

Actinides 93 International Conference  
 September 20-24, 1993  
 Santa Fe, New Mexico  
 Journal of Alloys and Compounds

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## Actinide Phosphonate Complexes in Aqueous Solutions

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## ABSTRACT

Complexes formed by actinides with carboxylic acids, polycarboxylic acids, and aminopolycarboxylic acids play a central role in both the basic and process chemistry of the actinides. Recent studies of f-element complexes with phosphonic acid ligands indicate that new ligands incorporating doubly ionizable phosphonate groups ( $-\text{PO}_3\text{H}_2$ ) have many properties which are unique chemically, and promise more efficient separation processes for waste cleanup and environmental restoration. Simple diphosphonate ligands form much stronger complexes than isostructural carboxylates, often exhibiting higher solubility as well. In this manuscript recent studies of the thermodynamics and kinetics of f-element complexation by 1,1 and 1,2 diphosphonic acid ligands are described.

## INTRODUCTION:

Coordination chemistry of the actinides has played a central role in both the first isolation of these important metals and in the subsequent description of their chemical properties. For example, the  $\alpha$ -hydroxyisobutyric acid cation exchange system depends on the consistent difference between the stability constants of adjacent trivalent lanthanides and actinides for mutual separation of individual members of the respective groups (1). The TALSPEAK process for separation of trivalent actinides from lanthanides (2), a difficult separation because of the great similarity of the aqueous

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 Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, Under contract number W-31-109-ENG-38

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chemistry of the groups, relies on the difference in stability of lanthanide and trivalent actinide complexes with the aminopolycarboxylate complexant diethylenetriamine-N,N,N',N'',N''-pentaacetic acid (DTPA) for successful target separations. Much of the systematics of lanthanide and actinide solution chemistry have been determined via studies of the complexation thermodynamics of chelation (3). Environmental behavior of the actinides is governed to a significant degree by their coordination chemistry, particularly complexation by carbonate, humic materials, and hydroxide (hydrolysis) (4).

Polycarboxylic and aminopolycarboxylic acid complexants commonly used in actinide isolation and waste treatment suffer from a few significant limitations. First, because of their strong affinity for hydrogen ions, they are relatively ineffective for complexing actinide cations in acidic solutions ( $\text{pH} < 2$ ). Secondly, their solubility and that of their f-element complexes is often limited. This characteristic can be selectively applied for isolation purposes (for example oxalate precipitation of trivalent and tetravalent actinides), but may represent a significant safety (e.g., criticality) hazard under unfavorable conditions. Thirdly, most carboxylate and (particularly) aminopolycarboxylate chelating agents are resistant to degradation. Their presence has been associated with the migration of radioactive elements from mixed waste disposal sites (5), and represents the primary source of radiolytic hydrogen being produced in waste storage tanks at various DOE sites (6).

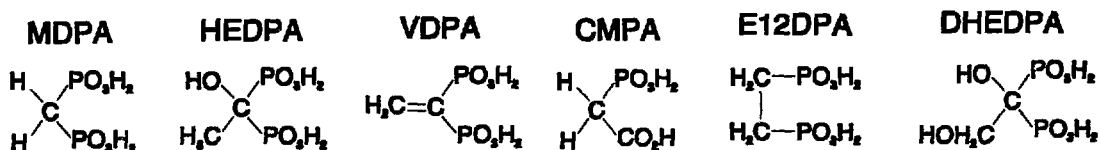
Considering these limitations, simple phosphonic acid chelating agents appear to represent a viable option for many of the applications of water soluble complexants in lanthanide/actinide chemistry. Diphosphonic acids have been recognized for a number of years as efficient complexants for many metal ions of importance in water treatment (7), but have been relatively poorly studied for the f-elements. We have in recent years conducted a detailed investigation of the basic solution chemistry of lanthanide and actinide complexes with diphosphonic acids of various geometries in order to systematize and correlate thermodynamic and kinetic data for these ligands with the much larger body of data on carboxylate and aminopolycarboxylate complexes. The following is a summary of our progress.

