Formation and Protonation of Aminopolyphosphonate Complexes of Alkaline-earth and Divalent Transition-metal Ions in Aqueous Solution

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The formation and protonation of *N*-methyliminobis(methylenephosphonic acid) (midmp, H_4L) and *N,N*-dimethylaminomethylphosphonic acid (dmamp, H_2L) complexes with alkaline-earth ($M = Mg^{2+}$, Ca^{2+}, Sr^{2+} or Ba^{2+}) and divalent transition metals ($M = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, or Cd^{2+}) have been investigated at 25.0 °C and at an ionic strength of 0.1 mol dm^{-3} (KNO_3) by means of potentiometry and ^{31}P NMR spectroscopy. The complex-formation constants, K_{ML}, for the alkaline-earth metals decrease with increasing ion size. The order of K_{ML} for the transition-metal complexes agrees with the Irving–Williams series for each ligand. The first protonation constants, K_{MHL}, of the alkaline earth–midmp and transition metal–dmamp complexes are quite large compared with the first protonation constants of the phosphonate group of the free ligand (the second protonation constants of the ligand K_{H_2L}), and decrease with increasing complex-formation constant. The values of K_{MHL} for the transition metal–midmp complexes are of the same order of magnitude as the value of K_{H_2L} for the ligand. The second protonation constants K_{MH_2L} of all complexes are smaller than K_{H_2L} and there is no significant difference among the complexes. The ^{31}P NMR spectra of the metal–ligand solutions have been measured at 25 °C as a function of pH and the chemical shift of each species was evaluated. The results of the potentiometric and NMR studies suggest that the M–N bond of the ML complex is weakened by a decrease in the number of methylenephosphonate groups of the ligand, *i.e.* protonation of midmp complexes of alkaline-earth and some transition metals and of all the dmamp complexes occurs at the nitrogen atom of the ligand, rupturing the M–N bond.

The aminopolyphosphonates are analogues of aminopolycarboxylates in which the carboxyl groups (CO_2^-) are substituted by phosphonate groups (PO_3^{2-}). Owing to the high negative charge of aminopolyphosphonates, *e.g.* unprotonated nitrilotris(methylenephosphonate) has six negative charges ($ntmp^{6-}$), their metal complexes are well suited for the study of metal complex protonation. Phosphonates containing one nitrogen atom are the most simple. Several kinds of C- or N-substituted derivatives of iminobis(methylenephosphonic acid)[1–5] and aminomethylphosphonic acid[1,2,6–8] have been synthesised and the complex-formation equilibria have been reported for some metal ions. The NMR behaviour of $Pt^{II}(NH_3)_2$ complexes[9] and luminiscence spectra of complexes of Eu^{3+} and Ce^{3+} were reported.[10] Nevertheless, no systematic study on the complex formation of these compounds has been done and the equilibrium constants are not always reliable. In previous papers we studied the complex-formation equilibria and NMR behaviour of ntmp complexes of alkaline-earth metals,[11] transition metals,[12] and rare-earth metals.[13] These results suggest that the M–N bond is ruptured in the protonated complexes of alkaline-earth and rare-earth metals and that protonation occurs on the nitrogen atom of the ligand, *i.e.* protonated ntmp co-ordinates to a metal ion through three phosphonate O^-.

In order to determine the effect of the number of phosphonate groups on complex structure, the complex formation of *N*-methyliminobis(methylenephosphonic acid) (H_4midmp) and *N,N*-dimethylaminomethylphosphonic acid (H_2dmamp) with alkaline-earth and divalent transition metals was investigated by means of potentiometry and NMR spectroscopy, and the results are discussed by comparison with those for the nitrilotris(methylenephosphonato) complex.

Experimental

Reagents.—*N*-Methyliminobis(methylenephosphonic acid) was synthesised from methylamine according to the method of Moedritzer and Irani[1] and recrystallized from 1 mol dm^{-3} HCl aqueous solution. *N,N*-Dimethylaminomethylenephosphonic acid was synthesised by the reaction of dimethylamine (74 g) and phosphorous acid (75 g) with formaldehyde (144 cm^3) in 7 mol dm^{-3} HCl (450 cm^3). The HCl and excess of formaldehyde were removed by evaporation. After dilution with water (700 cm^3), unreacted phosphorous acid was precipitated by $Ba(OH)_2$ at pH 9. Unreacted amine was removed by evaporation of the supernatant. After dilution with water (500 cm^3), the barium salt of the acid was precipitated by $Ba(OH)_2$ at pH 12. After the barium salt had been converted into the free acid by the reaction with sulfuric acid, crystals were obtained upon evaporation (yield: 53%). The purity was determined as > 99% by elemental analysis and ^{31}P NMR spectroscopy. The concentration of the stock solution of the free acid was determined by pH titration with standard KOH and the analysis of the titration curve.

