

Calorimetric and Laser Induced Fluorescence Investigation of the Complexation Geometry of Selected Europium-*gem*-Diphosphonate Complexes in Acidic Solutions[†]

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Details of the coordination chemistry of europium complexes with methanediphosphonic acid (MDPA), vinylidene-1,1-diphosphonic acid (VDPA), and 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) in acidic aqueous solutions have been investigated by titration calorimetry and laser-induced fluorescence. For the 1:1 complexes, thermodynamic parameters and complex hydration are consistent with those previously reported for europium complexes with the carboxylate structural analog malonate. In the 1:2 complexes, markedly different thermodynamic parameters and cation dehydration are observed. The second diphosphonate ligand adds to the 1:1 complex displacing four additional water molecules from the primary coordination sphere (as compared with two for the addition of a second malonate). This reaction is also characterized by a nearly zero entropy change. The results are rationalized using molecular mechanics to suggest an unusual geometry in which the diphosphonate ligands and bound water molecules are appreciably segregated in the europium coordination sphere. Intramolecular hydrogen bonding and second hydration sphere ordering are suggested to explain the low complexation entropies.

Introduction

Organophosphonic acids have been widely studied as complexing agents for transition and alkaline earth metal ions.¹ With most metal ions, these phosphonate ligands form stronger complexes than their carboxylate analogs. Most earlier studies of the complexation of lanthanide and actinide metal ions by organophosphonates has been directed to the aminopolymethylenephosphonates.²⁻⁶ The solubility for the lanthanide and actinide complexes with simple organophosphonates appears to be somewhat limited at elevated pH, but surprisingly strong complexes of moderate solubility have been observed in acidic solutions.⁷⁻¹⁰

The protonation constants and the stability constants for Eu(III) complexation have been reported for several substituted methylenediphosphonate ligands.⁷ The enhanced complexing ability of diphosphonate ligands (as compared with that of the

analogous dicarboxylates) was attributed to the decreased basicity of the phosphonate group(s) and the dominance of protonated complexes. It has been suggested that the presence of an extra oxygen donor atom in the phosphonate group may be responsible, at least to some degree, for the enhanced binding strength.¹⁰

To improve our understanding of the complexing ability of the diphosphonate complexes, we have conducted an investigation of the thermodynamics of protonation and of europium complexation reactions of methylenediphosphonic acid (MDPA), vinylidene-1,1-diphosphonic acid (VDPA), and 1-hydroxyethylene-1,1-diphosphonic acid (HEDPA). To complement the thermodynamic data, the approximate number of water molecules in the primary coordination sphere of the complexes was determined by laser induced fluorescence.¹¹

Experimental Section

MDPA, HEDPA, and VDPA were prepared as described in a previous publication.⁷ The purity of the acids was checked by titrimetric assay and by NMR spectroscopy. A Eu(ClO₄)₃ stock solution of 0.0767 M was prepared by dissolution of the necessary weighed amount of 99.95% pure Eu₂O₃ in analytical reagent grade perchloric acid. The acidity of the titrant solution of Eu(III) was adjusted to the desired pH by the addition of HClO₄. The perchloric acid titrant was prepared from analytical reagent grade HClO₄. The ionic strength of each solution was adjusted to 2.0 M by addition of NaClO₄.

The titration calorimeter at Florida State University has been described previously.¹² All enthalpy titrations were conducted at 25.00 °C at an ionic strength of 2.0 ± 0.1 M. In the ligand protonation experiments, solutions of known concentration of the tetrasodium salts of the diphosphonates (≈0.01 M) in NaClO₄ were titrated with standardized HClO₄/NaClO₄ solution (at 2.0 M ionic strength), while ligand titrations were performed in duplicate. In the metal complexation

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experiments, two titrations were run for each system under different sets of conditions. Solutions of 0.01 M diphosphonic acid/0.4 M HClO₄/1.6 M NaClO₄ (favoring the 1:1 complex EuH₃L) or 0.1 M diphosphonic acid/0.1 M HClO₄/1.9 M NaClO₄ (favoring the 1:2 complex Eu(H₃L)₂) were titrated with one of standardized Eu(ClO₄)₃ (0.0767 M) at 2.0 M (NaClO₄) ionic strength.

To check a report that the α -hydroxy group had a pK_a value of 11.13 in 0.1 M KCl,¹³ an enthalpy titration of HEDPA with 5 equiv of base present initially was performed. The heat of dilution of H⁺ for the conditions of these titrations was determined in a separate experiment.

To resolve the enthalpy titration data, the speciation of the metal ion and ligand was calculated using previously determined equilibrium constants for metal ion binding and for ligand protonation. The resolution of the cumulative heat (Q_{tot}) as a function of the species present was accomplished by a generic Newton-Raphson nonlinear regression program. Standard procedure for the propagation of errors were followed to establish the uncertainties in the final parameters.

Free energy data⁸ for ligand protonation and complex formation were used to establish the appropriate range of conditions to obtain the maximum formation of a particular species with minimum overlap with others. This was done through speciation calculations which indicated that the dominant europium-diphosphonate complexes in acid solution (0.1–2.0 M) are Eu(H₃L)₂²⁺ and Eu(H₃L)₂⁺. Attempts to determine the heats for formation of Eu(H₂L)⁺ and Eu(H₂L)₂⁻ complexes, dominant at pH > 2, were unsuccessful due to precipitation of unidentified Eu-diphosphonate solids.

