

1. Cover Sheet

FINAL REPORT

U.S. Department of Energy

f-Element Ion Chelation in Highly Basic Media

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Project Number: 54595

Grant Number: DE-FG0007-96ER14736

Grant Project Officer: William Millman and Ramoncita Massey

Project Duration: 10/96-9/00

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3. Executive Summary

A large body of data has been collected over the last fifty years on the chemical behavior of f-element ions. The ions undergo rapid hydrolysis reactions in neutral or basic aqueous solutions that produce poorly understood oxide-hydroxide species; therefore, most of the fundamental f-element solution chemistry has been accomplished in acidic solutions. The thorough development of acid-side f-element chemistry has allowed synthetic and separations chemists to rationally design advanced organic chelating ligands useful for highly selective partitioning and separation of f-element ions from complex acidic solution matrices. These ligands and new examples under development allow for the safe use and treatment of solutions containing highly radioactive species.

The U.S. Department of Energy, while performing its missions over the last fifty years, has produced large quantities of “waste” radioactive f-elements materials and fission products that have been stored pending analysis of permanent disposal options. Initially, much of the waste was stored dry or in the acidic aqueous solutions they were processed in. However, the corrosive nature of the acidic solutions led to neutralization and storage as basic solutions, sludges and precipitates. These materials must now be recovered, undergo partitioning in order to significantly reduce the waste volume and treatment to prepare the materials for solid-state immobilization. Unfortunately, the fundamental aqueous solution chemistry to support this objective is not well developed. As a result, this DOE/EMSP project was undertaken to address the following fundamental objectives: 1) study the chemical speciation of Sr and lanthanide (Ln) ions in basic aqueous media containing classical counter anions found in waste matrices; 2) prepare pyridine N-oxide phosphonates and phosphonic acids that might act as selective chelators for Ln ions in model basic pH waste streams; 3) study the binding of the new chelators

toward Ln ions and 4) examine the utility of the chelators as decontamination and dissolution agents under basic solution conditions.

The project has been successful in attacking selected aspects of the very difficult problems associated with basic pH solution f-element waste chemistry. In particular, the project has 1) shed additional light on the initial stages of Ln ion sol-gel-precipitate formulation under basic solution conditions; 2) generated new families of pyridine phosphonic acid chelators; 3) characterized the function of the chelators and 4) examined their utility as oxide-hydroxide dissolution agents. These findings have contributed significantly to an improved understanding of the behavior of Ln ions in basic media containing anions found in typical waste sludges as well as to the development of sludge dissolution agents.

The direct CMSP Relevance, Impact and Technology Transfer impacts are found in the creation of the fundamental science data. The findings will be described in peer reviewed journal articles, and the new chelator systems are under consideration for evaluation in applications involving actinide bearing wastes. The new chelating reagents are easily made and could be prepared in quantities suitable for large scale decontamination and dissolution processes involving sludges. Further studies will be required to assess specific performance in actinide ion bearing wastes.

The research program was completed at the University of New Mexico using postdoctoral, graduate student and undergraduate coworkers. The project was also performed with collaborative interactions involving Dr. Brian Rapko and Dr. Benjamin Hay at PNNL who were funded separately. The findings of the project have also stimulated very fruitful collaborations with Dr. Ken Nash and coworkers in the Chemistry Division at Argonne National

Laboratory. It is expected that the continued efforts to study our new chelators under practical conditions will be accomplished in conjunction with the ANL team.

4. Research Objectives

The U.S. Department of Energy (DOE) is charged with the task of safely remediating $\sim 1.5 \times 10^7$ ft³ of high level radioactive waste (HLW) stored in the DOE complex.^{1,2} Only a small fraction of the waste contains radioactive elements, but these species are responsible for most of the problems inherent in long term storage. The dominant emitters are cesium-137 and strontium-90; however, actinide species (Np, Pu, Am, Cm) and metal fission products are also significant radioactivity contributors. Most of the waste containing these elements was initially handled in nitric acid solutions during reprocessing; however, to reduce storage tank corrosion the solutions were made strongly alkaline. In addition, reprocessing efforts introduced a number of inorganic (e.g., CO₃²⁻) and organic (e.g., BPh₄⁻) ions, chelating agents (e.g., EDTA), and solvents. As a result, the radioactive elements in many storage tanks (e.g., at the Hanford facility) reside in complex solid and liquid matrices.^{3,4}

It has been proposed that the permanent disposal of the waste will require partitioning of low and high activity components while minimizing their volumes, particularly for the HLW fraction. The initial treatment may involve physical separation of the solid and liquid fractions, and there may be some washing of the solid fraction. It is anticipated that the liquid fractions will contain small concentrations of radioactive elements, and their speciation will likely be unknown. The majority of the radioactive elements in the HLW will appear in the solids fraction, again with largely unknown speciation. It may prove possible to directly handle the solid fraction with existing or planned solid waste immobilization concepts; however, the liquid waste will likely require further chemical processing and separations.

Existing liquid phase separation techniques, derived for actinide (An) ions in acidic media, will not provide for satisfactory partitioning of radioactive elements from the alkaline

HLW matrix. Vastly improved methods and approaches, suitable for basic media, will be required. Unfortunately, there does not exist a well-developed molecular chemistry knowledge base to support the derivation of the required separations. As pointed out in the original EMSP program announcement, one of the most vexing problems in designing advanced separations schemes for these alkaline matrix wastes is the general lack of information on fission product and actinide chemical speciation in strongly basic media. Some detailed information is available for carbonate-rich media;⁵ however, much less is known about hydroxide-rich systems.⁶⁻¹⁰ It is likely that, in hydroxide rich solutions, mixed monometallic and polymetallic oxide-hydroxide species form initially from hydrolysis and condensation processes, and some of the species may be soluble in aqueous base solution. In addition, suspended colloids or sols probably form along with the dominant solid precipitates and gels. Undocumented reports suggest that solubility of the oxide-hydroxide metallate species are enhanced by the presence of chelating ligands often present in waste tanks (e.g., EDTA).

Some clues about the chemical speciation of Ln and An ions in hydroxide-rich media may be gained from the literature of the aqueous hydrolysis of these ions.⁵⁻¹¹ A full description of this literature will not be presented, especially since it is described in a recent review,⁵ but some summarizing comments follow. First, it appears that hydrolysis processes are complex and pH-dependent. Furthermore, for several elements in selected oxidation states, it is confirmed that polynuclear oxide-hydroxide species are formed. Some of these species are soluble and some produce living (reactive) oligomers or polymers. Finally, based upon the extensive basic carbonate literature,⁵ it is probable that coordination chemistry of the polynuclear oxide-hydroxide species will be rich. This will be especially true where ligands are utilized that can

interrupt condensation reactions and compete for binding sites against bridging oxide and hydroxide connectivities in polynuclear species.

Some possible issues involved in the dissolution of precipitates or polymers are revealed by examination of the literature on dissolution of insoluble oxide minerals in natural aquatic systems.^{12,13} Stumm and others^{12,13} have devised models for the dissolution of alumina and ferrihydrite. They find that the breakdown of a slightly soluble oxide-hydroxides is controlled by the rates of surface reactions such as redox processes and ligand absorption. The ligand-based process is summarized by the following simplistic equations (Eq. 1-3):

1. Ligand Absorption



2. Precursor Complex Formation



3. Detachment



It is considered that the ligand, by precipitate or gel surface binding, serves to weaken internal Fe-O bonds leading to eventual release (dissolution) of small, molecular units to solution. The majority of ligands that have been studied for this type of application are organic chelating carboxylates (e.g., salicylate, oxalate, malonate, phthalate); however, ligands such as tripolyphosphate have also been found to enhance ferrihydrite dissolution.¹⁴

How do these features relate to the high pH chemistry of actinides and fission products? Some information can be gleaned from existing literature.^{8,9,15-20} In general, the Ln ions strongly

favor the +3 oxidation state, while the early actinides show more diversity by appearing in +3, +4, and +6 oxidation states. Heavier An ions favor the +3 oxidation state, especially in classical coordination compounds. The f-element ions are relatively large and the ionic radii show a relatively smooth contraction with increasing atomic number. Their bonding is largely dominated by ionic interactions, and in general, crystal field effects in complexes are relatively small to nonexistent and high coordination numbers (CN=7-10) are common. As a result of small crystal field/orbital orientation effects, the coordination polyhedra adopted in many solid state structures have irregular shapes, and structures in solution probably rapidly interconvert between various idealized geometries. The f-element ions are normally classes as “hard”, and they tend to form their strongest complexes with negatively charged ligands containing oxo donor centers. Ligands containing softer donor centers (e.g., N, P, and S) bind to f-element ions, but they typically do not compete effectively against water in aqueous solutions. Many oxo ligand complexes are kinetically labile; therefore, only the most stable complexes relative to aquo species are isolated from water solutions. These complexes often contain chelating ligands that provide additional thermodynamic and kinetic stability over their monofunctional ligand counterparts. Some of these features have close parallels with d-element (transition metal) ions; however, many of the coordination characteristics of f-element ions strongly contrast with the behavior of transition metal ions. Further, it would be inaccurate to conclude that the f-element ions are “monolithic” in their coordination behavior. Indeed, it is likely that actinide ions, particularly An(III), are “softer” than their Ln(III) counterparts, and they probably display d-orbital character to a greater degree.²¹

Although many of the fundamental features of f-element ion coordination chemistry have been revealed much of the information pertains to aqueous acidic solution chemistry. A great

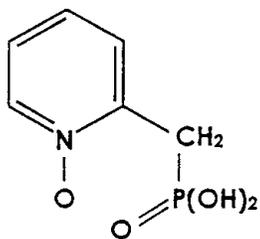
deal remains to be learned, particularly in areas that interface with important technical applications. One area that warrants additional exploration involves metal selective ligand design. For example, it is of fundamental interest to know whether it is possible to design and prepare ligands that recognize and bind to Ln and An ions in the presence of other metal ions. Such ligands are now available for the selective binding of some transition metals and Group 1 and 2 ions, and a rudimentary predictive framework has been established for construction of such ligands.²²⁻³¹ However, with the exception of Raymond's detailed studies of UO_2^{2+} , Th(IV), and Pu(IV) sequestering agents,²⁹ much less attention has been given to ligand design for f-element ions. Based on Raymond's studies and our own work, it appears that the strongest ligand/metal coordination conditions should be ones that contain multidentate O-donors efficiently packed around the f-element ion in a way that provides maximum numbers of ligand donor-metal interactions with minimum steric strain. Furthermore, based on discussions provided by Hancock and Martell,²⁵ it is expected that the overall stability of complexes of the highly charged f-elements will be enhanced by the presence of negatively charged oxygen atoms relative to neutral oxygen donors. On the other hand, ligand selectivity may be improved by introduction of neutral O-donor or N-donor centers.

