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Review

Uranium complexes of multidentate N-donor ligands

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Contents

Abstract

This review focuses on uranium cation coordination complexes with multidentate nitrogen-containing ligands appearing in the literature from 2000 to mid-2005, with reports prior to 2000 included where pertinent. In addition to the uranyl cation (UO_2^{2+}), special attention will be paid to tri and tetravalent uranium species, for which recent reports have provided new insights into actinide chemistry. The ligands discussed can be separated into five main categories: pyrrole, pyridine, amido, Schiff-base salicylidene-derived and other miscellaneous type ligands. Manipulation of the

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steric bulk and rigidity of these ligands is essential for exploring the reactivity and bonding behavior of uranium cations. Additionally, applications of such complexes, including small molecule activation, catalysis, actinide sensors and incorporation into liquid crystals will be discussed.

Keywords: Uranium; Actinides; Nitrogen; Pyrrole; Pyridine; Salen; Salophen; Amido; Scorpionate; Carbazone; Coordination complexes

1. Introduction

The inspiration behind the synthesis and investigation of uranium–nitrogen complexes generally derives from four basic motives, namely a desire to: (i) explore the fundamental chemistry of 5f-elements reactivity and coordination behavior; (ii) understand the bonding interactions between the metal center and ligand (ionic or covalent bonding); (iii) identify suitable trivalent actinide (An(III)) extractants for nuclear remediation and finally, (iv) explore possible applications of new complexes, such as in catalysis or as sensors.

The first motive needs no further clarification: the rarity and radioactivity of the actinide elements has restricted them from widespread study, leaving them as one of the few unexplored areas of the periodic table. Moreover, the bonding behavior of the lanthanides and actinides has been a subject of debate for nearly 40 years [1–3], a fact that underlies the second motive for investigation. Since the report of uranocene [U(COT)$_2$] by Streitwieser and Müeler-Westerhoff in 1968 [4], many groups have tried to prove, or disprove, covalent interactions between the actinide cations and various ligands. For instance, metal-to-ligand π-bonding has been observed in uranium–phosphorus complexes [5], and uranium–arene complexes [6] leading to the suggestion that a covalent interaction is possible with uranium. A number of complexes have also been reported in which the presence of nitrogen back donation with U(III) is proposed [7,8]. Evidence has also been put forth suggesting δ backbonding between amido groups and a U(II) center [9]. The synthesis of new uranium-containing complexes continues to be sought to understand better the covalent behavior of uranium and also to understand uranium coordination chemistry in general.

Another incentive for probing the extent of covalent interactions in actinide complexes derives from a desire to effect efficient actinide/lanthanide cation (An(III)/Ln(III)) separations. Over 60 years of nuclear weapons and energy production has lead to a significant amount of radioactive waste [10]. Ideally, uranium and plutonium cations could be separated from other waste and recycled. The actinides present in smaller quantities, in particular the so-called minor actinides Np(III), Am(III) and Cm(III), could then be transmuted into short-lived radionuclides by neutron irradiation. However, the presence of lanthanide cations in higher quantities than the minor actinides (as high as 20-fold excess in some instances) impedes this process. Therefore, an efficient means of separation of the lanthanides and actinides is necessary. However, effecting such separations has proved difficult, due to the similar reactivity and size of the trivalent actinides and lanthanides. Exploitation of the slightly covalent interactions present in the actinides towards ligands, as well as an observed preference for softer donor atoms, such as nitrogen, may provide the solution to the An(III)/Ln(III) separation problem [11]. Uranium, while not present in the trivalent coordination state in a significant amount in nuclear waste, is often chosen as a model for the minor actinides in extraction studies. Although not a perfect match in terms of electronic structure, U(III) salts often display reactivity that is similar to those of the minor actinides. This cation is also less radioactive and available in readily usable quantities.

Finally, a number of uranium-containing complexes have been shown to be useful in other applications, such as catalysis, anion and neutral molecule sensing and small molecule activation. These applications are providing a less specialized and easier-to-appreciate motivation for carrying out actinide-related chemical research.

This review will focus on recently reported (2000–June 2005) uranium complexes prepared from multidentate nitrogen-containing ligands. Where appropriate, articles published pre-2000 have been included for completeness. The attention of the reader is also directed to other reviews on the subject [12,13]. In particular, a recent review by Burns et al. provides an extensive survey of the actinide literature up until 2002 [13]. The present work will provide an up-to-date review of the literature, with a focus on complexes reported in organic solvents. A number of reports concerning the coordination of other actinide cations (especially thorium) have been published but the present discussion is limited to uranium complexes, since uranium remains by far the best studied of the actinide cations. While all stable uranium oxidation states (III–VI) will be discussed, special attention will be given to the U(III) oxidation state due to: (1) the numerous reports involving this cation that have appeared over the past few years and (2) its exceptional coordination chemistry. Another focus of the paper will be on the uranyl cation, UO_2^{2+}, also due to its prevalence in recent literature. Additionally, the ligands themselves are broken into four main categories: salen-derived Schiff-base ligands, pyrrole-, amido- and pyridine-based ligands, with an additional chapter devoted to newer systems. While other nitrogen-containing ligands have been used to effect uranium coordination, these four categories encompass the majority of the recent reports.

2. Salicylaldehyde-derivatives

The salen ligand has been known for some time and is well established in the area of metal coordination chemistry [14,15]. Made via a [2 + 1] condensation reaction from salicylaldehyde and a diamine, this ligand forms a tetradentate cleft with two nitrogen and two oxygen atoms (N_2O_2, also H_2L). Functionalization of either precursor is generally straightforward, and for this reason there are a number of salen analogues reported in the literature. For example, complexes of ‘salophen’, formed by condensation of salicylaldehyde with *o*-phenylenediamine, have found a number of applications, ranging from catalysis to sensors. Compartmental Schiff-base ligands, formed by substitution of salicylidene at the 6 position, typically with a hydroxy (abbreviated H_4L) or methoxy group, possess a hexadentate core, or more specifically, two pockets capable of cation coordination (N_2O_2 and O_4). These two asymmetric pockets have been shown to complex two different metals in addition to forming higher order polynuclear species.

Due to space constraints, mention of the salen–uranyl complexes will be limited to those that show potential utility for specific applications. Descriptions of preparative chemistry carried only for the sake of providing new complexes are generally excluded. The reader is directed to reviews, as well as to several recent literature reports, for a more complete coverage of this latter chemistry [16–19].

2.1. Salophen

Coordination of small molecules by uranyl salophen complexes is well documented [20,21]. As the uranyl cation typically adopts a pentacoordinate environment, the tetradentate salen ligand leaves one site open for coordination to another molecule. Early crystal structures included coordination of methanol, ethanol or water; coordination complexes involving pyridine, aniline, DMSO, and tetraphenyl phosphate have also been reported [20]. However, the 1987 report by Reinhoudt and coworkers [22] which showed coordination of urea to a uranyl salophen complex, is now viewed as being particularly seminal. In this work, it was demonstrated that a uranyl salophen ligand bearing an attached crown ether could coordinate urea within the crown ether moiety, with the urea–carbonyl oxygen coordinated in turn to the uranyl cation. Viewed in the fullness of time, it is clear that this work has paved the way for uranyl–Schiff-base ligands being used to coordinate not only other neutral molecules [23–26], but also anions.

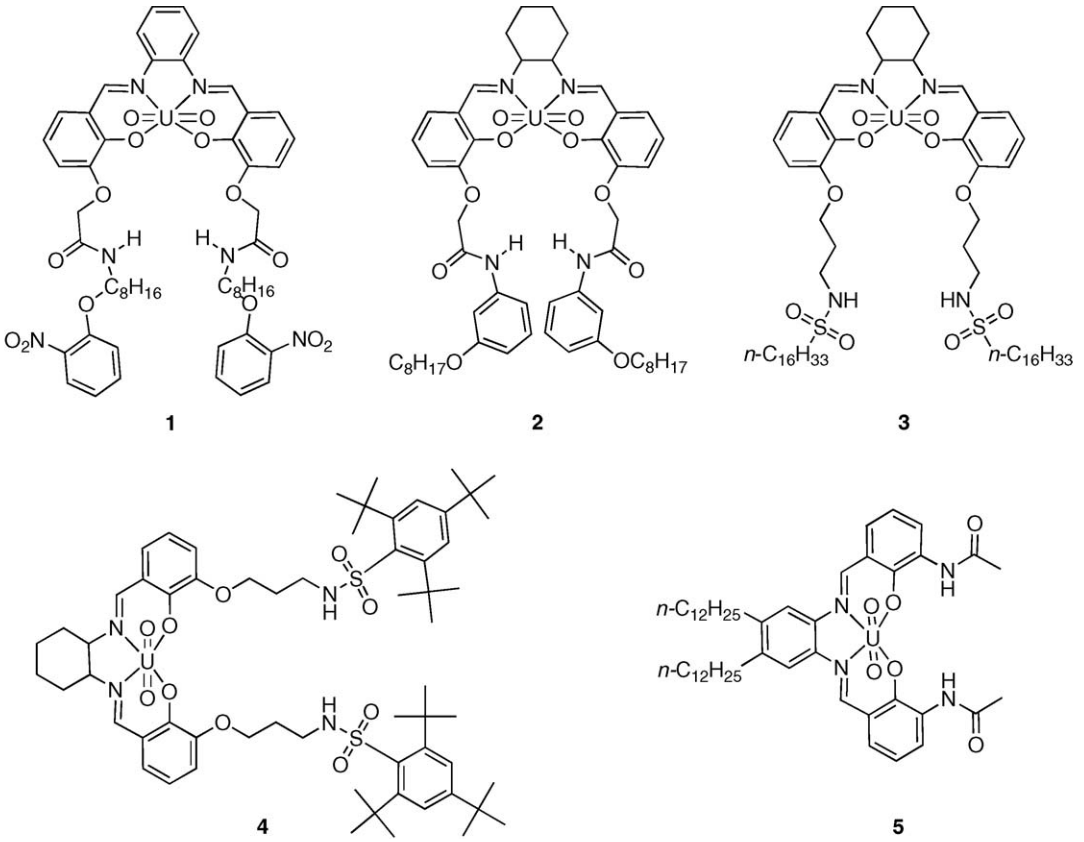
Early work in the field served to demonstrate that uranyl salophen complexes form strong complexes with $H_2PO_4^-$ [27,28]. Appreciating this, Reinhoudt and coworkers used neutral uranyl complexes (e.g., **1**–**5**) to study anion-facilitated transport through supported liquid membranes (SLM) [29]. SLM's consist [30] of an organic carrier solution (uranyl salophen in the present work) immobilized on a thin microporous film placed between two aqueous phases. Using an elegant, albeit complex, analysis, Reinhoudt and coworkers were able to report the Gibbs free energies of transfer, the diffusion coefficients (D_m), extraction coefficient (K_{ex}), and stability constant (K_a) for dihydrogen phosphate and chloride anions with five different uranyl salophene carriers (Scheme 1). It was concluded that uranyl complexes **3** and **4** derived from sulphone-containing ligands had the best selectivity for $H_2PO_4^-$ over Cl^-; they also displayed the highest extraction coefficients (out of the five uranyl salophens tested). Overall, this work not only served to confirm the viability of using uranyl salophens as neutral anion carriers, it also helped show that stability constants could be inferred from membrane transport studies. It thus has played an important historic role by demonstrating the utility of studies involving supported liquid membranes.

Wroblewski et al. reported the use of the uranyl salophenes as dihydrogenphosphate sensors when incorporated into a polymeric membrane [31,32]. With sufficient durability and lifetime, the uranyl salophen complexes could be used in ion selective membranes (ISM) or chemically modified field effect transistors (CHEMFETs). ISMs contain a membrane consisting of a plasticizer (a solvent used to promote plasticity), PVC, 1 wt.% carrier and 20 mol% of a salt (since the carrier is neutral, it was found ionic sites in the membrane-promoted selectivity) [31]. The membrane produced in this way is immobilized on a disk and mounted on an electrode, to form the final ISM setup. CHEMFETs involve membrane solutions of similar compositions as described for ISMs but which are then placed on top of the gate of a transistor. It was found that uranyl salophenes substituted with dodecoxy chains (e.g., **6**) showed increased solubility in the membrane and thus higher selectivity coefficients for dihydrogenphosphate (10^4 and 10^5) over the blank membrane. After analysis of a range of ionic salt concentrations and various plasticizers (which effect solvation of the carrier in the organic phase) it was concluded that optimal anion selectivity was reached when the membranes were formulated with of 2% of the ionophore (uranyl salophene) and 20 mol% of tetradecylammonium bromide (the ionic salt), as well as polar, aromatic plasticizers such as *o*-nitrophenyl octylether and 2-fluorophenyl 2-nitrophenyl ether.

Durability tests of the designed CHEMFETs were investigated in the context of probing dihydrogen-phosphate sensor selectivity. Unfortunately, the lipophilic uranyl salophen discussed above (**6**) was found to undergo significant degradation over the course of 2 weeks as evidenced by decreased dihydrogenphosphate selectivity. It was believed that formation, and subsequent precipitation, of a water–uranyl–salophen complex occurs, and that this process lowers the effective concentration of the carrier inside the membrane. Synthetic replacement of the dodecoxy groups in **6** by *t*-butyl groups on the salicylidene rings, giving **7**, improved the solubility in the membrane phase. With this new carrier, the initial selectivity was slightly enhanced, as was the lifetime of the sensor, with only a slight decrease in selectivity being observed after 2 weeks. Durability was also superior in that the amount of ammonium salt (from 20 to 5 mol%) present in the membrane could be reduced, albeit at the cost of a slight decrease in selectivity [33,34]. A subsequent re-investigation of the plasticizer as a function of selectivity and durability confirmed that the original plasticizer, *o*-nitrophenyl octylether, allows for the highest combination of phosphate selectivity and CHEMFET lifetime [34].

Reinhoudt and coworkers also developed an uranyl salophen electrode that demonstrated high selectivity for fluoride [35]. It was found that selectivity over halides, sulfate and nitrate increased with the addition of amide groups (capable of H bonds with F^-) and an augmentation of the overall lipophilic character, i.e. by moving from system **8** to **9** (Scheme 2).

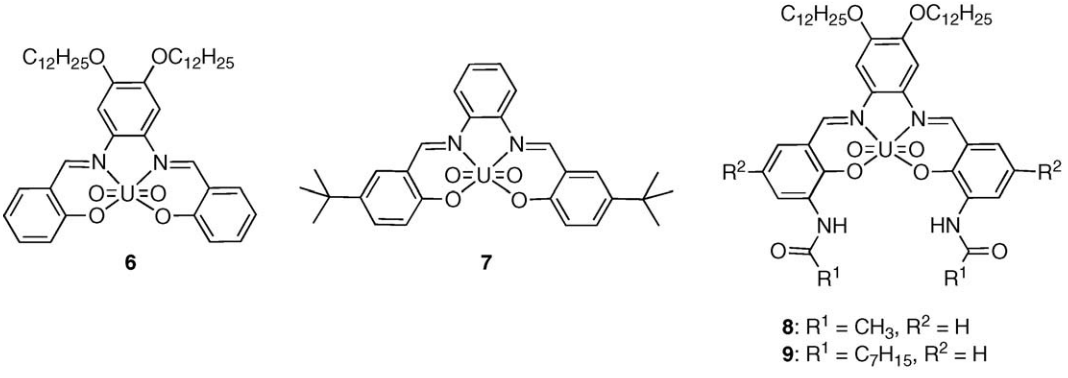
The role of uranyl salophen complexes (e.g., **10** and **11**) in catalysis has also been studied (Scheme 3). In the hopes of exploiting the uranyl salophen as a neutral Lewis acid, an acetate moiety was coordinated to the uranyl salophen complex. Kinetic



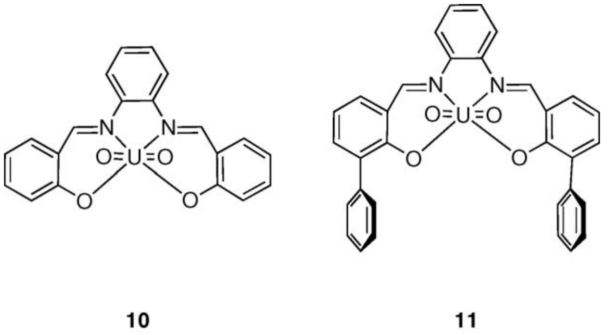
Scheme 1. Uranyl–salophen ligands tested in dihydrogenphosphate transport studies.

studies of ethanolysis and methanolysis catalyzed by these systems, provided evidence for ester cleavage [36]. Based on these studies, the ability of an open-chain bis-aryl uranyl salophen, **11**, to catalyze 1,4-thiol addition was explored [37]. The reaction of thiophenol with 2-cyclopenten-1-one in the presence of triethylamine in chloroform was found to proceed with a $t_{1/2}$ of 162 min. Upon the addition of uranyl salophen **10**, the $t_{1/2}$ was lowered to 13.4 min, while the bis-aryl uranyl salophen **11** demonstrated a $t_{1/2}$ of 3.8 min. The turnover frequencies (TOF) for these two catalysts were found to be 1.43 and 0.63 s^{-1}, respectively. Most likely, the superiority of **11** relative to **10** is due to attractive van der Waal's interactions between the 2-cyclopenten-1-one and the phenyl walls.

Further investigation of the above systems revealed that an enone–uranyl salophen complex forms via coordination of the enone carbonyl to the uranyl center. This 'activated' enone then reacts with a base–thiol complex. As expected, thiol addition in the presence of uranyl salophen **10** was nearly 900 times faster than the uncatalyzed version of the reaction. Thiol addition with the unsubstituted uranyl salophen **10** was found to be 2.4 times *faster* than with the bis-aryl uranyl salophen **11** [38]. To explain this finding, it was proposed that the steric constraints imparted by the two aryl groups hindered enone coordination to a greater extent than the enhancement provided by the aryl groups. However, in sub-saturated solutions, or those with unactivated enones present, thiol addition was an order of magnitude



Scheme 2. Uranyl salophens tested as anion sensors.



Scheme 3. Uranyl salophens tested for use a potential catalysts.

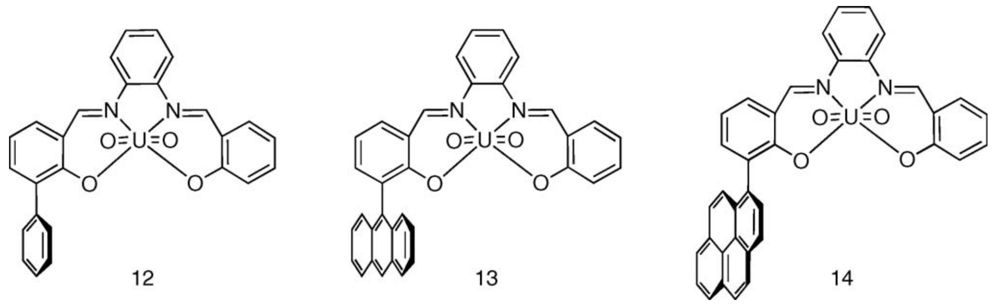
greater with the bis-aryl uranyl salophen **11**, a finding that led to the suggestion that the aryl groups, while sterically inhibitive, do aid in enone complexation. Thus, under these conditions, **11** acts as a more effective catalyst than **10**. The bis-aryl uranyl salophen **11** was also found capable of catalyzing the reaction of thiols with acyclic enones, such as ethyl vinyl ketone [38].