The equipment and procedures used for the laser fluorescence experiments have been described previously.¹⁴ The measurements were made on mixtures of varying concentrations of Eu(III) and diphosphonate. The fluorescence decay rates were correlated with the distribution of species to obtain the decay rate for each species which, in turn, provided the values of the hydration of the individual complexes.

Results

Typical plots of the calculated change in pH (a) and in experimental Q_{tot} (b) as a function of the titrant volume in acid titration of Na₄MDP are shown in Figure 1. The first two protonation reactions are observed without significant overlap, but the third and fourth protonations occur almost simultaneously (pK₂ = 2.35, pK₁ = 1.30). A significant correction must be made for the heat of dilution of excess H⁺ in the lower pH range. Equivalence points in the enthalpy titrations were determined from the intersections of the linear regression fits for the first two data segments, and from a quadratic fit for the first 10–12 points after the maximum in the Q_{tot} value. The total ligand and initial acid concentrations were calculated from these equivalence points which improved the accuracy of the fit parameters.

We have analyzed the data assuming that the measured heats correspond to reactions of the free or protonated ligand with a hydrogen ion. The cumulative heat for the protonation reactions can be defined as

$$Q_{\text{tot}} = Q_1 n_{\text{HL}} + Q_2 n_{\text{H}_2\text{L}} + Q_3 n_{\text{H}_3\text{L}} + Q_4 n_{\text{H}_4\text{L}} + Q_{\text{dil}} n_{\text{H}} \quad (1)$$

where $Q_i = -\Sigma \Delta H_i$; Q_{dil} is the heat of dilution of H⁺; n_{HL} is the number of moles of each protonated ligand species, and n_{H} is the number of moles of excess hydrogen ion. If we define the protonation constants as $\beta_{hi} = \pi K_{hi}$, the cumulative heat can be written in terms of the total ligand concentration (L_t):

$$Q_{\text{tot}} = -\frac{L_t \text{Vol}_t (\sum Q_i \beta_{hi} [\text{H}^+]^i)}{(1 + \sum \beta_i [\text{H}^+]^i)} + Q_{\text{dil}} n_{\text{H}} \quad (2)$$

Because the pH is not measured during the titration, the [H⁺]

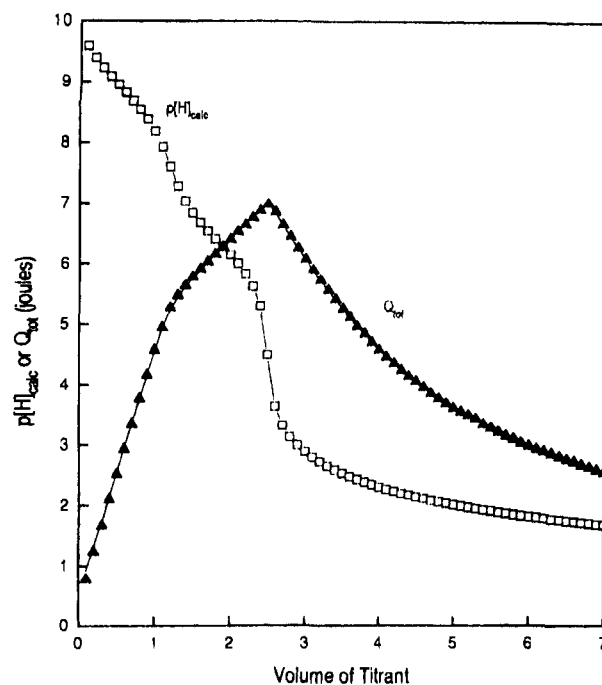


Figure 1. Results for the titration of a 0.01 M solution of the tetrasodium salt of methanediphosphonic acid (MDPA) with 0.395 M HClO₄/1.60 M NaClO₄. Solid line on Q_{tot} data is calculated based on the least-squares analysis of the data.

Table 1. Apparent^a Thermodynamic Parameters^b for Reactions of Methylendiphosphonic Acid (MDPA) at $T = 298$ K and $I = 2.0$ M (NaClO₄)

reaction	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/(mol K))
H + L \rightleftharpoons HL	-50.80(\pm 0.06)	-10.36(\pm 0.10)	+136(\pm 0.4)
H + HL \rightleftharpoons H ₂ L	-36.19(\pm 0.05)	-3.17(\pm 0.14)	+111(\pm 0.5)
H + H ₂ L \rightleftharpoons H ₃ L	-13.41 (\pm 0.06)	+7.83(\pm 0.14)	+71(\pm 0.5)
H + H ₃ L \rightleftharpoons H ₄ L	-7.42(\pm 0.57)	+5.75(\pm 0.24)	+44(\pm 2.0)
Eu + H ₃ L \rightleftharpoons Eu(H ₃ L)	-20.78(\pm 0.58)	+9.56(\pm 0.32)	+102(\pm 2)
Eu + 2H ₃ L \rightleftharpoons Eu(H ₃ L) ₂	-32.60(\pm 0.82)	+2.42(\pm 0.38)	+118(\pm 3)
Eu(H ₃ L) + H ₃ L \rightleftharpoons Eu(H ₃ L) ₂	-11.82(\pm 1.01)	-7.14(\pm 0.50)	+16(\pm 4)

^a These values are termed "apparent" as there has been no correction for possible Na⁺-L⁻ interaction. ^b The values in parentheses represent the 2 σ uncertainty limit. Charges are omitted for simplicity.

is calculated from the known concentration of total ligand and acid added at each point in the titration by application of mass balance criteria and the known protonation constants. The calculated [H⁺] is used with the β_{hi} values in eq 2 to resolve the individual heats (ΔH_i) as the least-squares fit parameters.

