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Stability and Structure of Ethylenedinitrilopoly(methylphosphonate) Complexes of the Divalent Transition Metal Ions in Aqueous Solution

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The formation and protonation of the complexes of a series of ethylenedinitrilopoly(methylphosphonic acids) (EDMP) $[(Me)_{2-p}(H_2O_3PCH_2)_pNC_2H_4N(Me)_{2-q}(CH_2PO_3H_2)_q$, $p = 0–2$, $q = 1–2]$ with divalent transition metal ions (M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} or Cd^{2+}) were investigated by means of potentiometry and ^{31}P NMR spectroscopy at 25.0 °C. The complex formation constants and protonation constants of these complexes were determined by pH titration. The ^{31}P NMR spectra of zinc and cadmium complexes were measured as a function of the pH, and the ^{31}P NMR chemical shifts of each chemical species were evaluated by using the equilibrium constants determined by pH titration. The results for EDMP complexes were compared with those of aminopoly(methylphosphonate) (NMP) $[(CH_3)_{3-r}N(CH_2PO_3H_2)_r$, $r = 1 – 3]$ complexes and alkaline earth metal EDMP complexes. The stability constants of the metal complexes increase upon increasing the number of the phosphonate groups and are around the same between the EDMP and NMP complexes of a given metal ion having the same total number of coordinating atoms. The stabilities of the edtmp ($p = q = 2$) complexes are around the same as those of the medtmp ($p = 1$, $q = 2$) complexes. These results reveal the structures in which two nitrogen atoms of the ethylenedinitrilopoly(methylphosphonate) co-ordinate to the transition metal ion in any complex. These structures are different from those of the corresponding alkaline earth metal complexes. The structures of the protonated complexes were estimated from the results of the protonation constants and the ^{31}P chemical shifts of the complexes.

The synthesis and properties of ethylenedinitrilotetra(methylphosphonic acid) (H_8edtmp), in which the carboxyl groups of ethylenedinitrilotetra(acetic acid) (H_4edta) are substituted by phosphonate groups, were first reported in 1956 by Westerback and Martell[1] and have been used for industrial purposes, such as a scale inhibitor, and for medical purposes, such as a magnetic resonance imaging agent and radiopharmaceuticals.[2–5] Various kinds of EDMP compounds have been synthesized[4–8] and complex formation has been studied.[1,7–21] Although the complex formation of the edtmp ligand has been intensively studied, there has been no systematic study of the other EDMP ligands, except for the alkaline earth metal complexes of EDMP.[8] Because the negative charge of the EDMP ligands is large, e.g. the charge of ethylenedinitrilotetra(methylphosphonate) is minus eight ($edtmp^{8-}$), the first protonation constants of the ligands are quite large. The protonation constants of edtmp have been determined by means of potentiometry.[9–12] Since this method is not suitable for the determination of the higher protonation constants, the reported valves of the protonation constants are scattered. The errors of the ligand protonation constants must cause a significant error in the determination of the formation constants and the protonation constants of complexes.[22] In a previous study, we determined the protonation constants by combining potentiometry with the NMR method and the complex formation constants of the alkaline earth metal ions with EDMP.[8] It was revealed that one of two nitrogen atoms of the ethylenediamine moiety does not co-ordinate to the metal ion.

We have studied the formation and protonation of monoaminopolymethylphosphonate $[(CH_3)_{3-r}N(CH_2PO_3H_2)_r$, $r = 1 – 3]$ (NMP) and $[N(CH_2COOH)_{3-r}(CH_2PO_3H_2)_r$, $r = 1 – 2]$ (NAMP) complexes with substitution-labile metal ions, such as the alkaline earth metals,[20–24] divalent transition metals[22,24,25] and lanthanide metals,[20] by means of potentiometry, NMR spectroscopy and calorimetry. The protonated complexes of the alkaline earth and lanthanide metal ions have the unusual structures. For example, protonation of the ntmp [nitrilotri(methylphosphonic acid)] complexes occurs on the nitrogen atom of the ligand, forming an *O*,*O*,*O*-tridentate complex with eight-membered chelate rings, where the nitrogen atom is not coordinated to the metal ion.[23] On the other hand, protonation takes place on the oxygen atom of phosphonate groups in divalent transition metal complexes.[25] In the case of midmp [*N*-methyliminobis(methylphosphonic acid)] and dmamp (*N*,*N*-dimethylaminomethylphosphonic acid) complexes, the first protonation takes place on the nitrogen atom in some transition metal complexes.[24]

