FINAL REPORT
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Rational Design of Metal Ion Sequestering Agents

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Executive Summary

Purpose

The technical achievement of producing deterrent nuclear weapons in the Cold War era left large amounts of radioactive and toxic wastes for a future, terminal disposal. Ultimately a geological repository will hold radioactive and transuranic waste, but the enormous liquid volume of the present waste requires separation, volume reduction and transformation into suitable waste forms. For environmental, safety and economic reasons, and because of the complexity and lengthy timeframe for resolving the waste issues, the Department of Energy has embarked on a program of basic science for application to the various waste problems.

The purpose of this project has been to study the fundamental coordination chemistry of the actinides, uranium, thorium, plutonium and americium, and the non-radioactive analogues, cerium, iron, neodymium, and gadolinium, used as actinide models. Using a biomimetic approach we have developed sequestering agents that selectively and strongly bind the actinides. We have determined the solid state structures and metal binding constants of the newly developed compounds with the metals mentioned above. The results of our studies indicate trends in the properties of the sequestering agents that allow us to appropriate certain compounds to the specific binding of certain metals under suitable conditions. The further development of these molecules includes structural refinements or the modification of polymers that can then be applied to waste processing, waste separations, chemical sensing, metal sequestration and other waste disposal projects.

Project Accomplishments

We have finished synthetic procedures and preliminary metal coordination studies with the dihydroxybenzenesulfonamides, a new class of ligands described in this report. A crystal structure of the iron(III)-sulfonamide complex has been elucidated. Metal binding constants for this class of ligand with iron, uranium, and thorium have been determined and indicate properties similar to the known compound Tiron.

We have determined the crystallographic structures of two thorium complexes with dihydroxyterephthalamide ligands. Also studied was the solution thermodynamic properties of these ligands with thorium.

Also synthesized were solid-phase polymers with hydroxypyridinone ligands. These functionalized polymers were studied for their plutonium sequestration capability.

In collaboration with researchers at Los Alamos National Laboratory, we have synthesized water-soluble chelating polymers that are effective in removing plutonium from dilute waste streams.

Also studied was a series of dihydroxyterephthalamide compounds as liquid-liquid extraction agents for the actinides. The synthesis and extraction efficiency of these compounds was investigated using iron(III), a model for plutonium(IV).

Relevance, Impact and Technology Transfer

We have synthesized solid-phase and water-soluble resins for actinide (especially plutonium) sequestering. LANL would like kilogram amounts of one of these water soluble polymers, “PDT” (Section on Plutonium, Part 2, WSCP) for pilot plant testing. Liquid-liquid extractant agents synthesized in this project will be evaluated for plutonium extracting abilities in future studies. We are preparing a patent on dihydroxysulfonamides for metal sequestering applications.

Our development of liquid-liquid extraction agents has drawn the attention of Dr. Bruce Moyer of Oak Ridge National Laboratory. We have formed a collaboration and submitted a proposal to test our ligands with simulated and actual tank wastes from the Savanna River Site.

Collaborations

We have ongoing collaborations with actinide researchers at other National Laboratories:

- Dr. Patricia W. Durbin, Lawrence Berkeley National Laboratory. "Biological Evaluation of New Actinide Chelating Agents"
- Dr. Glen E. Fryxell, Pacific Northwest National Laboratory. "Actinide-Specific Interfacial Chemistry of Monolayer Coasted Mesoporous Ceramics"
- Dr. Ben Hay, Pacific Northwest National Laboratory. "Architectural Design Criteria for f-Block Metal Sequestration Agents"
- Drs. Gordon D. Jarvinen and Barbara Smith, Los Alamos National Laboratory. "Water Soluble Polymer Supported Chelators"

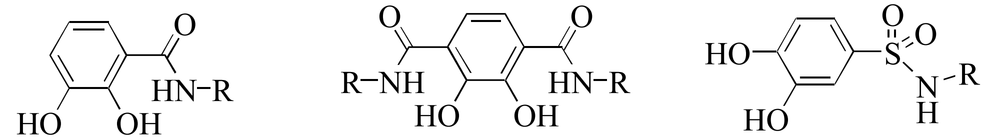
Research Objectives

The discriminate bonding of metal ions is a challenge to the synthetic chemist and a phenomenon of considerable practical importance.[1] An important feature of many technical applications is the specific or preferential binding of a single metal ion in the presence of many metals. Examples range from large-volume uses (e.g. ferric EDTA as a plant food, calcium complexing agents as water softeners or anticaking formulations) to very high technology applications (technetium complexation in radiopharmaceuticals, synthetic metalloenzymes). We are interested in efficient and discriminate binding of actinides for waste stream remediation.

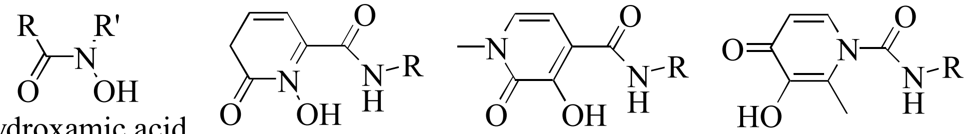
Actinides represent a major and long-lived contaminant in nuclear waste. While the separation of actinides from other radioactive components of waste, such as Sr and Cs, is relatively well established, the separation of actinides from each other and in complex solutions (e.g. those found in tank wastes) is not as well resolved. The challenge of designing metal-specific (actinide) ligands is facilitated by examples from nature. Bacteria synthesize Fe(III)-specific ligands, called siderophores, to sequester Fe(III) from the environment and return it to the cell. The similarities between Fe(III) and Pu(IV) (their charge-to-size ratios and acidity), make the siderophores prototypical for designing actinide-specific ligands.

The chelating groups present in siderophores are usually hydroxamic acids and catecholamides. We have developed derivatives of these natural products which have improved properties. The catechol derivatives are the 2,3-dihydroxyterephthalamides (TAMs), and 3,4-dihydroxysulfonamides (SFAMs), and the hydroxamic acid derivatives are three isomers of hydroxypyridinones, 1,2-HOPO, 3,2-HOPO, and 3,4-HOPO. All of these ligands are attached to molecular backbones by amides and a very important feature of HOPO and CAM ligands is a strong hydrogen bonds formed between the amide proton and the adjacent phenolic oxygen in the metal complex, thereby enhancing the stability (Figure 1).

Ligand Scheme


Catecholamide (CAM) Terephthalamide (TAM) Sulfonamide(SFAM)

Catecholates


Hydroxamic acid 1,2-HOPO 3,2-Me-HOPO 3,4-HOPO

Hydroxypyridinones (HOPO)

Metal-binding Motif

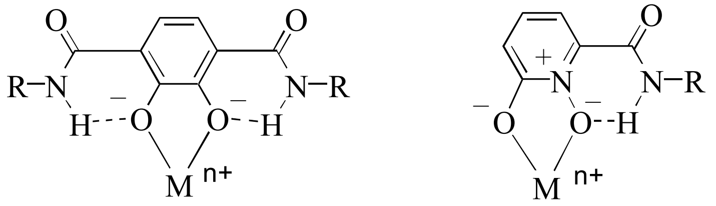


Figure 1. Generic structures of the ligands studied in this project as actinide sequestering agents; the prototypes are catecholate and hydroxamic acid natural products. With amido groups meta to phenolic oxygen atoms, a hydrogen-bond formed between the amide and catecholate oxygen enhances the stability of the resulting metal complex.

Summary Objectives and Key Results

This project addresses fundamental issues and requirements in developing hazardous metal ion separation technologies needed in the treatment and disposal of radioactive and chemical toxic waste. It encompasses the synthesis of new agents, followed by their characterization and evaluation, with the aim of optimizing their metal ion sequestering properties for use in applied technologies.

The research is focused on the following key areas:

1) basic design and synthesis of new metal ion specific sequestering ligands;
2) structural and thermodynamic investigations of these ligands and their complexes formed with the targeted metal ions – determination of stability constants and crystallization of the metal complexes;
3) development of sequestering agents and their incorporation into systems designed to be prototypes of inexpensive and highly effective materials for hazardous metal ion decontamination – solvent extraction studies, development of solid phase extractants, and investigation of water soluble chelating polymers.

Based on our studies, we anticipate that these new materials can be applied to the remediation of very dilute waste streams, separations in nonaqueous systems, and improvement of current separations technology in systems of basic aqueous (caustic) media.

Key recent results:

We have:
1) Synthesized a new class of multidentate ligands, the 3,4-dihydroxysulfonamides, which have nearly identical stability constants to Tiron, an inexpensive and powerful bidentate chelator that is highly charged and can only be used in aqueous solution.
2) Developed new solid phase metal chelating polymers which show excellent uptake of Pu(IV).
3) Developed, in collaboration with researchers at Los Alamos National Lab, 7 derivatives of water-soluble chelating polymers to be used in their polymer filtration process for the removal of dilute concentrations of Pu(IV) from waste streams.
4) Studied the fundamental coordination chemistry, through X-ray crystallography and stability constant determination, of actinides and actinide analogs (Fe, Zr, Ce, Th, UO_2^{2+}.) with dihydroxyterephalamides, dihydroxysulfonamides, and HOPOs.
5) Developed new liquid-liquid extraction agents.