Metal nitrates used were of analytical grade (Wako pure chemicals) and the concentrations of the stock solutions were determined by titration with standard ethylenediaminetetraacetate. All the solutions were prepared with distilled and deionized water (Organo, Puric Z).

Potentiometric Measurements.—The pH titration was carried out with an Orion Ion Analyzer EA 920 instrument under a nitrogen stream. The electromotive force (e.m.f.) of the glass electrode (Iwaki, glass electrode IW002 and calomel electrode IW0022) was measured as function of the concentrations of nitric acid (10^{-1}–10^{-4} mol dm^{-3}) and potassium hydroxide (10^{-1}–10^{-3} mol dm^{-3}) at 25.0 ± 0.1 °C ($I = 0.1$ mol dm^{-3} KNO_3, $pK_w = 13.82$). The pH (1–13) was evaluated from the emf by using this calibration curve. A solution of 10^{-2} mol dm^{-3} free ligand or metal–ligand mixture was titrated in a water-jacketed cell (25.0 ± 0.1 °C) with 0.1 mol dm^{-3} KOH at $I = 0.1$ mol dm^{-3} (KNO_3). The concentrations of ligand and metal ion were 10^{-2} mol dm^{-3} for the midmp systems and transition metal–dmamp systems. The concentrations in the Zn–midmp system were $c_{\text{midmp}} = c_{\text{Zn}} = 5 \times 10^{-4}$ mol dm^{-3} to prevent precipitation. In the alkaline-earth metal–dmamp systems, $c_{\text{dmamp}} = 10^{-2}$ and $c_{\text{M}} = 3 \times 10^{-2}$ mol dm^{-3}.

NMR *Measurements*.—The ^{31}P NMR spectra of ligand ($c_{\text{L}} = 3 \times 10^{-2}$ mol dm^{-3}) or metal–ligand equimolar solutions ($c_{\text{M}} = c_{\text{L}} = 3 \times 10^{-2}$ mol dm^{-3}) were measured by a JEOL-FT 90Q spectrometer (36.23 MHz for ^{31}P) with a 10 mm diameter sample tube at 25 ± 2 °C. The concentrations in the Zn^{2+}–midmp system were $c_{\text{M}} = c_{\text{L}} = 5 \times 10^{-4}$ mol dm^{-3}. Downfield shifts are denoted as positive. The external standard was 0.5% H_3PO_4 in D_2O and the chemical shift values reported are those corresponding to aqueous 85% H_3PO_4 as reference.

Results and Discussion

Complex Formation.—The hydrogen-ion concentration $[H^+]$ was calculated from the electromotive force in the titration of ligand H_rL or metal–H_rL solution with KOH (r = 4 for midmp and 2 for dmamp). The mean number of protons bound to the ligand and complexes, $\bar{n}_{\text{obs}}$, is obtained from equation (1) where c_{OH} and c_{L} are the total concentrations of KOH titrated and the ligand H_rL, respectively.

$$\bar{n}_{\text{obs}} = (rc_{\text{L}} - c_{\text{OH}} - [H^+] + [OH^-])/c_{\text{L}} \quad (1)$$

By using a successive protonation constant of the ligand dmamp or midmp defined by $K_{H_nL} = [H_nL]/[H][H_{n-1}L]$ the mean number of protons bound to ligand can be calculated from equation (2) where $\beta_n = \Pi K_{H_nL}$. The charges of the

$$\bar{n}_{\text{calc}} = \Sigma n[H_nL]/c_{\text{L}} = \Sigma n\beta_n[H]^n/(1 + \Sigma\beta_n[H]^n) \quad (2)$$

chemical species are omitted for simplicity. The values of K_{H_nL} were evaluated by our computer program. A set of K_{H_nL} giving a minimum sum of the squares of the deviations, $\Sigma(\bar{n}_{\text{obs}} - \bar{n}_{\text{calc}})^2$, was obtained by non-weighted non-linear regression. R factors $\{[\Sigma(\bar{n}_{\text{obs}} - \bar{n}_{\text{calc}})^2/\Sigma(\bar{n}_{\text{obs}})^2]^{\frac{1}{2}}\}$ of less than 0.01 were obtained for each titration of 30–40 data points. The successive protonation constants of the ligands (midmp and dmamp), thus obtained are listed in Table 1 together with those of ntmp.[1] The errors given were evaluated from uncertainty σ and duplicated titration data.

