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Stability and structure of ethylenedinitrilopoly(methylphosphonate) complexes of the alkaline-earth metal ions in aqueous solution

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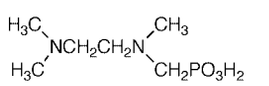
The formation and protonation of the complexes of a series of ethylenedinitrilopoly(methylphosphonic acids) (edmp) [$(H_2O_3PCH_2)_{2-p}Me_pNC_2H_4NMe_q(CH_2PO_3H_2)_{2-q}$; p, q = 0–2] with the alkaline-earth metal ions (M = Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+}) have been investigated by means of potentiometry and ^{31}P NMR spectroscopy at 25.0 °C. The complex formation and protonation constants of these complexes were determined by pH titration. The ^{31}P NMR spectra were measured as a function of pH and the shifts of each chemical species evaluated by using the equilibrium constants determined by pH titration. The results for edmp complexes were compared with those of aminopoly(methylphosphonic acid) [$Me_rN(CH_2PO_3H_2)_{3-r}$, r = 0–2] complexes. The stability constants of the metal complexes increase upon increasing number of phosphonate groups and are almost the same among the edmp having the same number of such groups irrespective of the number of nitrogen atoms. These results indicate a structure where one nitrogen atom of the phosphonate does not co-ordinate in any of the complexes. The first protonation takes place on this nitrogen atom.

Introduction

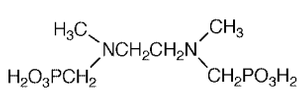
The properties of aminopolyphosphonates (APPs) in which the carboxyl groups of aminopolycarboxylates are substituted by phosphonate groups were first reported as early as 1949 by Schwarzenbach *et al.*[1] concurrently with those of aminopolycarboxylates (APCs) and have been used for industrial purposes such as in scale inhibition and for medical purposes such as magnetic resonance imaging agent.[2–6] Many kinds of these compounds have been synthesized[1,5–10] and complex formation has been studied.[9–29] The number of negative charges of APPs is much higher than that of the corresponding APCs, *e.g.* the charge of ethylenedinitrilotetra(methylphosphonate) is minus eight ($edtmp^{8-}$), while that of ethylenedinitrolotetraacetate is minus four ($edta^{4-}$). Thus, the metal complexes of aminopolyphosphonates easily form protonated species.

We have studied the formation and protonation of monoaminopolyphosphonic acid [$Me_rN(CH_2PO_3H_2)_{3-r}$, r = 0–2] complexes with substitution-labile metal ions such as the alkaline-earth metals,[25–27] divalent transition metals[27,28] and lanthanoid metals[29] by means of potentiometry, NMR spectroscopy and calorimetry. The unprotonated metal complexes of nitrilotris(methylphosphonic acid) (ntmp) have an ordinal structure, *i.e.* ntmp co-ordinates as an *N*,*O*,*O*,*O*-tetradentate ligand.[28] On the other hand, the protonated complexes of alkaline-earth and lanthanoid metals have unusual structures. That is, protonation occurs on the nitrogen atom of the ligand, rupturing the M–N bond and forming the *O*,*O*,*O*-tridentate complex with eight-membered chelate rings.[25,29] In the case of inert Co^{III}(polyamine) complexes such as *cis*-$[Co(en)_2(H_2O)_2]^{3+}$, APPs form *O*,*O*-bidentate complexes having an eight-membered chelate ring where the nitrogen atom of ligand does not co-ordinate.[30] The complex formation of ethylenedinitrilopoly(methylphosphonates) (edmp) has hardly been studied except for edtmp. The structure of the edtmp complexes is rather complicated.[26]

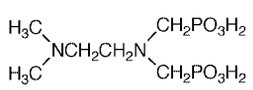
In the present study, the complex formation of a series of ethylenedinitrilopoly(methylphosphonate) with alkaline-earth metal ions was investigated by means of potentiometry and ^{31}P NMR spectrometry. The results are discussed by a comparison with monoaminopolyphosphonate and aminopolycarboxylate complexes.



