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Thermodynamics and hydration of the europium complexes of a nitrogen heterocycle methane-1,1-diphosphonic acid

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Received 19th May 2000, Accepted 27th July 2000

The enthalpies for formation of five Eu^{3+} complexes with *N*-piperidinomethane-1,1-diphosphonic acid (H_4pmdp) have been determined by titration calorimetry in 2 M (Na,H)ClO_4 media at 25 °C. Both protonation enthalpies and entropies, and the structure of H_4pmdp in the solid state indicate protonation of the piperidine nitrogen to give a zwitterion in the free ligand. Luminescent lifetime measurements show that the formation of the 1 : 1 and 1 : 2 Eu : L complexes of a variety of methane-1,1-diphosphonic acids liberates an average of 3.3 ± 0.1 water molecules per ligand from the Eu inner hydration sphere. The number of water molecules in the inner coordination sphere and the thermodynamic parameters of the complexes suggest that the structure of the Eu^{3+}–pmdp complexes and the strength of the Eu^{3+}–pmdp bonds are similar to those of other methane-1,1-diphosphonic acids despite the presence of the piperidine ring. However, the complexation entropies argue for weaker solvation of the Eu–pmdp complexes probably due to the hydrophobic character of the piperidine ring.

Introduction

The greater strength of diphosphonic acid chelating agents, as compared to polycarboxylic acids, is a manifestation of several interrelated characteristics of the diphosphonate moiety. The presence of an additional oxygen donor atom per phosphorus atom ($–PO_3H_2$ *vs.* $–CO_2H$) gives each phosphonate group a binding strength equivalent to 1.5 carboxylate groups.[1] In addition, the P=O bond has long been known to be highly polar,[2] a fact that allows diphosphonate ligands to form a variety of protonated complexes (MH_nL) with polyvalent metal ions. Complexes of Th^{4+} with fully protonated diphosphonic acids have been reported.[3] The ability of diphosphonic acids to form protonated complexes also encourages formation of an extensive intramolecular, interligand hydrogen bond network that stabilizes the 1 : 2 (Eu^{3+} : diphosphonate) complexes.[4] Because phosphonic acids also are more readily deprotonated than carboxylic acids, metal ions can more effectively compete with H^+ for truly anionic ligand binding sites in acidic solutions of diphosphonic acids. The latter characteristic is one of the most important features of these ligands as few carboxylic acids are acidic enough to be effective ligands in acidic media.

Because of these superior complexation properties in acidic solution, certain diphosphonic acid ligands are being developed to address specific needs in actinide separations. Numerous uses of diphosphonates in lanthanide and actinide separation chemistry have been described, including applications in surface decontamination,[5] in solvent extraction[6–8] or extraction chromatography,[9] and in the preparation of a polymer based cation exchange resin.[10] These powerful f-element complexants can be easily destroyed at the end of their useful life by raising the temperature or adding mild oxidizing agents,[6] which mitigates the possibility of ligand promoted actinide migration or radiolytic ligand decomposition and the associated gas generation in nuclear wastes.

The properties of the core methane diphosphonic acid functionality may be modified by derivatization. Alkyl-, hydroxy- and amino- derivatives of methane-1,1-diphosphonic acid have been studied as f-element complexants in aqueous solution (Fig. 1).[3,4,11–14] The lanthanide and actinide complexes of the various diphosphonic acids have exhibited moderate solubility in acidic solutions but only poor solubility in weakly acidic solutions.[4,11,13,15] However, transition metal complexes of nitrogen heterocycle substituted methane-1,1-diphosphonic acids have shown greater solubility than other methane-1,1-diphosphonic acids.[16] Therefore, we have studied the europium(III) complexation properties of *N*-piperidinomethane-1,1-diphosphonic acid, H_4pmdp.

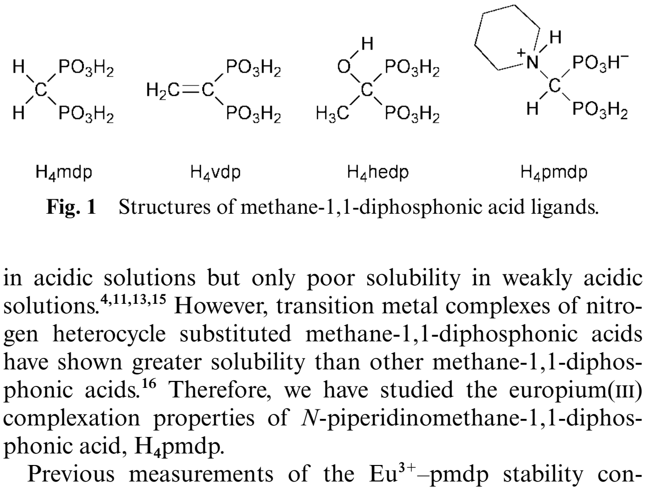

Fig. 1 Structures of methane-1,1-diphosphonic acid ligands.

Previous measurements of the Eu^{3+}–pmdp stability constants[12] showed that the *N*-piperidinomethane-1,1-diphosphonic acid complexes of trivalent lanthanide cations are more soluble than those of simpler diphosphonic acids. At the same time the ligands retain the ability to strongly complex trivalent f-element cations. The nitrogen heterocycle on the central (1- or α-) carbon lowers the pK_a of each phosphonate oxygen by 1–2 log units compared to non-amino diphosphonic acids. Despite the reduced H^+ affinity, binding of Eu^{3+} is not impaired. Moreover, the comparison of the Eu^{3+}–H_4pmdp stability constants with those of other diphosphonic acids suggests that the presence of a hydrogen bonding group attached to the central carbon atom, such as –OH or $–NR_2H^+$, further stabilizes lanthanide–diphosphonate complexes through interactions with the solvent water molecules.[12] The present work investigates this possibility through structural studies of the ligand and time-resolved laser-induced fluorescence and titration calorimetric measurements on Eu^{3+}–pmdp complexes.

