

Stability and structure of nitrilo(acetate–methylphosphonate) complexes of the alkaline-earth and divalent transition metal ions in aqueous solution

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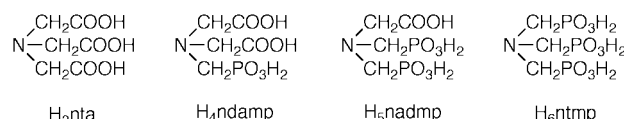
The formation and protonation of the complexes of acids $N(\text{CH}_2\text{COOH})_3-r(\text{CH}_2\text{PO}_3\text{H}_2)_r$, $r = 1$ (H_4ndamp) or 2 (H_5nadmp), with the alkaline-earth metal ions ($\text{M} = \text{Mg}^{2+}$, Ca^{2+} , Sr^{2+} or Ba^{2+}) and the divalent transition metal ions ($\text{M} = \text{Mn}^{2+}$, Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} or Cd^{2+}) have been investigated by means of potentiometry and ^{31}P NMR spectroscopy at 25 °C. The complex formation constants and protonation constants of these complexes were determined by pH titration. The ^{31}P NMR spectra of the ligand and metal–ligand solutions were measured as a function of pH and the ^{31}P NMR chemical shifts of each chemical species evaluated by using the equilibrium constants determined by pH titration. The stability constants of the metal complexes increase as the number of the ligand phosphonate groups ($r = 0-3$) increases. In the alkaline-earth metal complexes the first protonation takes place on the nitrogen atom except for $\text{Ca}-\text{ndamp}$ and $-\text{nadmp}$ complexes. In the transition metal complexes the formation constants follow the so-called Irving–Williams series although the $\text{Ni}-\text{nadmp}$ and $-\text{ntmp}$ ($r = 3$) complexes show a peculiar behavior. The change in the chemical shift of the complexes upon protonation supports the structures of the metal complexes predicted from the formation and protonation constants.

Introduction

The complex formation of *N*-phosphonomethyliminodiacetic acid (H_4ndamp) was first reported as early as 1949 by Schwarzenbach *et al.*, concurrently with those of aminopolycarboxylates (APCs).¹ Several studies on the complex formation of such *N*-bonded mixed acetic–methylphosphonic acids (NAMPs) have been reported.^{1–15} The values of the protonation constants of H_4ndamp do not vary much among these reports.^{1,2,5,7–9,12,16} However, those of *N*-carboxymethyliminodimethylphosphonic acid (H_5nadmp) show large disagreements because of the very high value of the first protonation constant.^{3,5,7,8,10,16} The number of negative charges of NAMPs is higher than that of the corresponding APC, *e.g.* the charge of deprotonated *N*-carboxymethyliminodimethylphosphonic acid is minus five (nadmp^{5-}), while that of nitrilotriacetate is minus three (nta^{3-}). Thus, the metal complexes of the former easily form protonated species. Although the complex formation of NAMPs with the alkaline-earth and transition metal ions has been studied, a systematic study for a series of metal ions has not been done. The errors of the ligand protonation constants must cause a significant error for the determination of the formation constants and protonation constants of complexes.

In previous studies we synthesized a series of aminopolymethylphosphonates (APPs) [nitrilopoly(methylphosphonates)]¹⁷ and ethylenedinitrilopoly(methylphosphonates)^{18,19} and reported the thermodynamic properties and NMR behavior of the protonated complexes of various kinds of metal ions.^{17,19–23} These studies revealed that the first protonation of the alkaline-earth metal and rare-earth metal complexes occurs on the nitrogen atom of the ligand with rupture of the $\text{M}-\text{N}$ bond and results in the formation of *O,O'*-chelates with eight-membered rings. The aminopolycarboxylates hardly form protonated complexes and the *O,O'*-chelate rings have never been reported for them.

In the present work the complex formation of NAMPs with the alkaline-earth and divalent transition metal ions was investigated by means of potentiometry and ^{31}P NMR spec-



troscopy. The effect of successive substitution of carboxylate by methylphosphonate [$\text{N}(\text{CH}_2\text{CO}_2\text{H})_3-r(\text{CH}_2\text{PO}_3\text{H}_2)_r$, $r = 0-3$] on the stabilities and structures of the complexes is discussed.

