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Coordination Chemistry with f-Element Complexes for an Improved Understanding of Factors That Contribute to Extraction Selectivity[†]

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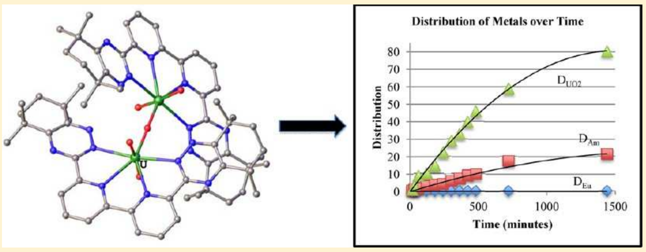
ABSTRACT: Here, we highlight some recent accomplishments in *f*-element coordination chemistry aimed at probing the fundamental chemical differences between the 4*f* elements, lanthanides, and the 5*f* elements, actinides. The studies of particular interest are those that target improving our knowledge of fundamental chemistry to aid in increased selectivity for extractions of actinides. Two components key to understanding the challenges of actinide separations are detailed here, namely, previously described separation methods and recent investigations into the fundamental coordination chemistry of actinides. Both are aimed at probing the critical features necessary for improved selectivity of separations. This is considered a critical goal in the safe remediation of contaminated sites and reprocessing of nuclear fuel sources used in either civilian and noncivilian energy production.



INTRODUCTION

The availability of adequate energy at a reasonable price is considered a requirement of modern society.[1−4] Rising energy costs and dependence on oil for energy will also limit manufacturing capabilities because petroleum products are also highly sought after as chemical feedstocks.[5,6] Some experts predict that the maximum allowable oil production using current methods will occur in the next 5−25 years, and, consequently, the need to have readily available alternatives is growing.[3] In the United States, at the end of 2010, 83% of energy used was from fossil fuels, while 8.4% was from nuclear power and 8% from renewable energy sources.[4] Roughly 13−14% of the world domestic electricity production is from nuclear sources, and nuclear power is the dominant source of electrical power for most of Europe.[7] Along with wind and solar power, nuclear energy is an attractive alternative energy source because it can generate significant amounts of energy with low atmospheric emissions;[8] however, the use of actinides in both military applications and nuclear fuels has resulted in a plethora of waste and contamination issues.[9−13] Critical issues including stockpile stewardship, long-term nuclear waste storage, and remediation remain.[3,4,14]

New technologies will be required to support the next generation of nuclear power production;[1,2,11,13,15] however, reprocessing of nuclear fuel wastes is made more difficult because of gaps remaining in our fundamental understanding of actinide chemistry and f-element chemistry. A recent resurgence of interest in the chemistry of actinides (in particular uranium, neptunium, and plutonium) has been inspired by a need to address these environmental concerns, to develop new separation technologies, and to continue to develop our fundamental understanding of the chemical behavior of actinides.[16−31]

BACKGROUND

In a typical light water reactor (LWR), the operational life span of a fuel rod is only about 3 years,[32] and only 5% of the energy content of the nuclear fuel rod is used.[1,11] Two reasons often cited for considering reprocessing are (1) to increase the available energy from fissile and fertile atoms and (2) to reduce hazards and costs for handling the high-level wastes from the resultant fission products (FPs).[33] Although recycling this remaining 95% of fissile material seems attractive from an efficiency standpoint, the generation and isolation of weapons-grade plutonium (^{239}Pu) and potential security risks that might lead to proliferation of nuclear weapons led to cessation of this technology in the United States during the Cold War.[3,34] Nations that use nuclear power technology to reprocess their spent fuel and recycle remaining fissile fractions have been able to develop a fuel cycle process that can provide up to 96% more energy than a once-through cycle process using the same initial amount of enriched uranium fuel.[8,11]

A key problem with the separation of spent nuclear fuel (SNF) is separation of trivalent actinides from the lanthanides produced as FPs. This is difficult because of their similar oxidation states, chemical properties, and ionic radii.[35−40] The problem of selective extraction of actinides has been an actively pursued area of research for over 60 years, with the first separation of uranium and plutonium done by the chemists during the Manhattan Project in the 1940s.[40−44] In the first separations described, the stability of UO_2^{2+} as well as the redox lability of plutonium (3+, 4+, and 6+ oxidation states) was

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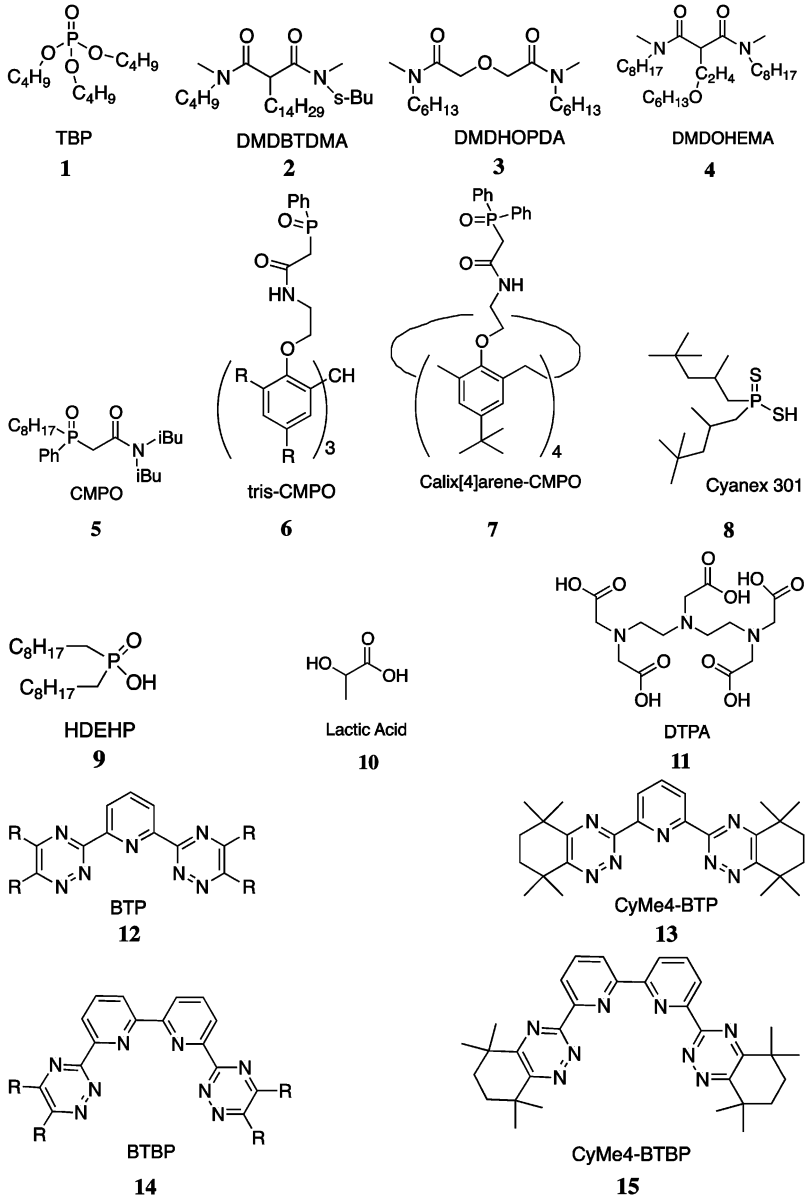
Table 1



exploited.[33,45] In these earliest processes, only plutonium was isolated by precipitating it in the reduced state as PuF_3 or PuF_4 along with all of the other FP-insoluble fluorides.[33,46] In order to get relatively pure plutonium, this precipitation process had to be repeated several times.[11]

Most industrially effective actinide–lanthanide separation methods are based on liquid–liquid extractions that take advantage of the difference in the chemistry of the lanthanides compared to the actinides, in particular, the stronger interactions of actinides with soft donor atoms such as chloride, nitrogen, phosphorus, or sulfur.[47] The formation of metallopolymers or precipitates can occur when organic ligands are used in the separation process. These problems can be overcome by optimizing the extraction conditions and performing the extraction from aqueous media containing small concentrations of actinides and other metals. While these methods can be highly effective in strongly acidic conditions, the ligand stability and, hence, extraction efficiency can be highly dependent upon the pH.[43] Other factors that can be of concern include other FPs, changes in the ionic strength, and ligand radiolytic stability. These are significant limitations, and thus alternatives continue to be explored.[48,49]

PUREX Process. The most widely used process for the removal of plutonium and uranium around the world is the Plutonium Uranium Recovery by EXtraction or "PUREX" process.[50,51] This process uses what has been the technologically most important extractant since 1954 tributyl phosphate (TBP, **1**; see Table 1) in a hydrocarbon solvent (usually kerosene or dodecane).[33,52,53] As a result of PUREX, the volume and radiotoxicity of highly radioactive and long-lived waste to be disposed of can be significantly reduced compared to the once-through fuel cycle.[53] Because this process has been used for several decades, there have been several milestones. First, high efficiency and reliability was achieved through the processing of large volumes of spent fuel.[52] Second, an increase in the production of high-quality UO_2 and mixed-oxide (MOX) fuels allows for improved LWRs and fast reactors.[52] Finally, the system has been modified to allow for the continuous decrease of solid waste volume, effluents, and environmental impact in terms of radiation doses.[52] Although the industry standard at present, the PUREX process remains far from perfect because it does not address the isolation of the minor actinides.[54,55] Continuous investigation on the subject has identified a number of promising extractant systems for actinide separations and their partitioning using solvent extraction procedures, either with proposals for TBP replacement or suggestions for other extractants to work as its complement as coextractants.