Experimental

The synthesis of H_4pmdp has been described previously.[12] The purity of the ligand was >99% by ^{31}P NMR and potentiometric titration. Water was purified to 18 MΩ cm with a Barnsted

DOI: 10.1039/b004038j

Table 1 Crystallographic data for H_4pmdp

Empirical formula	$C_6H_{15}NO_6P_2$
M/g mol^{-1}	259.14
Crystal system	Monoclinic
a/Å	8.0583(4)
b/Å	6.4558(3)
c/Å	18.8222(10)
β/°	95.591(1)
V/Å^3	974.52(8)
T/K	173
Space group	$P2_1/n$
Z	4
λ/Å	0.71073
D_c/g cm^{-3}	1.766
μ/mm^{-1}	0.457
Independent reflections (R_{int})	2289 (0.0787)
$R1^a$ (observed data)	0.0753
$wR2^b$ (observed data)	0.1973

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, with $F_o^2 > 2\sigma(F_o^2)$. ^{b} $wR2 = [\Sigma(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (°) for H_4pmdp

P(1)–O(1)	1.544(3)	P(1)–O(2)	1.549(3)
P(1)–O(3)	1.496(3)	P(1)–C(1)	1.829(3)
P(2)–O(4)	1.506(3)	P(2)–O(5)	1.572(3)
P(2)–O(6)	1.512(3)	P(2)–C(1)	1.855(3)
N–C(1)	1.514(4)	N–C(2)	1.510(4)
N–C(6)	1.504(4)	C(2)–C(3)	1.523(5)
C(3)–C(4)	1.521(6)	C(4)–C(5)	1.534(6)
C(5)–C(6)	1.525(5)	H(1)–O(6)	2.350(4)
O(3)–P(1)–O(1)	115.8(1)	O(3)–P(1)–O(2)	114.2(1)
O(1)–P(1)–O(2)	106.3(2)	O(3)–P(1)–C(1)	105.0(2)
O(1)–P(1)–C(1)	107.3(2)	O(2)–P(1)–C(1)	107.8(2)
O(4)–P(2)–O(6)	115.8(2)	O(4)–P(2)–O(5)	109.0(2)
O(6)–P(2)–O(5)	110.7(1)	O(4)–P(2)–C(1)	106.2(2)
O(6)–P(2)–C(1)	106.9(2)	O(5)–P(2)–C(1)	107.9(2)
C(6)–N–C(2)	110.8(3)	C(6)–N–C(1)	115.3(3)
C(2)–N–C(1)	111.6(2)	N–C(1)–P(1)	118.9(2)
N–C(1)–P(2)	111.6(2)	P(1)–C(1)–P(2)	111.6(2)

E-pure system. Ultrex grade 70% $HClO_4$ (Baker) and a 50% solution of semiconductor grade NaOH (Aldrich) were diluted, standardized by acidimetric titration to the phenolphthalein endpoint, and used to adjust the acidity of ligand solutions and titrants. A stock solution of $Eu(ClO_4)_3$ was prepared by dissolution of 99.9% Eu_2O_3 (Apache) in warm $HClO_4$. The Eu^{3+} concentration was measured by EDTA titration using xylenol orange indicator,[17] and the concentration of excess acid in the Eu solution was determined by the Gran method.[18] The ionic strength of the solutions was maintained at 2.00 ± 0.05 M by addition of a standardized $NaClO_4$ solution prepared from $NaClO_4{\cdot}H_2O$ (GFS Chemicals). The dissolved iron content of the background electrolyte solution was such that a 2 M solution of $NaClO_4$ contained $<1 \times 10^{-6}$ M iron as quantified spectrophotometrically using the tris(1,10-phenanthroline)iron(II) complex[19] and standard addition of $Fe(NO_3)_3$.

Crystals of H_4pmdp were grown from an aqueous solution of the ligand in 1.9 M $NaClO_4$ at p[H] = 1.0. A transparent single crystal of H_4pmdp was mounted on a fiber and transferred to the goniometer. The crystal was cooled to −100 °C during data collection using a stream of cold nitrogen gas. The space group was determined to be the centric $P2_1/n$ from the systematic absences. A summary of data collection parameters is given in Table 1. The geometrically constrained hydrogen atoms were placed in their calculated positions and allowed to ride on the bonded atom with $B = 1.2 \times U_{eq}(C)$. Hydrogen atoms on the phosphate oxygens were placed in calculated positions $[B = 1.2 \times U_{eq}(O)]$, with torsional freedom. H(1) was located from a difference Fourier map and allowed to ride on N with $B = 1.2 \times U_{eq}(N)$. Refinement of non-hydrogen atoms was carried out with anisotropic temperature factors.

CCDC reference number 186/2115.

See http://www.rsc.org/suppdata/dt/b0/b004038j/ for crystallographic files in .cif format.

Calorimetric measurements were made using the Argonne titration calorimeter.[20] Titrations were carried out in duplicate at 24.985 ± 0.005 °C beginning with 50 ml of pmdp solutions of varying concentration and acidity. The p[H] (p[H] = −log [H^+] in molar units) of each ligand solution was measured before the titrations as previously described.[12] The heats of protonation of pmdp were measured by titration of a Na_4pmdp with $HClO_4$, and are uncorrected for ion pairing between Na^+ and pmdp^{4-}. The heats of formation of the EuH_hpmdp$_l^{(3+h-4l)}$ complexes were measured by titration of 0.008, 0.012, 0.020 and 0.030 M H_4pmdp solutions with 0.102 M Eu^{3+}–0.104 M $HClO_4$–1.90 M $NaClO_4$ beginning at p[H] 1 or 2. The complexation enthalpy determinations were performed in duplicate. The heat of dilution of each titrant was measured by titration into 50 ml 1.99 M $NaClO_4$–0.01 M $HClO_4$. The solution composition at each point of a titration was calculated from the previously measured stability constants[12] and the volumes and the total concentrations of each component using the program LETAGROP ETITR[21] and a spreadsheet based speciation program.[22]