Experimental

Reagents

The acid H_4ndamp was synthesized by reaction of iminodiacetic acid (0.50 mol) and phosphorous acid (0.61 mol) with 150 cm³ 40% formaldehyde in 3.5 mol dm⁻³ HCl (420 cm³) according to the method of Moedritzer and Irani.²⁴ In a similar manner, H_5nadmp was synthesized by using glycine (0.50 mol) and phosphorous acid (1.22 mol). Their purities were determined to be 99.8% by ^{31}P NMR and pH titration. The phosphorus contents of the ligands determined by ICP (inductively coupled plasma)-MS are: Found 13.2%, Calc. ($\text{C}_5\text{H}_{10}\text{NO}_7\text{P}$) 13.6% for ndamp ; Found 23.1%, Calc. ($\text{C}_4\text{H}_{11}\text{NO}_8\text{P}_2$) 23.5% for nadmp . Metal nitrates used were 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 deionized water (Organo, Model-III).

Potentiometric measurements

The pH titrations were 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

Table 1 Protonation constants of ligands^a

	nta ^b	ndamp	nadmp	ntmp ^c
log K_{HL}	9.70	10.74 ± 0.05	11.8 ± 0.1 ^d	12.8
log $K_{\text{H}_2\text{L}}$	2.52	5.62 ± 0.03	6.41 ± 0.03	7.15
log $K_{\text{H}_3\text{L}}$	1.7	2.31 ± 0.03	5.02 ± 0.03	5.89
log $K_{\text{H}_4\text{L}}$		1.7 ± 0.1	2.07 ± 0.05	4.63
log $K_{\text{H}_5\text{L}}$			1.1 ± 0.1	1.4

^a $K_{\text{H}_n\text{L}} = [\text{H}_n\text{L}]/[\text{H}][\text{H}_{n-1}\text{L}]$, $I = 0.1$ (KNO₃), 25.0 °C. ^b Ref. 26. ^c Ref. 17. ^d Evaluated by ³¹P NMR spectroscopy.

water, $\text{p}K_{\text{w}} = 13.82$,²⁵ was used for the calibration. The pH, logarithm of reciprocal of the hydrogen ion concentration, was evaluated from the emf by using the calibration curve. A solution of 0.001–0.01 mol dm^{−3} ligand or metal–ligand (0.95:1) solution was titrated in a water-jacketed cell (25.0 ± 0.1 °C) with KOH solution ($I = 0.1$ mol dm^{−3}, KNO₃).

NMR Measurements

The ³¹P-¹H NMR spectra of ligand ($c_{\text{L}} = 0.01$ mol dm^{−3}) or equimolar metal–ligand solution ($c_{\text{M}} = c_{\text{L}} = 0.01$ or 0.005 mol dm^{−3}) were measured at various pH by a Varian Unity 500 FT-NMR Spectrometer (202.35 MHz for ³¹P) with a 10 mm diameter sample tube at 25 °C ($I = 0.1$ mol dm^{−3}, KNO₃). The external standard, which was placed in a 5 mm diameter concentric tube, was 0.5% H₃PO₄ in D₂O. The observed chemical shifts were converted into values referenced to aqueous 85% H₃PO₄.

Results and discussion

Protonation of ligands

The mean number of protons bound to the ligands, \bar{n}_{obs} , was calculated by using the hydrogen-ion concentration $[\text{H}^+]$ obtained from the electromotive force. The calculated value of the mean number of protons bound to a ligand, \bar{n}_{calc} , is obtained by using successive ligand protonation constants defined by $K_{\text{H}_n\text{L}} = [\text{H}_n\text{L}]/[\text{H}][\text{H}_{n-1}\text{L}]$. The values of $K_{\text{H}_n\text{L}}$ giving the minimum sum of the squares of the deviations, $\Sigma(\bar{n}_{\text{obs}} - \bar{n}_{\text{calc}})^2$, were obtained by a non-linear regression.^{17,19} The values of the protonation constants of ndamp and nadmp obtained from 30–40 data points are listed in Table 1 together with results for nta²⁶ and ntmp,¹⁷ where the value of K_{HL} of nadmp determined by ³¹P NMR measurement is listed and agrees with that obtained by pH titration ($\log K_{\text{HL}} = 11.9 \pm 0.3$) within experimental error. Although the reported values of the protonation constants of ndamp do not differ very much compared with those of the present results, those of nadmp show a large disagreement, particularly the first protonation constant, K_{HL} . It is generally difficult to determine reliable values of higher protonation constants by pH titration, thus the values reported for the first protonation constant of nadmp are considerably smaller than that determined here except for the value of Buglyó *et al.*¹⁴ ($\log K_{\text{HL}} = 11.49$). Spectroscopic methods such as NMR are suitable for the determination of protonation constants at high or low pH. Thus, the K_{HL} reported here must be reliable and reasonable in comparison with those of other APPs [Table 1 and ethylenedinitrilopoly(methylphosphonic acids)¹⁹].