(H_2tmedmp)



(H_4dmeddmp-*N*,*N*′)



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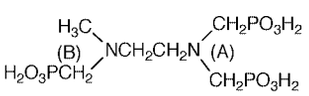
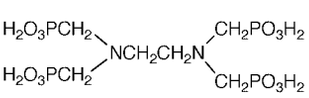


(H_6medtmp)



(H_8edtmp)

Experimental

Reagents

The compound $Me_2NCH_2CH_2NMeCH_2PO_3H_2$ (H_2tmedmp) was synthesized by reaction of *N*,*N*,*N*′-trimethylethylenediamine (0.19 mol) and phosphorous acid (0.39 mol) with 30 cm^3 40% formaldehyde in 5 mol dm^{-3} HCl (120 cm^3) according to the method of Medved' *et al.*[10] Its purity was determined to be 99.8% by ^{31}P,^{13}C and ^1H NMR and pH titration. The compounds $H_2O_3PCH_2NMeCH_2CH_2N(CH_2PO_3H_2)_2$ (H_6medtmp), $Me_2NCH_2CH_2N(CH_2PO_3H_2)_2$ [H_4dmeddmp(*N*,*N*)] and $H_2O_3PCH_2NMeCH_2CH_2NMeCH_2PO_3H_2$ [H_4dmeddmp(*N*,*N*′)] were

Table 1 Protonation constants of ethylenedinitrilopoly(methylphosphonic acids)[a]

	edtmp[b]	medtmp[b]	dmeddmp(*N*,*N*)[b]	dmeddmp(*N*,*N*′)[b]	tmedmp
log K_{HL}	13.0	12.6	12.5	11.46	10.65 ± 0.05
log K_{H_2L}	9.85	8.94	8.40	7.83	6.84 ± 0.03
log K_{H_3L}	7.87	7.06	6.15	5.68	4.20 ± 0.05
log K_{H_4L}	6.40	5.45	2.80	3.85	
log K_{H_5L}	5.12	2.89			
log K_{H_6L}	2.96	≈1			
log K_{H_7L}	<1				

[a] $K_{H_nL} = [H_nL]/[H][H_{n-1}L]$, $I = 0.1$ mol dm^{-3} (KNO_3), 25.0 °C. [b] Ref. 7.

synthesized as previously described.[7] Metal nitrates used were analytical grade (Wako pure chemicals) and the concentrations of the stock solutions were determined by titration with a standard ethylenedinitrilotetraacetate. All the solutions were prepared with deionized water (Organo, Model-III).

Potentiometric measurements

The pH titration was carried out with a Corning Research Model Ion Analyzer C-130 under a nitrogen stream. The electromotive force (emf) of the glass electrode (Iwaki, glass electrode IW002 and calomel electrode IW022) was calibrated by titration with nitric acid or potassium hydroxide at 25.0 ± 0.1 °C ($I = 0.1$ mol dm^{-3} KNO_3). The pH, logarithm of the reciprocal of the hydrogen ion concentration, was evaluated from the emf by using the calibration curve. A 0.005–0.01 mol dm^{-3} ligand solution or metal–ligand mixture was titrated in a water-jacketed cell (25.0 ± 0.1 °C) with 0.1 mol dm^{-3} KOH at an ionic strength of 0.1 mol dm^{-3} (KNO_3).

NMR Measurements

The ^{31}P-{^{1}H} NMR spectra of ligands ($c_L = 0.01$ mol dm^{-3}) or metal–ligand equimolar solutions ($c_M = c_L = 0.01$ mol dm^{-3}) were measured at various pH by a Varian Unity 500 FT-NMR spectrometer (202.35 MHz for ^{31}P) with a 10 mm diameter sample tube at 25 °C ($I = 0.1$ mol dm^{-3} KNO_3). The external standard, which was served by a 5 mm diameter concentric tube, was 0.5% H_3PO_4 in D_2O. The observed chemical shifts were converted to be values, referenced to aqueous 85% H_3PO_4.

Results and discussion

Formation constants

By using the hydrogen-ion concentration [H^+] obtained from the electromotive force, the mean number of protons bound to the ligand and complexes, $\bar{n}_{obs}$, was obtained. The calculated value of the mean number of protons bound to the ligand, $\bar{n}_{calc}$, is obtained by using successive protonation constants defined by $K_{H_nL} = [H_nL]/[H][H_{n-1}L]$. The latter values giving the minimum sum of the squares of the deviations, $\Sigma(\bar{n}_{obs} - \bar{n}_{calc})^2$, were obtained by a non-linear regression.[25–27] The values of the protonation constants of tmedmp obtained from 30–40 data points are listed in Table 1 together with the results of other edmp.[7]

The formation constant of the metal complex and its successive protonation constant are defined by $K_{ML} = [ML]/[M][L]$ and $K_{MH_mL} = [MH_mL]/[H][MH_{m-1}L]$. By the same process of non-linear regression as for the ligand, a set of K_{ML} and K_{MH_nL} values was evaluated.[25–27] The formation of hydroxo complexes such as M(OH)L was not observed under these experimental conditions. The logarithmic formation constants of the metal complexes and their protonation constants thus obtained are listed in Table 2. The distribution curves of the protonated species of medtmp (a) and the Ca^{2+}–medtmp complex (b) are shown as a function of pH in Fig. 1 as an example.