At present, about half of the world's SNF is produced in a once-through cycle, while the other half is reprocessed to recycle uranium and plutonium in the PUREX process.[56] Although geological repositories are generally considered the best option for the sequestration of such wastes, how to accomplish the required long-term surveillance and gain public acceptance of such repositories are lingering questions.[56] The option of partitioning actinides from high-level wastes (HLWs) represents one opportunity to reduce these uncertainties.[57] The waste stream from the PUREX process is highly radiotoxic and contains long-lived minor actinides (^{241}Am, ^{244}Cm, and ^{237}Np), lanthanide FPs, and short-lived corrosion products. This waste stream poses a major scientific challenge: develop a partitioning process with selectivity of the trivalent actinides over the trivalent lanthanides and synthesize an extractant that is able to perform in low pH and high radiation fields. Many separations currently in development are thus modifications of the PUREX process or are intended as final polishing steps, to reduce the amounts of HLWs requiring long-term geological storage, through the selective extraction of just the high-level α emitters—the actinides. Key to the development of a new extraction agent are that it is low cost, relatively easy to synthesize, and highly selective for actinides over a broad range of effective pH. It would also be preferable to have ligands that are resistant to radiolytic damage as well as easily strippable and incinerable to allow for ease of recovery of the metals without contributing to emissions or solid wastes.[1,2,14,40,44]

DIAMEX. The diamide extraction (DIAMEX) process was developed in the late 1980s by French researchers and proposes the use of diamides for the extraction of actinides from HLW nitric acid solutions as a finishing step after the PUREX reprocessing.[53] The main advantage proposed is the use of the carbon−hydrogen−oxygen−nitrogen (CHON) principle, which can allow for incineration of the separation materials at the end of their useful life and aid in minimizing the overall volume of wastes generated.[53] Presently, the most intensively studied diamide ligand suitable for extraction of tri-, tetra-, or hexavalent actinides is *N*,*N*′-dimethyl-*N*,*N*′-dibutyltetradecylmalonamide (DMDBTDMA, **2**). Good results have been reported on the use of DMDBTDMA in dodecane to extract Fe, as well as Am^{III},[58] U^{VI}, Np^{IV}, Sr^{II}, and Cs^{I} from different HNO$_3$ concentrations.[53] A modification of the ligand to *N*,*N*′-dimethyl-*N*,*N*′-dihexyl-3-oxapentanediamide (DMDHOPDA, **3**) and thenoyltrifluoroacetone (HTTA) in toluene or nitrobenzene was used for the extraction and mutual separation of actinides with III, IV, V, and VI oxidation states.[59] In a mixture of thorium, americium, uranium, and neptunium at pH 3 in 1 M NaClO$_4$, thorium can be extracted with 5 mM HTTA in toluene in the first step; then in a second step with 1 mM DMDHOPDA in toluene, americium can be extracted.[59] In the following step with 20 mM DMDHOPDA in toluene, uranium is extracted, and finally with 100 mM DMDHOPDA in nitrobenzene, neptunium is extracted into the organic phase.[59] Further research would be necessary for a final highly selective isolation of the actinide elements.[53] Using *N*,*N*′-dimethyl-*N*,*N*′-dioctyl-2-(2-(hexyloxy)ethyl)malonamide (DMDOHEMA, **4**) as an extractant, the efficiency of minor actinide recovery using high active waste can again be increased; it is sufficiently robust against hydrolysis and radiolysis, and because of the increased lipophilicity, the formation of third-phase solids or metallopolymers is suppressed.[55,60] Drawbacks that have been pointed out to the DIAMEX process are the structural complexity of the diamides compared to TBP and also the somewhat narrow range of HNO$_3$ concentrations that allow for good recovery of the trivalent actinides.[53]

TRUEX. The TRUEX, or transuranium extraction process, utilizes (*N*,*N*′-diisobutylcarbamoylmethyl)-octylphenylphosphine oxide (CMPO, **5**) where both the C═O and P═O groups act as ligating functions for extraction. The extracted complex contains three molecules of CMPO per cation.[61] Although powerful for extractions, CMPO by itself shows little discrimination between the 5*f* actinides and 4*f* lanthanides.[61] One of the first modifications in the TRUEX process was the addition of the PUREX process extractant (TBP), resulting in a new mixed-solvent system as an "all-purpose" actinide extractant from nitric acid waste solutions.[53] Several advantages were gained in the mixed-solvent system including enhanced distribution ratios of Am^{III} in 2 M HNO$_3$, suppressed distribution at low acidity for stripping, and good distribution between 0.5 and 6 M HNO$_3$.[62] The biggest benefit observed is improved extractant compatibility with aliphatic diluents with an increased metal loading capacity without third-phase formation.[62] After further investigation into a mixed-solvent CMPO−TBP system, problems arose with the stripping and subsequent recovery of the metals themselves, resulting from the high nitric acid concentration of the incoming loaded CMPO−TBP phase.[63] Although TRUEX using CMPO can readily sequester actinides, lanthanides are still extracted in quantities that complicate processing.[64] This further hinders the transmutation strategy because some isotopes of the extracted lanthanides have large neutron cross sections.[65−69]

The CMPO−actinide complexes produced in characterizing these systems have been extensively studied to investigate the effects of ligand modifications and process changes that might increase selectivity for actinides, such as the 3:1 CMPO-to-metal stoichiometry for the americium species.[64] In 2002, a modified CMPO−thorium crystal structure was reported. This ligand used three CMPO ligands attached to one triphenoxymethane molecule on the ideal 3:1 TRUEX stoichiometry for a coordination number for the thorium of 10 (Figure 1).[64] Six coordination sites are occupied by oxygen atoms from the three CMPO arms, with the remaining four sites occupied by oxygen atoms from the nitrates. Metal−oxygen bond distances range from 2.395 to 2.483 Å with a mean of 2.420 Å. Because the derivatized CMPO ligand is bulky, it does not allow for all of the nitrates to bind; this forms at 2+ cationic complex.[64]

In one strategy to selectively set the geometry of the CMPO groups and take advantage of preorganization for a chelate effect and perhaps increased selectivity of extractions, investigators attached the moieties to a variety of calixarene-like platforms. The selectivity for the actinides was found to increase in comparison to mono-CMPO extractants.[64] The most extensively studied was the use of the narrow and wide rims of calix[4]arenes (calix[4]arene-CMPO, **7**). For example, it was discovered that the CMPO moiety attached to the narrow rim of calix[4]arene is a much more efficient extractant for lanthanides and actinides than CMPO by itself.[61] In

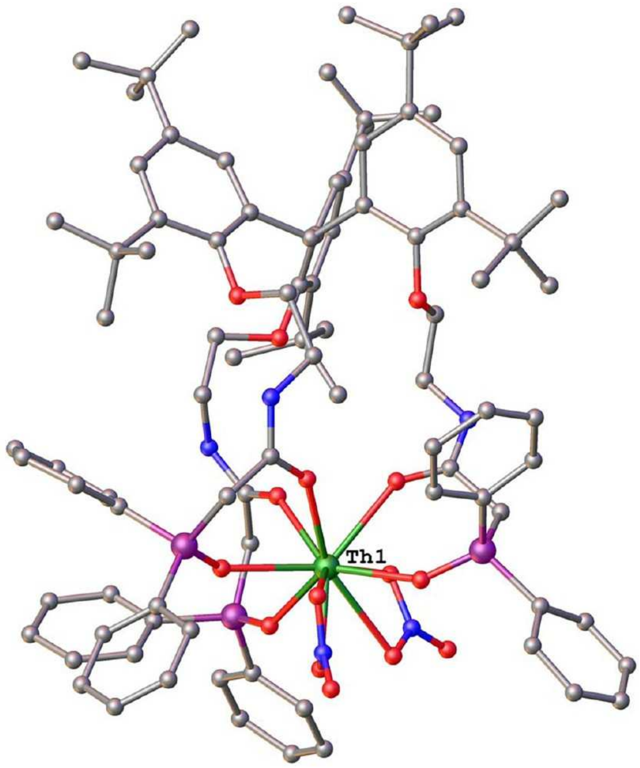


Figure 1. Projection of [tris(3,5-*tert*-butyl-2-(((diphenylphosphoryl)-acetamido)ethoxy)phenyl)Th$(NO_3)_2$]$(NO_3)_2$]. The carbon atoms are depicted as gray, the oxygen red, the nitrogen blue, and the central thorium atom green. For clarity, the structure is shown as a ball and stick projection and hydrogens have been omitted for clarity.[64,142]

comparison to CMPO functions of wide-rim calixarenes, a narrow-rim calixarene is a considerably better extractant for thorium and the extraction ability does not decrease for >2 M HNO_3.[61] However, lanthanide selectivity proved to be less predictable, with selectivity for some lanthanides equaling that of actinides.[64]