The value of K_{HL} is much larger than $K_{\text{H}_2\text{L}}$ and shows a good linear correlation with the number of phosphonate groups of the ligand. The results indicate that the first protonation takes place on the nitrogen atom. The succeeding protonations take place on the oxygen atoms of the phosphonate groups and are followed by protonation on the carboxylate groups. The differences of $\log K_{\text{H}_n\text{L}}$ and $\log K_{\text{H}_{n+1}\text{L}}$ between the protonations of the phosphonate groups in a given ligand are about 1.3 whereas those between phosphonate and carboxylate groups are about 3 units.

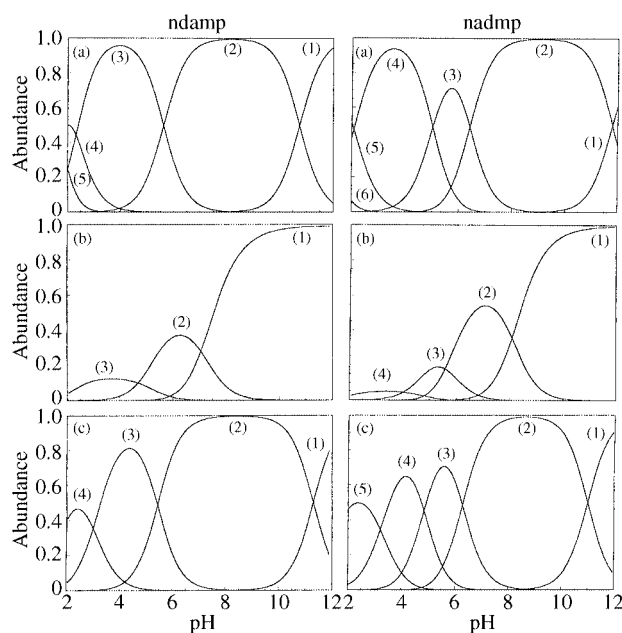


Fig. 1 Distribution diagrams: (a) ligand, (1) L, (2) HL, (3) H₂L, (4) H₃L, (5) H₄L, (6) H₅L, $c_{\text{L}} = 0.01$ mol dm^{−3}; (b) strontium complex, (1) ML, (2) M(HL), (3) M(H₂L), (4) M(H₃L), $c_{\text{L}} = c_{\text{Sr}} = 0.01$ mol dm^{−3}; (c) cadmium complex, (1) M(OH)L, (2) ML, (3) M(HL), (4) M(H₂L), (5) M(H₃L), $c_{\text{L}} = c_{\text{Cd}} = 0.005$ mol dm^{−3}.

