39(4) |
| C37 | C32 | 1.44(4) | C23 | C24 | 1.33(3) |
| C37 | C36 | 1.41(3) | C23 | C22 | 1.38(4) |
| C30 | C29 | 1.44(3) | C4 | C9 | 1.44(4) |
| C38 | C29 | 1.36(3) | C4 | C3 | 1.38(4) |
| C38 | C39 | 1.45(3) | C12 | C13 | 1.41(4) |
| O7 | C87 | 1.48(3) | C15 | C14 | 1.38(4) |
| C60 | C61 | 1.44(4) | C15 | C16 | 1.42(4) |
| C60 | C59 | 1.37(3) | C14 | C13 | 1.43(4) |
| C59 | C58 | 1.34(3) | Cl1 | C86 | 1.76(3) |
| C82 | C81 | 1.41(4) | Cl2 | C86 | 1.75(4) |
| C82 | C83 | 1.35(4) | C41 | C42 | 1.40(4) |
| C81 | C80 | 1.48(4) | C41 | C40 | 1.39(4) |
| C39 | N3 | 1.35(3) | C43 | C44 | 1.35(4) |
| C2 | C1 | 1.43(4) | C43 | C42 | 1.36(4) |
| C2 | C3 | 1.32(4) | C44 | C45 | 1.40(3) |
| C73 | C72 | 1.42(3) | C45 | C40 | 1.38(4) |

**Crystallographic Table 102** Bond Angles for **$Eu_2[L^{VII}]_3$**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| O3 | Eu1 | O4 | 70.1(7) | C59 | C60 | C61 | 121(3) |
| N1 | Eu1 | O4 | 162.5(7) | C60 | C61 | C62 | 119(3) |
| N1 | Eu1 | O3 | 94.0(7) | C58 | C59 | C60 | 123(3) |
| N2 | Eu1 | O4 | 132.6(8) | C83 | C82 | C81 | 118(4) |
| N2 | Eu1 | O3 | 146.0(8) | C82 | C81 | C76 | 124(4) |
| N2 | Eu1 | N1 | 64.8(8) | C80 | C81 | C76 | 116(3) |
| O1 | Eu1 | O4 | 94.5(7) | C80 | C81 | C82 | 120(3) |
| O1 | Eu1 | O3 | 74.3(6) | C82 | C83 | C84 | 125(3) |
| O1 | Eu1 | N1 | 73.6(7) | O3 | C29 | Eu1 | 41.9(13) |
| O1 | Eu1 | N2 | 119.8(7) | C30 | C29 | Eu1 | 133(2) |
| O2 | Eu1 | O4 | 81.5(7) | C30 | C29 | O3 | 118(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O2 | Eu1 | O3 | 143.8(7) | C38 | C29 | Eu1 | 97(2) |
| O2 | Eu1 | N1 | 109.9(7) | C38 | C29 | O3 | 125(3) |
| O2 | Eu1 | N2 | 70.2(8) | C38 | C29 | C30 | 117(3) |
| O2 | Eu1 | O1 | 86.4(7) | N3 | C39 | C38 | 123(3) |
| C29 | Eu1 | O4 | 91.7(7) | C3 | C2 | C1 | 123(4) |
| C29 | Eu1 | O3 | 21.6(6) | C72 | C73 | N6 | 122(3) |
| C29 | Eu1 | N1 | 72.6(8) | C68 | C73 | N6 | 118(3) |
| C29 | Eu1 | N2 | 128.0(8) | C68 | C73 | C72 | 120(3) |
| C29 | Eu1 | O1 | 71.7(7) | C19 | C28 | O2 | 124(3) |
| C29 | Eu1 | O2 | 156.5(7) | C27 | C28 | O2 | 116(3) |
| N4 | Eu1 | O4 | 68.8(7) | C27 | C28 | C19 | 120(3) |
| N4 | Eu1 | O3 | 101.8(7) | C50 | C51 | C52 | 122(4) |
| N4 | Eu1 | N1 | 123.3(8) | C12 | C17 | N2 | 116(3) |
| N4 | Eu1 | N2 | 72.8(7) | C16 | C17 | N2 | 122(3) |
| N4 | Eu1 | O1 | 163.0(7) | C16 | C17 | C12 | 122(3) |
| N4 | Eu1 | O2 | 87.8(7) | C71 | C72 | C73 | 119(3) |
| N4 | Eu1 | C29 | 110.8(7) | C10 | C11 | N1 | 125(3) |
| N3 | Eu1 | O4 | 105.3(7) | C20 | C25 | C26 | 119(3) |
| N3 | Eu1 | O3 | 68.6(7) | C24 | C25 | C26 | 127(3) |
| N3 | Eu1 | N1 | 73.8(7) | C24 | C25 | C20 | 113(3) |
| N3 | Eu1 | N2 | 79.7(8) | C37 | C32 | C31 | 120(3) |
| N3 | Eu1 | O1 | 127.9(7) | C33 | C32 | C31 | 122(3) |
| N3 | Eu1 | O2 | 143.2(7) | C33 | C32 | C37 | 118(3) |
| N3 | Eu1 | C29 | 60.3(8) | C1 | C10 | C11 | 124(3) |
| N3 | Eu1 | N4 | 62.9(8) | C9 | C10 | C11 | 117(3) |
| N6 | Eu2 | O4 | 79.3(7) | C9 | C10 | C1 | 118(3) |
| O3 | Eu2 | O4 | 71.0(7) | C34 | C35 | C36 | 120(4) |
| O3 | Eu2 | N6 | 115.5(7) | C50 | C49 | C48 | 115(3) |
| N5 | Eu2 | O4 | 114.7(7) | C20 | C19 | C28 | 121(3) |
| N5 | Eu2 | N6 | 65.7(8) | C18 | C19 | C28 | 116(3) |
| N5 | Eu2 | O3 | 76.9(7) | C18 | C19 | C20 | 122(3) |
| C57 | Eu2 | O4 | 152.8(7) | C35 | C36 | C37 | 118(3) |
| C57 | Eu2 | N6 | 117.1(8) | C56 | C47 | C48 | 118(3) |
| C57 | Eu2 | O3 | 82.0(8) | C46 | C47 | C48 | 121(3) |
| C57 | Eu2 | N5 | 60.7(9) | C46 | C47 | C56 | 121(3) |
| O6 | Eu2 | O4 | 95.1(7) | C27 | C26 | C25 | 124(3) |
| O6 | Eu2 | N6 | 74.0(8) | C78 | C77 | C76 | 123(3) |
| O6 | Eu2 | O3 | 160.2(7) | C34 | C33 | C32 | 117(4) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O6 | Eu2 | N5 | 122.5(7) | C53 | C52 | C51 | 121(4) |
| O6 | Eu2 | C57 | 109.9(8) | C54 | C55 | C56 | 117(3) |
| O5 | Eu2 | O4 | 162.9(7) | C2 | C1 | O1 | 119(3) |
| O5 | Eu2 | N6 | 117.4(7) | C10 | C1 | O1 | 123(3) |
| O5 | Eu2 | O3 | 96.8(7) | C10 | C1 | C2 | 118(3) |
| O5 | Eu2 | N5 | 72.5(8) | C47 | C48 | C49 | 120(3) |
| O5 | Eu2 | C57 | 17.0(7) | C53 | C48 | C49 | 123(3) |
| O5 | Eu2 | O6 | 93.3(7) | C53 | C48 | C47 | 118(3) |
| O7 | Eu2 | O4 | 75.8(7) | C19 | C20 | C25 | 117(3) |
| O7 | Eu2 | N6 | 149.1(7) | C21 | C20 | C25 | 122(3) |
| O7 | Eu2 | O3 | 73.1(6) | C21 | C20 | C19 | 121(3) |
| O7 | Eu2 | N5 | 142.6(8) | C79 | C78 | C77 | 121(3) |
| O7 | Eu2 | C57 | 93.1(8) | C19 | C18 | N2 | 130(3) |
| O7 | Eu2 | O6 | 90.2(7) | C48 | C53 | C52 | 117(3) |
| O7 | Eu2 | O5 | 89.4(7) | C54 | C53 | C52 | 121(3) |
| Eu2 | O4 | Eu1 | 108.9(8) | C54 | C53 | C48 | 122(3) |
| C56 | O4 | Eu1 | 122.0(18) | C47 | C56 | O4 | 124(3) |
| C56 | O4 | Eu2 | 127.2(18) | C55 | C56 | O4 | 112(3) |
| C74 | N6 | Eu2 | 127(2) | C55 | C56 | C47 | 124(3) |
| C73 | N6 | Eu2 | 113.8(19) | C46 | N4 | Eu1 | 126(2) |
| C73 | N6 | C74 | 119(3) | C45 | N4 | Eu1 | 115.4(19) |
| Eu2 | O3 | Eu1 | 109.9(8) | C45 | N4 | C46 | 119(3) |
| C29 | O3 | Eu1 | 116.5(17) | C39 | N3 | Eu1 | 123(2) |
| C29 | O3 | Eu2 | 133.5(18) | C40 | N3 | Eu1 | 116.4(19) |
| C11 | N1 | Eu1 | 129(2) | C40 | N3 | C39 | 120(3) |
| C12 | N1 | Eu1 | 113.5(19) | C71 | C70 | C69 | 121(3) |
| C12 | N1 | C11 | 117(3) | C79 | C80 | C81 | 124(4) |
| C76 | C75 | C84 | 127(3) | C7 | C8 | C9 | 123(3) |
| C74 | C75 | C84 | 121(3) | C4 | C5 | C6 | 123(3) |
| C74 | C75 | C76 | 112(3) | C7 | C6 | C5 | 119(3) |
| C63 | C64 | C65 | 124(3) | C68 | C69 | C70 | 121(3) |
| C17 | N2 | Eu1 | 112.9(19) | C22 | C21 | C20 | 118(3) |
| C18 | N2 | Eu1 | 124(2) | C22 | C23 | C24 | 116(3) |
| C18 | N2 | C17 | 122(3) | C26 | C27 | C28 | 119(3) |
| C66 | C65 | C64 | 123(3) | C9 | C4 | C5 | 116(3) |
| C60 | C65 | C64 | 119(3) | C3 | C4 | C5 | 124(3) |
| C60 | C65 | C66 | 118(3) | C3 | C4 | C9 | 120(3) |
| O6 | C84 | C75 | 127(3) | C8 | C9 | C10 | 122(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C83 | C84 | C75 | 113(3) | C4 | C9 | C10 | 119(3) |
| C83 | C84 | O6 | 119(3) | C4 | C9 | C8 | 119(3) |
| C57 | C66 | C65 | 121(3) | C59 | C58 | C57 | 122(3) |
| C67 | C66 | C65 | 120(3) | C17 | C12 | N1 | 118(3) |
| C67 | C66 | C57 | 119(3) | C13 | C12 | N1 | 121(3) |
| C67 | N5 | Eu2 | 125(2) | C13 | C12 | C17 | 120(3) |
| C68 | N5 | Eu2 | 115(2) | C16 | C15 | C14 | 120(3) |
| C68 | N5 | C67 | 119(3) | C4 | C3 | C2 | 122(3) |
| C81 | C76 | C75 | 113(3) | C13 | C14 | C15 | 120(3) |
| C77 | C76 | C75 | 128(3) | C49 | C50 | C51 | 122(4) |
| C77 | C76 | C81 | 119(3) | C23 | C24 | C25 | 128(4) |
| C66 | C57 | Eu2 | 99(2) | C6 | C7 | C8 | 121(3) |
| O5 | C57 | Eu2 | 30.3(14) | C53 | C54 | C55 | 121(3) |
| O5 | C57 | C66 | 125(3) | C15 | C16 | C17 | 118(3) |
| C58 | C57 | Eu2 | 143(2) | C73 | C68 | N5 | 117(3) |
| C58 | C57 | C66 | 115(3) | C69 | C68 | N5 | 125(3) |
| C58 | C57 | O5 | 120(3) | C69 | C68 | C73 | 118(3) |
| C62 | C63 | C64 | 118(3) | C33 | C34 | C35 | 127(4) |
| C61 | C62 | C63 | 122(3) | C40 | C41 | C42 | 120(3) |
| C75 | C74 | N6 | 126(3) | C70 | C71 | C72 | 120(3) |
| N5 | C67 | C66 | 129(3) | C42 | C43 | C44 | 124(4) |
| C1 | O1 | Eu1 | 137(2) | C14 | C13 | C12 | 119(3) |
| C84 | O6 | Eu2 | 136(2) | N4 | C46 | C47 | 126(3) |
| C32 | C31 | C30 | 120(3) | C45 | C44 | C43 | 118(3) |
| C28 | O2 | Eu1 | 128.3(19) | C23 | C22 | C21 | 123(4) |
| C32 | C37 | C38 | 116(3) | C43 | C42 | C41 | 117(3) |
| C36 | C37 | C38 | 124(3) | C44 | C45 | N4 | 123(3) |
| C36 | C37 | C32 | 120(3) | C40 | C45 | N4 | 117(3) |
| C29 | C30 | C31 | 123(3) | C40 | C45 | C44 | 120(3) |
| C57 | O5 | Eu2 | 133(2) | Cl2 | C86 | Cl1 | 109(2) |
| C29 | C38 | C37 | 123(3) | Cl4 | C85 | Cl3 | 102(2) |
| C39 | C38 | C37 | 115(3) | C80 | C79 | C78 | 118(4) |
| C39 | C38 | C29 | 121(3) | C41 | C40 | N3 | 123(3) |
| C87 | O7 | Eu2 | 132.7(17) | C45 | C40 | N3 | 117(3) |
| C61 | C60 | C65 | 119(3) | C45 | C40 | C41 | 120(3) |
| C59 | C60 | C65 | 120(3) | | | | |

**Crystallographic Table 103** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **$Eu_2[L^{VII}]_3$**.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H64 | 134(19) | -2038(14) | 8261(15) | 34(13) |
| H63 | -1009(19) | -2243(14) | 8679(16) | 41(13) |
| H62 | -2135(19) | -2354(14) | 7956(15) | 38(12) |
| H74 | 4335(18) | -1896(14) | 7063(15) | 25(12) |
| H67 | 1146(18) | -2197(14) | 7865(15) | 18(12) |
| H31 | -1053(19) | -444(13) | 6655(15) | 27(12) |
| H30 | 156(18) | -407(13) | 6367(15) | 29(12) |
| H7 | 1170(90) | 60(80) | 5820(50) | 65(10) |
| H61 | -2110(19) | -2274(14) | 6808(15) | 35(12) |
| H59 | -1349(18) | -2087(13) | 5889(15) | 21(12) |
| H82 | 4660(20) | -1561(14) | 4396(17) | 43(13) |
| H83 | 3400(20) | -1419(15) | 4574(16) | 44(13) |
| H39 | 1217(18) | -639(14) | 8838(15) | 29(12) |
| H2 | 560(20) | 1100(14) | 5499(16) | 41(13) |
| H51 | 7030(20) | 123(15) | 6643(16) | 46(13) |
| H72 | 4351(19) | -1735(14) | 8046(15) | 35(12) |
| H11 | 208(18) | 1526(13) | 7995(14) | 19(11) |
| H35 | -1116(19) | -285(14) | 9422(16) | 40(13) |
| H49 | 5540(20) | -106(15) | 8013(17) | 49(13) |
| H36 | 171(18) | -239(14) | 9163(16) | 33(12) |
| H26 | 5460(19) | 1763(14) | 6859(16) | 37(13) |
| H77 | 5386(19) | -1683(14) | 6987(16) | 37(13) |
| H33 | -1960(20) | -439(15) | 7553(17) | 56(14) |
| H52 | 6080(20) | 150(15) | 5819(17) | 50(13) |
| H55 | 3380(19) | 78(14) | 5657(16) | 40(13) |
| H78 | 6651(19) | -1719(14) | 6794(16) | 34(13) |
| H18 | 3492(19) | 1837(14) | 8812(14) | 22(12) |
| H70 | 2927(19) | -2014(14) | 9446(16) | 33(12) |
| H80 | 6030(20) | -1636(15) | 4848(18) | 61(14) |
| H8 | -895(19) | 1301(14) | 7830(16) | 33(12) |
| H5 | -2000(20) | 1497(15) | 5666(17) | 50(14) |
| H6 | -2770(20) | 1531(15) | 6511(16) | 43(13) |
| H69 | 1880(20) | -1979(14) | 8687(16) | 40(13) |
| H21 | 4670(20) | 1608(15) | 9279(17) | 50(14) |
| H23 | 6906(19) | 1774(14) | 8916(16) | 32(12) |

| | | | | |
|---|---|---|---|---|
| H27 | 4200(19) | 1549(14) | 6453(16) | 36(13) |
| H58 | -230(19) | -1917(14) | 5462(16) | 41(13) |
| H15 | 2060(20) | 1524(15) | 10429(17) | 54(14) |
| H3 | -680(20) | 1346(14) | 5284(17) | 42(13) |
| H14 | 760(20) | 1420(15) | 10068(16) | 53(14) |
| H50 | 6800(20) | 74(17) | 7720(19) | 79(16) |
| H24 | 6500(20) | 1759(15) | 7835(17) | 48(14) |
| H7a | -2200(19) | 1384(14) | 7594(16) | 40(13) |
| H54 | 4681(18) | 119(13) | 5433(15) | 27(12) |
| H16 | 2977(19) | 1560(14) | 9656(15) | 35(13) |
| H34 | -2080(20) | -410(16) | 8637(18) | 68(15) |
| H41 | 1980(19) | -332(14) | 9678(16) | 37(13) |
| H71 | 4163(19) | -1977(14) | 9134(15) | 33(12) |
| H43 | 4260(20) | -301(15) | 10183(17) | 53(14) |
| H13 | 350(20) | 1234(14) | 8933(16) | 46(13) |
| H46 | 4423(19) | -399(14) | 8123(15) | 27(12) |
| H44 | 4469(19) | -28(14) | 9136(16) | 37(13) |
| H22 | 5970(20) | 1708(15) | 9644(18) | 63(15) |
| H42 | 3040(20) | -417(15) | 10496(17) | 51(14) |
| H86a | 1280(20) | -2435(18) | 10535(17) | 101(17) |
| H86b | 1940(20) | -2101(18) | 10167(17) | 101(17) |
| H85a | 6390(30) | -2230(20) | 9260(20) | 150(20) |
| H85b | 5560(30) | -2280(20) | 8820(20) | 150(20) |
| H79 | 6990(20) | -1720(16) | 5694(18) | 68(15) |
| H87a | 1950(140) | -280(40) | 4800(60) | 160(20) |
| H87b | 1240(30) | 210(120) | 4770(50) | 160(20) |
| H87c | 2070(120) | 440(80) | 5089(17) | 160(20) |

Refinement model description

Number of restraints - 3, number of constraints - 119.

Details:

1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups

2. Restrained distances
O7-H7
0.87 with sigma of 0.01
C87-H7
1.989295 with sigma of 0.02
Eu2-H7
2.994132 with sigma of 0.02
3.a Secondary CH2 refined with riding coordinates:
C86(H86a,H86b), C85(H85a,H85b)
3.b Aromatic/amide H refined with riding coordinates:
C64(H64), C63(H63), C62(H62), C74(H74), C67(H67), C31(H31), C30(H30), C61(H61), C59(H59), C82(H82), C83(H83), C39(H39), C2(H2), C51(H51), C72(H72), C11(H11), C35(H35), C49(H49), C36(H36), C26(H26), C77(H77), C33(H33), C52(H52), C55(H55), C78(H78), C18(H18), C70(H70), C80(H80), C8(H8), C5(H5), C6(H6), C69(H69), C21(H21), C23(H23), C27(H27), C58(H58), C15(H15), C3(H3), C14(H14), C50(H50), C24(H24), C7(H7a), C54(H54), C16(H16), C34(H34), C41(H41), C71(H71), C43(H43), C13(H13), C46(H46), C44(H44), C22(H22), C42(H42), C79(H79)
3.c Idealised Me refined as rotating group:
C87(H87a,H87b,H87c)

## $Tb_2[L^{VII}]_3$

**Crystallographic Table 104** Crystal data and structure refinement for $Tb_2[L^{VII}]_3$

| | |
|---|---|
| Identification code | $Tb_2[L^{VII}]_3$ |
| Empirical formula | $C_{87}Cl_4N_6O_7Tb_2H_{62}$ |
| Formula weight | 1760.13 |
| Temperature/K | 180.45 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 17.4955(6) |
| b/Å | 20.5102(7) |
| c/Å | 20.6076(8) |
| α/° | 90 |
| β/° | 96.4934(10) |
| γ/° | 90 |
| Volume/Å$^3$ | 7347.3(5) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.5911 |
| m/mm$^{-1}$ | 2.118 |
| F(000) | 3511.0 |
| Crystal size/mm$^3$ | 0.3 × 0.28 × 0.15 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 2.34 to 54.96° |
| Index ranges | $-22 \le h \le 22$, $-26 \le k \le 26$, $-26 \le l \le 25$ |
| Reflections collected | 111448 |
| Independent reflections | 16845 [$R_{int}$ = 0.0508, $R_{sigma}$ = 0.0403] |
| Data/restraints/parameters | 16845/3/949 |
| Goodness-of-fit on $F^2$ | 1.084 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0610, $wR_2$ = 0.1273 |
| Final R indexes [all data] | $R_1$ = 0.0756, $wR_2$ = 0.1418 |
| Largest diff. peak/hole / e Å$^{-3}$ | 3.29/-1.56 |

**Crystallographic Table 105** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for $Tb_2[L^{VII}]_3$. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Tb1 | 2254.28(13) | 4429.63(12) | 2434.26(11) | 20.82(6) |
| Tb2 | 2083.24(13) | 6030.80(12) | 1446.19(11) | 22.83(7) |
| C40 | 3356(2) | 5132(2) | 3720(2) | 17.3(9) |

| | | | | |
|---|---|---|---|---|
| C68 | 3170(3) | 6724(2) | 2683(2) | 23.5(10) |
| N3 | 3406(2) | 5014(2) | 3053.0(19) | 22.6(9) |
| N5 | 3224(2) | 6575(2) | 2012(2) | 22.4(8) |
| O1 | 3100.1(19) | 3703.5(18) | 2085.2(17) | 26.5(8) |
| C29 | 3602(3) | 5042(2) | 1635(2) | 21.8(10) |
| C38 | 4192(3) | 5073(2) | 2151(3) | 25.4(11) |
| O2 | 1419(2) | 4009(2) | 1611.0(18) | 35.2(9) |
| O4 | 1433.6(18) | 5316.9(17) | 2083.2(16) | 22.7(7) |
| N2 | 1243(2) | 3858(2) | 2959(2) | 23.5(9) |
| O3 | 2864.3(18) | 5116.0(17) | 1738.5(16) | 23.1(7) |
| C45 | 2591(3) | 5214(2) | 3905(2) | 26.3(11) |
| C56 | 740(3) | 5341(2) | 2296(3) | 22.9(10) |
| C65 | 4865(3) | 6636(3) | 1023(3) | 29.0(11) |
| C46 | 1310(3) | 5386(2) | 3447(2) | 23.8(10) |
| C73 | 2428(3) | 6791(2) | 2874(2) | 23.1(10) |
| C74 | 1138(3) | 6958(3) | 2460(3) | 26.7(11) |
| O6 | 1069(2) | 6635(2) | 1090.6(18) | 33.1(9) |
| N1 | 2738(2) | 3718(2) | 3368.5(19) | 23.8(9) |
| C47 | 652(3) | 5346(2) | 2958(3) | 24(1) |
| O5 | 2772(2) | 6374(2) | 677.6(17) | 32.8(9) |
| C54 | -637(3) | 5412(3) | 2012(3) | 33.8(13) |
| C21 | -1100(3) | 3671(3) | 2382(3) | 33.0(12) |
| C37 | 4989(3) | 5021(3) | 2023(3) | 31.3(12) |
| C77 | -366(3) | 7087(3) | 2948(3) | 35.9(13) |
| C18 | 556(3) | 3689(2) | 2704(3) | 26.0(11) |
| C28 | 684(3) | 3871(3) | 1523(3) | 28.6(11) |
| C41 | 3960(3) | 5152(3) | 4207(3) | 37.8(14) |
| C19 | 238(3) | 3768(2) | 2040(3) | 25.5(11) |
| C1 | 3800(3) | 3558(2) | 2347(3) | 26.5(11) |
| C66 | 4058(3) | 6585(3) | 1137(3) | 26.4(11) |
| C72 | 2339(3) | 6901(3) | 3532(3) | 29.6(11) |
| C9 | 4793(3) | 3380(3) | 3271(3) | 30.8(12) |
| C10 | 3998(3) | 3483(2) | 3019(3) | 26.5(11) |
| C60 | 5061(3) | 6618(3) | 373(3) | 37.5(13) |
| C17 | 1441(3) | 3730(3) | 3637(2) | 25.7(10) |
| C20 | -587(3) | 3676(3) | 1894(3) | 26.9(11) |
| C44 | 2488(4) | 5316(3) | 4558(3) | 35.5(13) |
| C76 | -284(3) | 7052(2) | 2271(3) | 28.6(11) |

| | | | | |
|---|---|---|---|---|
| C30 | 3788(3) | 4950(3) | 994(3) | 31.9(12) |
| C4 | 5357(3) | 3325(3) | 2832(3) | 31.6(12) |
| C82 | -915(3) | 7047(3) | 1155(3) | 36.8(13) |
| C12 | 2230(3) | 3652(2) | 3857(2) | 24.8(10) |
| C11 | 3422(3) | 3453(3) | 3466(3) | 26.7(11) |
| C67 | 3877(3) | 6698(2) | 1786(3) | 27.1(11) |
| C53 | -763(3) | 5398(3) | 2679(3) | 34.3(13) |
| C81 | -968(3) | 7104(3) | 1833(3) | 32.9(12) |
| C34 | 6514(3) | 4889(3) | 1733(4) | 53.6(19) |
| C26 | -438(3) | 3678(3) | 729(3) | 42.7(15) |
| C16 | 913(3) | 3719(3) | 4096(3) | 34.1(13) |
| C57 | 3490(3) | 6475(3) | 607(3) | 31.0(12) |
| C69 | 3804(3) | 6780(3) | 3156(3) | 31.3(12) |
| C48 | -114(3) | 5356(3) | 3161(3) | 31.8(12) |
| C36 | 5617(3) | 5009(3) | 2527(3) | 42.1(15) |
| C31 | 4536(3) | 4903(3) | 867(3) | 33.1(12) |
| C64 | 5475(3) | 6678(3) | 1531(3) | 38.0(14) |
| C59 | 4467(4) | 6540(4) | -146(3) | 45.5(16) |
| C55 | 81(3) | 5383(2) | 1826(3) | 28.0(11) |
| C78 | -1063(4) | 7199(3) | 3170(4) | 44.7(15) |
| C32 | 5148(3) | 4944(3) | 1372(3) | 33.5(13) |
| C3 | 5123(3) | 3342(3) | 2154(3) | 34.9(13) |
| C84 | 450(3) | 6817(3) | 1349(3) | 29.8(12) |
| C13 | 2460(3) | 3568(3) | 4517(3) | 35.5(13) |
| C42 | 3852(4) | 5266(3) | 4854(3) | 45.9(16) |
| C58 | 3719(4) | 6468(3) | -35(3) | 39.7(14) |
| C83 | -245(3) | 6902(3) | 922(3) | 38.2(14) |
| C75 | 440(3) | 6929(2) | 2020(3) | 27.3(11) |
| C15 | 1151(4) | 3620(3) | 4752(3) | 43.6(15) |
| C2 | 4374(3) | 3453(3) | 1919(3) | 30.8(12) |
| C25 | -923(3) | 3618(3) | 1233(3) | 33.1(12) |
| C24 | -1726(3) | 3527(3) | 1093(3) | 39.5(14) |
| C27 | 322(3) | 3802(3) | 867(3) | 42.3(16) |
| C70 | 3711(3) | 6908(3) | 3804(3) | 36.2(13) |
| C63 | 6223(4) | 6718(4) | 1407(4) | 53.2(19) |
| C71 | 2974(3) | 6964(3) | 3988(3) | 38.5(14) |
| C23 | -2190(3) | 3510(3) | 1579(3) | 40.8(14) |
| C5 | 6145(3) | 3252(3) | 3080(4) | 43.5(16) |

| | | | | |
|---|---|---|---|---|
| C8 | 5054(3) | 3368(3) | 3949(3) | 39.1(14) |
| C14 | 1927(4) | 3543(3) | 4960(3) | 46.0(16) |
| C7 | 5823(4) | 3295(3) | 4166(4) | 50.9(18) |
| C43 | 3109(4) | 5351(3) | 5025(3) | 46.0(16) |
| C35 | 6354(3) | 4942(4) | 2377(4) | 55.6(19) |
| C33 | 5927(3) | 4883(3) | 1241(4) | 47.5(17) |
| C62 | 6407(4) | 6715(4) | 762(4) | 61(2) |
| C6 | 6377(3) | 3242(3) | 3734(4) | 50.6(18) |
| C22 | -1882(3) | 3592(3) | 2231(3) | 40.1(14) |
| C61 | 5842(4) | 6663(4) | 263(4) | 54.9(19) |
| O7 | 1538(3) | 5174(2) | 694(2) | 46.6(11) |
| C80 | -1680(3) | 7225(3) | 2079(4) | 44.9(16) |
| C52 | -1509(4) | 5407(3) | 2879(4) | 52.9(19) |
| C79 | -1729(4) | 7280(3) | 2735(4) | 46.8(16) |
| C51 | -1619(4) | 5355(4) | 3516(5) | 64(2) |
| C49 | -252(4) | 5289(3) | 3822(3) | 41.7(15) |
| C50 | -988(4) | 5292(4) | 3992(4) | 57(2) |
| N4 | 1984(2) | 5139(2) | 3391(2) | 23.4(9) |
| N6 | 1803(2) | 6718(2) | 2371(2) | 23.1(9) |
| C39 | 4026(3) | 5180(2) | 2822(3) | 27.0(11) |
| C85 | 1670(6) | 4966(5) | 55(5) | 84(3) |