Table 2 Equilibrium constants of formation (log K_{ML})[a] and protonation (log K_{MH_mL})[b] of the alkaline-earth metal complexes[c]

	MgL	CaL	SrL	BaL
edtmp[d]				
log K_{ML}	8.35	9.29	7.56	7.10
log K_{MHL}	10.07	9.45	10.08	10.26
log K_{MH_2L}	8.73	8.24	8.50	8.54
log K_{MH_3L}	6.86	6.74	6.91	7.05
log K_{MH_4L}	5.35	5.49	5.82	5.78
medtmp				
log K_{ML}	7.83	7.77	6.63	6.29
log K_{MHL}	8.91	9.04	9.45	9.57
log K_{MH_2L}	8.07	7.87	8.04	8.32
log K_{MH_3L}	5.74	5.91	6.23	6.47
log K_{MH_4L}	4.3	4.5	4.4	4.4
dmeddmp(*N*,*N*)				
log K_{ML}	5.36	4.85	3.84	3.37
log K_{MHL}	9.99	10.32	10.99	11.07
log K_{MH_2L}	7.4	7.4	7.8	7.8
dmeddmp(*N*,*N*′)				
log K_{ML}	5.67	4.27	3.27	3.12
log K_{MHL}	8.80	9.94	10.24	10.20
log K_{MH_2L}	6.9	7.0	7.2	7.3
tmedmp				
log K_{ML}	2.4	1.9	1.7	1.1
log K_{MHL}	9.8	10.1	10.0	9.1

[a] $K_{ML} = [ML]/[M][L]$. [b] $K_{MH_nL} = [MH_mL]/[MH_{m-1}L][H]$. [c] Errors of the logarithmic constants were estimated as ±0.02 for log K_{ML} [dmeddmp(*N*,*N*′), dmeddmp(*N*,*N*) and medtmp] and log K_{MHL} (medtmp); ±0.04 for log K_{MHL} [dmeddmp(*N*,*N*′) and dmeddmp(*N*,*N*)] and log K_{MH_2L}, log K_{MH_3L} (medtmp); ±0.1 for log K_{ML}, log K_{MHL} (tmedmp), log K_{MH_2L} [dmeddpm(*N*,*N*′), dmeddmp(*N*,*N*)] and log K_{MH_4L} (medtmp). [d] Ref. 26.

Phosphorus-31 NMR

The proton decoupled ^{31}P-{^{1}H} NMR spectra show one single peak except for that of medtmp, which consists of two signals with a peak area ratio of 2:1, corresponding to the $N(CH_2PO_3^{2-})_2$ (A) and $NMe(CH_2PO_3^{2-})$ (B) groups. Thus, the chemical shifts of the ligand are given by a linear combination of each protonated species, $\delta_{calc} = \Sigma\delta_{H_nL}X_{H_nL}$. The proportion of each species, X_{H_nL}, was calculated using the protonation constants, K_{H_nL}. A set of chemical shifts for each species, δ_{H_nL}, minimizing the sum of squares of the deviations, $\Sigma(\delta_{obs} - \delta_{calc})^2$, was evaluated by a non-linear regression.[25–27] The results for tmedmp are listed in Table 3 together with those for other edmp.

The 1:1 metal–ligand solution also shows a single ^{31}P-{^{1}H} NMR signal. The chemical shift changes of the ligand and metal–ligand solution are plotted as a function of pH in Fig. 2, where the results for the medtmp system are shown as an example. A set of chemical shifts for each complex, δ_{MH_nL}, was evaluated in the same manner as that for the ligand and are