The bis-aryl salophen complex **11** was found to demonstrate improved substrate specificity, in addition to displaying a higher rate of catalysis [39]. Reinhouldt and coworkers demonstrated that the association constant of the salophen uranyl complexes with various enones is increased from 10- to 100-fold (depending on the enone) when two phenyl walls (**11**) are 'added' to the parent complex (**10**). The notable exception to this rule is 6,6-dimethyl-2-cyclohexen-1-one for which the association constant with **11** was only doubled relative to what was seen for **10**. It was found that in certain situations, especially when steric bulk is present in the enones, the "addition" of only one aryl wall (cf. structures **12**–**14**) (Scheme 4) can increase the association constant, as demonstrated in another set of experiments [40]. Generally speaking, the resulting half-cleft systems were found to give rise to higher association constants as compared to the corresponding parent structures. Such findings provide support for the notion that only one phenyl group participates in van der Waal's interactions with the enones, while the additional aryl group serves as a steric blocking group, hindering the interaction of the enone with the uranyl cation. The influence of *gem*-dimethyl groups in the reaction of *n*,*n*-dimethyl-2-cyclohexen-1-one with benzenethiol was studied with respect to the rate of reaction. Rate experiments, as well as competition experiments, served to demonstrate that 6,6-dimethyl-2-cyclohexen-1-one was a preferred substrate and likewise served to demonstrate the high substrate specificity of catalyst **11**.

The inherent low symmetry of the uranyl–salophen complex has recently been demonstrated by NMR spectroscopy [41]. Due to its large radius, the uranyl cation sits slightly above the salophen ligand (as predicted by molecular modeling calculations and established by X-ray diffraction analysis). Theoretically, therefore, the use of an unsymmetric ligand could produce a chiral, non-racemic compound. In simple systems this promise has not as yet been realized. Most likely, this reflects the rapid interconversion of the putative enantiomers. Bulky substituents have, therefore been introduced, giving rise to systems such as **15** and **16**. With these systems, evidence for the formation of enantiomers was inferred from NMR spectroscopic studies. Similar analyses were used to support the conclusion that these enantiomers are able to recognize chiral guests [42]. An enantiomer made using *S*-naproxen was also crystallized and fully characterized [43].

A benzyloxy-substituted uranyl salophene has been shown to serve as a ditopic receptor for quaternary ammonium halide contact ion pairs and alkali-halide ion pairs such as CsF, KCl, RbCl and CsCl [44,45]. In all cases, the Lewis acidic uranyl cation contributed to the stabilization of the anion while cation–π interactions stabilized the bound cation near the aromatic sidearms. Crystal structures revealed a 1:1 binding stoichiometry between the metal salt and the uranyl salophen, which results in a 2:2 complex due to dimerization. A second receptor, with only one benzyloxy sidearm, formed a 2:1 uranyl salophen:salt complex, which again leads to a 4:2 complex due to dimerization. These solid state structural results were supported by comparative ^{1}H NMR studies that used an unsubstituted uranyl salophen as a control molecule.

Ikeda and coworkers have utilized salophen **10**, (*N*,*N*′-disalicylidene-*o*-phenlenediaminate) as a stabilizing ligand for the U(V) cation. Due to its low stability, the resulting U(V) complex was never actually isolated, although significant spectroscopic evidence consistent with its existence was put forth [46]. Mizuguchi et al. were the first to report a clean UV–vis spectrum of a pure U(V) species, $[UO_2(CO_3)_3]^{4-}$, which was characterized in aqueous media [47]. Subsequently, these researchers have focused attention on non-aqueous systems. Electrochemical and spectroelectrochemical studies were carried out with the complex UO_2(salophen)L, where L = DMSO or DMF [46]. The U(V) species was found to be stable in DMSO, while disassociation of the coordinating solvent was



Scheme 4. Mono-aryl uranyl salophens.

observed in DMF. The authors confirmed that the $5f^1$ absorption bands observed at 750 and 900 nm with low extinction coefficients were due to the U(V) species, as had been previously suggested [48]. It was later reported that at a potential of −1.73 V, the IR spectra of the dominant species in the $U^{VI}O_2$(salophen)DMSO/$U^{V}O_2$(salophen)$DMSO^-$ couple was that of the U(V) species (770 cm^{-1}), and this value was at a lower wavenumber than the U(VI) analogue (895 cm^{-1}) [49]. This decrease in frequency seen upon reduction is in accord with previous findings involving the $Am^{VI/V}$ and $Np^{VI/V}$ redox couples [50], leading the authors to conclude that the U=O bond strength was weakened as a result of metal-centered reduction. Interestingly, no spectral changes were observed for the salophen ligand, indicating the redox chemistry of the uranyl cation did not influence the coordination geometry of the ligand.

A comparison of three species, [$U^{V}O_2(dbm)_2$DMSO]-, [$U^{V}O_2$(salophen)DMSO]- and [$U^{V}O_2(CO_3)_3]_5$- (dbm = dibenzoylmethanate), confirmed the absorption bands of a U(V) complex at ∼650, 750, 900, 1400 and 1875 nm [51]. Mizuoka et al. ascribed these spectral features to f–f transitions within the $U^{V}O_2^+$ core.

2.2. *Salen*

Bastos et al. have reported uranyl cation detection in the presence of the salen ligand effected via cathodic adsorptive stripping voltammetry [52]. This system displayed a sensitivity for the uranyl cation over a range of 5.0–25.0 μg/l and demonstrated selectivity over a number of transition metals as well as thorium. Shamsipur et al. have reported that the naphthyl-derived salen (Scheme 5, **17**), when supported on a PVC membrane (plasticizer: dioctyl phthalate), shows selectivity for the uranyl cation over a wide range of transition, alkali, and alkali earth metals. Typical selectivity coefficients were found to be on the order of 10^{-2} or better, while the limit of detection for this membrane was ca. 7.0×10^{-8} M [53].

A report by Sah et al. discusses the properties of a salen type Schiff-base ligand produced from a sugar moiety, namely 4,6-*O*-ethylidene-β-D-glucopyranosylamine and salicylaldehyde or 3-methoxysalicylaldehyde [54]. The interactions of dioxo metal cations with the sugar moiety were then discussed. MoO_2^{2+} and VO_2^+ both produced *cis*-dioxo products with the transition metal bonded to one oxygen atom of the sugar, while the UO_2^{2+} cation formed a bond with an adjacent OH group present on monsaccharide. The uranyl complex formed a binuclear dimer where the ligand:metal ratio remained 1:1. The uranyl cation complex exhibited typical pentagonal-bipyramidal geometries with a U–U distance of 3.942(1) Å.

2.3. *Compartmental ligands*

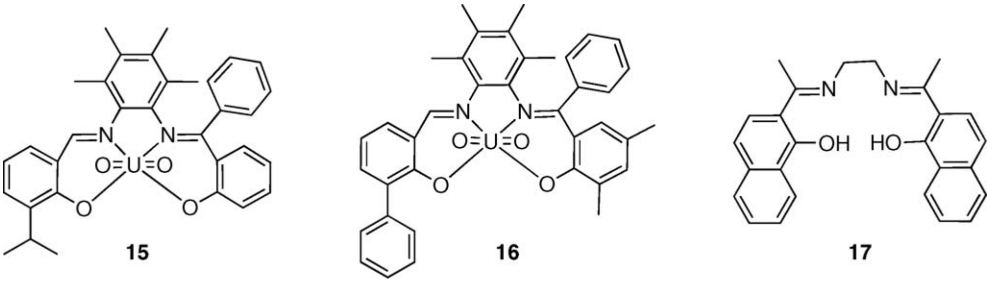
2.3.1. *Uranyl complexes*

The synthesis of an asymmetric compartmental Schiff-base macrocycle has been reported via a templation reaction involving the use of $UO_2(acac)_2\cdot 2H_2O$, a diformyl precursor (either 3,3′-(3,6-dioxaoctane-1,8-diyldioxy)bis(2-hydroxybenzaldehyde) or 3,3′-(3-oxapentane-1,5-diyldioxy)bis(2-hydroxybenzaldehyde)), and 1,2-diamino-3-azamethylpentane [55]. In this case, X-ray diffraction analysis, supported by IR and NMR spectroscopy, revealed that the uranyl cation occupies the N_3O_2 core, rather than the O_2O_3 or O_2O_4 crown-like site. Under similar conditions, Ln(III) cations were found to be complexed within the crown-like chamber. This difference in selectivity was considered ‘supramolecular evidence’ of the inherent preference of 5f cations for ‘soft’ donor ligands.

In 2003, Salmon et al. reported the first crystallographic evidence for heteronuclear uranium complexes [56]. Reaction of *N*,*N*′-bis(3-hydroxysalicylidene)-1,3-propanediamine (**25**) or *N*,*N*′-bis(3-hydroxysalicylidene)-2-methyl-1,2-propanediamine (**26**) with $Ni(acac)_2$ in THF and subsequent reaction with UCl_4 or $U(acac)_4$, produced a binuclear uranyl–nickel complex in which an *uranyl* cation (i.e., U(VI), rather than U(IV)) occupies the outer, O_4 pocket. It was postulated that, trace amounts of air and water in the flask served to effect oxidation of the metal center. Additionally, reaction of **25** with $Cu(acac)_2$ and subsequent reaction with $U(OTf)_4$ produced a tetranuclear complex in which two uranyl cations occupied the outer O_4 pocket in two separate ligands. One of the outer oxygen atoms of each dinuclear species is in turn coordinated to the U center of the other complex. The net result is the ‘assembled’ formation of a tetranuclear species. In this arrangement each U center has an O_7 environment [56].

2.3.2. *U(IV) complexes*

A U(IV) salen complex has recently been characterized by X-ray crystallography (Fig. 1). In this complex, the uranium center is bound inside the N_2O_2 pocket and also coordinated to two acetylacetone (acac) ligands [57]. This complex was formed by reaction of *N*,*N*′-bis(3-hydroxysalicylidene)-2-methyl-1,2-



Scheme 5. Enantiomeric salophens and salen for uranyl detection.

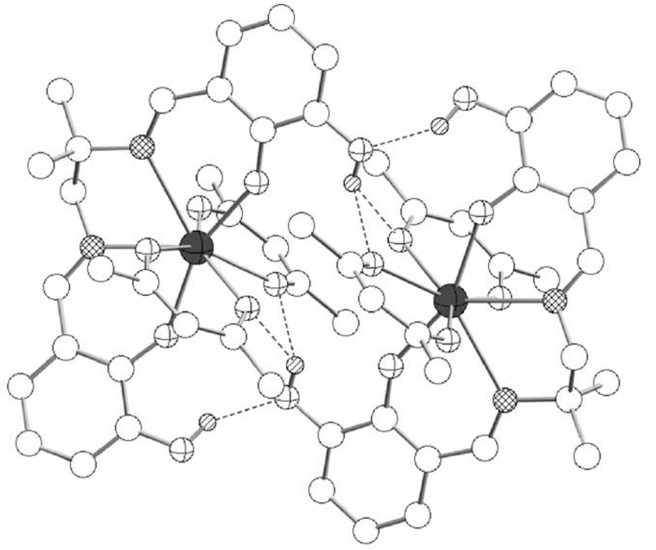


Fig. 1. Single crystal X-ray diffraction structure of a hydrogen-bonded dimer of [U(**26**)(acac)$_2$] [57]. Most hydrogen atoms have been removed for clarity. Here, the atom labels are as follows: ○=C; ▩=N; ⊕=O; ●=U; ▨=H.

propanediamine (**26**) with U(acac)$_4$ in THF. Perhaps the most interesting feature of this complex is the multiple hydrogen bond interactions, which serve to link two separate complexes thus stabilizing formation of a dimer.

Ligand transfer reactions between salen transition metal complexes and other transitional metal salts have been well documented [58]. Similarly, –H or –OMe substituted U(IV) salen complexes have been formed via displacement of a transition metal in the N_2O_2 core [59]. Variations in the ligand substitution pattern, as expressed in systems **18**–**25**, the choice of the uranium salt (U(acac)$_4$ or UCl$_4$), or the solvent (THF or pyridine) afforded a variety of mononuclear uranium complexes. A trinuclear (Cu$_2$U) complex, **32**, however, was formed from the reaction of [Cu(H$_2$**24**)] (Scheme 6) with U(acac)$_4$ in THF. In this complex, each copper cation is ligated within the N_2O_2 pocket of a salen ligand, while one uranium cation is coordinated to the O_4 pockets of both salen ligands. Under identical reaction conditions, the corresponding Co$_2$U, Ni$_2$U, Zn$_2$U, and Cu$_2$Zr complexes could be made [59].

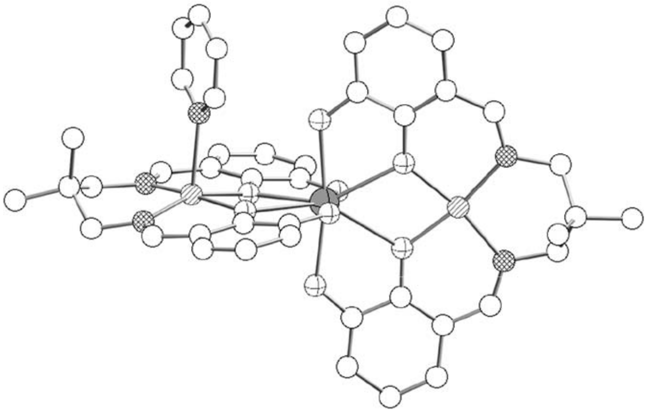
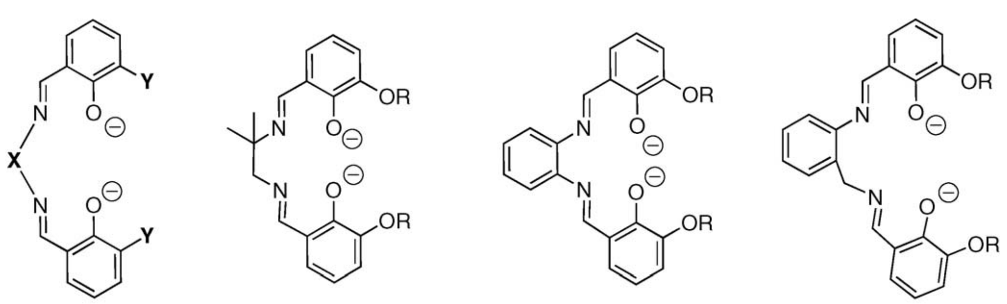


Fig. 2. Single crystal X-ray diffraction structure of trinuclear Cu$_2$U complex, **32** [59]. All hydrogen atoms have been removed for clarity. Here, the atom labels are as follows: ○ = C; ▩ = N; ⊕ = O; ● = U; ▨ = CU.

The most striking feature of these complexes is the linear arrangement of the three metal atoms. Magnetic studies of the Cu$_2$U and Cu$_2$Zr complexes did not indicate any Cu–Cu interactions present in the Cu$_2$U system. However, a ferromagnetic interaction was inferred between the U^{4+} and Cu^{2+} cations (based on comparative studies with the Cu$_2$Zr complex and previous results [60]). Further support for these proposed interactions was provided by the synthesis of additional Cu$_2$U trinuclear complexes **33** and **34**, using *N*,*N*′-bis(3-hydroxysalicylidene)-1,3-propanediamine (**25**), or *N*,*N*′-bis(3-hydroxysalicylidene)-2-dimethyl-1,2-propanediamine (**26**), respectively, as the ligands [61]. As with the other trinuclear complexes, and similar to what was seen with complex **32** shown in Fig. 2, the uranium center was found to occupy the O_4 pocket generated by two ligands linked together (Scheme 7). SQUID measurements provided evidence for a ferromagnetic Cu–U interaction in complexes of **32** and **33** but an antiferromagnetic interaction with the salen-derived uranium complex **34**. On the basis of these results, it was argued that both the ligand environment and the



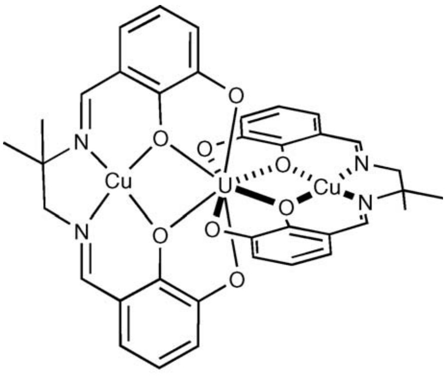
18: X = (CH$_2$)$_2$, Y = H
19: X = (CH$_2$)$_3$, Y = H
20: X = (CH$_2$)$_2$, Y = OMe
21: X = (CH$_2$)$_3$, Y = OMe
22: X = CH$_2$CMe$_2$CH$_2$, Y = OMe
23: X = (CH$_2$)$_2$, Y = OH
24; X = CH$_2$CMe$_2$CH$_2$, Y = OH
25: X = (CH$_2$)$_3$, Y = OH

26: R = H
27: R = Me

28: R = H
29: R = Me

30: R = H
31: R = Me

Scheme 6. Salen-derived ‘compartmental’ ligands.



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Scheme 7. Cu_2U trinuclear complex, **34** [58].

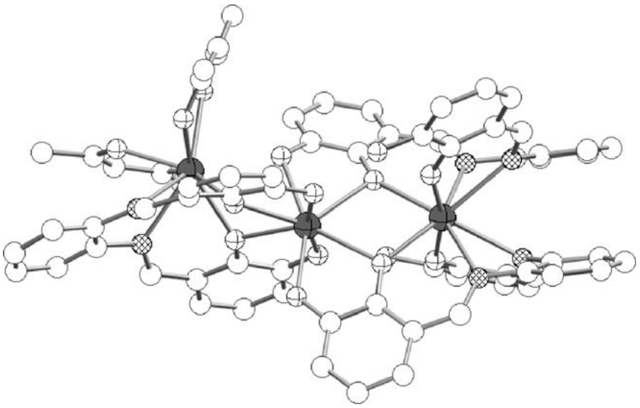


Fig. 4. Single crystal X-ray diffraction structure of $[U_3(\mathbf{28})(H\mathbf{28})_2(acac)_2]\cdot 3THF$ complex [62]. All hydrogen atoms have been removed for clarity. Here, the atom labels are as follows: ○ = C; ▨ = N; ⊕ = O; ● = U.

metal–metal distances strongly effect the Cu(II)–U(IV) interactions [61].

When salens $(H_2\mathbf{27})$, $(H_2\mathbf{29})$, $(H_2\mathbf{31})$, or $(H_2\mathbf{22})$ were reacted with $U(acac)_4$, 2:1 ligand-to-uranium complexes were formed [62]. X-ray diffraction analysis revealed that the ligands in these complexes adopt a meridional, rather than sandwich-like, orientation in the solid state (Fig. 3).