Methods and Results

A. New Ligand Development – 3,4-Dihydroxysulfonamides

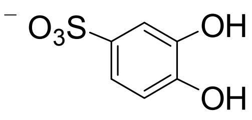
We have developed a new class of ligands, catechol sulfonamides (Figure 2), inspired by the sulfonated catecholates. The ligand Tiron (4,5-dihydroxy-1,3-benzenedisulfonic acid) has long been known as an excellent chelator for high oxidation state metals. However, this ligand is limited in its practical applications as it is only soluble in water and a bidentate chelator. We have chosen to investigate sulfonamide derivatives to take advantage of the excellent chelating properties and to provide a point of attachment for incorporation into an extractant scaffold. A 3-step synthesis was developed that installs a single sulfonamide in the 4-position of the catecholate ring. Ten sulfonamide bi- tetra- or hexadentate ligands have been synthesized.

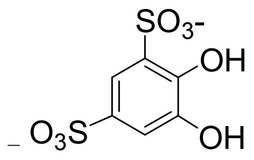
tiron

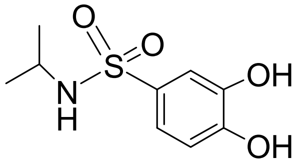
Generic sulfonamide

Figure 2. Tiron is an excellent chelator of Fe(III) and other high oxidation state metals. The dihydroxysulfonamide variant (right) has been investigated as a potential chelator in practical separation technologies.

The focus of this project is actinide waste remediation and accordingly we would like to study Pu(IV) or a M^{4+} analog as frequently as possible. However, the amount of heavy-metal or radioactive waste that could be generated by these studies prompts us to begin with Fe(III), a reasonable model for Pu(IV). Thus, protonation constants and Fe(III) stability constants were determined for N-*i*-propyl-3,4-dihydroxybenzenesulfonamide (*i*-PrSFAM) (Table 1). These numbers are summarized in the table below and the constants for Tiron and mono-sulfonated catechol are included for comparison.







		Tiron	*i*-PrSFAM
log K_{a1}	12.5	12.0	11.9
log K_{a2}	8.4	8.3	7.6
log K_{110}[a]	17.0	20.4	19.21
log K_{120}[a]	14.0	15.1	14.16
log K_{130}[a]	9.1	10.8	9.96
log β_{130}[b]	40.1	46.3	43.33
pM[c]	13.74	20.67	19.48

[a] Equilibrium constants with Fe(III). [b] $\beta_n = [ML_n] / [M^{n+}] [L^{2-}]^n$

[c] pM = -log $[M^{n+}]$ at pH 7.4, $[M^{n+}]$ = 0.1 mM, [L] = 1.0 mM.

Table 1. The protonation and Fe(III) stability constants of N-isopropyl, tiron and mono-sulfonated catechol are shown for comparison.

Examination of the pK_a values for *i*-PrSFAM, a typical sulfonamide, reveals the remarkable fact that the addition of *one* sulfonamide group to the catechol ring has a greater electron withdrawing effect on the catecholate protons than *two* sulfonate groups. However, this trend is not mirrored in a higher Fe(III) formation constant—the stability of the sulfonamide iron complex is intermediate between the two other ligands. We use Fe(III) as a preliminary model for studying Pu(IV). Still, this ligand is exceptional in its metal-binding ability. Since *i*-PrSFAM has higher formation constants with Fe(III) than the sulfonated catechol, we expect that bis-sulfonamides will have Fe(III) formation constants that are higher than the Fe(III) complex of Tiron.

B. Plutonium(IV) Background

For some time we have pursued a rational approach to the synthesis of actinide-specific sequestering agents that is based on siderophores. Some of the first indications that these ligands would be effective Pu(IV) chelating agents came from studies of Pu(IV) decorporation from mice.[2-5] Eight of the HOPO ligands studied promoted significantly more Pu excretion than an equal molar amount of $CaNa_3$-DTPA (the compound in present clinical use). For the three most promising compounds, there is no acute toxicity seen up to the highest dose administered, which was 1000 L mol/kg. They are promising therapeutic agents and also promising precursors for extraction agents as will be described.

To address the application of these types of ligands for plutonium waste remediation agents, we prepared agents for use as liquid/liquid extractants and tested them for their efficiency.[6] This research described an extracting agent, 1-hydroxy-6-N-octylcarboxamide-2(1H)-pyridinone (octyl-1,2-HOPO), which shows high specificity for Pu(IV) over a range of conditions. This work was initially performed under an ESP supported project and extended to the solid phase plutonium sequestering agents (described below) under this EMSP project.

Recent Pu (IV) Results.

1. Solid Supported Extractants.

The use of HOPO ligands as extraction agents was extended to solid-supported extractants. In collaboration with Dr. Darleane Hoffman's group at Lawrence Livermore National Laboratory, HOPO and CAM ligands were incorporated into solid phase sequestering agents and tested for Pu(IV) uptake from simulated waste streams.[7] Eleven polystyrene divinylbenzene resins were prepared by appending one of four ligands using a variety of linkers. The alkyl linkers varied in length from 0 to 6 carbons, which may result in bidentate or tetradentate coordination of the metal. Also, a diamine linker (dien) was examined that allowed two ligands to be in close proximity to ensure tetradentate chelation of the plutonium (Figure 3).

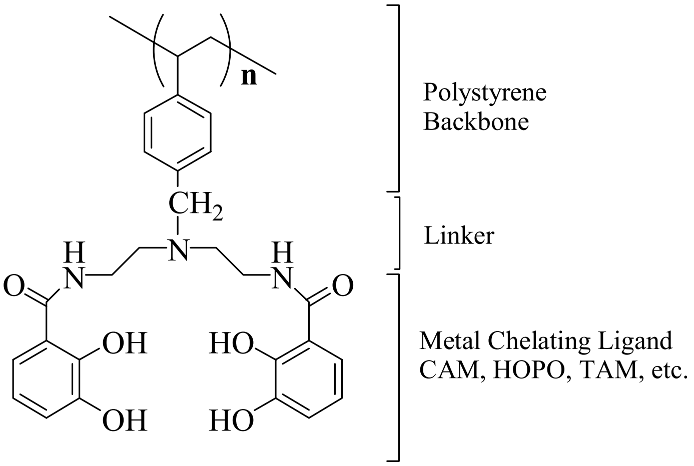


Figure 3. Functionalized polystyrene resins are efficient at Pu(IV) extraction under a variety of conditions.

In general, we found that all of these resins display fast kinetics of plutonium uptake and are very effective at sequestering plutonium in highly acidic solutions such as 2M HNO_3, in high ionic strength conditions such as 5M $NaNO_3$, in the presence of competing metals such as Fe(III), and in the presence of competing ligands such as EDTA. All of the resins show good chemical stability towards acid and base and have loading capacities of 70 to 90%. In addition, no dependence of the linker length was observed: a few octadentate ligands that were prepared did not show any improved uptake of Pu(IV) over the tetradentate ligands. A brief summary on the extraction results for the uptake of plutonium for 1,2-HOPO Dien resins follows:

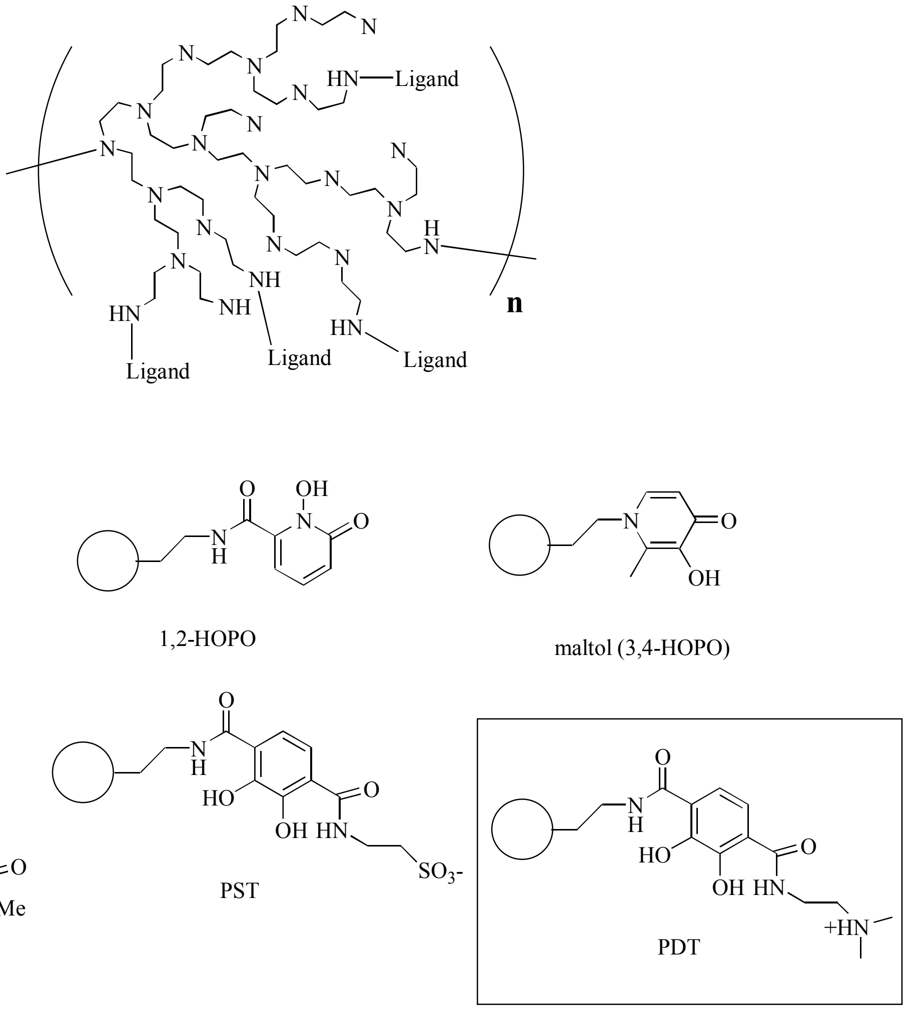
- Both Pu(IV) and Pu(VI) are extracted from aqueous solutions.
- Pu(IV) and Pu(VI) are extracted from acidic solutions at pH = 1. The extraction of Pu(VI) was slightly lower than that for Pu(IV) in the lower pH range.
- 90% of the Pu(IV) is selectively extracted from solutions containing a one thousand fold excess of Fe(III) at pH = l.
- Greater than 58% of the Pu(IV) is extracted from solutions containing up to a ten thousand fold excess of Fe(III) at pH = 1.
- Pu(IV) is extracted nearly quantitatively from aqueous solutions containing several hundred fold excesses of EDTA.