Table 3 The ^{31}P NMR chemical shifts (δ_{H_xL}) of ethylenedinitrilopoly(methylphosphonic acids)

	edtmp[a]	medtmp(A)[a,b]	medtmp(B)[a,c]	dmeddmp(*N*,*N*)[a]	dmeddmp(*N*,*N*′)[a]	tmedmp
δ_L	17.15	16.63	15.96	16.46	15.08	14.90 ± 0.03
δ_{HL}	11.50	15.54	8.12	16.15	11.17	14.15 ± 0.03
δ_{H_2L}	9.42	14.67	6.74	17.86	8.72	11.77 ± 0.05
δ_{H_3L}	11.83	17.89	6.67	19.75	8.67	6.4 ± 0.1
δ_{H_4L}	12.54	18.77	7.64	11.63	6.71	
δ_{H_5L}	12.94	10.65	7.03			
δ_{H_6L}	8.96					

[a] Ref. 7. [b] Iminodimethylenephosphonate group. [c] Iminomonomethylenephosphonate group.

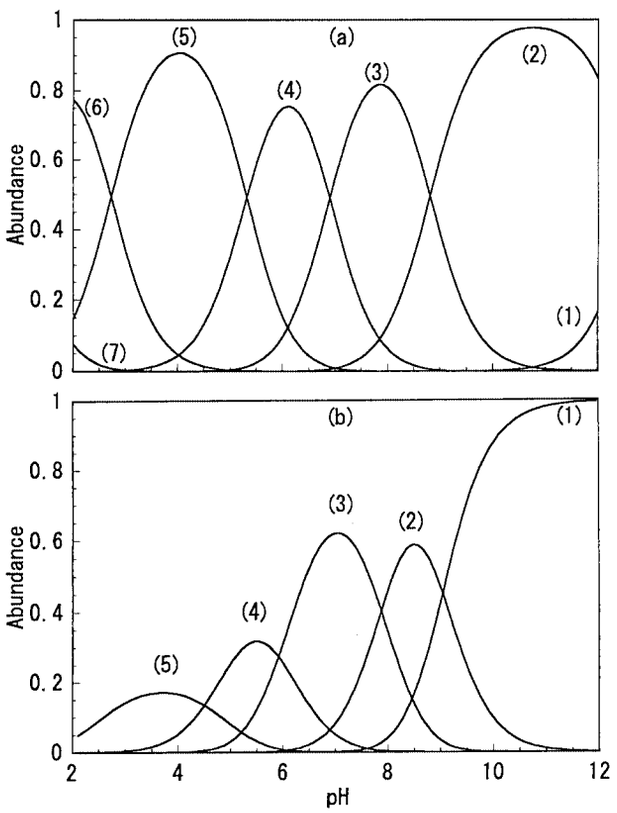


Fig. 1 Distribution diagrams: (a) ligand medtmp, (1) L, (2) HL, (3) H_2L, (4) H_3L, (5) H_4L, (6) H_5L, (7) H_6L, $c_L = 0.01$ mol dm^{-3}; (b) calcium–medtmp complex, (1) ML, (2) MHL, (3) MH_2L, (4) MH_3L, (5) MH_4L, $c_L = c_{Ca} = 0.01$ mol dm^{-3}.

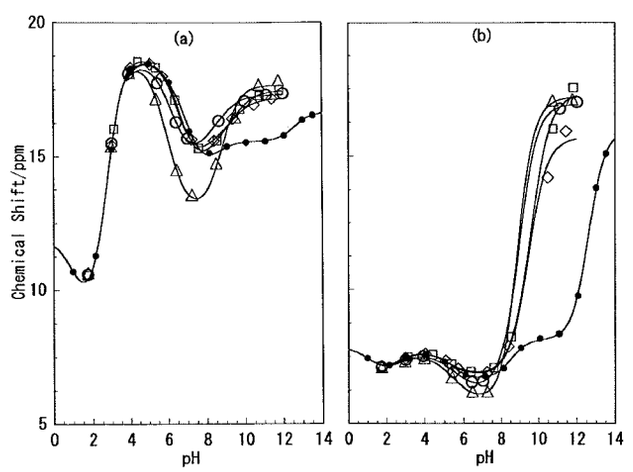


Fig. 2 Plots of ^{31}P NMR chemical shifts of the medtmp system as a function of pH: ●, ligand; △, Mg^{2+}; ○, Ca^{2+}; ◇, Sr^{2+}; □, Ba^{2+}. (a): iminodi(methylphosphonate); (b): methylimino(methylphosphonate).