## EXPERIMENTAL

This program began with the premise of preparing a new class of chelating agents designed to complex actinides strongly in acidic solutions, forming complexes with enhanced solubility (relative to polycarboxylates and aminopolycarboxylates). The ligands were designed to either possess an inherent, controllable instability, or to be readily decomposed in-situ by treatment with mild oxidizing

agents to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{H}_3\text{PO}_4$ . These ligands are called Thermally Unstable Complexants (TUCS). Their synthesis and use have been described in previous publications (8,9). The most efficient ligands are based on methanediphosphonic acid with various substituents designed to effect the thermal instability of the ligand and solubility of the complexes.

Examples of the first generation of diphosphonate complexants are shown below. MDPA (methanediphosphonic acid), CMPA (carboxymethanediphosphonic acid), and E12DPA (ethane-1,2-diphosphonic acid) are structurally analogous to malonate and succinate. The geometries represented by VDPA (vinylidene-1,1-diphosphonic acid), HEDPA (1-hydroxyethane-1,1-diphosphonic acid) and DHEDPA (1,2-dihydroxyethane-1,1-diphosphonic acid) have no stable carboxylic acid analogs.



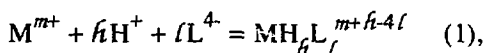
The ligands have been characterized by potentiometric titration and NMR spectroscopy. The 1,1-diphosphonates are tetrabasic acids having protonation constants comparable with those for EDTA (i.e.,  $\text{pK}_1 = 1.0-1.5$ ,  $\text{pK}_2 = 2.0-3.0$ ,  $\text{pK}_3 = 6.0-7.0$ ,  $\text{pK}_4 = 10.0-11.0$ , 8).

Metal complexes in acidic solutions have been characterized with respect to complex stability and stoichiometry by distribution methods (10-12). Complete investigations have been conducted for europium, thorium, and uranyl complexes, each with selected ligands shown above. MDPA, HEDPA, and VDPA complexes have been studied for all three metal ions. These cations are chosen to represent the three most important oxidation states of the actinides in process chemistry. Experimental observations for these cations may be applied with caution to describe the behavior of all actinides in a given oxidation state. Additional observations by potentiometric titration (13), NMR spectroscopy (13), laser induced fluorescence (14), titration calorimetry (14), and stopped-flow kinetics (15), which have been applied in selected systems, have been described elsewhere.

## RESULTS AND DISCUSSION

For the europium, thorium, and uranyl complexes with 1,1-diphosphonic acids in acid solutions, the observed complex stoichiometries fall within a relatively narrow spread of values. At trace concentration of metal ions, there is no evidence for polynuclear complexes. This is not true at higher

concentrations of the metal ion and higher pH, as will be described below. Considering the equilibrium:



$f=0$  for most polycarboxylate and aminopolycarboxylate ligands. For diphosphonate complexes in acidic solutions,  $f=2l$  or more, implying the dominance of protonated complexes under these conditions. The monoprotonated phosphonate moiety ( $-PO_3H^-$ ) is the principal binding group in acidic solutions, but the existence of diphosphonate complexes with the stoichiometry  $M(H_3L)_f$  implies that doubly protonated groups ( $-PO_3H_2$ ) also coordinate to the metal ions. Metal:ligand stoichiometries from 1:1 to 1:3 are observed (10-12).

f-Element cations behave in solution as hard acids, preferring interaction with strong base donor atoms like oxygen to soft base donors like sulfur. Electrostatic models are therefore most useful in correlating thermodynamic data. A linear correlation between the free energy ( $\Delta G$  or  $\log K$ ) for metal ion complex formation and ligand protonation has previously been discussed (3). In Figure 1 is shown such a linear correlation of  $\log \beta$  vs  $\Sigma pK_a$  (taken as the total hydrogen ion affinity) for polycarboxylate and aminopolycarboxylate complexes of europium, thorium, and uranyl (open symbols) compared with those for simple diphosphonate ligands (closed symbols). For a given degree of ligand acidity, the phosphonate containing complexants form complexes from 2 (europium) to 5 (thorium) orders of magnitude stronger than carboxylic acids. The phosphonate data is for the complexes identified in acidic solutions (i.e., protonated complexes). Insufficient data exists to predict whether this apparent enhancement will continue as the pH is raised.