2. Water-Soluble Chelating Polymers

The removal of actinides from waste streams presents challenging separation problems due to the complex and unique mixture of radioactive and non-radioactive components each stream contains. The classical approaches to separating actinide ions from solutions involve liquid-liquid extraction, ion exchange resins, or solid-supported chelators. Although, many advances have been made in the development of new extractants, ion exchange materials, and ligands for solid supports, any one of these techniques has the disadvantages of slow kinetics and mixed waste or colloid formation, and none are ideal for the removal or concentration of dilute amounts of radionuclides. Thus new approaches to waste stream remediation are required that can function in ways older techniques are not suited for.

In collaboration with Drs. Gordon Jarvinen, Barbara Smith, Norman Schroeder, and Tom Robison at Los Alamos National Lab, we are investigating Polymer filtration (PF) and water soluble chelating polymers (WSCP) used in combination as a very effective way to remove and concentrate Pu(IV) from dilute waste streams. The metal ion separation is accomplished with a molecular weight cutoff membrane that retains the WSCP with bound Pu(IV) while the smaller unbound molecules and ions pass through the membrane as the permeate. The scaffold for the WSCP is polyethyleneimine (PEI), a water soluble polymer with a molecular weight of at least 30,000 (Figure 4).

We are investigating TAM derivatives as the chelating agent for several reasons. First, the TAMs were chosen for the expected selectivity for Pu(IV) over trivalent metals such as Am(III) and Fe(III). Second, the TAMs are completely oxidizable. The most commonly used WSCP at LANL has phosphoric acid binding groups which, upon oxidation produce phosphates that interfere with glass waste forms and Pu-purification ion exchange columns. Finally, the second amide group allows us to install functional groups that can improve the solubility of the WSCP in water throughout the pH range. The previously examined HOPO derivatives had problems with solubility in certain pH ranges.



Me-3,2-HOPO

1,2-HOPO

maltol (3,4-HOPO)

TAM

PST

PDT

Figure 4. PEI, the scaffold for WSCP, is a highly branched water-soluble polymer of MW > 30,000 that permits the attachment of ligands at the primary amines. Shown are the six derivatives that were made, which incorporate our actinide-specific ligands. PDT (in the box) was the most promising and is discussed in detail.

Thus far, maltol, two HOPO ligands, and three TAM ligands have been incorporated into a WSCP. Our experiments show that HOPO-WSCP materials are excellent chelators for Am(III) and Pu(IV): at pH ~ 2 the K_d values are approximately 10^6. However, these materials do not discriminate between Am(III) and Pu(IV) and the polymer precipitates above pH 3.

One TAM derivative, PEI-dimethylaminoethylene-TAM (PDT), is the most promising WSCP thus far because it is soluble throughout a large pH range, shows strong discrimination for Pu(IV) over Fe(III) and Am(III), and competes against other complexing agents such as EDTA. The results discussed below were all obtained with PDT and the Pu(IV) concentration was approximately 10^{-8} M.

Pu(IV) Extraction. For Pu(IV) uptake, the K_d values at the highest is 4.8x10^{6} at pH 11.4 (99.8% extraction), 1.3x10^{6} at pH 4.5 (99.3% extraction) where the biggest jump occurs, and 1x10^{5} at pH 2.9 (91.1% extraction), a low pH value that still exhibits strong uptake (Figure 5).

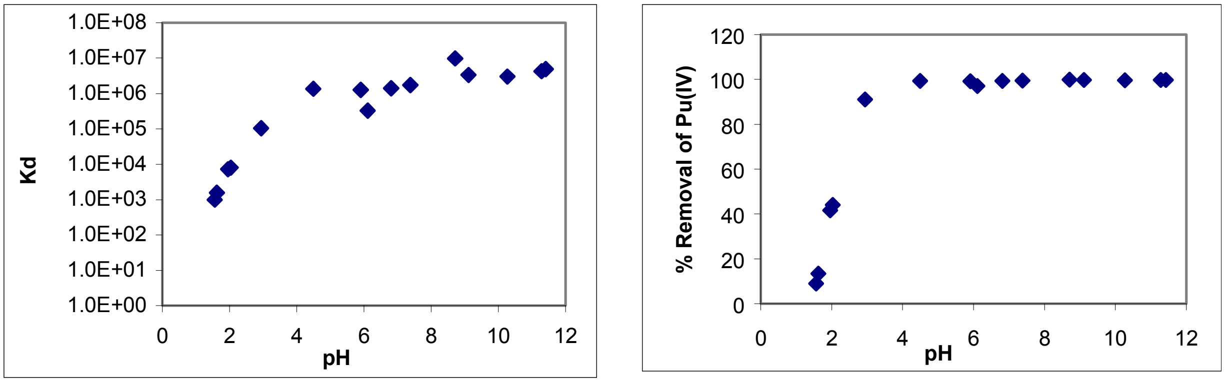


Figure 5. The graph on the left is a plot of Kd vs. pH for the uptake of Pu(IV) by PDT. The same data are plotted as % extraction vs. pH on the right.

Pu(IV) versus Am(III). The selectivity of TAMs for higher oxidation state metals is seen by comparing these results to the Am(III) uptake results (Figure 6). Again, the distribution coefficients increase with increasing pH, however this happens between pH 7 and 9. The distribution coefficient at pH 10.9 is 2.1x10^{6} (99.5% extraction), comparable with Pu(IV), and the biggest difference between the two metals is seen at pH 4.5 where K_d is 1.6x10^{3} for Am(III) (14% extraction) and 1.3x10^{6} for Pu(IV) (99.3% extraction).

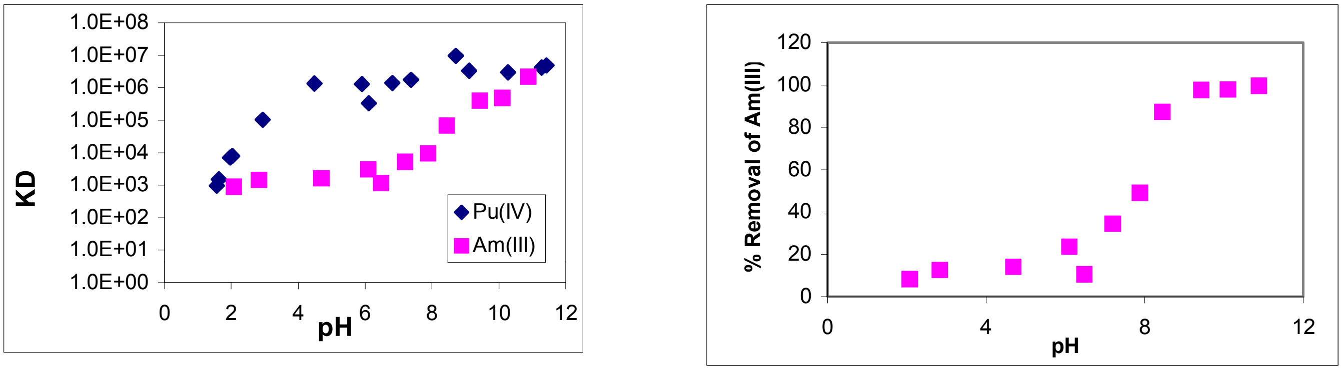


Figure 6. A comparision of Am(III) (pink squares) and Pu(IV) (blue diamonds) uptake by PDT is shown in the plot of Kd vs. pH on the left. The relation of Kd to % uptake for Am(III) is shown in the plot on the right.

Competition with Fe(III) or EDTA. To examine the effect of competing metals or ligands on the efficacy of Pu(IV) uptake by PDT, EDTA and Fe(III)competition experiments were conducted with an excess (2.5 mM) of these species (Figure 7). The graphs from both of these experiments show that neither one significantly interfered with the uptake of Pu(IV). The competition with Fe(III)shows that K_d is decreased slightly, however it still represents over 99% uptake of Pu(IV)

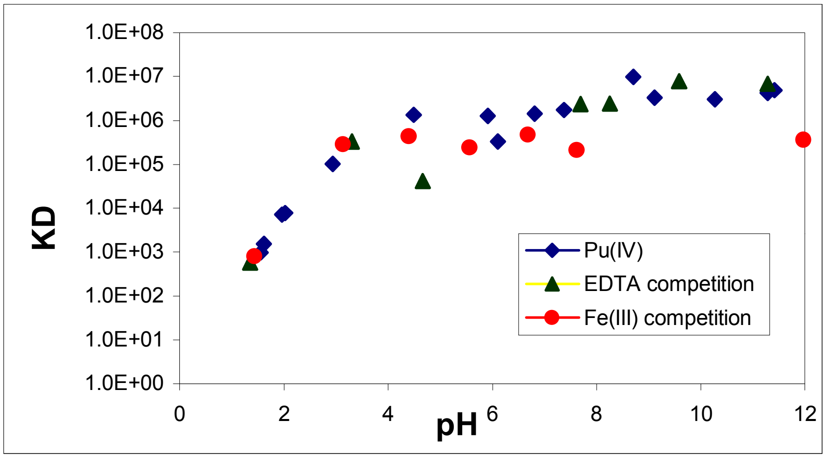


Figure 7. The uptake of Pu(IV) is not affected by the presence of 2.5 mM EDTA (green triangles) or Fe(III) (red circles).