Ligand architectural features or geometric "preorganization",²²⁻³² also play an important role in ligand design, and significant efforts have been given to developing a fundamental understanding of geometric effects through molecular modeling.³² For example, with most simple d-block metal ions, regular octahedral coordination fields are preferred. Complexes with bidentate ligands having five-membered chelate rings are often energetically favored over chelate structures having six-membered or larger rings, all else being equal. However, with f-element ions capable of adopting larger (CN = 7-12), more irregular coordination fields appear.

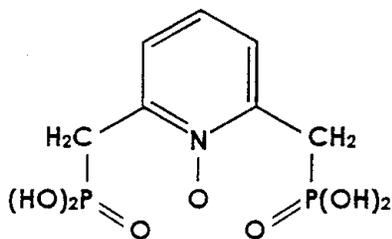
As a result, bidentate ligands that utilize six, seven, and even eight-membered chelate rings may be stabilized when the ligands display geometrical flexibility. It can also be expected that f-element specificity may be influenced by fine-tuning steric and electronic effects on a multifunctional ligand. For example, the introduction of one “softer” donor site, by charge or element modifications, on a multifunctional/multidentate ligand or the mixing of chelate ring sizes, may lead to enhanced specificity for f-elements.

Obviously, there is a diverse collection of ligand design features that might be pursued in the hunt for selective f-element chelators. Under past and present DOE-BES sponsorship, we have established a significant ligand design, synthesis, and coordination chemistry background for multifunctional phosphonates, CMP/CMPO derivatives, and phosphinopyridine N,P-oxides. All of that coordination chemistry has been investigated in either non-aqueous or acidic aqueous solutions. In the DOE/EMSP project (54595) we have extended our field of study into basic pH, aqueous media. The specific fundamental chemical objectives of the project as stated in the original proposal were:

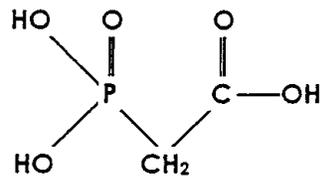
- to study the chemical speciation of Sr and Ln ions in basic media formed in aqueous solutions with and without classical chelation agents (e.g., EDTA, polyphosphates, and organic carboxylates);
- to prepare pyridine N-oxide phosphonate and phosphonoacetate chelators of the types **1**, **2** and **4** and characterize their ionization properties by titrimetric techniques;



1



2



4

- to study the interactions of **1**, **2** and **4** with soluble oxide-hydroxide metallate species and higher molecular weight sols, gels and precipitates containing Sr and Ln ions
- to study the interactions of newly designed phosphonate ligands with oxide-hydroxide metallate species.
- to transfer the fundamental coordination chemistry revealed here to research groups at LANL and PNNL that could utilize the results to improve tank waste treatment protocols.

5. Methods and Results

A. Solubility/Speciation of Ions in Basic Media

The hydration and hydrolysis of Ln (III) ions have been extensively studied and results have been thoroughly reviewed by Choppin³³ and Baes and Mesmer.¹¹ This work is especially pertinent because Ln (III) ions are present in waste, but also the ions serve as stable stand-ins for studies of An ions. As outlined in the original proposal, our intent in studying Ln (III) hydrolysis was not to add another decimal place in the accuracy of solubility products. Instead, we wanted to define a simple method that could be used for assessing ligand effects on hydrolysis. In evaluating the literature, we decided that light scattering measurements might provide an ideal, simple approach for following hydrolysis from sol-formation through to precipitation. This proved correct. In fact, Suzuki et al³⁴ reported use of light scattering to follow precipitation of Ln (III) ions using electrolytically generated OH⁻, and they reported pH shifts of ~ 0.3 to 0.6 pH units from the accepted values. All shifts were to lower pH when using their technique. They also observed that the larger ions had higher hydrolysis on-set pHs. Two mechanisms for hydrolysis were proposed. These depended upon electrolytic generation of OH⁻ from free water followed by reaction with Ln (H₂O)_n³⁺ species, or electrolytic conversion of Ln bound water.³⁴

In our studies, we have provided OH⁻ chemically in dilute solution without use of electrolysis, and we have followed hydrolysis via light scattering (nephelometry). We observe responses parallel to those reported by Suzuki et al, although the pH shifts are more like 0.2 to 0.4 pH units compared to the earlier data. Some representative data appear in Table 1. The key issue is that the light scattering probe works very well. This is especially important since this experiment could be very easily extended for use with hot actinide solutions using very small

Table 1. Typical Hydrolysis on-set pHs for $M(\text{NO}_3)_x$ Salts

Compound	pH
Sr $(\text{NO}_3)_2$	10.0
Y $(\text{NO}_3)_3$	6.5
La $(\text{NO}_3)_3$	7.6
Nd $(\text{NO}_3)_3$	6.8-7.0
Er $(\text{NO}_3)_3$	6.5

samples. It is also clear that the work could be extended to structural analyses of the growing polymer. Further, since the trends we observe are parallel to the Suzuki observations, it is apparent that mechanisms involving electrolytic generation of OH^- are probably not pertinent. All the electrolytic approach does is ensure steady production of OH^- . It does not change the issue of molecular level mixing inhomogeneity.

In our studies, we have also examined the effect of ionic strength. By addition of KNO_3 or KCl to the $\text{Ln}(\text{NO}_3)_3$ solutions, the pH on-set for hydrolysis shifts to lower pH with the effect slightly greater for Cl^- consistent with its poor complexing ability. Some representative data appear in Table 2. This observation is not unexpected; however, direct measures of this phenomenon seem to be missing from the literature. Since tank waste typically contain huge excess concentrations of anions, it can be expected that the precipitation of oxo-hydroxide species will occur at lower pHs than anticipated.

Table 2. Typical Hydrolysis on-set pHs for $M(NO_3)_x$ Salts Ionic Strength Shift

$M(NO_3)_3 = 0.01 \text{ M La}(NO_3)_3$

Salt conc	KNO ₃	pH	KCl
0.0M	7.6		7.6
0.1M	7.4		6.8
0.5M	7.2		6.7
1.0M	6.7		6.5
3.0M	6.5		6.3

As shown in Table 3 for $La(NO_3)_3$, some unexpected pH shift/precipitation reactions also occur with organic anions, some of which appear in tank waste. Acetic acid/acetate show little or no pH shift. This is not surprising since acetate is not a strongly coordinating anion. Benzoic, malonic, oxalic, phthalic and salicylic acids, to differing degrees, shift the pH on-set for hydrolysis. Obviously, these ions can dramatically affect processing of basic pH tank waste since they destabilize the soluble species far from their “normal” pH stability ranges. Two acids, citric and EDTA, strongly stabilize soluble species by shifting the on-set pH to high values, 14.0 or greater. This also is a very important observation since these values suggest that soluble ions could appear in effluents at pH values otherwise expected to cause precipitation.

Some effort was made to study this effect with simulant mixtures by using nephelometry and ICP-AES for analysis of the mixtures. In general, the observations are parallel with those presented in Table 3. However, the mixtures also showed some irreproducibility or lack of solution stability which made these systems difficult to study. As a result, these data are not

Table 3. Hydrolysis on-set pH for $M(\text{NO}_3)_x$ Salts Coordinating Counter Ion Shift.



Compound	M/L ratio	pH value	Observation
Acetic acid	1:3	7.6	Hydrolysis
	1:7	7.8	Hydrolysis
Acetylacetone	1:3	7.7	Solid Complex Formed
Benzoic Acid	1:3	5.0	Solid Complex Formed
Citric acid	1:3	>14.0	No Hydrolysis
Malonic acid	1:3	4.0	Solid Complex Formed
Oxalic acid	1:3	2.0	Solid Complex Formed
	1:6	2.0	Solid Complex Formed
Phthalic acid	1:3	5.0	Solid Complex Formed
Salicylic acid	1:3	6.3	Solid Complex Formed
EDTA	1:1	14.0	No hydrolysis

reported here. If these data should become important to understanding simulant behavior under some sludge processing schemes, these fundamental studies should be reopened. For our purpose, with the complexants of interest to us, this complex behavior can be avoided.

Finally, we examined the hydrolysis on-set pH shifts with three new pyridyl phosphoric acids and phosphono acetic acid, ligands **1-4**, as shown in Table 4 for $\text{La}(\text{NO}_3)_3$. The addition of **1** to $\text{La}(\text{NO}_3)_3$ followed by pH adjustment shows no evidence for hydrolysis until pH 8.2. This is similar to acetic acid. As the amount of **1** increases there is a shift in the pH on-set also

Table 4. Hydrolysis on-set pH for M(NO₃)_x Salts Coordinating Phosphonic Acid Shifts.

M(NO₃)₃ = 0.01M La(NO₃)₃

M/L Ratio/pH values for hydrolysis

Compound	1:1	1:2	1:3	1:4	Observation
1	8.2	8.6-8.9	9.4	9.4	No hydrolysis
2	13.4	13.7			No hydrolysis
3	2.0				Solid complex forms
4	2.0-3.0	2.0			Solid complex forms

similar to acetic acid except the shift is bigger. This is expected since this ligand (e.g. R = Ph) is found to be an excellent chelator.³⁵ This, in fact, suggests that **1** may be a good decontamination agent. Reagent **2** dramatically shifts the hydrolysis on-set to pH 13.4 at 1:1 and 13.7 at 2:1 concentrations. This behavior is closely related to EDTA. This also is consistent with the strong chelating properties of organo derivatives of **2**³⁵ in which the ligand acts as a tridentate chelator. This topic for the tetra acid is dealt with in a following section. Conversion of **2** to a diacid, such as **3**, results in immediate precipitation. This is most likely a result of complex formation and subsequent aqueous insolubility of this compound. This is not unsurprising since the Ph groups should result in aqueous insolubility. The complex, on the other hand, is soluble in polar organic solvents. Ligand **4** also shows complex formation with precipitation even at low acid concentrations.