While the meridional orientation was observed in the solid state, ^1H NMR spectroscopic analysis indicated that the sandwich-like orientation was present in as high as a 35% ratio of product, for $U(\mathbf{31})_2$ [62]. On the other hand, when these same ligands were reacted with UCl_4, the expected [63] mononuclear 1:1 metal:ligand species were formed [64]. Moreover, multinuclear complexes were formed when the ligand was altered (i.e. from *N*,*N′*-bis(3-methoxysalicylidene) to *N*,*N′*-bis(3-hydroxysalicylidene)) [62]. Reaction of $U(acac)_4$ with $H_2\mathbf{28}$, produced the trinuclear species, $[U_3(\mathbf{28})(H\mathbf{28})_2(acac)_2]\cdot 3THF$ (Fig. 4), in which no symmetry element was present.

A tetranuclear species, $[U_4(H\mathbf{30})_4(H_2\mathbf{30})_2]\cdot 5THF$, was formed when $U(acac)_4$ was reacted with a slight excess of $H_2\mathbf{30}$. This complex was described as possessing a dimeric structure consisting of dinuclear subunits joined by two bridging ligands [62]. Again, a change in the metalating agent, from $U(acac)_4$ to UCl_4, led to the formation of different products [64]. Reaction of $(H_2\mathbf{25})$ or $(H_2\mathbf{30})$ with UCl_4, each resulted in similar tetranuclear species with two bridging and two terminal ligands. It is important to note that while reactions of the salen-derived ligand **30** with either UCl_4 or $U(acac)_4$ led in both cases to the formation of tetranuclear species consisting of dinuclear subunits, the reaction with $U(acac)_4$ resulted in an overall neutral complex with little symmetry (vide supra). For instance, the use of UCl_4, in conjunction with a slight excess of ligand led to the co-crystallization of two centrosymmetric tetranuclear species that are best described in terms of an anionic-neutral pair, namely $[Hpy]_2[U_4(\mathbf{30})_2(H_2\mathbf{30})Cl_6][U_4(\mathbf{30})_2(H_2\mathbf{30})_2Cl_4(py)_2]$. In a separate experiment, a hexanuclear compound, $[Hpy]_2[U_6(\mathbf{26})_4Cl_{10}(py)_4]\cdot 6py$ was synthesized by reacting *N*,*N′*-bis(3-hydroxysalicylidene-2-methyl-1,2-propendiamine) $(H_2\mathbf{26})$ with UCl_4. The complex consisted of two trinuclear, rather than dinuclear, subunits joined by two bridging ligands (Fig. 5).

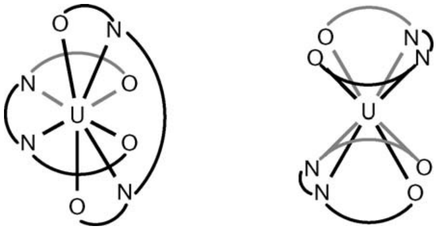


Fig. 3. Meridional and sandwich-like ligand orientations.

In 2004, Salmon et al. reported the formation of an octanuclear Schiff-base uranium complex, $(Hpy)_2[U_8\mathbf{28}_4Cl_{10}O_4]\cdot 10py$ (Fig. 6), from the reaction of $ZnH_2\mathbf{28}$ with 1 equivalent of UCl_4 in pyridine in the presence of 'adventitious oxygen' [65]. (However, it needs to be mentioned that attempts at reproducing these conditions were unsuccessful.) The complex can best be described as four $U_2\mathbf{28}Cl_2O$ units held together by μ_2-phenoxo, μ_4-oxo and μ_2-chloride bridges. In this complex, uranium cations occupy both the inner N_2O_2 and outer O_4 cavities of the salicylidene moiety. The only other previously reported uranium cluster with significant μ-oxo bridging was published in 2001 (vide infra) by Duval et al. [66].

3. Pyrrole-derived ligands

Porphyrins, conjugated macrocyclic systems containing four pyrroles linked in a 16-atom ring, are prevalent in nature and are well known for their diverse metalation chemistry. Porphyrin–actinide complexes have been reported; however, due to their relatively small core, the coordinated metal cations studied to date, Th(IV) or U(IV), typically sit out of the plane of the ring [67]. Such findings have inspired the study of porphyrin analogues as possible ligands for the stabilization of actinide complexes. To date, three such analogues have received particular attention and all three are discussed in detail below. The first of these is calix[4]pyrrole. This porphyrinogen-like macrocycle can be considered a 'saturated' porphyrin, with alkylated sp^3 carbons precluding the formation of conjugated systems; it has been well studied of late for its anion binding [68,69] and transition metal coordination properties [70,71]. Expanded por-

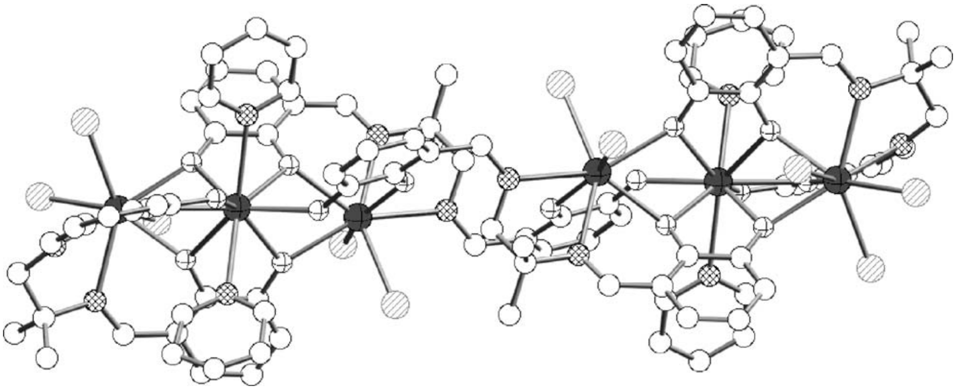


Fig. 5. Single crystal X-ray diffraction structure of the complex $[Hpy]_2[U_6(\mathbf{26})_4Cl_{10}(py)_4]\cdot 6py$ [64]. All hydrogen atoms have been removed for clarity. Here, the atom labels are as follows: ○ = C; ⊗ = N; ⊕ = O; ● = U; ▨ = Ci. .

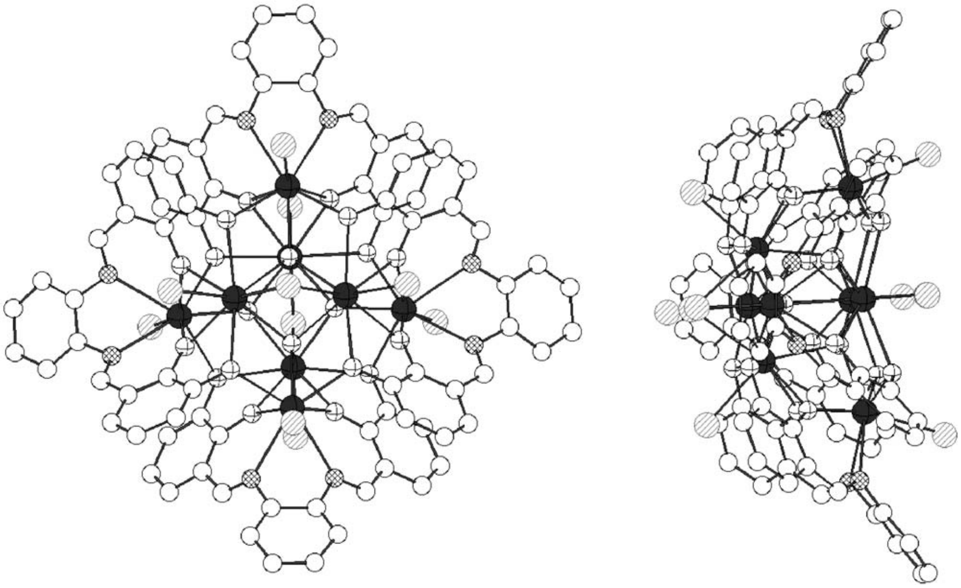


Fig. 6. Single crystal X-ray diffraction structure of $(Hpy)_2[U_8\mathbf{28}Cl_{10}O_4]\cdot 10py$ complex [65]. All hydrogen atoms have been removed for clarity. Here, the atom labels are as follows: ○ = C; ⊗ = N; ⊕ = O; ● = U; ▨ = Ci. .

phyrins define the second class of porphyrin analogues of interest in the actinide coordination area. Expanded porphyrins are conjugated macrocycles containing four or more pyrroles and 17 or more atoms in their inner core. This larger core size has led to suggestions that they would be particularly suited for the coordination of *f*-block cations. Finally, pyrrole-containing Schiff-base macrocycles, define a third set of porphyrin analogues of potential interest to the actinide chemist; they are appealing because they posses iminic, as well as pyrrolic, nitrogens, thus providing inherently unusual coordination environments.

3.1. *Calix[4]pyrrole*

Reaction of $UI_3(thf)_4$ and $([(\text{–}CH_2\text{–})_5]_4\text{–calix[4]pyrrole})[K(thf)]_4$, (hereafter, $(\text{calix[4]pyrrole})[K(thf)]_4$) resulted in a binuclear species bridged by an oxygen atom, $\{[(\text{calix[4]pyrrole})UK(thf)_3]_2(\mu_2\text{–}O)\}\cdot 2THF$, (**35**, Fig. 7) [72]. An X-ray

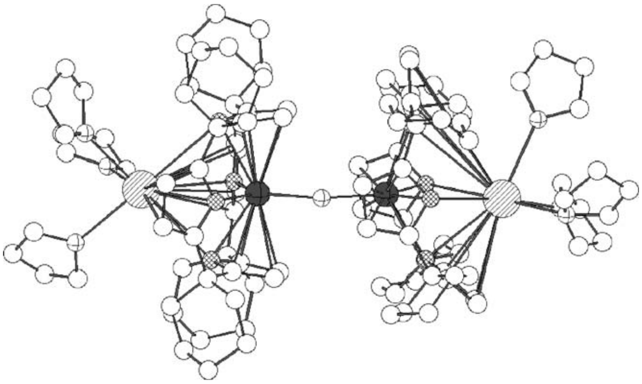


Fig. 7. Single crystal X-ray diffraction structure of $\{[(\text{calix[4]pyrrole})UK(thf)_3]_2(\mu_2\text{-}O)\}\cdot 2THF$ complex, **35** [72]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ⊗ = N; ⊕ = O; ● = U; ▨ = K. .

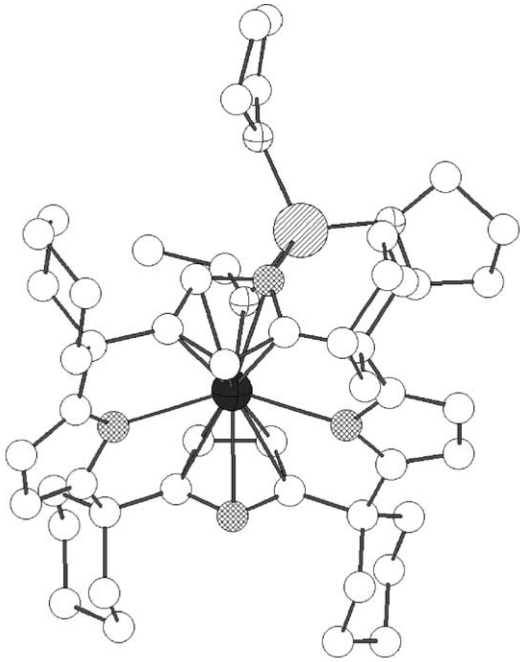


Fig. 8. Single crystal X-ray diffraction crystal X-ray structure of the (N-confused-calix[4]pyrrole)ULi(OC_2H_5)(thf)$_2$ complex, **36** [72]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▩ = N; ⊕ = O; ● = U; ▨= Li. .

diffraction analysis revealed that two pyrroles on opposite sides of the calix[4]pyrrole moiety are π-bound (η^5) to the now-tetravalent uranium center, with the other two pyrroles being σ-bound (η^1) to the uranium center through the pyrrole nitrogen atoms, in analogy to what is seen in the case of **37** (vide infra). The authors propose that during the course of the reaction, oxidation of the uranium centers is facilitated via the two-electron degradation of THF. In a different experiment, an excess of the corresponding lithium salt of calix[4]pyrrole was found to lead to the formation of the binuclear species, [(calix[4]pyrrole)ULi(thf)$_2$]$_2$·hexane [73]. As the in the previously described binuclear calix[4]pyrrole uranium complex (vide supra), the complex [(calix[4]pyrrole)ULi(thf)$_2$]$_2$·hexane is characterized by two U(IV) centers that are bound to the four pyrrole subunits in an η^1:η^5 fashion. However, rather than containing a μ-oxo bridge, in this case one the β-carbon of one of the pyrrole rings is deprotonated, thus forming an η^1 bond with the opposing uranium cation. In this case, it was hypothesized that the lithium salt aids in deprotonation of the pyrrole β-CH proton in question.

Substitution of UCl_3 for UI_3 in the reaction with (calix[4]pyrrole)[Li(thf)]$_4$, produced an unexpected N-confused calix[4]pyrrole uranium complex (**36**, Fig. 8) [72]. In this species, one lithium cation was coordinated to the nitrogen atom of the N-confused pyrrole, as well as to an ethoxide oxygen atom which, in turn, was coordinated to the uranium center. The authors inferred that the ethoxide residue was most likely produced via a process involving THF fragmentation.

It was concluded that the synthesis of three different complexes (vide supra) from a very similar starting material is indicative of a rather complicated mechanism and serves as proof for the high reactivity of the U(III) center. In an effort to limit the solvent influence in the reaction mechanism, DME, a more robust ether solvent, was used in the reaction of UI_3(dme)$_2$ with [(Et_8–calix[4]pyrrole)K_4(dme)$_2$]. In this case, the trivalent, mononuclear complex [(Et_8–calix[4]pyrrole)U(dme)][K(dme)] (**37**) is produced. In this complex, the uranium center is coordinated to the calix[4]pyrrole in an η^1:η^5 fashion, and to one solvent molecule [72].

The inherent reactivity of this monomer was also studied [74]. Towards this end, attempts at reduction using [K(naphthalenide)] under argon were made; this produced two complexes, **38** and **39**. The fact that **38** was formed led to the conclusion that deoxygenation (fragmentation) of the DME solvent molecule takes place during the course of the reaction, concurrent with the formation of a mixed valent U(III)/U(IV) μ-oxo complex. Complex **39**, was found to be an infinite anionic polymer (Fig. 9) which contains three potassium atoms for each U(III)–calix[4]pyrrole dimer. The U(III)–calix[4]pyrrole dimers were assembled in the polymeric matrix via a bridging Me_2SiO_2 and bridging K atom for each dimeric pair. It was implied by

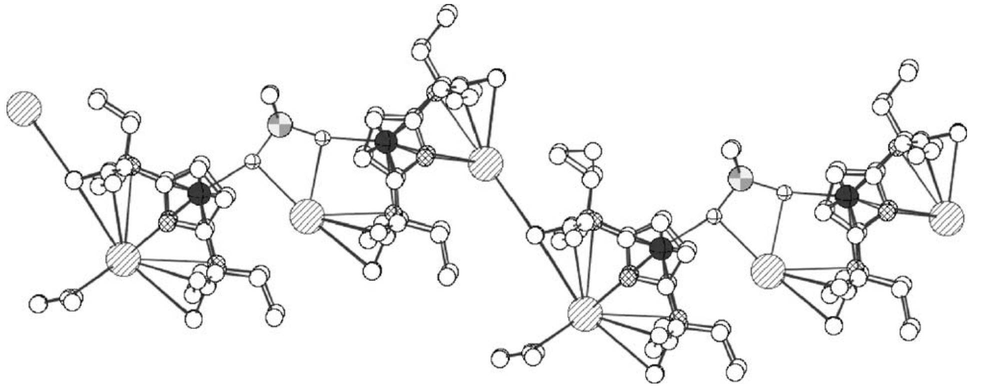
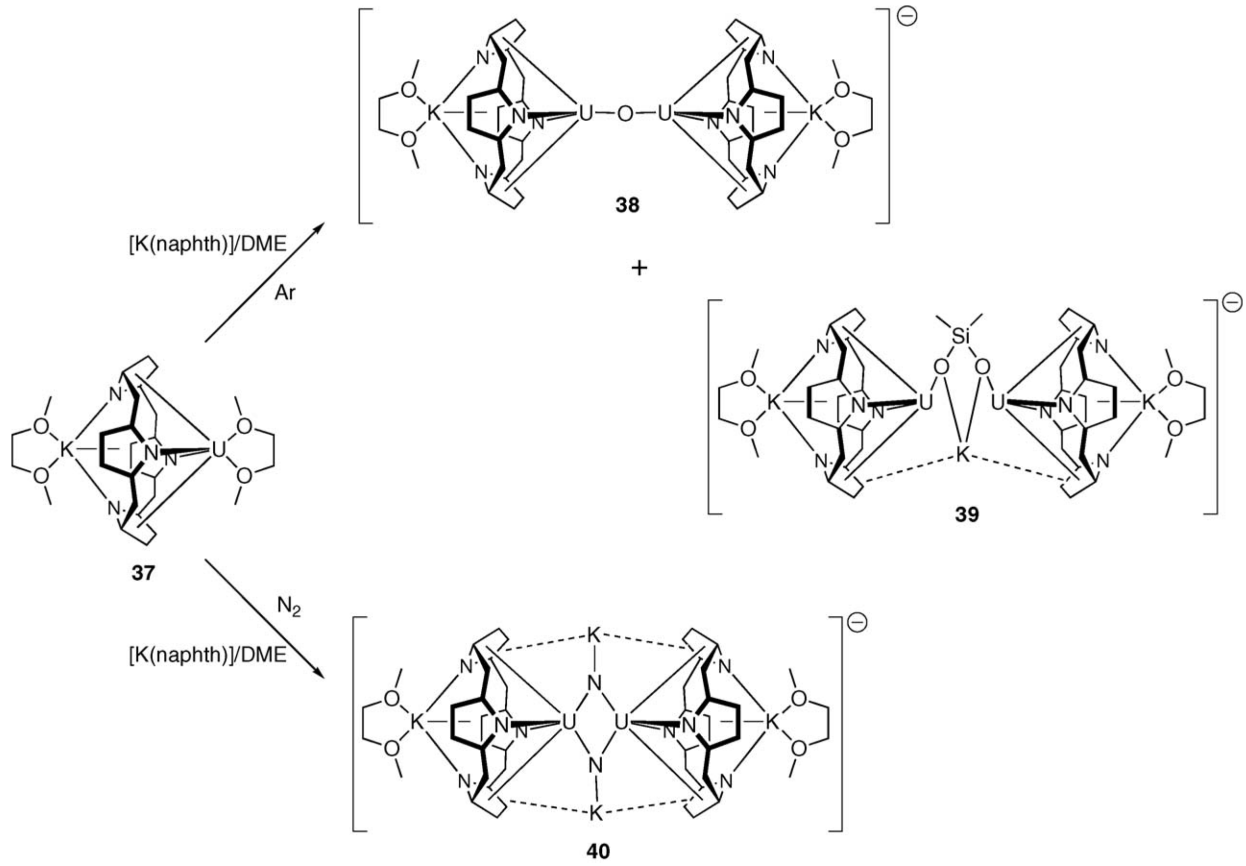


Fig. 9. Single crystal X-ray diffraction structure of complex **39**, an infinite anionic polymer containing U(III)-calix[4]pyrrole dimmers [74]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▩ = N; ⊕ = O; ● = U; ▨ = K; ◐ = S. .