The formation constant of the metal complex and its successive protonation constants are defined by $K_{\text{ML}} = [ML]/[M][L]$, $K_{MH_mL} = [MH_mL]/[H][MH_{m-1}L]$. The mean number of protons bound to the ligand and complexes are calculated from equation (3) where $\beta_{\text{M}} = \Pi K_{MH_mL}$. By the same

$$\begin{aligned}\bar{n}_{\text{calc}} &= (\Sigma n[H_nL] + \Sigma m[MH_mL])/c_{\text{L}} \\ &= (\Sigma n\beta_n[H]^n + \Sigma m K_{\text{ML}}\beta_m[M][H]^m)/\{1 + \Sigma\beta_n[H]^n \\ &\qquad + K_{\text{ML}}[M](1 + \Sigma\beta_m[H]^m)\} \quad (3)\end{aligned}$$

process of non-linear regression as for the ligand, a set of K_{ML} and K_{MH_mL} values giving a minimum sum of squares of the deviations, $\Sigma(\bar{n}_{\text{obs}} - \bar{n}_{\text{calc}})^2$, was evaluated. The errors of the constants were evaluated from duplicated titrations involving 30–40 data points. In the case of transition metal–dmamp complexes and complexes of Mn^{2+}, Fe^{2+} and Zn^{2+} with midmp, reliable titration curves were not obtained at high pH because of precipitation of the complex or metal hydroxide. In these systems, 15–30 data points were obtained for each titration. The logarithmic formation constants of the metal complexes and their protonation constants are listed in Table 2. The transition-metal complexes of midmp form hydroxo complexes, M(OH)L, at high pH, the protonation constant of which is defined by $K_{M(OH)L} = [ML]/[H][M(OH)L]$ and also listed in Table 2. Under the present experimental conditions, the extent of formation of complexes such as ML_2 or ML_3 is negligible.

The abundance of each species formed under the experimental conditions was calculated at various pH by our program using the constants listed in Tables 1 and 2. The distribution curves of the ligand midmp (*a*) and of its complexes with Sr^{2+} (*b*) and Cd^{2+} (*c*) are shown as a function of pH in Fig. 1.

The protonation constants of the ligand and formation

Table 1 Protonation constants of the ligands[a]

	dmamp	midmp	ntmp[b]
log K_1	10.9 ± 0.2	12.1 ± 0.2	12.8
	10.9 ± 0.1[c]	12.0 ± 0.1[c]	12.7[c]
log K_2	5.16 ± 0.03	6.04 ± 0.03	7.15
log K_3	1.3 ± 0.2	4.90 ± 0.03	5.89
log K_4		1.3 ± 0.2	4.63
log K_5			1.4

[a] $K_n = [H_nL]/[H_{n-1}L]$. [b] Ref. 11. [c] Evaluated from the ^{31}P NMR chemical shift.

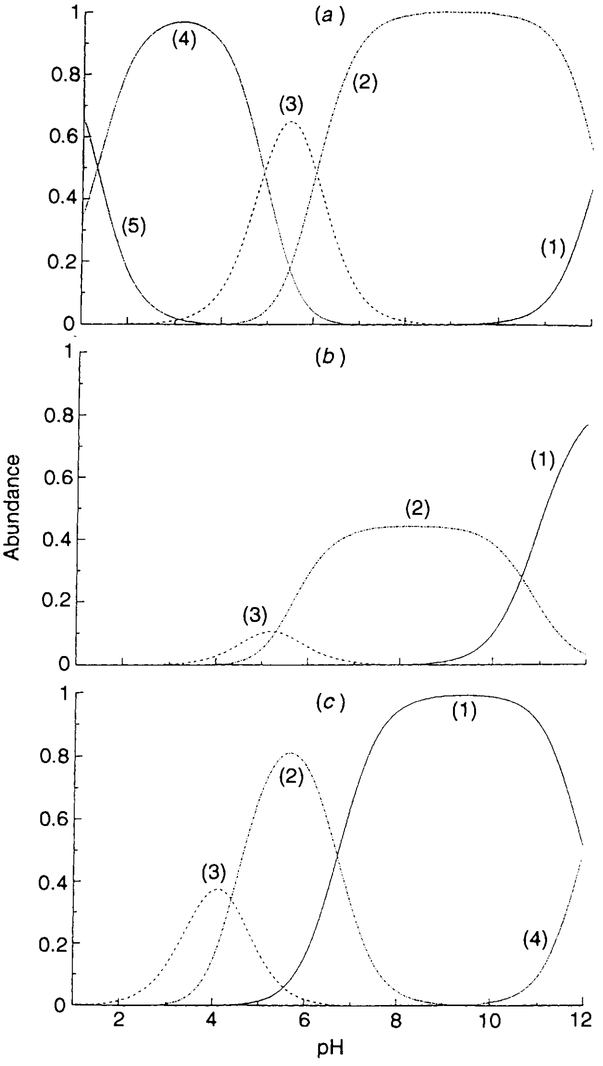

Fig. 1 Distribution diagrams: (*a*) ligand midmp, (1) L, (2) HL, (3) H_2L, (4) H_3L, (5) H_4L; (*b*) strontium- and (*c*) cadmium-midmp complexes, (1) ML, (2) MHL, (3) MH_2L, (4) M(OH)L. $c_{\text{L}} = 1 \times 10^{-2}$, $c_{\text{Sr}} = 3 \times 10^{-2}$, $c_{\text{Cd}} = 1 \times 10^{-2}$ M.