Cyanex. Cyanex 301 (**8**) is the respective dithio analogue of Cyanex 272, originally developed for selective extraction of zinc from calcium.[70] Increasing sulfur substitution increases the acidity of the extractants, making them more suited to extraction of soft Lewis acids, or softer Lewis acids in the case of actinides versus lanthanides.[71−73] Cyanex 301 can only differentiate between Am^{III} and lanthanides in solutions with a pH lower than 3.[32] An additional drawback is that Cyanex will decompose in these acidic solutions.[74−76] Studies have been undertaken to investigate different dithiophosphinic acids for minor actinide extractions.[74−76] A ligand involving an aromatic dithiophosphinic acid proved to be synthetically challenging but offered a more hydrolytically, radiolytically, and acidically stable system compared to Cyanex 301 while exhibiting a separation factor (SF) of ~100000 at low pH.[74] Changing this to dialkyl groups showed a significant effect on the extraction power but minimal impact on the selectivity with SFs of ~10000.[77] Bis(2-ethylhexyl)dithiophosphinic acid is the most promising of these because of its lower pH and high loading capacity.[77]

TALSPEAK. In principle, both TALSPEAK (Trivalent Actinide−Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes) and reverse TALSPEAK are based on the extraction of lanthanides using di(2-ethylhexyl)phosphoric acid (HDEHP, **9**), or a similar liquid cation exchanger, from a medium that selectively retains actinides in the aqueous phase as complexes with polyaminopolyacetic acid complexants.[78] In reverse TALSPEAK, the complexant solution is applied for selective stripping of actinides from a loaded organic phase.[78] TALSPEAK goes against the norm, instituting the use of a holdback agent such that lanthanides are extracted and actinides remain in the aqueous phase, in place of the typical strategy of extracting actinides into an organic phase.[78] HDEHP was initially used as an extractant in the 1950s in the extractions of lanthanides and actinides from mineral acid solutions.[79,80] HDEHP is a liquid cation exchanger and also a chelating agent that most typically forms a tris complex with trivalent lanthanides in the organic phase; distribution ratios were found to be nearly 10^5 for La^{3+} to Lu^{3+} and overlap significantly with those of the trivalent actinides.[78] Although separations of some individual members of the series (Am from Yb) are possible with HDEHP alone, this system is not useful for separation of these groups.[78] In the 1960s, Weaver and Kappelmann reported that, by altering the composition of the aqueous phase by substituting a solution containing moderate concentrations of carboxylic acids and lesser amounts of aminopolycarboxylic acids, the trivalent actinides could be separated from the trivalent lanthanides.[78,81] After a detailed investigation of the effects of different carboxylic acids and polyaminopolycarboxylic acids, they finally concluded that lactic acid (**10**) was the most suitable because of the high solubility of its lanthanide salts.[78,81] Diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid (DTPA, **11**) was also found to be the most suitable aminopolycarboxylate complexant because of its strong complex formation with actinides and higher solubility limits.[78,81] This, in turn, led to a complete group separation with DTPA in a selective partitioning due to the three amine nitrogen atoms in a specific coordination geometry.[78] While some advances have been made in the TALSPEAK process involving different organic extractants and holdback reagents, there is still a considerable potential for improvement by better matching of the extractant and holdback reagent complex strength while reducing the acidity of the organophosphorous extractant.[82]

SANEX. One of the principal obstacles to a process for the removal of americium and curium from the waste is the fact that a selective metal-binding reagent with the required properties of radiation stability, chemical stability, and solubility has yet to be identified.[65] Recently, 1,2,4-triazin-3-yloligopyridines (BTPs, **12**) have been identified as metal extractants specifically with the ability to separate actinides(III) and lanthanides(III) from nitric acid media.[65,83,84] These BTP molecules can bind as tridentate ligands to metal cations. If a metal binding agent is to be used to process radioactive waste, the extractant must be able to resist both radiolytic degradation and the effects of nitrogen oxoacids. Chemical attacks on the α-benzylic hydrogen atoms have been shown to be responsible for much of the degradation of BTPs by nitrogen oxoacids.[65,85]

In order to prevent degradation, the α-benzylic hydrogen atoms were replaced by alkyl groups and eventually without benzylic hydrogen atoms to form 2,6-bis(5,5,8,8,-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazine-3-yl)pyridine ($CyMe_4$-BTP, **13**).[65,85] This ligand with an annulated ring would prove to be more resistant to hydrolysis and radiolysis.[65] Although the rate of extraction is slower than that of other BTPs, the distribution ratio of americium was higher for the same time period and the SF between Am^{III} and Eu^{III} was an order of magnitude higher.[65] This molecule became the then standard for the SANEX or "Selective ActiNide EXtraction" process.[65]

To find better selectivity with improved kinetics and to allow easier stripping of the coordinated complexes 6,6′-bis(5,6-dialkyl[1,2,4]triazin-3-yl)[2,2′]bipyridines (BTBPs, **14**) have been developed.[85,86] BTBPs are quadridentate molecules consisting of two 1,2,4-triazin-3-yl groups linked by a central dipyridyl moiety.[66,67,87] Much like the original BTPs, alkyl groups where attached to the annulated rings on the BTBPs to begin with. The extraction efficiency toward trivalent actinides was lower than that with the BTPs but without compromising their selectivities (the Am^{III} distribution ratio is 3.9, and the SF for Am^{III} over Eu^{III} is 180).[85] With the longer alkyl chains on the BTBPs, the SFs of Am^{III} over the early lanthanides increased, but with a reduced ability to separate Am^{III} from heavier lanthanides. These ligands still had the problems of radiolytic degradation because of the α-benzylic hydrogen atoms.[88]

In this case, researchers decided to investigate putting the same aliphatic ring system from $CyMe_4$-BTP on the BTBPs ($CyMe_4$-BTBP, **15**), combining the high selectivity with the increased radiolytic resistance.[85] The ligand exhibited affinity toward trivalent actinides (almost too high to prevent backextraction) and high SFs over the lanthanides while maintaining stability versus nitric acid and radiolytic degradation, allowing recycling of the organic phase in a continuous SANEX process.[85] This ligand has become the reference system for the SANEX process.[89,90] Although the major drawback is the slow extraction kinetics, this can be improved with the addition of a phase-transfer catalyst such as DMDOHEMA or *N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide (TODGA), essentially combining the DIAMEX and SANEX processes.[68,89,90] A new improved BTP ligand has been synthesized, bis[2,6-(5,6,7,8-tetrahydro-5,9,9-trimethyl-5,8-methano-1,2,4-benzotriazin-3-yl)]pyridine (CA-BTP). This ligand is stable toward hydrolysis, high solubility in 1-octanol, and better equilibrium extraction kinetics reached within 10 min compared to 120 min for $CyMe_4$-BTBP.[68]

A new development is the introduction of cis-locked 1,10-phenanthrolines with 6,6′-bis(5,6-dialkyl[1,2,4]triazine-3-yl-[2,2′] ($CyMe_4$BTPhen).[91] It is thought that, by having a rigid cis conformation of the donor atoms, complex formation would be both more rapid and more thermodynamically favored compared to that of the bipyridine analogues.[91] The phenanthroline derivative showed better extraction kinetics in the four solvents tested compared to BTBP and that it is selective for Am over Eu, even at high acidity. As far as lanthanide separation, a similar trend in the distribution ratio between $CyMe_4$BTPhen and BTBP was observed.[91] Further applications of this ligand in coordination chemistry are being investigated.[91]

GANEX. GANEX, or group actinide extraction, is a two-step separation process being designed for the new "Generation IV" reactors.[91] Early concepts of separating actinides from lanthanides require an initial separation of both actinides and lanthanides from the PUREX raffinate and then a separate step to isolate the actinides.[69] Years of research have focused on this concept, but the two processes that have been given the most interest are the TALSPEAK process and the DIAMEX/SANEX processes.[69] Today, much of the focus in Europe has shifted toward a process that can replace PUREX by simultaneously removing all actinides either from the dissolved spent fuel or from dissolved fuel after the bulk of the uranium has been removed.[69,91] As proposed, this process—dubbed GANEX—has the potential to simplify this separation and eliminate some intermediate steps and may offer a greater degree of proliferation resistance because all actinides are routed together, unlike the TRUEX/TALSPEAK or DIAMEX/SANEX processes.[91] The proposed GANEX system will use two extractants, TBP (**1**) and BTBP (**14**) with cyclohexanone as a diluent.[69] All actinides are separated simultaneously from lanthanides as well as the fission and corrosion/activation products; thus, the complicated process of redox control of plutonium and neptunium can be avoided.[69]

Lanthanides as Models for Actinides in Structural Characterization. One concern in research characterizing the 5*f* elements or actinide complexes is the potential for radiological hazards. The additional expense that arises in working with these or in obtaining materials and equipment for dedicated use greatly increases the costs of such research. Because of this, it has often been found to be convenient to use other metal ions as less hazardous analogues for characterization. This allows for increased access to a wider range of analytical tools and for training of personnel. A good example of this is in the characterization thorium(IV) or uranium(IV) complexes as models for the more highly active plutonium(IV).[10,38,92,93]