**Crystallographic Table 106** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **$Tb_2[L^{VII}]_3$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Tb1 | 15.23(11) | 25.90(12) | 21.42(12) | -0.63(9) | 2.45(8) | -1.04(9) |
| Tb2 | 18.78(12) | 27.82(13) | 21.82(12) | 2.67(9) | 2.00(9) | 0.54(9) |
| C40 | 12(2) | 25(2) | 13(2) | -4.0(17) | -5.8(16) | -1.1(17) |
| C68 | 22(2) | 26(3) | 22(2) | -3(2) | 0.4(19) | 0.5(19) |
| N3 | 19(2) | 28(2) | 20(2) | 0.7(17) | 0.2(16) | 1.3(17) |
| N5 | 21(2) | 22(2) | 25(2) | 1.2(16) | 3.3(16) | 0.8(16) |
| O1 | 21.3(17) | 32(2) | 26.0(18) | 4.9(15) | 1.3(14) | -4.6(15) |
| C29 | 15(2) | 23(2) | 28(3) | 1.9(18) | 6.1(19) | 1.2(19) |
| C38 | 19(2) | 21(2) | 37(3) | -0.6(19) | 7(2) | 5(2) |
| O2 | 18.4(18) | 59(3) | 29(2) | -12.0(17) | 5.2(15) | -16.8(18) |
| O4 | 17.6(16) | 29.1(18) | 22.1(17) | 3.3(14) | 5.1(13) | -1.1(14) |
| N2 | 22(2) | 23(2) | 26(2) | -2.7(17) | 3.4(17) | -4.0(17) |
| O3 | 17.7(16) | 30.5(19) | 22.3(17) | 2.2(14) | 6.9(13) | 3.5(14) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C45 | 32(3) | 22(3) | 24(3) | -4(2) | 0(2) | 1(2) |
| C56 | 15(2) | 21(2) | 32(3) | 3.0(18) | 1.5(19) | 0(2) |
| C65 | 24(3) | 24(3) | 40(3) | -4(2) | 8(2) | -2(2) |
| C46 | 23(2) | 26(3) | 24(2) | -3(2) | 9.0(19) | -5(2) |
| C73 | 21(2) | 18(2) | 29(3) | 1.2(18) | -1.4(19) | 1.5(19) |
| C74 | 25(3) | 27(3) | 28(3) | 4(2) | 5(2) | -2(2) |
| O6 | 24.5(19) | 48(2) | 26.6(19) | 14.8(17) | 1.5(15) | 3.4(17) |
| N1 | 28(2) | 24(2) | 19(2) | -5.4(17) | 0.8(16) | 2.9(16) |
| C47 | 19(2) | 21(2) | 33(3) | -0.8(19) | 4(2) | -4(2) |
| O5 | 26.2(19) | 48(2) | 24.0(19) | 0.7(17) | 3.2(15) | 6.3(17) |
| C54 | 18(2) | 29(3) | 53(4) | 1(2) | -2(2) | -6(3) |
| C21 | 21(3) | 39(3) | 40(3) | -2(2) | 4(2) | -2(2) |
| C37 | 14(2) | 25(3) | 54(4) | 0(2) | 2(2) | 6(2) |
| C77 | 36(3) | 32(3) | 40(3) | 3(2) | 7(3) | 0(2) |
| C18 | 22(2) | 23(2) | 33(3) | -4(2) | 5(2) | -2(2) |
| C28 | 20(2) | 32(3) | 33(3) | -4(2) | 2(2) | -9(2) |
| C41 | 32(3) | 43(3) | 36(3) | -7(3) | -8(2) | 3(3) |
| C19 | 22(2) | 19(2) | 35(3) | -4.3(19) | 3(2) | -4(2) |
| C1 | 27(3) | 21(2) | 33(3) | -2(2) | 7(2) | -4(2) |
| C66 | 25(3) | 28(3) | 27(3) | -3(2) | 5(2) | 6(2) |
| C72 | 32(3) | 32(3) | 26(3) | 4(2) | 8(2) | -7(2) |
| C9 | 23(3) | 26(3) | 42(3) | 0(2) | -2(2) | -1(2) |
| C10 | 29(3) | 20(2) | 31(3) | 4(2) | 5(2) | 0(2) |
| C60 | 38(3) | 37(3) | 40(3) | -4(3) | 15(3) | 1(3) |
| C17 | 25(3) | 28(3) | 24(3) | -3(2) | 5(2) | -2(2) |
| C20 | 20(2) | 25(3) | 35(3) | -2(2) | 3(2) | -3(2) |
| C44 | 38(3) | 41(3) | 27(3) | -7(3) | 4(2) | -2(2) |
| C76 | 24(3) | 19(2) | 42(3) | 3(2) | 4(2) | -2(2) |
| C30 | 28(3) | 38(3) | 31(3) | -1(2) | 9(2) | -1(2) |
| C4 | 19(2) | 27(3) | 49(3) | 2(2) | 5(2) | 1(2) |
| C82 | 27(3) | 28(3) | 54(4) | 4(2) | -6(3) | 3(3) |
| C12 | 31(3) | 22(2) | 23(2) | 0(2) | 7(2) | -0.7(19) |
| C11 | 24(3) | 29(3) | 26(3) | 5(2) | -1(2) | 1(2) |
| C67 | 26(3) | 25(3) | 30(3) | -4(2) | 3(2) | -2(2) |
| C53 | 21(3) | 24(3) | 59(4) | 0(2) | 12(3) | -5(3) |
| C81 | 25(3) | 25(3) | 49(3) | 4(2) | 2(2) | 3(2) |
| C34 | 18(3) | 51(4) | 95(6) | -1(3) | 21(3) | -6(4) |
| C26 | 27(3) | 65(4) | 35(3) | -7(3) | 0(2) | -22(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C16 | 28(3) | 37(3) | 39(3) | -9(2) | 16(2) | -6(2) |
| C57 | 30(3) | 38(3) | 26(3) | 1(2) | 11(2) | 5(2) |
| C69 | 24(3) | 38(3) | 31(3) | -1(2) | -1(2) | 0(2) |
| C48 | 28(3) | 24(3) | 45(3) | -1(2) | 15(2) | -4(2) |
| C36 | 15(3) | 52(4) | 59(4) | -1(2) | 6(3) | 10(3) |
| C31 | 30(3) | 35(3) | 37(3) | 3(2) | 16(2) | 3(2) |
| C64 | 27(3) | 46(4) | 42(3) | -8(3) | 9(2) | -8(3) |
| C59 | 46(4) | 66(4) | 28(3) | 1(3) | 18(3) | 8(3) |
| C55 | 22(3) | 25(3) | 35(3) | 0(2) | -3(2) | -3(2) |
| C78 | 38(3) | 41(4) | 58(4) | -1(3) | 17(3) | -5(3) |
| C32 | 23(3) | 25(3) | 56(4) | 1(2) | 20(3) | -1(2) |
| C3 | 27(3) | 34(3) | 46(3) | 8(2) | 12(2) | 2(3) |
| C84 | 25(3) | 26(3) | 38(3) | 11(2) | 0(2) | -2(2) |
| C13 | 33(3) | 51(4) | 24(3) | -1(3) | 4(2) | 1(2) |
| C42 | 46(4) | 58(4) | 28(3) | -7(3) | -20(3) | -1(3) |
| C58 | 37(3) | 60(4) | 22(3) | 2(3) | 5(2) | 9(3) |
| C83 | 34(3) | 44(3) | 35(3) | 11(3) | -2(2) | 2(3) |
| C75 | 26(3) | 20(2) | 35(3) | 6(2) | 3(2) | 2(2) |
| C15 | 46(4) | 55(4) | 33(3) | -9(3) | 21(3) | -1(3) |
| C2 | 35(3) | 27(3) | 31(3) | 5(2) | 7(2) | 1(2) |
| C25 | 22(3) | 36(3) | 41(3) | -2(2) | 2(2) | -8(2) |
| C24 | 25(3) | 46(4) | 46(4) | -4(3) | -4(2) | -8(3) |
| C27 | 24(3) | 70(5) | 31(3) | -7(3) | 1(2) | -20(3) |
| C70 | 24(3) | 52(4) | 30(3) | -3(3) | -7(2) | -4(3) |
| C63 | 24(3) | 79(5) | 57(4) | -17(3) | 6(3) | -16(4) |
| C71 | 40(3) | 48(4) | 27(3) | 5(3) | 3(2) | -4(3) |
| C23 | 17(3) | 49(4) | 56(4) | -6(2) | -2(3) | -3(3) |
| C5 | 20(3) | 35(3) | 75(5) | 2(2) | 2(3) | 5(3) |
| C8 | 34(3) | 41(3) | 41(3) | 2(3) | -3(3) | 4(3) |
| C14 | 51(4) | 60(4) | 28(3) | -3(3) | 13(3) | 7(3) |
| C7 | 34(3) | 53(4) | 61(4) | -3(3) | -17(3) | -3(3) |
| C43 | 63(4) | 47(4) | 27(3) | -10(3) | 1(3) | -1(3) |
| C35 | 16(3) | 65(5) | 85(6) | -6(3) | 2(3) | 3(4) |
| C33 | 23(3) | 47(4) | 77(5) | 5(3) | 23(3) | -5(3) |
| C62 | 28(3) | 94(6) | 63(5) | -16(4) | 23(3) | -10(4) |
| C6 | 19(3) | 55(4) | 72(5) | 0(3) | -19(3) | 1(4) |
| C22 | 28(3) | 43(3) | 51(4) | -1(3) | 11(3) | 2(3) |
| C61 | 40(4) | 80(5) | 49(4) | -7(4) | 23(3) | -1(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O7 | 50(3) | 57(3) | 33(2) | -11(2) | 2(2) | -14(2) |
| C80 | 26(3) | 32(3) | 76(5) | 4(2) | 7(3) | 6(3) |
| C52 | 21(3) | 51(4) | 88(6) | 0(3) | 14(3) | -16(4) |
| C79 | 30(3) | 46(4) | 68(5) | 3(3) | 19(3) | -6(3) |
| C51 | 27(3) | 63(5) | 106(7) | -5(3) | 32(4) | -15(5) |
| C49 | 37(3) | 41(3) | 51(4) | -2(3) | 21(3) | -11(3) |
| C50 | 55(4) | 54(4) | 69(5) | -2(4) | 40(4) | -12(4) |
| N4 | 27(2) | 23(2) | 21(2) | -4.5(17) | 7.1(17) | -1.2(16) |
| N6 | 21(2) | 24(2) | 25(2) | 2.9(16) | 1.2(16) | -0.0(17) |
| C39 | 19(2) | 24(3) | 37(3) | -5(2) | -1(2) | 4(2) |

**Crystallographic Table 107** Bond Lengths for **$Tb_2[L^{VII}]_3$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Tb1 | N3 | 2.558(4) | C41 | C42 | 1.388(9) |
| Tb1 | O1 | 2.273(3) | C19 | C20 | 1.454(7) |
| Tb1 | O2 | 2.279(3) | C1 | C10 | 1.396(7) |
| Tb1 | O4 | 2.379(3) | C1 | C2 | 1.426(7) |
| Tb1 | N2 | 2.472(4) | C66 | C67 | 1.429(7) |
| Tb1 | O3 | 2.350(3) | C66 | C57 | 1.410(7) |
| Tb1 | N1 | 2.487(4) | C72 | C71 | 1.379(8) |
| Tb1 | N4 | 2.538(4) | C9 | C10 | 1.443(7) |
| Tb2 | N5 | 2.462(4) | C9 | C4 | 1.416(8) |
| Tb2 | O4 | 2.344(3) | C9 | C8 | 1.421(8) |
| Tb2 | O3 | 2.359(3) | C10 | C11 | 1.442(7) |
| Tb2 | O6 | 2.220(3) | C60 | C59 | 1.413(9) |
| Tb2 | O5 | 2.211(4) | C60 | C61 | 1.413(8) |
| Tb2 | O7 | 2.464(4) | C17 | C12 | 1.413(7) |
| Tb2 | N6 | 2.463(4) | C17 | C16 | 1.395(7) |
| C40 | N3 | 1.407(6) | C20 | C25 | 1.426(8) |
| C40 | C45 | 1.443(7) | C44 | C43 | 1.371(8) |
| C40 | C41 | 1.374(7) | C76 | C81 | 1.420(7) |
| C68 | N5 | 1.429(6) | C76 | C75 | 1.443(7) |
| C68 | C73 | 1.406(7) | C30 | C31 | 1.368(7) |
| C68 | C69 | 1.398(7) | C4 | C3 | 1.412(8) |
| N3 | C39 | 1.279(6) | C4 | C5 | 1.423(7) |
| N5 | C67 | 1.306(6) | C82 | C81 | 1.416(9) |
| O1 | C1 | 1.316(6) | C82 | C83 | 1.349(8) |
| C29 | C38 | 1.398(7) | C12 | C13 | 1.385(7) |

| | | | | | |
|---|---|---|---|---|---|
| C29 | O3 | 1.340(5) | C53 | C48 | 1.424(8) |
| C29 | C30 | 1.407(7) | C53 | C52 | 1.412(8) |
| C38 | C37 | 1.453(7) | C81 | C80 | 1.419(8) |
| C38 | C39 | 1.462(7) | C34 | C35 | 1.391(11) |
| O2 | C28 | 1.310(6) | C34 | C33 | 1.360(10) |
| O4 | C56 | 1.337(6) | C26 | C25 | 1.419(8) |
| N2 | C18 | 1.302(6) | C26 | C27 | 1.352(8) |
| N2 | C17 | 1.425(6) | C16 | C15 | 1.384(8) |
| C45 | C44 | 1.394(7) | C57 | C58 | 1.425(7) |
| C45 | N4 | 1.421(6) | C69 | C70 | 1.388(8) |
| C56 | C47 | 1.391(7) | C48 | C49 | 1.418(8) |
| C56 | C55 | 1.422(7) | C36 | C35 | 1.367(8) |
| C65 | C66 | 1.460(7) | C31 | C32 | 1.409(8) |
| C65 | C60 | 1.420(8) | C64 | C63 | 1.364(8) |
| C65 | C64 | 1.410(8) | C59 | C58 | 1.361(8) |
| C46 | C47 | 1.444(7) | C78 | C79 | 1.398(9) |
| C46 | N4 | 1.300(6) | C32 | C33 | 1.425(7) |
| C73 | C72 | 1.399(7) | C3 | C2 | 1.363(8) |
| C73 | N6 | 1.427(6) | C84 | C83 | 1.430(7) |
| C74 | C75 | 1.438(7) | C84 | C75 | 1.403(8) |
| C74 | N6 | 1.296(6) | C13 | C14 | 1.378(8) |
| O6 | C84 | 1.313(6) | C42 | C43 | 1.395(10) |
| N1 | C12 | 1.422(6) | C15 | C14 | 1.384(9) |
| N1 | C11 | 1.310(6) | C25 | C24 | 1.414(7) |
| C47 | C48 | 1.447(7) | C24 | C23 | 1.360(9) |
| O5 | C57 | 1.297(6) | C70 | C71 | 1.389(8) |
| C54 | C53 | 1.417(9) | C63 | C62 | 1.403(10) |
| C54 | C55 | 1.355(7) | C23 | C22 | 1.399(9) |
| C21 | C20 | 1.423(7) | C5 | C6 | 1.363(10) |
| C21 | C22 | 1.378(8) | C8 | C7 | 1.377(8) |
| C37 | C36 | 1.424(8) | C7 | C6 | 1.392(10) |
| C37 | C32 | 1.408(8) | C62 | C61 | 1.347(10) |
| C77 | C76 | 1.420(8) | O7 | C85 | 1.427(10) |
| C77 | C78 | 1.370(8) | C80 | C79 | 1.368(10) |
| C18 | C19 | 1.428(7) | C52 | C51 | 1.352(11) |
| C28 | C19 | 1.407(7) | C51 | C50 | 1.397(11) |
| C28 | C27 | 1.433(7) | C49 | C50 | 1.373(8) |

**Crystallographic Table 108** Bond Angles for $Tb_2[L^{VII}]_3$.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O1 | Tb1 | N3 | 87.71(13) | C28 | C19 | C18 | 123.7(5) |
| O2 | Tb1 | N3 | 161.95(13) | C20 | C19 | C18 | 117.1(5) |
| O2 | Tb1 | O1 | 84.37(13) | C20 | C19 | C28 | 119.0(5) |
| O4 | Tb1 | N3 | 101.99(12) | C10 | C1 | O1 | 123.2(5) |
| O4 | Tb1 | O1 | 142.84(12) | C2 | C1 | O1 | 117.9(5) |
| O4 | Tb1 | O2 | 75.47(14) | C2 | C1 | C10 | 118.9(5) |
| N2 | Tb1 | N3 | 124.53(13) | C67 | C66 | C65 | 117.4(5) |
| N2 | Tb1 | O1 | 110.59(13) | C57 | C66 | C65 | 119.8(5) |
| N2 | Tb1 | O2 | 73.51(13) | C57 | C66 | C67 | 122.7(5) |
| N2 | Tb1 | O4 | 93.36(13) | C71 | C72 | C73 | 120.4(5) |
| O3 | Tb1 | N3 | 68.71(12) | C4 | C9 | C10 | 119.6(5) |
| O3 | Tb1 | O1 | 80.94(12) | C8 | C9 | C10 | 123.1(5) |
| O3 | Tb1 | O2 | 93.98(13) | C8 | C9 | C4 | 117.2(5) |
| O3 | Tb1 | O4 | 69.90(11) | C9 | C10 | C1 | 119.6(5) |
| O3 | Tb1 | N2 | 161.48(13) | C11 | C10 | C1 | 121.7(5) |
| N1 | Tb1 | N3 | 73.11(13) | C11 | C10 | C9 | 118.5(5) |
| N1 | Tb1 | O1 | 71.56(13) | C59 | C60 | C65 | 118.7(5) |
| N1 | Tb1 | O2 | 119.16(15) | C61 | C60 | C65 | 119.4(6) |
| N1 | Tb1 | O4 | 145.60(13) | C61 | C60 | C59 | 121.9(6) |
| N1 | Tb1 | N2 | 65.18(14) | C12 | C17 | N2 | 117.2(4) |
| N1 | Tb1 | O3 | 133.31(12) | C16 | C17 | N2 | 124.1(5) |
| N4 | Tb1 | N3 | 63.26(13) | C16 | C17 | C12 | 118.6(5) |
| N4 | Tb1 | O1 | 143.80(13) | C19 | C20 | C21 | 123.1(5) |
| N4 | Tb1 | O2 | 129.42(13) | C25 | C20 | C21 | 116.8(5) |
| N4 | Tb1 | O4 | 68.82(12) | C25 | C20 | C19 | 120.1(5) |
| N4 | Tb1 | N2 | 74.10(13) | C43 | C44 | C45 | 120.5(6) |
| N4 | Tb1 | O3 | 105.56(12) | C81 | C76 | C77 | 116.6(5) |
| N4 | Tb1 | N1 | 79.17(14) | C75 | C76 | C77 | 123.5(5) |
| O4 | Tb2 | N5 | 115.87(12) | C75 | C76 | C81 | 119.7(5) |
| O3 | Tb2 | N5 | 79.90(13) | C31 | C30 | C29 | 121.2(5) |
| O3 | Tb2 | O4 | 70.35(11) | C3 | C4 | C9 | 119.0(5) |
| O6 | Tb2 | N5 | 118.55(14) | C5 | C4 | C9 | 119.8(6) |
| O6 | Tb2 | O4 | 96.52(13) | C5 | C4 | C3 | 121.2(5) |
| O6 | Tb2 | O3 | 161.22(14) | C83 | C82 | C81 | 121.7(5) |
| O5 | Tb2 | N5 | 73.53(14) | C17 | C12 | N1 | 115.3(4) |
| O5 | Tb2 | O4 | 159.70(14) | C13 | C12 | N1 | 124.9(5) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O5 | Tb2 | O3 | 95.10(13) | C13 | C12 | C17 | 119.6(5) |
| O5 | Tb2 | O6 | 93.80(14) | C10 | C11 | N1 | 125.2(5) |
| O7 | Tb2 | N5 | 148.99(15) | C66 | C67 | N5 | 126.7(5) |
| O7 | Tb2 | O4 | 74.27(13) | C48 | C53 | C54 | 118.6(5) |
| O7 | Tb2 | O3 | 76.42(14) | C52 | C53 | C54 | 122.2(6) |
| O7 | Tb2 | O6 | 87.28(16) | C52 | C53 | C48 | 119.3(6) |
| O7 | Tb2 | O5 | 88.85(15) | C82 | C81 | C76 | 118.5(5) |
| N6 | Tb2 | N5 | 66.17(13) | C80 | C81 | C76 | 119.9(6) |
| N6 | Tb2 | O4 | 76.86(13) | C80 | C81 | C82 | 121.7(6) |
| N6 | Tb2 | O3 | 114.69(12) | C33 | C34 | C35 | 119.7(6) |
| N6 | Tb2 | O6 | 73.39(14) | C27 | C26 | C25 | 121.2(6) |
| N6 | Tb2 | O5 | 122.99(14) | C15 | C16 | C17 | 120.9(5) |
| N6 | Tb2 | O7 | 142.95(14) | C66 | C57 | O5 | 123.0(5) |
| C45 | C40 | N3 | 116.1(4) | C58 | C57 | O5 | 118.7(5) |
| C41 | C40 | N3 | 126.3(5) | C58 | C57 | C66 | 118.2(5) |
| C41 | C40 | C45 | 117.6(5) | C70 | C69 | C68 | 121.1(5) |
| C73 | C68 | N5 | 117.2(4) | C53 | C48 | C47 | 119.4(5) |
| C69 | C68 | N5 | 124.0(5) | C49 | C48 | C47 | 122.7(5) |
| C69 | C68 | C73 | 118.8(5) | C49 | C48 | C53 | 117.8(5) |
| C40 | N3 | Tb1 | 115.8(3) | C35 | C36 | C37 | 120.3(7) |
| C39 | N3 | Tb1 | 126.4(3) | C32 | C31 | C30 | 121.1(5) |
| C39 | N3 | C40 | 117.8(4) | C63 | C64 | C65 | 121.7(6) |
| C68 | N5 | Tb2 | 114.6(3) | C58 | C59 | C60 | 121.6(5) |
| C67 | N5 | Tb2 | 127.9(3) | C54 | C55 | C56 | 121.1(5) |
| C67 | N5 | C68 | 117.3(4) | C79 | C78 | C77 | 121.0(6) |
| C1 | O1 | Tb1 | 128.8(3) | C31 | C32 | C37 | 119.7(5) |
| O3 | C29 | C38 | 121.0(4) | C33 | C32 | C37 | 119.1(6) |
| C30 | C29 | C38 | 119.4(4) | C33 | C32 | C31 | 121.1(6) |
| C30 | C29 | O3 | 119.6(4) | C2 | C3 | C4 | 121.0(5) |
| C37 | C38 | C29 | 120.0(5) | C83 | C84 | O6 | 117.9(5) |
| C39 | C38 | C29 | 121.2(4) | C75 | C84 | O6 | 123.3(5) |
| C39 | C38 | C37 | 118.7(5) | C75 | C84 | C83 | 118.8(5) |
| C28 | O2 | Tb1 | 136.2(3) | C14 | C13 | C12 | 120.8(6) |
| Tb2 | O4 | Tb1 | 109.50(13) | C43 | C42 | C41 | 119.8(5) |
| C56 | O4 | Tb1 | 117.9(3) | C59 | C58 | C57 | 122.1(6) |
| C56 | O4 | Tb2 | 132.5(3) | C84 | C83 | C82 | 121.4(6) |
| C18 | N2 | Tb1 | 128.5(4) | C76 | C75 | C74 | 118.9(5) |
| C17 | N2 | Tb1 | 114.2(3) | C84 | C75 | C74 | 121.6(5) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C17 | N2 | C18 | 117.2(4) | C84 | C75 | C76 | 119.5(5) |
| Tb2 | O3 | Tb1 | 110.02(13) | C14 | C15 | C16 | 119.8(5) |
| C29 | O3 | Tb1 | 122.8(3) | C3 | C2 | C1 | 121.4(5) |
| C29 | O3 | Tb2 | 126.1(3) | C26 | C25 | C20 | 118.4(5) |
| C44 | C45 | C40 | 119.9(5) | C24 | C25 | C20 | 119.9(5) |
| N4 | C45 | C40 | 115.4(4) | C24 | C25 | C26 | 121.7(5) |
| N4 | C45 | C44 | 124.6(5) | C23 | C24 | C25 | 121.0(6) |
| C47 | C56 | O4 | 121.8(4) | C26 | C27 | C28 | 122.4(6) |
| C55 | C56 | O4 | 118.4(5) | C71 | C70 | C69 | 119.4(5) |
| C55 | C56 | C47 | 119.7(5) | C62 | C63 | C64 | 120.3(6) |
| C60 | C65 | C66 | 119.4(5) | C70 | C71 | C72 | 120.5(5) |
| C64 | C65 | C66 | 123.3(5) | C22 | C23 | C24 | 120.5(5) |
| C64 | C65 | C60 | 117.3(5) | C6 | C5 | C4 | 121.6(6) |
| N4 | C46 | C47 | 125.1(5) | C7 | C8 | C9 | 120.9(6) |
| C72 | C73 | C68 | 119.7(5) | C15 | C14 | C13 | 120.3(6) |
| N6 | C73 | C68 | 116.2(4) | C6 | C7 | C8 | 121.8(7) |
| N6 | C73 | C72 | 124.1(5) | C42 | C43 | C44 | 120.2(6) |
| N6 | C74 | C75 | 127.3(5) | C36 | C35 | C34 | 121.4(7) |
| C84 | O6 | Tb2 | 133.6(3) | C32 | C33 | C34 | 121.0(7) |
| C12 | N1 | Tb1 | 114.7(3) | C61 | C62 | C63 | 119.8(6) |
| C11 | N1 | Tb1 | 126.0(3) | C7 | C6 | C5 | 118.7(6) |
| C11 | N1 | C12 | 119.0(4) | C23 | C22 | C21 | 119.7(6) |
| C46 | C47 | C56 | 121.2(4) | C62 | C61 | C60 | 121.5(6) |
| C48 | C47 | C56 | 119.5(5) | C85 | O7 | Tb2 | 134.6(5) |
| C48 | C47 | C46 | 119.2(5) | C79 | C80 | C81 | 121.5(6) |
| C57 | O5 | Tb2 | 138.1(3) | C51 | C52 | C53 | 121.2(7) |
| C55 | C54 | C53 | 121.6(5) | C80 | C79 | C78 | 118.9(6) |
| C22 | C21 | C20 | 122.1(6) | C50 | C51 | C52 | 120.2(6) |
| C36 | C37 | C38 | 123.0(5) | C50 | C49 | C48 | 120.7(7) |
| C32 | C37 | C38 | 118.5(5) | C49 | C50 | C51 | 120.7(7) |
| C32 | C37 | C36 | 118.4(5) | C45 | N4 | Tb1 | 116.8(3) |
| C78 | C77 | C76 | 122.0(6) | C46 | N4 | Tb1 | 122.9(3) |
| C19 | C18 | N2 | 126.8(5) | C46 | N4 | C45 | 120.0(4) |
| C19 | C28 | O2 | 123.2(5) | C73 | N6 | Tb2 | 114.8(3) |
| C27 | C28 | O2 | 118.4(5) | C74 | N6 | Tb2 | 126.0(3) |
| C27 | C28 | C19 | 118.4(5) | C74 | N6 | C73 | 118.9(4) |
| C42 | C41 | C40 | 122.0(6) | C38 | C39 | N3 | 125.4(5) |