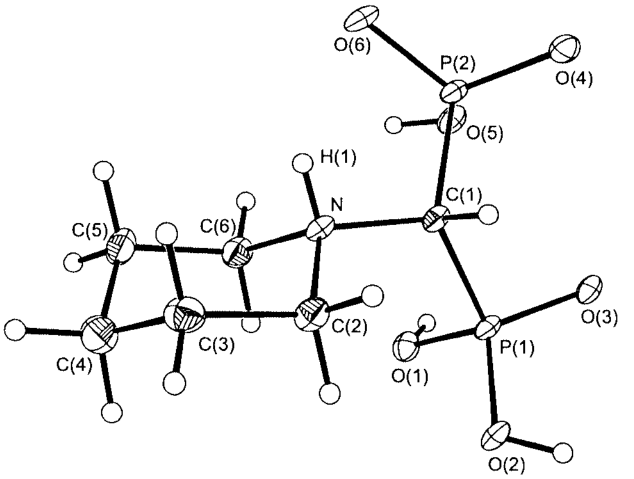

Fig. 2 ORTEP diagram of the *N*-piperidinomethane-1,1-diphosphonic acid zwitterion.

Time-resolved laser-induced fluorescence measurements of Eu^{3+}–pmdp solutions were conducted at 22–23 °C.[23] The solutions were prepared by dispensing known volumes of the Eu^{3+} titrant into 0, 0.008, 0.012, 0.020 and 0.030 M H_4pmdp solutions of the appropriate acidity. In addition, one solution containing 0.0294 M H_4pmdp–0.00101 M Eu^{3+}–0.100 M $DClO_4$–1.89 M $NaClO_4$ in 97.5 atom% D_2O (Aldrich) was prepared to measure k_{D_2O} in a solution with a high degree of Eu^{3+} complexation. Using these solutions, the luminescence decay of the europium $^5D_0$ state after excitation at 355 nm was measured by collection of all luminescence between 665 and 920 nm. Reported decay constants are the mean of five measurements. The Eu^{3+} speciation for each of the H_2O solutions was calculated as above and was correlated with the luminescence lifetime of each solution to obtain the number of OH oscillators coordinated for each europium species.

Results and discussion

Solid state structure of H_4pmdp

As shown in Fig. 2, molecules of H_4pmdp are zwitterions in the crystalline state, which is common for aminophosphonic acids.[24] The piperidine nitrogen is protonated, but the phosphonate group incorporating P(2) is only singly protonated.

Table 3 Measured thermodynamic parameters for the reactions of pmdp at $I = 2.0$ M and $T = 25$ °C

Reaction	*mhl*	ΔG^a/kJ mol^{-1}	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
$H^+ + pmdp^{4-} \rightleftharpoons Hpmdp^{3-}$	011	-65.6 ± 0.6	-54.4 ± 0.3	$+38 \pm 2$
$H^+ + Hpmdp^{3-} \rightleftharpoons H_2pmdp^{2-}$	021	-44.3 ± 0.2	-8.5 ± 0.4	$+120 \pm 1$
$H^+ + H_2pmdp^{2-} \rightleftharpoons H_3pmdp^-$	031	-26.4 ± 0.1	-1.3 ± 0.3	$+84 \pm 1$
$H^+ + H_3pmdp^- \rightleftharpoons H_4pmdp$	041	-11.5 ± 0.1	$+1.7 \pm 0.4$	$+44 \pm 1$
$H^+ + H_4pmdp \rightleftharpoons H_5pmdp^+$	051	-1.8 ± 0.6	$+19.9 \pm 0.9$	$+73 \pm 4$
$Eu^{3+} + H_3pmdp^- \rightleftharpoons Eu(H_3pmdp)^{2+}$	131	-22.5 ± 0.5	$+3.6 \pm 0.7$	$+87 \pm 3$
$Eu^{3+} + H_4pmdp \rightleftharpoons Eu(H_4pmdp)^{3+}$	141	-18.7 ± 1.0	$+4.5 \pm 1.5$	$+78 \pm 7$
$Eu^{3+} + 2\ H_3pmdp^- \rightleftharpoons Eu(H_3pmdp)_2{}^+$	162	-39.8 ± 0.4	-5.1 ± 0.5	$+116 \pm 2$
$Eu^{3+} + 2\ H_4pmdp \rightleftharpoons Eu(H_4pmdp)_2{}^{3+}$	182	-35.3 ± 0.6	$+1.5 \pm 0.7$	$+124 \pm 3$
$Eu^{3+} + 2\ H_4pmdp + H_3pmdp^- \rightleftharpoons Eu(H_4pmdp)_2(H_3pmdp)^{2+}$	1 11 3	-52.7 ± 0.5	-6.5 ± 0.4	$+155 \pm 2$
$Eu(H_3pmdp)^{2+} + H_3pmdp^- \rightleftharpoons Eu(H_3pmdp)_2{}^+$	162	-17.4 ± 0.6	-8.6 ± 0.8	$+29 \pm 4$
$Eu(H_4pmdp)^{3+} + H_4pmdp \rightleftharpoons Eu(H_4pmdp)_2{}^{3+}$	182	-16.7 ± 1.1	-3.0 ± 2.0	$+46 \pm 8$
$Eu(H_4pmdp)_2{}^{3+} + H_3pmdp^- \rightleftharpoons Eu(H_4pmdp)_2(H_3pmdp)^{2+}$	1 11 3	-17.3 ± 0.7	-7.9 ± 0.8	$+31 \pm 3$

[a] ΔG from ref. 12.

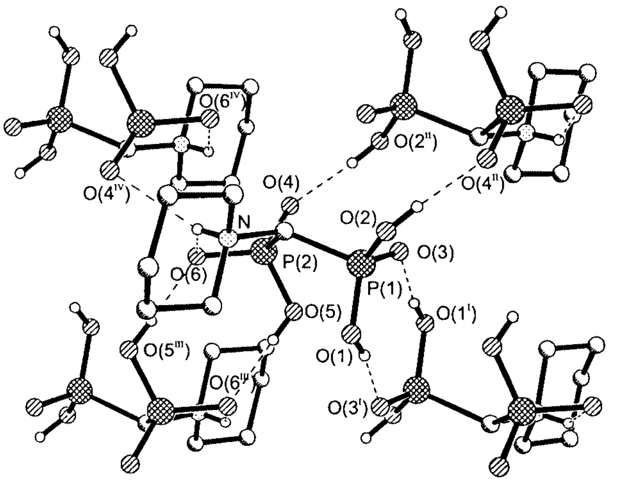

Fig. 3 Intermolecular hydrogen bonding in crystals of *N*-piperidinomethane-1,1-diphosphonic acid. Hydrogen bonds are indicated by dashed lines.