The pH on-set studies suggested that speciation studies by pH titrations might be informative. Initially, ligands **1** and **4** were examined. Several problems were encountered due to the insolubility of the complexes in water over a significant pH range. Titrations of Nd (III), Eu (III), Th (IV) and UO_2^{2+} with **2**, on the other hand were successful and representative data are presented in Figure 1. Titration of the ligand **2** (H_4L) shows two distinct ionizations: ($\text{H}_4\text{L} \rightarrow \text{H}_2\text{L}^{2-} + 2\text{H}^+$) and ($\text{H}_2\text{L}^{2-} \rightarrow \text{L}^{4-} + 2\text{H}^+$). The titration curves with each of the metals suggest the formation of several complexes. Modeling of each system has been attempted. Of course, the models are not unambiguous and additional work should be done to verify the models in each case. We have examined the Nd (III) system to the greatest accuracy and representative data are summarized in Figure 2. These results suggest that hydroxo (or oxohydroxo) species may be suppressed until $\text{pH} > 9$. These studies, we hoped would guide efforts to isolate individual complexes for full characterization studies. In the final analysis, we have not yet been able to isolate these species. They appear to be polymetallic clusters, but the stoichiometries and structures are still unknown.

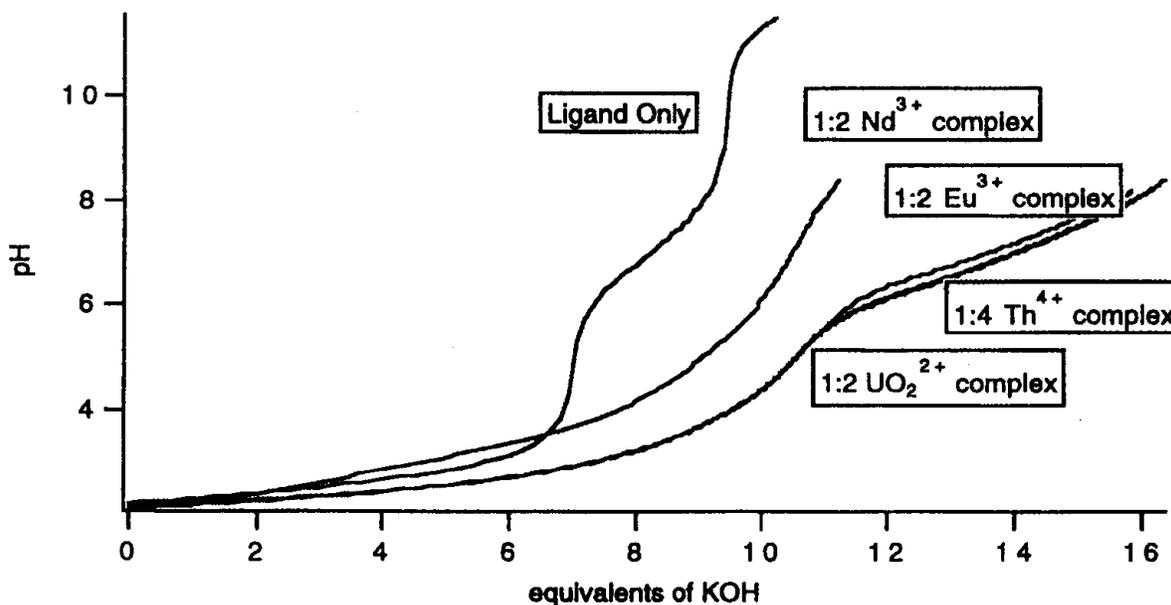


Figure 1. pH Titrations on Systems Containing Ligand **2** and Nd^{3+} , Eu^{3+} , Th^{4+} , UO_2^{2+}

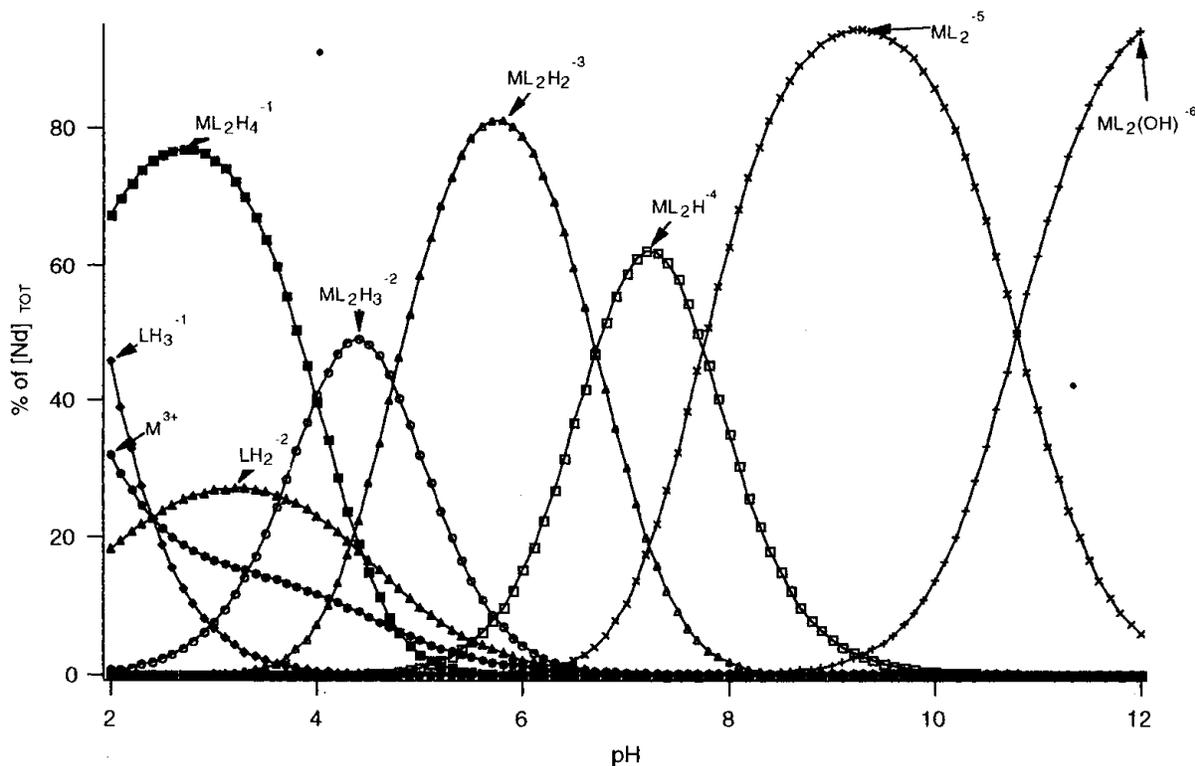


Figure 2. Speciation Behavior in Complexation by **2** with $\text{Nd}(\text{NO}_3)_3$ ($2.5 \times 10^{-3}\text{M}$).

B. Oxo-Hydroxide Metallate Growth Kinetics

We were interested in charting the kinetics of sol-gel hydrolysis of the Ln (III) ions in support of our efforts to isolate ligand stabilized, soluble oxo-hydroxide clusters prior to sol-gel formation and/or precipitation. Nephelometry was used to follow the oligomerization process and some typical data are presented in Figure 3. Here $\text{La}(\text{NO}_3)_3$ (0.01 M) was combined with aliquots of KOH and the light scattering followed with time. There is an initial rapid growth in polymer scattering which then tails off. The higher scattering at t_0 results from the problem of hydroxide mixing at the start of each run. We have attempted to “trap” the presumed oxo-

hydroxo intermediates early and late in the condensation process by adding both neutral ligands and the phosphoric acid chelators. This has proven unsuccessful, and this led to our studies of complex formation under hydrothermal reaction conditions.

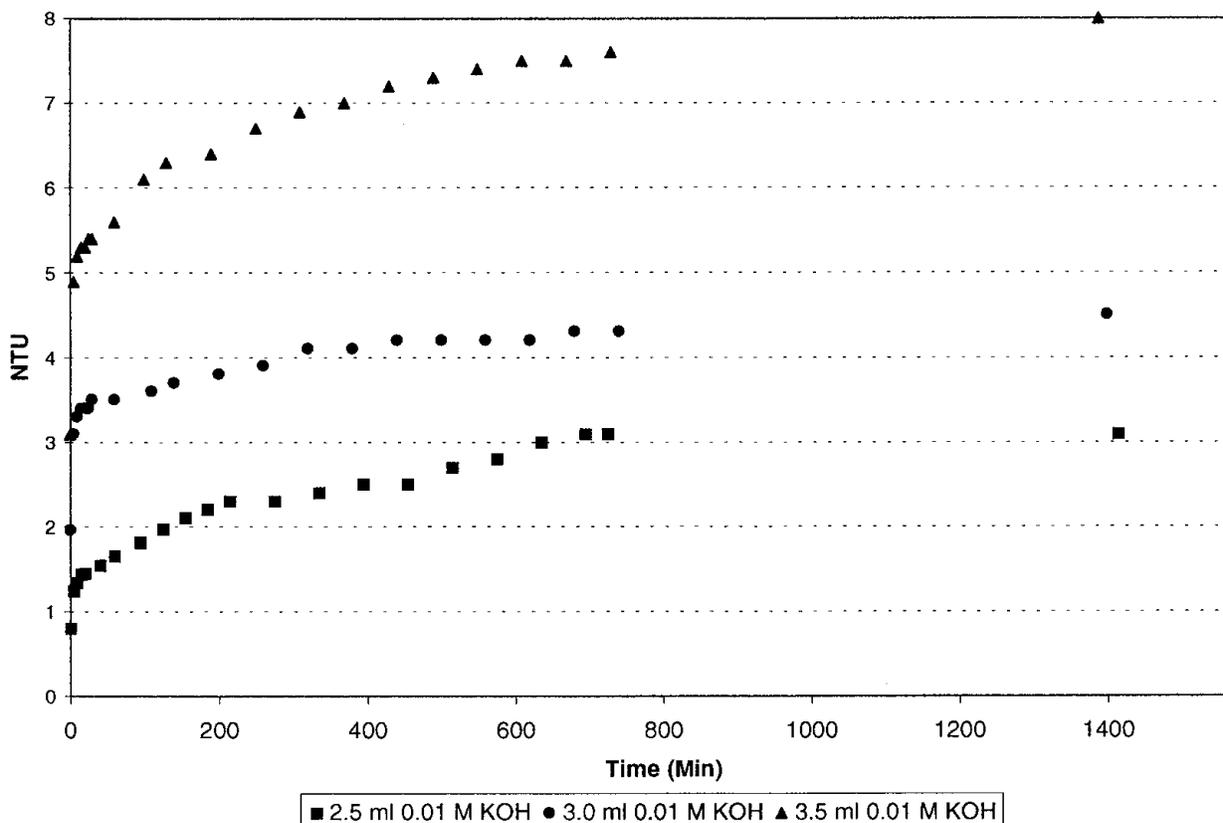
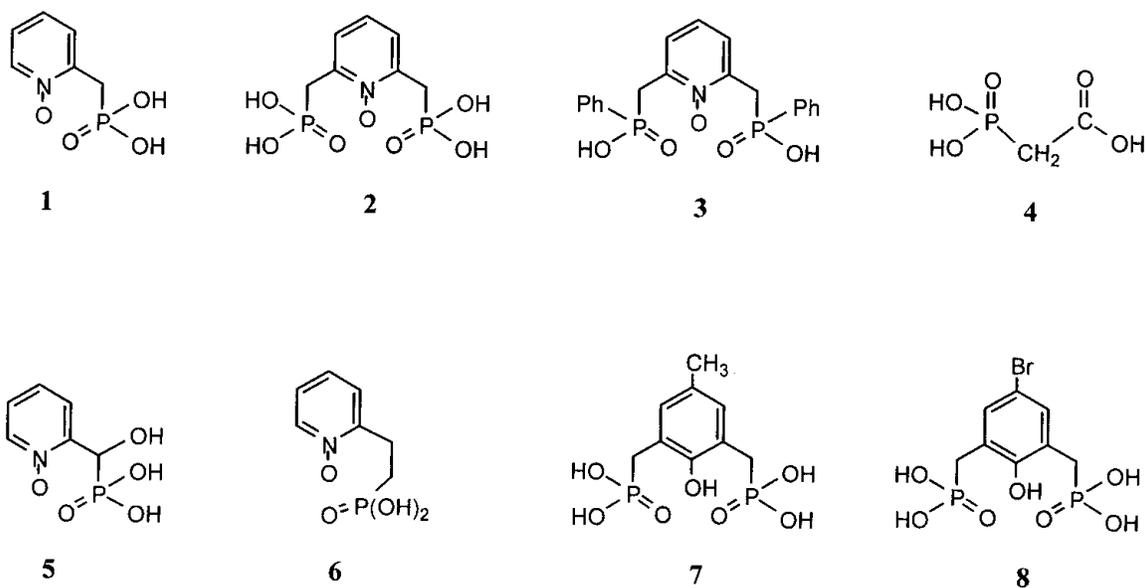