Table 4 The ^{31}P NMR chemical shifts of the alkaline-earth metal complexes[a]

	MgL	CaL	SrL	BaL
edtmp[b]				
δ_{ML}	16.94	17.67	17.41	17.49
δ_{MHL}	10.83	14.03	14.75	14.34
δ_{MH_2L}	8.04	12.87	14.14	13.52
δ_{MH_3L}	10.39	12.47	11.11	11.61
δ_{MH_4L}	10.89	12.23	13.72	13.74
medtmp				
$\delta_{ML(A)}$	17.63	17.26	17.13	17.45
$\delta_{MHL(A)}$	14.05	16.36	16.03	16.24
$\delta_{MH_2L(A)}$	12.52	15.06	15.01	14.73
$\delta_{MH_3L(A)}$	17.20	18.22	18.97	18.83
$\delta_{MH_4L(A)}$	17.3	17.0	17.0	17.2
$\delta_{ML(B)}$	17.21	16.96	15.72	17.40
$\delta_{MHL(B)}$	7.75	8.08	7.81	8.54
$\delta_{MH_2L(B)}$	5.72	6.23	6.83	6.90
$\delta_{MH_3L(B)}$	6.57	7.01	7.37	7.29
$\delta_{MH_4L(B)}$	6.4	7.1	7.6	7.7
dmeddmp(*N*,*N*)				
δ_{ML}	16.83	17.00	16.96	16.95
δ_{MHL}	15.64	15.90	16.01	15.94
δ_{MH_2L}	17.7	18.5	18.1	18.9
dmeddmp(*N*,*N*′)				
δ_{ML}	16.38	16.70	16.75	16.64
δ_{MHL}	9.92	11.34	11.36	11.09
δ_{MH_2L}	7.0	6.9	7.6	7.6
tmedmp				
δ_{ML}	14.26	14.96	14.97	15.14
δ_{MHL}	14.3	14.2	14.3	13.7

[a] Errors of chemical shifts were estimated as ±0.03 for δ_{ML} [tmedmp, dmeddmp(*N*,*N*′), dmeddmp(*N*,*N*) and medtmp] and δ_{MHL} (medtmp); ±0.05 for δ_{MHL} [dmeddmp(*N*,*N*′) and dmeddmp(*N*,*N*)] and δ_{MH_2L} and δ_{MH_3L} (medtmp); ±0.1 for δ_{MHL} (tmedmp), δ_{MH_2L} [dmeddmp(*N*,*N*′), dmeddmp(*N*,*N*)] and δ_{MH_4L} (medtmp). [b] Ref. 26.

listed in Table 4. The calculated chemical shifts of the medtmp complexes obtained by using these values are shown by solid lines in Fig. 2.

Structure of unprotonated complexes

The complex formation constants, log K_{ML}, of alkaline-earth metal ions with edmp are plotted in Fig. 3 together with those of one nitrogen atom ligands [ntmp, nitrilotris(methylphosphonic acid);[25] midmp, *N*-methyliminobis(methylphosphonic acid)[27] and dmamp, *N*,*N*-dimethylaminomethylphosphonic acid[27]], where results for some aminopolycarboxylates (APCs) are also depicted [edta;[31] nta, nitrilotriacetic acid;[32] mida, *N*-methyliminodiacetic acid[33]]. The stabilities of the complexes increase as the number of phosphonate groups increases. The stability

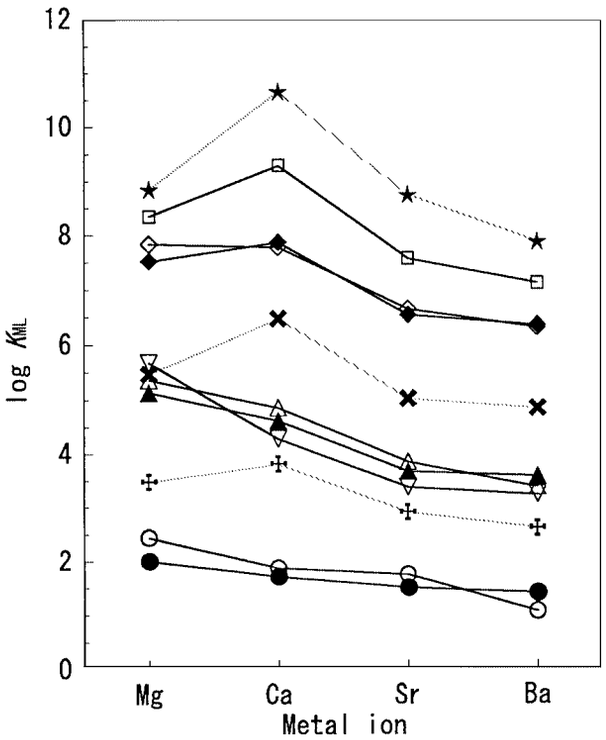
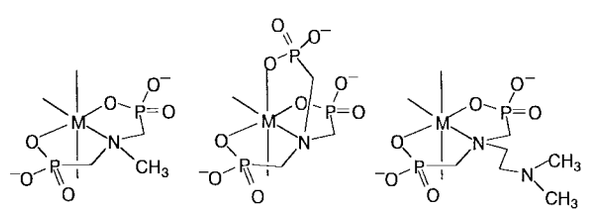