The P(2)–O bond distances (Table 2) bear this out. The bond distance of the protonated oxygen P(2)–O(5) is 1.572(3) Å, while the bond distances of the non-protonated oxygens of this phosphonate group, P(2)–O(6) and P(2)–O(4), have nearly identical separations of 1.512(3) and 1.506(3) Å respectively. In contrast, the P(1) phosphoryl group exhibits a pattern characteristic of diprotonation with one short [P(1)–O(3) 1.496(3) Å] and two long [P(1)–O(1) 1.544(3) Å and P(1)–O(2) 1.549(3) Å] bond distances.

Each phosphoryl oxygen is involved in both intra- and inter-molecular hydrogen bonding that causes each H_4pmdp molecule to interact with four neighboring molecules (Fig. 3). One oxygen, O(6), participates in a 2.350(4) Å intramolecular hydrogen bond with the amino proton and also in a 1.784(13) Å intermolecular bond with a phosphonic acid proton on another H_4pmdp molecule.

The remaining bond distances and angles of the methane-1,1-diphosphonic acid core of H_4pmdp are comparable to those found in other methane-1,1-diphosphonic acids, with the exception of the bond angles around C(1).[25,26] The size of the *N*-piperidine substituent on C(1) reduces the P(1)–C(1)–P(2) angle from 117.2° in methane-1,1-diphosphonic acid (H_4mdp) and 115.1° in 1-hydroxyethane-1,1-diphosphonic acid (H_4hedp) to 111.6(2)° in H_4pmdp. Both P–C bonds lengthen to reduce the strain between phosphonate groups caused by the reduction of the P(1)–C(1)–P(2) angle, an effect also noted for H_4hedp.[25] In addition, the intramolecular hydrogen bond between N–H(1) and O(6) results in a significant reduction in the N–C(1)–P(2) bond angle, 111.6(2)°, *versus* the N–C(1)–P(1) angle of 118.9(2)°.

The extensive interligand hydrogen bonding previously observed in crystal structures of H_4mdp and H_4hedp and in lanthanide–hedp complexes[27] is also seen in the H_4pmdp crystals. Eight, ten and twelve membered rings have been observed in crystals of H_4mdp,[26] while twelve membered rings have been reported for $H_4hedp{\cdot}H_2O$.[25] Despite the size of the piperidine substituent, these modes of bonding are also observed for H_4pmdp. As shown in Fig. 3, intermolecular hydrogen bond networks form two eight membered rings and a twelve membered ring with the surrounding H_4pmdp molecules within the unit cell.

Attempts to crystallize lanthanide–pmdp complexes were frustrated by the general solubility of the complexes and the positive charge present on the complexes of interest.

Protonation enthalpies of $pmdp^{4-}$

Analysis of the protonation enthalpies of the ligand was straightforward. The first four protonation reactions of $pmdp^{4-}$ occur with little overlap. However, the distributions of H_4pmdp and H_5pmdp^+ do overlap between p[H] 1 and 2 owing to the proximity of the lowest two pK_a values, 0.3 and 2.02. The protonation enthalpy of each $H_hpmdp^{(h-4)}$ species, ΔH_{H_hL}, was calculated using the Levenberg–Marquardt least squares algorithm implemented in the program Origin (Microcal) for 47 total data points with the equations

$$Q_{\mathrm{H}_h\mathrm{L}} = -\sum_{m=1}^{h} \Delta H_{\mathrm{H}_m\mathrm{L}} \qquad (1)$$

and

$$Q_i^{\text{total}} = \sum_{h=1}^{5} Q_{\mathrm{H}_h\mathrm{L}}\delta_i^{\mathrm{H}_h\mathrm{L}} + Q_{\mathrm{OH}}\delta_i^{\mathrm{OH}} + Q_{\mathrm{dil}}V_i^{\text{added}} \qquad (2)$$

where Q_{H_hL} is the cumulative molar heat of protonation of species H_hL, δ_i^X is the change in the number of moles of species X from the initial solution composition, Q_{dil} is the heat of dilution of the titrant (-1.06 J ml^{-1}), and V_i^{added} is the total volume of titrant added. The heat of neutralization of OH^-, Q_{OH}, is estimated to be $+56.9$ kJ mol^{-1} at $I = 2.0$ M from the compilation of Martell *et al.*[28] The cumulative reaction heat at each point *i* of a titration or Q_i^{total}, is defined as

$$Q_i^{\text{total}} = \sum_{j=1}^{i} q_j \qquad (3)$$

where q_j is the heat of reaction measured for each addition of titrant, with exothermic heats having a positive sign. Uncertainties in the fit parameters calculated from the covariance matrix are reported at the 2σ confidence level. Results of these computations are summarized in Table 3.

The protonation enthalpies and entropies give insight into the protonation sequence of this ligand. The large exothermic enthalpy observed for the first protonation reaction, −54.4 kJ mol^{-1}, and the relatively small entropy, +38 J K^{-1} mol^{-1}, are substantially different from those previously reported for the first two protonations of the phosphonate oxygens of three non-amino bearing methane-1,1-diphosphonic acids, which range between −15.7 and −2.0 kJ mol^{-1} for ΔH, and +99 and +136 J K^{-1} mol^{-1} for ΔS.[4] However the enthalpy and entropy for the first protonation reaction of pmdp^{4-} are consistent with those reported for protonation of piperidine derivatives (ΔH between −41 and −61 kJ mol^{-1} and ΔS between +9 and +58 J K^{-1} mol^{-1}).[28] This suggests that the piperidine nitrogen is protonated first.