**Crystallographic Table 109** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **$Tb_2[L^{VII}]_3$**.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H46 | 1245(3) | 5610(2) | 3841(2) | 28.6(12) |
| H74 | 1108(3) | 7178(3) | 2862(3) | 32.0(13) |
| H54 | -1067(3) | 5443(3) | 1687(3) | 40.6(15) |
| H21 | -898(3) | 3724(3) | 2826(3) | 39.6(15) |
| H77 | 76(3) | 7030(3) | 3256(3) | 43.0(15) |
| H18 | 234(3) | 3493(2) | 2990(3) | 31.2(13) |
| H41 | 4468(3) | 5086(3) | 4098(3) | 45.4(16) |
| H72 | 1837(3) | 6933(3) | 3664(3) | 35.5(14) |
| H44 | 1983(4) | 5362(3) | 4680(3) | 42.6(15) |
| H30 | 3386(3) | 4920(3) | 644(3) | 38.2(14) |
| H82 | -1364(3) | 7112(3) | 856(3) | 44.1(16) |
| H11 | 3550(3) | 3223(3) | 3864(3) | 32.0(13) |
| H67 | 4273(3) | 6882(2) | 2085(3) | 32.5(13) |
| H34 | 7031(3) | 4857(3) | 1637(4) | 64(2) |
| H26 | -651(3) | 3631(3) | 287(3) | 51.2(19) |
| H16 | 381(3) | 3782(3) | 3956(3) | 40.9(15) |
| H69 | 4308(3) | 6730(3) | 3033(3) | 37.5(14) |
| H36 | 5522(3) | 5047(3) | 2971(3) | 50.5(18) |
| H31 | 4646(3) | 4842(3) | 430(3) | 39.7(15) |
| H64 | 5361(3) | 6678(3) | 1971(3) | 45.6(16) |
| H59 | 4592(4) | 6539(4) | -582(3) | 54.6(19) |
| H55 | 144(3) | 5391(2) | 1374(3) | 33.5(13) |
| H78 | -1094(4) | 7222(3) | 3626(4) | 53.6(18) |
| H3 | 5493(3) | 3275(3) | 1857(3) | 41.9(15) |
| H13 | 2992(3) | 3526(3) | 4667(3) | 42.6(16) |
| H42 | 4281(4) | 5285(3) | 5180(3) | 55.0(19) |
| H58 | 3338(4) | 6412(3) | -397(3) | 47.7(17) |
| H83 | -236(3) | 6856(3) | 464(3) | 45.8(16) |
| H15 | 785(4) | 3604(3) | 5058(3) | 52.3(18) |
| H2 | 4232(3) | 3461(3) | 1461(3) | 37.0(14) |
| H24 | -1945(3) | 3478(3) | 652(3) | 47.5(17) |
| H27 | 627(3) | 3845(3) | 516(3) | 50.7(19) |
| H70 | 4148(3) | 6956(3) | 4119(3) | 43.5(16) |
| H63 | 6621(4) | 6747(4) | 1759(4) | 64(2) |
| H71 | 2908(3) | 7047(3) | 4432(3) | 46.2(16) |

| | | | | |
|---|---|---|---|---|
| H23 | -2727(3) | 3441(3) | 1476(3) | 49.0(17) |
| H5 | 6519(3) | 3209(3) | 2782(4) | 52.2(19) |
| H8 | 4693(3) | 3411(3) | 4258(3) | 46.9(16) |
| H14 | 2091(4) | 3474(3) | 5410(3) | 55.2(19) |
| H7 | 5980(4) | 3280(3) | 4622(4) | 61(2) |
| H43 | 3034(4) | 5434(3) | 5467(3) | 55.2(19) |
| H35 | 6766(3) | 4931(4) | 2719(4) | 67(2) |
| H33 | 6038(3) | 4837(3) | 802(4) | 57(2) |
| H62 | 6928(4) | 6749(4) | 677(4) | 73(3) |
| H6 | 6906(3) | 3200(3) | 3892(4) | 61(2) |
| H22 | -2211(3) | 3593(3) | 2568(3) | 48.1(17) |
| H61 | 5972(4) | 6657(4) | -172(4) | 66(2) |
| H7a | 1390(30) | 4821(12) | 891(10) | 69.9(17) |
| H80 | -2133(3) | 7270(3) | 1782(4) | 53.9(19) |
| H52 | -1943(4) | 5450(3) | 2560(4) | 63(2) |
| H79 | -2208(4) | 7371(3) | 2892(4) | 56.2(19) |
| H51 | -2125(4) | 5362(4) | 3640(5) | 76(3) |
| H49 | 170(4) | 5241(3) | 4152(3) | 50.1(18) |
| H50 | -1070(4) | 5252(4) | 4438(4) | 68(2) |
| H39 | 4411(3) | 5391(2) | 3111(3) | 32.5(13) |
| H85a | 1187(10) | 4990(30) | -236(9) | 125(4) |
| H85b | 2050(30) | 5250(20) | -112(14) | 125(4) |
| H85c | 1860(40) | 4517(13) | 75(7) | 125(4) |

**Crystallographic Table 110** Solvent masks information for **$Tb_2[L^{VII}]_3$**.

| Number | X | Y | Z | Volume | Electron count | Content |
|---|---|---|---|---|---|---|
| 1 | 0.000 | 0.000 | 0.500 | 7.0 | 0.0 | |
| 2 | 0.152 | 0.204 | 0.032 | 346.2 | 109.5 | 2DCM/H2O |
| 3 | 0.152 | 0.296 | 0.532 | 346.2 | 105.1 | 2DCM/H2O |
| 4 | 0.000 | 0.500 | 0.000 | 7.0 | 0.0 | |
| 5 | -0.152 | 0.704 | 0.468 | 346.2 | 112.3 | 2DCM/H2O |
| 6 | -0.152 | 0.796 | 0.968 | 346.2 | 107.9 | 2DCM/H2O |

Refinement model description

Number of restraints - 3, number of constraints - 113.

## $Dy_2[L^{VII}]_3$

**Crystallographic Table 111** Crystal data and structure refinement for $Dy_2[L^{VII}]_3$

| | |
|---|---|
| Identification code | $Dy_2[L^{VII}]_3$ |
| Empirical formula | $C_{87}H_{62}N_6O_7Dy_2Cl_4$ |
| Formula weight | 1770.30 |
| Temperature/K | 180.45 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 17.4752(9) |
| b/Å | 20.4942(11) |
| c/Å | 20.6008(10) |
| α/° | 90 |
| β/° | 96.4456(10) |
| γ/° | 90 |
| Volume/Å$^3$ | 7331.3(7) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.6038 |
| m/mm$^{-1}$ | 2.231 |
| F(000) | 3530.8 |
| Crystal size/mm$^3$ | 0.2 × 0.18 × 0.09 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 2.34 to 45.98° |
| Index ranges | $-19 \le h \le 19$, $-22 \le k \le 22$, $-22 \le l \le 22$ |
| Reflections collected | 94401 |
| Independent reflections | 10188 [$R_{int}$ = 0.0550, $R_{sigma}$ = 0.0357] |
| Data/restraints/parameters | 10188/2/958 |
| Goodness-of-fit on $F^2$ | 1.107 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0489, $wR_2$ = 0.0911 |
| Final R indexes [all data] | $R_1$ = 0.0618, $wR_2$ = 0.0967 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.12/-1.58 |

**Crystallographic Table 112** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for $Dy_2[L^{VII}]_3$. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Dy1 | 2906.80(18) | 6036.87(17) | 3535.16(16) | 19.23(10) |
| Dy2 | 2741.09(18) | 4440.98(16) | 2554.43(15) | 16.03(10) |
| O1 | 1910(3) | 3720(2) | 2914(2) | 21.5(11) |

| | | | | |
|---|---|---|---|---|
| O6 | 3900(3) | 6647(3) | 3898(2) | 30.4(13) |
| N6 | 3186(3) | 6722(3) | 2619(3) | 18.7(13) |
| O5 | 2233(3) | 6380(3) | 4307(2) | 30.7(13) |
| O2 | 3565(3) | 4039(3) | 3384(2) | 28.7(13) |
| N1 | 2260(3) | 3729(3) | 1631(3) | 19.8(13) |
| O3 | 2131(2) | 5126(2) | 3249(2) | 20.1(11) |
| N4 | 3009(3) | 5145(3) | 1600(3) | 16.9(13) |
| O4 | 3550(3) | 5328(2) | 2903(2) | 20.5(11) |
| C85 | 3316(8) | 4967(8) | 4933(7) | 109(5) |
| N5 | 1769(3) | 6576(3) | 2974(3) | 20.0(13) |
| N2 | 3755(3) | 3869(3) | 2038(3) | 19.3(13) |
| N3 | 1589(3) | 5018(3) | 1931(3) | 21.7(14) |
| C40 | 1657(4) | 5138(4) | 1258(3) | 23.1(17) |
| C45 | 2408(4) | 5214(3) | 1090(3) | 22.3(17) |
| C84 | 4524(4) | 6821(3) | 3646(4) | 24.9(18) |
| C83 | 5218(5) | 6914(4) | 4072(4) | 36(2) |
| C82 | 5895(4) | 7055(4) | 3848(4) | 34(2) |
| C81 | 5955(4) | 7110(4) | 3170(4) | 29.9(19) |
| C80 | 6667(4) | 7235(4) | 2928(5) | 36(2) |
| C79 | 6722(5) | 7291(4) | 2276(5) | 46(2) |
| C78 | 6066(5) | 7213(4) | 1838(5) | 41(2) |
| C77 | 5361(5) | 7099(4) | 2052(4) | 34(2) |
| C76 | 5278(4) | 7060(3) | 2727(4) | 23.9(17) |
| C75 | 4550(4) | 6939(3) | 2977(3) | 22.2(17) |
| C74 | 3856(4) | 6965(3) | 2533(4) | 22.8(17) |
| C73 | 2564(4) | 6797(3) | 2122(3) | 19.6(16) |
| C68 | 1817(4) | 6732(4) | 2303(4) | 26.0(18) |
| C67 | 1129(4) | 6699(3) | 3208(4) | 23.4(17) |
| C66 | 937(4) | 6582(3) | 3859(3) | 22.2(17) |
| C57 | 1513(4) | 6473(4) | 4380(4) | 26.9(18) |
| C58 | 1281(5) | 6464(4) | 5026(4) | 38(2) |
| C59 | 542(5) | 6533(4) | 5136(4) | 41(2) |
| C60 | -56(5) | 6617(4) | 4624(4) | 34(2) |
| C65 | 135(4) | 6640(4) | 3973(4) | 26.3(18) |
| C64 | -478(4) | 6684(4) | 3475(4) | 34(2) |
| C63 | -1232(5) | 6724(5) | 3594(5) | 49(3) |
| C62 | -1406(5) | 6719(5) | 4236(5) | 58(3) |
| C61 | -836(5) | 6654(5) | 4733(5) | 48(2) |

| | | | | |
|---|---|---|---|---|
| C69 | 1186(4) | 6785(4) | 1826(4) | 27.1(18) |
| C70 | 1283(5) | 6911(4) | 1185(4) | 33(2) |
| C71 | 2022(5) | 6971(4) | 1003(4) | 34(2) |
| C72 | 2644(4) | 6906(4) | 1463(4) | 26.9(18) |
| C18 | 4432(4) | 3701(3) | 2300(4) | 22.0(17) |
| C19 | 4760(4) | 3779(3) | 2964(3) | 18.9(16) |
| C20 | 5582(4) | 3691(3) | 3112(4) | 24.1(17) |
| C25 | 5912(4) | 3643(4) | 3770(4) | 30.0(19) |
| C24 | 6715(4) | 3549(4) | 3913(4) | 38(2) |
| C23 | 7182(4) | 3523(4) | 3433(4) | 39(2) |
| C22 | 6868(4) | 3595(4) | 2782(4) | 36(2) |
| C21 | 6091(4) | 3679(4) | 2631(4) | 29.6(19) |
| C26 | 5429(5) | 3706(5) | 4274(4) | 42(2) |
| C27 | 4659(4) | 3838(4) | 4131(4) | 36(2) |
| C28 | 4303(4) | 3893(4) | 3472(4) | 26.3(18) |
| C17 | 3554(4) | 3739(3) | 1362(3) | 19.2(16) |
| C12 | 2775(4) | 3660(3) | 1150(3) | 21.5(17) |
| C11 | 1579(4) | 3466(3) | 1536(3) | 20.3(16) |
| C10 | 1007(4) | 3492(3) | 1982(4) | 21.5(17) |
| C1 | 1213(4) | 3568(3) | 2658(3) | 20.9(16) |
| C2 | 628(4) | 3464(4) | 3083(4) | 26.5(18) |
| C3 | -116(4) | 3347(4) | 2849(4) | 29.7(19) |
| C4 | -357(4) | 3326(4) | 2173(4) | 26.7(18) |
| C9 | 204(4) | 3391(4) | 1734(4) | 25.2(17) |
| C8 | -53(5) | 3377(4) | 1060(4) | 36(2) |
| C7 | -824(5) | 3299(4) | 847(5) | 45(2) |
| C6 | -1370(5) | 3246(4) | 1289(5) | 43(2) |
| C5 | -1142(4) | 3259(4) | 1934(4) | 37(2) |
| C13 | 2546(4) | 3565(4) | 485(4) | 29.1(19) |
| C14 | 3077(5) | 3543(5) | 43(4) | 42(2) |
| C15 | 3850(5) | 3621(4) | 252(4) | 36(2) |
| C16 | 4090(5) | 3722(4) | 903(4) | 28.9(19) |
| C39 | 968(4) | 5182(3) | 2166(4) | 21.3(17) |
| C38 | 807(4) | 5078(4) | 2830(4) | 22.6(17) |
| C29 | 1394(4) | 5055(4) | 3343(4) | 22.3(17) |
| C30 | 1203(4) | 4960(4) | 3991(4) | 27.5(18) |
| C31 | 464(4) | 4911(4) | 4117(4) | 33(2) |
| C32 | -153(4) | 4947(4) | 3615(4) | 32(2) |

| | | | | |
|---|---|---|---|---|
| C37 | 6(4) | 5026(4) | 2961(4) | 27.1(18) |
| C36 | -618(4) | 5013(4) | 2462(5) | 38(2) |
| C35 | -1361(5) | 4942(5) | 2613(5) | 52(3) |
| C34 | -1520(5) | 4893(4) | 3258(5) | 48(3) |
| C33 | -930(5) | 4883(4) | 3751(5) | 46(2) |
| C46 | 3680(4) | 5391(3) | 1541(3) | 21.5(17) |
| C47 | 4345(4) | 5356(3) | 2032(3) | 18.5(16) |
| C56 | 4247(4) | 5353(3) | 2696(3) | 18.3(16) |
| C55 | 4905(4) | 5398(3) | 3162(4) | 22.8(17) |
| C54 | 5631(4) | 5425(4) | 2985(4) | 30.7(19) |
| C53 | 5754(4) | 5402(3) | 2316(4) | 29.5(19) |
| C52 | 6504(5) | 5411(4) | 2119(5) | 43(2) |
| C51 | 6624(5) | 5362(5) | 1485(5) | 54(3) |
| C50 | 5993(5) | 5299(5) | 1009(5) | 51(3) |
| C49 | 5251(5) | 5294(4) | 1168(4) | 33(2) |
| C48 | 5106(4) | 5359(3) | 1828(4) | 23.7(18) |
| C44 | 2510(5) | 5319(4) | 432(4) | 30.6(19) |
| C43 | 1886(5) | 5352(4) | -38(4) | 42(2) |
| C42 | 1151(5) | 5262(5) | 135(4) | 46(2) |
| C41 | 1033(5) | 5150(4) | 777(4) | 35(2) |
| O7 | 3453(3) | 5195(3) | 4282(2) | 39.0(14) |

**Crystallographic Table 113** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **$Dy_2[L^{VII}]_3$.** The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{12}$** | **$U_{13}$** | **$U_{23}$** |
|---|---|---|---|---|---|---|
| Dy1 | 14.73(18) | 26.6(2) | 16.55(18) | -4.48(15) | 2.64(13) | -2.37(15) |
| Dy2 | 10.01(17) | 23.27(19) | 14.92(17) | 0.33(14) | 1.88(12) | 1.19(15) |
| O6 | 20(3) | 47(4) | 24(3) | -16(3) | 5(2) | 0(3) |
| N6 | 7(3) | 21(3) | 27(3) | -2(3) | 0(3) | -4(3) |
| O5 | 24(3) | 47(4) | 22(3) | 1(3) | 6(2) | -7(3) |
| O2 | 12(3) | 52(4) | 22(3) | 4(2) | 3(2) | 10(3) |
| N1 | 18(3) | 22(3) | 19(3) | 1(3) | 4(3) | 3(3) |
| O3 | 13(3) | 26(3) | 22(3) | -4(2) | 4(2) | -2(2) |
| N4 | 5(3) | 22(3) | 24(3) | 1(3) | 3(2) | 0(3) |
| O4 | 14(3) | 29(3) | 19(3) | -2(2) | 3(2) | -2(2) |
| N5 | 17(3) | 23(3) | 21(3) | -1(3) | 8(3) | -1(3) |
| N2 | 16(3) | 17(3) | 25(3) | -3(3) | 4(3) | 5(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N3 | 17(3) | 22(3) | 26(3) | -1(3) | 2(3) | -2(3) |
| C40 | 19(4) | 31(5) | 18(4) | 4(3) | -4(3) | 5(3) |
| C45 | 26(4) | 14(4) | 27(4) | 5(3) | 4(3) | 4(3) |
| C84 | 24(4) | 13(4) | 36(5) | -9(3) | 0(4) | -7(3) |
| C83 | 37(5) | 40(5) | 29(5) | -14(4) | 0(4) | -2(4) |
| C82 | 20(4) | 33(5) | 45(5) | -7(4) | -7(4) | -2(4) |
| C81 | 25(4) | 18(4) | 47(5) | -8(3) | 6(4) | -3(4) |
| C80 | 19(4) | 24(5) | 63(6) | -1(4) | 3(4) | -2(4) |
| C79 | 31(5) | 38(6) | 74(7) | 1(4) | 25(5) | 10(5) |
| C78 | 31(5) | 42(5) | 54(6) | 2(4) | 24(4) | 9(5) |
| C77 | 32(5) | 28(5) | 42(5) | -2(4) | 7(4) | -2(4) |
| C76 | 24(4) | 14(4) | 35(5) | -4(3) | 10(3) | -1(3) |
| C75 | 22(4) | 17(4) | 27(4) | -6(3) | 1(3) | -2(3) |
| C74 | 22(4) | 22(4) | 25(4) | 2(3) | 6(3) | -1(3) |
| C73 | 23(4) | 16(4) | 21(4) | 0(3) | 4(3) | 1(3) |
| C68 | 24(4) | 28(5) | 28(4) | 3(3) | 8(3) | -3(3) |
| C67 | 25(4) | 18(4) | 27(4) | 4(3) | -2(3) | 0(3) |
| C66 | 22(4) | 20(4) | 26(4) | 1(3) | 10(3) | -7(3) |
| C57 | 28(5) | 28(5) | 26(4) | -3(4) | 10(4) | -5(3) |
| C58 | 33(5) | 55(6) | 28(5) | -2(4) | 10(4) | -11(4) |
| C59 | 44(6) | 54(6) | 27(5) | -1(5) | 12(4) | -12(4) |
| C60 | 31(5) | 37(5) | 39(5) | 2(4) | 18(4) | -5(4) |
| C65 | 22(4) | 22(4) | 37(5) | 2(3) | 14(4) | 1(4) |
| C64 | 24(4) | 42(5) | 37(5) | 9(4) | 10(4) | 7(4) |
| C63 | 36(5) | 64(7) | 48(6) | 10(5) | 8(4) | 17(5) |
| C62 | 27(5) | 81(8) | 70(7) | 16(5) | 26(5) | 13(6) |
| C61 | 40(6) | 64(7) | 45(6) | 1(5) | 24(5) | -3(5) |
| C69 | 19(4) | 34(5) | 28(4) | 0(3) | 2(3) | 0(4) |
| C70 | 30(5) | 39(5) | 27(5) | 3(4) | -4(4) | 7(4) |
| C71 | 36(5) | 46(5) | 22(4) | 0(4) | 8(4) | 1(4) |
| C72 | 21(4) | 32(5) | 29(4) | -6(3) | 4(3) | 8(4) |
| C18 | 18(4) | 14(4) | 36(5) | 2(3) | 11(3) | 2(3) |
| C19 | 17(4) | 15(4) | 24(4) | 1(3) | 1(3) | 7(3) |
| C20 | 18(4) | 17(4) | 38(5) | 0(3) | 8(3) | 11(3) |
| C25 | 22(4) | 30(5) | 39(5) | 3(4) | 4(4) | 14(4) |
| C24 | 21(4) | 46(6) | 43(5) | 0(4) | -7(4) | 13(4) |
| C23 | 10(4) | 44(6) | 62(6) | 1(4) | 0(4) | 5(5) |
| C22 | 20(4) | 43(5) | 46(5) | -2(4) | 11(4) | 1(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C21 | 19(4) | 30(5) | 39(5) | 1(3) | 3(4) | 3(4) |
| C26 | 37(5) | 61(6) | 27(5) | 6(5) | -3(4) | 22(4) |
| C27 | 26(4) | 60(6) | 23(4) | 14(4) | 5(3) | 17(4) |
| C28 | 22(4) | 26(4) | 31(4) | 0(3) | 4(3) | 12(4) |
| C17 | 24(4) | 15(4) | 18(4) | -1(3) | 2(3) | 3(3) |
| C12 | 26(4) | 18(4) | 21(4) | 6(3) | 6(3) | 4(3) |
| C11 | 21(4) | 23(4) | 17(4) | 5(3) | 0(3) | -1(3) |
| C10 | 16(4) | 17(4) | 31(4) | -1(3) | 3(3) | 2(3) |
| C2 | 32(5) | 28(4) | 21(4) | -1(4) | 9(3) | 5(3) |
| C3 | 18(4) | 29(5) | 46(5) | -2(3) | 20(4) | 2(4) |
| C4 | 18(4) | 22(4) | 40(5) | -1(3) | 4(4) | 0(4) |
| C9 | 25(4) | 21(4) | 28(4) | 2(3) | -3(3) | 0(3) |
| C8 | 26(5) | 37(5) | 42(5) | -4(4) | -9(4) | 7(4) |
| C7 | 42(6) | 42(6) | 47(6) | 2(4) | -12(5) | 3(5) |
| C6 | 16(4) | 42(6) | 66(7) | 0(4) | -19(4) | 4(5) |
| C5 | 20(4) | 34(5) | 57(6) | -6(4) | 7(4) | -1(4) |
| C13 | 27(4) | 35(5) | 25(4) | 0(4) | 1(4) | -3(4) |
| C14 | 46(6) | 57(6) | 22(5) | 0(5) | 7(4) | -2(4) |
| C15 | 43(5) | 36(5) | 33(5) | 11(4) | 21(4) | 5(4) |
| C16 | 31(5) | 29(5) | 29(5) | 10(4) | 15(4) | 7(4) |
| C39 | 8(4) | 18(4) | 36(5) | 0(3) | -3(3) | -1(3) |
| C38 | 16(4) | 23(4) | 30(4) | 4(3) | 8(3) | -3(3) |
| C29 | 13(4) | 25(4) | 31(4) | -3(3) | 9(3) | -8(3) |
| C30 | 21(4) | 32(5) | 31(5) | -4(4) | 12(3) | -4(4) |
| C31 | 31(5) | 33(5) | 40(5) | -6(4) | 20(4) | -4(4) |
| C32 | 22(4) | 21(4) | 55(6) | -1(3) | 18(4) | -6(4) |
| C37 | 17(4) | 21(4) | 44(5) | 2(3) | 6(4) | -6(4) |
| C36 | 22(5) | 37(5) | 56(6) | 0(4) | 7(4) | -3(4) |
| C35 | 10(4) | 61(7) | 84(8) | 1(4) | 4(5) | -8(6) |
| C34 | 16(5) | 44(6) | 85(8) | 1(4) | 18(5) | 1(5) |
| C33 | 33(5) | 41(6) | 69(7) | -4(4) | 27(5) | 4(5) |
| C46 | 33(5) | 15(4) | 19(4) | 9(3) | 11(3) | -1(3) |
| C47 | 15(4) | 11(4) | 32(4) | -2(3) | 10(3) | 2(3) |
| C56 | 10(4) | 16(4) | 29(4) | -2(3) | 6(3) | 3(3) |
| C55 | 15(4) | 22(4) | 32(4) | -2(3) | 4(3) | 5(3) |
| C54 | 16(4) | 27(5) | 48(5) | 1(3) | -2(4) | 0(4) |
| C53 | 19(4) | 15(4) | 56(6) | 0(3) | 12(4) | 0(4) |
| C52 | 20(5) | 36(5) | 75(7) | 6(4) | 15(5) | 9(5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C51 | 27(5) | 59(7) | 83(8) | 8(5) | 34(5) | 16(6) |
| C50 | 45(6) | 56(6) | 61(7) | 10(5) | 40(5) | 13(5) |
| C49 | 35(5) | 28(5) | 39(5) | 3(4) | 16(4) | 3(4) |
| C48 | 18(4) | 12(4) | 43(5) | 2(3) | 13(4) | 6(3) |
| C44 | 30(5) | 35(5) | 27(4) | 10(4) | 4(4) | 8(4) |
| C43 | 59(6) | 50(6) | 15(4) | 11(5) | -1(4) | 6(4) |
| C42 | 42(6) | 52(6) | 38(5) | 10(5) | -16(4) | 9(5) |
| C41 | 29(5) | 41(5) | 33(5) | 4(4) | -1(4) | 0(4) |
| O7 | 38(3) | 54(4) | 24(3) | 4(3) | -2(3) | 10(3) |