The thermodynamic parameters for the protonation reactions of MDPA, VDPA, and HEDPA are presented in Tables 1–3. The initial protonation reaction for each diphosphonate ligand is exothermic but the enthalpies become increasingly endothermic for additional protonations. The enthalpies for HEDPA are more exothermic than those for corresponding reactions of the other two diphosphonates. It was not possible to obtain a value of ΔH for the hydroxyl group protonation in HEDPA (pK_a > 13).

Previous reports^{15,16} of ion-pairing between the alkali cations and *gem*-diphosphonates suggest the existence of NaL³⁻, Na₂L²⁻, and NaHL²⁻. Except for NaL³⁻, the two reports do not agree on the identity of the species present. As a result, we cannot be definite about the extent that replacement of Na⁺

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Table 2. Apparent^a Thermodynamic Parameters^b for the Reactions of Vinylidene-1,1-diphosphonic Acid (VDPA) at $T = 298$ K and $I = 2.0$ M (NaClO_4)

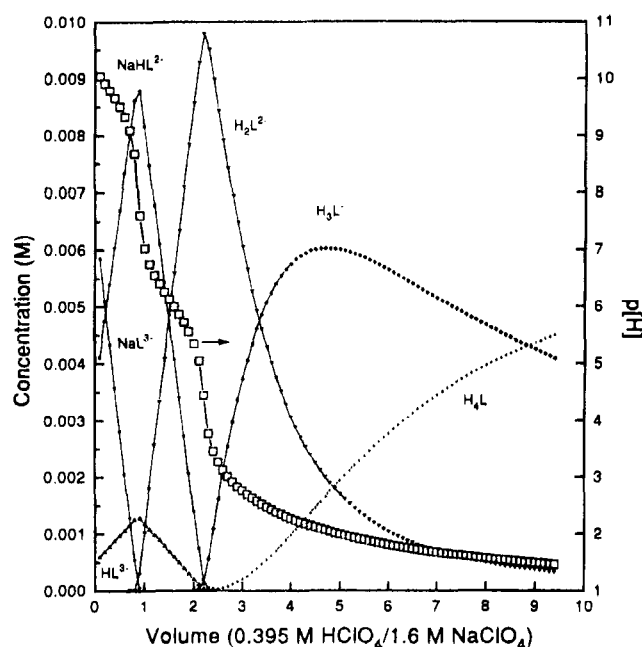
reaction	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/(mol K))
$\text{H} + \text{L} \rightleftharpoons \text{HL}$	-49.09(±0.06)	-11.50(±0.08)	+126(±0.3)
$\text{H} + \text{HL} \rightleftharpoons \text{H}_2\text{L}$	-34.30(±0.12)	-2.02(±0.12)	+108(±0.6)
$\text{H} + \text{H}_2\text{L} \rightleftharpoons \text{H}_3\text{L}$	-11.76(±0.05)	+8.69(±0.12)	+69(±0.4)
$\text{H} + \text{H}_3\text{L} \rightleftharpoons \text{H}_4\text{L}$	-8.05(±0.57)	+4.29(±0.40)	+41(±3.0)
$\text{Eu} + \text{H}_3\text{L} \rightleftharpoons \text{Eu}(\text{H}_3\text{L})$	-20.83(±0.58)	+11.05(±0.53)	+107(±3)
$\text{Eu} + 2\text{H}_3\text{L} \rightleftharpoons \text{Eu}(\text{H}_3\text{L})_2$	-33.33(±0.82)	+3.60(±0.74)	+123(±4)
$\text{Eu}(\text{H}_3\text{L}) + \text{H}_3\text{L} \rightleftharpoons \text{Eu}(\text{H}_3\text{L})_2$	-12.50(±1.00)	-7.45(±0.91)	+16(±5)

^a These values are termed "apparent" as there has been no correction for possible $\text{Na}^+ - \text{L}^-$ interactions. ^b The values in parentheses represent the $\pm 2\sigma$ error limit. Charges are omitted for simplicity.