If the piperidine nitrogen is protonated first, one would expect the enthalpies and entropies for the formation of H$_2$pmdp^{2-}, H$_3$pmdp$^-$ and H$_4$pmdp (Table 3) to correspond well with the values for the first, second and third protonations of the non-amino bearing diphosphonic acids. This is indeed the case. The last protonation step of pmdp^{4-}, $\mathrm{H^+ + H_4pmdp \rightleftharpoons H_5pmdp^+}$, should be substantially more endothermic and have a larger entropy change than those observed for the final protonation step of non-amino diphosphonic acids. Protonation of H$_4$pmdp to form fully protonated H$_5$pmdp$^+$ must weaken the hydrogen bond formed between the proton on the piperidine nitrogen and the unprotonated phosphonate oxygen. We would expect this to be a more endothermic and entropy increasing process than the simple protonation of a phosphonate oxygen. The thermodynamic parameters observed for the protonation of H$_4$pmdp (ΔH = +19.9 kJ mol^{-1}, ΔS = +73 J K^{-1} mol^{-1}) are consistent with this.

The crystal structure of H$_4$pmdp and the complete set of protonation enthalpies and entropies of H$_h$pmdp^{h-4} support our earlier conclusion, based on ^{31}P NMR spectroscopy,[12] that the pmdp ligand is a zwitterion in the Eu complexes studied.

Europium complexation

Because determination of the Eu^{3+}–H$_h$pmdp^{h-4} complexation enthalpies began with no metal in the titration vessel, the analysis was complicated only by the protonation equilibria of H$_3$pmdp$^-$ and H$_4$pmdp. The reactions considered were

$$\mathrm{Eu^{3+}} + l\,\mathrm{H}_{h/l}\mathrm{pmdp}^{h/l-4} \rightleftharpoons \mathrm{EuH}_h\mathrm{pmdp}_l^{\,3+h-4l} \quad (4)$$

$$\mathrm{H^+ + H_3pmdp^- \rightleftharpoons H_4pmdp} \quad (5)$$

and

$$\mathrm{H_5pmdp^+ \rightleftharpoons H^+ + H_4pmdp} \quad (6)$$

The experimental data and the multiple linear least squares regression fit for all of the Eu^{3+} titrations (192 total data points) are shown in Fig. 4 and the resolved parameters are tabulated in Table 3. The complexation enthalpies of species Eu$_m$H$_h$L$_l$, ΔH_{mhl}, were fit as the parameters of eqn. (7), where V_i^{total} is the

$$Q_i^{\text{total}} = -\sum_{mhl} (\Delta H_{mhl} V_i^{\text{total}}[\mathrm{Eu}_m\mathrm{H}_h\mathrm{L}_l]_i) - \Delta H_{\mathrm{H_5L}}\delta_i^{\mathrm{H_5L}} - \Delta H_{\mathrm{H_4L}}(-\delta_i^{\mathrm{H_5L}}) + Q_{\text{dil}}V_i^{\text{added}} \quad (7)$$

total volume and $\delta_i^{\mathrm{H}_h\mathrm{L}}$ is the change in the total number of moles of H$_h$L (including that present in the europium complexes) from the initial conditions. The heat of dilution of the Eu^{3+}–HClO$_4$ titrant was measured to be −0.11 J ml^{-1}. Unlike previous investigations of f-element diphosphonic acid complexes,[4,11] precipitates were not observed in these experiments even days after the titrations were completed. The greater solubility of the Eu–pmdp complexes allowed us to study a wider range of concentrations and metal–ligand stoichiometries, and obtain thermodynamic parameters for each of the five Eu–pmdp complexes previously reported to be present under these experimental conditions.

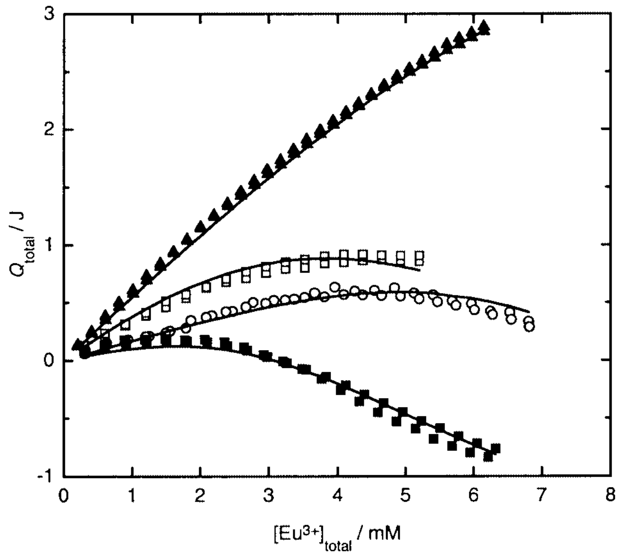

Fig. 4 Experimental and calculated (——) total heats observed for the titration of pmdp solutions with 0.102 M Eu(ClO$_4$)$_3$–0.104 M HClO$_4$–1.90 M NaClO$_4$. The calorimeter initially held 50 ml of (▲) 0.0295 M pmdp–1.96 M NaClO$_4$ at p[H] 1.008, (■) 0.00799 M pmdp–1.98 M NaClO$_4$ at p[H] 1.988, (○) 0.0197 M pmdp–1.96 M NaClO$_4$ at p[H] 1.994 or (□) 0.0119 M pmdp–1.87 M NaClO$_4$ at p[H] 1.007.

In aqueous solutions the formation of metal–ligand complexes is accompanied by changes in the hydration of both the metal ions and the ligands. The most obvious, and easily quantifiable changes in hydration occur when the metal and ligand form an inner sphere complex. In this process, water molecules are displaced from the inner coordination sphere of the metal ion and the donor atoms of the ligand. The entropy of complexation for f-element cations in aqueous solution is primarily associated with changes in the hydration of the metal cation and the ligands,[29] but ΔS can also include interactions with outer sphere solvent molecules and other phenomena only indirectly related to the metal–ligand bond.[30] Therefore, to augment the calorimetric measurements, the Eu inner coordination spheres of these complexes were studied by measurements of the emission spectra and the luminescence decay constants of Eu–pmdp solutions.