Fig. 3 Plots of the logarithmic formation constants of alkaline-earth metal complexes. □, edtmp; ★, edta; ◇, medtmp; ◆, ntmp; ✖, nta; △, dmeddmp(*N*,*N*); ▽, dmeddmp(*N*,*N*′); ▲, midmp; ✣, mida; ○, tmedmp; ●, dmamp.

of the complex of the ethylenedinitrilopoly(methylphosphonate) ligand hardly differs from that of the one nitrogen ligand having the same number of phosphonate groups, *i.e.* does not depend on the number of the nitrogen atoms of the ligand.

In the case of midmp complexes[27] all the co-ordinating atoms, *i.e.* two phosphonate oxygens and amino nitrogen, co-ordinate to the metal ion and form two chelate rings (Structure I). The formation constants of ntmp complexes, in which the methyl group of midmp is substituted by a methylphosphonate group, are much larger than these of midmp complexes. This indicates that the oxygen atom of the third phosphonate group co-ordinates giving three chelate rings (Structure II).[25]

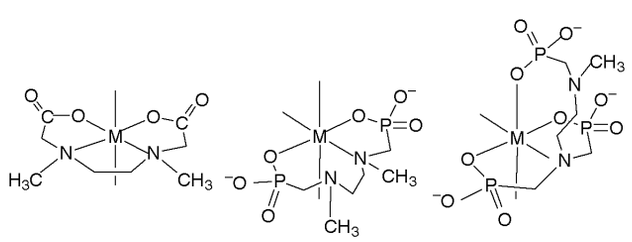


I II III

On the other hand, the formation constants of dmeddmp(*N*,*N*) complexes, in which the methyl group of midmp is substituted by the dimethylaminoethylene group [$C_2H_4NMe_2$], are the same order of magnitude as those of the midmp complexes. This indicates that the nitrogen atom of the dimethylamino group does not co-ordinate (Structure III). This structure is reasonable, because the co-ordination ability of nitrogen is quite low as seen from the fact that ethylenediamine hardly co-ordinates these metal ions. The situation of the tmedmp is the same as that of dmeddmp(*N*,*N*). That is, the formation constants of tmedmp complexes, in which the methyl group of dmamp is substituted by a dimethylaminoethylene group, are almost the same as those of the dmamp complexes. Thus, the nitrogen atom of the dimethylamino group does not co-ordinate.

In the case of the ligands having the phosphonate groups at both of the amino nitrogens [dmeddmp(*N*,*N*′), medtmp, edtmp] the complex formation constants are rather complicated. The stability constants, $K_{M(medtmp)}$, of the complexes of medtmp, in which one methyl group of the dimethylamino moiety of dmeddmp(*N*,*N*) is substituted by a methylphosphonate group, are larger than those of dmeddmp(*N*,*N*) complexes, $K_{M(dmeddmp(N,N))}$. This indicates that the oxygen atom of the third phosphonate group co-ordinates. However, the stability constants of the medtmp complexes, $K_{M(medtmp)}$, are comparable to those of ntmp, $K_{M(ntmp)}$, *i.e.* the co-ordinating ability of the $NCH_2PO_3^{2-}$ group is almost the same as that of phosphonate (PO_3^{2-}). The situation of the dmeddmp(*N*,*N*′) complexes, in which one methyl group of dimethylamino moiety of tmedmp is substituted by a methylphosphonate group, is the same as that of medtmp. That is, although the stability constants of dmeddmp(*N*,*N*′) are larger than those of tmedmp, they are almost the same as those of midmp complexes.