Formation constants

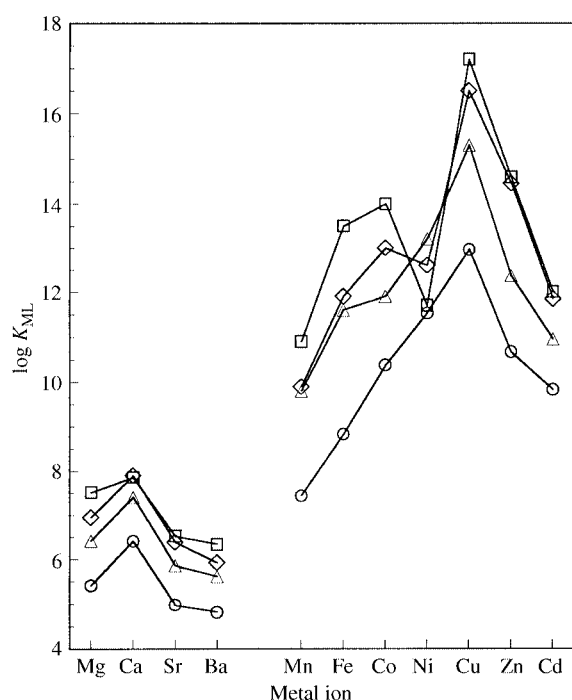
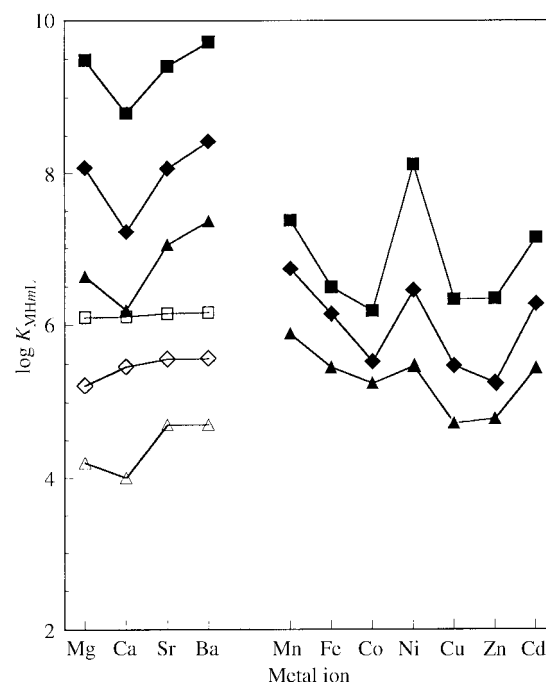
A set of formation constants of the metal complexes and their successive protonation constants, defined by $K_{\text{ML}} = [\text{ML}]/[\text{M}][\text{L}]$ and $K_{\text{MH}_n\text{L}} = [\text{MH}_n\text{L}]/[\text{H}][\text{MH}_{n-1}\text{L}]$, was evaluated by the same process of non-linear regression as for the ligand,^{17,19} taking into account the hydrolysis of the metal ions.²⁵ In the case of the transition metal complexes, the hydroxo complex, M(OH)L, is formed at high pH, whereas the formation of hydroxo complexes is not observed for the alkaline-earth metal complexes under these experimental conditions. The logarithmic formation constants of the metal complexes and their protonation constants thus obtained from 30–40 data points are listed in Table 2, where the formation constant of a hydroxo complex is defined by $K_{\text{M(OH)L}} = [\text{M(OH)L}]/[\text{ML}][\text{OH}]$. The distribution curves of the unprotonated and protonated species of ligands (a), strontium complexes (b) and cadmium complexes (c) are shown as a function of pH in Fig. 1 as an example. The complex formation constant, $\log K_{\text{ML}}$, of the alkaline-earth metal and divalent transition metal ions with NAMPs are plotted in Fig. 2 together with those of nta²⁷ and ntmp.^{21,22} The first protonation constants of the metal complexes and the second protonation constants of the alkaline-earth complexes with NAMPs are plotted in Fig. 3 together with those of ntmp.^{21,22}

Alkaline-earth metal complexes. The formation constants of alkaline-earth metal complexes increase as the metal ion size decreases, although the Mg²⁺ ion shows a decrease in K_{ML} ($\text{Mg}^{2+} < \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$) (Fig. 2). The size of Mg²⁺ is too small to form a stable complex and the formation of magnesium complexes might be entropy driven in the same manner as those of ntmp and ethylenedinitrilotetra(methylphosphonic acid) (edtmp).²⁰ The formation constants of alkaline-earth metal complexes increase as the number of ligand phosphonate groups (r) increases. The increments of ligand protonation constants with the substitution of a carboxylate group by one phosphonate group, $\Delta \log K_{\text{H}_n\text{L}}$, are almost the same irrespective of the number r , *i.e.* $\Delta \log K_{\text{HL}}$ is about 1.0 and $\Delta \log K_{\text{H}_2\text{L}}$ for the protonation on the phosphonate group is about 0.8 (Table 1). However, the increments of the stability of complexes ($\Delta \log K_{\text{ML}}$) decrease with increase in the number of ligand

Table 2 Formation constants ($\log K_{\text{ML}}$)^a and successive protonation constants ($\log K_{\text{MH}_n\text{L}}$)^b of the metal complexes^c