Figure 3. Light Scattering intensity vs. time for a solution of $\text{La}(\text{NO}_3)_3$ (0.1M) with added KOH.

C. Chelator/Decon Agent Synthesis

As mentioned above, it was anticipated that bifunctional and trifunctional phosphoric acids would be excellent chelators for f-element ions, and they might display useful oxide-hydroxide dissolution properties. Results described in Sections A and B confirm these suggestions. In this section, syntheses for these ligands are described. The primary chelators that have been prepared are those shown here as **1 – 9**. They have been obtained from several

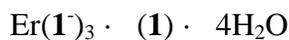
different routes and papers describing this work are in preparation.³⁶⁻³⁷ In most cases phosphonate derivatives with R = OEt or OSiMe₃ were prepared initially by Arbusov chemistry similar to that described previously in our group.³⁸ These compounds are subsequently hydrolyzed by use of HCl or HOAc. Considerable effort was given to perfecting simple, high yield procedures that would encourage large scale applications. All of the new ligands have been fully characterized by CHN analyses, IR, mass spectrometry and ¹H, ¹³C and ³¹P NMR spectroscopy.



D. Molecular Coordination Chemistry

It was important to characterize, at a molecular level, how these ligands function as dissolution agents in order that further chelator design could be accomplished. Initially, the coordination reactions were performed at 23 °C in water or MeOH solvent. Complexes formed easily and solid complexes were isolated in good yield. Characterization showed formation of 1:1, 2:1 and 3:1 complexes for the bifunctional ligands, and 1:1 and 2:1 complexes with

trifunctional ligands. In addition, each of these complexes was found to contain variable amounts of H₂O or MeOH in either the inner or outer coordination spheres. This is not unexpected since these are strong H-bonding solvent systems. Single crystals, suitable for x-ray diffraction studies, were not obtained, and spectroscopic data did not provide much unambiguous information on the structures of the complexes. Because of this, we turned our attention to studying the formation of complexes via hydrothermal conditions. On the surface, this would appear to be a poor choice since the compounds formed would seem to be unrelated to tank waste conditions. However, there are situations in these tanks that may approximate hydrothermal conditions due to the radiation field heating. The hydrothermal approach gave rise to the formation of numerous crystalline compounds, and a brief summary of those that have been fully structurally characterized is provided.



A view of the complex is shown in Figure 4 and a view of the unit cell contents appears in Figure 5. There are four Er atoms and thirty-two water molecules in the unit cell. The Er ion sits on a two-fold axis, and there are two unique ligands: two ligands are ordered monoanions ($\mathbf{1}^-$) while the other two are a disordered mixture of ($\mathbf{1}^-$) and neutral ($\mathbf{1}$). The eight N-O and P-O donor O atoms in the four chelating ligands form a square antiprism inner sphere coordination polyhedron. The bonded Er-O(P) distances are shorter than the Er-O(N) distances: 2.264 Å vs 2.423 Å. This difference is significantly larger than the differences found in neutral organophosphonate ligand derivatives.³⁵ This is consistent with the much higher electron density on the donor O atom in the anionic ligand. Figure 5 clearly shows the complex hydrogen bonding that serves to stabilize the structure.

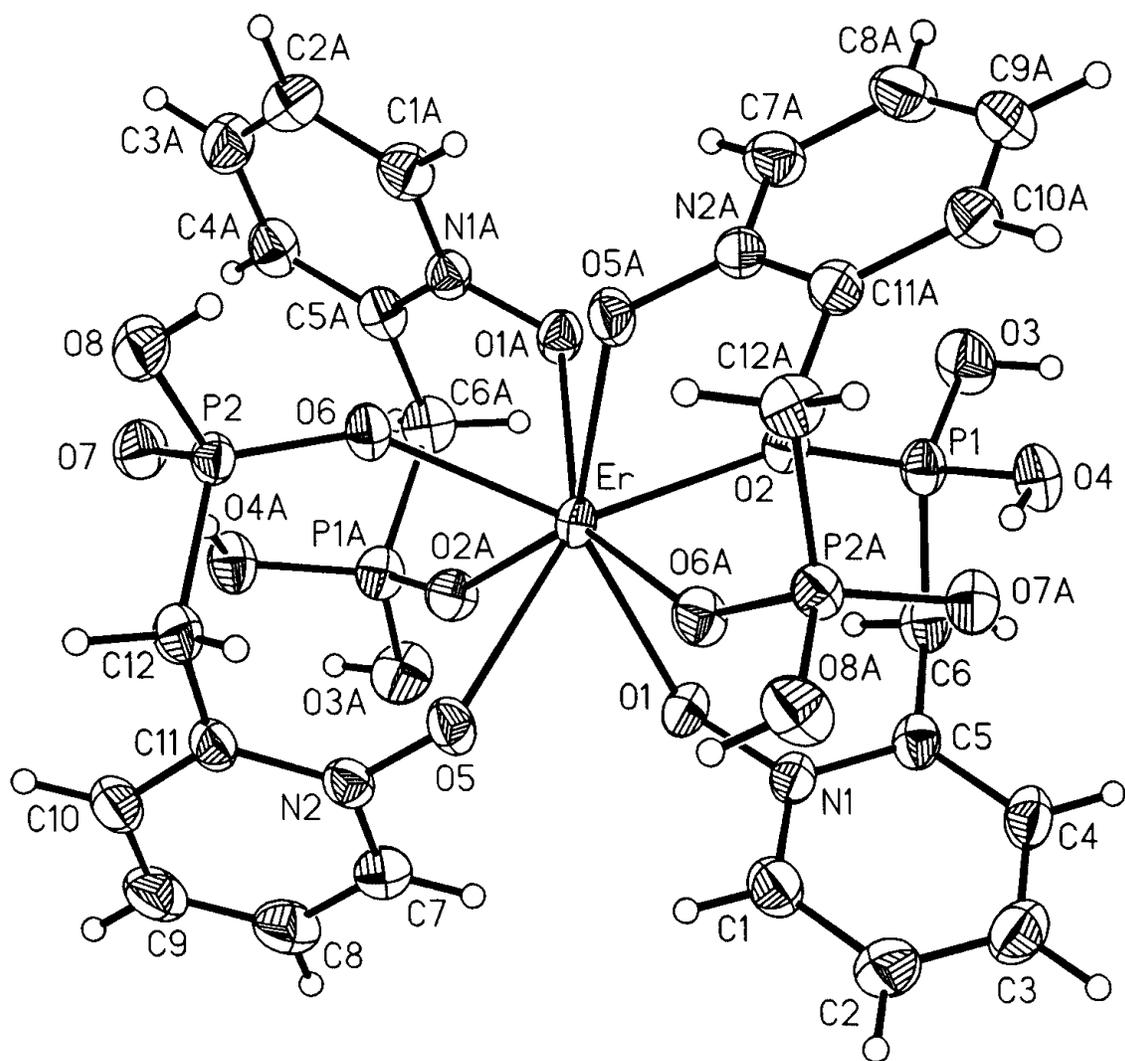


Figure 4. Molecular structure of $\text{Er}(\mathbf{1})_3 \cdot (\mathbf{1}) \cdot 4\text{H}_2\text{O}$.