**Crystallographic Table 114** Bond Lengths for **$Dy_2[L^{VII}]_3$.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Dy1 | O6 | 2.202(5) | C63 | C62 | 1.389(13) |
| Dy1 | N6 | 2.446(6) | C62 | C61 | 1.353(13) |
| Dy1 | O5 | 2.197(5) | C69 | C70 | 1.375(10) |
| Dy1 | O3 | 2.343(5) | C70 | C71 | 1.389(11) |
| Dy1 | O4 | 2.324(5) | C71 | C72 | 1.366(10) |
| Dy1 | N5 | 2.448(6) | C18 | C19 | 1.431(10) |
| Dy1 | O7 | 2.434(5) | C19 | C20 | 1.445(10) |
| Dy2 | O1 | 2.255(5) | C19 | C28 | 1.405(10) |
| Dy2 | O2 | 2.263(5) | C20 | C25 | 1.417(11) |
| Dy2 | N1 | 2.469(6) | C20 | C21 | 1.405(10) |
| Dy2 | O3 | 2.345(5) | C25 | C24 | 1.415(10) |
| Dy2 | N4 | 2.525(6) | C25 | C26 | 1.415(11) |
| Dy2 | O4 | 2.365(5) | C24 | C23 | 1.353(12) |
| Dy2 | N2 | 2.464(6) | C23 | C22 | 1.398(12) |
| Dy2 | N3 | 2.554(6) | C22 | C21 | 1.370(10) |
| O1 | C1 | 1.309(8) | C26 | C27 | 1.371(11) |
| O6 | C84 | 1.308(8) | C27 | C28 | 1.433(10) |
| N6 | C74 | 1.302(9) | C17 | C12 | 1.391(10) |
| N6 | C73 | 1.415(9) | C17 | C16 | 1.404(10) |
| O5 | C57 | 1.298(9) | C12 | C13 | 1.398(10) |
| O2 | C28 | 1.316(8) | C11 | C10 | 1.432(10) |
| N1 | C12 | 1.417(9) | C10 | C1 | 1.409(10) |
| N1 | C11 | 1.301(9) | C10 | C9 | 1.453(10) |
| O3 | C29 | 1.331(8) | C1 | C2 | 1.433(10) |
| N4 | C45 | 1.407(9) | C2 | C3 | 1.356(10) |
| N4 | C46 | 1.295(9) | C3 | C4 | 1.409(11) |

| | | | | | |
|---|---|---|---|---|---|
| O4 | C56 | 1.335(8) | C4 | C9 | 1.414(10) |
| C85 | O7 | 1.465(14) | C4 | C5 | 1.412(10) |
| N5 | C68 | 1.430(9) | C9 | C8 | 1.410(11) |
| N5 | C67 | 1.291(9) | C8 | C7 | 1.378(11) |
| N2 | C18 | 1.290(9) | C7 | C6 | 1.396(13) |
| N2 | C17 | 1.423(9) | C6 | C5 | 1.344(12) |
| N3 | C40 | 1.425(9) | C13 | C14 | 1.371(11) |
| N3 | C39 | 1.282(9) | C14 | C15 | 1.381(12) |
| C40 | C45 | 1.402(10) | C15 | C16 | 1.375(11) |
| C40 | C41 | 1.389(10) | C39 | C38 | 1.442(10) |
| C45 | C44 | 1.403(10) | C38 | C29 | 1.389(10) |
| C84 | C83 | 1.428(10) | C38 | C37 | 1.459(10) |
| C84 | C75 | 1.405(10) | C29 | C30 | 1.426(10) |
| C83 | C82 | 1.349(11) | C30 | C31 | 1.350(10) |
| C82 | C81 | 1.416(11) | C31 | C32 | 1.411(11) |
| C81 | C80 | 1.415(11) | C32 | C37 | 1.415(11) |
| C81 | C76 | 1.414(11) | C32 | C33 | 1.423(11) |
| C80 | C79 | 1.363(12) | C37 | C36 | 1.412(11) |
| C79 | C78 | 1.386(12) | C36 | C35 | 1.376(11) |
| C78 | C77 | 1.374(11) | C35 | C34 | 1.392(13) |
| C77 | C76 | 1.418(11) | C34 | C33 | 1.365(13) |
| C76 | C75 | 1.445(10) | C46 | C47 | 1.454(10) |
| C75 | C74 | 1.436(10) | C47 | C56 | 1.398(10) |
| C73 | C68 | 1.405(10) | C47 | C48 | 1.439(9) |
| C73 | C72 | 1.398(10) | C56 | C55 | 1.416(10) |
| C68 | C69 | 1.395(10) | C55 | C54 | 1.360(10) |
| C67 | C66 | 1.439(10) | C54 | C53 | 1.418(11) |
| C66 | C57 | 1.405(10) | C53 | C52 | 1.415(11) |
| C66 | C65 | 1.451(10) | C53 | C48 | 1.429(11) |
| C57 | C58 | 1.435(11) | C52 | C51 | 1.349(13) |
| C58 | C59 | 1.344(11) | C51 | C50 | 1.398(14) |
| C59 | C60 | 1.410(12) | C50 | C49 | 1.372(11) |
| C60 | C65 | 1.418(11) | C49 | C48 | 1.417(11) |
| C60 | C61 | 1.408(11) | C44 | C43 | 1.376(11) |
| C65 | C64 | 1.401(11) | C43 | C42 | 1.383(12) |
| C64 | C63 | 1.370(11) | C42 | C41 | 1.380(12) |

**Crystallographic Table 115** Bond Angles for **$Dy_2[L^{VII}]_3$**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| N6 | Dy1 | O6 | 73.62(18) | C65 | C66 | C57 | 120.7(6) |
| O5 | Dy1 | O6 | 92.19(19) | C66 | C57 | O5 | 123.8(6) |
| O5 | Dy1 | N6 | 122.98(19) | C58 | C57 | O5 | 119.0(7) |
| O3 | Dy1 | O6 | 161.84(18) | C58 | C57 | C66 | 117.2(7) |
| O3 | Dy1 | N6 | 115.03(17) | C59 | C58 | C57 | 122.2(8) |
| O3 | Dy1 | O5 | 95.45(17) | C60 | C59 | C58 | 122.2(8) |
| O4 | Dy1 | O6 | 97.64(17) | C65 | C60 | C59 | 118.5(7) |
| O4 | Dy1 | N6 | 77.02(17) | C61 | C60 | C59 | 122.5(8) |
| O4 | Dy1 | O5 | 159.69(18) | C61 | C60 | C65 | 119.0(8) |
| O4 | Dy1 | O3 | 70.37(15) | C60 | C65 | C66 | 119.1(7) |
| N5 | Dy1 | O6 | 118.2(2) | C64 | C65 | C66 | 124.0(7) |
| N5 | Dy1 | N6 | 66.32(18) | C64 | C65 | C60 | 116.9(7) |
| N5 | Dy1 | O5 | 74.02(18) | C63 | C64 | C65 | 123.0(8) |
| N5 | Dy1 | O3 | 79.85(17) | C62 | C63 | C64 | 119.2(9) |
| N5 | Dy1 | O4 | 115.84(17) | C61 | C62 | C63 | 120.0(8) |
| O7 | Dy1 | O6 | 87.10(19) | C62 | C61 | C60 | 121.9(8) |
| O7 | Dy1 | N6 | 142.81(18) | C70 | C69 | C68 | 121.2(7) |
| O7 | Dy1 | O5 | 88.50(19) | C71 | C70 | C69 | 119.7(7) |
| O7 | Dy1 | O3 | 76.67(18) | C72 | C71 | C70 | 119.7(7) |
| O7 | Dy1 | O4 | 74.37(17) | C71 | C72 | C73 | 122.0(7) |
| O7 | Dy1 | N5 | 149.14(18) | C19 | C18 | N2 | 128.4(7) |
| O2 | Dy2 | O1 | 83.80(17) | C20 | C19 | C18 | 118.0(6) |
| N1 | Dy2 | O1 | 71.95(17) | C28 | C19 | C18 | 122.0(6) |
| N1 | Dy2 | O2 | 119.95(19) | C28 | C19 | C20 | 119.9(6) |
| O3 | Dy2 | O1 | 80.65(16) | C25 | C20 | C19 | 119.9(7) |
| O3 | Dy2 | O2 | 92.98(17) | C21 | C20 | C19 | 123.2(7) |
| O3 | Dy2 | N1 | 133.25(17) | C21 | C20 | C25 | 116.9(7) |
| N4 | Dy2 | O1 | 144.41(17) | C24 | C25 | C20 | 119.8(7) |
| N4 | Dy2 | O2 | 129.67(17) | C26 | C25 | C20 | 118.9(7) |
| N4 | Dy2 | N1 | 79.32(18) | C26 | C25 | C24 | 121.3(7) |
| N4 | Dy2 | O3 | 105.63(17) | C23 | C24 | C25 | 121.2(8) |
| O4 | Dy2 | O1 | 142.11(16) | C22 | C23 | C24 | 119.6(7) |
| O4 | Dy2 | O2 | 75.08(18) | C21 | C22 | C23 | 120.2(8) |
| O4 | Dy2 | N1 | 145.94(17) | C22 | C21 | C20 | 122.2(8) |
| O4 | Dy2 | O3 | 69.64(15) | C27 | C26 | C25 | 120.8(7) |
| O4 | Dy2 | N4 | 68.91(16) | C28 | C27 | C26 | 122.1(7) |
| N2 | Dy2 | O1 | 110.59(17) | C19 | C28 | O2 | 124.4(7) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N2 | Dy2 | O2 | 74.05(18) | C27 | C28 | O2 | 117.6(7) |
| N2 | Dy2 | N1 | 65.48(18) | C27 | C28 | C19 | 118.0(7) |
| N2 | Dy2 | O3 | 161.25(17) | C12 | C17 | N2 | 117.0(6) |
| N2 | Dy2 | N4 | 74.36(17) | C16 | C17 | N2 | 123.5(6) |
| N2 | Dy2 | O4 | 93.56(17) | C16 | C17 | C12 | 119.4(7) |
| N3 | Dy2 | O1 | 88.18(17) | C17 | C12 | N1 | 116.4(6) |
| N3 | Dy2 | O2 | 161.36(18) | C13 | C12 | N1 | 124.4(7) |
| N3 | Dy2 | N1 | 72.86(18) | C13 | C12 | C17 | 119.0(6) |
| N3 | Dy2 | O3 | 69.06(17) | C10 | C11 | N1 | 125.6(6) |
| N3 | Dy2 | N4 | 63.13(17) | C1 | C10 | C11 | 121.2(6) |
| N3 | Dy2 | O4 | 101.98(17) | C9 | C10 | C11 | 119.1(6) |
| N3 | Dy2 | N2 | 124.58(18) | C9 | C10 | C1 | 119.6(6) |
| C1 | O1 | Dy2 | 128.9(4) | C10 | C1 | O1 | 123.2(6) |
| C84 | O6 | Dy1 | 132.8(4) | C2 | C1 | O1 | 118.9(6) |
| C74 | N6 | Dy1 | 125.7(5) | C2 | C1 | C10 | 117.8(6) |
| C73 | N6 | Dy1 | 114.6(4) | C3 | C2 | C1 | 122.0(7) |
| C73 | N6 | C74 | 119.3(6) | C4 | C3 | C2 | 121.7(7) |
| C57 | O5 | Dy1 | 137.4(5) | C9 | C4 | C3 | 118.5(7) |
| C28 | O2 | Dy2 | 135.8(4) | C5 | C4 | C3 | 121.3(7) |
| C12 | N1 | Dy2 | 114.2(4) | C5 | C4 | C9 | 120.1(7) |
| C11 | N1 | Dy2 | 125.9(5) | C4 | C9 | C10 | 120.0(7) |
| C11 | N1 | C12 | 119.7(6) | C8 | C9 | C10 | 122.5(7) |
| Dy2 | O3 | Dy1 | 109.89(17) | C8 | C9 | C4 | 117.5(7) |
| C29 | O3 | Dy1 | 126.3(4) | C7 | C8 | C9 | 120.6(8) |
| C29 | O3 | Dy2 | 122.5(4) | C6 | C7 | C8 | 121.1(8) |
| C45 | N4 | Dy2 | 116.8(4) | C5 | C6 | C7 | 119.7(8) |
| C46 | N4 | Dy2 | 123.0(5) | C6 | C5 | C4 | 121.1(8) |
| C46 | N4 | C45 | 119.9(6) | C14 | C13 | C12 | 120.9(7) |
| Dy2 | O4 | Dy1 | 109.88(18) | C15 | C14 | C13 | 120.1(8) |
| C56 | O4 | Dy1 | 132.1(4) | C16 | C15 | C14 | 120.1(7) |
| C56 | O4 | Dy2 | 117.9(4) | C15 | C16 | C17 | 120.4(7) |
| C68 | N5 | Dy1 | 115.2(4) | C38 | C39 | N3 | 125.7(7) |
| C67 | N5 | Dy1 | 127.1(5) | C29 | C38 | C39 | 121.3(6) |
| C67 | N5 | C68 | 117.6(6) | C37 | C38 | C39 | 118.7(6) |
| C18 | N2 | Dy2 | 128.0(5) | C37 | C38 | C29 | 120.0(7) |
| C17 | N2 | Dy2 | 113.6(4) | C38 | C29 | O3 | 122.0(6) |
| C17 | N2 | C18 | 118.4(6) | C30 | C29 | O3 | 118.9(6) |
| C40 | N3 | Dy2 | 114.9(4) | C30 | C29 | C38 | 119.1(6) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C39 | N3 | Dy2 | 125.7(5) | C31 | C30 | C29 | 121.3(7) |
| C39 | N3 | C40 | 119.3(6) | C32 | C31 | C30 | 121.6(7) |
| C45 | C40 | N3 | 116.3(6) | C37 | C32 | C31 | 119.3(7) |
| C41 | C40 | N3 | 123.5(7) | C33 | C32 | C31 | 121.2(8) |
| C41 | C40 | C45 | 120.2(7) | C33 | C32 | C37 | 119.5(8) |
| C40 | C45 | N4 | 116.4(6) | C32 | C37 | C38 | 118.6(7) |
| C44 | C45 | N4 | 124.8(6) | C36 | C37 | C38 | 123.1(7) |
| C44 | C45 | C40 | 118.7(7) | C36 | C37 | C32 | 118.3(7) |
| C83 | C84 | O6 | 118.7(7) | C35 | C36 | C37 | 120.5(9) |
| C75 | C84 | O6 | 123.9(6) | C34 | C35 | C36 | 121.2(9) |
| C75 | C84 | C83 | 117.4(7) | C33 | C34 | C35 | 119.8(8) |
| C82 | C83 | C84 | 122.4(8) | C34 | C33 | C32 | 120.6(9) |
| C81 | C82 | C83 | 121.3(7) | C47 | C46 | N4 | 125.2(6) |
| C80 | C81 | C82 | 121.8(7) | C56 | C47 | C46 | 120.3(6) |
| C76 | C81 | C82 | 118.7(7) | C48 | C47 | C46 | 119.3(6) |
| C76 | C81 | C80 | 119.4(8) | C48 | C47 | C56 | 120.3(6) |
| C79 | C80 | C81 | 121.6(8) | C47 | C56 | O4 | 121.9(6) |
| C78 | C79 | C80 | 119.2(8) | C55 | C56 | O4 | 119.1(6) |
| C77 | C78 | C79 | 121.1(8) | C55 | C56 | C47 | 119.0(6) |
| C76 | C77 | C78 | 121.3(8) | C54 | C55 | C56 | 122.1(7) |
| C77 | C76 | C81 | 117.3(7) | C53 | C54 | C55 | 120.5(7) |
| C75 | C76 | C81 | 119.3(7) | C52 | C53 | C54 | 121.6(8) |
| C75 | C76 | C77 | 123.4(7) | C48 | C53 | C54 | 119.3(7) |
| C76 | C75 | C84 | 120.4(6) | C48 | C53 | C52 | 119.0(8) |
| C74 | C75 | C84 | 120.8(6) | C51 | C52 | C53 | 121.7(9) |
| C74 | C75 | C76 | 118.8(7) | C50 | C51 | C52 | 119.3(8) |
| C75 | C74 | N6 | 127.4(7) | C49 | C50 | C51 | 121.7(9) |
| C68 | C73 | N6 | 117.3(6) | C48 | C49 | C50 | 120.2(8) |
| C72 | C73 | N6 | 124.6(6) | C53 | C48 | C47 | 118.7(7) |
| C72 | C73 | C68 | 118.0(7) | C49 | C48 | C47 | 123.3(7) |
| C73 | C68 | N5 | 115.8(6) | C49 | C48 | C53 | 117.9(7) |
| C69 | C68 | N5 | 124.8(6) | C43 | C44 | C45 | 120.8(8) |
| C69 | C68 | C73 | 119.3(7) | C42 | C43 | C44 | 119.7(8) |
| C66 | C67 | N5 | 128.2(7) | C41 | C42 | C43 | 120.8(8) |
| C57 | C66 | C67 | 121.1(6) | C42 | C41 | C40 | 119.8(8) |
| C65 | C66 | C67 | 118.0(7) | | | | |

**Crystallographic Table 116** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic

Displacement Parameters ($Å^2 \times 10^3$) for **$Dy_2[L^{VII}]_3$**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H85a | 2890(40) | 5220(40) | 5080(20) | 163(7) |
| H85b | 3180(60) | 4503(15) | 4912(12) | 163(7) |
| H85c | 3780(20) | 5030(50) | 5237(13) | 163(7) |
| H83 | 5202(5) | 6875(4) | 4530(4) | 43(2) |
| H82 | 6340(4) | 7119(4) | 4150(4) | 41(2) |
| H80 | 7118(4) | 7282(4) | 3228(5) | 43(3) |
| H79 | 7204(5) | 7381(4) | 2123(5) | 55(3) |
| H78 | 6104(5) | 7240(4) | 1382(5) | 49(3) |
| H77 | 4922(5) | 7044(4) | 1741(4) | 41(2) |
| H74 | 3889(4) | 7184(3) | 2131(4) | 27(2) |
| H67 | 736(4) | 6891(3) | 2913(4) | 28(2) |
| H58 | 1663(5) | 6407(4) | 5388(4) | 46(3) |
| H59 | 418(5) | 6524(4) | 5573(4) | 49(3) |
| H64 | -365(4) | 6686(4) | 3034(4) | 41(2) |
| H63 | -1631(5) | 6756(5) | 3243(5) | 59(3) |
| H62 | -1925(5) | 6761(5) | 4325(5) | 70(3) |
| H61 | -966(5) | 6632(5) | 5168(5) | 58(3) |
| H69 | 681(4) | 6732(4) | 1947(4) | 33(2) |
| H70 | 848(5) | 6958(4) | 869(4) | 39(2) |
| H71 | 2094(5) | 7057(4) | 561(4) | 41(2) |
| H72 | 3146(4) | 6935(4) | 1331(4) | 32(2) |
| H18 | 4753(4) | 3499(3) | 2016(4) | 26(2) |
| H24 | 6931(4) | 3503(4) | 4355(4) | 45(3) |
| H23 | 7720(4) | 3457(4) | 3537(4) | 47(3) |
| H22 | 7195(4) | 3585(4) | 2443(4) | 43(2) |
| H21 | 5890(4) | 3731(4) | 2186(4) | 35(2) |
| H26 | 5640(5) | 3657(5) | 4717(4) | 50(3) |
| H27 | 4353(4) | 3894(4) | 4479(4) | 43(3) |
| H11 | 1451(4) | 3237(3) | 1138(3) | 24(2) |
| H2 | 766(4) | 3478(4) | 3542(4) | 32(2) |
| H3 | -483(4) | 3278(4) | 3149(4) | 36(2) |
| H8 | 308(5) | 3421(4) | 751(4) | 43(3) |
| H7 | -986(5) | 3282(4) | 391(5) | 54(3) |
| H6 | -1901(5) | 3201(4) | 1135(5) | 52(3) |
| H5 | -1516(4) | 3222(4) | 2234(4) | 44(3) |
| H13 | 2014(4) | 3515(4) | 336(4) | 35(2) |

| | | | | |
|---|---|---|---|---|
| H14 | 2913(5) | 3475(5) | -407(4) | 50(3) |
| H15 | 4217(5) | 3604(4) | -54(4) | 43(3) |
| H16 | 4622(5) | 3781(4) | 1044(4) | 35(2) |
| H39 | 581(4) | 5390(3) | 1879(4) | 26(2) |
| H30 | 1605(4) | 4930(4) | 4342(4) | 33(2) |
| H31 | 357(4) | 4850(4) | 4555(4) | 40(2) |
| H36 | -524(4) | 5055(4) | 2018(5) | 46(3) |
| H35 | -1772(5) | 4925(5) | 2270(5) | 62(3) |
| H34 | -2038(5) | 4868(4) | 3354(5) | 57(3) |
| H33 | -1039(5) | 4833(4) | 4190(5) | 55(3) |
| H46 | 3743(4) | 5611(3) | 1144(3) | 26(2) |
| H55 | 4837(4) | 5410(3) | 3613(4) | 27(2) |
| H54 | 6058(4) | 5459(4) | 3311(4) | 37(2) |
| H52 | 6934(5) | 5453(4) | 2441(5) | 52(3) |
| H51 | 7132(5) | 5370(5) | 1364(5) | 65(3) |
| H50 | 6079(5) | 5258(5) | 564(5) | 62(3) |
| H49 | 4833(5) | 5247(4) | 834(4) | 40(2) |
| H44 | 3015(5) | 5367(4) | 310(4) | 37(2) |
| H43 | 1960(5) | 5435(4) | -480(4) | 50(3) |
| H42 | 723(5) | 5279(5) | -191(4) | 55(3) |
| H41 | 527(5) | 5080(4) | 889(4) | 41(2) |
| H7a | 3501(3) | 4835(3) | 4067(2) | 59(2) |

**Crystallographic Table 117** Solvent masks information for **$Dy_2[L^{VII}]_3$**.

| Number | X | Y | Z | Volume | Electron count | Content |
|---|---|---|---|---|---|---|
| 1 | 0.347 | 0.204 | 0.465 | 322.5 | 105.0 | 2DCM/1H2O |
| 2 | 0.347 | 0.296 | 0.965 | 322.5 | 101.1 | 2DCM/1H2O |
| 3 | -0.347 | 0.704 | 0.035 | 322.5 | 102.0 | 2DCM/1H2O |
| 4 | -0.347 | 0.796 | 0.535 | 322.5 | 98.2 | 2DCM/1H2O |

Refinement model description

Number of restraints - 0, number of constraints - 114.