Pu(IV) desorption from surfaces. Pu is known to form a soluble polymer in basic solutions and to adsorb to glass surfaces. An experiment was conducted to see if PDT could solubilize this adsorbed Pu. This was done by adding Pu(IV) to two basic solutions of 0.1M $NaNO_3$ and counting the radioactivity of the feed solutions at regular intervals. As expected, the radioactivity of the solution decreased with time as the Pu(IV) adsorbed to the glass surfaces. After four hours PDT was added to one of the solutions and the activity of the feed solution slowly recovered to normal counts after 2 days (Figure 8). This experiment indicated that the TAM ligands can solubilize Pu(IV) that had adsorbed to a glass surface.

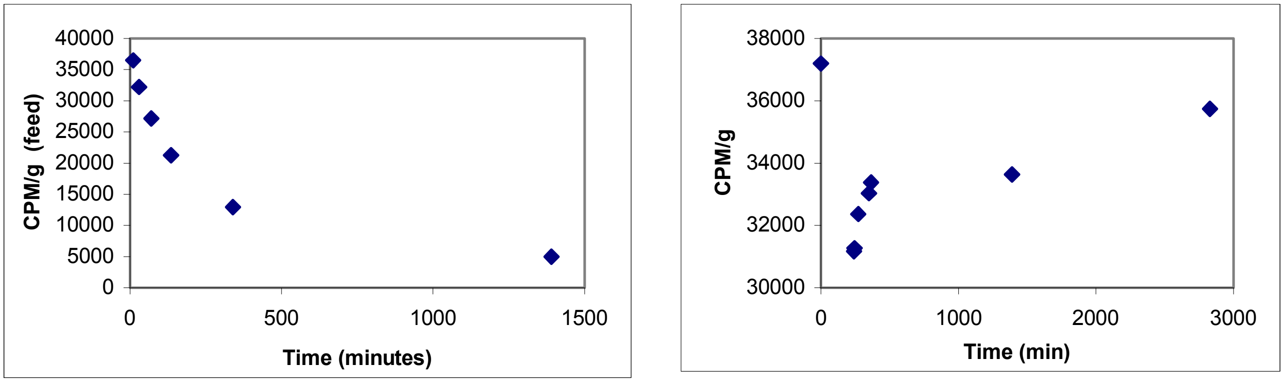


Figure 8. The graph on the left shows the decrease of cpm over time of a basic Pu(IV) solution as the Pu(IV) adsorbs to the glass surfaces. The graph on the right illustrates that TAMs can solubilize Pu(IV) that has adsorbed on a glass surface by the recovery of the cpm when PDT is added after four hours.

In conclusion, PDT has been shown to be an excellent derivative of PEI for use in PF system for the removal of dilute concentrations of Pu(IV) from simulated waste streams. Currently, PDT is being synthesized on a large scale for pilot plant testing of Pu(IV) removal from LANL waste streams.

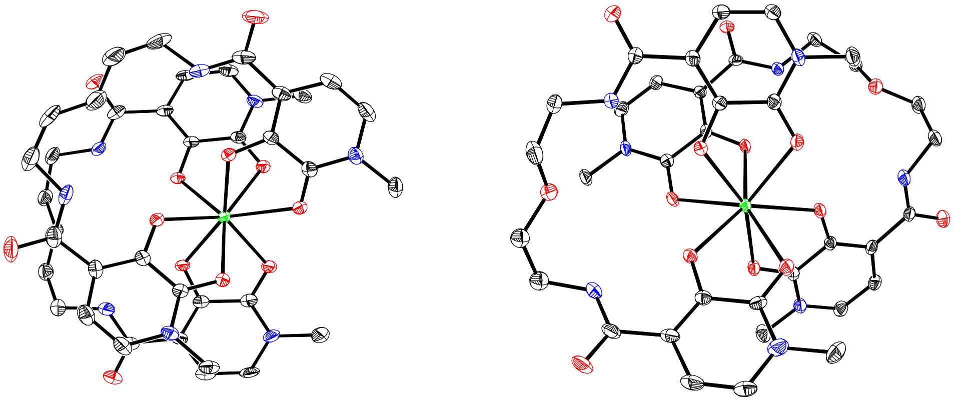
C. Cerium(IV) background.

The similarities between Fe(III) and Pu(IV) were used initially to design ligands for Pu(IV) sequestering and decorporation agents. However, for more direct molecular-level studies it is advantageous to have a non-radioactive metal cation that has a similar size and coordination number to Pu(IV). The identical charges, nearly equal radii, and similar solution chemistry of Ce(IV) and Pu(IV) make the former ion an excellent model for the latter. Ce(IV) offers a special advantage in modeling Pu(IV) complexation because of its electrochemistry which allows one to determine even very large formation constants for Ce(IV) complexes from those of the corresponding Ce(III) complexes and the redox potentials of the Ce(IV)/Ce(III) pairs. Earlier work investigated the catecholato and tironato complexes of cerium(IV),[8,9] and supports Ce(IV) as a model of Pu(IV) coordination.

Recent Ce(IV) Results.

The Ce(IV) complexes of previously synthesized bi-, tetra-, hexa-, and octadentate ligands incorporating 1,2- and Me-3,2-hydroxypyridinone (1,2-HOPO, Me-3,2-HOPO) groups were characterized by solid state structures and by solution thermodynamic studies. [10] Electrochemical measurements of the Ce(III)/(IV) redox couple allow for the determination of even very large formation constants for the Ce(IV) complexes versus the corresponding Ce(III) complexes. In all cases, the formal potential for Ce(IV)/Ce(III) saturated complexes was approximately 1.6 V lower than the formal potential for the aqueous Ce(IV)/Ce(III) pair (+ 1.7 V vs. NHE), meaning that the Ce(IV) tetra- Me-3,2-HOPO complexes on average have stability constants of 10^{47}.[10] Calculation of the pM values at select pH values imply that HOPO ligands are able to bind Pu(IV) strongly even at very low pH. Additionally, the experimental results of Pu(IV) sequestering by HOPO ligands discussed above substantiate the claim that Ce(IV) is a good model for Pu(IV).

The structures of three Ce(IV)-Me-3,2-HOPO complexes were determined by single crystal X-ray diffraction studies (Figure 9). Least-squares shape analysis of these 8-coordinate complexes demonstrated that subtle changes in the ligand backbone can vary the coordination polyhedron from nearly a trigonal dodecahedron to nearly a square antiprism. This conformational flexibility implies that the central ion has no preference towards a specific coordination geometry. One additional deduction from our study is that simple (bidentate) HOPO fragments attached by a small linker, or on polymer support may also act as effective sequestering agents. This hypothesis is corroborated by the similar formal potentials of all Ce(IV)/Ce(III) pairs (see preceding paragraph) and by tests of polystyrene-supported 1,2-HOPO ligands with Pu(IV) conducted at LLNL.[6,7]



Crystal structure of Ce(L^5)$_2$ **Crystal structure of Ce(L^6)$_2$**

Figure 9. The solid state structures of two Ce-HOPO complexes.

D. Thorium(IV) background

We have also investigated Th(IV) as a model of Pu(IV). Ce(IV) coordination chemistry can often be complicated by redox chemistry. Thus, direct titrations of our ligands to determine stability constants with Ce(IV) cannot be done. However, Th(IV) can be directly titrated with our ligands to determine stability constants. One caveat is that Th(IV) has a larger ionic radius (hence a lower charge density) that manifests itself in lower overall stability constants than those expected for Pu(IV).

Recent Th(IV) Results

The crystal structures and stability constants of Th(IV) with simple TAM and HOPO ligands have been determined.