Table 3. Apparent^a Thermodynamic Parameters^b for the Reactions of 1-Hydroxyethylene-1,1-diphosphonic Acid (HEDPA) at $T = 298$ K and $I = 2.0$ M (NaClO_4)

reaction	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/(mol K))
$\text{H} + \text{L} \rightleftharpoons \text{HL}$	-52.05(±0.05)	-15.72(±0.24)	+122(±0.8)
$\text{H} + \text{HL} \rightleftharpoons \text{H}_2\text{L}$	-35.39(±0.06)	-5.80(±0.18)	+99(±0.6)
$\text{H} + \text{H}_2\text{L} \rightleftharpoons \text{H}_3\text{L}$	-12.56(±0.06)	+4.26(±0.16)	+56(±0.6)
$\text{H} + \text{H}_3\text{L} \rightleftharpoons \text{H}_4\text{L}$	-8.90(±0.57)	+2.42(±0.32)	+38(±2.2)
$\text{Eu} + \text{H}_3\text{L} \rightleftharpoons \text{Eu}(\text{H}_3\text{L})$	-24.14(±0.58)	+5.06(±0.67)	+98(±3)
$\text{Eu} + 2\text{H}_3\text{L} \rightleftharpoons \text{Eu}(\text{H}_3\text{L})_2$	-40.35(±0.74)	-9.49(±0.83)	+104(±4)
$\text{Eu}(\text{H}_3\text{L}) + \text{H}_3\text{L} \rightleftharpoons \text{Eu}(\text{H}_3\text{L})_2$	-16.21(±0.94)	-14.55(±1.12)	+6(±5)

^a These values are termed "apparent" as there has been no correction for possible $\text{Na}^+ - \text{L}^-$ interactions. ^b The values in parentheses represent the $\pm 2\sigma$ error limit. Charges are omitted for simplicity.

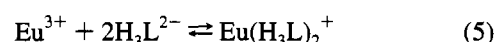
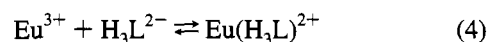
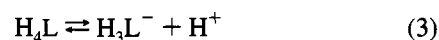
**Figure 2.** Probable speciation of 0.01 M HEDPA in 2.0 M NaClO_4 solution in the course of enthalpy titration with 0.395 M $\text{HClO}_4/1.60$ M NaClO_4 based on the $\text{Na}^+ - \text{HEDP}$ ion pairing equilibrium data¹⁶ at 0.5 M ionic strength and protonation constants⁷ at 2.0 M ionic strength.

by H^+ contributes to the observed "protonation" data. If we choose to apply the equilibrium constants of Carroll and Irani¹⁶ for 0.5 M ionic strength, we can calculate the probable speciation in a representative titration of HEDPA under the conditions of the enthalpy titrations (Figure 2). For the first two protonation reactions, multiple and overlapping reactions contribute. However, the sodium ion pairing reactions do not affect the analysis

of the europium complexation experiments as these complexation experiments were conducted in acidic solutions.

Assuming the speciation presented in Figure 2 is representative of the present experiments, we have estimated the enthalpies of a number of protonation/ Na^+ ion pairing reactions for HEDPA. This analysis is only semi-quantitative, as the effect of variation in ionic strength is not considered, and the identity of species is not confirmed. Reported values of $\log \beta$, ΔH , and ΔS values for formation of NaHEDP^{3-} in 0.5 M ionic strength are, respectively, 2.07, +1.7 kJ/mol, +46 J/(mol K).¹⁶ We estimate $\Delta H = -11$ kJ/mol for the reaction $\text{H}^+ + \text{NaL}^{3-} = \text{HL}^{3-} + \text{Na}^+$ from the ΔH for $\text{H}^+ + \text{L}^{4-}$ reported by Vasilev et al.¹⁷

Analysis of the Eu^{3+} complexation titrations was complicated by the presence of both free H_4L and H_3L^- in 0.4 M or 0.1 M acid. The calculated speciation of the metal ion and ligand for the Eu-VDP titrations is shown in Figure 3. The observed heat is composed of contributions from three reactions



plus the heat of dilution of Eu^{3+} . The observed total heat (Q_{tot}) can be given as:

$$Q_{\text{tot}} = \Delta H_{\text{M}(\text{H}_3\text{L})}[\text{EuH}_3\text{L}]\text{Vol}_1 + \Delta H_{\text{M}(\text{H}_3\text{L})_2}[\text{Eu}(\text{H}_3\text{L})_2]\text{Vol}_1 + \Delta H_{\text{dil}}[\text{Eu}^{3+}]\text{Vol}_1 + \Delta H_{\text{H}_4\text{L}}([\text{H}_4\text{L}]_0\text{Vol}_0 - [\text{H}_4\text{L}]\text{Vol}_1) \quad (6)$$

The enthalpy of ionization of H_4L is taken from Tables 1–3. The small protonation constants ($\text{p}K_1 = 1.3\text{--}1.6$) associated with reaction 3 have relatively large uncertainties ($\pm 0.1\text{--}0.2$).

The heat of dilution of Eu^{3+} can be estimated from the titration represented by Figure 4a. In this titration, speciation calculations indicate the formation of a single complex species, $\text{EuH}_3\text{L}^{2+}$, with excess Eu^{3+} ; $\text{Eu}(\text{H}_3\text{L})_2^+$ represents less than 5% of the total europium. To a good approximation, the total heat (Q_{cor} – observed heats corrected for ligand protonation heats) can be attributed to the formation of $\text{EuH}_3\text{L}^{2+}$ and the heat of dilution of Eu^{3+} . A linear fit of Q_{cor} vs millimoles ($\text{EuH}_3\text{L}^{2+}$) for Eu-VDP, under the conditions of Figure 4a, gives a correlation of 0.999, suggesting that the heat of dilution of Eu(III) is probably negligible. The final fits and reported parameters are based on the assumption $\Delta H_{\text{dil}}(\text{Eu}) = 0$. The resolved heats of complex formation for equilibria 4 and 5 and the stepwise data for formation of the 1:2 complexes are given in Tables 1–3.