## $Er_2[L^{VII}]_3$

**Crystallographic Table 118** Crystal data and structure refinement for $Er_2[L^{VII}]_3$

| | |
|---|---|
| Empirical formula | $C_{87}H_{66}Er_2N_6O_9$ |
| Formula weight | 1674.04 |
| Temperature/K | 180.65 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.309(2) |
| b/Å | 17.582(4) |
| c/Å | 18.939(4) |
| α/° | 82.655(4) |
| β/° | 86.443(4) |
| γ/° | 82.386(4) |
| Volume/Å$^3$ | 3371.2(12) |
| Z | 2 |
| $\rho_{calc}$mg/mm$^3$ | 1.6490 |
| m/mm$^{-1}$ | 2.542 |
| F(000) | 1676.2 |
| Crystal size/mm$^3$ | 0.11 × 0.09 × 0.06 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 2.18 to 44.92° |
| Index ranges | $-11 \le h \le 11$, $-18 \le k \le 18$, $-20 \le l \le 20$ |
| Reflections collected | 26445 |
| Independent reflections | 8754 [$R_{int}$ = 0.1455, $R_{sigma}$ = 0.1934] |
| Data/restraints/parameters | 8754/3/435 |
| Goodness-of-fit on $F^2$ | 0.941 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0608, $wR_2$ = 0.1208 |
| Final R indexes [all data] | $R_1$ = 0.1226, $wR_2$ = 0.1462 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.74/-2.53 |

**Crystallographic Table 119** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for $Er_2[L^{VII}]_3$. $U_{eq}$is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Er1 | -1088.2(5) | 2144.3(3) | 3232.8(3) | 19.31(19) |
| Er2 | 2357.3(5) | 2229.5(3) | 2366.5(3) | 18.54(19) |
| O1 | -2279(7) | 1207(5) | 3534(4) | 32(2) |
| N2 | -2165(8) | 3332(5) | 2603(4) | 16(2) |

| | | | | |
|---|---|---|---|---|
| O3 | -2039(7) | 2807(5) | 4055(4) | 28(2) |
| O4 | 669(6) | 2839(4) | 3055(3) | 21.1(19) |
| O5 | 3138(7) | 1424(4) | 3275(4) | 27(2) |
| O6 | 3446(6) | 3023(4) | 2867(4) | 22(2) |
| O7 | 638(6) | 1510(4) | 2606(3) | 18.6(19) |
| O8 | 93(7) | 1487(5) | 4214(4) | 29(2) |
| O9 | 1789(8) | 1951(5) | 4990(5) | 48(3) |
| O10 | 3662(8) | 2654(5) | 4305(4) | 45(2) |
| N1 | -2113(8) | 1949(6) | 2166(5) | 24(2) |
| C0aa | -2617(10) | 3987(7) | 2875(6) | 27(3) |
| N3 | 3768(8) | 1199(5) | 1875(4) | 20(2) |
| N4 | 4029(8) | 2686(5) | 1496(4) | 19(2) |
| N5 | 1375(8) | 2031(5) | 1235(4) | 18(2) |
| N6 | 1275(8) | 3426(5) | 1633(4) | 19(2) |
| C1 | -2560(10) | 1343(7) | 2021(6) | 21(3) |
| C2 | -2622(10) | 635(7) | 2497(6) | 18(3) |
| C3 | -2550(10) | 621(7) | 3240(6) | 22(3) |
| C4 | -2863(10) | -70(7) | 3688(6) | 28(3) |
| C5 | -3068(10) | -709(8) | 3419(6) | 33(3) |
| C6 | -2976(10) | -745(7) | 2684(6) | 25(3) |
| C7 | -2765(10) | -64(7) | 2197(6) | 22(3) |
| C8 | -2657(10) | -144(7) | 1472(6) | 30(3) |
| C9 | -2760(11) | -838(7) | 1218(6) | 32(3) |
| C10 | -2990(11) | -1488(8) | 1703(7) | 43(4) |
| C11 | -3067(11) | -1448(8) | 2407(6) | 38(3) |
| C12 | -2145(10) | 2598(7) | 1628(6) | 21(3) |
| C13 | -2072(10) | 2561(7) | 885(6) | 28(3) |
| C14 | -2099(10) | 3204(7) | 388(6) | 24(3) |
| C15 | -2143(10) | 3913(7) | 631(6) | 29(3) |
| C16 | -2199(10) | 3983(7) | 1341(6) | 24(3) |
| C17 | -2165(10) | 3330(7) | 1861(6) | 23(3) |
| C18 | -2651(10) | 4127(7) | 3593(6) | 20(3) |
| C19 | -2427(10) | 3530(7) | 4142(6) | 27(3) |
| C20 | -2656(11) | 3709(8) | 4863(6) | 36(3) |
| C21 | -3034(12) | 4427(8) | 5022(7) | 48(4) |
| C22 | -3187(11) | 5047(7) | 4466(6) | 31(3) |
| C23 | -3553(11) | 5819(8) | 4621(7) | 43(4) |
| C24 | -3667(12) | 6435(8) | 4118(7) | 46(4) |

| | | | | |
|---|---|---|---|---|
| C25 | -3352(12) | 6297(8) | 3407(7) | 48(4) |
| C26 | -3009(11) | 5560(8) | 3222(6) | 36(3) |
| C27 | -2970(10) | 4912(7) | 3748(6) | 22(3) |
| C28 | 3321(11) | 667(7) | 3408(6) | 28(3) |
| C29 | 3606(10) | 179(7) | 2870(6) | 21(3) |
| C30 | 3980(10) | 486(7) | 2170(6) | 24(3) |
| C31 | 4315(10) | 1403(7) | 1184(6) | 22(3) |
| C32 | 4480(10) | 2177(7) | 974(6) | 17(3) |
| C33 | 4502(10) | 3349(7) | 1455(6) | 20(3) |
| C34 | 4217(10) | 3920(7) | 1930(6) | 17(3) |
| C35 | 3771(10) | 3708(7) | 2635(6) | 21(3) |
| C36 | 3748(10) | 4272(7) | 3134(6) | 30(3) |
| C37 | 4026(10) | 4984(7) | 2920(6) | 33(3) |
| C38 | 4372(11) | 5231(7) | 2215(6) | 27(3) |
| C39 | 4495(10) | 4699(7) | 1700(6) | 27(3) |
| C40 | 4869(12) | 4969(8) | 1016(7) | 46(4) |
| C41 | 5241(14) | 5691(9) | 829(8) | 64(5) |
| C42 | 5120(13) | 6199(9) | 1343(7) | 61(4) |
| C43 | 4653(12) | 5977(8) | 2006(7) | 48(4) |
| C44 | 4967(10) | 2398(7) | 295(6) | 25(3) |
| C45 | 5337(10) | 1879(7) | -191(6) | 31(3) |
| C46 | 5139(11) | 1136(8) | 13(6) | 35(3) |
| C47 | 4632(11) | 889(8) | 684(6) | 38(4) |
| C48 | 3630(10) | -658(7) | 3036(6) | 25(3) |
| C49 | 3490(10) | -960(7) | 3747(6) | 28(3) |
| C50 | 3350(11) | -468(8) | 4294(7) | 37(4) |
| C51 | 3247(11) | 320(7) | 4130(6) | 32(3) |
| C52 | 3418(11) | -1790(8) | 3924(7) | 45(4) |
| C53 | 3539(11) | -2258(8) | 3397(6) | 39(4) |
| C54 | 3632(11) | -1946(8) | 2692(7) | 41(4) |
| C55 | 3694(10) | -1169(7) | 2516(6) | 29(3) |
| C56 | 1353(9) | 2650(6) | 674(5) | 15(3) |
| C57 | 1298(10) | 3378(7) | 898(6) | 21(3) |
| C58 | 753(9) | 4049(7) | 1880(5) | 19(3) |
| C59 | 686(10) | 4198(7) | 2608(6) | 19(3) |
| C60 | 602(10) | 4982(7) | 2768(6) | 21(3) |
| C61 | 678(11) | 5607(7) | 2238(7) | 36(3) |
| C62 | 658(12) | 6344(9) | 2410(7) | 52(4) |

| | | | | |
|---|---|---|---|---|
| C63 | 518(12) | 6486(9) | 3125(7) | 48(4) |
| C64 | 480(11) | 5899(8) | 3653(7) | 44(4) |
| C65 | 519(11) | 5121(7) | 3472(6) | 28(3) |
| C66 | 504(10) | 4511(7) | 4030(6) | 29(3) |
| C67 | 572(10) | 3767(7) | 3870(6) | 24(3) |
| C68 | 675(10) | 3604(7) | 3153(6) | 17(3) |
| C69 | 1332(10) | 4024(7) | 366(6) | 24(3) |
| C70 | 1341(10) | 3929(7) | -336(6) | 29(3) |
| C71 | 1396(10) | 3205(7) | -551(6) | 32(3) |
| C72 | 1399(10) | 2568(7) | -52(6) | 28(3) |
| C73 | 943(10) | 1402(7) | 1135(6) | 24(3) |
| C74 | 871(9) | 721(6) | 1647(5) | 18(3) |
| C75 | 671(9) | 817(7) | 2377(6) | 16(3) |
| C76 | 456(9) | 165(6) | 2872(6) | 20(3) |
| C77 | 431(10) | -543(7) | 2665(6) | 25(3) |
| C78 | 637(10) | -678(7) | 1942(6) | 24(3) |
| C79 | 889(10) | -41(7) | 1421(6) | 20(3) |
| C80 | 1171(11) | -193(8) | 719(6) | 35(3) |
| C81 | 1191(11) | -924(8) | 533(7) | 41(4) |
| C82 | 932(11) | -1539(8) | 1034(7) | 42(4) |
| C83 | 657(10) | -1417(7) | 1728(6) | 34(3) |
| C84 | 1152(12) | 2378(8) | 5521(6) | 50(4) |
| C85 | 4879(14) | 2213(9) | 4315(8) | 79(5) |
| C1aa | -479(13) | 1080(9) | 4810(7) | 73(5) |

**Crystallographic Table 120** Anisotropic Displacement Parameters ($Å^2×10^3$) for **$Er_2[L^{VII}]_3$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Er1 | 25.1(3) | 12.0(4) | 20.6(4) | -0.6(3) | -2.5(3) | -2.0(3) |
| Er2 | 23.7(3) | 10.5(4) | 21.1(4) | 0.8(3) | -4.0(3) | -2.5(3) |

**Crystallographic Table 121** Bond Lengths for **$Er_2[L^{VII}]_3$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Er1 | O1 | 2.182(8) | C24 | C25 | 1.408(15) |
| Er1 | N2 | 2.436(8) | C25 | C26 | 1.380(16) |
| Er1 | O3 | 2.172(7) | C26 | C27 | 1.413(15) |
| Er1 | O4 | 2.301(7) | C28 | C29 | 1.408(15) |
| Er1 | O7 | 2.318(7) | C28 | C51 | 1.427(14) |

| | | | | | |
|---|---|---|---|---|---|
| Er1 | O8 | 2.373(7) | C29 | C30 | 1.416(14) |
| Er1 | N1 | 2.420(9) | C29 | C48 | 1.461(15) |
| Er2 | O4 | 2.337(7) | C31 | C32 | 1.397(15) |
| Er2 | O5 | 2.205(7) | C31 | C47 | 1.386(15) |
| Er2 | O6 | 2.233(7) | C32 | C44 | 1.378(13) |
| Er2 | O7 | 2.301(7) | C33 | C34 | 1.421(14) |
| Er2 | N3 | 2.414(9) | C34 | C35 | 1.406(13) |
| Er2 | N4 | 2.451(8) | C34 | C39 | 1.445(15) |
| Er2 | N5 | 2.508(8) | C35 | C36 | 1.452(15) |
| Er2 | N6 | 2.535(9) | C36 | C37 | 1.329(15) |
| O1 | C3 | 1.301(12) | C37 | C38 | 1.390(14) |
| N2 | C0aa | 1.337(13) | C38 | C39 | 1.423(15) |
| N2 | C17 | 1.406(12) | C38 | C43 | 1.384(16) |
| O3 | C19 | 1.309(13) | C39 | C40 | 1.373(15) |
| O4 | C68 | 1.381(12) | C40 | C41 | 1.371(18) |
| O5 | C28 | 1.313(13) | C41 | C42 | 1.392(18) |
| O6 | C35 | 1.307(12) | C42 | C43 | 1.347(16) |
| O7 | C75 | 1.340(12) | C44 | C45 | 1.380(15) |
| O8 | C1aa | 1.399(13) | C45 | C46 | 1.353(16) |
| O9 | C84 | 1.409(13) | C46 | C47 | 1.382(14) |
| O10 | C85 | 1.385(15) | C48 | C49 | 1.389(14) |
| N1 | C1 | 1.283(12) | C48 | C55 | 1.410(15) |
| N1 | C12 | 1.428(13) | C49 | C50 | 1.421(15) |
| C0aa | C18 | 1.409(14) | C49 | C52 | 1.465(16) |
| N3 | C30 | 1.302(13) | C50 | C51 | 1.372(16) |
| N3 | C31 | 1.415(12) | C52 | C53 | 1.363(15) |
| N4 | C32 | 1.434(13) | C53 | C54 | 1.379(15) |
| N4 | C33 | 1.313(12) | C54 | C55 | 1.372(16) |
| N5 | C56 | 1.420(13) | C56 | C57 | 1.391(14) |
| N5 | C73 | 1.285(12) | C56 | C72 | 1.398(13) |
| N6 | C57 | 1.404(12) | C57 | C69 | 1.422(14) |
| N6 | C58 | 1.285(12) | C58 | C59 | 1.432(13) |
| C1 | C2 | 1.447(14) | C59 | C60 | 1.441(15) |
| C2 | C3 | 1.411(13) | C59 | C68 | 1.372(14) |
| C2 | C7 | 1.446(15) | C60 | C61 | 1.398(15) |
| C3 | C4 | 1.451(15) | C60 | C65 | 1.381(14) |
| C4 | C5 | 1.337(15) | C61 | C62 | 1.372(16) |
| C5 | C6 | 1.399(14) | C62 | C63 | 1.405(16) |

| | | | | | |
|---|---|---|---|---|---|
| C6 | C7 | 1.448(15) | C63 | C64 | 1.344(16) |
| C6 | C11 | 1.419(15) | C64 | C65 | 1.446(16) |
| C7 | C8 | 1.394(14) | C65 | C66 | 1.408(15) |
| C8 | C9 | 1.385(15) | C66 | C67 | 1.372(15) |
| C9 | C10 | 1.408(16) | C67 | C68 | 1.418(13) |
| C10 | C11 | 1.342(15) | C69 | C70 | 1.360(13) |
| C12 | C13 | 1.413(14) | C70 | C71 | 1.378(15) |
| C12 | C17 | 1.409(15) | C71 | C72 | 1.369(15) |
| C13 | C14 | 1.375(14) | C73 | C74 | 1.449(14) |
| C14 | C15 | 1.378(15) | C74 | C75 | 1.413(13) |
| C15 | C16 | 1.364(13) | C74 | C79 | 1.456(14) |
| C16 | C17 | 1.412(15) | C75 | C76 | 1.417(14) |
| C18 | C19 | 1.387(15) | C76 | C77 | 1.355(14) |
| C18 | C27 | 1.440(15) | C77 | C78 | 1.418(14) |
| C19 | C20 | 1.437(14) | C78 | C79 | 1.434(15) |
| C20 | C21 | 1.338(16) | C78 | C83 | 1.408(15) |
| C21 | C22 | 1.415(16) | C79 | C80 | 1.396(14) |
| C22 | C23 | 1.423(16) | C80 | C81 | 1.373(16) |
| C22 | C27 | 1.408(14) | C81 | C82 | 1.387(16) |
| C23 | C24 | 1.346(16) | C82 | C83 | 1.366(14) |

**Crystallographic Table 122** Bond Angles for **$Er_2[L^{VII}]_3$.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| N2 | Er1 | O1 | 116.9(3) | C18 | C19 | O3 | 124.7(11) |
| O3 | Er1 | O1 | 92.4(3) | C20 | C19 | O3 | 117.1(11) |
| O3 | Er1 | N2 | 74.3(3) | C20 | C19 | C18 | 118.2(12) |
| O4 | Er1 | O1 | 162.1(3) | C21 | C20 | C19 | 122.7(13) |
| O4 | Er1 | N2 | 81.0(3) | C22 | C21 | C20 | 119.5(13) |
| O4 | Er1 | O3 | 94.2(3) | C23 | C22 | C21 | 120.7(12) |
| O7 | Er1 | O1 | 100.3(3) | C27 | C22 | C21 | 120.6(12) |
| O7 | Er1 | N2 | 115.5(3) | C27 | C22 | C23 | 118.7(12) |
| O7 | Er1 | O3 | 156.9(2) | C24 | C23 | C22 | 123.4(13) |
| O7 | Er1 | O4 | 68.3(2) | C25 | C24 | C23 | 117.2(14) |
| O8 | Er1 | O1 | 80.9(3) | C26 | C25 | C24 | 122.0(13) |
| O8 | Er1 | N2 | 150.3(3) | C27 | C26 | C25 | 120.4(12) |
| O8 | Er1 | O3 | 81.7(3) | C22 | C27 | C18 | 118.5(11) |
| O8 | Er1 | O4 | 83.6(2) | C26 | C27 | C18 | 123.5(11) |
| O8 | Er1 | O7 | 81.4(2) | C26 | C27 | C22 | 117.9(12) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N1 | Er1 | O1 | 73.3(3) | C29 | C28 | O5 | 123.0(11) |
| N1 | Er1 | N2 | 66.5(3) | C51 | C28 | O5 | 118.8(10) |
| N1 | Er1 | O3 | 124.5(3) | C51 | C28 | C29 | 118.2(11) |
| N1 | Er1 | O4 | 115.7(3) | C30 | C29 | C28 | 120.2(11) |
| N1 | Er1 | O7 | 78.0(3) | C48 | C29 | C28 | 120.7(10) |
| N1 | Er1 | O8 | 143.2(3) | C48 | C29 | C30 | 118.9(10) |
| O5 | Er2 | O4 | 94.0(2) | C29 | C30 | N3 | 128.0(11) |
| O6 | Er2 | O4 | 79.3(2) | C32 | C31 | N3 | 118.4(10) |
| O6 | Er2 | O5 | 80.7(3) | C47 | C31 | N3 | 124.0(11) |
| O7 | Er2 | O4 | 68.0(2) | C47 | C31 | C32 | 117.5(11) |
| O7 | Er2 | O5 | 80.7(2) | C31 | C32 | N4 | 114.5(9) |
| O7 | Er2 | O6 | 140.8(2) | C44 | C32 | N4 | 125.6(10) |
| N3 | Er2 | O4 | 159.2(3) | C44 | C32 | C31 | 119.8(10) |
| N3 | Er2 | O5 | 73.1(3) | C34 | C33 | N4 | 127.2(10) |
| N3 | Er2 | O6 | 113.4(3) | C35 | C34 | C33 | 119.8(10) |
| N3 | Er2 | O7 | 93.5(3) | C39 | C34 | C33 | 119.5(10) |
| N4 | Er2 | O4 | 134.3(3) | C39 | C34 | C35 | 120.5(10) |
| N4 | Er2 | O5 | 114.6(3) | C34 | C35 | O6 | 123.4(10) |
| N4 | Er2 | O6 | 71.7(3) | C36 | C35 | O6 | 119.1(10) |
| N4 | Er2 | O7 | 147.4(3) | C36 | C35 | C34 | 117.5(10) |
| N4 | Er2 | N3 | 66.4(3) | C37 | C36 | C35 | 121.2(11) |
| N5 | Er2 | O4 | 106.6(2) | C38 | C37 | C36 | 122.6(12) |
| N5 | Er2 | O5 | 132.8(3) | C39 | C38 | C37 | 119.6(11) |
| N5 | Er2 | O6 | 143.9(3) | C43 | C38 | C37 | 121.3(12) |
| N5 | Er2 | O7 | 69.2(2) | C43 | C38 | C39 | 119.0(11) |
| N5 | Er2 | N3 | 73.4(3) | C38 | C39 | C34 | 118.2(10) |
| N5 | Er2 | N4 | 80.2(3) | C40 | C39 | C34 | 124.6(11) |
| N6 | Er2 | O4 | 70.6(3) | C40 | C39 | C38 | 117.2(12) |
| N6 | Er2 | O5 | 161.8(3) | C41 | C40 | C39 | 123.0(13) |
| N6 | Er2 | O6 | 86.8(3) | C42 | C41 | C40 | 118.5(15) |
| N6 | Er2 | O7 | 101.4(3) | C43 | C42 | C41 | 120.0(15) |
| N6 | Er2 | N3 | 124.4(3) | C42 | C43 | C38 | 121.8(13) |
| N6 | Er2 | N4 | 73.2(3) | C45 | C44 | C32 | 122.5(12) |
| N6 | Er2 | N5 | 63.2(3) | C46 | C45 | C44 | 117.0(12) |
| C3 | O1 | Er1 | 135.6(7) | C47 | C46 | C45 | 122.5(12) |
| C0aa | N2 | Er1 | 127.2(7) | C46 | C47 | C31 | 120.6(12) |
| C17 | N2 | Er1 | 113.9(7) | C49 | C48 | C29 | 118.0(10) |
| C17 | N2 | C0aa | 118.5(9) | C55 | C48 | C29 | 123.8(11) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C19 | O3 | Er1 | 138.7(7) | C55 | C48 | C49 | 118.0(11) |
| Er2 | O4 | Er1 | 111.4(3) | C50 | C49 | C48 | 120.7(12) |
| C68 | O4 | Er1 | 126.9(6) | C52 | C49 | C48 | 119.0(11) |
| C68 | O4 | Er2 | 119.6(6) | C52 | C49 | C50 | 120.2(11) |
| C28 | O5 | Er2 | 133.3(7) | C51 | C50 | C49 | 120.8(12) |
| C35 | O6 | Er2 | 131.6(6) | C50 | C51 | C28 | 121.0(12) |
| Er2 | O7 | Er1 | 112.1(3) | C53 | C52 | C49 | 120.0(12) |
| C75 | O7 | Er1 | 126.3(6) | C54 | C53 | C52 | 120.2(13) |
| C75 | O7 | Er2 | 121.5(6) | C55 | C54 | C53 | 120.5(12) |
| C1aa | O8 | Er1 | 124.1(7) | C54 | C55 | C48 | 122.1(12) |
| C1 | N1 | Er1 | 128.7(8) | C57 | C56 | N5 | 114.5(9) |
| C12 | N1 | Er1 | 113.3(7) | C72 | C56 | N5 | 125.0(11) |
| C12 | N1 | C1 | 117.9(9) | C72 | C56 | C57 | 120.5(11) |
| C18 | C0aa | N2 | 127.8(11) | C56 | C57 | N6 | 118.2(10) |
| C30 | N3 | Er2 | 125.7(8) | C69 | C57 | N6 | 123.9(11) |
| C31 | N3 | Er2 | 114.8(7) | C69 | C57 | C56 | 117.8(10) |
| C31 | N3 | C30 | 119.4(9) | C59 | C58 | N6 | 126.7(10) |
| C32 | N4 | Er2 | 115.1(7) | C60 | C59 | C58 | 119.4(10) |
| C33 | N4 | Er2 | 126.4(7) | C68 | C59 | C58 | 120.8(11) |
| C33 | N4 | C32 | 118.5(9) | C68 | C59 | C60 | 119.7(10) |
| C56 | N5 | Er2 | 116.6(7) | C61 | C60 | C59 | 122.4(11) |
| C73 | N5 | Er2 | 123.9(7) | C65 | C60 | C59 | 119.1(11) |
| C73 | N5 | C56 | 119.5(9) | C65 | C60 | C61 | 118.4(12) |
| C57 | N6 | Er2 | 114.6(7) | C62 | C61 | C60 | 121.0(12) |
| C58 | N6 | Er2 | 125.4(7) | C63 | C62 | C61 | 120.3(14) |
| C58 | N6 | C57 | 119.9(9) | C64 | C63 | C62 | 120.6(15) |
| C2 | C1 | N1 | 125.9(11) | C65 | C64 | C63 | 119.0(13) |
| C3 | C2 | C1 | 121.1(11) | C64 | C65 | C60 | 120.6(11) |
| C7 | C2 | C1 | 118.6(10) | C66 | C65 | C60 | 121.1(12) |
| C7 | C2 | C3 | 120.2(10) | C66 | C65 | C64 | 118.4(11) |
| C2 | C3 | O1 | 123.0(11) | C67 | C66 | C65 | 119.2(11) |
| C4 | C3 | O1 | 119.5(10) | C68 | C67 | C66 | 121.1(11) |
| C4 | C3 | C2 | 117.4(11) | C59 | C68 | O4 | 124.1(10) |
| C5 | C4 | C3 | 122.3(12) | C67 | C68 | O4 | 116.0(10) |
| C6 | C5 | C4 | 121.2(12) | C67 | C68 | C59 | 119.8(11) |
| C7 | C6 | C5 | 120.0(11) | C70 | C69 | C57 | 120.2(12) |
| C11 | C6 | C5 | 120.8(11) | C71 | C70 | C69 | 121.3(12) |
| C11 | C6 | C7 | 119.3(11) | C72 | C71 | C70 | 119.9(12) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C6 | C7 | C2 | 117.9(10) | C71 | C72 | C56 | 120.2(12) |
| C8 | C7 | C2 | 125.0(11) | C74 | C73 | N5 | 127.0(11) |
| C8 | C7 | C6 | 117.0(11) | C75 | C74 | C73 | 118.5(11) |
| C9 | C8 | C7 | 122.3(12) | C79 | C74 | C73 | 121.5(10) |
| C10 | C9 | C8 | 119.6(12) | C79 | C74 | C75 | 119.8(10) |
| C11 | C10 | C9 | 120.6(13) | C74 | C75 | O7 | 121.7(10) |
| C10 | C11 | C6 | 121.2(13) | C76 | C75 | O7 | 119.7(10) |
| C13 | C12 | N1 | 125.4(11) | C76 | C75 | C74 | 118.7(11) |
| C17 | C12 | N1 | 116.8(10) | C77 | C76 | C75 | 122.0(11) |
| C17 | C12 | C13 | 117.7(11) | C78 | C77 | C76 | 122.0(11) |
| C14 | C13 | C12 | 123.2(12) | C79 | C78 | C77 | 118.2(11) |
| C15 | C14 | C13 | 117.8(11) | C83 | C78 | C77 | 122.2(11) |
| C16 | C15 | C14 | 121.5(12) | C83 | C78 | C79 | 119.5(11) |
| C17 | C16 | C15 | 121.5(12) | C78 | C79 | C74 | 119.2(10) |
| C12 | C17 | N2 | 115.6(10) | C80 | C79 | C74 | 123.2(11) |
| C16 | C17 | N2 | 126.2(11) | C80 | C79 | C78 | 117.6(11) |
| C16 | C17 | C12 | 118.2(11) | C81 | C80 | C79 | 121.1(13) |
| C19 | C18 | C0aa | 121.8(11) | C82 | C81 | C80 | 121.4(13) |
| C27 | C18 | C0aa | 118.0(10) | C83 | C82 | C81 | 119.4(14) |
| C27 | C18 | C19 | 120.1(10) | C82 | C83 | C78 | 121.0(12) |