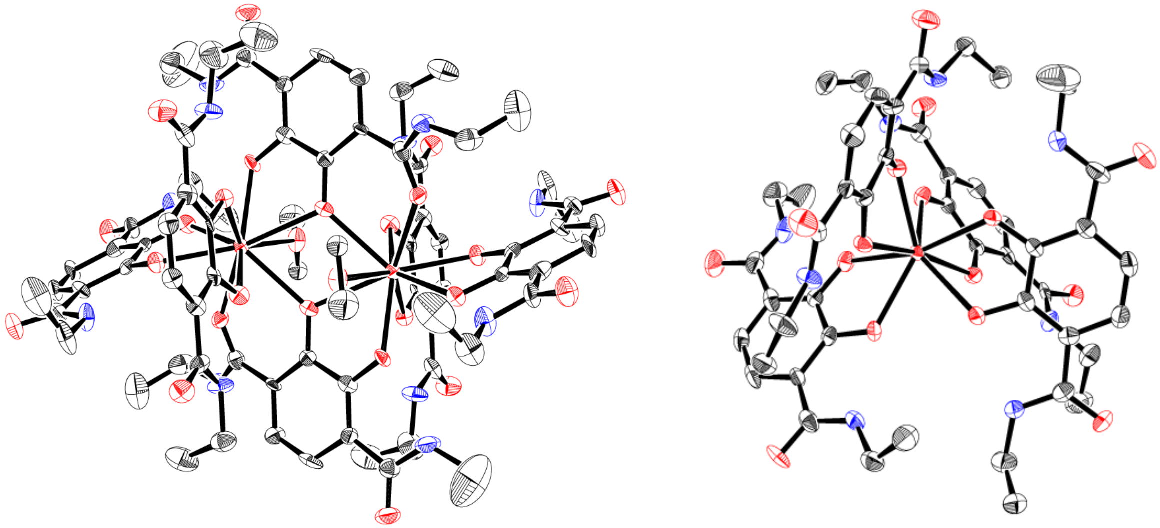
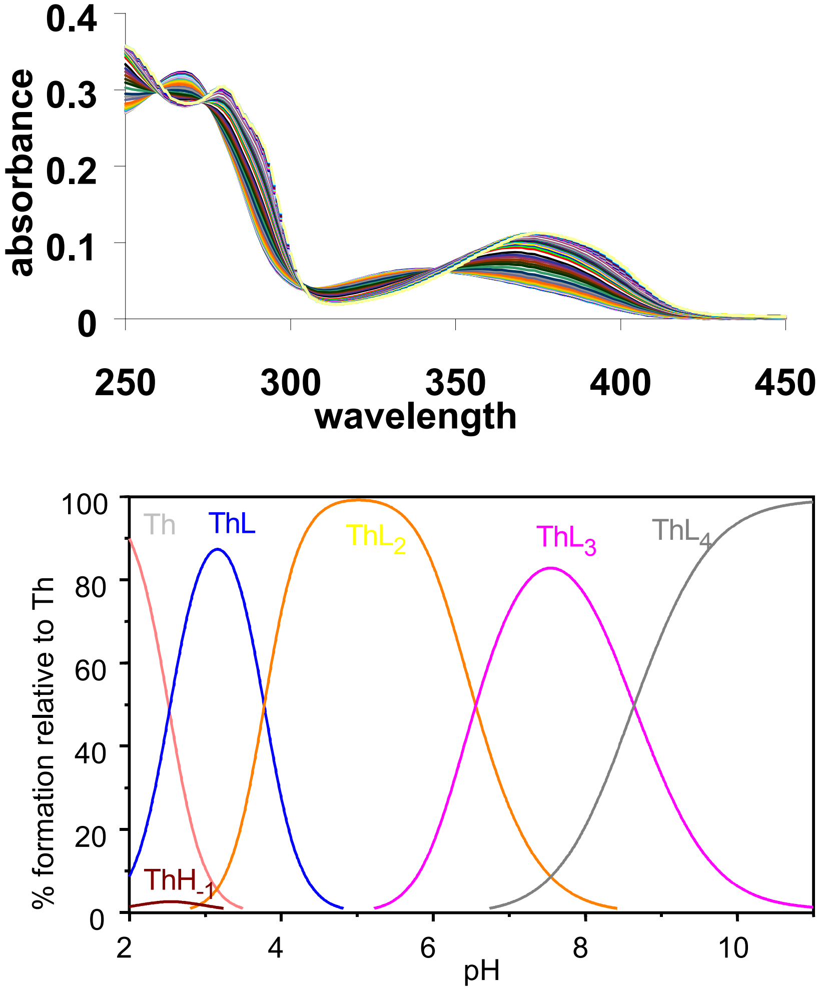


Figure 10. Two x-ray crystal structures were obtained for Th(IV) with a TAM. On the left is a $Th_2[TAM]_6$ dimer in which the Th(IV) is 9 coordinate. On the right is a discrete $Th[TAM]_4$ complex in which the Th(IV) is 8 coordinate.

Th-TAMs. For the ligand ethyl-TAM, two different structures were obtained (Figure 10). One is the expected coordination of 4 TAMs to the Th(IV) to produce an 8-coordinate structure with bicapped-trigonal prismatic geometry. The second structure was obtained when the synthesis of the metal complex was performed under slightly different conditions. The resulting complex is a Th_2TAM_3 dimer. The coordination around the Th(IV) consists of two TAM units bound in the expected catecholate fashion. The third TAM also binds with its catecholate oxygen atoms, however one of the catecholate oxygen atoms bridges to the second Th(IV). The amide that is ortho to this phenol is rotated 180^o and oriented such that the amide oxygen binds to the second Th(IV) in a *salicylate* mode (refer to Figure 1 for a schematic of this hydrogen bond). In this case, the bridging TAM exhibits both orientations of the amide. In total, each Th(IV) is coordinated by 5 phenolic oxygen atoms, 2 bridging phenolic oxygen atoms, one amide oxygen, and one MeOH, for a total coordination number of 9. These two structure indicated to us that Th(IV) can fluctuate between 8 and 9 coordinate and that the hydrogen bond (which gives approximately 1.2 kcal/mol of extra stability) can be broken to provide for a ninth coordinating atom to the Th(IV).

The stability constants for ethylTAM with Th(IV) were determined by monitoring the changes in the UV-Vis spectrum as a function of pH (Figure 11). The data was fit to a model of successive addition of ligands to the metal center (ML, ML_2, ML_3, ML_4) and no mixed ligand-hydroxide species were observed. The overall formation constant (β140) for the $Th(TAM)_4$ complex is $10^{42.3}$. This value is approximately the same as the formation constant for the $Fe(TAM)_3$ complex, which is indicative of the role of charge density in the formation constants. Thus, it is expected that the formation constant for the Pu(TAM)$_4$ complex will be higher than those of the Th(IV) complex. However, this is still a strong Th(IV) chelator. The speciation diagram indicates that the complex fully forms around pH 10, and this ligand also prevents the hydrolysis of Th(IV).



Log K_{MLH}

$K_{110} = 15.2$

$K_{120} = 12.8$

$K_{130} = 8.2$

$K_{140} = 6.1$

$\beta_{140} = 42.3$

Figure 11. Stepwise stability constants for Th(IV) with TAM ligands were determined by spectrophotometric titration and the overall formation constant is $10^{42.3}$. Sample spectra from the titration are shown above and a speciation diagram (calculated for 10^{-4} M Ligand and 10^{-5} M Th(IV)) is shown below.

Th-HOPOs. The formation constants for the Th(IV)/N-Pr-3,2-HOPO complexes were determined by spectrophotometric titration (Table 2) and the results are listed along with the similar 1,2-HOPO and 3,4-HOPO complexes.

The spectra were fit using the following model:

$$\mathrm{Th(L^2)_3^+} + \mathrm{HL} \leftrightarrow \mathrm{Th(L^2)_4} + \mathrm{H^+}$$
$$\mathrm{Th(L^2)_4} + \mathrm{OH^-} \leftrightarrow \mathrm{Th(OH)\,(L^2)_3} + \mathrm{L^-}$$
$$\mathrm{Th(OH)\,(L^2)_3} + \mathrm{OH^-} \leftrightarrow \mathrm{Th(OH)_2(L^2)_2} + \mathrm{L^-}$$
$$\mathrm{Th(OH)_2(L^2)_2} + \mathrm{2OH^-} \leftrightarrow \mathrm{Th(OH)_4} + \mathrm{2(L^2)^-}$$

The formation constant log β_{140} for the 8-coordinate complex ThL_4, 38.3, is intermediate between the formation constants of the 8-coordinate complexes of the 1,2-HOPO derivative (36.0) and the 3,4-HOPO derivative (41.8) indicating that the stability of these complexes follows the acidity of the ligand and is mainly electrostatic interaction between the positive Th(IV) ion and the negatively charged ligands. Sterics and more covalent types of bonding are less important or not present in the complexes as would be expect from a closed d-shell ion like Th(IV). The speciation as a function of pH was calculated to illustrate the differences between the 3 ligands with respect to their acidity (Figure 12).