In the titration of HEDPA with $\text{Eu}(\text{ClO}_4)_3$, the formation of a copious white precipitate was noted upon completion of the titration for both the 1:1 and 1:2 complexes. However, subsequent tests of the kinetics of precipitation indicated that the precipitation reaction was slow, and probably did not interfere through the first 14–18 points of each titration. Assuming that the speciation calculations described the actual reactions occurring for this portion of the Eu-HEDP titration curves, the data for the two titrations were combined and analyzed using eq 6. The relatively large error limits on these data are a manifestation of the increased uncertainty caused by the shortened data set.

The laser fluorescence results are presented in Table 4. For the Eu-MDPA and Eu-HEDPA systems, concentrations of the

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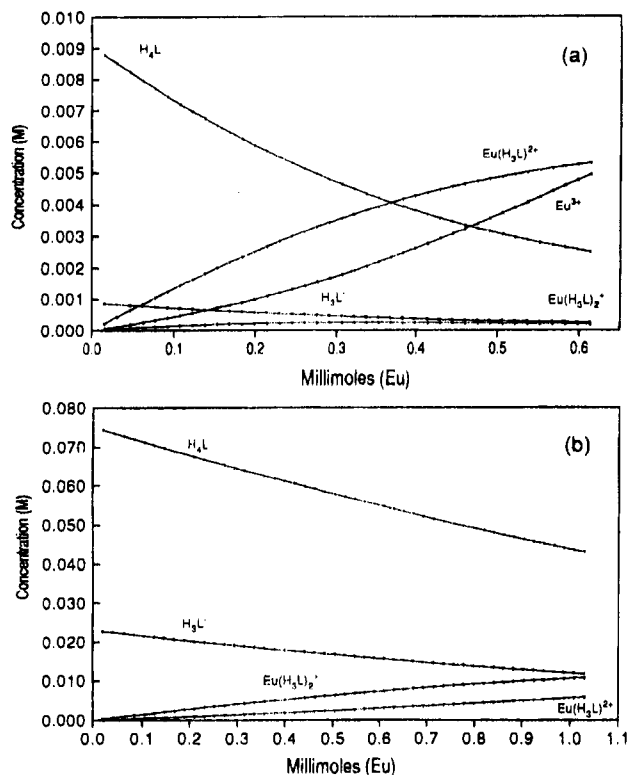


Figure 3. Calculated speciation for the titration of vinylidene-1,1-diphosphonic acid (VDPA) with $\text{Eu}(\text{ClO}_4)_3$. (a) titrant 0.067 M $\text{Eu}(\text{ClO}_4)_3$, 0.400 M HClO_4 , 1.2 M NaClO_4 ; titrand $[\text{VDPA}] = 0.01$ M. (b) titrant 0.105 M $\text{Eu}(\text{ClO}_4)_3$, 0.400 M HClO_4 , 1.59 M NaClO_4 . (b) titrant 0.105 M $\text{Eu}(\text{ClO}_4)_3$, $[\text{HClO}_4] = 0.10$ M, $[\text{NaClO}_4] = 1.27$ M; titrand $[\text{VDPA}] = 0.100$ M, $[\text{HClO}_4] = 0.10$ M, $[\text{NaClO}_4] = 1.86$ M.

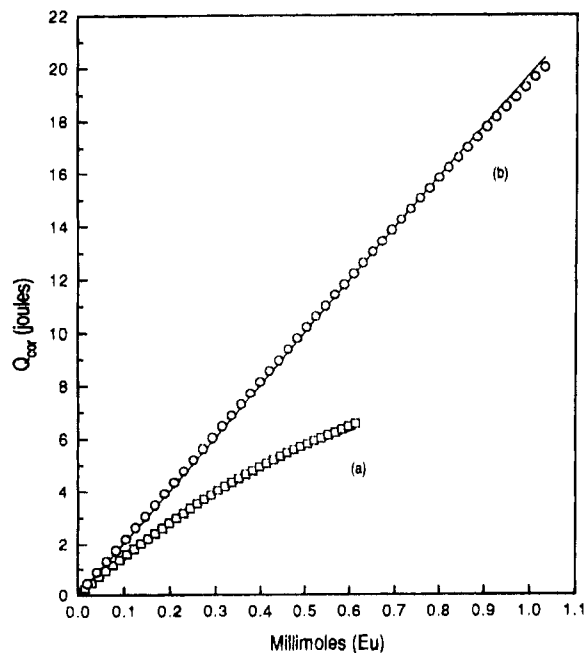


Figure 4. Experimental and calculated cumulative heats (corrected for ligand protonation) as a function of the number of millimoles of europium added in the titrations: (a) titrant 0.067 M $\text{Eu}(\text{ClO}_4)_3$, 0.400 M HClO_4 , 1.2 M NaClO_4 ; titrand $[\text{VDPA}] = 0.01$ M. (b) titrant 0.105 M $\text{Eu}(\text{ClO}_4)_3$, 0.400 M HClO_4 , 1.59 M NaClO_4 ; titrand $[\text{VDPA}] = 0.100$ M, $[\text{HClO}_4] = 0.10$ M, $[\text{NaClO}_4] = 1.27$ M; titrand $[\text{VDPA}] = 0.100$ M, $[\text{HClO}_4] = 0.10$ M, $[\text{NaClO}_4] = 1.86$ M. Calculated values are based on least-squares analysis of the data for both experiments.