Scheme 8. Reaction scheme for **38**–**40** [74]. The ethyl groups have been removed for clarity. K(napth) = potassium naphthlide.

the authors that the high reactivity of the U(III) center was again demonstrated by this chemistry and that it was induced in part by the presence of Me_2SiO_2 resulting from silicon grease present in the reaction flask. Reaction of the monomer, **37**, with [K(napthalenide)dme] under N_2 produced an unprecedented U(V)/U(IV) complex, **40**, in which a nitrogen molecule, from the N_2 atmosphere, is coordinated to each uranium center, as well as to a potassium cation (Scheme 8).

In a separate experiment, two equivalents of $UI_3(thf)_4$ were reacted with one equivalent $[(Et_8\text{–calix[4]pyrrole})][Li(thf)]_4$ to form a binuclear complex containing two trivalent uranium centers coordinating one calix[4]pyrrole unit. Each uranium center is coordinated to all four pyrrolic moieties, as in the complexes previously described (vide supra), as well as to two iodide anions. The result is that these metal atoms are present in a tetragonally distorted octahedral geometry. The U–U distance is 3.4515(5) Å. A somewhat geometrically similar U(III)/U(IV) complex (**41**, Fig. 10) was obtained by partial reduction of UCl_4 prior to the reaction with $(Et_8\text{–calix[4]pyrrole})[Li(thf)_4]$. The U–U distance was found to be 3.365(3) Å with both uranium centers being present in geometries that are roughly octahedral.

Magnetic moments were calculated for both complexes and provided support for the conclusion that **41** is a mixed valence, U(III)/U(IV) species in which the metal centers are held in close proximity. It is important to note that the U–U distances in

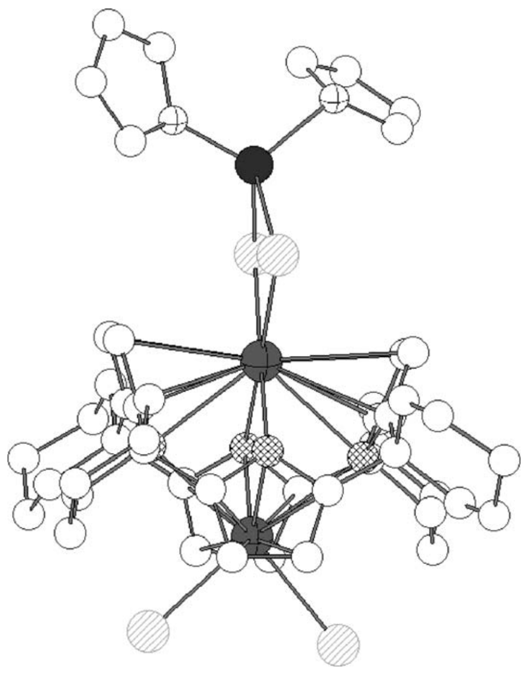


Fig. 10. Single crystal X-ray diffraction structure of the U(III)/U(IV) calix[4]pyrrole complex, **41** [74]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ⊗ = N; ⊕ = O; ● = U; ⊘ = Cl.

these systems are among the shortest seen in uranium chemistry. However, magnetic data gave no evidence for U–U bonding. DFT calculations provided support for the presence of a weakly coupled antiferromagnetic interaction between the mixed valent atoms [73].

3.2. Porphyrins and expanded porphyrins

Lomova and Andrianova recently reported double and triple-decker complexes of uranium and tetraphenylporphyrin (TPP). Reaction of TPP with $UO_2(OAc)_2$ in phenol, produced the double-decker U(IV)$(TPP)_2$ and U(III)$(TPP)_3$ in 18 and 14% yield, respectively. The complexes were characterized by UV–vis, IR, and ^{1}H NMR spectroscopy [75].

In 2001 Sessler et al. reported that an expanded porphyrin, hexaphyrin (1.0.1.0.0.0), generally referred to as isoamethyrin (**42**) [24], was able to coordinate the uranyl cation, as well as the neptunyl cation [76]. It was shown that the macrocycle twisted slightly to accommodate the uranyl cation while adopting an aromatic structure (Fig. 11). Crystal structures of the $UO_2{}^{2+}$ and $NpO_2{}^+$ complexes revealed that the macrocycle, formally a 24 π-electron system as originally prepared, underwent oxidation upon coordination of these actinyl cations to produce an aromatic, 22 π-electron species.

The combination of metal coordination and oxidation dramatically changes the color of the macrocycle in solution (from a golden yellow for the free base to a red for the metal-coordinated species) and is accompanied by a five-fold increase of the extinction coefficient ($\varepsilon \sim 60{,}000\,dm^3\,mol^{-1}\,cm^{-1}$ for acid salt compared to $\varepsilon \sim 330{,}000\,dm^3\,mol^{-1}\,cm^{-1}$ for the UO_2 complex). This dramatic color change led Sessler and coworkers to propose that isoamethyrin may have a role to play as an actinide cation sensor [77]. It was reported that, under the appropriate solvent conditions, the detection limit for $UO_2{}^{2+}$ fell into the ppb range assuming a UV–vis spectrometer signal:noise ratio of 10:1. Furthermore, preliminary results [77] showed that a number of transition metals (with the exception of Cu^{2+}) did not induce the same color change as seen with the actinides, leading to the suggestion that this macrocycle possessed good actinide selectivity (Fig. 12).

Fig. 12. Colors of MeOH–CH_2Cl_2 (95:5 v/v) solutions of isoamethyrin (1.02×10^{-4} M) containing four equivalent of Et_3N. Acetate salts were used for this study, with the exception of $Cd(NO_3)_2$ [77].

3.3. Oligopyrrolic Schiff bases

Pyrrole-containing Schiff bases are generally considered to fall within the expanded porphyrin family [78]. As a class, they have displayed a rich metalation chemistry. Not surprisingly, it has been the transition metals and lanthanides that have been most extensively studied. However, over the past few years a number of actinide–Schiff-base expanded porphyrin complexes have been reported. Much of this chemistry has been treated in recent reviews [78,79] and, therefore, only a brief discussion is included here.

The uranyl cation has proven useful in template reactions involving the production of pyrrole Schiff-base macrocycles, a synthetic approach that has been exploited by Sessler et al. [81,82]. For instance, the condensation of *o*-phenylenediamine with a diformyl pyrrole in the presence of uranyl acetate and

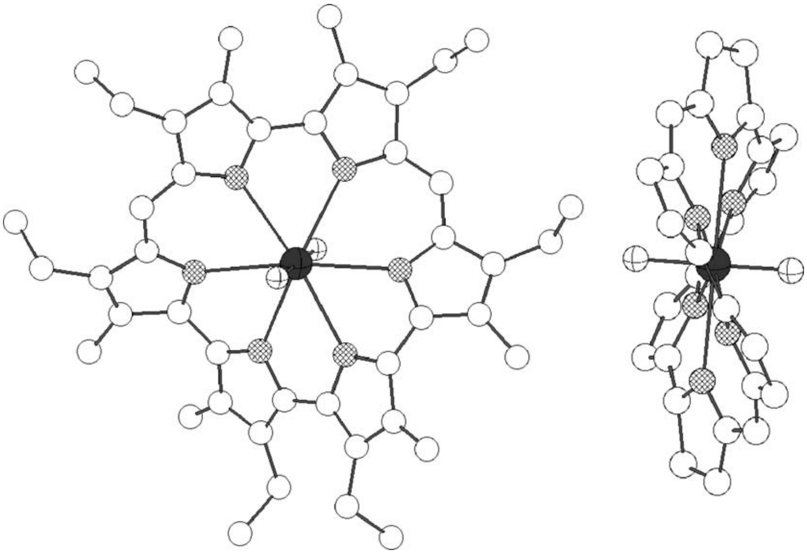


Fig. 11. Single crystal X-ray diffraction structure of UO_2-**42** [76]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▨ = N; ⊕ = O; ● = U.
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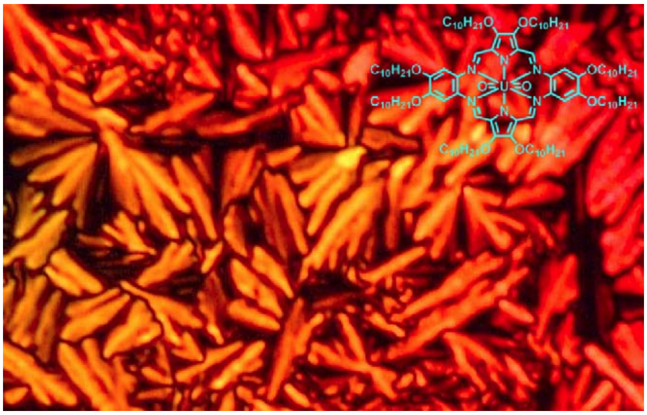


Fig. 13. Uranyl complex **45** as observed by photomicrography at 124 °C. For this system, the mesophase is stable between 108 and 135 °C [80].

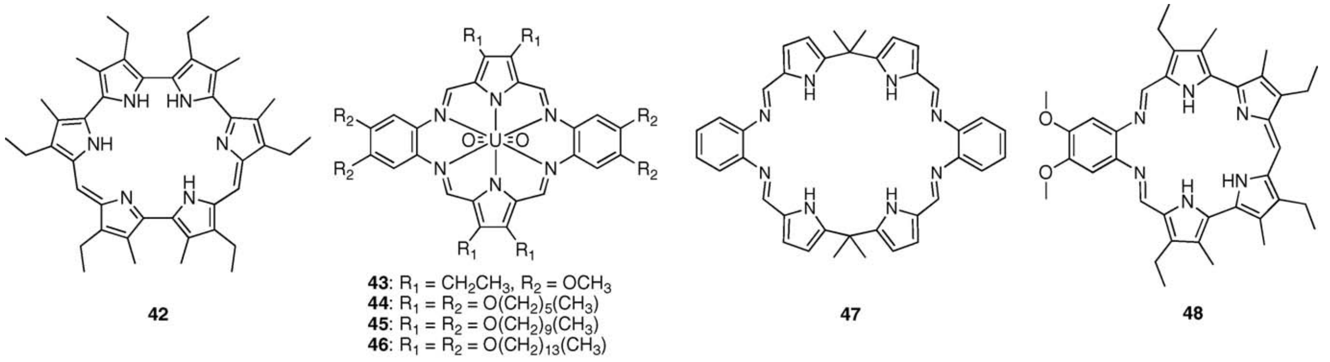
a proton sponge produced the fully conjugated Schiff-base systems **43**–**46**, macrocycles that as a group have come to be referred to as alaskaphyrins. The fully conjugated environment provided by the alaskaphyrins was found to be well suited for the coordination of the uranyl cation. In fact, in most cases analyzed by X-ray diffraction analysis, the UO_2^{2+} center was found to fit perfectly in the macrocycle core [82].

While pyrrole Schiff-base macrocycles, such as the alaskaphyrins and various congeners have been known for many years, an application in the area of liquid crystals has emerged recently. While uranyl liquid crystals [83] and Schiff-base liquid crystals [84] have been previously reported, it is only recently that these two intellectual themes were merged. This was done via the template-mediated production of a novel uranyl-alaskaphyrin liquid crystal by Sessler et al. [80]. Here, several functionalized diformyl pyrroles were condensed with *o*-phenylenediamine derivatives in the presence of a proton sponge and uranyl acetate (the source of the UO_2^{2+} template) to give macrocycles **44**–**46**. The octa-decyloxy and octa-tetradecyloxy alaskaphyrins (**45** and **46**) were found to produce columnar mesophases, whose nature was apparent from photomicrography (Fig. 13). It is believed that the combination of planarity of the macrocycle and intermolecular π-stacking is responsible for the observed liquid crystalline properties of these novel materials [80].

The ability of alasakphyrin to coordinate the uranyl, neptunyl and plutonyl cations [85] has also been analyzed by molecular modeling. A DFT study was performed on all three coordination complexes in order to gain a better understanding of the coordination environment between the metal and macrocycle [86]. It was concluded that alkyl and electron-donating substituents on the β-position of the pyrrole actually weaken the interactions between the uranyl cation with the ligand. In addition, the binding energy between the dioxo metal and ligand was predicted to decrease upon moving across the periodic table (i.e., U > Np > Pu). It is important to note, however, that the most stable oxidation state of these cations varies with environment. It is known [87], for instance, that in an aqueous environment neptunium is most stable in its pentavalent oxidation state, while plutonium is most stable in its tetravalent oxidation state. Thus, these theoretical analyses are likely to be most useful as guides for future experiments, rather than as predictions per se.

Macrocycles of type **47** are known to coordinate Pd [88] and Fe in different conformations [89]. However, in a recent communication by Arnold et al. [90] the formation of a uranyl complex using this polypyrrolic Schiff-base macrocycle was reported [91]. Specifically, it was found that reaction of the free base form of **47** with an uranyl amide, $[UO_2(THF)_2\{N(SiMe_3)_2\}_2]$ (Fig. 14), yielded an asymmetric mononuclear complex with the uranyl cation occupying one pocket of the Pac-man-like ligand (Scheme 9). One of the trans diaxal uranyl-oxygen atoms points into the open dipyrromethane compartment, presumably as the result of hydrogen bonding interactions. By contrast, the other oxo oxygen atom is oriented “exo” to the ligand. Reaction with an excess of pyridine served to replace the THF molecule but did not change the overall coordination sphere of the uranyl cation (which remained roughly pentagonal bipyrimidal) [90].

Grandephyrin, **48**, made by a [1 + 1] condensation reaction of a diformyl bisbipyrrole with a diamine, has been shown to coordinate the uranyl cation via a mode that involves all six nitrogen atoms (four pyrrolic, two Schiff-base iminic). Upon complexation, the macrocycle shifts from its slightly ruffled shape to planar, while providing a complex with roughly C_2 symmetry (cf. Fig. 15), although some disorder is present in the pyrrole subunits furthest from the imine nitrogen atoms. Based on ^1H NMR spectroscopic analysis, it was suggested that this latter disorder is present in the solution as well as in the solid state. As



42

43: $R_1 = CH_2CH_3$, $R_2 = OCH_3$
44: $R_1 = R_2 = O(CH_2)_5(CH_3)$
45: $R_1 = R_2 = O(CH_2)_9(CH_3)$
46: $R_1 = R_2 = O(CH_2)_{13}(CH_3)$

47

48

Scheme 9. Isoamethyrin, uranyl alaskaphyrins, macrocycle **47** and grandephyrin.

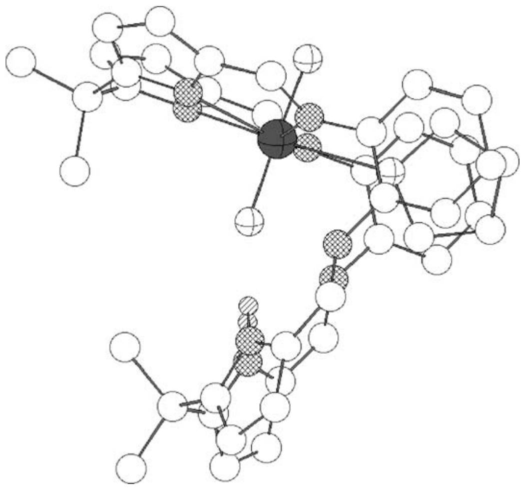


Fig. 14. Single crystal X-ray diffraction structure of the uranyl complex formed from the polypyrrolic Schiff-base macrocycle **47** [90]. Most hydrogen atoms have been removed for clarity. Atom labels are as follows: ○=C; ▩=N; ⊕=O; ●=U; ▨=H.

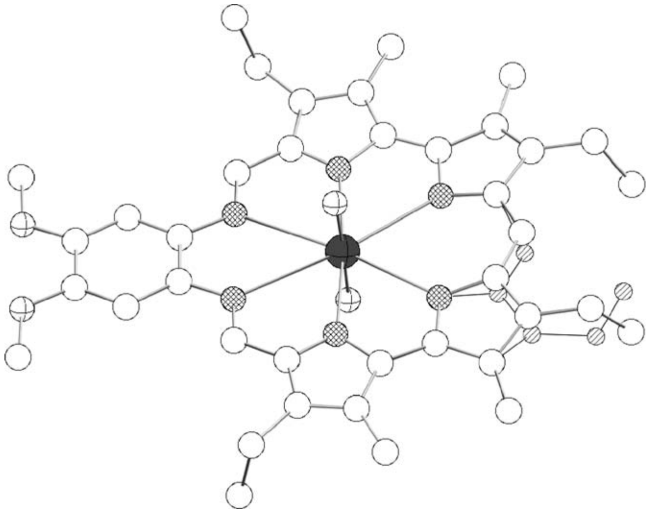


Fig. 15. Single crystal X-ray diffraction structure of UO_2-**48** [85]. All hydrogen atoms have been removed for clarity. The disordered C atoms are presented as hashed spheres. Atom labels are as follows: ○ = C; ▩ = N; ⊕ = O; ● = U.

is seen in Fig. 15, the uranyl cation is slightly shifted towards the disordered pyrrolic nitrogens. It is rationalized that the disorder reflects the strain placed on the ligand to accommodate the large uranyl cation. The uranyl cation, with six nitrogens in its equatorial plane, can be considered to have a distorted hexagonal bipyrimidal geometry [85].

4. Polyamido-derived ligands

Due to space limitations, work done with the exclusive intent of actinide extraction or developing monodentate amido ligands will be excluded from this review. The interested reader is directed towards more extensive reviews on these subjects [13,92].

4.1. Bidentate

Sarsfield et al. [93] have utilized bulky bidentate chelating ligands, $PhC(NSiMe_3)_2$ (NCN) and $Ph_2P(NSiMe_3)_2$ (NPN), to effect coordination of the uranyl cation and have reported unusual binding geometries for the resulting complexes. A different kind of complex, namely $[UO\{OB(C_6F_5)_3\}(NCN)_2]$, was obtained through a metathesis reaction involving two equivalents Na[NCN] with $UO_2Cl_2(thf)_3$ and subsequent reaction with two equivalents of $B(C_6F_5)_3$. Based on X-ray diffraction analysis and IR and Raman spectroscopy, it was found that, while the uranyl unit remains linear, a U=O–B interaction lengthens the U=O bond [94]. It was postulated that this weakening is due to electronic effects resulting from the electron-donating nature of the ligands, as opposed to steric interactions. Additionally, it was shown that an oxo-bridged dimer, $[Na(thf)UO_2(NCN)_2]_2(\mu\text{-}O)$, fortuitously formed by hydrolysis of a U-tris(NCN) complex, had the second lowest uranyl stretching frequency reported to date [93].