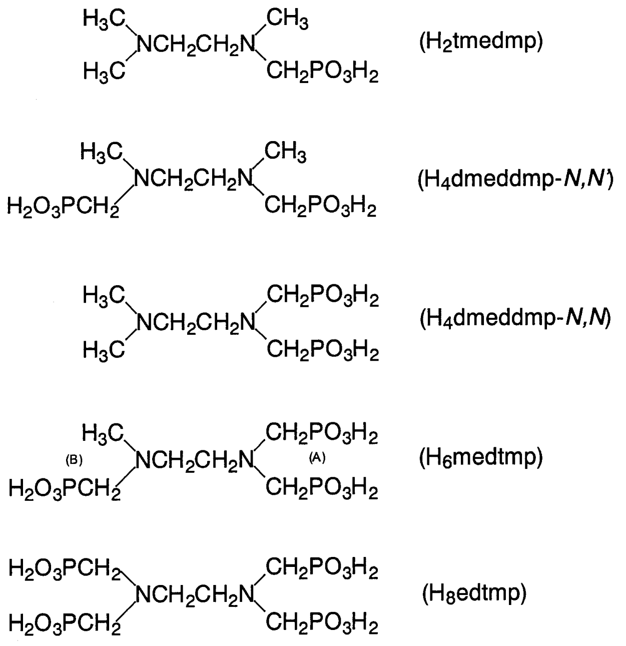
In the present work, the complex formation of a series of ethylenedinitrilopoly(methylphosphonate) with divalent transition metal ions was investigated by means of potentiometry and ^{31}P NMR spectrometry (Scheme 1). The results are discussed by a comparison with these of monoaminopolymethylphosphonate complexes and the alkaline earth metal EDMP complexes.

Experimental

Reagents. The compounds $H_2O_3PCH_2NMeC_2H_4N(CH_2PO_3H_2)_2$ (H_6medtmp), $Me_2NC_2H_4N(CH_2PO_3H_2)_2$ [H_4dmeddmp(*N*,*N*)], $H_2O_3PCH_2NMeC_2H_4NMeCH_2PO_3H_2$ [H_4dmeddmp(*N*,*N′*)] and $Me_2NC_2H_4NMeCH_2PO_3H_2$ (H_2tmedmp) were synthesized as previously described.[6,8] The compound $(H_2O_3PCH_2)_2NC_2H_4N(CH_2PO_3H_2)_2$ (H_8edtmp) was obtained from Dojin Chemicals. The metal nitrates were of analytical grade (Wako Pure Chemicals) and the concentrations of the stock solutions were determined by titration with a standard ethylenediaminetetraacetate. All of the solutions were prepared with deionized water (Organo, Model-III).

Potentiometric Measurements. The pH titration was carried out with a Corning Research Model C-130 Ion Analyzer 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 ionization constant of water, $pK_w = 13.82$,[26] was used for the calibration. The pH, logarithm of the reciprocal of the hydrogen ion concentration, was evaluated from the emf by using the calibration curve. A solution of 0.001–0.005 mol dm^{-3} metal–ligand mixture was titrated in a water-jacketed cell (25.0 ± 0.1 °C) with KOH at an ionic strength of 0.1 mol dm^{-3} (KNO_3).

NMR Measurements. The $^{31}P\{^1H\}$ NMR spectra of zinc and cadmium-ligand equimolar solutions ($c_M = c_L = 0.005$ 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 of an aqueous 85% H_3PO_4 reference.



Scheme 1.

Results and Discussion

Formation Constants. The pH titration curves of medtmp and transition metal complexes are shown in Fig. 1. 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 using the hydrogen-ion concentration $[H^+]$ obtained from the electromotive force, the mean number of protons bound to the complexes, $\bar{n}_{obs}$, was calculated. The calculated value of the mean number of protons bound to complexes, $\bar{n}_{calc}$, is obtained by using successive protonation constants of the complexes. The values of K_{ML} and K_{MH_mL} giving the minimum sum of the squares of the deviations, $\sum(\bar{n}_{obs} - \bar{n}_{calc})^2$, were obtained by a non-linear regression.[21,23,24] The standard derivation of the mean number of protons bound to a ligand, $\bar{n}_{obs}$, is less than 0.016 for any potentiometric titration. The hydroxo complexes M(OH)L is formed at a high pH, and the formation constant of hydroxo complexes is defined by $K_{M(OH)L} = [M(OH)L]/[ML][OH]$. The logarithmic formation constants of the metal complexes, their protonation constants and formation constants of thus-obtained hydroxo complexes are listed in Table 1. Although some constants reported by Motekaitis[11] for edtmp complexes (M: Co, Ni, Cu and Zn) agree fairly well with our results, the results of Mn and Cd–edtmp complexes differ from our results.[9,12] Some constants reported by Medved′ [7] for dmeddmp(*N*,*N′*) complexes (M: Ni and Cu) agree fairly well with our results, but others have not been determined. The constants of medtmp, dmeddmp(*N*,*N*) and tmedmp with the transition metal ions have not been determined. The distribution curves of the protonated species of medtmp (a) and Zn^{2+}-medtmp complex (b) are shown as a function of the pH in Fig. 2 as an example.