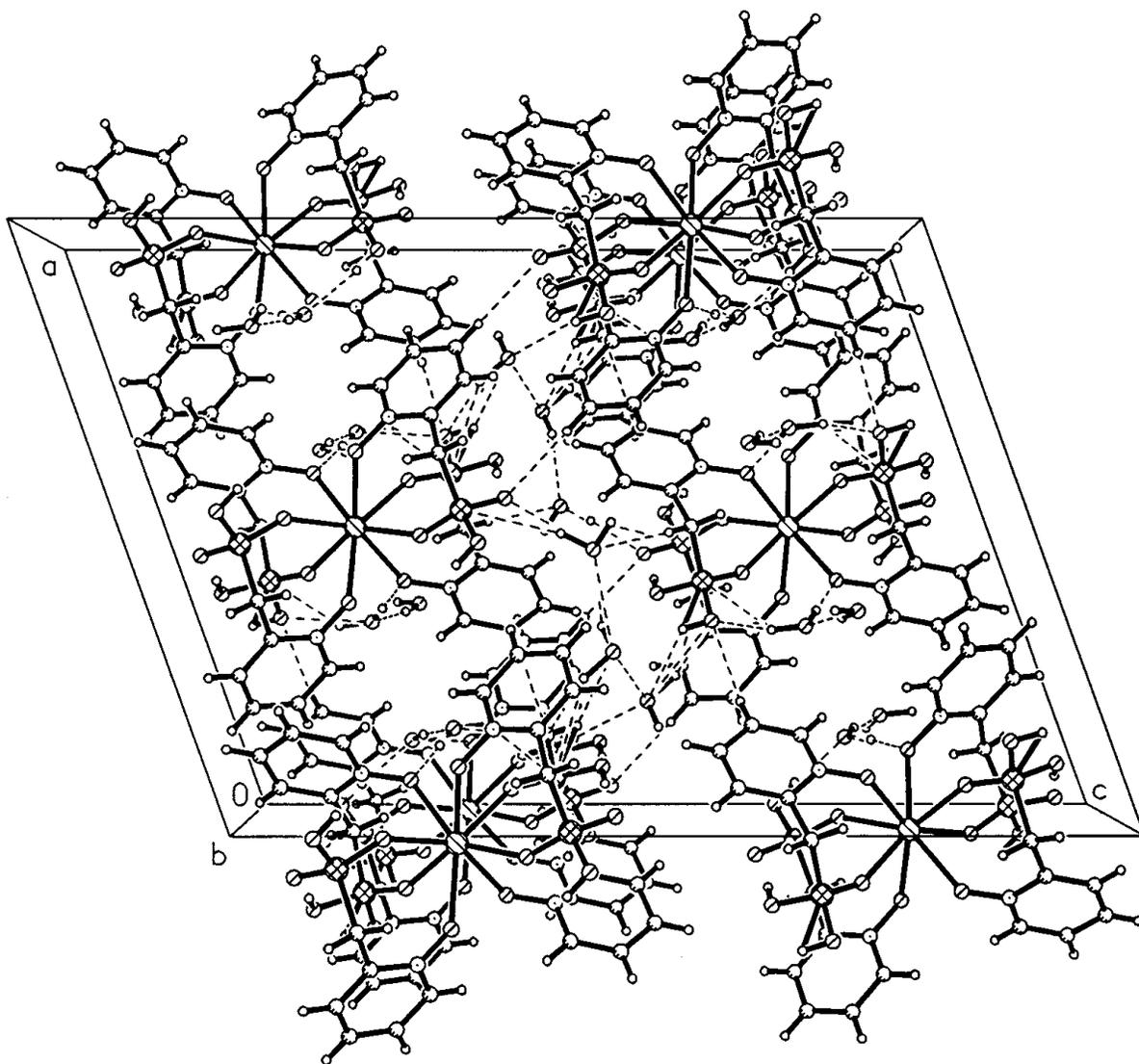
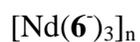


Figure 5. Unit cell contents for $\text{Er}(\mathbf{1}')_3 \cdot (\mathbf{1}) \cdot 4\text{H}_2\text{O}$.



In order to determine how the enlargement of the pendent chelating arm affects the binding of the bifunctional ligand class, the structure of a Nd (III) complex of $\mathbf{6}$ was determined. This compound forms an intriguing polymeric structure shown in Figures 6-8. The asymmetric unit contains $1/3 [\text{Nd}(\mathbf{6})_3]$. There are two unique Nd atoms occupying the **a** and **b** positions. These positions have $\bar{3}$ point symmetry with each Nd octahedrally bound to six ($\mathbf{6}$) groups.

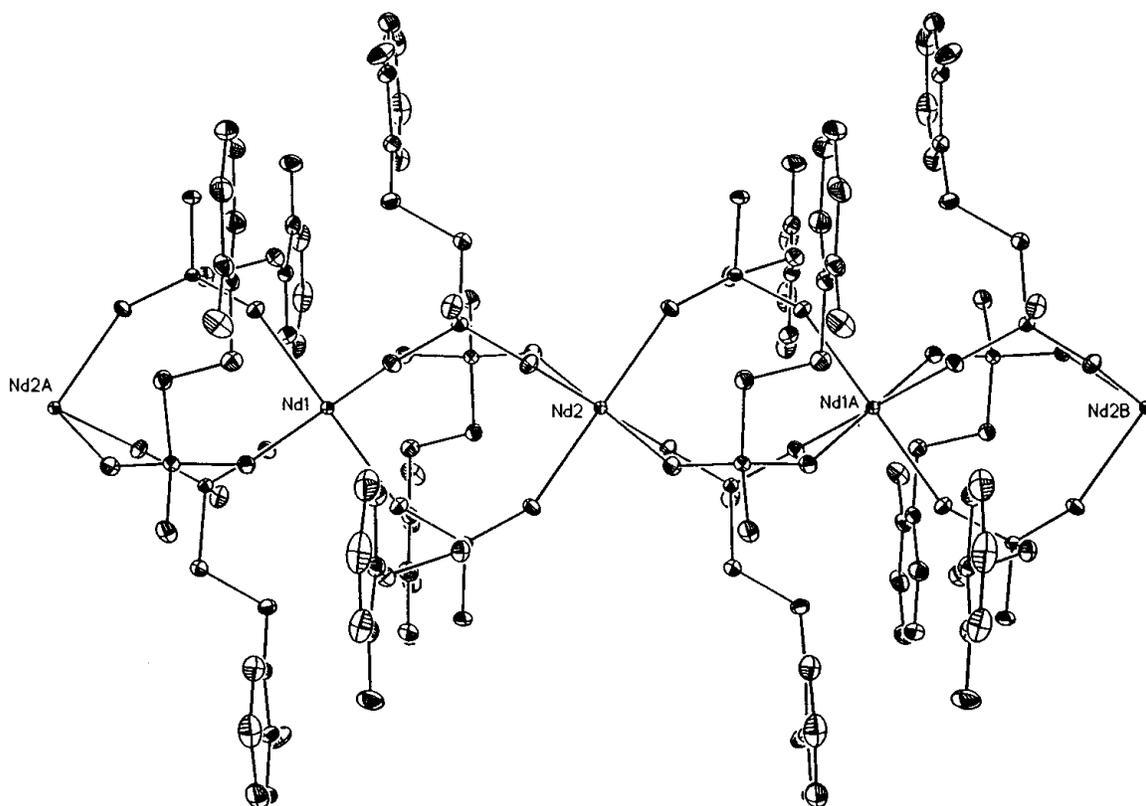


Figure 6. Molecular structure of $[\text{Nd}(\mathbf{6})_3]_n$

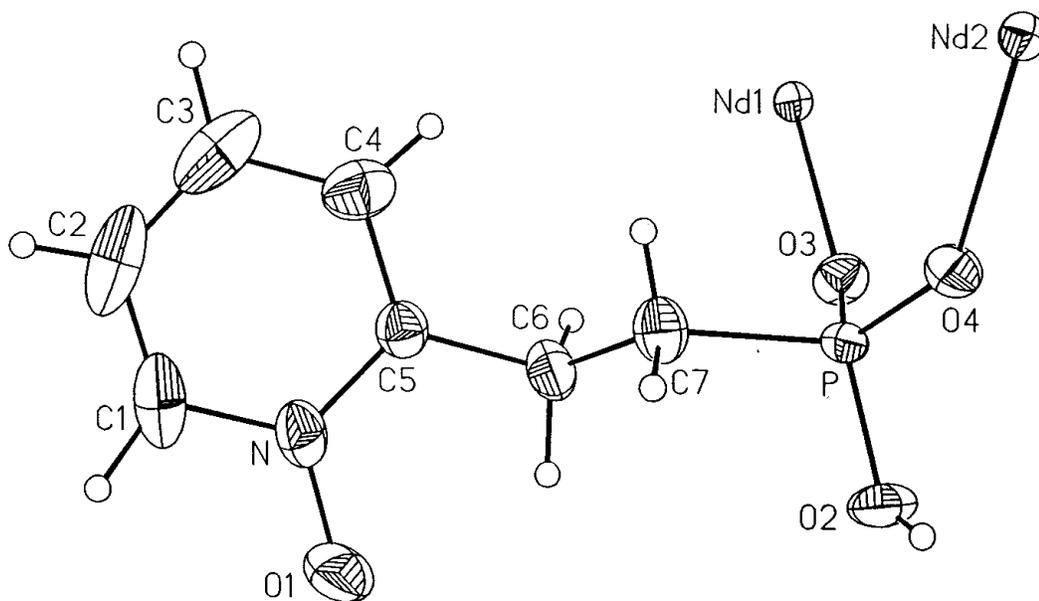


Figure 7. Ligand **6** bridging interaction between two Nd ions.

Each of **6** is bound to both kinds of Nd atoms (Figure 7) forming a chain along the o,o,z direction. The Nd-O distances are essentially identical, and the ligand acts as a bridging ligand instead of as a chelate (Figure 7).

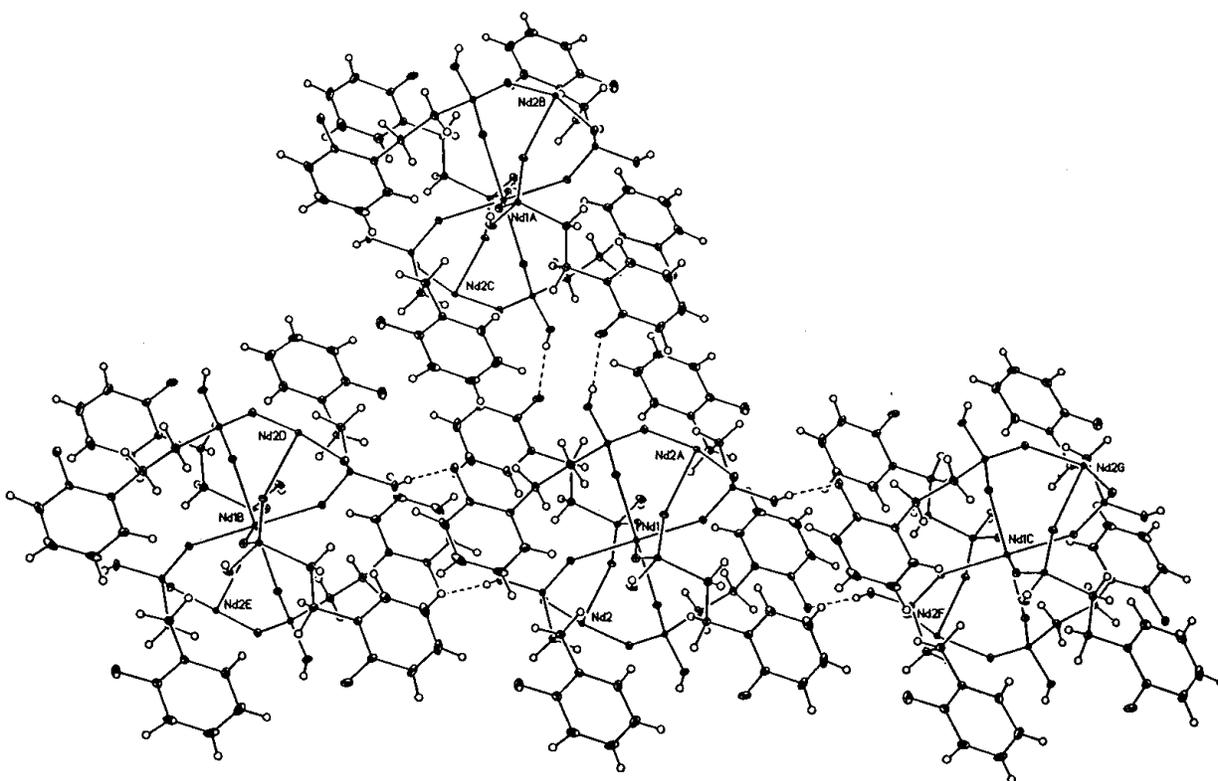


Figure 8. View of bridged bonding and hydrogen bonding in $[\text{Nd}(\mathbf{6})_3]_n$

There is significant hydrogen bonding that stabilizes the chain structure (Figure 8). The structure adopted suggests that the extra CH_2 group between the pyridine ring and the $\text{P}=\text{O}$ group disfavors chelation and promotes bridging.