In separate work, Sarsfield et al. have reported a uranyl complex, $[UO_2Cl\{\eta^3\text{-}CH(Ph_2PNSiMe_3)_2\}(thf)]$, containing a uranyl-methine bond [95]. The system exists in the form of a dimer, with each uranyl cation coordinated to two nitrogens and the central carbon atom of the bis(iminophosphorano)methide ligand, in addition to two bridging chlorides and linear oxo atoms. Interestingly, the ligand is displaced from the equatorial position of the uranyl cation; the methane carbon is described as displaced by ∼18°. In contrast, the U–N bond of a nitrogen-containing analogue, $[UO_2Cl\{\eta^3\text{-}N(Ph_2PNSiMe_3)_2\}(thf)]$, in which the uranyl cation is coordinated to three nitrogen atoms, was shown to remain closer to the uranyl equatorial plane [96].

A homoleptic U(III) tris(amidinate) complex has been reported and its catalytic activity has been compared to similar lanthanide complexes [97]. Reaction of UCl_4 in THF with $[LiMeC(NCy)_2](thf)]_2$ (Cy = cyclohexyl) produced the mononuclear complex, $[U\{RC(NCy)_2\}_3Cl]$ (R = Me, *n*-Bu). Subsequent reduction with Li in THF cleanly afforded the trivalent tris(amidinate) complex, $[U\{MeC(NCy)_2\}_3]$ (**49**, Fig. 16). It was stated that the U–N distance for the U(III) complex was 0.025 Å shorter than what one would expect for a purely ionic bonding model. Attempts at polymerization of ε-caprolactone with **49** proved unsuccessful, a result that was thought by the authors to reflect rapid oxidation to a U(IV) species.

4.2. Tridentate

Wilson et al. studied An(IV) (An = U and Th) coordination using the bulky chelating silylamino(disilylamido) ligand, $[Me_3SiN\{CH_2CH_2NSiMe_3\}_2]^{2-}$ (abbreviated as $[NN_2]^{2-}$), after finding that this ligand afforded interesting chemistry in the case of the transition metals [98]. The mono-diamidoamine complex, $[M(NN_2)Cl_2(THF)]$ (M = U, Th), (**50**, M = U) as well as the minor side product, a bis-diamidoamine complex $[M(NN_2)_2]$ (M = U, Th), were readily formed upon addition of MCl_4 (M = U, Th) with $Li_2[NN_2]$. Recrystallization of the uranium complexes from toluene resulted in green crystals of the dimeric species,

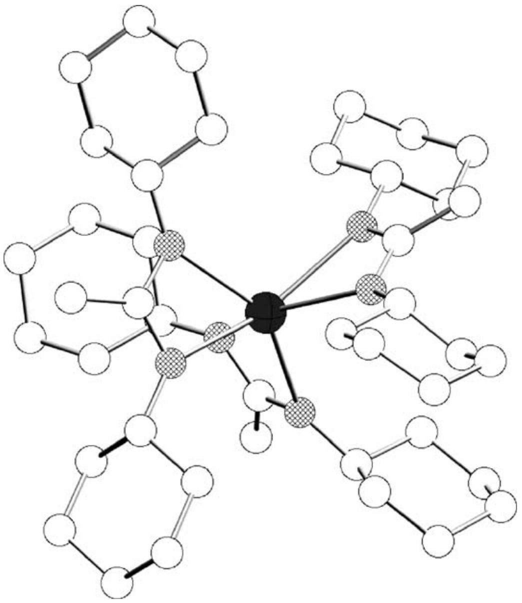


Fig. 16. Single crystal X-ray diffraction structure of complex **49** [97]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▨ = N; ● = U. .

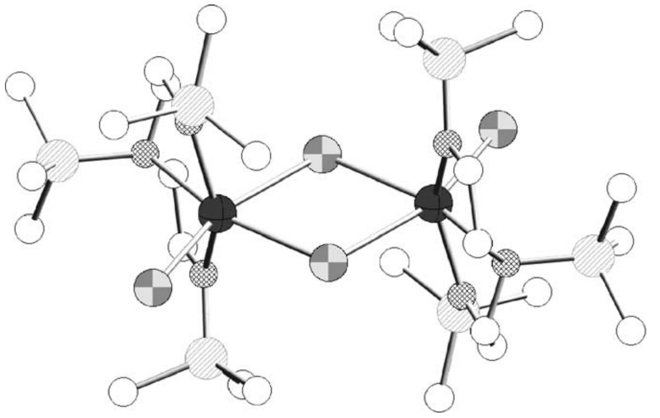


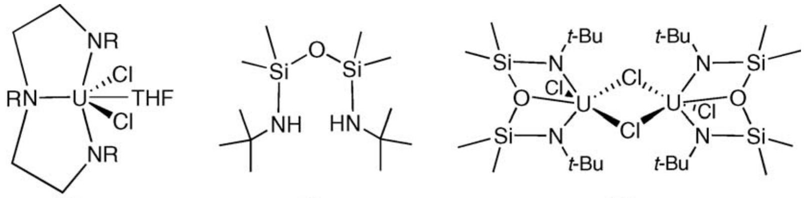
Fig. 17. Single crystal X-ray diffraction structure of **51**, $[U(Me_3SiN\{CH_2CH_2NSiMe_3\}_2)Cl_2]_2$ [98]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▨ = N; ● = U; ▨ = Si; ◐ = Cl. .

$[U(NN_2)Cl_2]_2$, **51**, and permitted characterization by X-ray diffraction methods (Fig. 17) [98].

In separate work, Jantunen et al. reported actinide coordination with a diamido ether ligand, $[(CH_3)_3CNH(Si(CH_3)_2)]_2O$ (H_2*t*-BuNON, **52**) [99]. Addition of Li_2[*t*-BuNON] to a THF slurry of MCl_4 (M = U, Th) at −30 °C afforded the dimeric bis-(diamino) complex $\{[t\text{-BuNON}]MCl_2\}_2$ (**53**, M = U), with no evidence for formation of the mono-product being obtained (Scheme 10). Attempts to effect methylation of **53** through addition of CH_3MgBr led to formation of a halide exchange product $\{[t\text{-BuNON}]UBr_2\}_2$, rather than the desired compound. Treatment of $\{[t\text{-BuNON}]UCl_2\}_2$ with two equivalents of C_3H_5MgCl afforded a mononuclear disubstituted allyl complex, $[t\text{-BuNON}]U(\eta\text{-}C_3H_5)_2$. While VT NMR (toluene-$d_8$) studies were inconclusive, based on IR analysis (KBr) it was suggested that, in the solid state, at least one of the allyl molecules is coordinated to the uranium center in an η^1 fashion. Treatment of $\{[t\text{-BuNON}]UCl_2\}_2$ with two equivalents of $LiCH_2Si(CH_3)_3$ in toluene afforded a monomeric species with two $CH_2Si(CH_3)_3$ groups coordinated to the metal center. Additionally, the complex $[t\text{-BuNON}]U(C_5(CH_3)_5)Cl$ was formed when **53** was treated with two equivalents of NaCp*. ^{1}H NMR and IR analysis led to the conclusion that the Cp* anion was bound in an η^5 fashion. Subsequent alkylation of this complex with one equivalent of CH_3MgBr in the presence of excess *p*-dioxane resulted in the formation of the corresponding alkylated complex, $[t\text{-BuNON}]U(C_5(CH_3)_5)CH_3$, in high yields.

In an effort to probe the coordination chemistry of this reactive species, the Meyer group has developed a novel ligand system for the U(III) cation. Specifically, these researchers found that reaction of $[U(N(SiMe_3)_2)_3]$ with 1,4,7-tris(3,5-di-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane ($(ArOH)_3$tacn; **54**) produced the six-coordinate U(III) species, $[((ArO)_3\text{tacn})U]$ (**56**) [7]. In this product, the U(III) center is formally bound to anionic aryloxide groups, while coordination to the tacn macrocycle presumably serves to protect the reactive uranium center from unwanted side reactions. It was thus proposed that this complex contains only one open reactive site, which is additionally 'shielded' (or protected) by the *tert*-butyl aryloxide substituents.

While a crystal structure of the six coordinate complex has remained elusive, presumably due to its exceptional reactivity, crystals suitable for X-ray diffraction were obtained by recrystallization in actetonitrile; this resulted in a complex (**58**) wherein the U(III) center is coordinated to an acetonitrile molecule, and which can thus be considered seven-coordinate (Fig. 18) [7,100]. The magnetic moment of complexes **56** and **58** both vary significantly with temperature (1.77 μ_B at 5 K to 2.92 μ_B at 300 K for **56**, and 1.66 μ_B at 4 K to 2.90 μ_B at room temperature and 3.40 at 350 K for **58** with no plateau observed at that temperature) [7,100]. These magnetic moments are lower than would



50 **52** **53**

Scheme 10. Mono-diamidoamine actinide complex **50** and bis-diamino actinide complex **53** formed from ligand **52** (R = $SiMe_3$).

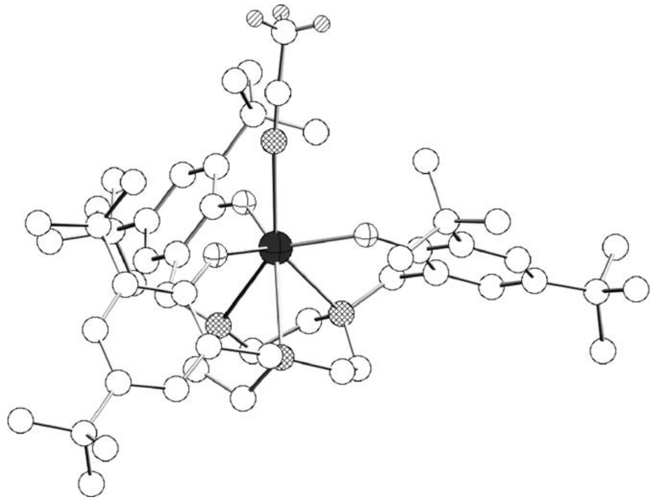


Fig. 18. Single crystal X-ray diffraction structure of [((ArO)$_3$tacn)U(NCCH$_3$)], **58** [7]. Most hydrogen atoms have been removed for clarity. Atom labels are as follows: ○=C; ⊛=N; ⊕=O; ●=U; ▨=H. .

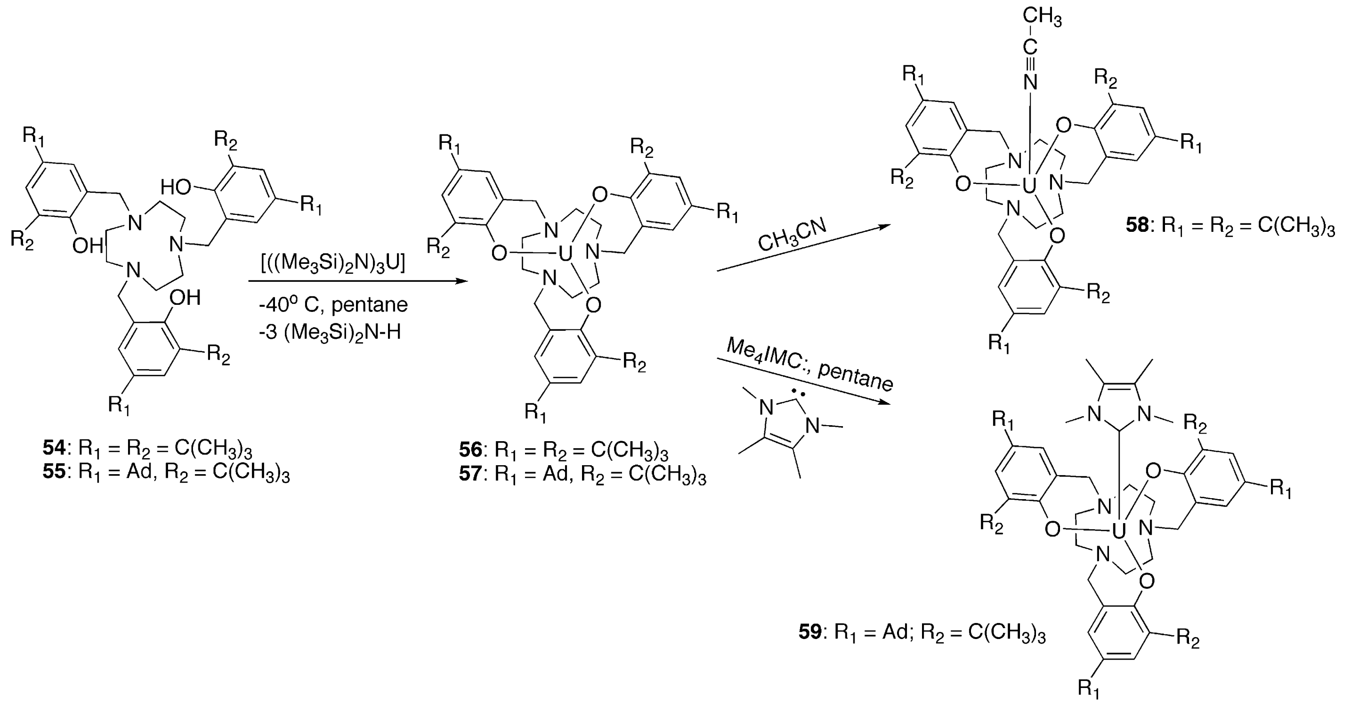
be expected for an f^3 uranium species with a $^4I_{9/2}$ ground state. In line with the DFT calculations, it was thus proposed that the depressed magnetic moments could reflect covalency present in the U(III) system, which would serve to quench spin–orbit coupling thereby reducing the magnetic moment [7].

Attempts at recrystallization of **56** from either Et$_2$O or THF led to the formation of the oxidized species, [((ArO)$_3$tacn) U^{IV}(OAr)], and the binuclear species, [{((ArO)$_3$tacn)U^{IV}}$_2$(μ-O)] [100] (Scheme 11). The enhanced reactivity of **56** was further studied by molecular modeling (DFT calculations), from which it was concluded that complex **56** showed reactivity behavior similar to a di-radical, namely that it might be reactive toward small molecules [100].

Reaction of **56** with one equivalent of trimethylsilyl azide led to the formation of two complexes. The major product, [((ArO)$_3$tacn)UN(Si(CH$_3$)$_3$))], was found to be a green U(V) imido complex. The short U–N(imido) distance of 1.991(4) and 1.985(5) Å, and a nearly linear U–N–Si(CH$_3$)$_3$ angle of 168.9(3)° and 178.5(3)°, were considered indicative of multiple bonding interactions between the uranium and nitrogen (imido) atoms. The side product from this reaction was a colorless U(IV) species, [((ArO)$_3$tacn)U(N$_3$)]. DFT calculations and Mülliken population analysis of the reported structures led to the proposal that covalent interactions were present in the U(V) imido species but not in the U(IV) species. In fact, the magnetic moments recorded for the U(IV) species, while temperature dependant, were found to be in agreement with theoretically determined values, while those for the U(V) species were found to be lower than theoretical values, with a result that was consistent with the DFT calculations (vide supra) [7].

Alkane (C–H) activation was observed upon addition of excess cyclohexane, cyclopentane, methylcyclohexane, methylcyclopentane or neohexane to a solution of **56** in *n*-pentane. Generally, the complexes formed followed the formula [(ArO)$_3$tacn)U(alkane)]·(cy-alkane), in which the activated alkane was coordinated to the U(III) center in a η^2 fashion through a C–H bond [101].

It was found that an increase in the steric bulk around the uranium center did not hinder reactivity [102]. The complex, [((^{Ad}ArO)$_3$tacn)U] (**57**), in which adamantyl groups were added to the aryloxide ligands, was synthesized in 67% yield and was observed to react readily with 1,3,4,5-tetramethyl-imidazol-2-ylidene (Me$_4$IMC:) to afford a deep purple complex charac-



Scheme 11. Synthesis of various [U(OAr)$_3$(tacn)] complexes [7,102] (Ad = adamantyl).

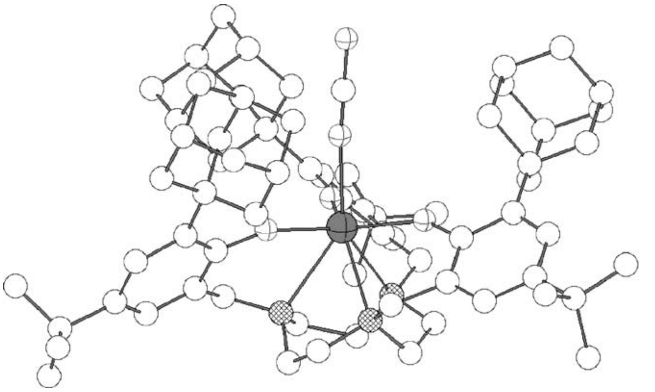


Fig. 19. Single crystal X-ray diffraction structure of the complex $[((^{Ad}ArO)_3tacn)U(OCO)]$, **60** [103]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▨ = N; ⊕ = O; ● = U.

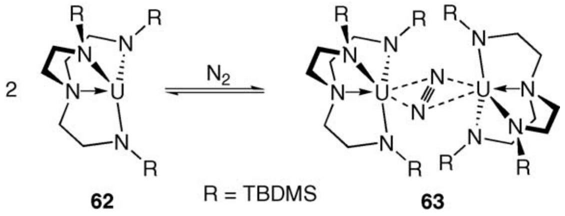
terized as $[((^{Ad}ArO)_3tacn)U(Me_4IMC{:})]$ (**59**). It was believed that the carbene was coordinated to the uranium center via a π-bonding interaction [102].

CO_2 activation has also been structurally proven with the adamantly derivatized complex [103]. Exposure of the unsaturated U(III) complex **56** to CO_2 led to an immediate color change (from green to colorless), which was found to be caused by formation of a U(IV) complex in which a reduced molecule of CO_2 was coordinated to the uranium center in a linear η^1 (–OCO) fashion (**60**, Fig. 19).

The $[(SiMe_2NPh)_3tacn]^{3-}$ ligand has been utilized by Marques and coworkers, as an ancillary ligand for U(IV). The reaction of $Na_3[(SiMe_2NPh)_3tacn]$ with one equivalent of $[UI_3(thf)_4]$ in toluene led to the formation of the six-coordinate complex, $[U\{(SiMe_2NPh)_3tacn\}]\cdot 0.5C_7H_8$, **61**. Reaction of **61** with a stoichiometric amount of benzyl chloride produced a seven-coordinate species $[U\{(SiMe_2NPh)_3tacn\}Cl]$, while addition of I_2 to a solution of **61** in toluene gave the corresponding iodide complex, $[U\{(SiMe_2NPh)_3tacn\}I]$ [104].