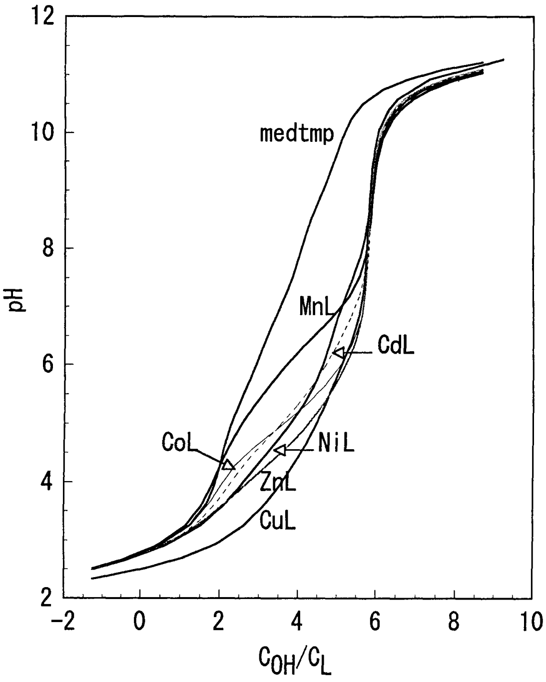


Fig. 1. The pH titration curves of medtmp and the transition metal complexes. $c_L = c_M = 0.005$ mol dm^{-3}.

Table 1. Equilibrium Constants of Formation ($\log K_{ML}$),[a] Protonation ($\log K_{MHmL}$)[b] and Formation of Hydroxo Complex ($\log K_{M(OH)L}$)[c] of the Divalent Metal Complexes[d]

	MnL	CoL	NiL	CuL	ZnL	CdL
edtmp						
$\log K_{ML}$	13.5	17.27	16.64	23.2	19.1	16.90
$\log K_{MHL}$	8.87	8.28	8.92	7.73	8.22	8.72
$\log K_{MH2L}$	7.21	6.45	7.32	6.10	5.92	6.93
$\log K_{MH3L}$	6.17	5.23	5.43	4.67	4.94	5.44
$\log K_{MH4L}$	4.9	4.3	4.3	3.8	4.1	4.9
$\log K_{M(OH)L}$	1.8	1.5	1.4	1.7	1.7	1.1
medtmp						
$\log K_{ML}$	12.61	16.27	15.88	24.0	18.01	15.82
$\log K_{MHL}$	6.96	6.02	7.42	6.15	5.95	6.68
$\log K_{MH2L}$	6.45	5.30	5.46	4.65	4.94	5.57
$\log K_{MH3L}$	5.05	3.90	4.41	3.62	3.90	4.53
$\log K_{MH4L}$	4.0	3.7	3.1	1.8	2.9	3.7
$\log K_{M(OH)L}$	2.8	2.0	2.4	1.7	1.9	2.0
dmeddmp(*N*,*N*)						
$\log K_{ML}$	9.68	14.03	13.79	17.8	15.04	12.47
$\log K_{MHL}$	7.66	5.09	5.75	5.64	5.42	6.50
$\log K_{MH2L}$	6.0	4.6	4.5	3.7	3.5	5.0
$\log K_{M(OH)L}$	2.7	2.6	1.3	3.0	1.7	1.8
dmeddmp(*N*,*N′*)						
$\log K_{ML}$	9.78	12.80	13.96	19.5	13.07	12.48
$\log K_{MHL}$	6.59	5.60	5.70	4.45	5.54	5.78
$\log K_{MH2L}$	5.9	4.7	4.7	3.7	4.5	4.9
$\log K_{M(OH)L}$	1.9	2.1	1.8	2.0	3.0	1.3
tmedmp						
$\log K_{ML}$	5.49	7.91	9.14	13.4	8.41	8.20
$\log K_{MHL}$	7.9	4.2	4.5	3.8	4.7	5.0
$\log K_{M(OH)L}$	3.6	3.4	3.0	4.1	4.7	3.1