The relative stabilities of the complexes among the APPs is quite different from that of the APC complexes. For example, the formation constant of the magnesium dmedda(*N*,*N*′) complex (log $K_{Mg(dmedda(N,N'))}$ 5.7)[34] is larger than that of magnesium–mida complex (log $K_{Mg(mida)}$ 3.44) and comparable to that of the Mg–nta complex (log $K_{Mg(nta)}$ 5.46). These results indicate that all co-ordinating atoms (two nitrogen and two oxygen) co-ordinate in the dmedda(*N*,*N*′) complexes (Structure IV).



IV V VI

On the other hand, the co-ordination ability of the $NCH_2PO_3^{2-}$ group is almost the same as that of phosphonate in the case of APP complexes. This may indicate that the nitrogen atom of the former group does not co-ordinate and an eight-membered chelate ring is formed. Thus, the structures of the dmeddmp(*N*,*N*′) and medtmp complexes must be given by V and VI. This difference of the structures between the APP and APC complexes might be caused by the difference in the geometry of the carboxylate group (CCO_2^-; triangle) and phosphonate group (CPO_3^{2-}; tetrahedron). The structures that the protonated complexes of ntmp and midmp with alkaline-earth metal ions, M(Hntmp) and M(Hmidmp), have involving eight-membered chelate rings[25,27] support this.

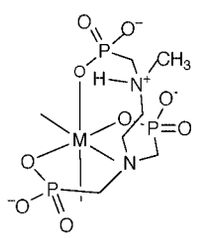
As seen from Fig. 3, the stabilities of the APP complexes are generally higher than those of the corresponding APC complexes. The differences in logarithmic stability constants of one-nitrogen ligands are 1–2 units, *e.g.* log $K_{Mg(ntmp)}$ − log $K_{Mg(nta)}$ = 2.06 and log $K_{Mg(midmp)}$ − log $K_{Mg(mida)}$ = 1.69. The difference between two-nitrogen ligands is much smaller, *e.g.* log $K_{Mg[dmeddmp(N,N')]}$ − log $K_{Mg[dmedda(N,N')]}$ = 0. This indicates the unstable structure of the dmeddmp(*N*,*N*′) complexes (Structure V). In the case of the edtmp complexes, the stabilities of the complexes are much smaller than those of edta complexes. The stability constants of edta complexes with alkaline-earth metal ions are about 4 units larger than those of the nta complexes, because the number of chelate rings increases from 3 to 5. On the other hand, the stability of the edtmp complexes is not so high compared with that of ntmp, *i.e.* the differences in logarithmic stability constants are about 1. These results indicate that at least one of the nitrogen atoms of edtmp is not co-ordinating.

In the case of APC complexes, the stability of Mg^{2+} complexes is lower than that of Ca^{2+}, although the stability of the complexes increases as the size of the metal ion decreases (Ba^{2+} to Ca^{2+}) (Fig. 3). The size of Mg^{2+} is too small to form a stable complex with APCs and the formation of the Mg^{2+} complexes is entropy driven. On the other hand, in the case of APP complexes, the stability of Mg^{2+} complexes is higher than that of Ca^{2+} complexes except for edtmp and ntmp. The difference in the formation constants between Mg^{2+} and Ca^{2+} complexes of edtmp and ntmp (APPs) is much less than that of edta and nta (APCs). The high negative charge of the phosphonate group (PO_3^{2-}) compared with the carboxylate group (CO_2^-) must be advantageous for the ionic interaction with the Mg^{2+} ion and the flexibility of the eight-membered chelate ring of the APC complex may loosen the strain caused by chelation to the small ion Mg^{2+}.

Protonation of metal complexes

The large values of the first protonation constants indicate that the first protonation occurs on the imino nitrogen atom. The values of the second protonation constants are still relatively large and the difference between the second and third protonation (log K_{H_3L} − log K_{H_2L}) is much smaller than that between the first and second (log K_{HL} − log K_{H_2L}). These results indicate that the structures of the diprotonated and higher protonated ligands are rather complicated, *i.e.* protonation occurs on both the nitrogen atom and phosphonate oxygen atoms. These structures were supported by the results of ^{31}P NMR spectra.[26]

The fact that the first protonation constant of the complex, log K_{MHL} (Table 2), is larger than second protonation constant of the ligand indicates the first protonation occurs on the nitrogen atom not co-ordinating to the metal ion as shown in Structure VII, where M(Hmedtmp) is depicted as an example.