Table 2 Equilibrium constants of formation and protonation of midmp and dmamp complexes

	Mg	Ca	Sr	Ba	Mn	Fe	Co	Ni	Cu	Zn	Cd
dmamp											
log K_{ML}[a]	2.0	1.7	1.5	1.5 ± 0.2	4.22		4.80	5.07	8.06	5.45	5.17 ± 0.1
log K_{MHL}[b]					8.98		8.45	8.01	5.45	7.46	7.60 ± 0.1
midmp											
log K_{ML}[a]	5.13	4.61	3.66	3.57 ± 0.04	8.24[c]	9.12[c]	9.27	9.59	14.32	10.44[c]	10.18 ± 0.02
log K_{MHL}[b]	9.72	10.13	10.61	10.62 ± 0.04	7.93	6.97	6.59	6.26	4.38	5.83[c]	6.71 ± 0.04
log K_{MH_2L}[b]	5.0	5.1	5.3	5.4 ± 0.1	4.54	4.28	4.42	4.58	3.40		4.43 ± 0.1
log $K_{M(OH)L}$[d]							11.3	12.1	10.8		12.0 ± 0.2

[a] K_{ML} = [ML]/[M][L]. [b] K_{MH_mL} = [MH$_m$L]/[H][MH$_{m-1}$L]. [c] Errors of the logarithmic constants were estimated as ±0.1. [d] $K_{M(OH)L}$ = [ML]/[H]-[M(OH)L].

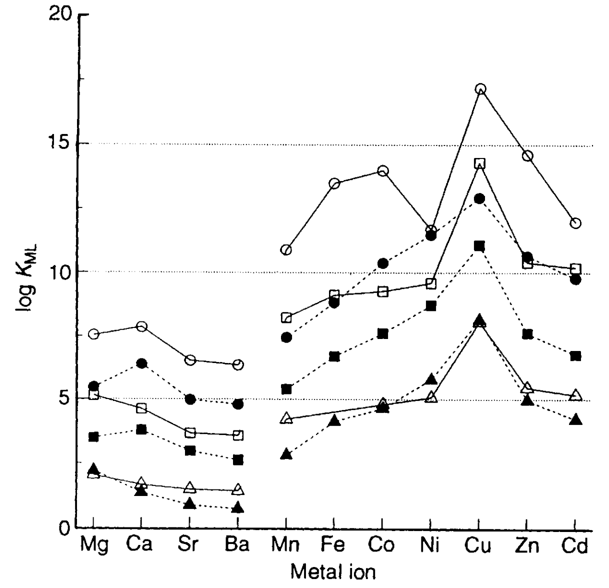

Fig. 2 Plots of logarithmic formation constants of aminopolyphosphonate (open symbols) and aminopolycarboxylate (closed symbols), log K_{ML}, as a function of metal ion: ○, ntmp; □, midmp; △, dmamp; ●, nta; ■, mida; ▲, glycine

constants of complexes of Cu^{2+} with dmamp agree within experimental errors with those reported previously.[8d] Although reported values of the protonation constants of ethyliminobis(methylenephosphonate)[4] show a reasonable agreement with the results for midmp (Table 1), the complex-formation constants show discrepancies of about one unit from our data, even if the effect of substitution of the methyl with the ethyl group is taken into consideration.

The first protonation constant of the ligand, K_{HL} (Table 1), increases with increasing number of methylene phosphonate groups, whereas that of aminopolycarboxylate ligands is scarcely changed by the number of carboxylate groups [log K_{HL} = 9.78, 9.65 and 9.71 for *N*,*N*-dimethylglycine,[14] *N*-methyliminodiacetic acid (H_2mida)[15] and nitrilotriacetic acid (H_3nta),[16] respectively]. The high negative charge of the phosphonate group (PO_3^{2-}) compared with the carboxyl group (CO_2^-) may account for the high basicity of the nitrogen atom of the aminopolyphosphonates.