a) $K_{ML} = [ML]/[M][L]$. b) $K_{MHmL} = [MH_mL]/[MH_{m-1}L][H]$. c) $K_{M(OH)L} = [M(OH)L]/[ML][OH]$. d) Errors of the logarithmic constants were estimated as ±0.02 for $\log K_{ML}$ and $\log K_{MHL}$ (medtmp and edtmp) except for copper complexes, Mn and Zn edtmp; ±0.04 for $\log K_{MHL}$ [dmeddmp(*N*,*N′*) and dmeddmp(*N*,*N*)] and $\log K_{MH2L}$, $\log K_{MH3L}$ (medtmp and medtmp); ±0.1 for $\log K_{ML}$ (copper complexes and Mn and Zn edtmp), $\log K_{MHL}$ (tmedmp), $\log K_{MH2L}$ [dmeddmp(*N*,*N′*) and dmeddmp(*N*,*N*)], $\log K_{MH4L}$ (medtmp and edtmp) and $\log K_{M(OH)L}$.

In aminopolycarboxylate (APC) complexes, the formation constants of the transition metal complexes are smaller than those of the corresponding aminopolyphosphonate (APP) complexes. APC complexes do not form higher protonated complexes. The edta complexes form only monoprotonated complexes and the protonation constants are very small ($\log K_{MHL} \approx 3$).[26]

Phosphorus-31 NMR. The 1:1 metal-ligand solution shows a single $^{31}P\{^1H\}$ NMR signal. The medtmp ligand system shows two singlet peaks that correspond to two types of phosphonate groups. Thus, the chemical shifts of complexes are given by a linear combination of each protonated species, $\delta_{calc} = \sum \delta_{H_nL}X_{H_nL} + \sum \delta_{MH_mL}X_{MH_mL}$, where X_{H_nL} and X_{MH_mL} refer to the proportion of H_nL and MH_mL. A set of chemical shifts for each complex, δ_{MH_mL}, minimizing the sum of the square of the deviation, $\sum(\delta_{obs} - \delta_{calc})^2$, was evaluated by a non-linear regression by using the ligand chemical shifts and equilibrium constants for the ligand and already determined complexes.[21,23,24] The chemical-shift changes of the ligand and metal-ligand solution are plotted as a function of the pH in Fig. 3, where the results of the medtmp system [(A): $-N(CH_2PO_3^{2-})_2$, (B): $-N(CH_3)(CH_2PO_3^{2-})$] are shown as an example. In the region of a steep chemical-shift change (pH 3–5), the NMR signals of metallic complexes are quite broad. The chemical shifts of each thus-obtained complex are listed in Table 2. The solid lines in Fig. 3 show the calculated curves of the chemical shifts of the medtmp complex obtained by using these values.

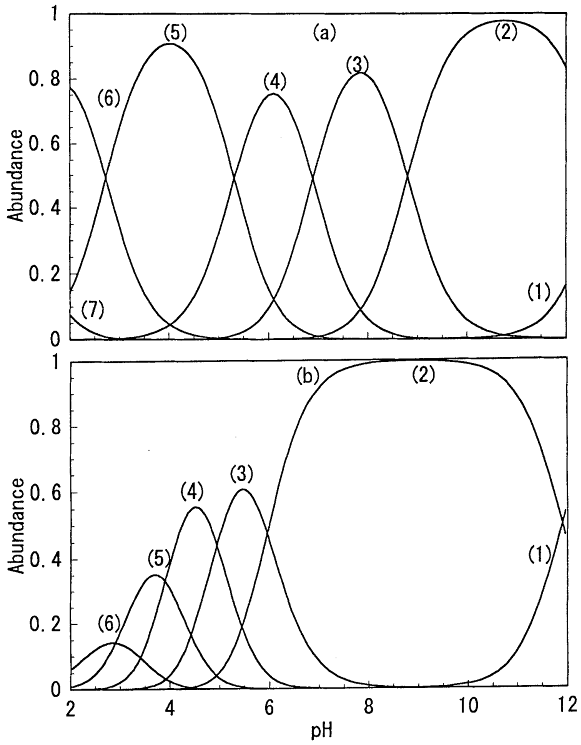


Fig. 2. Distribution diagrams: (a) ligand medtmp. (1) L, (2) HL, (3) H_2L, (4) H_3L, (5) H_4L, (6) H_5L, (7) H_6L. c_L = 0.005 mol dm^{-3}; (b) zinc-medtmp complex, (1) M(OH)L, (2) ML, (3) MHL, (4) MH_2L, (5) MH_3L, (6) MH_3L, (6) MH_4L. $c_L = c_{Zn}$ = 0.005 mol dm^{-3}.