Complexation of the Eu^{3+} aquo ion by H$_3$pmdp$^-$ and H$_4$pmdp is accompanied by small changes in the emission spectra from the Eu ^{5}D$_1$ and ^{5}D$_0$ states. As depicted in Fig. 5, variation in the composition of the solutions has little impact on the band positions even though the luminescence lifetimes, and thus the hydration numbers, vary significantly (Table 4). This is attributed to complex formation merely replacing one set of oxygen donors (water molecules) with oxygen donors from pmdp. However, small changes in the shape of the normalized emission bands are apparent, demonstrating that the distribution of Eu species is indeed different for each solution.[31] The band at 617 nm shows the most variation with solution composition.

The number of OH oscillators in the inner coordination sphere of Eu^{3+}, Tb^{3+} or Cm^{3+} complexes has been reported to be proportional to the decay constants of the excited species due to energy transfer between excited electronic states of the metal center and vibrational bands of coordinated OH groups.[32,33] The average number of water molecules present in the Eu inner coordination sphere, $n_{\mathrm{H_2O}}$ or the average hydration number, was calculated for the solutions in Table 4 from the observed luminescence decay constant using Horrocks and Sudnick's equation [eqn. (8)],[32] where $k_{\mathrm{H_2O}}$ and $k_{\mathrm{D_2O}}$ are the

$$n_{\mathrm{H_2O}} = 1.05 \times 10^{-3}\,(k_{\mathrm{H_2O}} - k_{\mathrm{D_2O}}) \quad (8)$$

Table 4 Fluorescence lifetimes and calculated species distributions of Eu–pmdp solutions, $I = 2.0$ M and $T = 22.5 \pm 0.5$ °C

Solution composition/mmol L^{-1}			Percent Eu^{3+} present in complex *mhl* $Eu_mH_h(pmdp)_l$							
$[pmdp^{4-}]_{total}$	$[Eu^{3+}]_{total}$	p[H]	1 0 0	1 3 1	1 4 1	1 6 2	1 8 2	1 11 3	k_{H_2O}/s^{-1}	n_{H_2O}
0.00	1.01	0.998	100.0	0.0	0.0	0.0	0.0	0.0	9457	9.6
7.46	6.07	1.776	16.7	43.2	16.6	14.0	7.2	2.3	5894	5.9
11.27	5.05	0.998	5.7	10.6	24.4	2.5	46.0	10.8	5191	5.1
18.93	6.07	1.809	0.7	13.5	4.8	32.5	14.3	34.1	3241	3.1
29.22	1.01	1.005	0.1	0.8	1.8	1.7	30.5	65.2	3396	3.3
29.41	1.01	1.0[a]							220[a]	

[a] k_{D_2O}: Measurement made in 97.5 atom% D_2O, $-\log [D^+]$ estimated using equilibrium constants measured in H_2O.

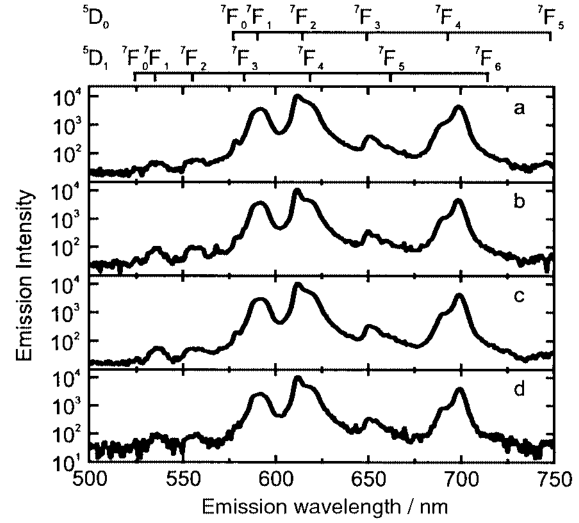

Fig. 5 Emission spectra from the $^5D_1$ and $^5D_0$ states of the $EuH_h(pmdp)_l$ complexes present in the solutions of Table 4 normalized to the same intensity for the peak at 611.8 nm. Total concentrations of pmdp were (a) 0.00746 M, (b) 0.01127 M, (c) 0.01893 M and (d) 0.02922 M. The assignments of the observed bands appear above along with tick marks denoting the expected centers[40] of aquated Eu^{3+} emission bands.

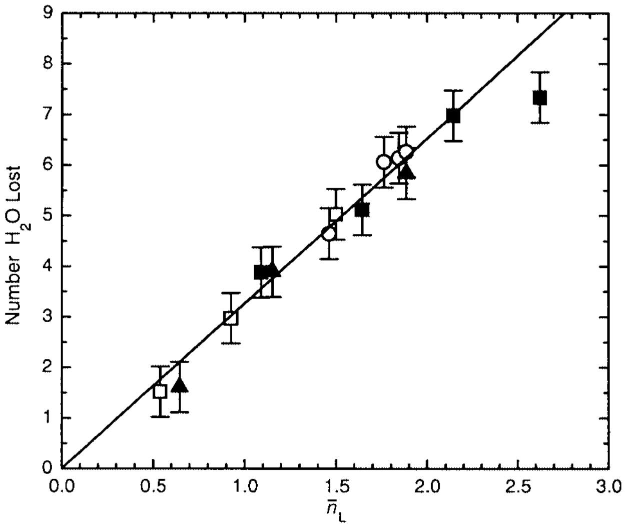

Fig. 6 The average number of water molecules displaced from the inner coordination sphere of europium–diphosphonic acid complexes as a function of the average number of diphosphonic acid ligands bound to europium: (■) pmdp, (□) mdp, (○) vdp, (▲) hedp and (——) linear fit.