complexant were varied at constant metal ion concentration and acidity to permit measurements to be made at varying concen-

Table 4. Fluorescence Decay Rates for Eu Complexes of MDPA, VDPA, and HEDPA^a

A. Eu-MDPA						
$[\text{L}]_i$	$[\text{Eu}^{3+}]$	$[\text{EuH}_3\text{L}^{2+}]$	$[\text{Eu}(\text{H}_3\text{L})_2^+]$	$k (10^{-3} \text{ s}^{-1})$	$av h$	
0.5 M total acidity, $I = 2.0$ M (NaClO_4), $[\text{Eu}]_i = 0.01$ M						
0.008	0.0047	0.0047	0.0002	8.14	8.2	
0.02	0.0017	0.0073	0.0008	6.99	7.0	
0.09	0.0002	0.0043	0.0054	5.36	5.3	
B. Eu-HEDPA						
$[\text{L}]_i$	$[\text{Eu}^{3+}]$	$[\text{EuH}_3\text{L}^{2+}]$	$[\text{Eu}(\text{H}_3\text{L})_2^+]$	$k (10^{-3} \text{ s}^{-1})$	$av h$	
0.5 M total acidity, $I = 2.0$ M (NaClO_4), $[\text{Eu}]_i = 0.01$ M						
0.008	0.0048	0.0048	0.0003	8.10	8.2	
0.02	0.0008	0.0068	0.0022	6.18	6.2	
0.09	0.0001	0.0027	0.0067	4.46	4.4	
C. Eu-VDPA						
pH	$[\text{EuH}_3\text{L}^{2+}]$	$[\text{Eu}(\text{H}_3\text{L})_2^+]$	$[\text{Eu}(\text{H}_2\text{L})_2^-]$	$k (10^{-3} \text{ s}^{-1})$	$av h$	
$[\text{L}]_i = 0.10$ M, $I = 2.0$ M (NaClO_4), $[\text{Eu}]_i = 0.01$ M						
0.3	0.0049	0.0049		5.71	5.7	
1.0	0.0022	0.0074	0.0002	4.49	4.4	
1.5	0.0011	0.0067	0.0016	4.30	4.2	
1.8	0.0004	0.0043	0.0043	3.97	3.8	
D. Average Number of H_2O Molecules						
ligand	$\text{Eu}(\text{H}_3\text{L})_2^{2+}$	$\text{Eu}(\text{H}_3\text{L})_2^+$	$\text{Eu}(\text{H}_2\text{L})_2^-$			
MDPA	7.2	2.6				
HEDPA	6.7	3.4				
VDPA	7.5	3.2	2.8			

^a All concentrations in M.

trations of the free metal and the $\text{EuH}_3\text{L}^{2+}$ and $\text{Eu}(\text{H}_3\text{L})_2^+$ complexes. Solutions of 0.01 M $\text{Eu}/0.1$ M VDPA were studied as a function of pH (between 0.3 and 1.8) in a constant ionic strength medium of 2.0 M (NaClO_4). The average number of hydroxy groups attached to Eu(III) in the inner coordination sphere was determined from the fluorescence decay rates according to the equation in ref 14 and the hydration of each of the complexes determined. The values in Table 4 have an uncertainty of ± 1 hydroxy group (or ± 0.5 H_2O molecules).

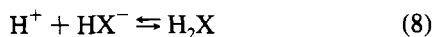
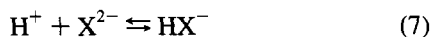
Discussion

Thermodynamic parameters for the protonation of HEDP have been reported by Vasil'ev et al.¹⁷⁻¹⁹ who used calorimetry to determine enthalpies for the first, second, and third protonation reactions of HEDP. They obtained -9.2 , -2.1 , and $+8.8$ kJ/mol for ΔH_i ($i = 1-3$) at zero ionic strength by extrapolation of results at different ionic strengths using $(\text{H}_3\text{C})_4\text{NCl}$ as the supporting electrolyte; the corresponding entropy values are $+201$, $+138$, and $+126$ J/(mol K). Miodusky²⁰ used temperature coefficient titration data to obtain enthalpy values of -19.2 , -8.6 , $+2.7$, and $+5.0$ kJ/mol for the four consecutive protonation reactions of HEDP. The respective entropy values are $+130$, $+95$, $+54$, and $+40$ J/(mol K). Our results are in closer agreement with Miodusky's data. Both our values and those of Miodusky's include a contribution from ion association between HEDP^{4-} and Na^+ (or K^+). Using the results of Carroll and Irani²¹ on Na^+ and K^+ binding to HEDP, we can correct our first protonation values to -14.0 kJ/mol for the enthalpy and $+185$ J/(mol K) for the entropy. Additional work in

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- (19) Vasil'ev, V. P.; Orlova, T. D.; Mar'ina, T. B. *Zh. Obshch. Khim.* **1984**, *54*, 514.
- (20) Mioduski, T. *Talanta* **1980**, *27*, 299.
- (21) Carroll, R. L.; Irani, R. R. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2971.

progress in 0.1 M NaClO₄²² is consistent with our present results in 2.0 M NaClO₄. Values of the heats for the second through fourth protonation reactions are in reasonable agreement from all three sets of data.