The complex formation constants with the aminopolyphosphonates (dmamp, midmp, ntmp[11,12]) are plotted in Fig. 2 together with those of the aminopolycarboxylates (glycine,[17,18,*] mida[15] and nta[16,19]). The plots for the alkaline-earth metal complexes are roughly parallel for dmamp, midmp and ntmp, although those of dmamp and midmp do not show a maximum at Mg^{2+} as is observed for the most simple aminocarboxylate glycine. The formation constants of the transition-metal complexes of dmamp and midmp follow the so-called Irving–Williams series ($K_{MnL} < K_{FeL} < K_{CoL} < K_{NiL} < K_{CuL} > K_{ZnL} > K_{CdL}$). Although the value of K_{ML} for the Ni–ntmp complex is considerably smaller than that predicted by this order, the complexes of midmp and dmamp show no irregularity for Ni.

The complex-formation constants of dmamp, K_{ML}, are almost the same as those of glycine for both alkaline-earth and transition metals. In the case of midmp and ntmp, the stability constants are quite large compared with those of mida and nta. The increase in the formation constants with increasing number of phosphonate groups is much larger than that upon increasing number of carboxylate groups. This might be attributed to the higher negative charge of the phosphonate groups (PO_3^{2-}) and indicate that the ionic nature of the bond is important in the aminopolyphosphonate complexes. The formation constants of the complexes of Mn^{2+}, Ni^{2+}, Cd^{2+} and Cu^{2+} with ntmp are relatively smaller than the values predicted from the effect of the number of methylenephosphonate groups. In these complexes the co-ordination of the third phosphonate might be weakened by electrostatic repulsion between the phosphonate groups.

The successive protonation constants K_{MH_mL} of the aminopolyphosphonate complexes are plotted as a function of the formation constant of the metal complex, K_{ML}, in Fig. 3, where in order to normalize the basicity of the ligand the difference between the protonation constant of the metal complex and the second protonation constant of the ligand (*i.e.* the first protonation of the phosphonate group), log K_{MH_mL} − log K_{H_2L}, is employed. The first protonation constants, K_{MHL}, of the alkaline-earth metal complexes of midmp are much higher than the second protonation constant of the ligand (log K_{MHL} − log K_{H_2L} > 0), *i.e.* the protonation constant of the metal complex is much larger than that of the phosphonate group of the ligand. The plot of log K_{MHL} − log K_{H_2L} *vs.* log K_{ML} for the alkaline-earth-metal complexes shows a linear correlation with a negative slope, *i.e.* the protonation constant of the metal complex decreases with increasing M–N bond strength. These facts indicate that the M–N bond of the alkaline-earth-metal complexes of midmp (structure **I**) is ruptured by the first protonation and that protonation occurs on the nitrogen atom of midmp of the complex (structure **II**).

As reported previously,[11] the ntmp complexes of alkaline-earth metals also have a similar structure to **II**. The fact that the plot of log K_{MHL} − log K_{H_2L} *vs.* log K_{ML} for the midmp complex falls on almost the same line as that for the ntmp complex (Fig. 3, solid line) indicates that both complexes have the same structure, *i.e.* protonation occurs at the nitrogen atom. Aminopolyacid complexes having an eight-membered chelate ring such as that in structure **II** have never been reported. The

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[*] Since there is no complete data set for the formation constant of the dimethylglycine complex, the results for the glycine complexes are cited. Although the complex-formation constants of the latter are 0.5–1 unit smaller than those of dimethylglycine, this difference is not that significant for the following discussion.

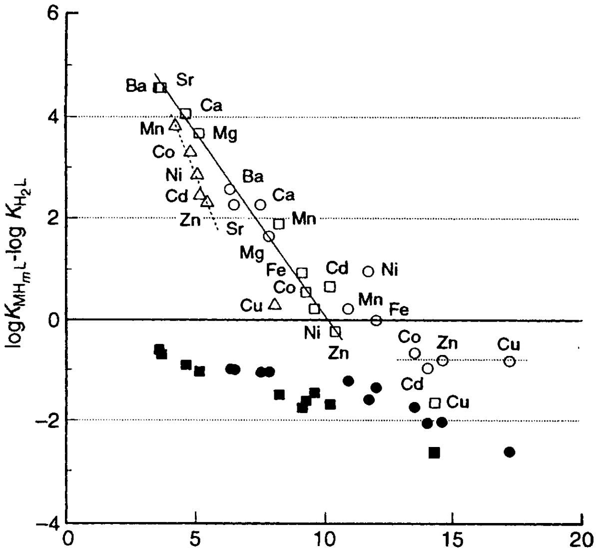
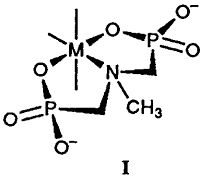
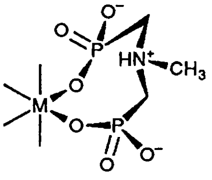


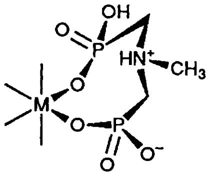
Fig. 3 Plot of log K_{MH_nL} − log K_{H_2L} as a function of the logarithmic formation constants of the metal complexes, log K_{ML}: ○, ntmp; □, midmp; △, dmamp. Open symbols, K_{MHL}; closed symbols, K_{MH_2L}.