luminescence decay constants of Eu^{3+} complexes in H_2O and D_2O, respectively. The decay constant of Eu^{3+} in D_2O was taken as 300 ± 10 s^{-1} for all the solutions based on the data for $Eu(ClO_4)_3$ in $NaClO_4$ reported by Lis and Choppin.[34] In a blank experiment to verify the validity of this assumption, Eu was primarily present as $Eu(D_4pmdp)_2^{3+}$ and $Eu(D_4pmdp)_2(D_3pmdp)^{2+}$. In this case k_{D_2O} was 220 s^{-1} (Table 4). This indicates that interactions with the ligand slightly increase the decay rate of the Eu luminescence. However the decrease in k_{D_2O} caused by complexation was not factored into the analysis since in this worst case it is equivalent to only 0.1 water molecules, which is much less than the uncertainty of these n_{H_2O} measurements, ±0.5 water molecules.[32] The hydration number measured for Eu^{3+} aquo cation in 2 M $NaClO_4$, 9.6, is in excellent agreement with previous results.[34,35]

In Fig. 6 the average number of water molecules liberated from the Eu inner coordination sphere by mdp, vdp (vinylidene-1,1-diphosphonic acid), hedp and pmdp binding is correlated with the average number of diphosphonate ligands bound to a europium cation, $\bar{n}_L$.[36] Values of n_{H_2O} for mdp, hedp and vdp were recalculated from the experimental data reported by Nash *et al.*[4] The calculation is made assuming that each phosphonate group is coordinated to the metal ion, that changes in ligand protonation do not effect the number of inner-sphere water molecules, and that the O–H oscillator of each coordinated POH group (*i.e.* each molecule of H_4pmdp, H_3mdp^-, H_3hedp^- or H_3vdp^- coordinated) contributes an apparent 0.5 H_2O molecules to n_{H_2O}. This coordination mode has been previously suggested for H_3mdp^- by molecular mechanics calculations[4] and has been observed in the solid state for $Nd(H_2hedp)(H_3hedp)$.[27] The correlation indicates that the number of water molecules liberated from the Eu inner coordination sphere by diphosphonic acid complexation is independent of the identity of the diphosphonic acid and the average number of bound ligands until the 1 : 3 Eu : L complex becomes the dominant species. Omitting the datum at $\bar{n}_L = 2.6$, linear regression finds the average number of water molecules liberated per bound diphosphonic acid to be 3.3 ± 0.1.

Previous luminescence studies of Eu^{3+} complexation by carboxylic acid ligands have typically shown an approximately one for one replacement of inner sphere water molecules by ligand donor atoms.[32] For example, malonic acid, the carboxylic acid analogue of mdp, is bidentate. It replaces 2.3 inner sphere water molecules on formation of the 1 : 1 Eu complex.[37] Similarly a tridentate ligand, oxydiacetic acid, or a tetradentate ligand, ethylenediaminediacetic acid, replaces 2.9 or 3.9 water molecules, respectively.[38] In this light, formation of the 1 : 1 and 1 : 2 Eu : diphosphonate complexes, which liberates three water molecules per complexed diphosphonate, might involve tridentate diphosphonate ligands with one monodentate and one bidentate phosphonate group in each ligand. Although this coordination mode has not been observed in the solid state, it is in perfect agreement with the thermodynamic observation that each diphosphonate group has a binding strength comparable to three monodentate carboxylate ligands.[1] Alternately, since a phosphonate group is larger than a corresponding carboxylate, the greater steric requirements of the two phosphonates in a methane-1,1-diphosphonic acid could be sufficient to expel an additional water molecule from the Eu inner coordination sphere, even if each phosphonate group is monodentate.

The dehydration caused by the addition of a third ligand to $Eu(H_4pmdp)_2^{3+}$ is a less straightforward process. Only 1.1 water

Table 5 Comparison of thermodynamic parameters for formation of Eu–L complexes in 2.0 M $NaClO_4$ and 25 °C. Values for mdp, vdp and hedp taken from ref. 4

Reaction	ΔH/kJ mol^{-1}			
	L = mdp^{4-}	vdp^{4-}	hedp^{4-}	Hpmdp^{3-}
Eu + H_2L				+3.6
Eu + H_3L	+9.6	+11.1	+5.1	+4.5
Eu(H_2L) + H_2L				−8.6
Eu(H_3L) + H_3L	−7.1	−7.5	−14.6	−3.0
Eu$(H_3L)_2$ + H_2L				−7.9

Reaction	ΔS/J K^{-1} mol^{-1}			
	L = mdp^{4-}	vdp^{4-}	hedp^{4-}	Hpmdp^{3-}
Eu + H_2L				+87
Eu + H_3L	+102	+107	+98	+78
Eu(H_2L) + H_2L				+29
Eu(H_3L) + H_3L	+16	+16	+6	+46
Eu$(H_3L)_2$ + H_2L				+31

molecules are displaced, which leaves 1.6 ± 0.5 H_2O in the Eu inner coordination sphere. If all three pmdp ligands were tridentate, the total Eu coordination number would be 10.6. High coordination numbers are possible for the trivalent lanthanides, but it is not clear why the addition of a third tridentate diphosphonate ligand would only displace one water molecule. Previous studies of the 1 : 2 Eu^{3+} : diphosphonic acid complexes in solution point toward a low symmetry complex, where the three inner-sphere water molecules are arranged on one side of the Eu with the two diphosphonic acid molecules on the other side.[4] Addition of a third diphosphonate ligand could retain this lopsided structure in order to form additional interligand hydrogen bonds. Such an arrangement would leave some room on one side of the complex for one to two water molecules. To achieve this configuration and form the interligand hydrogen bond network, however, one or more of the pmdp ligands in the tris complex could be bidentate (with two monodentate phosphonates). The total coordination number would then be between 7.6 and 9.6 depending on the number of bidentate pmdp molecules, in agreement with the value (8–9) favored by aqueous trivalent lanthanide complexes. Such a change in the coordination mode of the ligands could also account for the unusual order of the emission intensities of the Eu–pmdp complexes.