Complex	xyz	log β_{xyz}
Th/PR-1,2-HOPO	140	36.0(3)
	13-1	24.9(2)
	12-2	12.1(2)
Th/PR-3,4-HOPO-N	140	41.8(5)
	130	35.8(2)
	120	25.0(8)
	110	13.5(2)
Th/PR-3,2-HOPO	140	38.3(3)
	130	31.9(3)
	13-1	26.6(2)
	12-2	13.3(2)

Table 2 Formation Constants for the Th(IV) – HOPO complexes

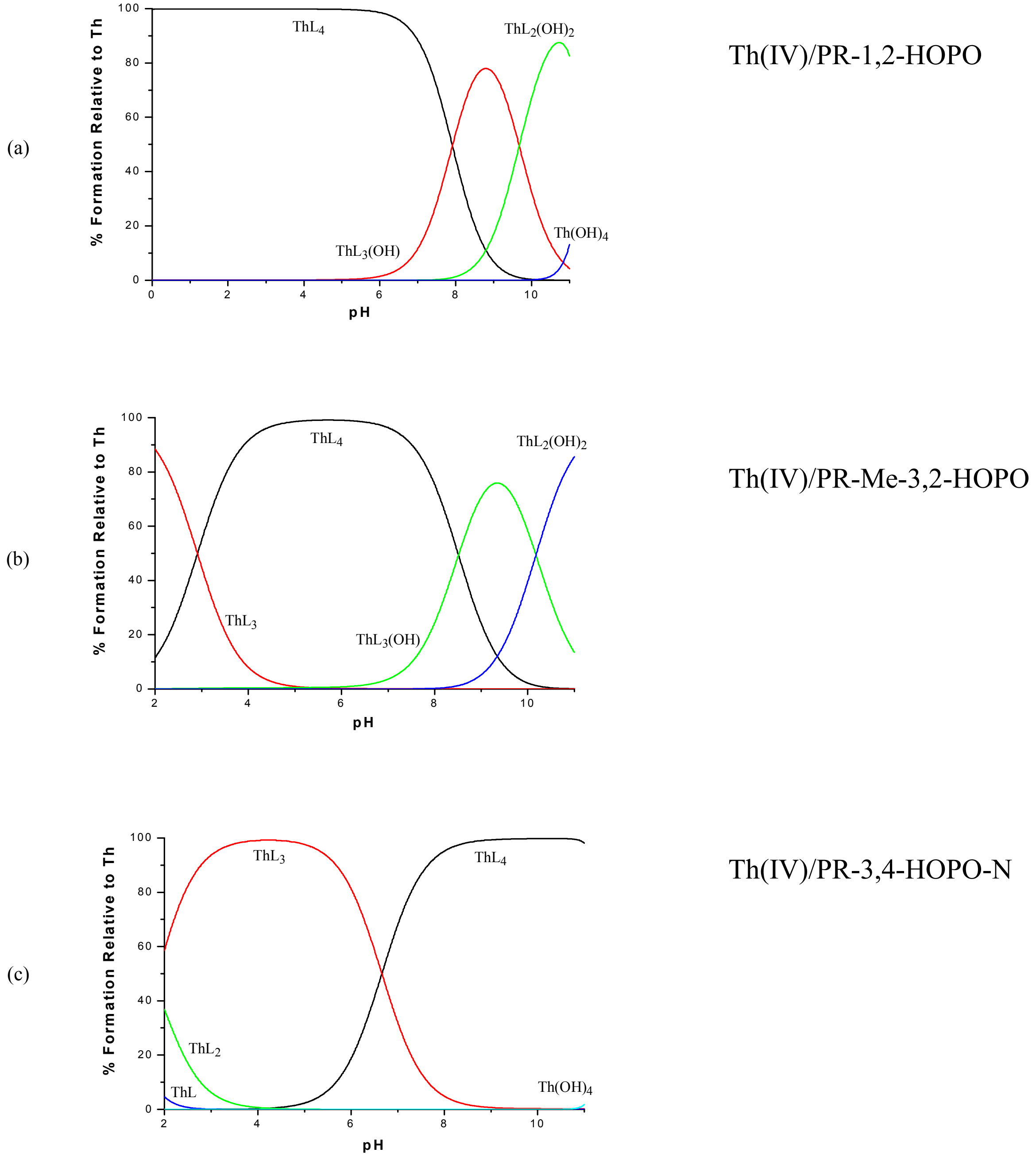


Figure 12. Species distribution of (a). Th(IV)/PR-1,2-HOPO, (b) Th(IV)/PR-Me-3,2-HOPO and (c) Th(IV)/PR-3,4-HOPO-N system for solutions containing 1 x 10^{-4} M Th^{4+} and 1 x 10^{-3} M ligands.

In the crystal structure of Th(IV)PR-Me-3,2-HOPO each thorium atom is nine coordinate with eight oxygen donors from the four PR-Me-3,2-HOPO ligands, and one amide oxygen donor from one of the PR-Me-3,2-HOPO ligands of the adjacent thorium complex. A structural diagram (ORTEP) of this compound is shown in Figure 13. The coordination polyhedron in the crystal structure of Th(L^4)$_4$·H_2O was assigned to be best described as a moncapped square-antiprism.

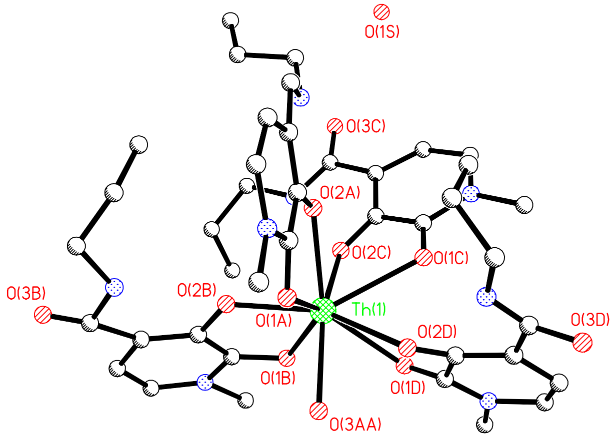


Figure 13. ORTEP of Th(IV)(PR-Me-3,2-HOPO)$_4$. The coordinated oxygen on the bottom is an amide from a neighboring complex.

Previous work indicated that the bidentate Me-3,2-HOPO ligand forms extraordinarily stable complexes with Th(IV) at low pH. The bis-bidentate ligand, 5LiO-Me-3,2-HOPO was also evaluated for an expected high stability constant. Thus, a low pH titration was conducted to determine the 1:1 stability constants and examine how stable this complex is in highly acidic conditions. However, the extraordinary stability of the complex is indicated by the lack of any dissociation within the pH regime of the experiment. A graph of absorbance varied with pH is shown in Figure 14; the salient point is the complex is *intact* even to a pH of 1.4.

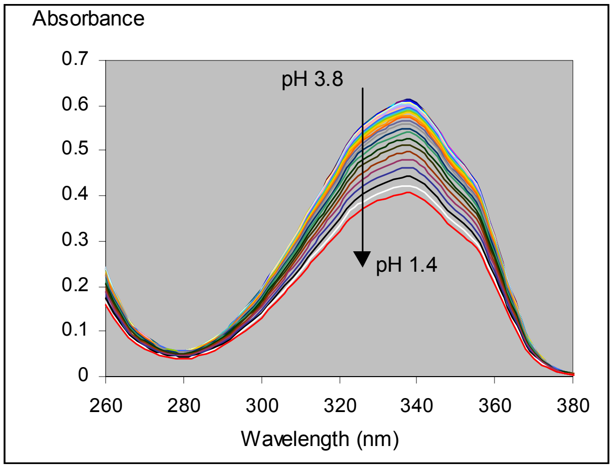


Figure 14. Low pH titration of Th^{4+} with 5LIO-Me-3,2-HOPO (1:1). Dilution only leads to a decrease in absorbance, no other species are evident over the pH range of the experiment.

Thorium-IPSFAMs. To address the stability of actinides with the sulfonamide catechols, spectrophotometric titrations with Th(IV) were carried out. Refined stability constants for this model are also included in Table 3, and are further illustrated in a species distribution diagram, Figure 15. Further work will include additional examination of actinide binding properties and potentially applying these ligands to radioactive waste stream remediation activities.

Species		Th(IPSFAM)
ML	$\log \beta_{110}$	16.8
ML_2	$\log \beta_{120}$	31.1
ML_2OH	$\log \beta_{12-1}$	26.4
ML_3	$\log \beta_{130}$	42.1
ML_4	$\log \beta_{140}$	48.4
		pM = 19.2

Table 3. Log β_{MLH} values for IPSFAM with Th(IV).

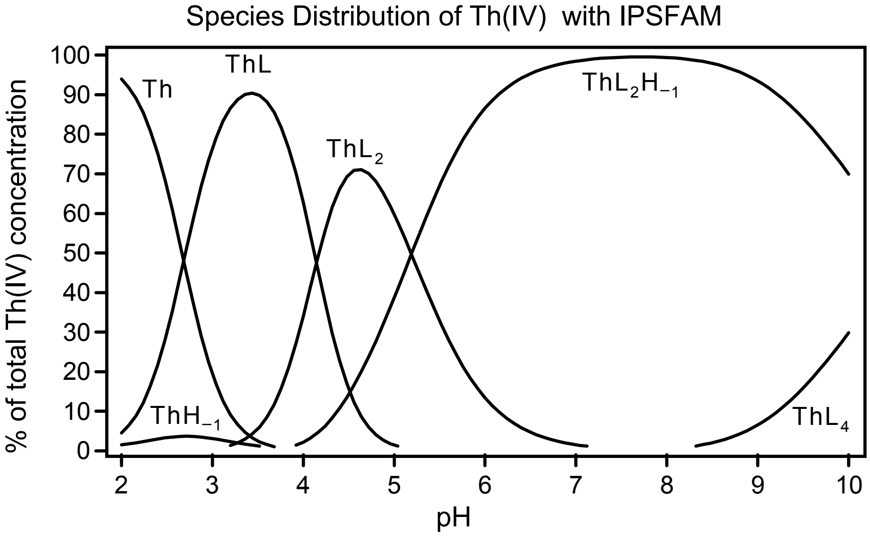


Figure 15. Speciation Plot for the Th:IPSFAM system. [M] = $3e^{-4}$, [L] = $1.3e^{-3}$.

E. Uranium Background.

The use of depleted uranium metal in armor piercing munitions has led to greater concentrations of this heavy metal in the environment, especially on training ranges and in theaters where the weapons have been used operationally. The wider occurrence of this metal may have future health impact on people that come into regular contact. As such, there is interest in the development of chelators, decorporation agents and specific ligands for the predominant hazardous form of uranium in the environment, the uranyl cation (UO_2^{2+}). Previous ligand design and synthesis in our research group [11,12] had produced selective uranyl chelators such as the one depicted in Figure 16.