Because of their similar ionic radii, lanthanides are often also seen as suitable coordination models for actinides. Both the 4*f* and 5*f* elements have large ionic radii, preferring large coordination numbers (8 or 9); they all possess flexible coordination geometries, and they all can act as Lewis acids in solutions.[10,94] Also, actinides in 3+ coordination, trivalent states exhibit ionic radii similar to those of the trivalent lanthanides in the same column of the periodic table. (The eight-coordinate ionic radii are 1.066 Å for Eu, 1.053 Å for Gd, and 1.090 Å for Am.)[35,36] There is a critical caveat in that, although they are similar in size and preferred coordination geometry, it can be misleading to assume their chemistry is similar. Lanthanides can be useful structural models; however, the radial extension of the 5*f* orbitals is further than the 4*f* orbitals. Because of this, the 5*f* orbitals of actinides are able to interact with the molecular orbitals of potential ligands. This, in effect, causes bonds of the 5*f* element to have more covalent character; actinides can therefore form more stable complexes with molecules such as BTPs than lanthanides can.[1,10,95−98]

In another example, plutonium has very unique properties and can be present in up to five different oxidation states in aqueous solutions (3+, 4+, 5+, 6+, and 7+). Cerium is the only lanthanide that is stable in the 4+ state in aqueous solutions or normal atmospheric conditions, and the similarities in the electrochemistry between $Ce^{III/IV}$ and $Pu^{III/IV}$ can make for useful comparisons. In an application like chelating metal ions from the body (decorporation), the need to separate Ce from Pu would be limited, and thus not a problem, but this could potentially be a problem in environmental cleanup or waste remediation.[99] Late actinides are more like lanthanides in that they prefer the trivalent oxidation state; however, there is an inherent flaw in relying on modeling based on lanthanides to determine what small differences in the difference between the 4*f* and 5*f* elements could be exploited for actinide selective extractions. Such modeling can be a powerful tool, yet many systems still make critical assumptions in characterizing the f-element chemistry, and this can lead to missteps. A critical need for modern techniques for characterizing the chemistry of the actinides and their metal complexes still exists.

BTP and BTBP Ligands. Once it was demonstrated that tetradentate molecules like BTBP (**14**) were able to bind and extract europium,[100] more detailed investigations of the actinide and lanthanide complexes with BTBP (**14**) and BTP (**12**) were undertaken by Foreman and others.[96,97,101] Additional complexes of these and related ligands have been prepared with lanthanides. A key objective was to characterize significant differences between these structures and those formed with other terdentate azaaromatic ligands whose SFs are much lower.[102] The solids prepared in this series of experiments with BTBP (**14**) resulted in complexes of a 1:1 metal-to-C2-BTBP ratio, and while ligands such as *N*,*N*′-bis[1-(pyridin-2-yl)ethylidene]ethane-1,2-diamine[103] have a flexible aliphatic section and so are able to change shape to suit the demands of the metal, the BTBP (**14**) ligands are more rigid and, therefore, are less able to change shape to suit the metal.[101] It is likely that the smaller steric demands of the 1,2,4-triazin-3-yl ring by comparison with the 2-pyridinyl ring allows the nitrogen atoms to approach more closely to the metal atom and contributes to the greater ability of the BTP (**12**) ligands to adopt the geometry required for metal binding.[101] Enhanced SF values for BTP (**12**) were found to be due to the formation of the $[ML_3]^{3+}$ cation.[102] From this same series of ligands, additional complexes with lanthanides (Sm−Lu) were prepared because these are of size similarto those of Eu^{III} and Am^{III}, which were used in the previously published extraction study.[102] It seems likely that the electronic properties of the ligand, particularly those of the donor nitrogen atoms, must be responsible for its exceptional extraction properties.[104]

When R-BTP (R = Me, Et, Pr) was used to prepare complexes with the later lanthanides, $[ML_3]^{3+}$ cations were consistently observed for all lanthanides in the presence of a variety of complex ions and/or neutral ligand species.[104] With the larger earlier lanthanides, this was not observed in the presence of nitrate despite varying experimental conditions. Instead centrosymmetric isostructural dimers $[M_2L_2(NO_3)_6]$ formed with M = La, Nd,[106] Pr, and Sm (see Figure 2).[104] Without the alkyl groups, 12-coordinante complexes of stoichiometry $[LnL_2(NO_3)_3]$ with Ln = Pr and Nd were formed. These structures are isomorphous, containing C_2 symmetry with an orthorhombic crystal system and a *Pbcn* space group. The Nd−N bond distances range from 2.70 to 2.77 Å compared to the alkyl-substituted BTP, which was 2.59−2.68 Å, while the Pr−N bond distance ranges from 2.73 to 2.76 Å. This is yet another instance of the unique properties of this family of BTP ligands. While there is no obvious correlation between its unusual complexation properties and the high SFs, it seems likely that the electronic properties of the ligand must be responsible.[104]

A second series of coordination complexes with Ce^{III} and U^{III} were prepared with the Me-BTP and *n*-Pr-BTP ligands.[105] The chemical formula for the cerium Me-BTP complex was determined as $[Ce(Mebtp)_3]I_3{\cdot}9C_5H_5N$ and crystallized in the *P*2/*n* space group, while the cerium n-Pr-BTP complex was determined as $[Ce(n\text{-}Prbtp)_3]I_3{\cdot}3C_5H_5N$ and crystallized in the *Pc* space group. The uranium *n*-Pr-BTP complex was determined as $[U(n\text{-}Prbtp)_3]I_3{\cdot}C_5H_5N$ and crystallized in the $P\bar{1}$ space group. The M−N(py) distance ranges from 2.624 to 2.641 Å with an average of 2.63 Å, whereas the M−N(triazine) distance ranges from 2.598 to 2.625 Å with a mean value of 2.61 Å. Similar distances were found for *n*-Pr-btp, indicating that the different alkyl groups at the 5 and 6 positions of the triazine moiety have no significant effect on the metal coordination sphere. These average distances appear longer than the corresponding distances in the other $[Ln(n\text{-}Prbtp)_3]^{3+}$ cations, in agreement with variation of the ionic radii of the metals. In the $[U(n\text{-}Prbtp)_3]^{3+}$ cation, the U−N(py) bond lengths vary from 2.52 to 2.56 Å and the U−N(triazine) distances range from 2.52 to 2.57 Å. These M−N distances are shorter than those found in the cerium analogue, by 0.09 and 0.06Å, if the average values are considered, while U^{III} and Ce^{III} have similar ionic radii. This could reflect some U−N *π*-back-bonding and some degree of covalency in the U−N bond (see Figure 3).[105]

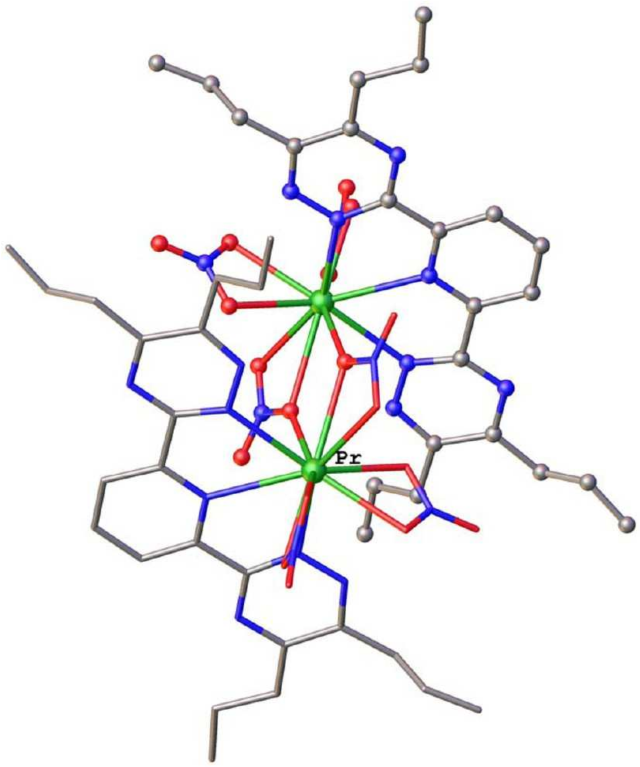


Figure 2. Projection of $[Pr_2(L1)_2(NO_3)_6]$. One ligand is shown as ball-and-stick, and another is shown as tube. The carbon atoms are depicted in gray, the oxygen atoms red, and the nitrogen atoms blue, and the central praseodymium atom is in green. The model is shown as a ball-and-stick projection, lacking hydrogen atoms for clarity.[102,142]

Using the ligand C_2-BTBP, Foreman and co-workers prepared complexes with 12 of the 14 different lanthanide metals, La, Ce, Pr, Nd, Sm, Eu, Dy, Ho, Er, Yb, Lu, and Y (see Figure 4).[101] La to Sm would all contain the formula $[M(NO_3)L]{\cdot}nH_2O$, where *n* is equal to 1 or 1.5, and crystallize in the monoclinic *P*2/*c* space group with C_2 symmetry. All of the resultant metal−ligand complexes are 10-coordinate except for Lu, which is 9-coordinate, which reflects the fact that Lu is the smallest of the lanthanides. Eu, Dy, Ho, Er, and Yt, all have the formula $[M(NO_3)_3L]{\cdot}MeCN$. As would be expected with the fixed geometry of the ligand, the M−N bond distances get shorter as the metal gets bigger; the bonds get smaller with M−N(pyr) from 2.741 Å for La to 2.450 Å for Yb. The M−N distance for the triazine nitrogen atom also decreased from 2.704 to 2.461 Å. These are the first reported examples of lanthanides bonded to a tetradentate aromatic ligand. One distinguishable feature is the N2−M−N22 angle, which ranges from 175.6° for La to 164.3° for Y, demonstrating that, as the