Structure of Unprotonated Complexes. The complex formation constants, $\log K_{ML}$, of the divalent transition metal ions with EDMP are plotted in Fig. 4 together with those of the alkaline earth metal complexes and one nitrogen atom NMP ligands, ntmp,[22] midmp and dmamp[24] complexes. The stabilities of the complexes increase as the number of phosphonate groups increases. In the case of alkaline earth metal complexes, the stabilities of the EDMP complexes are comparable to those of one-nitrogen NMP ligands having the same number of phosphonate groups in spite of an increase in the number of nitrogen atoms. This fact indicates that one of the two nitrogen atoms of the ethylenediamine moiety does not co-ordinate to the alkaline earth metal in the EDMP complexes. On the other hand, for the divalent transition metal complexes, the stability of the EDMP complexes is higher than that of the NMP com-

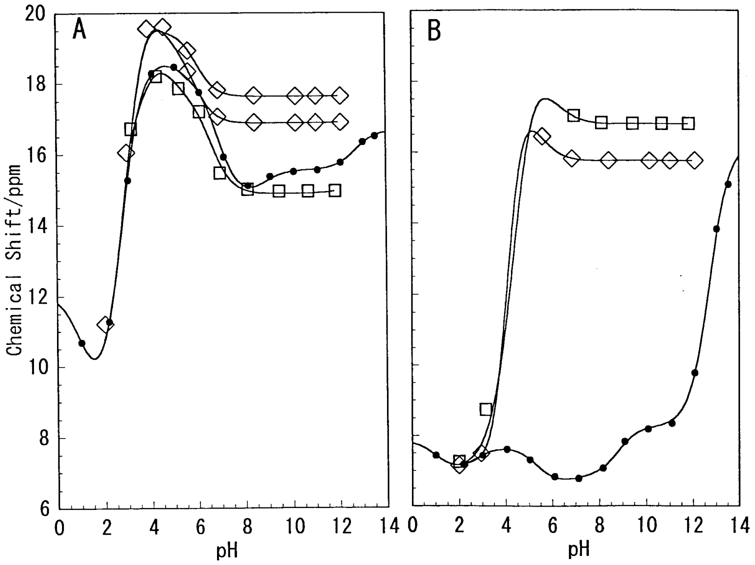


Fig. 3. Plots of ^{31}P NMR chemical shiits of the medtmp system as a function of pH: •, ligand; ◇, ZnL; □, CdL. (A): iminodi(methylphosphonate); (B): methylimino(methylphosphonate). The signal of ZnL(A) is separated two peaks at high pH.

Table 2. The ^{31}P NMR Chemical Shift of Zinc and Cadmium Complexes[a)]

	ZnL			CdL	
edtmp					
δ_{ML}	16.46			15.51	
δ_{MHL}	16.36			16.19	
δ_{MH2L}	17.58			17.34	
δ_{MH3L}	18.28			17.04	
δ_{MH4L}	17.6			17.3	
medtmp[b)]	(A)		(B)	(A)	(B)
δ_{ML}	17.63	16.88	15.75	14.89	16.79
δ_{MHL}	19.46	18.78	16.42	17.30	17.40
δ_{MH2L}	19.51		18.19	17.99	
δ_{MH3L}	20.9		6.5	18.9	13.9
δ_{MH4L}	10.0		7.2	16.1	7.1
$\delta_{M(OH)L}$	17.64	16.90	15.76	15.02	16.79
dmeddmp(*N*,*N*)					
δ_{ML}	17.05			16.03	
δ_{MHL}	19.25			17.21	
δ_{MH2L}	19.2			19.6	
$\delta_{M(OH)L}$	16.36			15.57	
dmeddmp(*N*,*N*′)					
δ_{ML}	15.87			14.61	
δ_{MHL}	13.11			16.93	
δ_{MH2L}	6.8			6.9	
$\delta_{M(OH)L}$	16.10			14.50	
tmedmp					
δ_{ML}	16.21			14.69	
δ_{MHL}	7.0			8.3	
$\delta_{M(OH)L}$	16.71			14.47	

a) Errors of chemical shifts were estimated as ±0.03 for δ_{ML}, δ_{MHL} (medtmp and edtmp) and $\delta_{M(OH)L}$; ±0.05 for δ_{MHL} [dmeddmp(*N*,*N*′) and dmeddmp(*N*,*N*)], δ_{MH2L} (medtmp and edtmp) and δ_{MH3L} (edtmp); ±0.1 for δ_{MHL} (tmedmp), δ_{MH2L} [dmeddmp(*N*,*N*′) and dmeddmp(*N*,*N*)], δ_{MH3L} (medtmp); δ_{MH4L} (medtmp and edtmp). b) (A). iminodimethylenephosphonate group; (B). iminomonomethylenephosphonate group.