This molecular unit has a two-fold axis passing through the Er atom, so the asymmetric unit is $\frac{1}{2} [\text{Er}(\mathbf{5})_3 (\mathbf{5}) \cdot 8\text{H}_2\text{O}]$. The molecular unit closely resembles that of $\text{Er}(\mathbf{1})_3 (\mathbf{1}) \cdot 4\text{H}_2\text{O}$, and a view is shown in Figures 9. The inner coordination sphere is a square antiprism of ligand

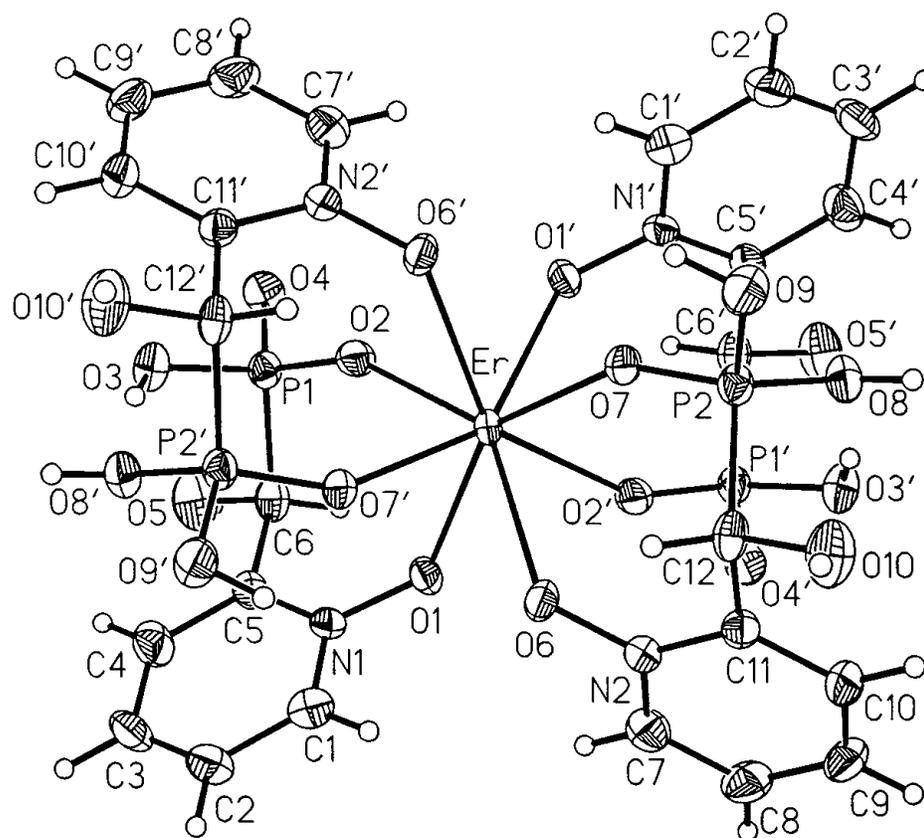


Figure 9. Molecular structure of $\text{Er}(\mathbf{5}^-)_3 \cdot (\mathbf{5}) \cdot 8\text{H}_2\text{O}$

O atoms similar to that found for the structure involving **1**. The unit cell contents for this molecule are shown in Figure 10 without H-bonding interactions represented.

$\text{Nd}(\mathbf{2}^{2-})(\mathbf{2}^-)(\text{H}_2\text{O})_{4/3}$

This structure is very unusual in that it contains two unique ligand fragments. One ligand is a dianion, while the other is a monoanion. Each forms a tridentate chelate on each Nd as shown in Figure 11. Each Nd is seven coordinate with the coordination polyhedron approximating a monocapped trigonal prism. Six of the oxygen atoms come from the tridentate

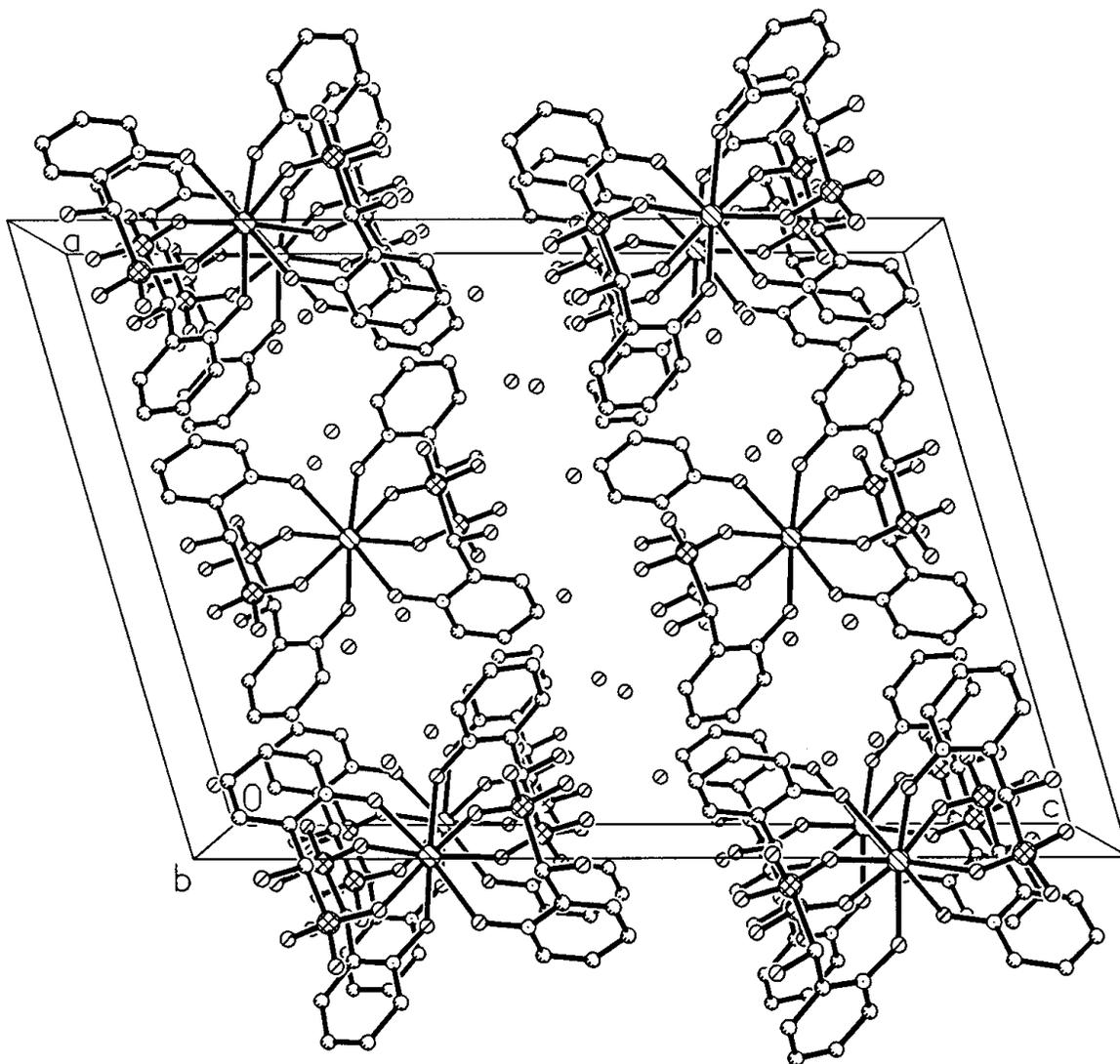


Figure 10. Unit cell contents for $\text{Er}(\mathbf{5}^-)_3 \cdot (\mathbf{5}) \cdot 8\text{H}_2\text{O}$