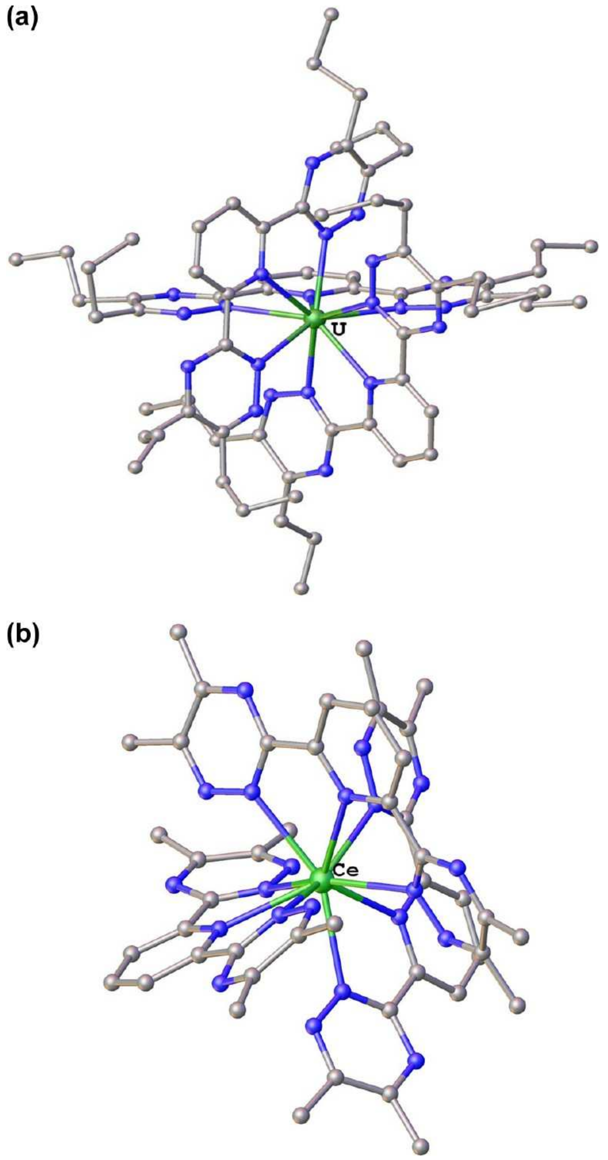


Figure 3. Projections of (a) $[U(Pr^{n}btp)_3]^{3+}$ and (b) $[Ce(Mebtp)_3]^{3+}$. Ball-and-stick models are shown, lacking hydrogen atoms for clarity. The carbon atoms are depicted in gray, the oxygen atoms red, the nitrogen atoms blue, and the *f* element atoms green.[105,142]

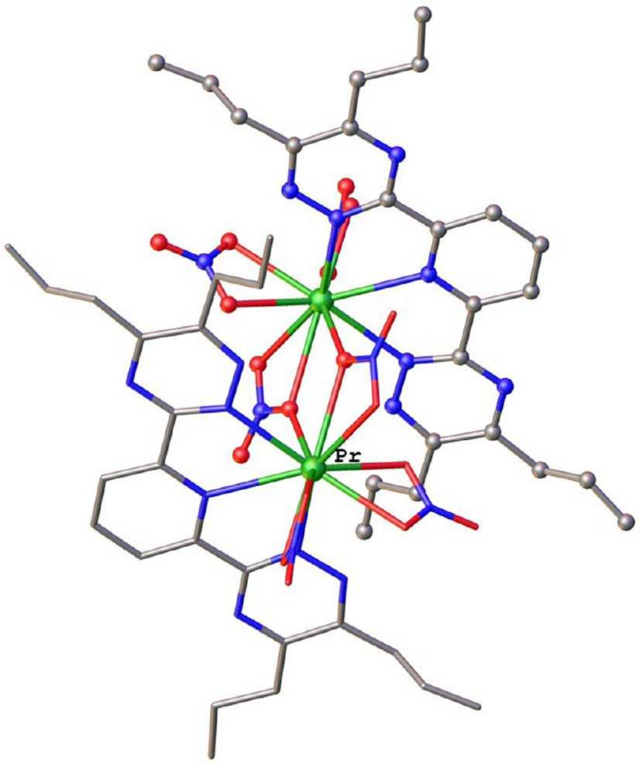


Figure 4. Projection of $[Pr_2(L1)_2(NO_3)_6]$. One ligand is shown as a ball and stick projection, and another is shown as a tube projection. The hydrogen atoms have been omitted for clarity. The carbon atoms are depicted in gray, the oxygen atoms red, the nitrogen atoms blue, and the central praseodymium atom is in green.[105,142]

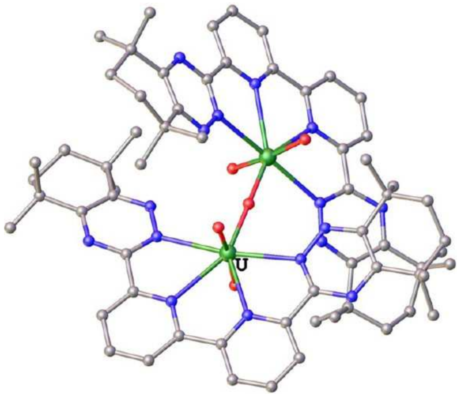


Figure 5. Projection of $[(UO_2)(CyMe_4BTBP))_2(\mu\text{-}O]^{2+}$. The carbon atoms are depicted in gray, the oxygen atoms red, the nitrogen atoms blue, and the central uranium atoms in green. The model is shown as a ball-and-stick projection, lacking hydrogen atoms for clarity.[101,142].

metal is decreased in size, it is pulled more toward the ligand cavity.[101]

Because bi- and tridentate polypyridine ligands led to uranyl compounds with unprecedented structures, it was decidedly of interest to determine the coordination geometry of the uranyl ion with the tetradentate BTBP ligands, and an analogous structure has been reported with the uranyl cation (UO_2^{2+}) and the $CyMe_4$-BTBP ligand by Berthet (see Figure 5).[106] Using $UO_2(OTf)_2$ and $UO_2I_2(thf)_3$ metal salts mixed with $CyMe_4$-BTBP produced $[UO_2(CyMe_4BTBP)(py)][OTf]_2\cdot 3py$, $[UO_2I(CyMe_4BTBP)][I]\cdot CH_3CN$, and $[UO_2(OEt)(CyMe_4BTBP)][OTf]\cdot EtOH$ and one dinuclear complex, $UO_2(CyMe_4BTBP)_2(\mu\text{-}O)][I]_2\cdot py$. All of these metal complexes are found in the usually pentagonal-bipyramidal configuration, forming seven-coordinate complexes with the ligand and with an X atom [X = N, I, or O] defining the equatorial plane. The U−N(BTBP) distances vary from 2.474 to 2.605 Å, with mean values between 2.52 and 2.57 Å, smaller in the dicationic derivative. The U−N distances of the triazine groups average 2.486−2.545 Å and are roughly 0.05 Å smaller than the central pyridyl moieties, which average 2.542−2.593 Å. The difference in distances is not likely due to the Lewis basicity of the nitrogen atoms because a stronger interaction of the Lewis acid group $(UO_2)^{2+}$ would be expected with the stronger nitrogen atoms on the pyridyl groups, but rather this can be ascribed to the cavity size of the rigid planar ligands as well as the size of the metal ions. The planarity of the tetradentate ligand in a one-to-one metal−ligand complex is in striking contrast with the conformation of the terdentate

2,2′:6′,2″-terpyridine ligand, which exhibits strong distortions with the bending out of the equatorial plane. This feature may be related to the different cavity sizes of the terdentate and tetradentate ligands.[106]

5*f* Coordination Compounds. Currently, 3936 of the 4165 (94.5%) structures containing a 5*f* element reported to the Cambridge Crystallographic Data Centre, CCDC, are composed of structures containing thorium and uranium, while 1869 of the 4165 (44.9%) structures contain the UO_2^{2+} ion.[107] One reason that the overwhelming majority of the reported actinide structures contain the thorium or uranium atoms is because these atoms provide long-lived radioisotopes with lower radioactive emissions. These elements provide an easier in vitro approach when starting from their simple salts, while starting from an in vivo waste slurry adds additional safety concerns; however, for understanding separation processes, it is critical to establish bonding parameters across the 5*f* series.[108−110] The ligands described below have been looked at for liquid−liquid extraction of trivalent lanthanides and actinides of different oxidation states. Generally, a multidentate ligand that contains soft donors, such as nitrogen and sulfur, is used for such separations. Because the behavior of the 5*f* elements has been studied much less, it is a tougher task to predict ligands that would have optimum efficiency and selectivity in separations as well as to provide an optimal coordination environment for these 5*f* metal ions in the solid state.[110]

In 2006 and 2007, uranyl complexes coordinated to a series of amino alcohol bis(phenolate) ligands were reported. The two amino alcohol bis(phenolate) ligands bind the uranyl metal centers in a bidentate fashion, with the ligand forming the equatorial plane. The coordination number of these complexes is 6 and is best described as octahedral, with the -yl oxygen atoms binding at the axial positions and the remaining equatorial sites filled by the amino alcohol bis(phenolate) ligands.[111,112]