I



II



III

protonation of the nitrogen atom of the complex is attributed to the very high proton affinity of the nitrogen atom of aminopolyphosphonates (*e.g.* log K_{HL} = 12.1 for midmp and 9.56 for mida[15]). The higher negative charge of the phosphonate compared with the carboxylate group may enable the formation of a structure such as **II**.

The first protonation constants of most of the transition-metal complexes of ntmp, K_{MHL}, are smaller than K_{H_2L} and almost the same irrespective of the metal ion (Fig. 3, dotted line). These results indicate that the protonation of these complexes occurs on the phosphonate O^-, without rupture of the M–N bond.[12] Since the M–N bond of alkaline-earth-metal complexes is very weak,[20] it is easily ruptured by protonation. In contrast, the M–N bond of the transition-metal complexes is so strong that protonation occurs on the phosphonate O^-. On the other hand, K_{MHL} of the midmp complexes of the transition metals is of the same order of magnitude as the second protonation constant of the ligand or more or less larger than it and decreases with increasing formation constant, K_{ML}. These results indicate that the protonation of some metal complexes of midmp occurs at the nitrogen atom even for transition metals. In particular, in the case of cadmium the first protonation constant is significantly larger than that of the zinc complex in spite of the small difference in formation constants K_{ML} between them. The value of K_{MHL} − log K_{H_2L} for the manganese complex is large and falls on the same line as for the alkaline-earth-metal complexes. Consquently, the protonated species of these complexes may have structure **II**. The number of phosphonate groups and chelate rings of the midmp complexes (two) is fewer than those of ntmp complexes (three). Thus the stability of the former is much smaller than that of the latter. Consequently, in the case of complexes having relatively weak M–N bonds such as those of $Mn^{2+}(d^5)$ or $Cd(d^{10})$, this bond in the midmp complexes might be ruptured upon protonation.

All the second protonation constants of midmp–transition-metal complexes, K_{MH_2L}, are smaller than the second protonation constant of the ligand. The values of log K_{MH_2L} − log K_{H_2L} do not differ much between the midmp and ntmp complexes and between alkaline-earth- and transition-metal complexes. These results are quite reasonable, *i.e.* the second protonation of complexes occurs on the phosphonate group (structure **III**) and the protonation on the phosphonate O^- is scarcely affected by the M–L bond strength.

The first protonation constants, K_{MHL}, of transition-metal complexes of dmamp are larger than log K_{H_2L} of dmamp and decrease with increasing formation constant K_{ML}. Consequently, the protonation of the metal chelate complex occurs on the nitrogen atom, *i.e.* the protonated ligand co-ordinates to the metal ion by the phosphonate group in a monodentate manner, $Me_2NH^+CH_2PO_3^{2-}$–M. The complex-formation constant of the metal ion with monoprotonated dmamp [M + Hdmamp $\rightleftharpoons$ M(Hdmamp)] is calculated as log K^{HL}_{MHL} = 1.9–2.2 except for Cu^{2+} (log K^{HL}_{CuHL} = 2.5). These values are comparable to the formation constant of the *N*,*N*,*N*-trimethylamino(methylphosphonate) ($Me_3N^+CH_2PO_3^{2-}$) complex (log K_{ML} is reported as 2.18 for Cu^{2+}.[8c] The plot of K_{MHL} for the dmamp complexes (Fig. 3, broken line) is relatively lower than those of midmp and ntmp. This may be explained by the lack of a chelate ring in the protonated complexes of dmamp, M(Hdmamp), *i.e.* the stability of the protonated complexes of midmp and ntmp are enhanced by the chelate effect.

The formation constant of the hydroxo complex was determined for the transition metal–midmp system (Table 2), although the formation of such complexes was not observed for the ntmp system. Owing to the relatively low negative charge of the midmp complex, $[M(midmp)]^{2-}$ deprotonation if a water molecule co-ordinating to the metal ion, $[M(H_2O)_3(midmp)]^{2-} \rightleftharpoons [M(H_2O)_2(OH)(midmp)]^{3-} + H^+$, is much easier than that for the ntmp complex having a large negative charge, $[Mn(ntmp)]^{4-}$. The equilibrium constants of the midmp complexes [$K_{M(OH)L}$ = [ML]/[H][M(OH)L], Table 2] are comparable to those of the nta complexes, [M(nta)] (log $K_{M(OH)L} \approx 11$).