The best indication of the relative affinity of phosphonate and carboxylate complexants should be provided by a comparison of the physical properties metal complexes with structural analogs. Toward this end, we studied the thermodynamics and laser-induced luminescence decay of europium complexes with MDPA (14). The former experiment addresses the energetics of complex formation while the latter assesses the degree of inner-sphere hydration of the complexes (17). The thermodynamic parameters for the formation of 1:1 and 1:2 complexes between europium(III) and MDPA or malonate are given in Table 1. The dominant form of the MDPA ligand under the experimental conditions is  $H_3L^-$ . Available thermodynamic data for malonate describes complexes with  $L^{2-}$ . The complexation equilibria with appropriate change in inner-sphere hydration are shown in equa-

tions 2-5:

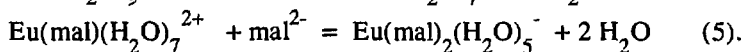
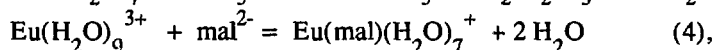
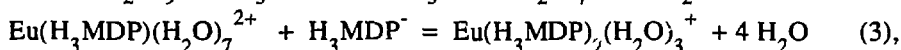
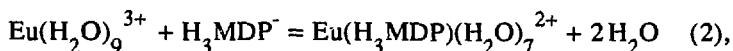


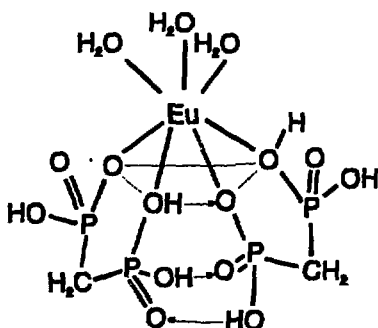
Table 1. Thermodynamic parameters for europium complexation by MDPA and malonate.

Complex	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol-K)
$\text{Eu}(\text{H}_3\text{MDP})^{2+}$	-20.8	+9.6	+102
$\text{Eu}(\text{H}_3\text{MDP})_2^+$	-11.9	-7.1	+16
$\text{Eu}(\text{mal})^+$	-20.7	+13	+113
$\text{Eu}(\text{mal})_2^-$	-15.4	+7	+75

Hydration of the free ligand is ignored in these equations, but should not be appreciably different for  $\text{H}_3\text{MDP}^-$  and  $\text{mal}^{2-}$ . Formation of a chelate ring typically requires the displacement of two solvent molecules from the inner-coordination sphere. The increased degrees-of-freedom due to the larger number of solute species in the solution implies increased entropy, which accounts in part for the "chelate effect". The data for the 1:1 complexes for the formation of  $\text{Eu}(\text{mal})^+$  and  $\text{Eu}(\text{H}_3\text{MDP})^{2+}$  are very similar indicating similar structures for the two complexes. However, while  $\text{Eu}(\text{mal})_2^-$  formation is typically driven by a favorable entropy,  $\text{Eu}(\text{H}_3\text{MDP})_2^+$  derives its stability from an exothermic heat and a small favorable entropy. Observation of such a small entropy change when nominally two excess water molecules are forced from the inner coordination sphere represents a significant departure from what is typically observed for polycarboxylate and aminopolycarboxylate complexes of the elements.