In a continuation of this line of research, uranyl complexes coordinated with a series of diaminobis(phenolates) were reported.[113,114] Two types of structures are reported: 1:1 and 2:1 ligand-to-metal ratios. In the 1:1 complexes, the coordination number around the uranium center is 7, and is best described as pentagonal-bipyramidal polyhedra. The two -yl oxygen atoms are found at the axial positions, and the equatorial plane is defined by two different pentagons, depending on whether the central nitrogen atom in the ligand is an imine or an ammonium. In the imine-type ligands, four coordination sites are filled by oxygen atoms, two from the ligand and two from a bidentate nitrate. In the ammonium-type ligands, the N−U bond is replaced by a water molecule. In the 2:1 complexes, the coordination number around the uranium center is 6, and they are best described as octahedral. Figure 6 shows the 2:1 ligand-to-metal complex of $[UO_2(N',N'$-bis(2-hydroxy-3-methoxy-5-(propen-2-yl)benzyl-N-(2-aminoethyl)-morpholine$)_2]\cdot 2CH_3CN$. The two -yl oxygen atoms are found at the axial positions, and the equatorial plane is defined by four oxygen atoms, two from each ligand.[114]

In 2007, it was reported that derivatives of the ligand TBP used in the PUREX process formed coordination structures with uranyl, UO_2^{2+}, and perrhenate, RhO_4^-.[115] The perrhenate ion is of interest because it has been shown to be a suitable mimic for pertechnetate (TcO_4^-), another potentially hazardous FP that is also a β emitter and readily transportable in aqueous media.[116] The two complexes reported are similar, with the difference being the TBP ligand derivative. In both structures, the coordination number of the uranium is 7, and they are best described as pentagonal-bipyramidal polyhedra. The -yl oxygen atoms are found at the two axial positions. Three sites of the equatorial pentagon are occupied by oxygen atoms from the perrhenate anion. The remaining two sites are occupied by the oxygen atoms of the TBP derivative ligand.[115]

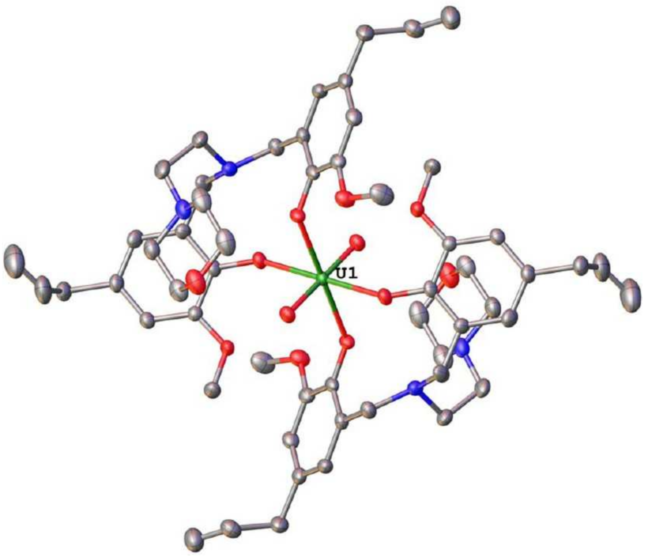


Figure 6. Thermal ellipsoid projection of $[UO_2(N',N'$-bis(2-hydroxy-3-methoxy-5-(propen-2-yl)benzyl-N-(2-aminoethyl)-morpholine$)_2]\cdot 2CH_3CN$. The carbon atoms are depicted in gray, the oxygen atoms red, and the nitrogen atoms blue, the central uranium atom is in green, and the hydrogen atoms are omitted for clarity.[105,142].

The first 5*f*-BTBP complex, bis(triazinyl)bipyridine, was reported in 2008.[106] This report also contains three mononuclear and a dinuclear UO_2-BTBP complex and also a dinuclear UO_2-TPTZ complex, tripyridyltriazine. In all five of these structures, the coordination number around the uranium site is 7, and they are best described as pentagonal-bipyramidal polyhedra, with the -yl oxygen atoms found at the two axial positions. In the four BTBP complexes, the BTBP ligand coordinates the uranium center in a tetradentate fashion, which defines the equatorial plane.[106]

Schnaars et al. reported three complexes, $AnX_2(^{Ar}acnac)_2$, where ^{Ar}acnac = (ArNC(Ph)CHC(Ph)O and Ar = 3,5-*t*-$Bu_2C_6H_3$, containing uranium and plutonium in 2011.[110] Among the interesting features of this report are that both the uranium and plutonium metals in the 4+ oxidation state were used to prepare complexes and that a comprehensive look at that oxidation state was sought. Two of the isostructural complexes contain U^{IV}, with the difference being the halides, Cl or I, bonded to the metal center. The Pu^{IV} structure will be discussed below. The β-ketoiminate ligand, containing a hard and a soft donor, was used because of its ability to stabilize weak Lewis acids, UO_2^{2+}, and thus was thought to be able to coordinate to the stronger Lewis acids, An^{IV}. The coordination number around the uranium center is 6, and they are best described as distorted octahedral polyhedra. The halides are found at the axial positions, and the ^{Ar}acnac ligands are found in the equatorial plane and are trans to each other, as seen in the isostructural $PuI_2(^{Ar}acnac)_2$ shown in Figure 11. The differing halides do not affect the bonding parameters of the ^{Ar}acnac ligand.[110]

Salen-type and Schiff base UO_2^{2+} structures were reported by our group in the last 5 years.[117−119] The coordination number of the uranium center, in both the salen-type and Schiff base systems, is 7, and they are best described by pentagonal-bipyramidal polyhedra. These salen-type ligands, called the salen quinoxolinols or salqu ligands, were designed with a quinoxaline backbone to enable the readily distinguishable properties by either fluorescence or UV−vis between different metal complexes. In the UO_2^{2+} structures, the -yl oxygen atoms sit at the axial positions, while the two oxo-coordination and two aza-coordination sites of the ligand occupy four of the positions in the pentagon. The remaining site of the pentagon is occupied by a solvent molecule. The ligand must twist from planar to accommodate the uranyl ion, resulting in a large change in the overlap of the π bonds in the conjugated backbone in the system and, consequently, a large change in the spectroscopy.[117]

In the asymmetric Schiff base structures, the -yl oxygen atoms sit at the axial positions while the equatorial pentagonal coordination is very different. Two ligands bind two metals and exclude the solvent molecule, forming a dinuclear U_2O_2 species. This U_2O_2 species is composed of two uranium sites, bridged by alkoxyl and hydroxyl oxygen atoms. The shape of this species forms a diamond, and each vertex alternates between uranium and oxygen atoms. (See, for example, ligand (*E*)-3-[(2-hydroxybenzylidene)amino]propane-1,2-diol; Figure 7.) The coordinating pentagon around the metal ion is composed of a phenolic oxygen atom, imine nitrogen atom, and bridging alkoxyl and hydroxyl groups, with the remaining site of the pentagon occupied by a solvent molecule.[119] These ligand systems offer the U···U interaction found at 3.8794 Å in Figure 7 of $[UO_2(3\text{-}(2\text{-hydroxybenzylideneamino})\text{propane-1,2-diol})]_2 \cdot C_3H_7NO$. In this series of complexes prepared with different substituents on the aryl backbone, the resultant complexes were always dinuclear 2:2 metal−ligand complexes. Simple extraction studies proved that they could be effective for removing uranyl from aqueous solutions (up to 99% in 24 h); however, the presence of iron or copper in mixed solutions would later demonstrate some complications to selective extractions. Hydrolysis of this extraction agent does occur, but at extreme pH conditions (i.e., 1−3 and 13−14), this is important because nuclear waste is found at high and low pH and a one-ligand processing system will need a stable ligand over a wide pH range.[20,119,120]

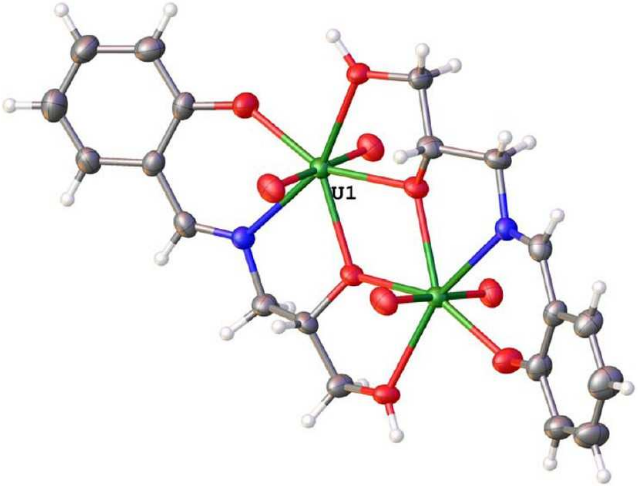


Figure 7. Thermal ellipsoid projection of $[UO_2(3\text{-}(2\text{-hydroxybenzylideneamino})\text{propane-1,2-diol})]_2 \cdot C_3H_7NO$. The carbon atoms are depicted in gray, the hydrogen atoms white, the oxygen atoms red, the nitrogen atoms blue, and the central uranium atoms green.[119,142]

With additional bridged structures, an attempt was made to limit the formation of dinuclear complexes to go after a 1:1 ligand-to-metal complex with the preparation of a 2,2′-[(1*E*,1′*E*)-[(2-hydroxypropane-1,3-diyl)bis(azanylylidene)]bis(methanylylidene)]diphenol ligand.[120] In these structures, the coordination number of the uranium site is 7, and they are best described as pentagonal-bipyramidal polyhedra. The -yl oxygen atoms sit at the axial positions, while the equatorial pentagonal coordination is different. The 1:2 ligand-to-metal pentagon is composed of a phenolic oxygen atom, an imine nitrogen atom, and bridging alkoxyl and hydroxyl groups, with the remaining site of the pentagon occupied by a solvent molecule. The 2:2 ligand-to-metal pentagon geometry is the same as the 2:1 in that the bite angles and bond distances are very similar, but one bridging hydroxyl group has been replaced by a coordinating solvent molecule. In the presence of uranyl, these Schiff base complexes are very stable, in particular compared to their transition-metal counterparts, and may be useful in akaline nuclear waste solutions.[20,119,120] This still may be of use as a final backextraction polishing step in that the ligand could be used to retain uranium in organic solutions after adjustment to a basic pH, which would release complexed transition metals.