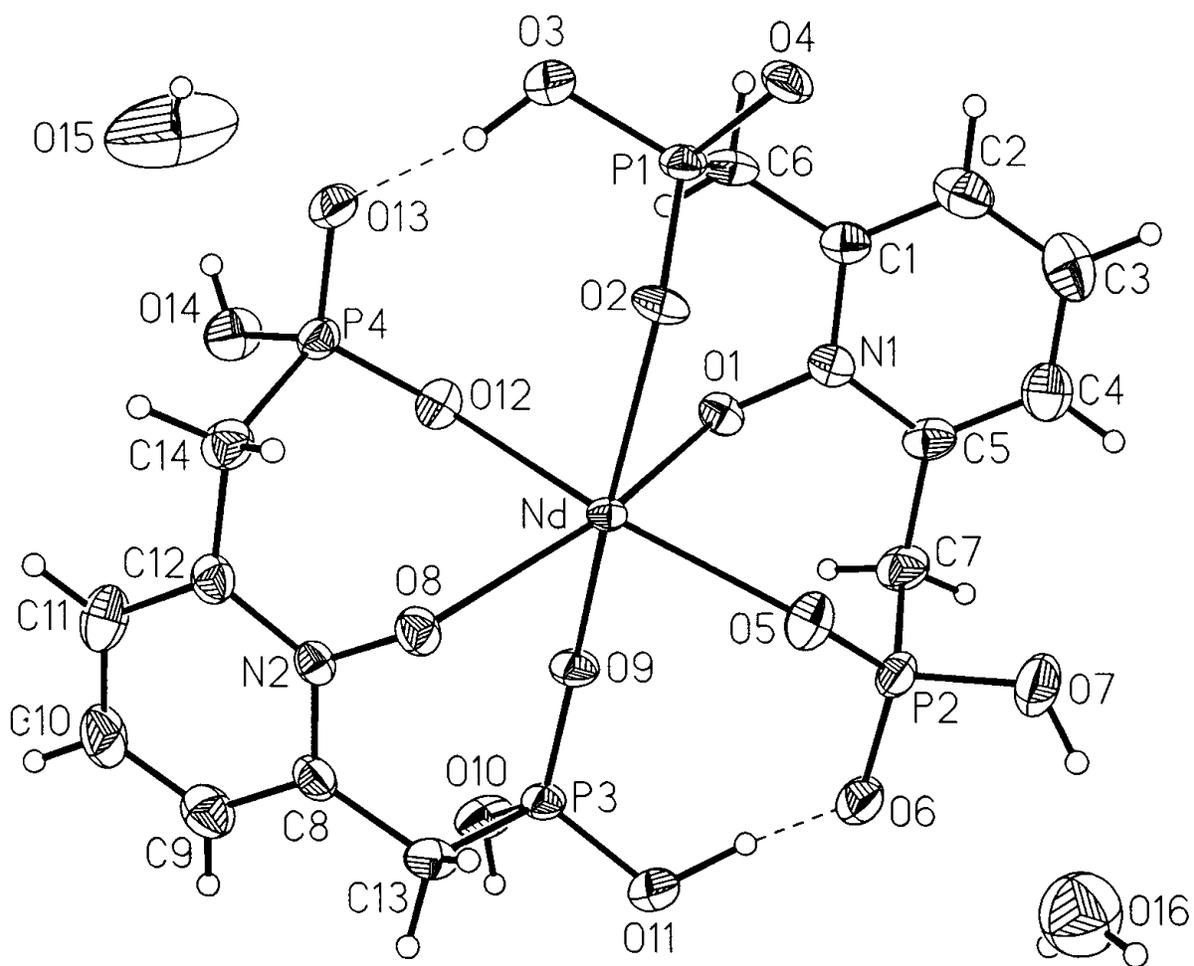


Figure 11. Molecular structure for $\text{Nd}(\mathbf{2}^{2-})(\mathbf{2}) \cdot (\text{H}_2\text{O})_{4/3}$

N-O and P-O groups. The seventh position is occupied by one of the phosphonate oxygens on the dianionic ligand. The result is a polymer chain structure. The Nd-O(P) and Nd-O(N) distances are similar. There is an extensive hydrogen bonding network for the complex that helps to stabilize the chain along the *c* axis as shown in Figure 12.

in Figure 13. Under the conditions of the reaction, the phenoxy group is not involved in the coordination.

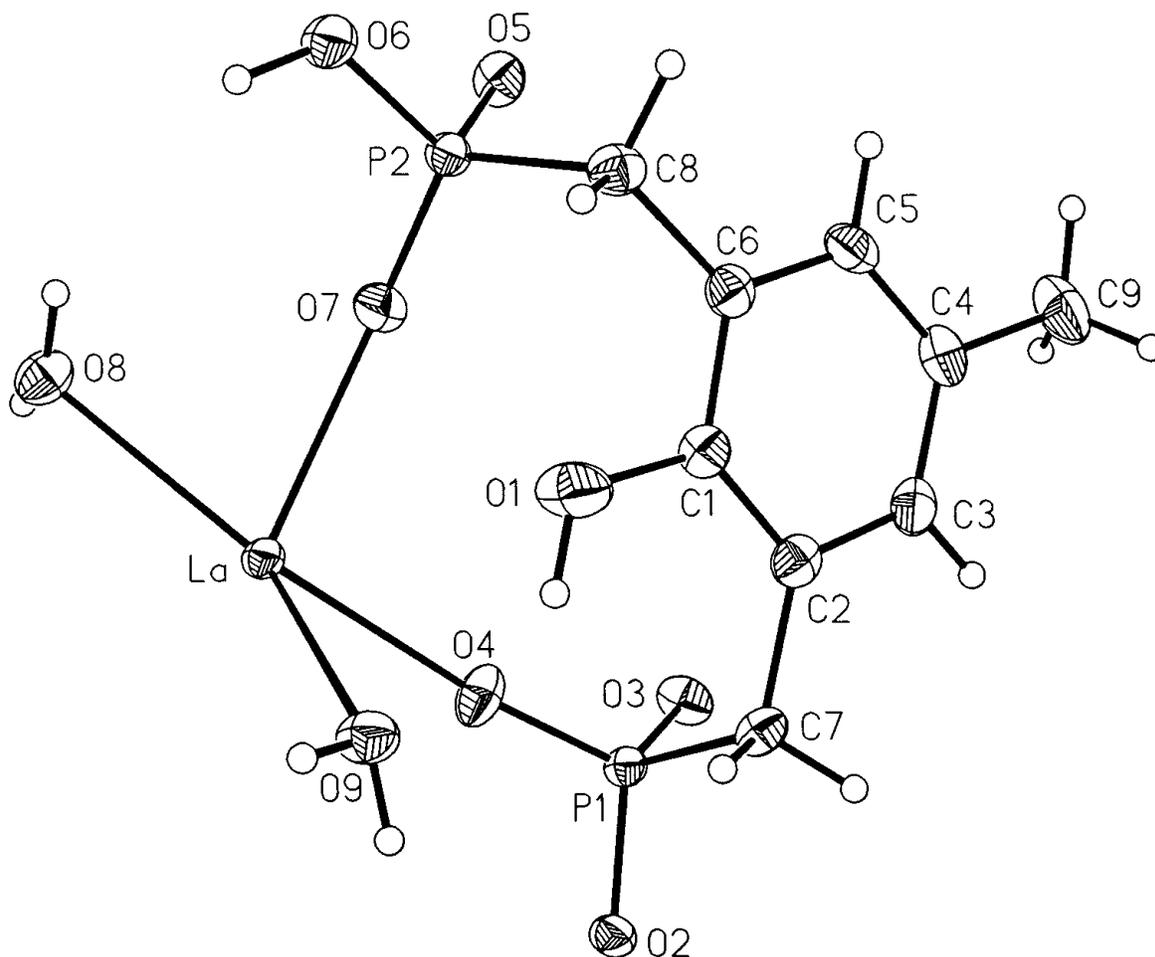


Figure 13. Molecular unit in $\text{La}(\text{7}^2)(\text{H}_2\text{O})_2$

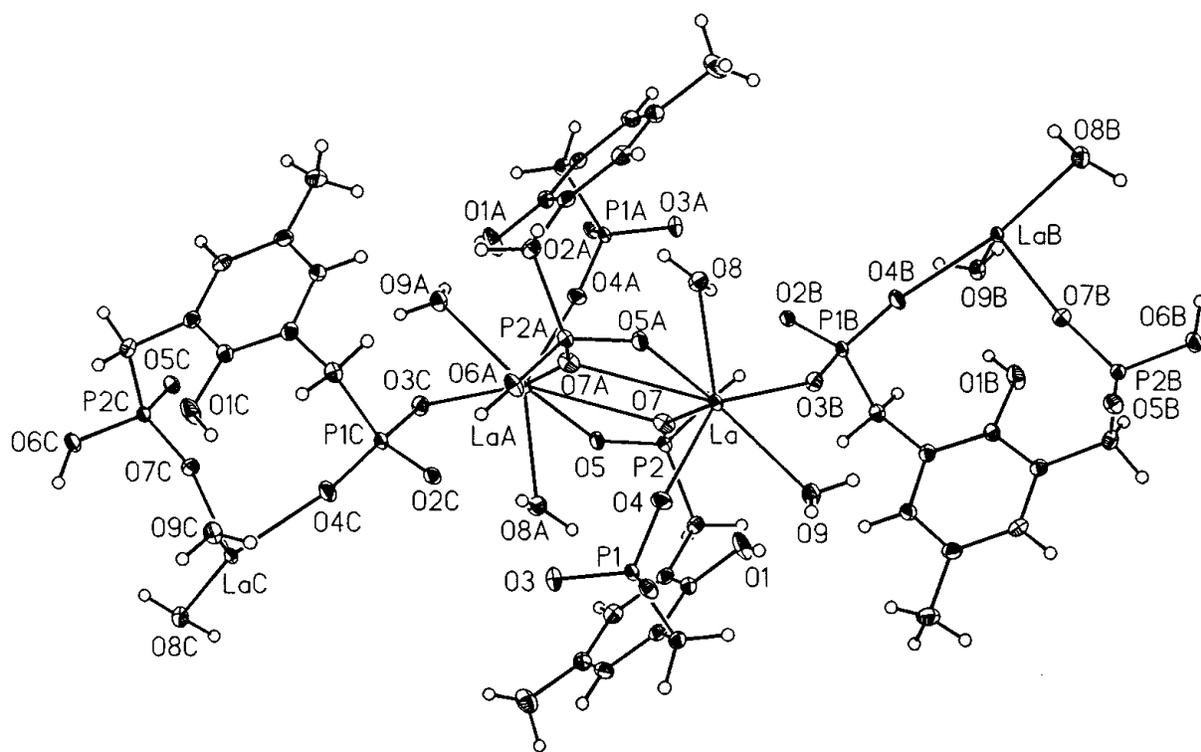


Figure 14. Chain structure for $\text{La} (7^{2+}) \cdot (\text{H}_2\text{O})_2$

6. Relevance, Impact and Technology Transfer

- a) As outlined in Section 4, this project involved development of fundamental science that would enable more practical, site-specific studies. To this end, the project was successful. The results suggest that studies of the precipitate-dissolution kinetics of f-element tank waste should be carefully reevaluated especially where metastable sol-gel clusters may be present. These species are likely to be chemically dynamic and may, without proper attention, result in mobilized species. Knowledge of this chemistry is crucial to successful treatment of tank waste.
- b) This project was not undertaken to address immediate field application issues since this was not part of the original proposal call. However, with further study on actinide ions, we expect to find that the new phosphonic acid chelators developed in the project will be useful as sludge solvers and decon agents. We also expect that the sol-gel dissolution information gained will be useful to those in the national laboratories studying dissolution/mobilization mechanisms.
- c) We believe our results should be of interest to those on the other side of the “Valley of Death.” However, it has been a slow process putting together the bridge. Over the last year, bridge building with the Chemistry Division at Argonne National Laboratory has led to the initial efforts to study phosphonic acid dissolution of f-element species. That work will continue as best possible without direct funding.
- d) The project’s primary impact has been in manpower training. Students trained have chosen to enter other areas of chemistry following completion of their projects for reasons that will not be discussed. The project has attracted attention at LANL and ANL, and these groups will use the results to push ahead with their separately funded projects. The original

goal of interfacing with B. Hay and B. Rapko at PNL was not highly successful, but this was due to the huge scope of the PNL effort and the fact that our collaboration was not at the top of the list for their EMSP project. The top systems were very productive for the PNL team so the collaborators never had time to explore the secondary systems. We were also unsuccessful in establishing a direct coworker to do solution calorimetry, again because of collaboration breakdowns.