VII

The results of ^{31}P NMR chemical shift change on protonation corroborate the structures of the protonated complexes. That is, the ^{31}P NMR chemical shifts of the protonated complexes, δ_{MH_mL} (Table 4), are quite similar to those of the corresponding "free" ligands, δ_{H_mL} (Table 3), irrespective of the kinds of ligands and metal ions, *i.e.* the chemical shifts of unprotonated and protonated edmp do not change upon co-ordination. The chemical shift change of the protonated complexes is plotted as a function of the number of protons (m) bound to the complex in Fig. 4, where the results for the calcium complexes are depicted as an example; similar patterns were obtained for the other metal complexes.

In the case of the medtmp complexes, the phosphonates of iminodi(methylphosphonate) [$N(CH_2PO_3^{2-})_2$, signal A] and methylimino(methylphosphonate) [$MeN(CH_2PO_3^{2-})$, signal B] are not equivalent, thus in the ^{31}P-{^1H} NMR two separate signals are observed. Signal A hardly changes upon the first protonation of the complex, whereas signal B shows a large upfield shift. It was demonstrated that protonation on the nitrogen atom causes a large upfield shift to the ^{31}P NMR signal ($\Delta\delta \approx 10$) corresponding to the methylphosphonate binding *via* N. Consequently, the results of the chemical shift change for

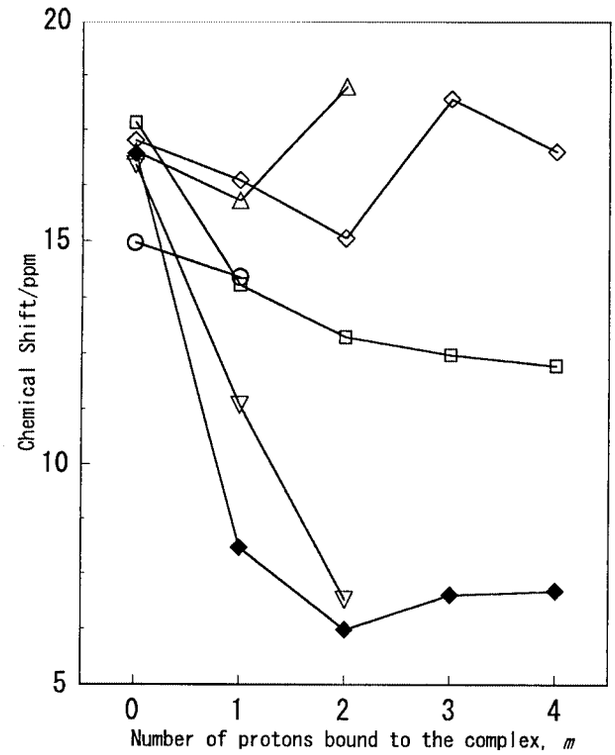


Fig. 4 Plots of ^{31}P NMR chemical shifts of calcium complexes (CaH_mL) as a function of the number of protons bound, m. □, edtmp; ◇, medtmp(A); ◆, medtmp(B); △, dmeddmp(N,N); ▽, dmeddmp(N,N'); ○, tmedmp.

medtmp complexes corroborate that the first protonation of the complex occurs on the nitrogen atom of the phosphonate B moiety, *i.e.* the nitrogen atom of methylimino(methylphosphonate) moiety not co-ordinating (Structure VII).

The small chemical shift change upon the first protonation of the dmeddmp(N,N) and tmedmp complexes supports the protonation of the nitrogen atom of the dimethylamino moiety. The ^{31}P NMR signals of the edtmp and dmeddmp(N,N') complexes show an upfield shift upon protonation but the extent is considerably smaller than 10 ppm. In the case of these ligands both the imino(methylphosphonate) groups of the ligand [$N(CH_2PO_3^{2-})_2$ or $NMe(CH_2PO_3^{2-})$] are equivalent. The fact that the protonated species of the complex show only one ^{31}P NMR signal indicates the quite fast protonation equilibrium and the signals of the protonated and unprotonated moieties of the complex are averaged. Thus, the monoprotonated complexes show an intermediate value of upfield shift and higher protonation causes a further upfield shift. The chemical shift of the ligand complexes except for dmeddmp(N,N') does not show a distinct upfield change upon higher protonation. These results support the structures estimated from protonation constants, *i.e.* partial protonation on the phosphonate oxygen and the imino nitrogen in the higher protonated complexes. The large upfield shift upon the second protonation of the dmeddmp(N,N'), where the total chemical shift change is about 10 ppm, may indicate that the both of the nitrogen atoms are protonated in the diprotonated complex.

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