Phosphorus-31 NMR Spectroscopy.—In spite of the presence of many kinds of protonated species H_nL, the proton-decoupled ^{31}P NMR spectra of the ligand solutions show only one sharp singlet at any pH. The chemical shifts for midmp are plotted as a function of pH in Fig. 4. These observations indicate that proton exchange of H_nL is very fast and the chemical shift of the ligand solution can be written as a linear combination of the chemical shifts of each species present as in equation (4), where

$$\delta_{calc} = \Sigma\delta_n X_{H_nL} \tag{4}$$

δ_n and X_{H_nL} are the chemical shift and proportions of each unprotonated or protonated species of ligand, H_nL, respectively. The proportions of the chemical species at a given pH were calculated by using the ligand protonation constants determined by potentiometry. A set of chemical shifts for each species of ligand, δ_n, giving a minimum sum of squares of deviations between the observed and calculated chemical shifts, $\Sigma(\delta_{obs} - \delta_{calc})^2$, was evaluated by a non-weighted non-linear regression with our computer program. The values thus obtained are listed in Table 3 together with results for ntmp.[1] The calculated chemical shifts for ligand midmp are shown in Fig. 4 by a solid line, and show good agreement with the experimental results.

As the ^{31}P NMR signal of the ligand shows a steep upfield shift corresponding to the first protonation, a relatively accurate value of the first protonation constant, K_{HL}, can be obtained. Although the pH titration method is generally poor for the determination of protonation constants at high pH, spectroscopic methods are suitable for such a system. The value of K_{HL}

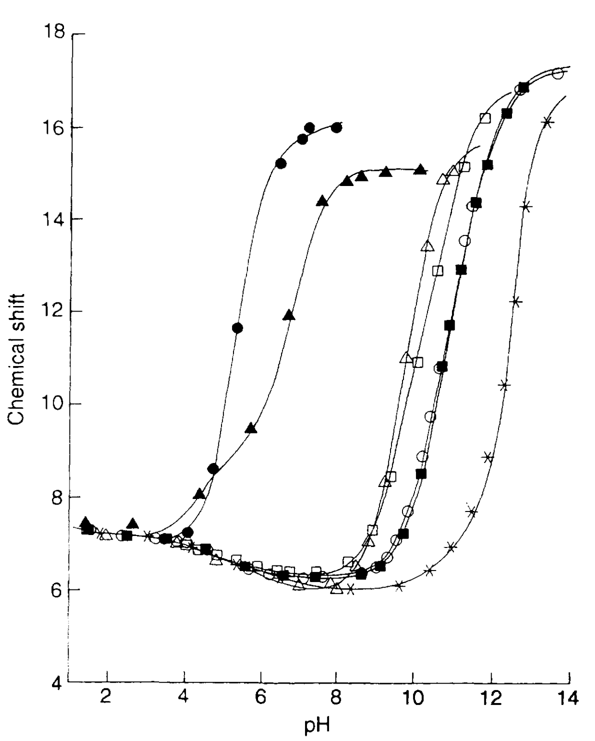


Fig. 4 Plot of ^{31}P NMR chemical shifts of the midmp system as a function of pH. ✱, Ligand. Metal–midmp solutions: △, Mg^{2+}; □, Ca^{2+}; ○, Sr^{2+}; ■, Ba^{2+}; ●, Zn^{2+}; ▲, Cd^{2+}

Table 3 The ^{31}P NMR chemical shifts of the ligands

	dmamp	midmp	ntmp*
δ_L	15.55	16.16	18.03
δ_{HL}	5.84	5.85	6.66
δ_{H_2L}	7.26	6.22	6.73
δ_{H_3L}		7.01	8.50
δ_{H_4L}			7.15

* Ref. 11.

Table 4 The ^{31}P chemical shifts of dmamp and midmp complexes

	Mg	Ca	Sr	Ba	Zn	Cd
dmamp						
δ_{ML}	15.2	14.9	15.2	15.2	13.1	14.0
δ_{MHL}					7.0	8.4
midmp						
δ_{ML}	15.88	16.54	17.26	17.06	16.4	15.01
δ_{MHL}	6.37	6.75	6.78	6.73	17.0	9.11
δ_{MH_2L}	6.54	6.94	7.21	7.29		7.84
$\delta_{M(OH)L}$						14.3

obtained from the chemical shift change is listed in Table 1 and is in good agreement with that obtained by potentiometry.