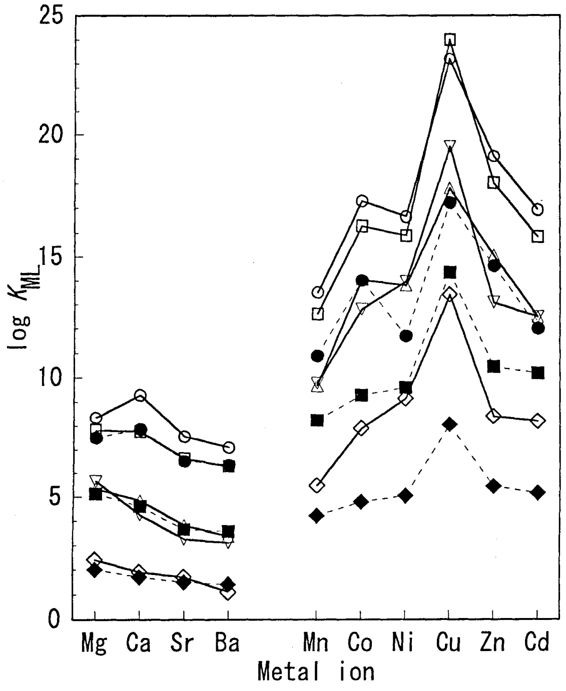


Fig. 4. Plots of the logarithmic formation constants of the metal complexes. ○, edtmp; □, medtmp; △, dmeddmp(*N*,*N*); ▽, dmeddmp(*N*,*N*′); ◇, tmedmp; ●, ntmp; ■, midmp; ◆, dmamp. K_{ML} = [ML]/[M][L].

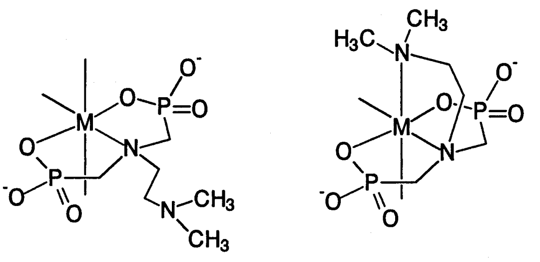
plexes having the same number of phosphonate groups, and is around the same as that of NMP which have the same total number of the co-ordination atoms, i.e., nitrogen atoms and phosphonate groups.

The formation constants of dmeddmp(*N*,*N*) complexes of the alkaline earth metal are the same order of magnitude as those of the midmp complexes, whereas those of the divalent transition metal complexes are larger than those of the midmp complexes and are around the same as those of the ntmp complexes. These facts indicate that the nitrogen atom of the dimethylamino group of dmeddmp(*N*,*N*) coordinates to the metal ions in the transition metal complexes (Structure **II**), but not in the alkaline earth metal complexes (Structure **I**) (Chart 1). The difference in the structures of the dmeddmp(*N*,*N*) complexes between the transition and alkaline earth metal is explained by the high coordination ability of the nitrogen atom to the transition metal ions.[26]

The situation concerning the stabilities of the dmeddmp(*N*,*N′*) and the medtmp complexes are similar to that of the dmeddmp(*N*,*N*) complexes. That is, the formation constants of the dmeddmp(*N*,*N′*) complexes with transition metal ions are almost the same as these of dmeddmp(*N*,*N*), and those of the medtmp complexes are larger than those of the dmeddmp(*N*,*N*) complexes. Consequently, in the case of the transition metal complexes of EDMP, all of the coordinating atoms, i.e., two nitrogen atoms and one oxygen atom of every phosphonate groups, coordinate to the metal ions. On the other hand, in the alkaline earth metal complexes, the one nitrogen atom does not coordinate to the metal ions, and one eight-membered chelate ring is formed.[8]

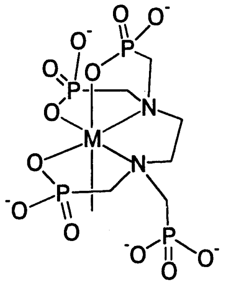
In spite of increasing in one phosphonate group compared with medtmp, the formation constants of the edtmp complexes with transition metal ions are almost the same as those of the medtmp complexes. In the case of aminopolycarboxylate complexes, the formation constants of edta complexes are larger than those of hedta [*N′*-(2-hydroxyethyl)ethylenediaminetri(acetic acid)] complexes,[26] which suggests six dentate coordination to the metal ions. Thus, the results concerning the stabilities of the EDMP complexes indicate that the edtmp complexes have a similar coordination structure as those of medtmp, i.e., one of the four phosphonate groups does not coordinate to the metal ion (structure **III**) (Chart 2). An electrostatic repulsion caused by a highly negative charge (edtmp^{-8}) of the phosphonate groups might prevent coordination of the fourth phosphonate group.