The all-aza [cyclo[6]pyrrole (UO_2)] coordination complex was reported in 2007.[121] The ligand was first noted in the synthesis of cyclo[8]pyrrole.[122] The authors held that cyclo[6]pyrrole would bind uranyl more readily than the earlier reported cyclo[8]pyrrole because of its cavity size and favorable donor number. The coordination number of the uranium site is 8, and is best described as a hexagonal bipyramidal polyhedron. The -yl oxygen atoms are found at the axial position, and the nitrogen atoms from the ligand define the hexagonal equatorial plane. This is the first metal complex of the cyclo[*N*]pyrrole series of expanded porphyrins.[121,123]

In 2009 and 2010, uranyl structures of the bis(Me-3,2-HOPO), 3-hydroxy-*N*-methylpyridin-2-one, ligand derivatives were reported.[123] The uranium sites in the reported structures have a coordination number of 7, and they are best described as bicapped pentagonal polyhedra. This ligand architecture coordinates the uranyl unit in a tetradentate, through the four Me-3,2-HOPO oxygen atoms, fashion leaving one site open for coordination through another ligand or a solvent. In 2011, two uranyl structures of a MeTAM (methyl terephlalamide) ligand were reported.[123] Previous studies have demonstrated that the MeTAM ligand can act as a decorporation agent and was found to be more effective in reducing $[UO_2^{2+}]$ in the kidneys and deposited bone than the HOPO ligands.[10,124]

In the past 15 years, coordination structures that contain neptunium have been few and far between. The first transuranic ether inclusion complex, $[NpO_2([18]\text{crown-6})][X]$ (where X = ClO_4^- or $CF_3SO_3^-$), with single-crystal diffraction data, was reported by Clark and co-workers in 1998 (see Figure 9). The NpO_2^+ ion is of particular interest because of the problems associated with extracting it from high-level nuclear waste, stemming from the neptunyl's low positive charge and relatively high solubility in aqueous media.[125] This also makes neptunyl of great potential environmental and health consequence because it could be easily transported in groundwater and

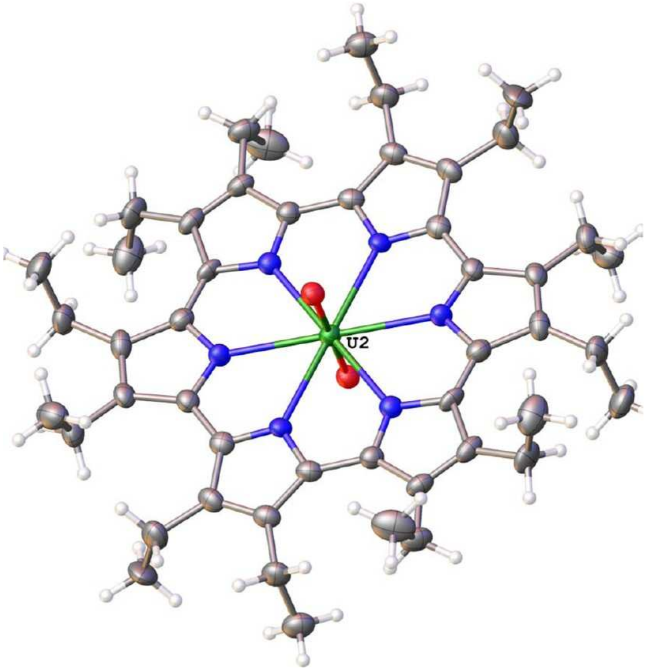


Figure 8. Thermal ellipsoid projection of [cyclo[6]pyrrole (UO_2)]. The carbon atoms are depicted in gray, the hydrogen atoms white, the oxygen atoms red, and the nitrogen atoms blue, and the central uranium atom is in green.[121]

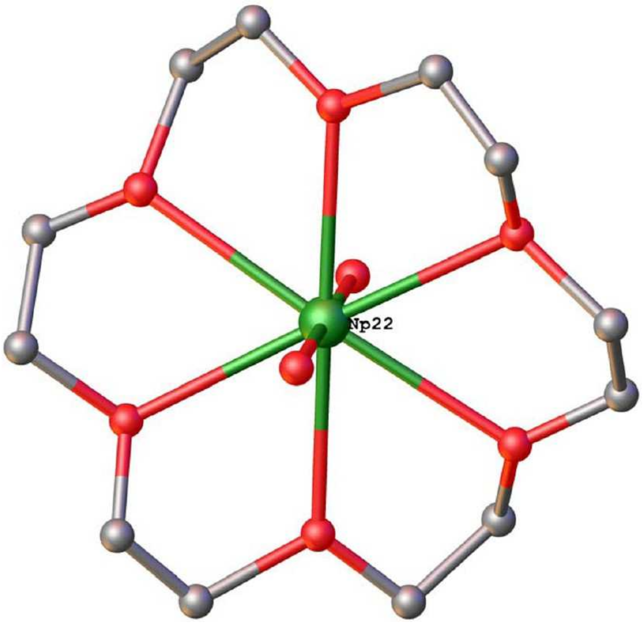


Figure 9. Ball-and-stick projection of $[NpO_2([18]crown\text{-}6)]^+$. The chlorate anion and the hydrogen atoms have been omitted for clarity. The carbon atoms are depicted in gray and the oxygen atoms red, and the central neptunium atom is in green.[128,142].

readily introduced into the food chain after a waste spill.[126,127] The Np═O bond length of 1.800 (5) Å is unusually short for a NpO_2^+ ion; it is found at a distance 0.05 Å shorter than the $[NpO_2(H_2O)_5]^+$ ion.[108] The [18]crown-6 ligand completely encapsulates the NpO_2^+ ion. The Np^V center is best described by an approximate hexagonal bipyramidal polyhedron. The short -yl oxygen atoms are found at the axial positions, and the ligands O_{ether} coordinate, forming the equatorial hexagonal plane. This is the first reported neptunium complex that was characterized by single-crystal X-ray diffraction with the radiation source from a synchrotron. The Np^V center, in the complex $[NpO_2(C_6H_{16}N_2O_3)_2]ClO_4$, is best described as a hexagonal bipyramidal polyhedron. Two of the eight sites are from the -yl oxygen atoms, found at 1.729 Å. The hexagonal plane is defined by the six oxygen atoms from the two ligands.[108]

The neptunium(V) hexaphyrin complex was reported in 2001.[128] The Np^V center has a coordination number of 8, and they are best described as hexagonal-bipyramidal polyhedra. The -yl oxygen atoms are found at the axial positions. The remaining six coordination sites are filled by nitrogen donors from the hexaphyrin ligand. The hexaphyrin ligand does have a slight twist when bound to the NpO_2^+ center, but the distortion is not as pronounced as in the uranyl hexaphyrin structure described in the same paper. The authors reason that the larger ionic radius of NpO_2^+ is a better fit for the hexaphyrin ligand as opposed to the uranyl unit.[128] It was later characterized with substituted versions of this ring to determine how this distortion affects coordination.[129] This was the first reported all-aza-coordinating system for neptunium, and its selectivity for actinides and intense color were characterized in potential sensing applications.[130−133]

Of the actinide structures reported in the CCDC, the 134 neptunium-containing and 77 plutonium-containing crystal structures represent 3.2 and 1.8% of the actinide compounds reported, respectively (CCDC database search). The remaining 0.5% of the actinide structures reported are the rest of the actinides besides those previously described (i.e., not U, Th, Pu, or Np). This is a concerning problem as the fundamental bonding parameters and coordination chemistry behavior need to be understood to be able to intelligently design ligands for separations, and ultimately to formulate new processes using these ligands.