A plausible rationale for this observation is provided by molecular modeling. Molecular mechanics calculations using several different modeling programs (Alchemy, CAChe, SYBYL) indicate a significant positive charge on the phosphorus in MDPA. This leads to a 1,4 electrostatic attraction (i.e., attraction between atoms not directly bound) between the partially positive phosphorus and the

negatively charged oxygens of the second phosphonate ligand. The programs predict a distorted tetragonal pyramidal arrangement of europium and the four bonding oxygens of the two phosphonate groups, as shown below.



With both ligands thus crowded into a single hemisphere around the cation, interligand hydrogen bonding between the triprotonated ligands becomes a significant source of added complex stability, contributing to both a negative enthalpy (through the formation of additional hydrogen bonds), and a smaller net entropy by increasing order in the complex. The extensive ordering implied by such an arrangement coupled with the potential for further second-sphere ordering of solvent molecules combine to reconcile the observed thermodynamic parameters.

Uranyl complexes with phosphonate containing ligands have been studied in the greatest detail because they are amenable to study by several different techniques. Distribution studies (12) with MDPA, VDPA, HEDPA, E12DPA, and CMPA indicate a marked preference for 1:2 complexes in most cases, even at very low concentrations of the ligand. Substitution of carboxylate for phosphonate (in studies of CMPA) or extension of the carbon backbone (E12DPA) results in reduced complex stability. In all cases, the observed complexes are significantly stronger than those with isostructural carboxylates. Molecular mechanics calculations suggest that the hydrogen ions bound to phosphonate may be most favorably oriented for a hydrogen bonding interaction with the "-yl" oxygens of uranyl, but the  $\alpha$ -hydroxy group of HEDPA probably is not.

The complexes between uranyl and MDPA are sufficiently soluble to permit study of this system by potentiometry and NMR spectroscopy (13). Providing that the ligand is maintained in 2-fold or greater excess over the uranyl ion, good solubility (at 0.01M total metal ion) is observed from pH 2 to 10. A series of titrations at 0.005 M MDPA containing uranyl at 1:8, 1:6, 1:4, 1:3, and 1:2 mole ra-

tios were best fit by assuming 1:2 complexes are dominant at both low and high pH. In the pH range from 5 to 8, polynuclear species are indicated. Best fits are obtained assuming metal:ligand stoichiometries of 2:2 and 2:3.

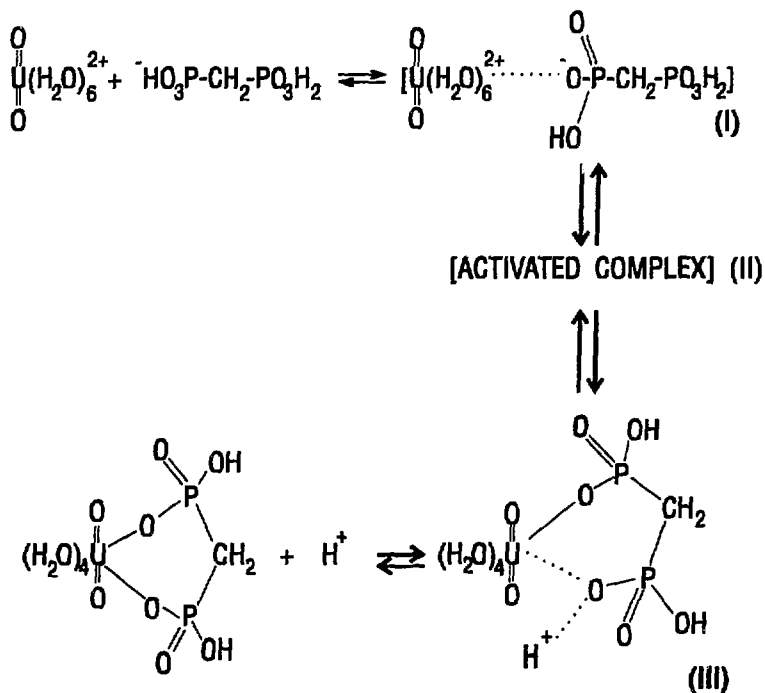
The potentiometric analysis is complemented by  $^{31}\text{P}$  spectroscopy. Decoupled spectra of solutions at the same mole ratios as the potentiometric experiments run as a function of pH produce singlet peaks (at room temperature) corresponding to the free ligand (17.0 ppm relative to an external  $\text{H}_3\text{PO}_4$  capillary reference), the 1:2 complex (23.0 ppm), and the polynuclear complex (27.2 ppm) (Figure 2a). The observation of singlet peaks for each of the complexes indicates high symmetry for the complexes, and implies relatively slow exchange between the complexes and the free ligand. At reduced temperature, some splitting of the second complex peak (27.2 ppm) is indicated. These three resonances increase and decrease in a manner consistent with the stoichiometric ratios suggested by the potentiometry, as shown in Figure 2b for a solution containing 0.005 M MDPA and 0.0017 M uranyl. Minor broadening of the  $^{23}\text{Na}$  resonance at high pH is taken as an indication of labile sodium ion binding to  $\text{UO}_2\text{L}_2^{6-}$  complex at high pH. The phosphorus environment represented by the resonance at 27.2 ppm probably corresponds to a diphosphonate group bridging two uranyl cations.