The $^{31}P-\{^1H\}$ NMR spectra of metal–ligand (midmp) solutions also show a single peak. The chemical shifts are plotted in Fig. 4 as a function of pH and can be written as in equation (5), where δ_m and X_{MH_mL} are the chemical shift and

$$\delta_{calc} = \Sigma\delta_n X_{H_nL} + \Sigma\delta_m X_{MH_mL} \qquad (5)$$

proportion of each species of complex, MH_mL, respectively. A set of chemical shifts for each complex, δ_m, giving a minimum square sum $\Sigma(\delta_{obs} - \delta_{calc})^2$ were evaluated by non-linear regression by using the ligand chemical shifts and equilibrium constants for the ligand and complexes already determined.

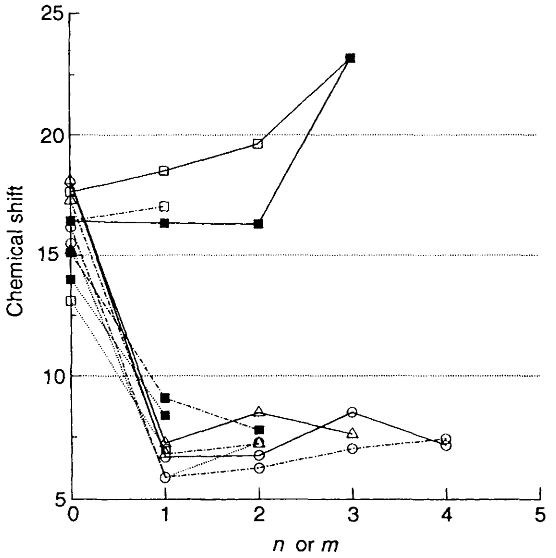


Fig. 5 Plots of the ^{31}P chemical shift of the ligand and complexes of Sr^{2+}, Zn^{2+} and Cd^{2+} with aminopolyphosphonates as a function of the number of protons bound to the ligand (H_nL), *n*, or complex (MH_mL), *m*. ○, ligand; △, Sr^{2+}; □, Zn^{2+}; ■, Cd^{2+}. Ligands: ——, ntmp; – • –, midmp; • • • • •, dmamp

The chemical shifts for unprotonated and protonated complexes are listed in Table 4. The calculated values for the metal–midmp systems are shown in Fig. 4 as solid lines and are in good agreement with the experimental results.

The chemical shifts of the unprotonated ligand species are almost the same for the different ligands (δ_L = 16–18), although they slightly decrease with decreasing number of phosphonate groups. Upon protonation of the nitrogen atom of the ligand, the chemical shifts show a steep upfield shift ($\delta_{HL} \approx 6$). Higher extents of protonation ($n \geqslant 2$), *i.e.* protonation at the phosphonate group, do not result in any significant change in chemical shift. Although the chemical shifts δ_{ML}, of the unprotonated complexes Zn^{2+} and Cd^{2+} are somewhat smaller than those of alkaline-earth metals, they are substantially the same as that, δ_L, of the unprotonated ligand, *i.e.* the effect on the chemical shift of co-ordination of ligand to the metal ion is much smaller than that caused by protonation of the nitrogen atom of the ligand.

The chemical shifts of ligands H_nL and complexes MH_mL of alkaline-earth (Sr^{2+} is shown as an example) and transition metals (Zn^{2+} and Cd^{2+}) are plotted in Fig. 5 as a function of the number of protons attached to these species, *n* or *m*, together with those of ntmp.[11,12] The ^{31}P NMR behaviour of the complexes upon protonation may be classified into two groups: 1, the chemical shift shows a large upfield shift upon the first protonation in the same manner as that of the ligand; 2, the chemical shifts of the protonated complexes do not show an upfield shift and do not so differ from that of the unprotonated complex. As reported previously,[11] an upfield shift of the complex upon protonation (group 1) indicates protonation at the nitrogen atom of the complex (structure **II**). All the protonated complexes of the alkaline-earth metals show an upfield shift (group 1).

On the other hand, in the case of the zinc and cadmium complexes the change in the chemical shift of the complexes upon protonation depends on the ligand. Both the complexes of Zn^{2+} and Cd^{2+} with ntmp belong to group 2 and protonation occurs on the phosphonate group.[11] In the case of the midmp complexes, the upfield shift for the cadmium complex predicts protonation at nitrogen, whereas the zinc complex shows the same protonation behaviour as that of the ntmp complex (group 2). Both of the complexes of Zn^{2+} and Cd^{2+} with dmamp show group 1 behaviour, indicating that dmamp is protonated at the nitrogen atom and co-ordinates to the metal by phosphonate acting as a monodentate ligand. Consequently, the results of the ^{31}P NMR study strongly support the structures of the aminopolyphosphonate complexes predicted by the protonation constants. That is, the strength of the M–N bond decreases with decreasing number of methylenephosphonate groups even if the stability of the complex, K_{ML}, does not vary.

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