The formation constants of divalent metal complexes follow the so-called Irving–Williams series ($K_{\mathrm{M}n\mathrm{L}} < K_{\mathrm{CoL}} < K_{\mathrm{NiL}} < K_{\mathrm{CuL}} > K_{\mathrm{ZnL}} > K_{\mathrm{CdL}}$), except for nickel complexes. Thus, nickel complexes show a peculiar behavior in the same manner as those of the NAMP complexes.[22] When the ligands have an iminodimethylphosphonate group, i.e., dmeddmp(*N*,*N*), medtmp and edtmp, the formation constants of nickel complexes are smaller than those of cobalt complexes in the same way as the ntmp complexes. These results indicate that the coordination of the phosphonate oxygen in the axial position is relatively weak in nickel complexes.



I **II**

Chart 1.



III

Chart 2.

Protonation of Metal Complexes. The first protonation constants, log K_{MHL}, of the divalent transition metal ions with EDMP are plotted in Fig. 5 together with those of the alkaline earth metal complexes. As can be seen from Fig. 5, the first protonation constants of the divalent transition metal complexes are much smaller than those of the corresponding alkaline earth metal complexes, except for the edtmp complexes. In the case of the alkaline earth metal complexes, the first protonation constants are large. This indicates that the first protonation takes place on the nitrogen atom not coordinating to the metal ion. In contrast to the alkaline earth metal complexes, the first protonation constants are small in the transition metal com-

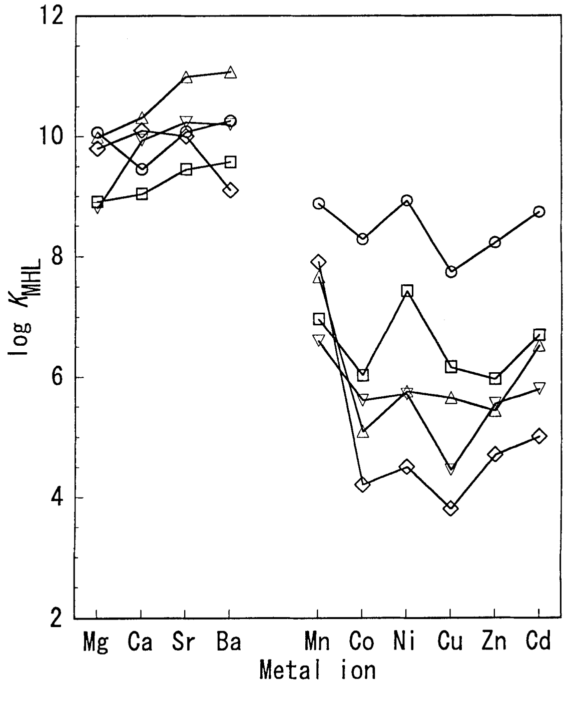


Fig. 5. Plots of the logarithmic first protonation constants of the metal complexes. K_{MHL} = [MHL]/[ML][H]. Symbols: see Fig. 4.

plexes, indicating that the first protonation takes place on the oxygen atom.

Although the formation constants of the edtmp complexes with transition metal ions are around the same as those of the medtmp complexes, the first protonation constants of the edtmp complexes are much larger than those of the medtmp complexes. These results support that the one oxygen atom of the phosphonate group of edtmp does not coordinate to the metal ion (Structure **III**), and that the first protonation takes place on it (Structure **IV**) (Chart 3). In the nickel edtmp complex, the first protonation constant does not differ very much from those of the other metal complexes, but the second protonation constant of Ni-edtmp is relatively larger than those of the other metal complexes (Table 2). These results suggest that one of the axial positions of the nickel complex is not coordinated by a phosphonate group, and the other is weakly coordinated by a phosphonate group in the Ni-edtmp complex. The electronic spectra indicate that this complex has a hexa-coordinated structure due to the coordination of a water molecule. The first protonation constants of the Mn–tmedmp and –dmeddmp(*N*,*N*) complexes are very large compared with those of other metal complexes, and larger than those of other ligand complexes. These results might indicate that the first protonation takes place on the nitrogen atom of the $-N(CH_3)_2$ group.