4.3. Tetradentate

A number of triamido–uranium complexes were reported in the 90's [105–112], with the majority of reports discussing U(IV) products. Notable exceptions include a mixed valent (III/IV) complex reported by Roussel et al. in 1996 [113]. Attempted reduction of a U(IV) complex, $[(NN'_3)UCl]_2$ $[NN'_3 = N(CH_2CH_2NSiBu^tMe_2)_3]$, with a potassium mirror resulted in the formation of the mixed valent species $\{[(NN'_3)U]_2(\mu\text{-}Cl)\}$. Sublimation of this mixed valent structure allowed for isolation of the trivalent species, $[U(NN'_3)]$, **62**. Two molecules of this latter trivalent species have been shown to react with dinitrogen to form the complex, $[\{U(NN'_3)\}_2(\mu_2\text{-}\eta{:}^2\eta^2\text{-}N_2)]$, **63**, where the uranium centers participate in a side-on bridging mode with one molecule of nitrogen [114]. Not only was this the first complex of a dinitrogen–actinide complex, but the process was shown to be reversible. Consistent with this reversibility, the N–N bond length in **63** was found to be roughly the same as that in dinitrogen gas (1.109(7) Å for **63** versus 1.0975 Å for N_2).



Scheme 12. Reversible coordination of N_2 [115].

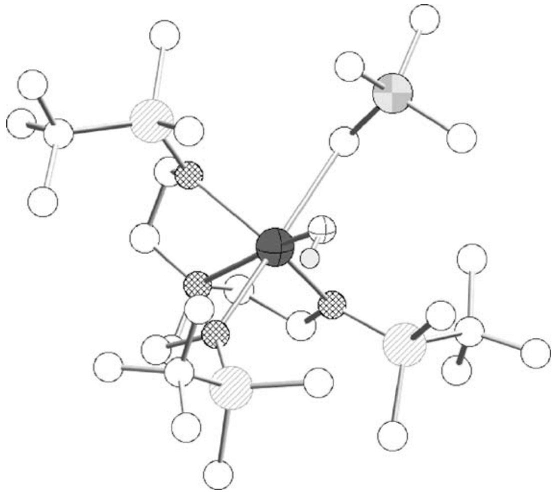
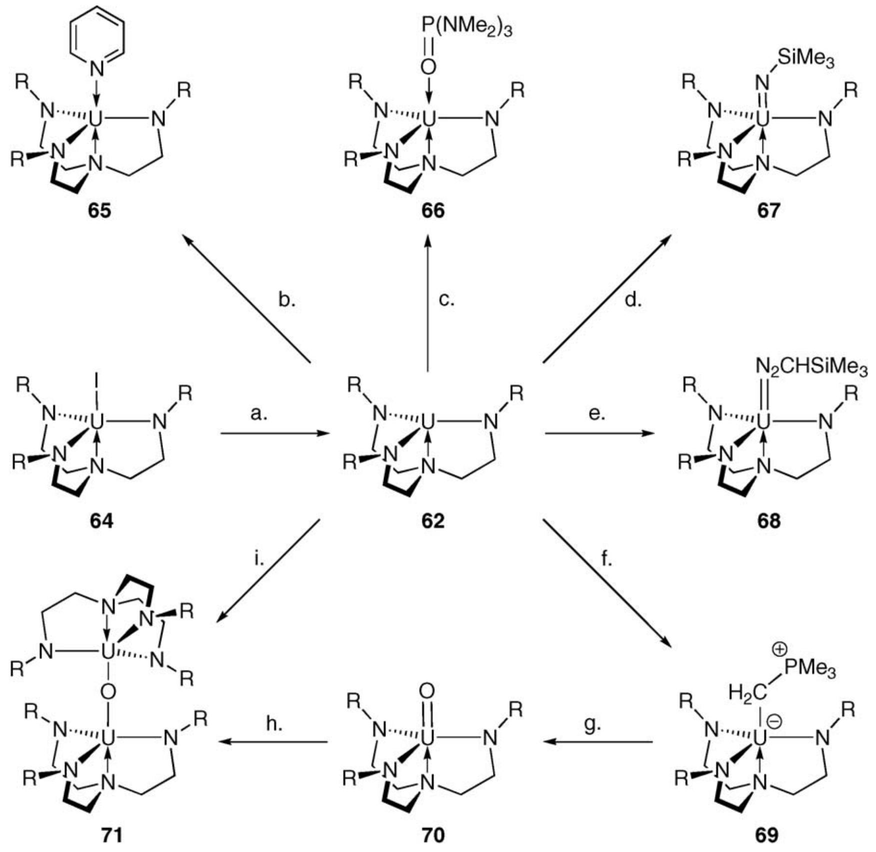


Fig. 20. Single crystal X-ray diffraction structure of $[U(NN'_3)(OH)(CH_2PMe_3)]$, **72** [117]. Most hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▨ = N; ● = U.

Based on this bond length, as well as UV–vis spectral comparisons and magnetic susceptibility measurements, it was concluded that the U(III) centers in **63** did not undergo oxidation upon coordination of N_2 (Scheme 12). It was postulated that the interlocking triamido ligands present in **63** preclude a lengthening of the N–N bond by sterically inhibiting any appreciable reduction in the U–U distance, a necessary step in N–N bond elongation [115].

A more straightforward synthesis of **62** was reported via reduction of **64**, $[U(NN'_3)I]$ [116], to produce the deep purple $U(NN'_3)$ species [117]. While a crystal structure of this complex has remained elusive, it was established as being the trivalent species by ^1H NMR and IR spectroscopy. Reaction with HMPA produced the trivalent uranium species, $[U(NN'_3)\{OP(NMe_2)_3\}]$ (**66**), as established by X-ray crystallography. Addition of trimethylsilylazide to **62** caused an immediate color change, from purple to red, and produced the imido, U(V) species, $[U(NN'_3)(NSiMe_3)]$ (**67**).

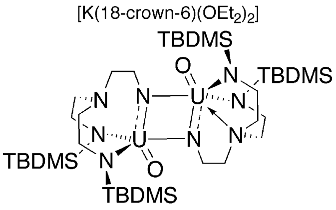
Addition of trimethylsilyldiazomethane to **62** led to the formation of a complex in which the uranium center was coordinated to $N_2CHSiMe_3$ through the terminal nitrogen atom. Unfortunately, attempts at N_2 removal were unsuccessful. Addition of trimethylphosphorane ($H_2C=PMe_3$) to **62** was found to produce the phosphorane adduct **69**. An interesting side product of this reaction was the U(IV) hydroxide species $[U(NN'_3)(OH)(CH_2PMe_3)]$ (**72**, Fig. 20). While a



Scheme 13. Synthesis of complexes **62** and **65**–**71**: (a) K, (b) pyridine, (c) HMPA, (d) trimethylsilylazide, (e) trimethylsilyldiazomethane, (f) methylene trimethylphosphorane, (g) Me_3NO, (h) **61**, and (i) Me_3NO [117].

crystal structure of this complex was obtained, its isolation has not been reproduced. In an attempt to form the alkylidene product from the phosphorane adduct, trimethylamine *N*-oxide was added. What was obtained was the pentavalent complex $U(NN'_3)O$, **70**. Adding an additional equivalent of **62** to this latter product yielded the U(IV) μ-oxo dimer (**71**) (Scheme 13). Unless otherwise noted, these complexes were characterized by elemental analysis, ^1H NMR and UV–vis spectroscopy, and magnetic susceptibility measurements [117].

Duval et al. have utilized bulky triamidoamine ligands with the objective of generating a *cis*-dioxo uranium complex [118]. These workers found that reaction of $[K(18\text{-crown-}6)]_2[UO_2(Cl)_4]$ with $Li_3[N(CH_2CH_2NSi\text{-}t\text{-}BuMe_2)_3]$ in THF resulted in a formally mixed valent U(V)/U(IV) oxo-imido dimer (**73**) (Scheme 14) with an overall negative charge. Abstraction of a silyl group and an oxo group from the starting uranyl complex is necessary for the formation of **73**. Together, the U_2N_2 core forms a rhombus structure with the uranium geometry best described as being capped triganol bipyramid. While not unprecedented, the rarity of only three equatorial ligands in a uranium complex has been noted.



73

Scheme 14. U(V)/U(IV) dimer, **73**.

Transamination of $[U(COT)(N\{SiMe_3\}_2)_2]$ with tetraazadodecane produced a dinuclear complex (**74**, Fig. 21) [119]. This complex was found to have one of the shortest U–U distances known, 3.3057(9) Å, without a formal U–U bond being present.

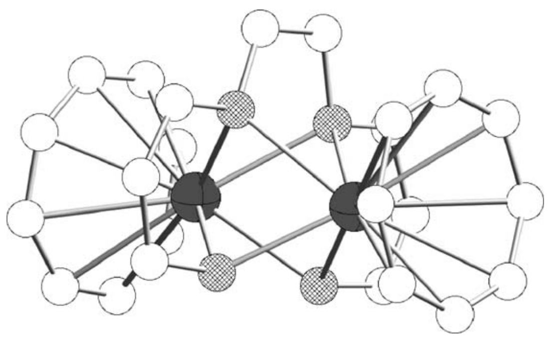


Fig. 21. Single crystal X-ray diffraction structure of **74** [119]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▨ = N; ● = U. .

5. Pyridine-derived ligands

Results detailing the ability of 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines to effect the extraction An(III) over Ln(III) cations [120,121] have led to an increased interest in pyridine-based ligands for actinide coordination. While it the extraction of the minor actinides (e.g., Am(III) and Cm(III)) from the lanthanide-containing mixtures that is of interest in terms of nuclear waste remediation [10], the difficulty of such studies has prompted the study of U(III)–pyridine ligands as surrogates for Am(III). Uranium(III) is much less radioactivie than Am(III) and has the further advantage of being available in readily usable quantities [122–124]. It should be noted, however, that the transplutonium elements have traditionally displayed reactivity features that are more similar to those of the 4f series than does uranium [125]. Thus, the suitablility of U(III) as an analogue for americium in the analysis of covalent interactions remains the subject of debate [126]. Despite these concerns, pyridine-based ligands have been shown to enhance liquid–liquid extractions of uranium and the minor actinides from Ln/An mixtures. The uranium complexes reported recently may also provide insights into the uranium coordination chemistry.

5.1. Bidentate

Berthet et al. have reported two uranyl complexes, $[UO_2(OTf)_2(bpy)_2]$ and a solvate of $[UO_2(phen)_3][OTf]_2$ (phen = 1,10-phenanthroline, Scheme 15) in which the ligands adopt a rhombohedral, as opposed to the typical distored bipyramidal geometry, around the uranyl cation [127,128]. The formation of this unusual geometry was attributed to the use of triflate as the counter anion, in conjunction with an anhydrous organic solvent and $UO_2Cl_2(thf)_3$ as the starting uranyl salt. For the $[UO_2(OTf)_2(bpy)_2]$ and $[UO_2(phen)_3][OTf]_2$ complexes, the maximum deviation of an individual atom from the mean plane of the uranyl cation (typically the equatorial plane) was 0.61 and 0.71 Å, respectively. These values are some of the largest reported for a uranyl complex.

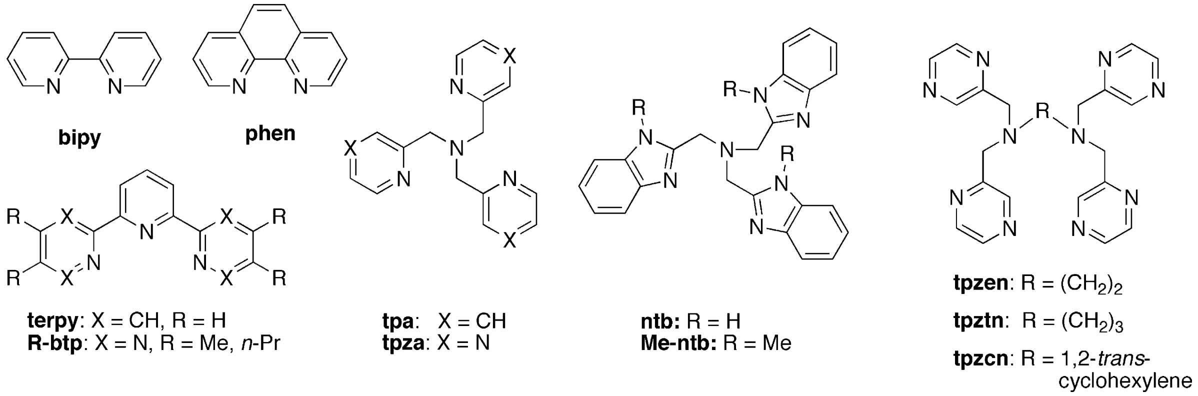
In an effort to understand the bonding character of the 5f cations, Ephritikhine and coworkers [122] studied the trivalent uranium cation within the cadre of studies designed to analyze the binding behavior of An(III) and Ln(III) with respect to bidentate and terdentate pyridine-containing ligands. Initial studies were conducted with 2,2′-bipyridine (bipy) (Scheme 15), a model ligand used to compare the stability constants, as well as enthalpy and entropy energies, in the case of UI_3, NdI_3 and CeI_3. Based on VT-NMR spectroscopic studies performed in anhydrous pyridine it was inferred that 1:1, 1:2 and 1:3 metal:ligand complexes are formed in the case of all three metals investigated, with the 1:2 species dominating at room temperature (as $MI_3(bipy)_2(py)_n$ $n = 1$ for M = Nd and Ce, and $n = 1.5$ when M = U, as inferred from elemental analysis). However, the stability constants were found to be small, with uranium showing only slightly higher binding affinity than the lanthanides. Subsequent investigations, made using conductivity measurements, indicate that the counter ion (I^-) and the solvent (pyridine) have an adverse effect on the interaction between bipy and the studied metals, thereby reducing the stability constants [122].

Charushnikova and Den Auwer have reported the synthesis and crystal structure of a number of molecular adducts formed between uranyl nitrate and terpy and bipy. In all the complexes the U(VI) has a hexagonal bipyramide geometry. The U–N bond lengths are identical whether bipy or terpy are used as the equatorial ligands. The only difference observed between the $UO_2(bipy)^{2+}$ and $UO_2(terpy)^{2+}$ complexes was in the U–O bond lengths between the uranyl metal center and the additional (i.e., non-nitrogen) equatorial ligands, e.g. NO_3^-, OH^-, H_2O, and O_2 [129].

5.2. Tridentate

A mixed-ligand uranyl complex, in which a uranyl cation is coordinated to both 2,2′-methylenediphenolate and 2,6-bis[(dimethylamino)methyl]pyridine, has been reported [130].

Berthet et al. reported crystal structures for 1:1, 1:2 UO_2:terpyridine (terpy) complexes by reaction of $[UO_2(OTf)_2]$ with one or two molar equivalents, as well as an excess, of terpy in acetonitrile, pyridine and a mixture of ethanol and acetonitrile, respectively [127]. It was reported that for the $[UO_2(terpy)_2][OTf]_2$ complex, the uranyl coordination geometry was rhombohedron, rather than the typical distorted bipyrimidal observed with the uranyl cation. While the terpy deviation



Scheme 15. Various pyridine, pyrazine, and 1,2,4-triazine-based ligands.

from the equatorial plane was significant at 0.49 Å (it was stated that typical deviations are no greater than 0.2 Å), the uranyl bipy and phen complexes also reported by Berthet et al. (specifically $[UO_2(OTf)_2(bipy)_2]$ and $[UO_2(phen)_3][OTf]_2$ showed a higher degree of deviation (0.61 and 0.71 Å, respectively).

Terpyridine-functionalized ligands were shown to have higher selectivity for An(III) over Ln(III) than bipy in numerous competition and liquid–liquid extraction studies [120,121]. For this reason, a number of analogues of this ligand have been synthesized and studied.

Binding affinities for the interaction between 2,2′:6′,2″-terpyridine (Scheme 14) and UI_3, CeI_3, or NdI_3 have been reported [124]. The complex $[UI_2(terpy)_2(py)]I$ was produced in quantitative yields from the reaction of two molar equivalents of terpy with $UI_3(py)_4$. Competition studies, involving a 2:1:1 solution of terpy:$UI_3(py)_4$:$CeI_3(py)_4$, revealed a separation factor of three in favor of U(III). To probe further the coordination behavior of the terpy-like ligands, triazine was incorporated into this scaffold in place of pyridine. The resulting systems, 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine (R-btp where R = Me or *n*-Pr) (Scheme 15), were analyzed in competition studies by Iveson et al. [123]. Mixing this ligand in almost any ratio with a uranium(III) salt gave rise to the 1:3, U:R-btp, or tris–R-btp complex almost immediately. A competition experiment, involving the use of a 1:1:1 solution of R-btp (R = Me), UI_3, and CeI_3, produced only the uranium(III) complex. In fact, the Ce(III) complex was evident only after the addition of 3–6 equivalents of R-btp. Based on these findings (supported by ^1H NMR spectrometric titrations), the reported separation factor for U^{III}/Ce^{III} was >20! Of the three pyridine-based ligands presented thus far, (bipy, terpy, and R-btp), R-btp not displayed only the highest affinity for f-block cations, it also showed the highest selectivity for uranium cations.

Due to the perceived poor lability of the MI_3 salts, acetonitrile, believed to aid the dissociation, rather than pyridine was used as solvent in the synthesis of the tris(terpy) complexes [131]. When the triflate salts, ($M(OTf)_3$, M = U, Ce), were used in conjunction with acetonitrile as the solvent, the tris(R-btp) complex was easily formed. Under similar conditions, the tris(terpy) complex formed as a mixture with the bis(terpy) complex. However, with an excess of terpy, the corresponding tris(terpy) (**75**, Fig. 22) complexes were formed. Higher association constants for the formation of both the bis- and tris-(terpy) U(III) complexes relative to the corresponding Nd(III) or Ce(III) species were observed, as determined via ^1H NMR techniques [132].

A comparison of numerous crystal structures provided a rationale for the observed selectivity of terpy and R-btp for U(III) over La, Ce, or Nd (the structures studied were $[M(terpy)_3]I_3\cdot 2MeCN$ (M = La, Ce, Nd, U), $[Ce(n\text{-}Pr\text{-}btp)3]I_3\cdot 3py$, $[U(n\text{-}Pr\text{-}btp)_3]I_3\cdot 4py$, $[La(Me\text{-}btp)_3][OTf]_3\cdot MeCN$, $[Ce(Me\text{-}btp)_3][OTf]_3\cdot MeCN$, and $[Ce(Me\text{-}btp)_3][OTf]_2I\cdot 2py$). In all cases analyzed, the U–N distance was shorter than the Ln–N distance, leading to the suggestion that U–N π back donation plays an important role in the overall bonding process. This structural difference was more pronounced in the case of the R-btp complexes than in those derived from terpy, providing important solid state support for the NMR spectroscopic studies from which a higher binding affinity for the U–R-btp versus U–terpy complexes was inferred [131].