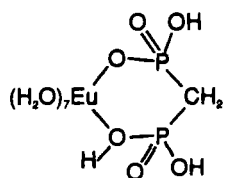
We can explore the effect of the structural differences between H⁺ binding in carboxylates and phosphonates by comparing the data for the third and fourth protonation reactions of MDP (the H₂L²⁻ and H₃L⁻ species) with the first and second protonation of malonate anion defining X²⁻ as H₂L²⁻ and Mal²⁻ and HX⁻ as H₃L⁻ and HMal⁻, the reactions are



The free energy for the malonate protonation reactions, $\Delta G_1 = -28.9$ kJ/mol and $\Delta G_2 = -14.8$ kJ/mol²³ are greater than the values for the MDP system of -13.4 kJ/mol and -7.4 kJ/mol, respectively. This difference reflects the greater basicity of the carboxylate oxygen. The corresponding protonation enthalpies and entropies for malonate are 2.0 kJ/mol and +104 J/(mol K) compared to 7.8 kJ/mol, and +71 J/(mol K) for H₂MDP²⁻. The difference in entropy values for eq 7 most likely is due to greater dehydration of Mal²⁻ than of H₂MDP²⁻ upon protonation. The enthalpies would also reflect a difference in hydration which would lead us to expect more positive values for the malonate system. The more negative enthalpy must reflect the greater basicity of the carboxylate relative to the phosphonate group. The entropy change for eq 8 is the same for both systems (45 ± 1 J/mol⁻¹/K⁻¹), indicating similar dehydration. It also suggests that any structural differences between the HX⁻ and H₂X species are similar in both systems. Again, the stronger basicity for HMal⁻ relative to that of H₃MDP⁻ is reflected in the more negative enthalpy.

For the europium complexation reactions, we were able to study only the formation of Eu(H₃L)²⁺ and Eu(H₃L)₂⁺ as the insolubility of the Eu³⁺ + H₂L²⁻ system precluded study of the thermodynamics of Eu(H₂L)_{*n*}^{3-2*n*} complexation. The values in Tables 1–3 indicate that the previously reported⁷ higher stability of Eu(H₃HEDP)²⁺ relative to Eu(H₃MDP)²⁺ and Eu(H₃VDP)²⁺ derives from a less endothermic ΔH as the complexation entropy is constant within the experimental accuracy of the measurements.

The positive ΔH and ΔS values for Ln(III) complexation with carboxylate ligands can be interpreted as due to the strong contribution of dehydration of the interacting cation and anion.²⁴ Presumably, the positive values of these parameters for Eu(III) interaction with the diphosphonate ligands also reflects dehydration. Table 4 reports a loss of about 1.5 water molecules from Eu(III) upon formation of Eu(H₃L)²⁺ with all three diphosphonate ligands. By contrast, it was reported that two water molecules are lost in the formation of EuMal⁺.¹⁴ Consider the following structure:

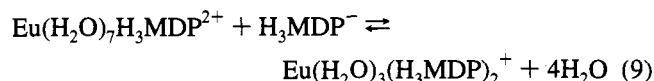


All hydroxyls attached to the metal ion can quench the luminescence; H₂O having two hydroxyl vibrators quenches

about twice as efficiently as a single OH group. The configuration in this structure is consistent with a "hydration number" of 7.5 as the protonated phosphonate group contributes one OH to quenching of europium fluorescence. It suggests an entropy change corresponding to the loss of two water molecules upon complexation. The similar hydration for HEDP, MDP, and VDP complexes suggests that the α -hydroxy group of HEDP is not directly coordinated to the metal ion.

Crystal structures indicate that six-membered rings are dominant in lanthanide phosphonate complexes. For example, the crystal structure²⁵ for the monophosphonate complex Lu-cilicinate (Lu(PO₃HCH₂CH₂NH₃)₃(ClO₄)₃·3D₂O) shows that the monoprotonated phosphonate group bridges two lutetium metal ions in an octahedral coordination environment. Shkol'nikova et al.²⁶ have reported that the Er(III) in the crystal structure of H(Er(H₂HEDP)₂)·H₂O is characterized by a local 8-fold coordination, and only six-membered-rings. In this crystal structure, phosphonate groups bridge two metal ions and the α -hydroxy group of HEDPA is not bound. The water molecule in the crystal is not coordinated to the cation.