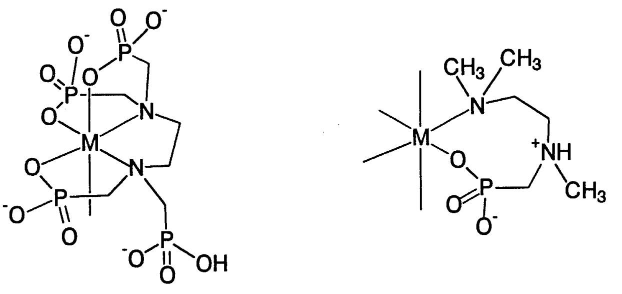

IV **V**

Chart 3.

The chemical-shift change of the protonated complexes is plotted as a function of the number of protons (*m*) bound to the zinc and cadmium complexes (Fig. 6), where the results of calcium complexes are also depicted as an example of the alkaline earth metal complexes. When protonation occurs on the nitrogen atom bound to the phosphonate group, the ^{31}P chemical-shift of this phosphonate group shows about a 10 ppm upfield shift.[23] The behavior of the chemical shift change due to protonation of the complexes is classified into two patterns according to the structure of the ligands. If the ligands have an iminodimethylphosphonate group, the first and second protonations do not cause a large chemical shift change. This indicates that the first and second protonations take place on the oxygen atoms in the same manner as the ntmp complexes.[22]

In the case of the medtmp, the phosphonates of $-N(CH_2PO_3^{2-})_2$, signal A, and $-NCH_3(CH_2PO_3^{2-})$, signal B, are observed as two separated signals. In the case of the zinc complex, signal A of mono-, unprotonated and hydroxo complexes is separated into two peaks (Fig. 3, mark: diamond). That is, the two phosphonate groups of iminodimethylenephosphonate are not equivalent each other, and an exchange between them is slow. The chemical shift of EDMP complexes having the $-N(CH_3)(CH_2PO_3^{2-})$ group shows a large upfield shift at some protonation step. These results indicate protonation of the nitrogen atom of this group at that step. That is, the M–N bond is ruptured and an eight-membered chelate ring is formed in the protonated complexes. This coordination manner is the same as that of the NMP complexes.[24] That is, the strength of the M–N bond decreases as the number of methylenephosphonate groups or negative charges decreases. The structure of protonated complexes of tmedmp is shown in Structure **V** as an example.

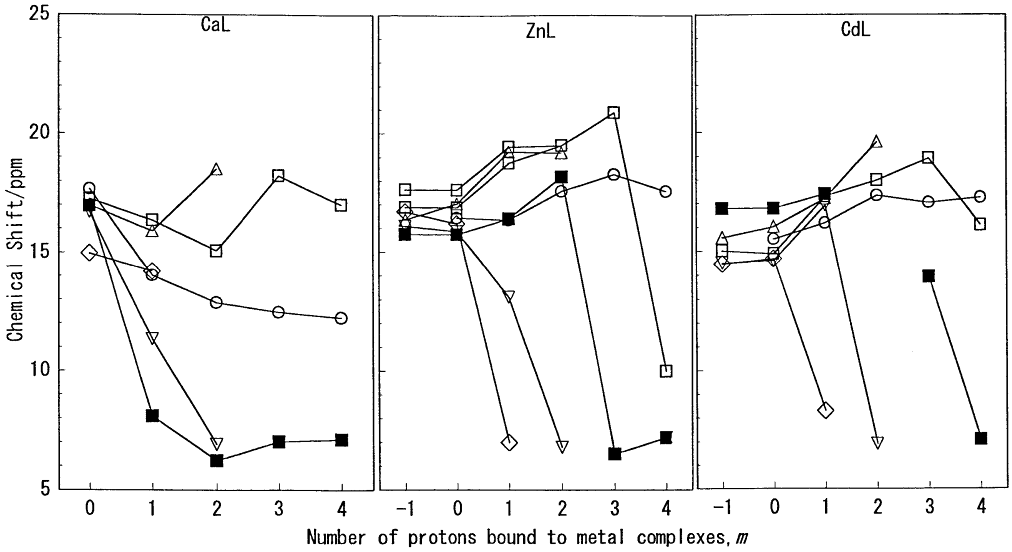


Fig. 6. Plots of ^{31}P NMR chemical shifts of calcium, zinc and cadmium complexes as a function of the number of protonation bound, *m*. ○, edtmp; □, medtmp(A); ■, medtmp(B); △, dmeddmp(*N*,*N*); ▽, dmeddmp(*N*,*N*′); ◇, tmedmp.

The hydroxo complexes, M(OH)L, are formed by the deprotonation of the water molecule coordinating to the metal ion of the complexes. A quite small change in the chemical shift by deprotonation indicates that the structure of the complexes hardly changes due to deprotonation.

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