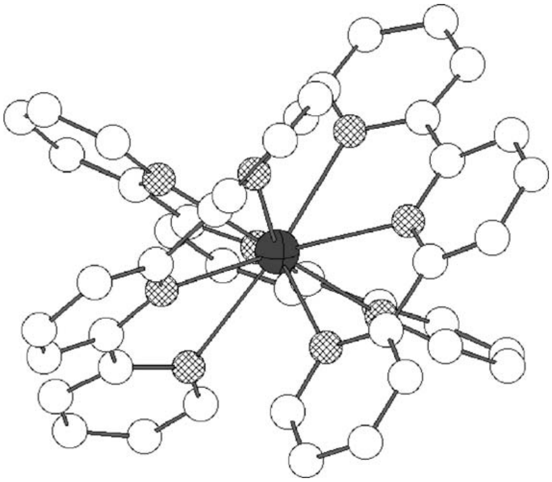


Fig. 22. Single crystal X-ray diffraction structure of uranium tris(terpy) complex, **75** [131]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▩ = N; ● = U. .

Trace amounts of oxygen and water led to the oxidation of the $[UX_2(terpy)_2(py)]X$ (X = I or OTf) complexes to the corresponding U(IV) tri and tetranuclear μ-oxo species. The trinuclear complex, $[\{UI(terpy)_2(\mu\text{-}O)\}_2\{UI_2(terpy)\}]I_4$, **76**, was found to contain two μ-oxo bridges between the three uranium cations. The tetranuclear complex, $[\{U(OTf)(terpy)_2(\mu\text{-}O)(\mu\text{-}OTf)U(terpy)\}_2(\mu\text{-}OTf)_2(\mu\text{-}O)][OTf]_4\text{-}py\text{-}MeCN$, **77**, was again found to contain μ-oxo bridges between the uranium centers, but also included bridging triflate ligands between each uranium. The most striking feature of these two complexes (Figs. 23 and 24) is the linear arrangement of the cations, with uranium–oxygen–uranium angles ranging from 158 to 173° [132].

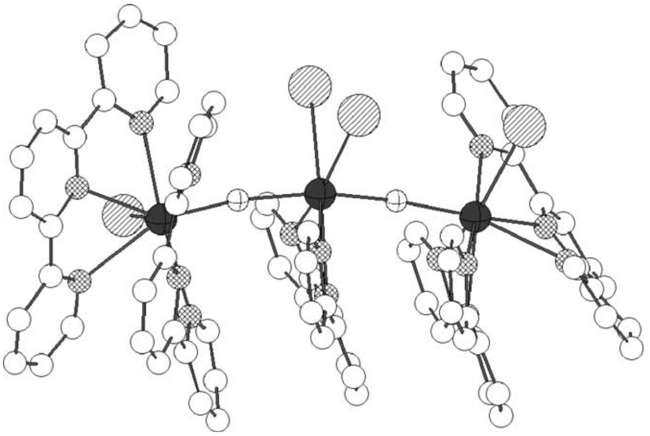


Fig. 23. Single crystal X-ray diffraction structure of **76** [132]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▩ = N; ⊕ = O; ● = U; ▨ = I. .

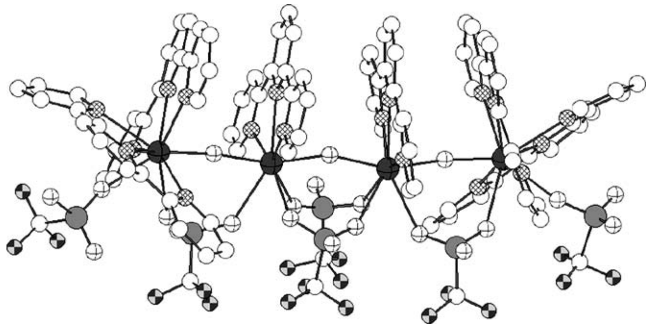


Fig. 24. Single crystal X-ray diffraction structure of **77** [132]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▨ = N; ⊕ = O; ● = U; ◐ = F; ● = S.

5.3. *Tetradentate*

Mazzanti et al. have used tripodal N-donor ligands to bind various An(III) cations selectively relative to the Ln(III) cations [8,133]. In doing so, they sought to determine concurrently the percentage of covalent character in typical An–N bonds. For the tripodal ligand, tris(benzimidazol-2-ylmethyl)amine (ntb) (Scheme 15), mono- and bis-complexes were obtained from reaction with $[UI_3(thf)_4]$ or $LaI_3(py)_4$ in pyridine [8]. The authors concluded, based on NMR spectroscopic studies, that the $[M(ntb)_2]I_3$ (M = U, La) complexes are formed after addition of only 0.5 equivalents of ntb. When the ligand tris[(2-pyridyl)methyl]amine (tpa) (Scheme 15) was used, the complex, $[M(tpa)I_3(py)]$ (M = La, U) was formed with evidence of the bis–tpa complex appearing only after the addition of more than one equivalent of tpa. Reaction of $UI_3(thf)_4$ with tpa in acetonitrile produced the complex $[U(tpa)_2]I_3{\cdot}3CH_3CN$ cleanly. Based on X-ray diffraction analysis it was concluded that the uranium is eight coordinates and in a distorted cube geometry with the two tpa ligands adopting a right-handed helical arrangement, thus creating a chiral species [134]. On the other hand, based on X-ray diffraction analysis of the mono-tpa complexes, $[M(tpa)I_3(py)]$ (M = U, La), it was inferred that the metal center is an eight coordinate in a highly distorted dodecahedron environment. While a comparison of the U and La mono-tpa complexes revealed that one pyridyl group had a shorter than expected U–N distance, suggesting a covalent interaction between tpa and U(III), generally, only minimal differences in the M–N length between La and U for the ligand (tpa) were observed [8].

In analogy to the U–terpy complex, the U–tpa complex was found to be reactive towards oxidation and hydrolysis [134]. For instance, reaction of $[U(tpa)_2]I_3$ with trace amounts of H_2O/O_2 in acetonitrile led to the formation of the corresponding U(IV) hydroxo complex, $[U(tpa)_2(OH)_2]I_2{\cdot}3CH_3CN$ (**78**, Fig. 25). In this complex, the metal is 10-coordinate with the iodide anions not being formally coordinated, making this complex the first crystallographically characterized uranium(IV) species to contain terminal hydroxides as the only anionic ligands.

Attempts at forming this complex by reacting the starting U(III) species with oxygen-free water in acetonitrile produced the trinuclear complex, $\{[U(tpa)(\mu\text{-}O)I]_3(\mu_3\text{-}I)\}{\cdot}3CH_3CN$ (**79**, Fig. 26). Intriguing aspects of this structure include the six-membered ring created by the uranium cations and the 3 μ-oxo atoms, as well as the bridging iodide atom which coordinates all three uranium centers. The mono- and bis-methoxo U(IV) complexes, $[U(tpa)I_3(OMe)]$ and $[U(tpa)I_2(OMe)_2]$, were isolated when various amounts of methanol were added to an acetonitrile solution containing tpa and $UI_3(thf)_4$. It was postulated that oxidation of the uranium cation is facilitated through formation of methoxide anion and subsequent coordination to the uranium center [134].

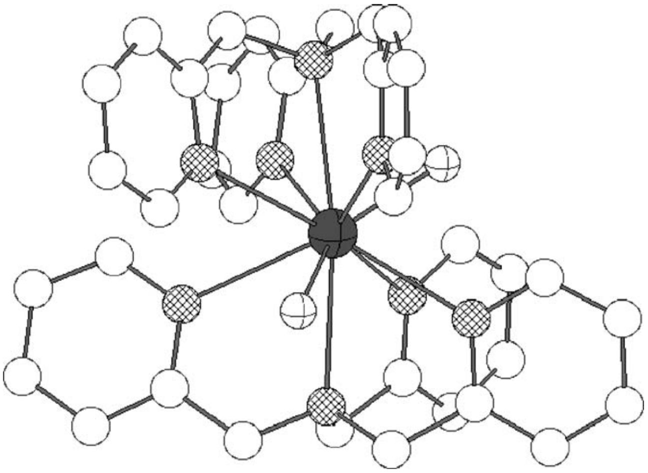


Fig. 25. Single crystal X-ray diffraction structure of **78** [134]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▨ = N; ⊕ = O; ● = U.

A comparison of the previously reported results leads to the suggestion that for the pyridine-based ligands, terpy, tpa, btp, and ntb, less basic nitrogen atoms increase the separation in favor of An(III) in liquid–liquid An(III)/Ln(III) extractions. With this trend in mind, the tripodal ligand tris[(2-pyrazinyl)methyl]amine (tpza) (Scheme 15), which had been previously shown to extract Am(III) more strongly than Eu(III)

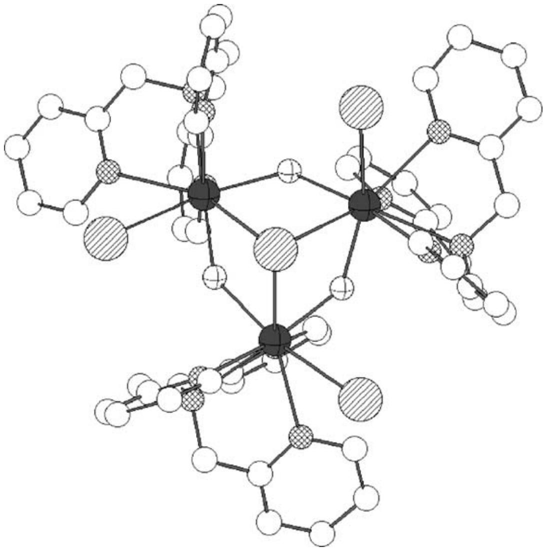


Fig. 26. Single crystal X-ray diffraction structure of **79** [134]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▨ = N; ⊕ = O; ● = U; ▧ = I.

[135], was investigated further [133]. The softer character of the tpza ligand is believed to lead to stronger, and possibly more covalent, interactions with the actinides. Unlike tpa, it was found that tpza only formed 1:1 complexes with U(III) or La(III), i.e. [M(tpza)I_3(MeCN)] (M = La and U), leading the authors to suggest that it binds these cations less strongly than tpa, most likely due to its lower σ-donor ability [133]. An NMR spectroscopic competition study performed in THF, involving the use of a 1:1:1 ratio of $LaI_3(thf)_4$, $UI_3(thf)_4$ and tpza, was thus undertaken. The ratio of formation constants ($K_{U(tpza)}/K_{La(tpza)}$) of [M(tpza)I_3] (M = U, La) was found to be 3.3 ± 0.5 in favor of the uranium complex. It is important to note that when the solvent was changed to pyridine, the difference between the two formation constants ($K_{U(tpza)}$ and $K_{La(tpza)}$) was negligible. X-ray diffraction quality single crystals for both metals were obtained as acetonitrile and THF adducts. On average, in the acetonitrile complexes comparable $M{-}N_{py}$ distances were found, with the largest difference occurring in the $M{-}N_{MeCN}$ bond; the $U{-}N_{MeCN}$ distance was found to be 2.610(10) Å while the $La{-}N_{MeCN}$ distance was found to be 2.662(4) Å. In addition, the length of the N≡C acetonitrile bond was found to be increased in the uranium complex (it normally shortens upon coordination). In the case of the THF complexes, shortened $M{-}N_{py}$ bonds were generally found for the uranium complex relative to the corresponding lanthanum species (the average decrease is 0.046 Å shorter), an observation that led the authors to conclude that the uranium cation is held more tightly than the La cation. It was also suggested that acetonitrile, which can act as a π-acceptor ligand, competes with the tpza for electron back donation from the U(III) center. THF, on the other hand, is a σ-donor and no such competition occurs, allowing for back donation from the U cation to the ligand, which, in turn, leads to shorter $U{-}N_{py}$ distances. DFT calculations produced similar results, namely a decrease in the $M{-}N_{py}$ distance upon passing from La to U, as well as an increase in the C–N distance for the U–acetonitrile complex. These theoretical results were believed to support the idea of back donation from the trivalent uranium cation to the coordinating ligand. This complements previous studies that have provided support for the notion that U(III) is able to act as a π-donor in the presence of strong π-acceptors [136].

5.4. *Hexadentate*

With the knowledge that the softer nitrogen donors present in pyrazinyl-containing ligands, as compared to pyridine-based ligands, increase U(III) versus Ln(III) selectivity, Karmazin et al. synthesized tetrapodal ligands to investigate the influence of flexibility on selectivity [137,138]. In particular, three new neutral N-donor ligands were synthesized, namely *N*,*N*,*N*,*N*-tetrakis(2-pyrazinylmethyl)ethylenediamine (tpzen), *N*,*N*,*N*,*N*-tetrakis(2-pyrazinylmethyl)-*trans*-1,2-cyclohexanediamine (tpzcn) and *N*,*N*,*N*,*N*-tetrakis(2-pyrazinylmethyl)trimethylenediamine (tpztn) (Scheme 15). Based on extraction studies involving Eu(III) and Am(III), it was concluded that, in the series, tpzen, tpzcn, and tpztn, only the ligand tpzen had a higher separation factor than the more rigid tpza [137]. An analysis of the crystal structures of [M(tpztn)I_2]I·xCH_3CN and [M(tpzcn)I_2]I·xCH_3CN (M = La, Ce, Nd and U), as well as that of [Lu(tpztn)(CH_3CN)2]I_3·CH_3CN, led to the conclusion, that in spite of the lack of observed Ln(III)/An(III) selectivity, the metal–ligand interactions in the case of tpztn and tpzcn were similar to those for tpza [138]. The reduction in the U(III)–N_{pz} distance seen with tpztn (0.042 Å shorter than the average $La{-}N_{pz}$ distance) was similar to what was seen in the case of the tpza ligand, suggesting a similar metal to nitrogen interaction in the case of both complexes. Such inferences were also drawn in the case of the tpzcn complexes; in fact, for [M(tpzcn)I_2]I, the difference between the average $U{-}N_{pz}$ and $La{-}N_{pz}$ distances is 0.054 Å — the largest observed out of the three complexes.

It is important to note that on passing from La to Ce and from La to Nd, the average metal–N distances decrease in accord with what one would expect for a reduction in ionic radius. However, the average U–N distance is significantly *shorter* that what would be expected for a purely ionic interaction. The complexes [M(tpzcn)I_2]I·xCH_3CN were found to adopt a double helical conformation in the solid state, as revealed by single crystal X-ray diffraction analysis, as well as in solution, as inferred from ^1H NMR spectroscopic analyses. Analysis of the Lu(tpztn) and Nd(tpztn) complexes by ^1H NMR spectroscopy also led to the conclusion that two C_2-symmetric double helical enantiomers are present in solution.

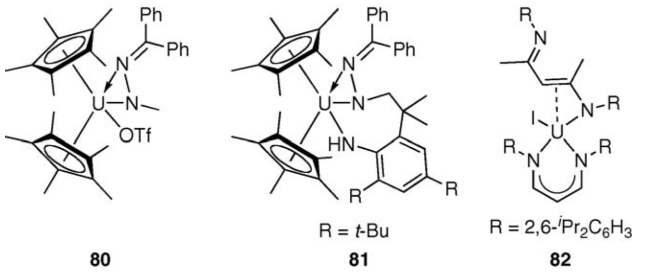
While further studies are clearly in order, the results presented above, when considered in concert, allow for a near-unique comparison of 4f and 5f isostructural nitrogen-containing complexes. They thus set the stage for future studies involving these and other kinds of ligand systems, including those involving other donor atoms.

5.5. *Macrocyclic*

Recently, the uranyl templated synthesis of a number of macrocycles derived from 2,6-diformyl- and 2,6-diacetylpyridine and various di-, tri-, and tetra-amines were reported by Mostafa and Aicha [139]. Due to low solubility, the complexes were generally characterized by IR, elemental analysis, thermal studies, and magnetic and electronic spectroscopy. The IR results (bands at ∼1600, 610, and 430 cm^{-1}, as well as at 3446–3420 cm^{-1}) led the authors to conclude that the UO_2^{2+} center is coordinated via the pyridyl nitrogen, and that either H_2O, EtOH, or hydroxo bridges are present in the complex. In short, two to three uranyl cations are believed to be coordinated to these macrocycles, with the Schiff-base nitrogens or pyridyl nitrogens merely donating electron density to the cations. It is believed the uranyl cations form covalent (ionic) bonds with the hydroxo oxygen atoms or acetate anions as necessary to complete their coordination sphere [139]. Unfortunately, the lack of structural data limits the pedagogical utility of this work.

5.6. *Pyrazine-derived*

The concept of π-back bonding between uranium centers and nitrogen-containing ligands represents one of the central



Scheme 16. Hydrazonato and diketiminato uranium complexes.

themes guiding currently ligand design. It has been argued that significant electron donation from the uranium center may lead to metal oxidation [140]. Consistent with such a hypothesis, it was reported that coordination of pyrazine to a solution of $[U(C_5H_4R)_3]$ (R = *t*-Bu, $SiMe_3$) resulted in the formation of a dimeric species wherein one pyrazine was coordinated to two uranium centers. An unusually short average U–N distance (2.322 Å) was observed and was considered by the authors as being more reminiscent of a U(IV) center than one involving a pure U(III) cation. This 'oxidation' was rationalized in terms of significant π-back donation. Reductive elimination occurred with the addition of a coordinating solvent, such as THF or pyridine. The authors noted, however, that oxidation of other actinide cations, such as Am(III) or Cm(III), is more difficult and was not expected to be observed under similar conditions.

Berthet and coworkers have recently reported a number of monodentate, pyridine-derived complexes with U(III) and Ce(III) [141]. In a typical reaction, the tris(cyclopentadienyl)-derivative $[M(C_5H_4R)_3]$ (M = Ce, U; R = ^tBu, $SiMe_3$) was reacted with and excess of the ligand to form $[M(C_5H_4R)_3L]$ (L = pyridazine, pyrimidine, pyrazine, 3,5-dimethylpyrazine, *s*-triazine, pyridine, 2-picoline, 3,5-lutidine, and 3-chloropyridine). While these are monodentate complexes and hence will not be discussed in detail, it is worth noting that the complexes all displayed a shorter U–N bond length versus the Ce–N bond length, in agreement with expectations.

6. Other miscellaneous ligands

6.1. Hydrazonato and diketiminato complexes

While investigating the reactivity of a new organometallic U(IV) complex, $[(C_5Me_5)_2U(CH_3)(OTf)]_2$ (**80**), Kiplinger et al. discovered an unprecedented hydrazonato actinide complex [142]. The peculiar structural features of complex **80**, in which an alkyl fragment, as well as a triflate ligand, are coordinated to the same metal center, is of particular interest since it provides a new entry into U(IV) chemistry. To test the reactivity of **80**, it was treated with dipheynldiazomethane; this yielded the unprecedented U(IV) hydrazonato complex, $(C_5Me_5)_2U(\eta^2(N,N')\text{-}CH_3NN{\equiv}CPh_2)$ (OTf) (**81**) [142]. A similar complex, in which the triflate was exchanged for a chloride, was obtained upon treatment of $(C_5Me_5)_2U(Me)Cl$ with the same diphenyldiazomethane reagent (Scheme 16). In related work, Kiplinger et al., reported the synthesis of a U(V) bis(amide) complex, **82**, formed via a cyclometallation reaction that was believed to occur during mild thermolysis of $(C_5Me_5)_2U(=N\text{–}2,4,6\text{-}tBu_3C_6H_2)(\text{–}N\text{–}N{=}CPh_2)$ [143].