**Crystallographic Table 123** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **$Er_2[L^{VII}]_3$**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H1 | -2880(10) | 1360(7) | 1558(6) | 26(4) |
| H4 | -2925(10) | -69(7) | 4191(6) | 34(4) |
| H5 | -3281(10) | -1146(8) | 3733(6) | 40(4) |
| H8a | -2508(10) | 292(7) | 1140(6) | 36(4) |
| H9 | -2675(11) | -874(7) | 721(6) | 39(4) |
| H10 | -3092(11) | -1959(8) | 1529(7) | 52(5) |
| H11 | -3185(11) | -1899(8) | 2727(6) | 46(4) |
| H13 | -2000(10) | 2067(7) | 722(6) | 34(4) |
| H14 | -2088(10) | 3161(7) | -108(6) | 29(4) |
| H15 | -2135(10) | 4364(7) | 296(6) | 35(4) |
| H16 | -2261(10) | 4483(7) | 1490(6) | 29(4) |
| H20 | -2535(11) | 3300(8) | 5242(6) | 43(4) |
| H21 | -3198(12) | 4521(8) | 5504(7) | 57(5) |
| H23 | -3727(11) | 5905(8) | 5105(7) | 51(4) |

| | | | | |
|---|---|---|---|---|
| H24 | -3947(12) | 6942(8) | 4236(7) | 55(5) |
| H25 | -3376(12) | 6724(8) | 3044(7) | 58(5) |
| H26 | -2799(11) | 5489(8) | 2738(6) | 43(4) |
| H30 | 4442(10) | 127(7) | 1880(6) | 28(4) |
| H33 | 5100(10) | 3460(7) | 1065(6) | 25(4) |
| H36 | 3529(10) | 4129(7) | 3624(6) | 36(4) |
| H37 | 3987(10) | 5338(7) | 3262(6) | 39(4) |
| H40 | 4871(12) | 4641(8) | 654(7) | 56(5) |
| H41 | 5574(14) | 5841(9) | 360(8) | 77(6) |
| H42 | 5368(13) | 6703(9) | 1225(7) | 73(5) |
| H43 | 4512(12) | 6342(8) | 2340(7) | 57(5) |
| H44 | 5052(10) | 2929(7) | 156(6) | 30(4) |
| H45 | 5714(10) | 2036(7) | -648(6) | 38(4) |
| H46 | 5357(11) | 769(8) | -317(6) | 43(4) |
| H47 | 4500(11) | 363(8) | 803(6) | 46(4) |
| H50 | 3327(11) | -688(8) | 4779(7) | 45(4) |
| H51 | 3124(11) | 639(7) | 4504(6) | 39(4) |
| H52 | 3288(11) | -2001(8) | 4406(7) | 55(5) |
| H53 | 3560(11) | -2801(8) | 3515(6) | 46(4) |
| H54 | 3653(11) | -2271(8) | 2326(7) | 49(4) |
| H55 | 3783(10) | -970(7) | 2027(6) | 35(4) |
| H58 | 372(9) | 4453(7) | 1545(5) | 23(3) |
| H61 | 744(11) | 5521(7) | 1751(7) | 43(4) |
| H62 | 740(12) | 6760(9) | 2043(7) | 63(5) |
| H63 | 450(12) | 7001(9) | 3238(7) | 58(5) |
| H64 | 428(11) | 5993(8) | 4137(7) | 53(5) |
| H66 | 446(10) | 4613(7) | 4513(6) | 34(4) |
| H67 | 550(10) | 3355(7) | 4245(6) | 29(4) |
| H69 | 1348(10) | 4525(7) | 501(6) | 28(4) |
| H70 | 1308(10) | 4369(7) | -685(6) | 35(4) |
| H71 | 1432(10) | 3148(7) | -1044(6) | 38(4) |
| H72 | 1433(10) | 2069(7) | -200(6) | 33(4) |
| H73 | 638(10) | 1382(7) | 675(6) | 29(4) |
| H76 | 327(9) | 225(6) | 3363(6) | 23(4) |
| H77 | 269(10) | -961(7) | 3015(6) | 30(4) |
| H80 | 1352(11) | 217(8) | 363(6) | 42(4) |
| H81 | 1387(11) | -1011(8) | 50(7) | 50(4) |
| H82 | 945(11) | -2041(8) | 895(7) | 50(4) |

| | | | | |
|---|---|---|---|---|
| H83 | 476(10) | -1838(7) | 2071(6) | 40(4) |
| H84a | 1130(70) | 2045(14) | 5977(11) | 76(6) |
| H84b | 1630(40) | 2820(30) | 5570(30) | 76(6) |
| H84c | 250(30) | 2570(40) | 5390(20) | 76(6) |
| H85a | 5540(20) | 2520(19) | 4440(50) | 119(8) |
| H85b | 4850(30) | 1750(30) | 4670(40) | 119(8) |
| H85c | 5110(40) | 2050(50) | 3842(15) | 119(8) |
| H10a | 3530(50) | 2880(50) | 3891(14) | 67(4) |
| H8 | 890(30) | 1530(50) | 4320(30) | 44(3) |
| H1aa | -990(80) | 700(40) | 4654(8) | 110(7) |
| H1ab | 208(14) | 810(40) | 5120(30) | 110(7) |
| H1ac | -1060(70) | 1442(11) | 5070(30) | 110(7) |
| H0aa | -2957(10) | 4409(7) | 2545(6) | 32(4) |
| H9a | 2470(60) | 2140(40) | 4840(40) | 72(4) |

Refinement model description

Number of restraints - 3, number of constraints - 125.

Details:

N/A

## $Lu_2[L^{VII}]_3$

**Crystallographic Table 124** Crystal data and structure refinement for $Lu_2[L^{VII}]_3$

| | |
|---|---|
| Empirical formula | $C_{88}H_{63}Cl_4Lu_2N_6O_8$ |
| Formula weight | 1824.26 |
| Temperature/K | 180.65 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 17.3991(17) |
| b/Å | 20.433(2) |
| c/Å | 20.680(2) |
| α/° | 90 |
| β/° | 96.1761(13) |
| γ/° | 90 |
| Volume/Å$^3$ | 7309.6(12) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.6576 |
| m/mm$^{-1}$ | 2.897 |
| F(000) | 3629.3 |
| Crystal size/mm$^3$ | 0.19 × 0.16 × 0.15 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 2.36 to 52.74° |
| Index ranges | $-21 \le h \le 21$, $-25 \le k \le 25$, $-25 \le l \le 25$ |
| Reflections collected | 76877 |
| Independent reflections | 14911 [$R_{int}$ = 0.0553, $R_{sigma}$ = 0.0387] |
| Data/restraints/parameters | 14911/3/977 |
| Goodness-of-fit on $F^2$ | 2.488 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.1865, $wR_2$ = 0.4959 |
| Final R indexes [all data] | $R_1$ = 0.1983, $wR_2$ = 0.5228 |
| Largest diff. peak/hole / e Å$^{-3}$ | 5.69/-11.33 |

**Crystallographic Table 125** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for $Lu_2[L^{VII}]_3$. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Lu1 | 2271.0(3) | 4440.2(3) | 2482.5(2) | 55.9(3) |
| Lu2 | 2082.3(3) | 6010.9(3) | 1524.0(2) | 59.9(3) |
| O4 | 1448(5) | 5289(5) | 2130(4) | 53.4(18) |
| O1 | 3093(5) | 3751(5) | 2093(4) | 61(2) |

| | | | | |
|---|---|---|---|---|
| O5 | 2723(5) | 6371(6) | 737(4) | 72(3) |
| O3 | 2839(5) | 5120(4) | 1781(4) | 58(2) |
| N3 | 3385(6) | 5010(5) | 3086(5) | 54(2) |
| O2 | 1497(5) | 4048(5) | 1650(4) | 67(2) |
| N1 | 2725(7) | 3757(5) | 3371(5) | 56(2) |
| C40 | 3363(8) | 5117(6) | 3747(7) | 62(3) |
| N4 | 1987(6) | 5128(5) | 3402(5) | 57(2) |
| C39 | 4035(7) | 5158(7) | 2828(6) | 58(3) |
| C38 | 4188(8) | 5050(7) | 2163(6) | 61(3) |
| N5 | 3181(6) | 6558(5) | 2069(5) | 55(2) |
| C45 | 2591(8) | 5205(6) | 3904(6) | 57(3) |
| C68 | 3177(9) | 6684(7) | 2748(7) | 66(3) |
| C32 | 5116(9) | 4920(8) | 1363(8) | 71(4) |
| C29 | 3589(7) | 5033(6) | 1660(6) | 57(3) |
| N2 | 1289(6) | 3873(5) | 2965(5) | 55(2) |
| C47 | 635(6) | 5350(6) | 2996(7) | 54(3) |
| C53 | -763(8) | 5373(7) | 2714(7) | 62(3) |
| C10 | 4010(7) | 3487(7) | 3013(6) | 60(3) |
| C30 | 3750(8) | 4943(7) | 1024(6) | 65(3) |
| C1 | 3784(7) | 3574(7) | 2347(7) | 62(3) |
| O7 | 1549(6) | 5207(5) | 776(4) | 66(2) |
| C11 | 3428(7) | 3482(7) | 3456(6) | 60(3) |
| C4 | 5350(7) | 3303(7) | 2786(7) | 64(3) |
| C54 | -628(7) | 5413(8) | 2061(8) | 70(4) |
| C60 | 5024(10) | 6598(10) | 401(8) | 84(4) |
| C55 | 90(7) | 5365(6) | 1872(7) | 58(3) |
| C34 | 6522(10) | 4838(9) | 1695(10) | 93(6) |
| C73 | 2374(8) | 6765(5) | 2909(5) | 53(3) |
| C65 | 4825(8) | 6634(6) | 1038(8) | 68(3) |
| O6 | 1107(6) | 6610(6) | 1132(5) | 79(3) |
| C41 | 3984(11) | 5137(9) | 4218(7) | 82(5) |
| C19 | 291(8) | 3787(7) | 2058(7) | 64(3) |
| C7 | 5842(9) | 3305(8) | 4105(8) | 74(4) |
| C77 | -406(10) | 7067(7) | 2947(9) | 76(4) |
| C81 | -977(9) | 7085(8) | 1834(7) | 71(3) |
| C44 | 2503(10) | 5309(7) | 4580(7) | 69(3) |
| C69 | 3796(9) | 6738(7) | 3192(7) | 67(3) |
| C78 | -1114(12) | 7228(7) | 3141(9) | 84(5) |

| | | | | |
|---|---|---|---|---|
| C37 | 4996(7) | 5018(6) | 2040(7) | 59(3) |
| N6 | 1788(6) | 6676(5) | 2407(5) | 56(2) |
| C74 | 1125(7) | 6932(7) | 2474(6) | 61(3) |
| C57 | 3418(7) | 6443(7) | 653(6) | 60(3) |
| C31 | 4518(9) | 4907(9) | 889(8) | 77(4) |
| C25 | -861(8) | 3624(8) | 1219(7) | 67(3) |
| C36 | 5642(7) | 4999(8) | 2521(9) | 74(4) |
| C46 | 1328(8) | 5363(7) | 3483(5) | 59(3) |
| C76 | -306(9) | 7037(8) | 2290(9) | 78(4) |
| C17 | 1435(8) | 3733(7) | 3645(6) | 63(3) |
| C70 | 3700(9) | 6897(7) | 3830(8) | 72(4) |
| C21 | -1072(10) | 3669(7) | 2351(7) | 74(4) |
| C66 | 4030(10) | 6568(8) | 1181(7) | 72(4) |
| C72 | 2313(10) | 6880(6) | 3574(8) | 71(4) |
| C24 | -1665(9) | 3571(9) | 1050(6) | 77(4) |
| C67 | 3843(8) | 6673(7) | 1830(6) | 63(3) |
| C56 | 776(7) | 5346(6) | 2364(7) | 58(3) |
| C9 | 4792(9) | 3367(8) | 3256(7) | 71(4) |
| C20 | -540(9) | 3666(7) | 1875(8) | 70(3) |
| C75 | 424(7) | 6906(8) | 2039(7) | 64(3) |
| C13 | 2468(7) | 3538(8) | 4520(7) | 72(4) |
| C48 | -115(8) | 5353(6) | 3182(7) | 64(3) |
| C82 | -888(8) | 7037(7) | 1170(8) | 67(3) |
| C3 | 5104(9) | 3325(7) | 2129(8) | 73(4) |
| C83 | -224(10) | 6892(9) | 948(8) | 81(4) |
| C12 | 2236(9) | 3667(7) | 3849(7) | 67(3) |
| C18 | 611(8) | 3700(7) | 2712(6) | 62(3) |
| C5 | 6161(9) | 3232(7) | 3009(9) | 77(4) |
| C26 | -340(11) | 3664(9) | 756(9) | 86(5) |
| C16 | 891(9) | 3733(8) | 4080(8) | 71(4) |
| C43 | 3095(12) | 5337(10) | 5039(7) | 87(5) |
| C35 | 6379(10) | 4903(9) | 2355(9) | 86(5) |
| C2 | 4361(8) | 3463(7) | 1903(7) | 67(3) |
| C84 | 477(8) | 6805(7) | 1398(7) | 70(4) |
| C27 | 425(8) | 3812(9) | 875(7) | 78(4) |
| C59 | 4380(11) | 6535(11) | -128(9) | 94(6) |
| C33 | 5901(9) | 4876(9) | 1233(8) | 80(4) |
| C42 | 3868(10) | 5231(9) | 4882(7) | 77(4) |

| | | | | |
|---|---|---|---|---|
| C71 | 2910(11) | 6924(9) | 4018(7) | 80(4) |
| C28 | 753(8) | 3896(7) | 1557(6) | 61(3) |
| C58 | 3645(9) | 6444(9) | 7(8) | 78(4) |
| C64 | 5438(9) | 6667(9) | 1533(8) | 78(4) |
| C80 | -1730(9) | 7196(11) | 2062(10) | 95(6) |
| C6 | 6375(9) | 3269(10) | 3650(8) | 89(5) |
| C15 | 1131(10) | 3615(8) | 4739(8) | 78(4) |
| C61 | 5770(14) | 6660(9) | 271(9) | 100(6) |
| C63 | 6190(10) | 6645(12) | 1364(10) | 101(6) |
| C23 | -2163(9) | 3498(8) | 1537(9) | 79(4) |
| C22 | -1846(9) | 3568(8) | 2177(8) | 78(4) |
| C14 | 1916(11) | 3536(10) | 4942(8) | 88(5) |
| C8 | 5074(10) | 3355(9) | 3919(7) | 80(4) |
| C52 | -1496(10) | 5424(8) | 2935(10) | 82(4) |
| C49 | -267(9) | 5275(8) | 3848(7) | 71(4) |
| C50 | -1019(10) | 5303(9) | 4036(9) | 83(4) |
| C79 | -1808(11) | 7289(8) | 2690(8) | 82(5) |
| C51 | -1655(9) | 5352(10) | 3561(11) | 100(6) |
| C62 | 6357(12) | 6689(12) | 741(10) | 106(7) |
| C85 | 1614(8) | 5060(6) | 105(6) | 60 |

**Crystallographic Table 126** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **$Lu_2[L^{VII}]_3$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{12}$** | **$U_{13}$** | **$U_{23}$** |
|---|---|---|---|---|---|---|
| Lu1 | 48.1(4) | 66.0(4) | 54.5(4) | 0.51(19) | 9.3(2) | -1.78(19) |
| Lu2 | 53.7(4) | 69.9(4) | 56.9(4) | 7.4(2) | 9.8(2) | 2.6(2) |
| O4 | 44(4) | 74(5) | 44(4) | 6(4) | 14(3) | 1(3) |
| O1 | 50(4) | 75(5) | 61(5) | 11(4) | 18(4) | -18(4) |
| O5 | 55(5) | 108(8) | 56(5) | -8(5) | 18(4) | 17(5) |
| O3 | 59(5) | 49(4) | 72(5) | 10(3) | 34(4) | 17(4) |
| N3 | 43(5) | 71(6) | 51(5) | -6(4) | 17(4) | 1(4) |
| O2 | 40(4) | 101(7) | 60(5) | -19(4) | 1(4) | -29(5) |
| N1 | 63(6) | 59(5) | 46(4) | -4(5) | 5(4) | 0(4) |
| C40 | 59(7) | 54(6) | 74(8) | -3(5) | 7(6) | 10(5) |
| N4 | 55(6) | 57(5) | 60(5) | -14(4) | 12(4) | -5(4) |
| C39 | 37(5) | 71(7) | 66(7) | 1(5) | 6(5) | 12(6) |
| C38 | 58(7) | 68(7) | 59(6) | 4(6) | 20(5) | 6(5) |
| N5 | 52(5) | 52(5) | 63(5) | 1(4) | 9(4) | -4(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C45 | 63(7) | 64(7) | 46(5) | -11(5) | 11(5) | 4(5) |
| C68 | 70(8) | 59(7) | 71(8) | 1(6) | 16(6) | -14(6) |
| C32 | 60(8) | 79(9) | 76(9) | 15(7) | 21(6) | 4(7) |
| C29 | 39(5) | 70(7) | 65(7) | 3(5) | 21(5) | 13(5) |
| N2 | 60(6) | 49(5) | 58(5) | -1(4) | 20(4) | 3(4) |
| C47 | 26(4) | 58(6) | 79(8) | -3(4) | 10(4) | -7(5) |
| C53 | 56(7) | 61(7) | 69(7) | 3(5) | 8(6) | 5(6) |
| C10 | 48(6) | 66(7) | 67(7) | 0(5) | 17(5) | -6(5) |
| C30 | 63(8) | 86(9) | 50(6) | 1(6) | 29(5) | -5(6) |
| C1 | 45(6) | 75(8) | 67(7) | 5(5) | 13(5) | 2(6) |
| O7 | 77(6) | 70(5) | 49(4) | 12(5) | 4(4) | -5(4) |
| C11 | 48(6) | 67(7) | 63(7) | -11(5) | -3(5) | 6(5) |
| C4 | 45(6) | 79(8) | 70(7) | -8(6) | 17(5) | -8(6) |
| C54 | 30(5) | 81(9) | 98(10) | 1(5) | -1(6) | -7(7) |
| C60 | 74(10) | 109(13) | 73(9) | 3(9) | 24(7) | 12(8) |
| C55 | 45(6) | 60(6) | 67(7) | -2(5) | 5(5) | -1(5) |
| C34 | 62(9) | 94(11) | 129(15) | 20(8) | 35(9) | 38(11) |
| C73 | 83(8) | 36(4) | 39(4) | 2(5) | 5(5) | 11(4) |
| C65 | 62(8) | 51(6) | 92(10) | 7(5) | 19(7) | -4(6) |
| O6 | 61(6) | 106(8) | 69(6) | 43(6) | 6(4) | 21(5) |
| C41 | 86(11) | 92(11) | 64(8) | -40(9) | -5(7) | 3(7) |
| C19 | 59(7) | 64(7) | 69(7) | 0(6) | 10(6) | -12(6) |
| C7 | 61(8) | 74(8) | 83(9) | 12(6) | -7(7) | -21(7) |
| C77 | 73(9) | 65(8) | 94(11) | -6(7) | 28(8) | -9(7) |
| C81 | 70(9) | 76(9) | 70(8) | 8(7) | 18(7) | 8(6) |
| C44 | 82(10) | 60(7) | 64(7) | -1(7) | 2(6) | -9(6) |
| C69 | 61(8) | 57(7) | 81(8) | 3(6) | 3(6) | 8(6) |
| C78 | 110(13) | 46(6) | 99(11) | -10(7) | 23(10) | -7(7) |
| C37 | 43(6) | 56(6) | 80(8) | 10(5) | 15(5) | 14(5) |
| N6 | 50(5) | 60(5) | 60(5) | 8(4) | 15(4) | 4(4) |
| C74 | 49(6) | 70(7) | 65(7) | 4(5) | 9(5) | -2(6) |
| C57 | 51(6) | 76(8) | 55(6) | 8(5) | 20(5) | 2(5) |
| C31 | 54(8) | 105(12) | 78(9) | -6(7) | 29(7) | 10(8) |
| C25 | 51(7) | 87(9) | 62(7) | 6(6) | 3(5) | -17(6) |
| C36 | 40(6) | 75(8) | 107(12) | -9(6) | 9(6) | 4(7) |
| C46 | 61(7) | 75(7) | 42(5) | 7(6) | 5(5) | 4(5) |
| C76 | 61(8) | 68(8) | 108(12) | 14(6) | 22(8) | 8(8) |
| C17 | 59(7) | 74(8) | 55(6) | 14(6) | 12(5) | 8(5) |

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|---|---|---|---|---|---|---|
| C70 | 66(8) | 65(7) | 83(9) | -4(6) | 1(7) | -22(7) |
| C21 | 88(10) | 68(8) | 72(8) | 19(7) | 28(7) | 16(6) |
| C66 | 82(10) | 73(8) | 63(7) | 6(7) | 16(7) | 17(6) |
| C72 | 87(10) | 45(6) | 87(9) | 13(6) | 37(8) | -4(6) |
| C24 | 71(9) | 109(12) | 48(6) | -12(8) | -1(6) | -4(7) |
| C67 | 59(7) | 73(8) | 58(6) | 3(6) | 12(5) | -15(6) |
| C56 | 47(6) | 54(6) | 72(7) | 1(5) | 6(5) | -16(5) |
| C9 | 66(8) | 75(8) | 70(8) | 20(7) | -3(6) | 6(6) |
| C20 | 59(8) | 60(7) | 93(10) | 2(6) | 16(7) | -9(6) |
| C75 | 41(6) | 80(8) | 74(8) | 1(5) | 15(5) | 6(6) |
| C13 | 41(6) | 110(11) | 65(7) | 26(7) | 7(5) | -17(7) |
| C48 | 53(7) | 58(6) | 85(9) | 2(5) | 30(6) | 2(6) |
| C82 | 50(6) | 59(7) | 88(9) | 12(5) | -10(6) | -2(6) |
| C3 | 72(9) | 55(7) | 98(10) | 14(6) | 38(8) | 4(6) |
| C83 | 69(9) | 89(10) | 82(10) | 12(8) | 1(7) | 14(8) |
| C12 | 72(8) | 65(7) | 68(7) | -1(6) | 26(6) | -12(6) |
| C18 | 66(8) | 64(7) | 57(6) | -3(6) | 8(5) | 0(5) |
| C5 | 60(8) | 59(7) | 110(12) | 18(6) | 0(7) | 3(7) |
| C26 | 86(11) | 94(11) | 80(10) | 8(9) | 21(8) | -19(8) |
| C16 | 58(8) | 75(8) | 84(9) | -9(6) | 24(7) | -11(7) |
| C43 | 96(12) | 106(12) | 55(7) | -2(10) | -12(7) | 3(8) |
| C35 | 65(9) | 92(11) | 103(12) | -20(8) | 10(8) | -6(9) |
| C2 | 62(8) | 69(7) | 70(7) | 3(6) | 15(6) | -9(6) |
| C84 | 63(8) | 68(8) | 80(9) | 25(6) | 22(7) | 7(6) |
| C27 | 45(6) | 128(13) | 59(7) | -4(7) | -10(5) | -25(8) |
| C59 | 73(10) | 128(16) | 88(11) | -2(10) | 33(9) | -8(11) |
| C33 | 55(8) | 112(12) | 81(9) | 1(8) | 36(7) | 5(8) |
| C42 | 79(10) | 89(10) | 64(8) | -14(8) | 7(7) | -19(7) |
| C71 | 85(11) | 94(11) | 60(7) | -1(9) | -2(7) | 15(7) |
| C28 | 54(7) | 74(8) | 56(6) | 11(6) | 4(5) | -7(5) |
| C58 | 66(9) | 97(11) | 77(9) | 4(8) | 30(7) | 21(8) |
| C64 | 56(8) | 99(11) | 83(9) | -22(7) | 23(7) | -24(8) |
| C80 | 47(7) | 120(15) | 116(14) | -4(8) | 4(8) | 23(11) |
| C6 | 51(7) | 134(15) | 81(10) | -35(9) | 1(7) | 6(9) |
| C15 | 75(9) | 85(10) | 79(9) | 7(8) | 35(7) | 15(7) |
| C61 | 140(18) | 86(11) | 81(11) | -30(12) | 49(12) | -2(9) |
| C63 | 53(9) | 139(17) | 113(14) | 6(10) | 12(9) | 13(13) |
| C23 | 62(8) | 76(9) | 98(11) | -6(7) | 10(7) | 8(8) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C22 | 66(9) | 87(10) | 82(9) | -3(7) | 20(7) | -17(8) |
| C14 | 84(11) | 118(14) | 66(8) | -11(10) | 23(8) | 14(8) |
| C8 | 81(10) | 95(11) | 62(8) | 15(9) | 1(7) | -10(7) |
| C52 | 63(9) | 78(9) | 108(13) | 0(7) | 26(8) | 1(8) |
| C49 | 73(9) | 76(8) | 69(8) | -4(7) | 31(7) | 2(6) |
| C50 | 78(10) | 94(11) | 85(10) | 4(8) | 41(8) | -4(8) |
| C79 | 100(12) | 68(8) | 85(10) | 20(8) | 48(9) | 2(7) |
| C51 | 46(8) | 112(14) | 146(18) | -2(8) | 31(9) | -33(12) |
| C62 | 93(13) | 145(19) | 90(12) | -22(13) | 53(11) | -9(12) |