The first structure reported of an organic extraction agent with a plutonium metal resolved by single-crystal analysis was $[Pu(\mathbf{1})_2(NO_3)_2][(NO_3)_2]$, where **1** is the trifunctional ligand 2,6-$[(C_6H_5)_2P(O)CH_2]_2$.[109] The coordination number around the plutonium center is 10, and is best described as a distorted bicapped square antiprism polyhedron. All 10 of the inner-sphere coordinating atoms are oxygen atoms. Two of the ligands bind the plutonium center in a tridentate fashion; each ligand binds once through the $O_{pyridine\ N\text{-}oxide}$ and twice through the $O_{phosphoryl}$ sites. The M−O_{ligand} bond distances of the plutonium(IV) structure are shorter than those of the thorium(IV) complex. While the actinide contraction is not as linear as the lanthanide contraction, it still exists, and these systems are evidence of this. Typically, a ligand that forms complexes with the lighter actindes forms shorter bonds with the heavier actinides.[109] Later, the complex $[Pu(\mathbf{2})_2(NO_3)_3{}^+]$-$[Pu(NO_3)_6{}^{2-}]_{0.5}$ was reported, where **2** is the bifunctional ligand 2-$[(C_6H_5)_2P(O)CH_2]C_5H_4NO$. The coordination number of this complex is 10, and the polyhedron is best described as an average of a bicapped antiprism and a sphenocorona. There are two idealized 10-vertex polyhedra: one is a bicapped antiprism, and the other is a sphenocorona. The complex is not described by either of these polyhedra; it is better described as a combination of the two. These complexes are examples of and could lead to the further development of phosphinopyridine ligands in separations of nuclear waste.[134]

Linear and cyclic hydroxamates containing the building block 1-amino-5-hydroxaminopentane as a building block have been found in the naturally occurring compounds known as siderophores. Bacteria have developed these compounds as a way to sequester naturally occurring iron.[135] While plutonium does not occur naturally, these complexes were of interest because they are potentially useful in medical treatments as chelators for iron and aluminum overload.[10,135−139] The first plutonium siderophore complex to be structurally characterized was $[Al(H_2O)_6][Pu(DFE)(H_2O)_3]_2(CF_3SO_3)_5 \cdot 14H_2O$. The coordination number around the plutonium metal center is 9, and is best described as a distorted tricapped trigonal prism. The ligand coordinates the metal center through six oxygen atoms: three from $O_{carbonyl}$ and three from $O_{oximate}$. Three water molecules complete the coordination sphere. This compound is the first discrete molecule structurally characterized with a Pu^{IV} ion that is nine-coordinate.[112] These siderophore-type complexes are interesting because they biologically function to separate a metal from the environment, transport it across an organic layer, and release the metal under the desired conditions.

The first structure of a plutonium(IV) hydroxypyridonate (HOPO) was reported in 2005. The complex is modeled after coordination systems found in the naturally occurring siderophores, with two *N*-methyl-3-hydroxy-2-pyridinone linked by a five-membered ether linker. The coordination number of the plutonium atom is 8, and is best described as bicapped trigonal prism. The metal complex is formed by two 5LIO(Me-3,2-HOPO) ligands and one plutonium atom. The 5LIO(Me-3,2-HOPO) ligand contains two types of oxygen atoms: the phenolic and amide nitrogen oxygen atoms. Four oxygen atoms from each ligand bind the plutonium metal in a sandwich-type complex, as seen in Figure 10. In part because of the flexible geometry allowed by the plutonium ion, this is the first structure to have two different chiralities of the metal complex in one unit cell.[140] This structure was later followed by other related 1,2-HOPO plutonium(IV) and plutoniuum(IV) maltol structures, which were reported with the comparable cerium(IV) structures for comparison. There was a remarkable difference between these structures, which had very dissimilar geometries, although they had similar size metal ions, and it points to a significant concern about the viability of cerium(IV) as a model for plutonium(IV).[19,141]

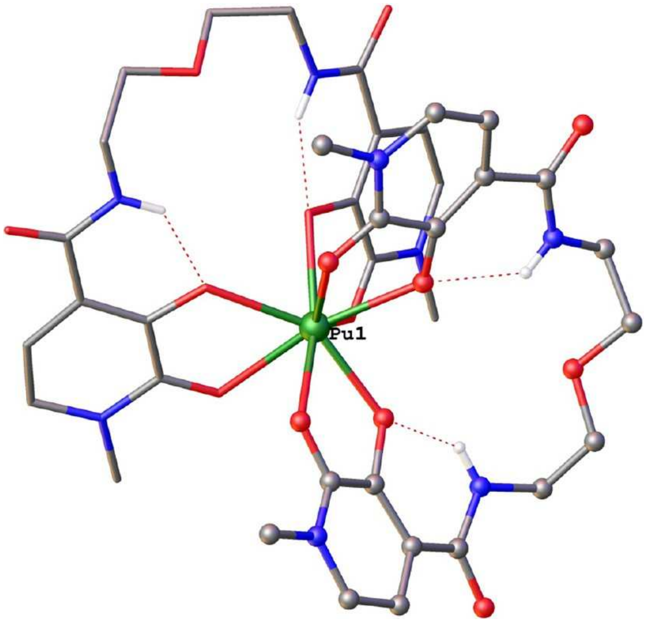


Figure 10. Projection of [Pu(5LIO(Me-3,2-HOPO)$_2$)]. One ligand is shown as ball-and-stick and the other as tube, lacking non-hydrogen-bonding hydrogen atoms for clarity. The carbon atoms are depicted in gray, the oxygen atoms red, and the nitrogen atoms blue, and the central plutonium atom is in green.[140,142]

As described above, three isostructural compounds with the general formula $AnX_2(^{Ar}acnac)_2$ were reported. The $PuI_2(^{Ar}acnac)_2$ ligand is shown in Figure 11. The starting material for the plutonium isostructure was Pu^0, partially because of the lack of suitable Pu^{IV} starting materials. This structure reported is the first example of a Pu−I bond. The actinide contraction and ionic bonding models alone are not enough to explain the difference in the An−O and An−N bond lengths of the $PuI_2(^{Ar}acnac)_2$ and $UI_2(^{Ar}acnac)_2$ isostructures. The ^{Ar}acnac ligand may be a useful probe in elucidating an all-enclusive comparative bonding study of actinides because it is not limited by the cavity size or sterics. The solid-state plutonium structures reported within have one common feature, excluding $PuI_2(^{Ar}acnac)_2$; this feature is that the metal center is completely bound by oxygen atoms.[110]

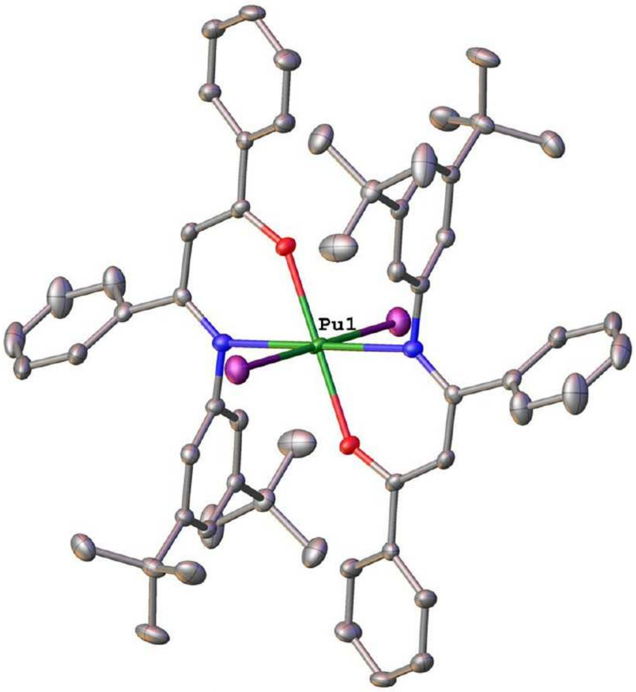


Figure 11. Projection of $PuI_2(^{Ar}acnac)_2$, model shown as a ball and stick projection, lacking hydrogens for clarity. The carbon atoms are depicted in gray, the oxygen atoms red, the nitrogen atoms blue, the iodine atoms as purple and the central plutonium atom is in green.[110,142]

In general, soft donors are preferred for separation purposes, yet with the data reported to the CCDC, hard donors appear favored for the isolation of single crystals suitable for X-ray diffraction. One reason for the lack of plutonium-containing structures deposited into the CCDC is the lack of readily available starting materials. This is complicated by the fact that materials must be carefully handled and that plutonium can have up to five oxidation states in aqueous solutions. Thus, preparing solutions containing ions in a single oxidation state for use in metal complexations requires additional preparation.

CONCLUSIONS

In the continued pursuit of an improved closed nuclear fuel cycle, many concerns regarding the safe recycling or recovery of fissionable materials remain. These concerns and a persistent need to protect ourselves and our environment from radioactive materials containing actinides will require that additional research in many areas continue, including not only separations and analytical chemistry but also fundamental coordination chemistry to define what parameters can be used to optimize separations. Although some of the systems currently in place are quite mature, there is still room for the development of new separation technologies and new fundamental discoveries. Inorganic coordination chemistry with the 4*f* and 5*f* elements allows for not only the support of such new systems but also an improved understanding of their fundamental chemistry, relativistic effects, and the differences between the chemical behavior of the 4*f* and 5*f* orbitals. The relatively small amount of structural data available (especially compared to many of the first-row transition-metal elements) hinders the ability to adequately evaluate computational methods and characterizations. New models will be required to continue to probe and elucidate the chemistry and environmental behavior of these important elements.

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Notes

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DEDICATION

†The authors dedicate this manuscript to Professor Kenneth N. Raymond on the occasion of his 70th birthday.

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