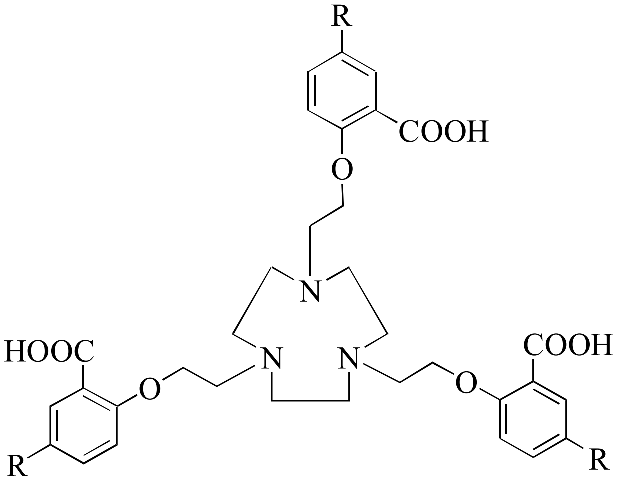


Figure 16. Selective Uranyl (UO_2^{2+}) complexing ligand. ETAC (R = H) or DETAC (R = decyl).

We have recently found that subtle changes in ligand backbone and thus, coordination geometry, strongly affect the properties of tetradentate HOPO ligands in complexes with uranyl (UO_2^{2+}).[4,13] It was found that the extent of decorporation of the uranyl ion from mice had a strong dependence on the length of the linker between the two HOPO units. Crystallization of these UO_2^{2+} 3,2-HOPO complexes demonstrated a basic feature: two bidentate chelating HOPO ligands plus an oxygen donor from a solvent coordinate in the equatorial plane of the ion (Figure 17). The complex with two bidentate ligands (HL^1) illustrated that the plane of the ligands also lie in this equatorial plane. However, in the tetradentate ligand series, the length of the linker (3, 4, or 5 carbons) affected the deviation from planarity of the ligand. The 3-carbon linker (HL^3) showed the highest deviation, and the 5-carbon linker (HL^5) almost exactly matched the coordination geometry of the two unlinked HOPOs. Ligand HL^5 was the one that was most effective at UO_2^{2+} decorporation. Thus, a strong dependence of decorporation efficacy versus deviation from planarity was observed with this series of ligands.

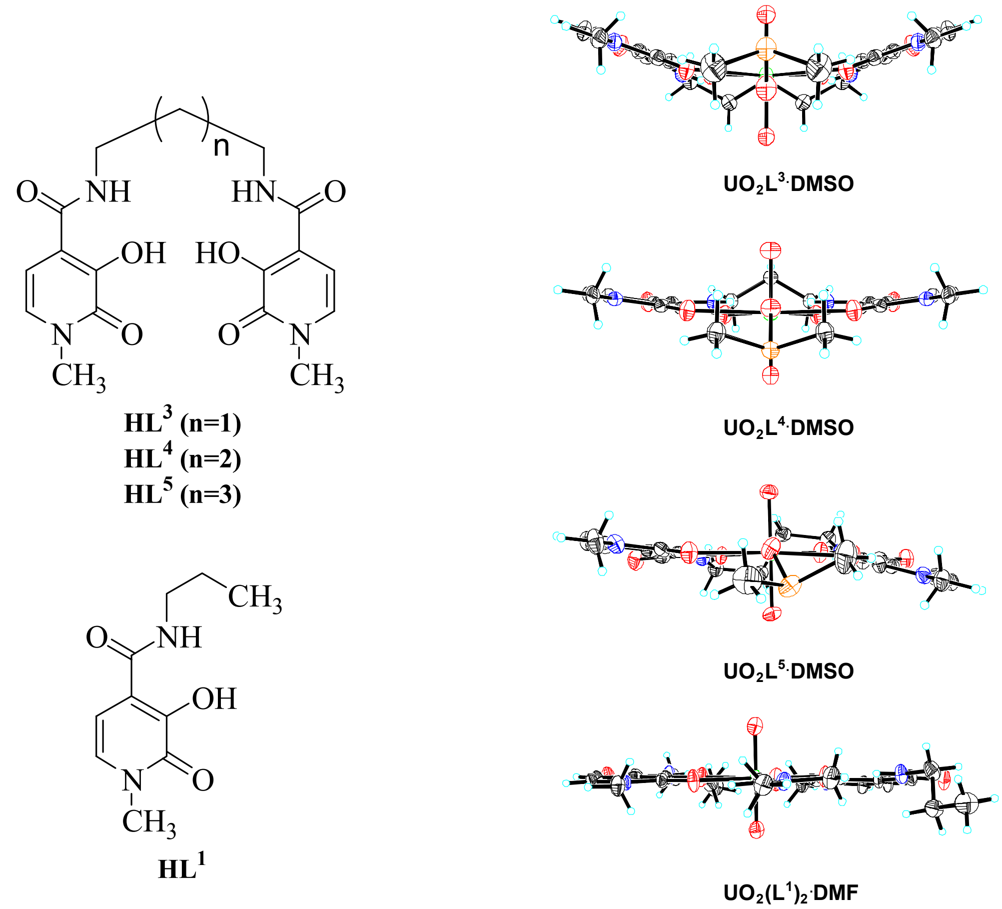


Figure 17. Ligand architecture and side-on view of the solid state structures of select uranyl-HOPO complexes. This orientation shows the deviation from planarity due to linker size, a critical factor in uranyl sequestering efficacy.

Recent Uranium Results.

Uranyl-SFAMs. The solution thermodynamic measurements for uranyl with IPSFAM were first approximated to those of UO_2^{2+} with Tiron.[14] A model of UO_2^{2+} with IPSFAM was generated to estimate experimental conditions for titrations of this system. The expected species were ML, ML_2, and $ML_2(OH)$; an ML_3 species, though not expected, was included in initial data refinements for completeness. Experiments at a M:L ratio of 1:2.3 revealed the species ML, ML_2, ML(OH), and $ML_2(OH)$ as present in the titration (Table 4). The sulfonamide ligand behaves almost identically to Tiron, which suggests that the higher negative charge on tiron may not play a large role in thermodynamic stability. Overall, the sulfonamide ligands have potential for development in applications where the properties of Tiron are desired, but the local negative charge of that ligand is not.

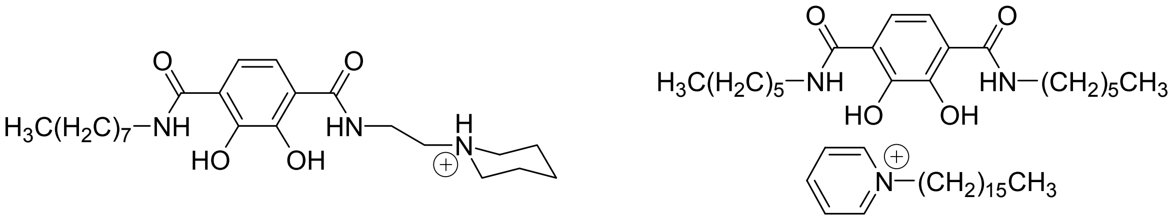
Species		IPSFAM	Tiron[a]
$(UO_2)LOH$	$\log \beta_{11\text{-}1}$	7.9 (1)	8.09[b]
$(UO_2)L$	$\log \beta_{110}$	14.1 (2)	14.29
$(UO_2)L_2OH$	$\log \beta_{12\text{-}1}$	14.6 (1)	16.58[b]
$(UO_2)L_2$	$\log \beta_{120}$	24.6 (1)	26.58
	$p\,UO_2^{2+}$	11.25	11.45

[a] Taken from reference 14. [b] Estimated.

Table 4. Comparison of solution thermodynamic constants determined for UO_2^{2+} with IPSFAM and those with Tiron. (25° C, 0.1 M KCl, # exps. = 5)

F. Liquid-Liquid Extraction

We are currently examining terephthalamide ligands (TAMs) as liquid-liquid extractants. These ligands form stable Th(IV) and Ce(IV) complexes and are expected to be excellent chelators for Pu(IV), particularly in basic media. Since the coordination of 4 of these ligands to Pu(IV) would result in an anionic complex, we have developed two strategies to form neutral complexes to facilitate extraction into the organic phase (Figure 18): 1) incorporation of a positively charge substituent into one of the ligand side arm will result in a neutral metal complex, and 2) a lipophillic counter-cation in addition to a lipophillic TAM ligand will permit extraction into the organic phase as an ion co-pair.



Approach #1 **Approach #2**

Figure 18. Recently developed TAM ligands for liquid/liquid extractants.

The results determined for Fe(III) extraction will be discussed here, with the expectation that the chemistry will transfer directly to plutonium extraction. To evaluate the extraction of Fe(III), it was necessary to develop a competition method in which a competing ligand (Tiron) was used in the aqueous phase. We expect the TAM ligands to function best at pHs above 5, so a water soluble ligand was required to prevent $Fe(OH)_3$ precipitation. Secondly, because the stability constants of the TAMs with Fe(III) are high and we expect the distribution coefficients to also be high, we want to maintain conditions where the metal ion is not 100% extracted. This allows for a more accurate determination of distribution coefficients and extraction constants. The effect of Tiron can later be subtracted out of the extraction equilibrium and K_{ex} determined.