**Crystallographic Table 127** Bond Lengths for **$Lu_2[L^{VII}]_3$.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Lu1 | O4 | 2.316(9) | C34 | C35 | 1.42(2) |
| Lu1 | O1 | 2.219(8) | C34 | C33 | 1.36(2) |
| Lu1 | O3 | 2.307(7) | C73 | N6 | 1.387(15) |
| Lu1 | N3 | 2.480(10) | C73 | C72 | 1.410(17) |
| Lu1 | O2 | 2.218(8) | C65 | C66 | 1.45(2) |
| Lu1 | N1 | 2.374(10) | C65 | C64 | 1.40(2) |
| Lu1 | N4 | 2.457(10) | O6 | C84 | 1.338(15) |
| Lu1 | N2 | 2.371(10) | C41 | C42 | 1.42(2) |
| Lu2 | O4 | 2.295(8) | C19 | C20 | 1.48(2) |
| Lu2 | O5 | 2.196(8) | C19 | C18 | 1.417(19) |
| Lu2 | O3 | 2.276(8) | C19 | C28 | 1.397(19) |
| Lu2 | N5 | 2.390(10) | C7 | C6 | 1.39(2) |
| Lu2 | O7 | 2.375(9) | C7 | C8 | 1.35(2) |
| Lu2 | O6 | 2.177(8) | C77 | C78 | 1.38(2) |
| Lu2 | N6 | 2.375(10) | C77 | C76 | 1.39(2) |
| O4 | C56 | 1.317(14) | C81 | C76 | 1.42(2) |
| O1 | C1 | 1.311(15) | C81 | C82 | 1.40(2) |
| O5 | C57 | 1.250(15) | C81 | C80 | 1.46(2) |
| O3 | C29 | 1.366(13) | C44 | C43 | 1.33(2) |
| N3 | C40 | 1.390(17) | C69 | C70 | 1.39(2) |
| N3 | C39 | 1.336(14) | C78 | C79 | 1.45(3) |
| O2 | C28 | 1.325(16) | C37 | C36 | 1.42(2) |
| N1 | C11 | 1.339(16) | N6 | C74 | 1.288(15) |
| N1 | C12 | 1.384(16) | C74 | C75 | 1.436(18) |
| C40 | C45 | 1.427(18) | C57 | C66 | 1.46(2) |
| C40 | C41 | 1.37(2) | C57 | C58 | 1.433(17) |

| | | | | | |
|---|---|---|---|---|---|
| N4 | C45 | 1.405(16) | C25 | C24 | 1.410(19) |
| N4 | C46 | 1.270(16) | C25 | C20 | 1.41(2) |
| C39 | C38 | 1.444(17) | C25 | C26 | 1.39(2) |
| C38 | C29 | 1.392(18) | C36 | C35 | 1.38(2) |
| C38 | C37 | 1.457(16) | C76 | C75 | 1.447(18) |
| N5 | C68 | 1.427(17) | C17 | C12 | 1.42(2) |
| N5 | C67 | 1.322(16) | C17 | C16 | 1.375(18) |
| C45 | C44 | 1.438(17) | C70 | C71 | 1.47(2) |
| C68 | C73 | 1.481(19) | C21 | C20 | 1.42(2) |
| C68 | C69 | 1.34(2) | C21 | C22 | 1.37(2) |
| C32 | C37 | 1.453(19) | C66 | C67 | 1.430(18) |
| C32 | C31 | 1.35(2) | C72 | C71 | 1.31(2) |
| C32 | C33 | 1.422(18) | C24 | C23 | 1.41(2) |
| C29 | C30 | 1.385(16) | C9 | C8 | 1.406(19) |
| N2 | C17 | 1.431(15) | C75 | C84 | 1.36(2) |
| N2 | C18 | 1.288(17) | C13 | C12 | 1.43(2) |
| C47 | C46 | 1.485(16) | C13 | C14 | 1.37(2) |
| C47 | C56 | 1.356(18) | C48 | C49 | 1.438(18) |
| C47 | C48 | 1.401(15) | C82 | C83 | 1.32(2) |
| C53 | C54 | 1.40(2) | C3 | C2 | 1.36(2) |
| C53 | C48 | 1.41(2) | C83 | C84 | 1.46(2) |
| C53 | C52 | 1.40(2) | C5 | C6 | 1.34(2) |
| C10 | C1 | 1.403(18) | C26 | C27 | 1.36(2) |
| C10 | C11 | 1.439(17) | C16 | C15 | 1.40(2) |
| C10 | C9 | 1.420(18) | C43 | C42 | 1.43(3) |
| C30 | C31 | 1.396(18) | C27 | C28 | 1.473(17) |
| C1 | C2 | 1.449(17) | C59 | C58 | 1.35(2) |
| O7 | C85 | 1.437(14) | C64 | C63 | 1.39(2) |
| C4 | C9 | 1.451(19) | C80 | C79 | 1.33(2) |
| C4 | C3 | 1.38(2) | C15 | C14 | 1.39(2) |
| C4 | C5 | 1.443(19) | C61 | C62 | 1.33(3) |
| C54 | C55 | 1.352(17) | C63 | C62 | 1.35(3) |
| C60 | C65 | 1.40(2) | C23 | C22 | 1.38(2) |
| C60 | C59 | 1.49(3) | C52 | C51 | 1.36(3) |
| C60 | C61 | 1.36(3) | C49 | C50 | 1.406(19) |
| C55 | C56 | 1.483(17) | C50 | C51 | 1.40(3) |

**Crystallographic Table 128** Bond Angles for **$Lu_2[L^{VII}]_3$**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O1 | Lu1 | O4 | 139.6(3) | C59 | C60 | C65 | 117.0(15) |
| O3 | Lu1 | O4 | 69.1(3) | C61 | C60 | C65 | 121.2(18) |
| O3 | Lu1 | O1 | 79.5(3) | C61 | C60 | C59 | 121.6(16) |
| N3 | Lu1 | O4 | 103.3(3) | C56 | C55 | C54 | 120.3(13) |
| N3 | Lu1 | O1 | 89.0(3) | C33 | C34 | C35 | 117.3(15) |
| N3 | Lu1 | O3 | 70.7(3) | N6 | C73 | C68 | 116.9(10) |
| O2 | Lu1 | O4 | 73.9(4) | C72 | C73 | C68 | 114.2(12) |
| O2 | Lu1 | O1 | 81.4(3) | C72 | C73 | N6 | 128.8(13) |
| O2 | Lu1 | O3 | 89.7(4) | C66 | C65 | C60 | 121.6(15) |
| O2 | Lu1 | N3 | 159.5(3) | C64 | C65 | C60 | 116.5(14) |
| N1 | Lu1 | O4 | 145.7(3) | C64 | C65 | C66 | 121.6(14) |
| N1 | Lu1 | O1 | 74.6(4) | C84 | O6 | Lu2 | 130.8(9) |
| N1 | Lu1 | O3 | 135.4(4) | C42 | C41 | C40 | 120.4(17) |
| N1 | Lu1 | N3 | 73.1(4) | C18 | C19 | C20 | 119.9(13) |
| N1 | Lu1 | O2 | 120.8(4) | C28 | C19 | C20 | 117.5(13) |
| N4 | Lu1 | O4 | 69.3(3) | C28 | C19 | C18 | 122.0(13) |
| N4 | Lu1 | O1 | 146.6(4) | C8 | C7 | C6 | 121.4(15) |
| N4 | Lu1 | O3 | 106.2(3) | C76 | C77 | C78 | 120.4(18) |
| N4 | Lu1 | N3 | 63.5(3) | C82 | C81 | C76 | 118.4(14) |
| N4 | Lu1 | O2 | 130.6(4) | C80 | C81 | C76 | 119.9(15) |
| N4 | Lu1 | N1 | 79.3(4) | C80 | C81 | C82 | 121.7(15) |
| N2 | Lu1 | O4 | 92.8(3) | C43 | C44 | C45 | 123.2(16) |
| N2 | Lu1 | O1 | 111.3(4) | C70 | C69 | C68 | 120.1(14) |
| N2 | Lu1 | O3 | 159.4(4) | C79 | C78 | C77 | 122.9(17) |
| N2 | Lu1 | N3 | 125.3(3) | C32 | C37 | C38 | 114.6(12) |
| N2 | Lu1 | O2 | 75.2(4) | C36 | C37 | C38 | 125.9(13) |
| N2 | Lu1 | N1 | 65.3(4) | C36 | C37 | C32 | 119.1(12) |
| N2 | Lu1 | N4 | 74.9(3) | C73 | N6 | Lu2 | 116.7(7) |
| O5 | Lu2 | O4 | 158.9(4) | C74 | N6 | Lu2 | 125.8(9) |
| O3 | Lu2 | O4 | 70.0(3) | C74 | N6 | C73 | 117.4(11) |
| O3 | Lu2 | O5 | 96.6(3) | C75 | C74 | N6 | 128.8(13) |
| N5 | Lu2 | O4 | 116.8(3) | C66 | C57 | O5 | 123.7(11) |
| N5 | Lu2 | O5 | 75.5(4) | C58 | C57 | O5 | 119.7(13) |
| N5 | Lu2 | O3 | 81.4(3) | C58 | C57 | C66 | 116.4(12) |
| O7 | Lu2 | O4 | 74.6(3) | C30 | C31 | C32 | 122.3(14) |
| O7 | Lu2 | O5 | 86.7(4) | C20 | C25 | C24 | 121.5(13) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O7 | Lu2 | O3 | 77.0(3) | C26 | C25 | C24 | 122.4(14) |
| O7 | Lu2 | N5 | 150.1(3) | C26 | C25 | C20 | 116.0(14) |
| O6 | Lu2 | O4 | 99.4(4) | C35 | C36 | C37 | 121.2(16) |
| O6 | Lu2 | O5 | 88.4(4) | C47 | C46 | N4 | 125.6(11) |
| O6 | Lu2 | O3 | 160.9(4) | C81 | C76 | C77 | 117.7(14) |
| O6 | Lu2 | N5 | 117.7(4) | C75 | C76 | C77 | 124.4(16) |
| O6 | Lu2 | O7 | 85.0(4) | C75 | C76 | C81 | 117.7(15) |
| N6 | Lu2 | O4 | 78.0(3) | C12 | C17 | N2 | 112.1(11) |
| N6 | Lu2 | O5 | 123.1(4) | C16 | C17 | N2 | 125.5(13) |
| N6 | Lu2 | O3 | 116.5(3) | C16 | C17 | C12 | 122.0(13) |
| N6 | Lu2 | N5 | 66.3(4) | C71 | C70 | C69 | 118.1(14) |
| N6 | Lu2 | O7 | 142.6(4) | C22 | C21 | C20 | 120.7(15) |
| N6 | Lu2 | O6 | 75.0(4) | C57 | C66 | C65 | 119.8(12) |
| Lu2 | O4 | Lu1 | 109.6(3) | C67 | C66 | C65 | 119.7(14) |
| C56 | O4 | Lu1 | 119.6(8) | C67 | C66 | C57 | 120.4(13) |
| C56 | O4 | Lu2 | 129.9(8) | C71 | C72 | C73 | 123.9(15) |
| C1 | O1 | Lu1 | 129.0(8) | C23 | C24 | C25 | 120.1(13) |
| C57 | O5 | Lu2 | 135.9(9) | C66 | C67 | N5 | 128.3(13) |
| Lu2 | O3 | Lu1 | 110.6(3) | C47 | C56 | O4 | 127.9(11) |
| C29 | O3 | Lu1 | 121.3(7) | C55 | C56 | O4 | 115.5(11) |
| C29 | O3 | Lu2 | 127.0(7) | C55 | C56 | C47 | 116.5(11) |
| C40 | N3 | Lu1 | 117.8(7) | C4 | C9 | C10 | 117.6(13) |
| C39 | N3 | Lu1 | 123.7(8) | C8 | C9 | C10 | 124.7(15) |
| C39 | N3 | C40 | 118.2(11) | C8 | C9 | C4 | 117.6(14) |
| C28 | O2 | Lu1 | 134.4(8) | C25 | C20 | C19 | 122.2(13) |
| C11 | N1 | Lu1 | 124.8(8) | C21 | C20 | C19 | 120.9(15) |
| C12 | N1 | Lu1 | 116.9(9) | C21 | C20 | C25 | 116.5(14) |
| C12 | N1 | C11 | 118.2(11) | C76 | C75 | C74 | 119.2(14) |
| C45 | C40 | N3 | 111.6(11) | C84 | C75 | C74 | 118.5(12) |
| C41 | C40 | N3 | 126.8(14) | C84 | C75 | C76 | 122.2(14) |
| C41 | C40 | C45 | 121.5(14) | C14 | C13 | C12 | 118.5(13) |
| C45 | N4 | Lu1 | 116.0(8) | C53 | C48 | C47 | 120.9(13) |
| C46 | N4 | Lu1 | 125.3(9) | C49 | C48 | C47 | 122.3(14) |
| C46 | N4 | C45 | 118.3(11) | C49 | C48 | C53 | 116.6(12) |
| C38 | C39 | N3 | 126.6(12) | C83 | C82 | C81 | 123.3(14) |
| C29 | C38 | C39 | 121.1(11) | C2 | C3 | C4 | 122.0(13) |
| C37 | C38 | C39 | 116.9(13) | C84 | C83 | C82 | 120.5(15) |
| C37 | C38 | C29 | 121.8(11) | C17 | C12 | N1 | 115.7(13) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C68 | N5 | Lu2 | 117.4(8) | C13 | C12 | N1 | 126.0(14) |
| C67 | N5 | Lu2 | 126.2(8) | C13 | C12 | C17 | 118.2(12) |
| C67 | N5 | C68 | 115.6(11) | C19 | C18 | N2 | 127.0(13) |
| N4 | C45 | C40 | 117.8(11) | C6 | C5 | C4 | 118.0(15) |
| C44 | C45 | C40 | 116.1(13) | C27 | C26 | C25 | 125.9(16) |
| C44 | C45 | N4 | 125.8(12) | C15 | C16 | C17 | 118.8(14) |
| C73 | C68 | N5 | 110.3(12) | C42 | C43 | C44 | 120.4(16) |
| C69 | C68 | N5 | 126.8(13) | C36 | C35 | C34 | 121.2(17) |
| C69 | C68 | C73 | 122.9(13) | C3 | C2 | C1 | 120.9(14) |
| C31 | C32 | C37 | 121.5(13) | C75 | C84 | O6 | 126.3(14) |
| C33 | C32 | C37 | 115.6(14) | C83 | C84 | O6 | 116.0(14) |
| C33 | C32 | C31 | 122.9(14) | C83 | C84 | C75 | 117.6(13) |
| C38 | C29 | O3 | 120.8(11) | C28 | C27 | C26 | 118.0(15) |
| C30 | C29 | O3 | 119.1(12) | C58 | C59 | C60 | 121.0(16) |
| C30 | C29 | C38 | 120.1(11) | C34 | C33 | C32 | 125.1(15) |
| C17 | N2 | Lu1 | 116.8(8) | C43 | C42 | C41 | 118.2(15) |
| C18 | N2 | Lu1 | 129.3(9) | C72 | C71 | C70 | 120.3(15) |
| C18 | N2 | C17 | 113.8(11) | C19 | C28 | O2 | 124.1(12) |
| C56 | C47 | C46 | 115.9(10) | C27 | C28 | O2 | 116.0(12) |
| C48 | C47 | C46 | 121.8(12) | C27 | C28 | C19 | 119.8(13) |
| C48 | C47 | C56 | 122.4(12) | C59 | C58 | C57 | 123.7(17) |
| C48 | C53 | C54 | 117.5(12) | C63 | C64 | C65 | 118.6(16) |
| C52 | C53 | C54 | 124.3(14) | C79 | C80 | C81 | 121.8(17) |
| C52 | C53 | C48 | 117.8(14) | C5 | C6 | C7 | 122.4(15) |
| C11 | C10 | C1 | 119.0(12) | C14 | C15 | C16 | 119.5(13) |
| C9 | C10 | C1 | 121.7(12) | C62 | C61 | C60 | 122.2(17) |
| C9 | C10 | C11 | 119.2(12) | C62 | C63 | C64 | 122.7(19) |
| C31 | C30 | C29 | 119.5(14) | C22 | C23 | C24 | 117.4(15) |
| C10 | C1 | O1 | 125.2(11) | C23 | C22 | C21 | 123.1(15) |
| C2 | C1 | O1 | 117.3(12) | C15 | C14 | C13 | 122.7(15) |
| C2 | C1 | C10 | 117.6(12) | C9 | C8 | C7 | 120.6(16) |
| C85 | O7 | Lu2 | 135.0(8) | C51 | C52 | C53 | 126.0(17) |
| C10 | C11 | N1 | 127.5(12) | C50 | C49 | C48 | 122.2(16) |
| C3 | C4 | C9 | 119.7(13) | C51 | C50 | C49 | 119.8(15) |
| C5 | C4 | C9 | 119.8(14) | C80 | C79 | C78 | 116.7(15) |
| C5 | C4 | C3 | 120.5(13) | C50 | C51 | C52 | 116.6(15) |
| C55 | C54 | C53 | 122.1(13) | C63 | C62 | C61 | 117.8(18) |

**Crystallographic Table 129** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **$Lu_2[L^{VII}]_3$**.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H39 | 4437(7) | 5354(7) | 3110(6) | 70(3) |
| H30 | 3341(8) | 4906(7) | 683(6) | 78(4) |
| H7 | 1370(70) | 4840(30) | 928(13) | 98(3) |
| H11 | 3556(7) | 3258(7) | 3856(6) | 72(3) |
| H54 | -1054(7) | 5476(8) | 1739(8) | 84(4) |
| H55 | 156(7) | 5344(6) | 1423(7) | 69(3) |
| H34 | 7030(10) | 4771(9) | 1579(10) | 112(7) |
| H41 | 4493(11) | 5089(9) | 4099(7) | 98(6) |
| H7a | 6021(9) | 3295(8) | 4555(8) | 88(5) |
| H77 | 17(10) | 6976(7) | 3264(9) | 91(5) |
| H44 | 1996(10) | 5359(7) | 4703(7) | 83(4) |
| H69 | 4300(9) | 6668(7) | 3069(7) | 80(4) |
| H78 | -1149(12) | 7303(7) | 3590(9) | 101(6) |
| H74 | 1095(7) | 7171(7) | 2865(6) | 73(3) |
| H31 | 4624(9) | 4872(9) | 449(8) | 93(5) |
| H36 | 5565(7) | 5053(8) | 2966(9) | 89(5) |
| H46 | 1274(8) | 5564(7) | 3890(5) | 71(3) |
| H70 | 4134(9) | 6985(7) | 4138(8) | 86(4) |
| H21 | -889(10) | 3742(7) | 2795(7) | 89(5) |
| H72 | 1811(10) | 6929(6) | 3708(8) | 85(4) |
| H24 | -1871(9) | 3586(9) | 605(6) | 92(5) |
| H67 | 4246(8) | 6848(7) | 2126(6) | 76(4) |
| H13 | 2995(7) | 3455(8) | 4669(7) | 86(5) |
| H82 | -1327(8) | 7112(7) | 865(8) | 80(4) |
| H3 | 5466(9) | 3242(7) | 1826(8) | 87(5) |
| H83 | -202(10) | 6845(9) | 494(8) | 97(5) |
| H18 | 291(8) | 3492(7) | 2994(6) | 75(3) |
| H5 | 6531(9) | 3161(7) | 2710(9) | 92(5) |
| H26 | -536(11) | 3580(9) | 317(9) | 103(5) |
| H16 | 361(9) | 3810(8) | 3937(8) | 85(4) |
| H43 | 3007(12) | 5429(10) | 5475(7) | 105(6) |
| H35 | 6799(10) | 4881(9) | 2688(9) | 104(6) |
| H2 | 4217(8) | 3487(7) | 1447(7) | 80(4) |
| H27 | 737(8) | 3860(9) | 528(7) | 94(5) |
| H59 | 4486(11) | 6559(11) | -569(9) | 113(7) |

| | | | | |
|---|---|---|---|---|
| H33 | 6001(9) | 4874(9) | 790(8) | 97(5) |
| H42 | 4292(10) | 5223(9) | 5213(7) | 93(5) |
| H71 | 2830(11) | 6975(9) | 4463(7) | 96(5) |
| H58 | 3256(9) | 6376(9) | -345(8) | 94(5) |
| H64 | 5343(9) | 6704(9) | 1975(8) | 94(5) |
| H80 | -2178(9) | 7202(11) | 1755(10) | 114(7) |
| H6 | 6911(9) | 3270(10) | 3799(8) | 107(6) |
| H15 | 762(10) | 3590(8) | 5045(8) | 94(5) |
| H61 | 5877(14) | 6684(9) | -169(9) | 120(8) |
| H63 | 6604(10) | 6597(12) | 1700(10) | 122(7) |
| H23 | -2697(9) | 3404(8) | 1432(9) | 94(5) |
| H22 | -2180(9) | 3545(8) | 2510(8) | 93(5) |
| H14 | 2073(11) | 3479(10) | 5393(8) | 106(6) |
| H8 | 4723(10) | 3381(9) | 4239(7) | 96(5) |
| H52 | -1919(10) | 5516(8) | 2618(10) | 98(5) |
| H49 | 155(9) | 5202(8) | 4171(7) | 85(4) |
| H50 | -1097(10) | 5289(9) | 4484(9) | 100(5) |
| H79 | -2294(11) | 7389(8) | 2835(8) | 98(5) |
| H51 | -2172(9) | 5337(10) | 3670(11) | 120(7) |
| H62 | 6874(12) | 6739(12) | 643(10) | 128(8) |
| H85a | 1293(8) | 4679(6) | -27(6) | 90 |
| H85b | 1439(8) | 5437(6) | -164(6) | 90 |
| H85c | 2155(8) | 4964(6) | 49(6) | 90 |

**Crystallographic Table 130** Solvent masks information for **$Lu_2[L^{VII}]_3$**.

| Number | X | Y | Z | Volume | Electron count | Content |
|---|---|---|---|---|---|---|
| 1 | 0.155 | 0.209 | 0.033 | 327.6 | 127.0 | 3DCM |
| 2 | 0.155 | 0.291 | 0.533 | 327.6 | 121.2 | 3DCM |
| 3 | -0.155 | 0.709 | 0.467 | 327.6 | 131.6 | 3DCM |
| 4 | -0.155 | 0.791 | 0.967 | 327.6 | 125.9 | 3DCM |

Refinement model description

Number of restraints - 3, number of constraints - 113.

Details:

1. Others
Fixed Uiso: C85(0.06) H85a(0.09) H85b(0.09) H85c(0.09)

## $UO_2[L^{VII}]$

**Crystallographic Table 131** Crystal data and structure refinement for **$UO_2[L^{VII}]$**

| | |
|---|---|
| Empirical formula | $C_{60}H_{48}Cl_8N_4O_{10}U_2$ |
| Formula weight | 1744.75 |
| Temperature/K | 180.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 15.4659(12) |
| b/Å | 19.3294(14) |
| c/Å | 22.2346(16) |
| α/° | 90 |
| β/° | 106.655(1) |
| γ/° | 90 |
| Volume/Å$^3$ | 6368.1(8) |
| Z | 4 |
| $\rho_{calc}$mg/mm$^3$ | 1.8197 |
| m/mm$^{-1}$ | 5.476 |
| F(000) | 3269.1 |
| Crystal size/mm$^3$ | 0.18 × 0.12 × 0.1 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection | 2.84 to 51.52° |
| Index ranges | $-18 \le h \le 18$, $-23 \le k \le 23$, $-27 \le l \le 27$ |
| Reflections collected | 74217 |
| Independent reflections | 12168 [$R_{int}$ = 0.0706, $R_{sigma}$ = 0.0463] |
| Data/restraints/parameters | 12168/0/759 |
| Goodness-of-fit on $F^2$ | 1.094 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0440, $wR_2$ = 0.0935 |
| Final R indexes [all data] | $R_1$ = 0.0628, $wR_2$ = 0.1031 |
| Largest diff. peak/hole / e Å$^{-3}$ | 3.33/-1.96 |

**Crystallographic Table 132** Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for **$UO_2[L^{VII}]$**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| U1 | -802.24(16) | 10935.58(14) | 554.71(13) | 17.87(8) |
| U2 | -2483.41(17) | 9914.97(14) | -1991.78(13) | 19.85(8) |
| O1 | 225(3) | 10825(3) | 343(2) | 23.9(11) |
| O2 | -326(3) | 10031(3) | 1230(2) | 23.5(11) |

| | | | | |
|---|---|---|---|---|
| O3 | -1824(3) | 11064(3) | 749(2) | 23.4(11) |
| O4 | -1513(3) | 9961(3) | -83(2) | 24.0(11) |
| O5 | -1643(3) | 10049(3) | -2663(3) | 30.9(13) |
| O6 | -1256(3) | 10646(3) | -1350(2) | 23.5(11) |
| O8 | -3149(3) | 10648(3) | -2297(2) | 28.1(12) |
| N1 | -53(4) | 11368(3) | 1634(3) | 22.2(14) |
| N2 | -549(4) | 12221(3) | 667(3) | 23.1(14) |
| N3 | -3892(4) | 9209(3) | -2061(3) | 24.2(14) |
| N4 | -3194(4) | 9318(3) | -3020(3) | 24.6(14) |
| C1 | -595(4) | 9919(4) | 1739(4) | 25.0(17) |
| C2 | -627(5) | 10446(4) | 2162(4) | 25.7(17) |
| C3 | -182(5) | 11103(4) | 2133(4) | 26.9(18) |
| C4 | 485(5) | 11975(4) | 1665(4) | 25.5(17) |
| C5 | 234(5) | 12422(4) | 1155(4) | 27.0(17) |
| C6 | -1082(6) | 12710(4) | 365(4) | 28.8(18) |
| C7 | -1882(5) | 12597(4) | -146(4) | 25.9(17) |
| C8 | -1992(5) | 11999(4) | -516(3) | 23.5(16) |
| C9 | -2736(5) | 11942(4) | -1059(4) | 27.3(17) |
| C10 | -3366(6) | 12453(5) | -1205(4) | 33.1(19) |
| C11 | -3300(6) | 13061(4) | -848(4) | 33.8(19) |
| C12 | -2553(6) | 13145(4) | -312(4) | 33(2) |
| C13 | -2519(8) | 13759(5) | 31(4) | 49(3) |
| C14 | -3185(9) | 14251(5) | -152(5) | 63(3) |
| C15 | -3925(8) | 14162(6) | -668(5) | 60(3) |
| C16 | -3973(7) | 13576(5) | -1002(5) | 48(3) |
| C18 | 752(6) | 13007(5) | 1136(4) | 39(2) |
| C19 | 1505(6) | 13145(5) | 1641(5) | 44(2) |
| C20 | 1741(5) | 12707(5) | 2148(4) | 37(2) |
| C21 | 1249(5) | 12111(4) | 2176(4) | 28.8(18) |
| C22 | -1007(5) | 10309(5) | 2667(4) | 35(2) |
| C23 | -1199(6) | 10840(6) | 3044(5) | 50(3) |
| C24 | -1625(9) | 10693(7) | 3502(6) | 73(4) |
| C25 | -1895(10) | 10017(8) | 3579(6) | 81(4) |
| C26 | -1719(9) | 9489(7) | 3222(6) | 73(4) |
| C27 | -1287(6) | 9629(5) | 2754(4) | 43(2) |
| C28 | -1162(6) | 9100(5) | 2345(4) | 42(2) |
| C29 | -849(5) | 9233(4) | 1846(4) | 31.3(19) |
| C31 | -3699(5) | 10179(4) | -992(4) | 22.8(16) |

| | | | | |
|---|---|---|---|---|
| C32 | -4516(5) | 9862(4) | -1345(4) | 24.5(17) |
| C33 | -5342(5) | 10030(4) | -1198(4) | 26.6(17) |
| C34 | -5328(5) | 10493(4) | -707(4) | 29.4(18) |
| C35 | -4487(5) | 10799(4) | -370(4) | 30.9(19) |
| C36 | -3715(5) | 10646(4) | -503(4) | 28.3(18) |
| C37 | -6132(5) | 10647(5) | -551(4) | 34(2) |
| C38 | -6927(5) | 10349(5) | -871(4) | 37(2) |
| C39 | -6958(5) | 9908(5) | -1363(4) | 37(2) |
| C40 | -6194(5) | 9754(5) | -1533(4) | 32(2) |
| C41 | -4508(5) | 9334(4) | -1794(4) | 27.1(18) |
| C42 | -3998(5) | 8625(4) | -2468(4) | 27.8(18) |
| C43 | -3655(5) | 8689(4) | -2986(4) | 28.7(18) |
| C44 | -3206(5) | 9561(5) | -3565(4) | 31.8(19) |
| C45 | -2687(5) | 10127(5) | -3681(4) | 31.3(19) |
| C46 | -1880(5) | 10315(4) | -3232(4) | 28.9(18) |
| C47 | -1277(6) | 10788(5) | -3396(4) | 39(2) |
| C48 | -1508(7) | 11086(5) | -3978(5) | 47(2) |
| C49 | -2327(7) | 10933(5) | -4437(5) | 45(2) |
| C50 | -2932(6) | 10458(5) | -4293(4) | 40(2) |
| C51 | -3749(7) | 10335(6) | -4752(5) | 56(3) |
| C52 | -3943(8) | 10660(7) | -5323(5) | 65(3) |
| C53 | -3349(9) | 11123(6) | -5467(6) | 69(3) |
| C54 | -2569(8) | 11266(6) | -5030(5) | 60(3) |
| C55 | -3752(6) | 8141(5) | -3405(4) | 37(2) |
| C56 | -4192(6) | 7540(5) | -3330(5) | 45(2) |
| C57 | -4510(7) | 7474(5) | -2807(5) | 50(3) |
| C58 | -4416(6) | 8010(5) | -2377(4) | 39(2) |
| O0aa | -2919(3) | 10028(3) | -1085(2) | 26.2(12) |
| O1aa | -1408(3) | 11481(3) | -385(2) | 23.6(11) |
| Cl7 | -7846(4) | 12606(3) | -1649(3) | 160(2) |
| Cl8 | -5953(4) | 12463(3) | -1023(4) | 182(3) |
| Cl9 | -5981(4) | 11775(3) | -2822(4) | 182(3) |
| Cl10 | -5554(4) | 10499(4) | -3289(3) | 163(2) |
| C0aa | -5254(10) | 11112(9) | -2679(8) | 107(6) |
| C1aa | -6978(16) | 12067(10) | -1402(14) | 240(17) |
| O3aa | -1847(3) | 9173(3) | -1669(3) | 28.7(12) |
| Cl1 | -1475(4) | 8048(3) | 197(2) | 126.9(18) |
| Cl2 | -3313(4) | 8092(2) | -611(2) | 115.1(16) |

| | | | | |
|---|---|---|---|---|
| Cl6 | -3014(7) | 12149(4) | 1825(3) | 224(4) |
| Cl0a | -4357(5) | 12405(4) | 754(4) | 252(5) |
| C2aa | -3113(19) | 12262(13) | 1074(11) | 249(17) |
| C3aa | -2137(12) | 8081(8) | -540(8) | 114(6) |