Given the similarities of the complexation induced inner sphere dehydration between the europium complexes of mdp, vdp, hedp and pmdp revealed in Fig. 6, the similar trends in the complexation enthalpies and entropies shown in Table 5 are not surprising. Despite the consistent change in the average number of water molecules in the europium inner hydration sphere caused by addition of the first and second diphosphonate ligands, the complexation entropies for the addition of the second ligand are much smaller than for the addition of the first. The complexation enthalpies for the addition of the second ligand are exothermic, in contrast to the endothermic ΔH values of the 1 : 1 complexes. This trend continues with the formation of the 1 : 3 Eu : pmdp complex, $Eu(H_4pmdp)_2(H_3pmdp)^{2+}$. The sign and magnitude of the 1 : 1 and 1 : 2 complexation entropies and enthalpies of mdp, vdp and hedp were previously taken as indications of extensive interligand–intracomplex hydrogen bonding between the diphosphonate ligands bound to a europium center and possibly also with outer sphere water molecules.[4] The similar trends for Eu–pmdp complexation indicate that interligand–intracomplex hydrogen bonding is also important for pmdp.

If the presence of a hydrogen bonding group on the α-carbon stabilizes the complexes through interactions with solvent molecules, the ΔH and ΔS values for H_3hedp^- and H_4pmdp complexation should closely resemble each other. The complexation enthalpies for $Eu(H_3hedp)^{2+}$ and $Eu(H_4pmdp)^{3+}$ are similar, and are approximately 5 kJ mol^{-1} more exothermic than those of the corresponding H_3mdp^- and H_3vdp^- complexes that lack the additional hydrogen bonding group. Likewise, the complexation entropies for $Eu(H_3hedp)^{2+}$ and $Eu(H_4pmdp)^{3+}$ are less positive than those of $Eu(H_3mdp)^{2+}$ and $Eu(H_3vdp)^{2+}$, which indicates greater ordering through hydrogen bonding in the hedp and pmdp complexes as compared to the mpd and vdp complexes.

However, the close relationship between ΔH and ΔS for the 1 : 1 H_3hedp^- and H_4pmdp complexes is not present for the 1 : 2 complexes. In this case the $Eu(H_4pmdp)_2{}^{3+}$ complexation enthalpies and entropies better resemble those of the 1 : 2 H_3mdp^- and H_3vdp^- complexes. The three principal factors considered thus far, dehydration of the Eu^{3+} inner hydration sphere; formation of an interligand hydrogen bond network; and the presence of an additional hydrogen bonding group on the *α*-carbon, cannot be the sole determinants of the thermodynamic parameters for the bis and tris Eu–pmdp complexes.

There are two significant structural differences between pmdp and the other three diphosphonic acids that could explain the differences: the presence of the amine group on the α-carbon and the associated six membered piperidine ring. Direct participation of the amino functionality through formation of a Eu–N bond is an unlikely explanation for the difference. First, the hydroxo group of hedp, which is in the same position as the piperidine nitrogen, does not coordinate lanthanide cations in the solid state.[15] Second, the low p[H] of the solutions studied and the high basicity of the piperidine nitrogen argue for protonation of the nitrogen lone pair, making it unavailable for complexation. Third, if a metal–amine bond were formed, the binding of Eu^{3+} by H_hpmdp^{h-4} should be weaker than the binding of the trivalent actinide cation with the same radius, Cf^{3+},[39] due to a greater covalent character in actinide bonds with nitrogen donors.[29] The stability constants of Cf^{3+}–pmdp complexes are not significantly different than the equivalent Eu^{3+} complexes.[8] Fourth, amine complexation is generally an exothermic process, but as shown in Table 5 the complexation enthalpies of pmdp are not significantly more exothermic than those of the other phosphonic acids. Finally, the extent of dehydration of the europium inner hydration sphere is independent of the structure of the diphosphonic acid, while complexation by the amino group should displace an additional water molecule from the inner hydration sphere. Thus the formation of a Eu–N bond is improbable.

The differences between the Eu complexation enthalpies and entropies of pmdp on one hand and of mdp, vdp and hedp on the other would then seem to arise from the size and hydrophobicity of the piperidine substituent, and not from a substantial difference in the metal–ligand or ligand–ligand interactions. Addition of a piperidine ring to the diphosphonic acid core roughly doubles the molecular volume of a methane-1,1-diphosphonic acid, and gives the ligand a metal binding, very hydrophilic half containing the diphosphonic acid moiety, and a hydrophobic half consisting of the aliphatic portion of the piperidine ring. As shown in Fig. 6, the size of the diphosphonate ligand does not significantly effect the number of water molecules released from the inner coordination sphere. Therefore the diphosphonate portion of the ligand, not the piperidine ring, must displace the water molecules from the inner coordination sphere. However, the piperidine ring can interact with the water molecules in the second hydration sphere that are not probed by the Horrocks' luminescence lifetime technique. Simple models based on the bond distances and angles found in the H_4pmdp and $Eu(H_3hedp)_2{}^{+}$[27] crystal structures predict that the piperidine ring extends between 5.1 and 7.8 Å from the europium center when complexed, allowing the piperidine ring to interact with outer sphere water molecules. To the extent that the piperidine ring of complexed pmdp interacts with water molecules in the outer hydration sphere rather than bulk water, the complexation entropies of pmdp should be larger (more positive) than those of mdp, vdp and hedp, as is the case for the 1 : 2 and 1 : 3 Eu : pmdp complexes. Consequently, the multiple piperidine rings present in the bis and tris Eu–pmdp complexes subsume a large portion of the second hydration sphere causing dehydration and solvent reorganization in this semi-ordered solvent zone.

Even though the inner sphere hydration of the Eu^{3+} complexes of methane-1,1-diphosphonic acids measured from the luminescence lifetimes is independent of the ligand's substituents, comparatively large, hydrophobic substituents such as a piperidine ring do affect the thermodynamic parameters, making it difficult to observe finer details like the hydrogen bonding interactions of the piperidine nitrogen.

Acknowledgements

We thank P. G. Rickert for the synthesis of H_4pmdp and L. R. Morss for his assistance in the execution of the calorimetric experiments. This work was supported by the United States Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract number W-31-109-ENG-38.

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