Direct investigation of the kinetics of uranyl complexation by diphosphonic acids in acidic solutions was performed by stopped-flow spectrophotometry (15). In this system, ArsenazoIII is used as an indicator of free metal ion. Complexation kinetics are investigated by observing the rate of disappearance of free metal ion upon mixing with MDPA, EDPA, or E12DPA under pseudo-first order conditions (diphosphonate ligand in excess). The reaction proceeds as a first-order approach to equilibrium.

Table 2. Rate and activation parameters for formation and dissociation of uranyl phosphonate complexes. Values in parentheses represent  $\pm 1\sigma$  uncertainty limit.

Ligand	$k_f(\text{M}^{-1}\text{s}^{-1})$	$k_d(\text{M}^{-1}\text{s}^{-1})$	$\Delta H^*$ (kJ/mol)	$\Delta S^*$ (J/mol-K)
MDPA	6813(320)		38.0(1.4)	-44(4)
		31.3(2.1)	44.8(2.4)	-66(8)
HEDPA	7715(146)		38.8(0.6)	-40(2)
		27.5(2.0)	57.8(20.9)	-22(62)
E12DPA	216(24)		46.8(0.1)	-43(1)
		47.4(2.6)	44.2(4.1)	-65(13)

librium thus permitting determination of both formation and dissociation rates for the respective 1:1 complexes. Rate constants and activation parameters are shown in Table 2. Activation parameters for both formation and dissociation reactions indicate an associative process as the rate determining step. Dissociation is catalyzed by acid. The probable mechanism is:



It has been noted previously that differences in actinide complex stabilities are most often the result of different dissociation rates for the complexes (17,18). Association rates are typically at or near the diffusion-controlled limit. For the phosphonate complexes, however, dissociation rates are similar for MDPA, HEDPA, and E12DPA while complex formation rates differ to determine relative complex stability.

### CONCLUSION

Phosphonic acid ligating groups bring to the design of new chelating agents for actinides a number of unique properties. Phosphonic acid groups appear to be capable of forming strong complexes in acidic solutions. As most actinide processing is done in acid, this property suggests great potential for the use of suitable phosphonate ligands for improved separations processes. Though not a topic of discussion for this paper, diphosphonate ligands have been prepared which incorporate a de-



gree of thermal instability to minimize waste disposal problems often associated with the use of organic chelating agents. Because complexes are formed with protonated phosphonate groups, significant opportunity exists for intramolecular hydrogen bonding and solute-solvent interaction for actinide-phosphonate complexes in acidic solutions. In contrast with most polycarboxylate ligands, complexation rates are relatively slow (millisecond lifetimes) thus enabling detailed studies of the rates and mechanism of actinide phosphonate complexation reactions.

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