Using approach #1, the unsymmetric TAM was found to be an excellent extractant at pH values above 5 using $CHCl_3$ as the extracting solvent. K_{ex} at pH 7.4 is approximately 10^{12}. Removing the pK_as of the ligand from the extraction equilibrium allowed us to calculate the proton-independent K_{ex} (essentially the K_{ex} at high pH) of 10^{45}. This is indeed an extraction system that needs to be evaluated with Pu(IV).

Using approach #2, we also discovered that the symmetric, lipophilic dihexyl-TAM ligand would extract Fe(III) into ethyl acetate if a suitably lipophilic counter cation, cetylpyridinium, was used. The distribution coefficients is about 10^{10} - 10^{11} for 2 to 5 molar equivalents of ligand.

Approach #2 is highly promising because the ligands are inexpensive and efficiently synthesized and the counter-cation is commercially available. The synthesis of symmetric TAMs has been drastically improved by developing a general procedure that avoids the protection and deprotection of the catecholate oxygen atoms. This streamlines the synthesis by reducing the synthetic steps from six to two and reduces the cost of synthesis by approximately 80% (Figure 19).

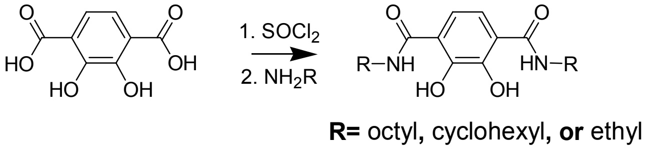


Figure 19. An efficient 2-step synthesis of the TAMs has been developed.

Relevance, Impact and Technology Transfer

A. Focus on DOE-EM problems

The general outlook of this research proposal, in accord with stated DOE and EMSP identified needs and specific goals, is to promote the following:

1. Provide separations technologies to process, concentrate and immobilize a wide spectrum of radioactive and hazardous waste at DOE sites.
2. Coordinate separations technologies within DOE-EM.
3. Foster future expertise in separations technologies.
4. Transfer separations technologies between DOE and the industrial sector.

Our laboratory and this research proposal identify the following seven areas of applied research as essential to furthering the goals of hazardous waste remediation as outlined by the DOE. These are:

1. Complete removal of dilute radionuclides from aqueous phases.
2. Solid-Liquid separations
3. Novel ion exchangers.
4. Advanced solvent extractions and liquid-liquid separations.

5. Selective sorbents and ligands.
6. Effective heavy element sequestering agents for highly basic media (pH >7)
7. Other separations areas.

B. How will this project improve technology, cleanup, etc.?

The development of metal-specific chelating agents paves the way for better extractants for the selective, efficient removal radionuclides from waste streams.
Selective agents and technologies can reduce the number of process steps, lead to a reduction in waste volume and net amount of HLW.
Improved technical processes can reduce risks to process and decontamination workers.

C. How does the project bridge the gap between research and technology?

This project has brought us into contact with more researchers in the applied science side of the DOE needs. The research in our group identifies, develops, and characterizes new ligands that are remarkably well suited for actinide chelation under a variety of conditions. Through our collaborations with researchers at national labs (PNNL, LANL, LBNL, LLNL) we are incorporating our ligands into several polymeric supports and evaluating our ligands for new separation technologies. Our focus is basic research with applications research conducted by our present and future collaborators.

D. Project's Impact?

LANL would like kilogram amounts of PDT (Section on Plutonium, Part 2, WSCP) for pilot plant testing. The production of this material is within our capability.

E. What new capacity, equipment or expertise has been developed?

Solid phase and water soluble resins for actinide sequestering; liquid-liquid extractant ligands.

F. How have the scientific capabilities of collaborating scientists been improved?

We have established links with applied research groups at Lawrence Livermore National Laboratory, Los Alamos National Laboratory, and Pacific Northwest National Laboratory.

G. How has this research advanced our understanding in the area?

H. What additional scientific or other hurdles must be overcome before the results of this project can be successfully applied to DOE Environmental Management problems?

I. Have any other government agencies or private enterprises expressed interest in the project? Please provide contact information.

LANL

Project Productivity

Did the project accomplish all of the proposed goals? The needs, results and prospects from the research with actinides drew our attention and efforts solely to this larger portion of the proposal. (The original proposal included research into Pb(II) and other heavy metal sequestering agents, approximately 20%.)

Was the project on schedule? Yes.

Was the work plan revised? No.

Personnel Supported

- Christine Gramer, Graduate Student
- Modi Wetzler, Graduate Student
- Nicole S. Wieland, Graduate Student
- Tom Mohs, Post-doctoral Researcher
- Emil Radkov, Post-doctoral Researcher
- David Van Horn, Post-doctoral Researcher
- Jide Xu, Staff Scientist
- Kenneth N. Raymond, Principle Investigator

Publications

Xiangdong Feng, L. Rao, Thomas R. Mohs, Jide Xu, Y. Xia, Glen E. Fryxell, Jun Liu, Kenneth N. Raymond. “Self-Assembled Monolayers on Mesorporous Silica, A Super Sponge for Actinides.” In Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries IV, Ceramic Transactions 93, James C. Marra and Gregory T. Chandler, Eds.; The American Ceramic Society, Ohio; 1999, p. 35-42.

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Pihong Zhao, Vadium V. Romanovski, Donald W. Whisenhunt, Jr., Darleane C. Hoffman, Thomas R. Mohs, Jide Xu and Kenneth N. Raymond. “Extraction of Plutonium by Chelating Hydroxypyridone and Catecholamide Resins.” *Solvent Extraction and Ion Exchange* **1999**, *17*, 1327-1353.

Xu, J.; Radkov, E.; Ziegler, M.; Raymond, K. N. "Plutonium(IV) Sequestration: Structural and Thermodynamic Evaluation of the Extraordinarily Stable Cerium(IV) Hydroxypyridinonate Complexes." *Inorg. Chem.* **2000**, *39*, 4156-4164.

Interactions

A. Meetings: [Meeting Name, Date, Title of Poster or Presentation, Attendee(s)]

- United Engineering Foundation “Metal Separation Technologies Beyond 2000” June 1999, “The Development of 2,3-Dihydroxyterephthalamides as Actinide Extractants” Christine J. Gramer
- ACS National Meeting, April 2000, “The Development of 2,3-Dihydroxyterephthalamides as Actinide Extractants” Christine J. Gramer
- ACS National Meeting, August 1999, “Ligands for Actinide Extraction : 2,3-Dihydroxyterephthalamides and 3,4-Dihydroxysulfonamides” Christine J. Gramer
- ACS National Meeting, April 1999, “The Development of 2,3-Dihydroxyterephthalamides as Actinide Extractants” Christine J. Gramer
- EMSP Actinide Chemistry Workshop, November 9-10,1999 “The Development of 2,3-Dihydroxyterephthalamides as Actinide Extractants.” Christine Gramer and David Van Horn.
- EMSP National Workshop, April 24-28, 2000 “Catechols and Hydroxypyridinones in Actinide Specific Complexation: Bridging Basic Chemistry and Remediation Technology.” Christine Gramer and David Van Horn.
- EMSP Sensors Initiative Workshop, June 19-20,2000 “Catechols and Hydroxypyridinones in Actinide Specific Complexation.” David Van Horn
- Plutonium Futures-The Science, July 10-13, 2000 “Catechols and Hydroxypyridinones in Actinide Chemistry.” David Van Horn.

- ACS National Meeting, April 1-6, 2000 “Comparison of the Aqueous Actinide and Lanthanide Coordination Chemistry of Dihydroxyterephthalamide, Dihydroxybenzene-sulfonamide, and Hydroxypyridinone Ligands.” David Van Horn.

B. Consultation: None

C. Collaborations:

- “Biological Evaluation of New Actinide Chelating Agents” – Collaboration with Dr. Patricia W. Durbin, Lawrence Berkeley National Laboratory.

- “Actinide-Specific Interfacial Chemistry of Monolayer Coasted Mesoporous Ceramics” – Collaboration with Dr. Glen E. Fryxell, Pacific Northwest National Laboratory.

- “Architectural Design Criteria for f-Block Metal Sequestration Agents” – Collaboration with Dr. Ben Hay, Pacific Northwest National Laboratory.

- “Water Soluble Polymer Supported Chelators” – Collaboration with Drs. Gordon D. Jarvinen and Barbara Smith, Los Alamos National Laboratory.

Transitions

Please refer to “Relevance, Impact and Technology Transfer”

Patents

We are preparing a patent that covers the synthesis and application of the dihydroxysulfonamide ligand system.

Future Work

The results from this project have pointed to the use of HOPO ligands as selective uranyl (UO_2^{2+}) sensors. We have started a collaboration with Heino Nitsche (LBNL) to do our own direct solution studies on Pu(IV). Activities will include determinations of stability constants in aqueous media with various ligands, tests to evaluate liquid-liquid extraction(LLX) agents, and the collection of crystallographic data. Our experience in this area has also led to a collaborative proposal with researchers at ORNL and SRTC on using some of the ligands described above for LLX of waste streams of caustic radioactive solutions at the Savanna River Site.

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Feedback

The EMSP program has facilitated more contact between our basic research activities and people with interests in applied technology activities.

We feel the most success has come about by having personnel visit collaborators and interact with them and the technical problem face to face for longer periods of time (up to a few weeks). These meetings facilitate information exchange about the exact nature of the problem, the capabilities needed or expected, and the focus of the research.