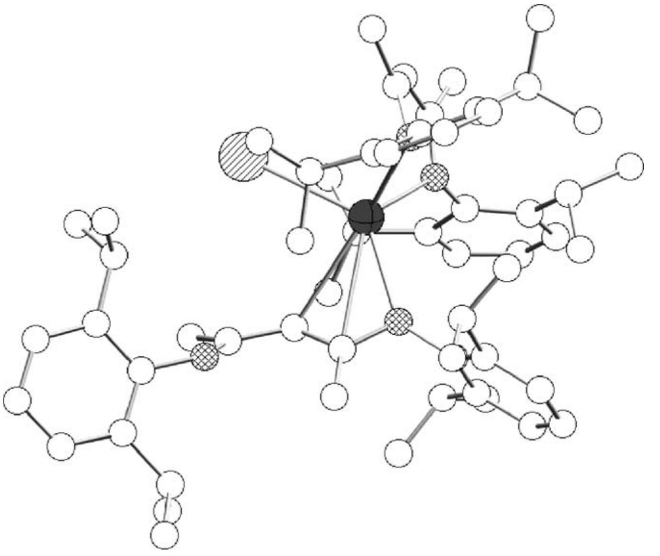
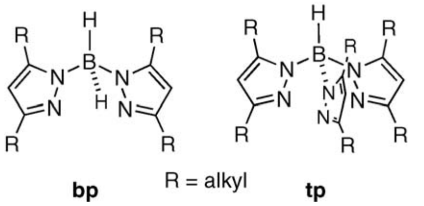


Fig. 27. Single crystal X-ray diffraction structure of bis(β-diketimidato)uranium(III) iodide complex, **83** [145]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▩ = N; ● = U; ▨ = I.

β-Diketiminato ligands have been utilized as ancillary ligands for main group elements, transitional metals, and lanthanides in organometallic non-aqueous chemistry [144]. Kiplinger and coworkers have explored their use in actinide chemistry. In particular, these researchers reported a novel bis(β-diketimidato)uranium(III) iodide complex, **83** (Fig. 27), that displays an uncommon η^3-(*N*,*C*,*C*′)-1-azaallyl bonding mode for the nacnac (nacnac$^-$ = [Ar]NC(Me)CHC(Me)N[Ar]) ligand. The complex was obtained in moderate yields by reaction of $UI_3(thf)_4$ with K(nacnac) at ambient temperature. The authors explain the interesting η^3-(*N*,*C*,*C*′) coordination of the diketiminato ligand to the U center by invoking what are believed to be unfavorable steric interactions at the metal center. They also explain their results in terms of specific electronic factors [145,146].

6.2. Scorpionate complexes

Scorpionate ligands have been used as flexible and versatile polydentate ligands for the coordination of a wide variety of metal ions [147]. Dihydrobis(pyrazoyl)borates (bp) and hydrotris(pyrazoyl)borates (tp) (Scheme 17) have been investigated in reaction with $[UI_3(thf)_4]$ [148–152].



Scheme 17. Dihydrobis(pyrazoyl)borate (bp) and hydrotris(pyrazoyl)borate (tp) ligands.

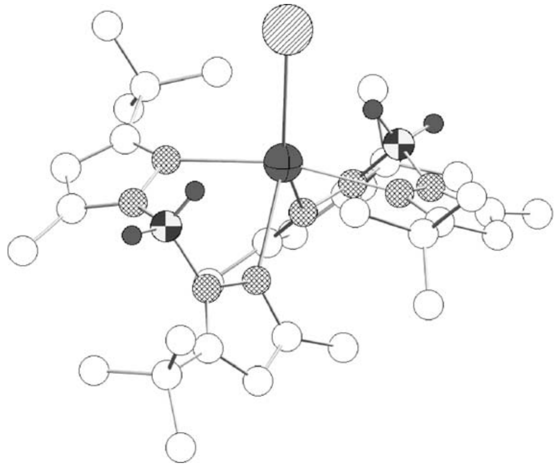


Fig. 28. Single crystal X-ray diffraction structure of **84** [149]. Most hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▨ = N; ● = U; ▨ = I; ◐ = B; ● = H. .

The nature of the complexes formed depends largely on the bulkiness of the substituent on the three position of the pyrrazole ring. The homoleptic complex $[\mathrm{U}\{\kappa^3\text{-bp}^{\mathrm{iPr2}}\}_3]$ was formed from the overnight reaction at room temperature of dihydrobis(3,5-diisopropylpyrazoyl)borate with $[\mathrm{UI}_3(\mathrm{thf})_4]$. The nine-coordinate U(III) center seen in this complex is stabilized by six nitrogen atoms from the pyrazoyl moieties, as well as by three bridging B–H···U three center bonds. The net result is a tricapped trigonal prismatic geometry [150].

Subsequent studies of the dihydrobis(pyrazoyl)borates as ligands for trivalent actinides have led to the isolation of the first bis-asymmetric heteroscorpionate U(III) complexes. In particular, reaction of $[\mathrm{UI}_3(\mathrm{thf})_4]$ with two equivalents of bis(*t*-Bu,Me)bp in toluene, was found to give rise to $[\mathrm{U}\{\kappa^3\text{-H}(\mu\text{-H})\mathrm{B}(\mathrm{pz}^{t\mathrm{Bu,Me}})(\mathrm{pz}^{\mathrm{Me},t\mathrm{Bu}})\}_2\mathrm{I}]$ (**84**, Fig. 28), a complex whose formation was postulated to result from an unprecedented isomerization at an f-element center. Although a serendipitous result, this finding is important because it helps provide a better understanding of the steric and electronic demands of the U(III) center towards bp ligands. It also helped inspire the synthesis of another asymmetric complex, namely $[\mathrm{U}\{\kappa^3\text{-H}(\mu\text{-H})\mathrm{B}(\mathrm{pz}^{t\mathrm{Bu,Me}})(\mathrm{pz}^{\mathrm{Me2}})\}_2\mathrm{I}]$ [149].

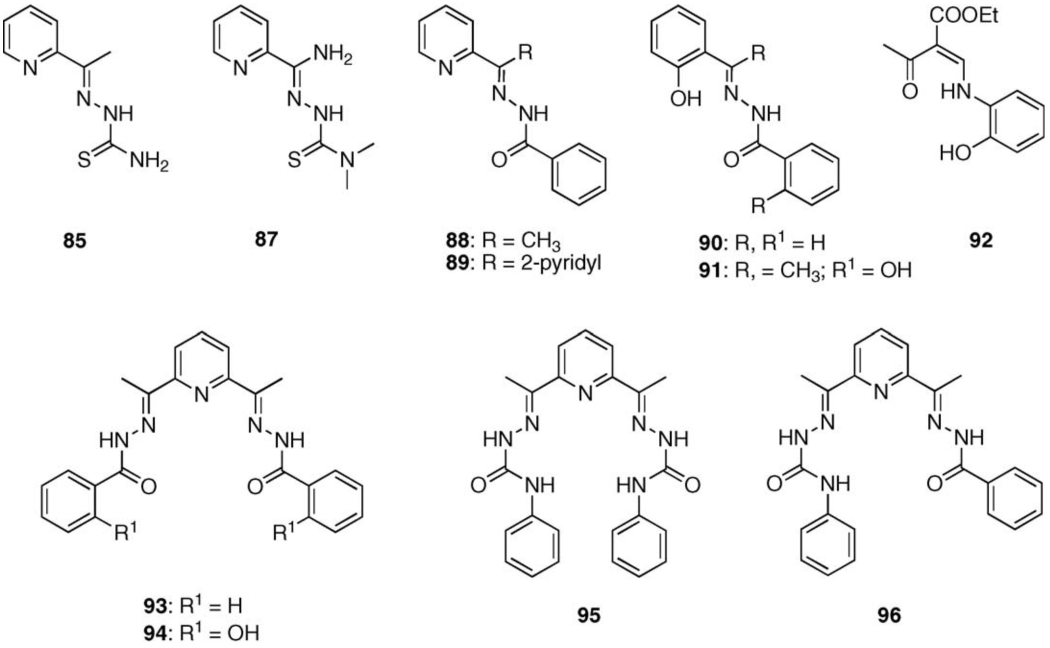
Initial results revealed that the use of tp ligands led to the formation of unstable 1:1 U:scorpionate complexes, such as $[\mathrm{UI}_2\{\kappa^3\text{-tp}^{i\mathrm{Pr2}}\}(\mathrm{thf})_x]$ [151]. However, when neutral co-ligands were present during the synthesis, complexes of the general formula $[\mathrm{UI}_2\{\kappa^3\text{-tp}^{i\mathrm{Pr2}}\}(\mathrm{ligand})_x]$ could be isolated as stable species. As neutral co-ligands, bipy, triphenyphosphine oxide, pyridine, and pyrazole could all be employed [148].

Trofimenko and coworkers have shown that the reaction between UCl_4 and a thalium salt of $\mathrm{tp}^{\mathrm{Ms}}$ produced a stable $\mathrm{UCl}_3\mathrm{tp}^{\mathrm{Ms*}}$ complex ($\mathrm{tp}^{\mathrm{Ms*}} = [\mathrm{HB(3\text{-}Mspz)_2(5\text{-}Mspz)}]^-$) formed via isomerization of the $\mathrm{tp}^{\mathrm{Ms}}$ ligand. Although $\mathrm{UCl}_3\mathrm{tp}^{\mathrm{Ms}}$ crystals were obtained, presumably fortuitously, no reproducible synthetic pathway to this complex was ever achieved [153].

Other examples of stable U(tp) scorpionate complexes were reported by Marques and coworkers. In this study, $[\mathrm{UI}(\mathrm{tp}^{\mathrm{Me2}})_2]$ was reacted with a stoichiometric amount of $\mathrm{KN(C_6H_5)_2}$ or $\mathrm{KN(SiMe_3)_2}$ to yield the corresponding complexes, $[\mathrm{U}(\mathrm{tp}^{\mathrm{Me2}})_2\{\mathrm{N(C_6H_5)_2}\}]$ and $[\mathrm{U}(\mathrm{tp}^{\mathrm{Me2}})_2\{\mathrm{N(SiMe_3)_2}\}]$. Attempted synthesis of the Sm or Nd analogues proved unsuccessful. The authors concluded that the starting material, $[\mathrm{UI}(\mathrm{tp}^{\mathrm{Me2}})_2]$, provides a new convenient entry into U(III) scorpionate chemistry [154].

6.3. Carbazone-derived complexes

Abram and et al. have undertaken a systematic study of the coordination chemistry of the uranyl cation with carbanzonato



85

87

88: R = CH_3
89: R = 2-pyridyl

90: R, R^1 = H
91: R, = CH_3; R^1 = OH

92

93: R^1 = H
94: R^1 = OH

95

96

Scheme 18. Carbazone-derived ligands.

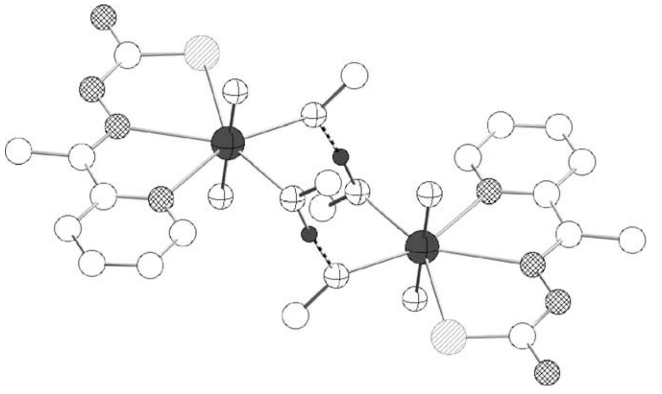


Fig. 29. Single crystal X-ray diffraction structure of UO_2(APTSC)(MeOH)(MeO) dimer, **86** [155]. Most hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▩ = N; ⊕ = O; ● = U; ▨ = S; ● = H.
.

and similar ligands (cf. Scheme 18 for ligand structures). It was found that reaction of $UO_2(NO_3)_2$ or $[NBu_4]_2[UO_2Cl_4]$ with multi-donor ligands resulted in the formation of a number of different complexes, ranging from mono- to tri-nuclear species. First, reaction of the uranyl nitrate salt with a thiosemicarbazone, HAPTSC (**85**), in methanol produced a complex, but only after the addition of Et_3N [155]. The resulting dimeric complex, UO_2(APTSC)(MeOH)(MeO), **86**, has the two subunits joined via hydrogen bonding interactions involving the methanolic ligands (Fig. 29). Reaction of either uranyl nitrate or uranyl chloride as the metal source with a similar ligand **87**, synthesized from 2-pyridineformamide and 2-dimethylthiosemicarbazone, led to different complexes, depending only on the solvent used [156]. Addition of a slightly different ligand, **88**, to either uranyl salt in methanol resulted in the formation of $[UO_2($**88**$)(MeOH)(MeO)]_2$, in analogy to what was seen in the case of **87**. However, reaction of the same reagents in acetonitrile produced a dimeric, hydroxo-bridged $[UO_2($**88**$)(\mu\text{-}OH)]_2$.

Ligand substitution reactions, involving the use of either **88** or **89**, produced more stable 1:2 metal-to-ligand complexes, wherein the metal centers were eight-coordinate [157]. Substitution of pyridine for a 2-phenolyl group, as in **90**, and using $UO_2(NO_3)_2$ as the starting material, resulted in the formation of a 1:3 metal:ligand complex, $[UO_2(HL_5)(H_2L_5)_2](NO_3)$, in which only one of the ligands was deprotonated. The synthetic addition of another hydroxyl group on the phenyl moiety, i.e. via the use of ligand **91**, led to the formation of an anionic dimeric complex. A trinuclear complex was formed upon addition of **92** to a uranium salt. This complex contained a μ_3-oxo ligand that coordinated all three uranium cations [158].

Ligands **93** and **94** were also studied. These species were found to support the formation of 1:1 uranyl complexes [157]. It is important to note, however, that in forming such complexes, the hydroxyl groups of **94** remains protonated and does not participate in the coordination of the uranyl cation, as established by NMR spectroscopic and X-ray diffraction analyses. Both seven-coordinate uranyl complexes easily add an additional solvent molecule, DMSO or pyridine, to form the corresponding eight-coordinate complex. Similar reactivity was observed with ligands **95** and **96**; however, the additional solvent molecules did not coordinate as easily [159]. The iminic nitrogens of the three complexes derived from ligands **93–96** were found to be deprotonated, and it was postulated that typical amide delocalization occurred.

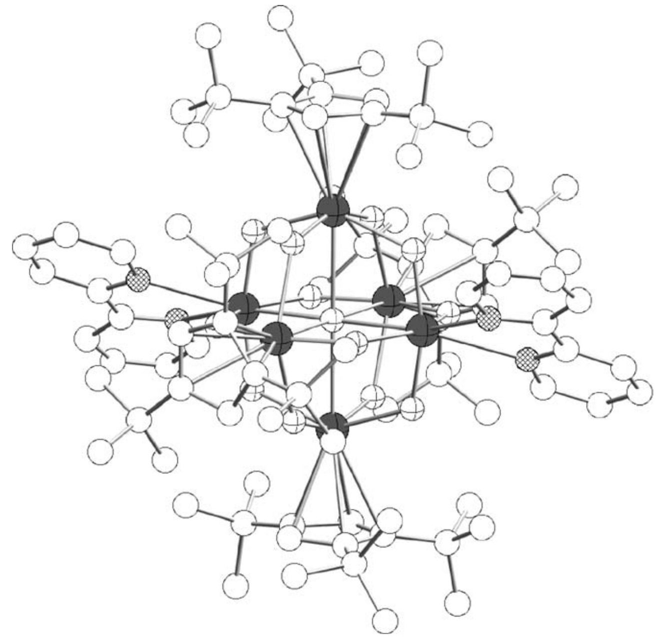


Fig. 30. Single crystal X-ray diffraction structure of the uranyl hexanuclear cluster compound, **97**, of Duval et al. [66]. All hydrogen atoms have been removed for clarity. Atom labels are as follows: ○ = C; ▩ = N; ⊕ = O; ● = U. .

6.4. Uranium clusters

In 2001, Duval et al. [66] reported the isolation of a uranium cluster with significant μ-oxo bridging. In an attempt to produce the uranium dioxo-species, an organometallic starting material, $[Cp^*UCl_2]$ ($Cp^* = 1,2,4\text{-}t\text{Bu}_3C_5H_2$), was reduced with KC_8 in THF followed by addition of two equivalents of pyridine *N*-oxide. What resulted was a cluster complex, **97**, wherein μ-oxo bridging interactions dominate (Fig. 30). This complex is also characterized by the presence of two terminal bipyridine units, which act as 'trapping ligands' on the two 'axial' uranium cations of the central octahedral U_6O_{13} core.

Another polynuclear uranium species was reported in 2002 by Moisan et al. [160]. These researchers found that adventitious traces of oxygen, presumably entering the reaction flask as the result of prolonged heating of a 1:1 mixture of octamethyl-5,5-di(2-pyridyl)ferrocene with UCl_4 in CH_2Cl_2, led to the formation of a U_8 cluster, $H_2[Fe(cp^*py)_2][U_8Cl_{24}O_4(cp^*py)_2]$ (cp^*py = tetramethyl-5-(2-pyridyl)cyclopentadiene). This U_8 cluster was put forward as being the highest order 'non-uranyl' uranium assembly reported to date.

7. Conclusions

The range of uranium complexes discussed in this review highlight not only the utility of multidentate nitrogen-donor ligands, but also the versatility of the uranium cation in its various oxidation states. The advent of nuclear materials provided an important early incentive to study the chemistry of uranium in aqueous environments [92,161]. By contrast, uranium chemistry in non-aqueous solvents has traditionally received little attention. In spite of the recent growth in reports dealing with U(III) complex formation and reactivity, it is clear that our understanding of low valent uranium chemistry remains far from fully developed. Further work in this area is thus to be encouraged.

As compared to the low valent uranium cations, the uranyl cation, $UO_2{}^{2+}$, is relatively well studied. However, again, most work involving this cation has focused on its behavior in aqueous solutions. As detailed in this review, efforts to make rationally designed, free-standing uranyl complexes have increased significantly in recent years.

While it has not proved possible in this review to cover the actinide-related chemistry of all nitrogen-containing ligands, efforts were made to discuss in considerable detail neutral and anionic ligands of varying base-strengths, rigidity, and donor atom number. Taken in concert, these ligands permit the stabilization of uranium complexes in four different oxidation states (i.e., (III), (IV), (V), and (VI)) and are thus likely to constitute essential tools as the coordination chemistry of uranium continues to develop.

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