For the formation of the 1:2 H₃MDP⁻ complex



the fluorescence decay rate indicates the loss of four water molecules from the inner coordination sphere (Table 4). The thermodynamic parameters are $\Delta H_2 = -7.1$ kJ/mol, $\Delta S_2 = +16$ J/(mol K). Thermodynamic parameters for the Eu-VDP complex are nearly identical while for Eu(H₃HEDP)₂⁺ the entropy is even smaller and the enthalpy more exothermic.

We assume that the low complexation entropy, combined with the loss of four water molecules from the inner coordination sphere of the metal, implies that Eu(H₃MDP)₂(H₂O)₃⁺ must have a highly ordered structure. It has been observed that the increased order resulting from the formation of a five- or six-membered ring approximately compensates for the translational and rotational freedom gained with the release of a water molecule to the bulk solution phase.²⁷ For this system, total compensation for the excess dehydration would seem to require the formation of three such rings. Intramolecular-interligand hydrogen bonding effects associated with the addition of the second H₃MDP⁻ ligand could account for such a contribution. In addition, the fluorescence results indicate only the water molecules that are lost from the inner coordination sphere. They do not necessarily require the release of those water molecules to the bulk solution. As the phosphonate groups are extensively protonated in the complex, many opportunities for solvent-complex hydrogen bonding exist. This second sphere ordering combined with the formation of rings between bound ligands (also through hydrogen bonding) should lead to a highly ordered complex and, presumably, a very low net entropy. The existence of a network of hydrogen bonds would also lead to a more exothermic complexation heat, consistent with observation. The large exothermic complexation enthalpy for addition of a second HEDP also correlates with this model.

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(24) Nancollas, G. H. *Interactions in Electrolyte Solutions*; Elsevier: Amsterdam 1966; pp 133–140.

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(26) Shkol'nikova, L. M.; Masyuk, A. A.; Polyanchuk, G. V.; Afonin, K. G.; Poznyak, A. L.; Zavodnik, V. E. *Koord. Khim.* **1989**, *15*, 1424; *Chem. Abstr.* **1990**, *112*, 46099y.

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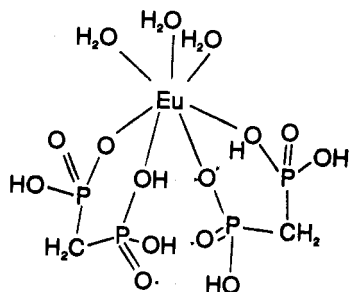


Figure 5. Proposed structure for $\text{Eu}(\text{H}_3\text{MDP})_2(\text{H}_2\text{O})_3^+$.

To test this hypothesis, the Eu + Mal and Eu + MDP systems were subjected to molecular mechanics calculations using the programs Alchemy, DTMM, CAChe, and Sybyl. Each of these programs were performed using the parameters generated by the manufacturer. None of the model calculations account for second sphere solvation, dielectric constant effects, or the dynamics of solution reactions and must be interpreted with caution. However, all four sets of modeling calculations suggest a similar arrangement of the ligands around the europium cation. It should be noted that the ionic interactions with the europium cation results in an optimum arrangement of coordinating groups around the metal ion due to a balance between electrostatic and steric effects. All four programs indicate that the $\text{Eu}(\text{H}_3\text{MDP})_2^+$ complex adopts a structure in which the two ligands essentially surround about two-thirds of the europium spherical surface leaving the remaining one-third exposed for interaction with solvent water molecules. A structure consistent with the modeling for $\text{Eu}(\text{H}_3\text{MDP})_2(\text{H}_2\text{O})_3^+$ is given in Figure 5.

The protonated phosphonate groups on the two ligands are oriented to permit the formation of at least two intramolecular hydrogen bonds. Inner-sphere water molecules must assume a tripodal orientation in the available space. Sybyl calculations suggest the basis of this arrangement is electrostatic attraction between atoms not bonded. It is likely a result of attraction between the partial positive charge on the phosphorus atoms

on one ligand and the negative charge of the oxygens of the second ligand.

There is at least one report in the literature of such an arrangement of ligands and solvent molecules.²⁸ Van Der Sluys et al. report that in the solid state $\text{UCl}_4(\text{THF})_3$ has a configuration in which the three solvent molecules are arranged as suggested in the $\text{Eu}(\text{H}_3\text{MDP})_2^+$ complex with the four chloride ions adjacent. Those authors cite the tripodal arrangement of solvent molecules as counterintuitive, suggesting that it results from crystal packing forces. The modeling calculations suggest perhaps there is a better explanation based on intramolecular electrostatic forces.

Conclusions

Complexation heats, fluorescence decay rates, and molecular modeling calculations have been combined with earlier data on the free energies to elucidate structural details of europium complexation reactions with MDP, VDP, and HEDP. $\text{Eu}(\text{H}_3\text{L})^{2+}$ forms six-membered-ring chelates with thermodynamic parameters and inner-sphere dehydration typical for such complexation. Upon addition of a second H_3L^- ligand, four water molecules are lost from the inner coordination sphere of the cation in the 1:1 complex accompanied by exothermic heats and small positive entropies. A likely structural model for these complexes, derived from molecular mechanics calculations, indicates an asymmetric placement of the ligands about the cation, with extensive interligand, intracomplex hydrogen bonding.

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