- e) Our chemical treatment systems are not yet ready for large scale trials. This may be appropriate following small scale tests at ANL during the next year.
- f) The capabilities of the UNM team have been improved by addition of the ICP which adds analytical capability to the group not present before. In addition, the newly formed collaborations at LANL on plutonium structural chemistry and at ANL on actinide solution thermodynamics will enhance our BES program and may allow the lab groups to seek applications based EMSP funding.
- g) The results greatly enhance our understanding of how Ln (III) ions behave in basic aqueous solutions. We have developed a totally new and powerful set of chelators that bind Ln (III) ions, and we expect that they will alter the solution behavior of An species.
- h) The chelators need to be tested on pure f-element systems and then on simulant mixtures containing actinides. This can only be done at one of the National Labs. Once the behavior is characterized, then it should be possible to design a separation “system” that utilizes the new chelators.
- i) ANL Chemistry Division (K. Nash) has interest in our chelators, and we have begun a collaboration. LANL (M. Neu) will continue to collaborate on structural studies if other funds are found.

7. Project Productivity

The project accomplished its proposed basic science goals, although not in the detail originally expected. The program was immensely successful in the aspects of chelator design, synthesis, coordination chemistry and dissolution analysis. The project was not successful in the proposed application of some instrumental techniques (mass spectrometry and NMR) to structural studies of Ln/chelator clusters. However, this was anticipated to some degree. The project was successful in crystallographic analyses of cluster formation.

8. Personnel Supported

a) Faculty

R. T. Paine, Chemistry Dept., UNM

b) Visiting Faculty

G. L. Wood, Chemistry Dept., Valdosta State University

c) Post doctorals

Xin-min Gan, Chemistry Dept., UNM

Evelyn Bond, Chemistry Dept., UNM

d) Graduate Students

Evelyn Bond, Chemistry Dept. UNM

Sahrah Parveen, Chemistry Dept., UNM

Claudia Tan, Chemistry Dept., UNM

Yufeng Wen, Chemistry Dept., UNM

Chunai Cai, Chemistry Dept., UNM

- e) Undergraduate Students
Greg Claycomb, Chemistry Dept., UNM
Jesse Stanchfield, Chemistry Dept., UNM
Nathan Kersten, Chemistry Dept., UNM
Nathan Donart, Chemistry Dept., UNM
- f) Staff Collaborator
Eileen Duesler

9. Publications

Peer Reviewed Journal Articles

- a) Gan, X.; Duesler, E.N.; Paine, R.T. “Synthesis and Coordination Chemistry of Bifunctional Pyridylphosphonic Acid Chelators” in preparation.
- b) Gan, X.; Duesler, E.N.; Paine, R.T. “Synthesis and Lanthanide Dissolution Properties of Trifunctional Pyridylphosphonic Acid Chelators” in preparation.
- c) Paine, R.T.; Duesler, E.N.; Bond, E.M. “Synthesis of Aminophosphonic Acid Chelator Fragments: Implications for Dendrimer Synthesis” in preparation.
- d) Gan, X.; Duesler, E.N.; Paine, R.T. “Dissolution Properties of Pyridylphosphonic Acid Chelators for Metal Hydroxides” in preparation.

In addition, it is expected that three additional articles will be prepared on structural studies involving pyridylphosphonic acids and two on thermodynamic studies. Work is still in progress on these projects without funding.

The papers will be properly acknowledged.

10. Interactions

a) Meetings

1. The PI attended the EMSP workshop/conferences in Chicago, July 1998 and Albuquerque 1999. A poster was presented at the Atlanta meeting, 2000.
2. The PI presented a paper at An-97 Baden-Baden, 1997.
3. E. Bond presented a paper at 55th Southwest Regional Meeting, Oct. 1999.

b) Consultants

None

c) Collaborations

1. With M. Neu, LANL
2. With K. Nash, ANL
3. With B. Hay, B. Rapko, PNL

11. Transitions

Beyond the interactions and collaborations described above, we are not aware of others. We have had discussions with two entities regarding chelator scale-up, but the talks are only preliminary until data are available for actinide dissolution.

12. Patents

None

13. Future Work

Potentially, much remains to be done, and descriptions are provided in Section 5.

14. Literature Cited

1. Fryberger, T.B.; Kuhn, W.L.; Watson, J.S. *Efficient Separations and Processing Integrated Program, Technology Summary*, DOE-EM-0126P, U.S. Department of Energy, Washington, D.C., 1994.
2. Fryberger, T.B.; Kuhn, W.L.; Watson, J.S. *Efficient Separations and Processing Integrated Program, Strategic Plan*, U.S. Department of Energy, Washington, D.C., 1994, and references therein.
3. Strachan, D.M.; Schulz, W.W.; Reynolds, D.A. *Hanford Site Organic Waste Tanks: History, Waste Properties, and Scientific Issues*, PNL-8473, Pacific Northwest Laboratory, Richland, Washington, 1993, and references therein.
4. Gephart, R.E.; Lundgren, R.E. *Hanford Tank Clean Up: A Guide to Understanding the Technical Issues*, PNL-10773, Pacific Northwest National Laboratory, Richland, WA, 1995.
5. Clark, D.L.; Hobart, D.E.; Neu, M.P. *Chem Rev* 1995, 95, 25, and references therein.
6. Seaborg, G.T.; Katz, J.J. "The Actinide Elements"; McGraw-Hill Book Co: New York, 1954.
7. Katz, J.J.; Seaborg, G.T. "The Chemistry of Actinide Elements"; Methuen: New York, 1957.
8. Soloveichik, G.L. in "Encyclopedia of Inorganic Chemistry"; Vol. 1, p. 2; King, R.B. Ed.; Wiley: New York, 1994, and references therein.
9. Cotton, S.A. in "Encyclopedia of Inorganic Chemistry"; Vol. 7, p. 3595; King, R.B.: New York, 1994, and references therein.

10. Fuger, J. *Radiochem Acta* **1992**, 59, 81.
11. Baes, C.F., Jr.; Mesmer, R.E. "The Hydrolysis of Cations"; Wiley: New York, 1976.
12. Stumm, W.; Wieland, E. in "Aquatic Chemical Kinetics"; Ch 13, Stumm, W. Ed.; Wiley: New York, 1990.
13. Schindler, P.W.; Stumm, W. in "Aquatic Surface Chemistry"; Ch. 4, Stumm, W. Ed.; Wiley: New York, 1987.
14. Lin, C.-F.; Benjamin, M.M. *Environ. Sci. Tech.* 24, 126 (**1990**).
15. Bagnall, K.W. "The Actinide Elements"; Elsevier: Amsterdam, 1972.
16. Keller, C. "The Chemistry of the Transuranium Elements"; Verlag Chemie: Berlin, 1971.
17. The Actinides, Vol. 5 of "Comprehensive Inorganic Chemistry"; Pergamon Press: Oxford, 1973.
18. "Lanthanides and Actinides", Vol. 7 of MTP International Review of Sciences, Inorganic Chemistry Bagnall, K.W., Ed.; Butterworth: London, Series 1, 1972; Series 2, 1975.
19. Greenwood, N.N.; Earnshaw, A., "Chemistry of the Elements"; Pergamon Press: Oxford, 1984.
20. "The Lanthanides", Vol. 4 of Comprehensive Inorganic Chemistry; Pergamon Press: Oxford, 1984.
21. Burns, C.J.; Bursten, B.E. *Comm. Inorg. Chem.* 9, 61(1989).
22. Gene, R.J.; Mobley, T.W.; Harrowfield, J.M.; Sargeson, A.M.; Snow, M.R. *J. Amer. Chem. Soc.*, 107, 899 (1985) and references therein.
23. Lehn, J.-M. *Science*, 227, 849 (1985); Lehn, J.M. *Angew. Chem. Intl. Ed. Engl.* 27, 89 (1988).

24. Cram, D.J. *Angew. Chem. Intl. Ed.*, 27, 1009 (1988); *Science*, 240, 760 (1988); Cram, D.J.; Trueblood, K.N. *Top. Curr. Chem.*, 98, 43 (1981); Cram, D.J.; Kaneda, T.; Helgeson, R.C.; Brown, S.B.; Knobler, C.B.; Maverick, E.; Trueblood, K.N. *J. Amer. Chem. Soc.*, 107, 3645 (1985).
25. Hancock, R.D.; Martell, A.E. *Chem. Rev.*, 89, 1875 (1989).
26. Wolfgang, K.; Vögtle, F. *Angew. Chem. Intl. Ed.*, 23, 714 (1984).
27. Bradshaw, J.S.; Krakowiak, K.E.; Izatt, R.M. *Azacrown Macrocycles*, Taylor, E.C. Ed., J. Wiley, New York, 1993 and references therein.
28. Gokel, G.W.; Korzeniowski, S.H. *Macrocyclic Polyether Synthesis*, Springer-Verlag, Berlin, 1982 and references therein.
29. Garrett, T.M.; Miller, P.W.; Raymond, K.N.; McMurry, T.J.; Garrett, T.M. *Pure Appl. Chem.*, 60, 545 (1988); Raymond, K.N.; Garrett, T.J. *Pure Appl. Chem.*, 60, 1807 (1988) and references therein.; Franczyk, T.S.; Czerwinski, K.R.; Raymond, K.N. *J. Am. Chem. Soc.*, 114, 8138 (1992).
30. Walkowiak, W.; Brown, P.R.; Shukla, J.P.; Bartsch, R.A., *J. Membr. Sci.*, 32, 59 (1987).
31. Moyer, B.A.; Baes, C.F.; Bryan, S.A.; Burns, J.H.; Case, B.N.; Lumetta, G.J.; McDowell, W.J.; Sachleben, R.A. in "Proceedings of the First Hanford Separation Science
ort No: PNL-SA-21775 pg. III-39, May 1993.
32. Hancock, R.D. *Prog. Inorg. Chem.* 37, 187 (1989).
33. Rizkalla, E.N.; Choppen, G.R. *Handbook on the Physics and Chemistry of Rare Earths* 15, 393 (1991).
34. Suzuki, Y.; Nagayama, T.; Sekine, M.; Mizuno, A.; Yamaguchi, K. *J. Less Common Metals* 126, 351 (1986).

15. Feedback

None