**Crystallographic Table 133** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **$UO_2[L^{VII}]$**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| U1 | 13.80(12) | 19.81(15) | 19.73(14) | -0.97(10) | 4.36(10) | -3.72(11) |
| U2 | 14.37(13) | 21.43(15) | 22.28(15) | -0.88(10) | 2.92(10) | -3.19(12) |
| O1 | 20(2) | 30(3) | 24(3) | -2(2) | 10(2) | -4(2) |
| O2 | 21(2) | 24(3) | 24(3) | -1(2) | 6(2) | -3(2) |
| O3 | 19(2) | 29(3) | 24(3) | -2(2) | 8(2) | -7(2) |
| O4 | 17(2) | 24(3) | 28(3) | 1(2) | 2(2) | -2(2) |
| O5 | 22(3) | 47(4) | 26(3) | -4(2) | 9(2) | -4(3) |
| O6 | 16(2) | 25(3) | 28(3) | -1(2) | 5(2) | -5(2) |
| O8 | 22(3) | 32(3) | 28(3) | -1(2) | 3(2) | -3(2) |
| N1 | 20(3) | 22(3) | 24(3) | -4(2) | 6(3) | -6(3) |
| N2 | 30(3) | 19(3) | 22(3) | -9(3) | 10(3) | -6(3) |
| N3 | 22(3) | 25(4) | 26(3) | -7(3) | 6(3) | -5(3) |
| N4 | 21(3) | 26(4) | 25(4) | -2(3) | 3(3) | -8(3) |
| C1 | 11(3) | 33(5) | 28(4) | 0(3) | 1(3) | -2(4) |
| C2 | 16(3) | 33(5) | 25(4) | 2(3) | 1(3) | 2(4) |
| C3 | 18(4) | 37(5) | 23(4) | -3(3) | 3(3) | -10(4) |
| C4 | 21(4) | 26(4) | 32(4) | -9(3) | 12(3) | -17(4) |
| C5 | 33(4) | 24(4) | 27(4) | -1(3) | 13(3) | -4(3) |
| C6 | 44(5) | 19(4) | 22(4) | 3(4) | 8(4) | 2(3) |
| C7 | 36(4) | 22(4) | 23(4) | -1(3) | 13(3) | 4(3) |
| C8 | 31(4) | 22(4) | 20(4) | 1(3) | 13(3) | 2(3) |
| C9 | 31(4) | 23(4) | 28(4) | -2(3) | 8(3) | 0(3) |
| C10 | 36(4) | 39(5) | 23(4) | 8(4) | 7(4) | 7(4) |
| C11 | 48(5) | 28(5) | 26(4) | 10(4) | 11(4) | 8(4) |
| C12 | 56(5) | 19(4) | 28(5) | 0(4) | 16(4) | 5(4) |
| C13 | 83(8) | 30(5) | 31(5) | 12(5) | 13(5) | -2(4) |
| C14 | 102(9) | 28(6) | 54(7) | 26(6) | 15(7) | -3(5) |
| C15 | 94(9) | 52(7) | 33(6) | 42(6) | 16(6) | 11(5) |
| C16 | 68(7) | 41(6) | 34(5) | 23(5) | 13(5) | 8(4) |
| C18 | 41(5) | 36(5) | 38(5) | -16(4) | 9(4) | -10(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C19 | 48(5) | 35(5) | 50(6) | -23(4) | 17(5) | -9(5) |
| C20 | 26(4) | 40(5) | 43(5) | -13(4) | 5(4) | -22(4) |
| C21 | 24(4) | 32(5) | 29(4) | -1(3) | 6(3) | -11(4) |
| C22 | 26(4) | 48(6) | 31(5) | -8(4) | 9(4) | -2(4) |
| C23 | 47(6) | 67(7) | 42(6) | -12(5) | 22(5) | -9(5) |
| C24 | 92(9) | 86(10) | 57(7) | -21(8) | 48(7) | -21(7) |
| C25 | 104(10) | 98(11) | 55(8) | -33(9) | 48(7) | 6(8) |
| C26 | 98(10) | 75(9) | 55(7) | -29(7) | 36(7) | 10(7) |
| C27 | 41(5) | 54(6) | 34(5) | -6(4) | 12(4) | 9(5) |
| C28 | 46(5) | 36(5) | 42(5) | -6(4) | 8(4) | 14(4) |
| C29 | 23(4) | 29(5) | 40(5) | -1(3) | 4(3) | 7(4) |
| C31 | 16(3) | 28(4) | 26(4) | 1(3) | 8(3) | -1(3) |
| C32 | 22(4) | 27(4) | 23(4) | -4(3) | 4(3) | -1(3) |
| C33 | 24(4) | 31(5) | 26(4) | -1(3) | 10(3) | 3(4) |
| C34 | 22(4) | 37(5) | 30(4) | 1(3) | 7(3) | 4(4) |
| C35 | 27(4) | 34(5) | 32(5) | -2(3) | 9(3) | -13(4) |
| C36 | 15(3) | 41(5) | 26(4) | -9(3) | 0(3) | -6(4) |
| C37 | 28(4) | 40(5) | 35(5) | 6(4) | 12(4) | 0(4) |
| C38 | 23(4) | 53(6) | 39(5) | 7(4) | 16(4) | 8(5) |
| C39 | 18(4) | 47(6) | 42(5) | -7(4) | 4(3) | 4(4) |
| C40 | 19(4) | 46(5) | 32(5) | -6(3) | 6(3) | -5(4) |
| C41 | 19(4) | 25(4) | 38(5) | -5(3) | 9(3) | -3(4) |
| C42 | 23(4) | 28(4) | 31(5) | -3(3) | 4(3) | -7(4) |
| C43 | 18(4) | 32(5) | 35(5) | -4(3) | 7(3) | -10(4) |
| C44 | 27(4) | 39(5) | 26(5) | -1(4) | 1(3) | -8(4) |
| C45 | 31(4) | 41(5) | 24(4) | -3(4) | 10(3) | -2(4) |
| C46 | 24(4) | 35(5) | 33(5) | 0(3) | 14(3) | -3(4) |
| C47 | 33(5) | 40(5) | 43(5) | -8(4) | 11(4) | -3(4) |
| C48 | 56(6) | 43(6) | 50(6) | -13(5) | 29(5) | 0(5) |
| C49 | 55(6) | 35(5) | 42(6) | 0(4) | 12(5) | 3(5) |
| C50 | 46(5) | 38(5) | 35(5) | 1(4) | 10(4) | 4(4) |
| C51 | 48(6) | 75(8) | 41(6) | -6(5) | 5(5) | 19(6) |
| C52 | 64(7) | 77(8) | 42(6) | -6(6) | -3(5) | 18(6) |
| C53 | 90(9) | 65(8) | 47(7) | -1(7) | 13(6) | 23(6) |
| C54 | 79(8) | 52(7) | 53(7) | -9(6) | 26(6) | 12(6) |
| C55 | 33(4) | 45(6) | 36(5) | -5(4) | 13(4) | -15(4) |
| C56 | 45(5) | 41(6) | 52(6) | -16(4) | 19(5) | -26(5) |
| C57 | 58(6) | 37(6) | 58(7) | -25(5) | 22(5) | -19(5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C58 | 40(5) | 37(5) | 44(5) | -18(4) | 18(4) | -12(4) |
| O0aa | 13(2) | 36(3) | 29(3) | -4(2) | 5(2) | -8(3) |
| O1aa | 29(3) | 19(3) | 22(3) | 3(2) | 7(2) | -1(2) |
| Cl7 | 160(5) | 115(4) | 191(6) | 1(4) | 29(5) | -40(4) |
| Cl8 | 145(5) | 124(4) | 234(7) | -30(4) | -13(5) | 72(5) |
| Cl9 | 100(4) | 132(5) | 334(10) | 27(3) | 96(5) | 76(5) |
| Cl10 | 109(4) | 170(6) | 178(6) | -26(4) | -12(4) | 1(5) |
| C0aa | 79(10) | 131(15) | 106(13) | 24(10) | 18(9) | 44(11) |
| C1aa | 180(20) | 79(14) | 340(40) | -38(14) | -130(20) | 64(18) |
| O3aa | 23(3) | 26(3) | 35(3) | 1(2) | 5(2) | -7(3) |
| Cl1 | 163(4) | 117(4) | 106(3) | -72(3) | 46(3) | 5(3) |
| Cl2 | 163(4) | 108(3) | 88(3) | 65(3) | 59(3) | 20(2) |
| Cl6 | 319(11) | 169(6) | 137(5) | -71(7) | -10(6) | -49(5) |
| Cl0a | 152(6) | 239(8) | 303(10) | 96(6) | -36(6) | -151(8) |
| C2aa | 370(30) | 250(30) | 260(20) | 250(30) | 290(30) | 190(20) |
| C3aa | 168(16) | 87(11) | 135(15) | -18(11) | 119(14) | 8(11) |

**Crystallographic Table 134** Bond Lengths for **$UO_2[L^{VII}]$**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| U1 | O1 | 1.795(5) | C22 | C23 | 1.408(13) |
| U1 | O2 | 2.285(5) | C22 | C27 | 1.414(13) |
| U1 | O3 | 1.771(5) | C23 | C24 | 1.393(14) |
| U1 | O4 | 2.424(5) | C24 | C25 | 1.396(17) |
| U1 | N1 | 2.491(6) | C25 | C26 | 1.368(18) |
| U1 | N2 | 2.516(6) | C26 | C27 | 1.415(14) |
| U1 | O1aa | 2.288(5) | C27 | C28 | 1.418(14) |
| U2 | O5 | 2.259(5) | C28 | C29 | 1.357(12) |
| U2 | O6 | 2.466(5) | C31 | C32 | 1.420(10) |
| U2 | O8 | 1.769(5) | C31 | C36 | 1.419(11) |
| U2 | N3 | 2.538(6) | C31 | O0aa | 1.315(8) |
| U2 | N4 | 2.515(6) | C32 | C33 | 1.445(10) |
| U2 | O0aa | 2.311(5) | C32 | C41 | 1.431(11) |
| U2 | O3aa | 1.771(5) | C33 | C34 | 1.407(11) |
| O2 | C1 | 1.330(9) | C33 | C40 | 1.418(10) |
| O5 | C46 | 1.315(10) | C34 | C35 | 1.430(11) |
| N1 | C3 | 1.290(10) | C34 | C37 | 1.415(11) |
| N1 | C4 | 1.428(9) | C35 | C36 | 1.344(11) |
| N2 | C5 | 1.428(10) | C37 | C38 | 1.360(12) |

| | | | | | |
|---|---|---|---|---|---|
| N2 | C6 | 1.307(10) | C38 | C39 | 1.377(13) |
| N3 | C41 | 1.282(9) | C39 | C40 | 1.373(11) |
| N3 | C42 | 1.425(10) | C42 | C43 | 1.404(11) |
| N4 | C43 | 1.424(10) | C42 | C58 | 1.396(11) |
| N4 | C44 | 1.294(10) | C43 | C55 | 1.390(11) |
| C1 | C2 | 1.397(11) | C44 | C45 | 1.424(12) |
| C1 | C29 | 1.422(11) | C45 | C46 | 1.403(11) |
| C2 | C3 | 1.454(11) | C45 | C50 | 1.452(12) |
| C2 | C22 | 1.433(11) | C46 | C47 | 1.428(11) |
| C4 | C5 | 1.390(11) | C47 | C48 | 1.366(13) |
| C4 | C21 | 1.409(10) | C48 | C49 | 1.411(14) |
| C5 | C18 | 1.396(11) | C49 | C50 | 1.412(13) |
| C6 | C7 | 1.437(11) | C49 | C54 | 1.418(14) |
| C7 | C8 | 1.400(11) | C50 | C51 | 1.399(13) |
| C7 | C12 | 1.455(11) | C51 | C52 | 1.370(14) |
| C8 | C9 | 1.412(10) | C52 | C53 | 1.384(16) |
| C8 | O1aa | 1.324(9) | C53 | C54 | 1.342(16) |
| C9 | C10 | 1.360(11) | C55 | C56 | 1.380(13) |
| C10 | C11 | 1.404(12) | C56 | C57 | 1.392(13) |
| C11 | C12 | 1.411(12) | C57 | C58 | 1.389(12) |
| C11 | C16 | 1.410(12) | Cl7 | C1aa | 1.66(2) |
| C12 | C13 | 1.404(12) | Cl8 | C1aa | 1.74(2) |
| C13 | C14 | 1.376(14) | Cl9 | C0aa | 1.675(16) |
| C14 | C15 | 1.379(15) | Cl10 | C0aa | 1.760(19) |
| C15 | C16 | 1.346(14) | Cl1 | C3aa | 1.665(19) |
| C18 | C19 | 1.393(12) | Cl2 | C3aa | 1.781(17) |
| C19 | C20 | 1.373(13) | Cl6 | C2aa | 1.65(2) |
| C20 | C21 | 1.392(12) | Cl0a | C2aa | 1.87(3) |

**Crystallographic Table 135** Bond Angles for **$UO_2[L^{VII}]$**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| O2 | U1 | O1 | 86.4(2) | C16 | C11 | C10 | 121.7(8) |
| O3 | U1 | O1 | 178.5(2) | C16 | C11 | C12 | 119.5(8) |
| O3 | U1 | O2 | 95.1(2) | C11 | C12 | C7 | 118.8(7) |
| O4 | U1 | O1 | 92.4(2) | C13 | C12 | C7 | 124.4(8) |
| O4 | U1 | O2 | 78.29(17) | C13 | C12 | C11 | 116.8(8) |
| O4 | U1 | O3 | 88.0(2) | C14 | C13 | C12 | 121.0(10) |
| N1 | U1 | O1 | 95.2(2) | C15 | C14 | C13 | 122.2(10) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| N1 | U1 | O2 | 69.53(19) | C16 | C15 | C14 | 117.8(9) |
| N1 | U1 | O3 | 85.3(2) | C15 | C16 | C11 | 122.7(10) |
| N1 | U1 | O4 | 146.34(19) | C19 | C18 | C5 | 119.0(9) |
| N2 | U1 | O1 | 91.1(2) | C20 | C19 | C18 | 120.6(8) |
| N2 | U1 | O2 | 132.69(19) | C21 | C20 | C19 | 121.8(8) |
| N2 | U1 | O3 | 87.8(2) | C20 | C21 | C4 | 117.5(8) |
| N2 | U1 | O4 | 148.99(19) | C23 | C22 | C2 | 122.4(8) |
| N2 | U1 | N1 | 63.7(2) | C27 | C22 | C2 | 119.2(8) |
| O1aa | U1 | O1 | 88.7(2) | C27 | C22 | C23 | 118.1(8) |
| O1aa | U1 | O2 | 157.47(18) | C24 | C23 | C22 | 120.7(11) |
| O1aa | U1 | O3 | 89.9(2) | C25 | C24 | C23 | 120.1(11) |
| O1aa | U1 | O4 | 79.95(17) | C26 | C25 | C24 | 120.7(11) |
| O1aa | U1 | N1 | 132.88(19) | C27 | C26 | C25 | 119.9(11) |
| O1aa | U1 | N2 | 69.34(19) | C26 | C27 | C22 | 120.4(10) |
| O6 | U2 | O5 | 79.84(18) | C28 | C27 | C22 | 118.7(8) |
| O8 | U2 | O5 | 92.0(2) | C28 | C27 | C26 | 120.8(10) |
| O8 | U2 | O6 | 91.7(2) | C29 | C28 | C27 | 122.2(8) |
| N3 | U2 | O5 | 131.93(19) | C28 | C29 | C1 | 119.6(8) |
| N3 | U2 | O6 | 148.02(18) | C36 | C31 | C32 | 119.4(6) |
| N3 | U2 | O8 | 90.7(2) | O0aa | C31 | C32 | 121.9(7) |
| N4 | U2 | O5 | 68.63(19) | O0aa | C31 | C36 | 118.7(6) |
| N4 | U2 | O6 | 148.43(19) | C33 | C32 | C31 | 118.8(7) |
| N4 | U2 | O8 | 87.9(2) | C41 | C32 | C31 | 120.7(7) |
| N4 | U2 | N3 | 63.5(2) | C41 | C32 | C33 | 120.2(7) |
| O0aa | U2 | O5 | 158.85(18) | C34 | C33 | C32 | 120.1(7) |
| O0aa | U2 | O6 | 79.01(17) | C40 | C33 | C32 | 123.1(7) |
| O0aa | U2 | O8 | 88.7(2) | C40 | C33 | C34 | 116.9(7) |
| O0aa | U2 | N3 | 69.17(18) | C35 | C34 | C33 | 118.6(7) |
| O0aa | U2 | N4 | 132.51(18) | C37 | C34 | C33 | 120.3(7) |
| O3aa | U2 | O5 | 90.1(2) | C37 | C34 | C35 | 121.0(8) |
| O3aa | U2 | O6 | 89.0(2) | C36 | C35 | C34 | 121.8(7) |
| O3aa | U2 | O8 | 177.8(2) | C35 | C36 | C31 | 121.3(7) |
| O3aa | U2 | N3 | 87.5(2) | C38 | C37 | C34 | 120.6(8) |
| O3aa | U2 | N4 | 92.5(2) | C39 | C38 | C37 | 119.9(8) |
| O3aa | U2 | O0aa | 89.5(2) | C40 | C39 | C38 | 121.1(8) |
| C1 | O2 | U1 | 124.3(4) | C39 | C40 | C33 | 121.2(8) |
| C46 | O5 | U2 | 128.7(5) | C32 | C41 | N3 | 127.9(7) |
| C3 | N1 | U1 | 123.5(5) | C43 | C42 | N3 | 116.7(7) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C4 | N1 | U1 | 115.3(5) | C58 | C42 | N3 | 123.8(7) |
| C4 | N1 | C3 | 121.1(6) | C58 | C42 | C43 | 119.5(7) |
| C5 | N2 | U1 | 114.7(5) | C42 | C43 | N4 | 115.6(7) |
| C6 | N2 | U1 | 127.3(5) | C55 | C43 | N4 | 125.0(7) |
| C6 | N2 | C5 | 117.8(6) | C55 | C43 | C42 | 119.4(8) |
| C41 | N3 | U2 | 127.5(5) | C45 | C44 | N4 | 126.2(7) |
| C42 | N3 | U2 | 113.9(4) | C46 | C45 | C44 | 120.1(8) |
| C42 | N3 | C41 | 118.5(6) | C50 | C45 | C44 | 119.9(7) |
| C43 | N4 | U2 | 115.9(5) | C50 | C45 | C46 | 119.5(8) |
| C44 | N4 | U2 | 124.8(5) | C45 | C46 | O5 | 122.0(7) |
| C44 | N4 | C43 | 119.2(7) | C47 | C46 | O5 | 118.2(7) |
| C2 | C1 | O2 | 122.2(7) | C47 | C46 | C45 | 119.7(8) |
| C29 | C1 | O2 | 117.6(7) | C48 | C47 | C46 | 120.0(8) |
| C29 | C1 | C2 | 120.1(7) | C49 | C48 | C47 | 122.3(9) |
| C3 | C2 | C1 | 119.9(7) | C50 | C49 | C48 | 119.1(9) |
| C22 | C2 | C1 | 119.7(7) | C54 | C49 | C48 | 121.4(9) |
| C22 | C2 | C3 | 120.0(7) | C54 | C49 | C50 | 119.4(9) |
| C2 | C3 | N1 | 125.2(7) | C49 | C50 | C45 | 119.2(8) |
| C5 | C4 | N1 | 116.5(7) | C51 | C50 | C45 | 123.2(9) |
| C21 | C4 | N1 | 122.4(7) | C51 | C50 | C49 | 117.6(9) |
| C21 | C4 | C5 | 121.1(7) | C52 | C51 | C50 | 120.7(10) |
| C4 | C5 | N2 | 115.4(7) | C53 | C52 | C51 | 121.8(11) |
| C18 | C5 | N2 | 124.5(7) | C54 | C53 | C52 | 119.0(11) |
| C18 | C5 | C4 | 120.0(7) | C53 | C54 | C49 | 121.5(10) |
| C7 | C6 | N2 | 124.8(7) | C56 | C55 | C43 | 121.4(8) |
| C8 | C7 | C6 | 121.5(7) | C57 | C56 | C55 | 118.9(8) |
| C12 | C7 | C6 | 118.7(7) | C58 | C57 | C56 | 121.0(9) |
| C12 | C7 | C8 | 119.6(7) | C57 | C58 | C42 | 119.8(8) |
| C9 | C8 | C7 | 119.9(7) | C31 | O0aa | U2 | 132.0(5) |
| O1aa | C8 | C7 | 122.3(7) | C8 | O1aa | U1 | 128.6(4) |
| O1aa | C8 | C9 | 117.8(7) | Cl10 | C0aa | Cl9 | 110.8(9) |
| C10 | C9 | C8 | 120.0(8) | Cl8 | C1aa | Cl7 | 114.9(12) |
| C11 | C10 | C9 | 122.8(8) | Cl0a | C2aa | Cl6 | 101.1(9) |
| C12 | C11 | C10 | 118.8(7) | Cl2 | C3aa | Cl1 | 114.3(8) |

**Crystallographic Table 136** Hydrogen Atom Coordinates (Å×$10^4$) and Isotropic Displacement Parameters (Å$^2$×$10^3$) for **$UO_2[L^{VII}]$**.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| H29 | -800(5) | 8870(4) | 1569(4) | 38(2) |
| H28 | -1301(6) | 8636(5) | 2424(4) | 50(3) |
| H21 | 1421(5) | 11808(4) | 2526(4) | 35(2) |
| H20 | 2255(5) | 12813(5) | 2489(4) | 45(3) |
| H19 | 1858(6) | 13546(5) | 1635(5) | 52(3) |
| H18 | 594(6) | 13308(5) | 783(4) | 47(3) |
| H9 | -2797(5) | 11547(4) | -1321(4) | 33(2) |
| H10 | -3871(6) | 12397(5) | -1564(4) | 40(2) |
| H23 | -1035(6) | 11303(6) | 2985(5) | 60(3) |
| H24 | -1733(9) | 11052(7) | 3763(6) | 87(4) |
| H25 | -2204(10) | 9923(8) | 3883(6) | 97(5) |
| H26 | -1886(9) | 9028(7) | 3288(6) | 87(4) |
| H13 | -2029(8) | 13835(5) | 396(4) | 58(3) |
| H14 | -3133(9) | 14667(5) | 83(5) | 75(4) |
| H15 | -4386(8) | 14503(6) | -782(5) | 72(4) |
| H16 | -4481(7) | 13506(5) | -1357(5) | 58(3) |
| H47 | -715(6) | 10896(5) | -3102(4) | 46(3) |
| H48 | -1104(7) | 11407(5) | -4077(5) | 56(3) |
| H58 | -4636(6) | 7958(5) | -2022(4) | 47(3) |
| H57 | -4795(7) | 7056(5) | -2744(5) | 60(3) |
| H56 | -4276(6) | 7178(5) | -3630(5) | 54(3) |
| H55 | -3509(6) | 8181(5) | -3750(4) | 45(3) |
| H36 | -3167(5) | 10854(4) | -264(4) | 34(2) |
| H35 | -4475(5) | 11119(4) | -43(4) | 37(2) |
| H51 | -4174(7) | 10023(6) | -4668(5) | 68(3) |
| H52 | -4500(8) | 10565(7) | -5629(5) | 78(4) |
| H53 | -3491(9) | 11337(6) | -5868(6) | 83(4) |
| H54 | -2170(8) | 11597(6) | -5121(5) | 71(4) |
| H40 | -6236(5) | 9457(5) | -1880(4) | 39(2) |
| H39 | -7518(5) | 9708(5) | -1589(4) | 44(3) |
| H38 | -7461(5) | 10445(5) | -756(4) | 44(3) |
| H37 | -6116(5) | 10962(5) | -220(4) | 40(2) |
| H4a | -2096(4) | 10015(16) | -190(20) | 36.0(17) |
| H4b | -1370(30) | 9583(4) | 135(10) | 36.0(17) |
| H6a | -1436(14) | 10850(20) | -1059(18) | 35.3(17) |

| | | | | |
|---|---|---|---|---|
| H6b | -791(14) | 10387(5) | -1180(20) | 35.3(17) |
| H3 | 30(5) | 11357(4) | 2513(4) | 32(2) |
| H6 | -930(6) | 13174(4) | 492(4) | 35(2) |
| H41 | -5022(5) | 9040(4) | -1908(4) | 32(2) |
| H44 | -3598(5) | 9340(5) | -3921(4) | 38(2) |
| H0aa | -4637(10) | 11286(9) | -2639(8) | 129(7) |
| H0ab | -5251(10) | 10889(9) | -2278(8) | 129(7) |
| H1aa | -7122(16) | 11728(10) | -1111(14) | 290(20) |
| H1ab | -6905(16) | 11808(10) | -1768(14) | 290(20) |
| H2aa | -2766(19) | 12669(13) | 1004(11) | 300(20) |
| H2ab | -2916(19) | 11847(13) | 888(11) | 300(20) |
| H3aa | -1984(12) | 8501(8) | -743(8) | 137(7) |
| H3ab | -2005(12) | 7675(8) | -771(8) | 137(7) |

Refinement model description

Number of restraints - 0, number of constraints - 90.

Details:

N/A

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