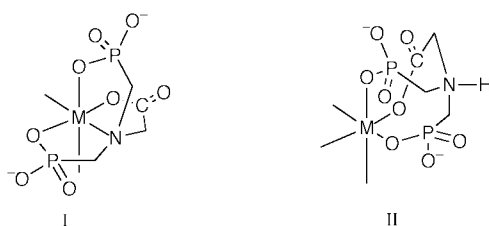
	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺	Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺	Cd ²⁺
nta ^d											
$\log K_{\text{ML}}$	5.41	6.41	4.98	4.82	7.44	8.83	10.38	11.53	12.96	10.67	9.83
$\log K_{\text{M(OH)L}}^e$						3.2	3.0	2.9	4.7	3.7	2.6
ndamp											
$\log K_{\text{ML}}$	6.41	7.41	5.86	5.61	9.8	11.6	11.9	13.2	15.3	12.36	10.95
$\log K_{\text{MHL}}$	6.63	6.19	7.05	7.36	5.89	5.45	5.24	5.46	4.72	4.78	5.44
$\log K_{\text{MH}_2\text{L}}$	4.2	4.0	4.7	4.7	4.6	3.6	2.9	2.4	2.2	2.1	3.0
$\log K_{\text{M(OH)L}}^e$					2.7		2.5	3.0	3.9	3.3	2.5
nadmp											
$\log K_{\text{ML}}$	6.95	7.90	6.38	5.93	9.9	11.9	13.0	12.6	16.5	14.46	11.84
$\log K_{\text{MHL}}$	8.07	7.22	8.06	8.42	6.73	6.14	5.52	6.45	5.47	5.25	6.27
$\log K_{\text{MH}_2\text{L}}$	5.22	5.46	5.56	5.57	4.77	4.56	4.49	4.88	3.78	4.22	4.83
$\log K_{\text{M(OH)L}}^e$	4.0	3.7	4.0	3.8	3.1	4.1	2.7	3.0	2.8	2.7	3.2
ntmp ^f											
$\log K_{\text{ML}}$	7.52	7.86	6.52	6.34	10.9	13.5	14.0	11.7	17.2	14.6	12.0
$\log K_{\text{MHL}}$	9.42	8.80	9.41	9.72	7.37	6.49	6.18	8.11	6.33	6.34	7.14
$\log K_{\text{MH}_2\text{L}}$	6.10	6.11	6.15	6.16	5.93	5.41	5.09	5.56	4.53	5.12	5.76
$\log K_{\text{M(OH)L}}^e$	4.8	4.9	5.0	5.1	4.7	4.2	3.6	3.5	3.5	3.9	4.0

^a $K_{\text{ML}} = [\text{ML}]/[\text{M}][\text{L}]$. ^b $K_{\text{MH}_n\text{L}} = [\text{MH}_n\text{L}]/[\text{MH}_{n-1}\text{L}][\text{H}]$. ^c Errors of the logarithmic constants were estimated as ± 0.02 for $\log K_{\text{ML}}$ (A.E.–ndamp, A.E.–nadmp and Zn, Cd complexes) and $\log K_{\text{MHL}}$ (nadmp); ± 0.04 for $\log K_{\text{MHL}}$ (ndamp) and $\log K_{\text{MH}_2\text{L}}$ (nadmp); ± 0.1 for $\log K_{\text{ML}}$ (Mn, Fe, Co, Ni and Cu–ndamp and –nadmp), $\log K_{\text{MH}_2\text{L}}$ (ndamp), $\log K_{\text{MH}_2\text{L}}$ (nadmp) and $\log K_{\text{M(OH)L}}$ (ndamp and nadmp). ^d Refs. 27–29. ^e $K_{\text{M(OH)L}} = [\text{M(OH)L}]/[\text{ML}][\text{OH}]$. ^f Refs. 21, 22.

**Fig. 2** Plots of the logarithmic formation constants of metal complexes. ○, nta; △, ndamp; ◇, nadmp; □, ntmp.**Fig. 3** Plots of the logarithmic protonation constants of metal complexes. ndamp: ▲, $\log K_{\text{MHL}}$; △, $\log K_{\text{MH}_2\text{L}}$. nadmp: ◆, $\log K_{\text{MHL}}$; ◇, $\log K_{\text{MH}_2\text{L}}$. ntmp: ■, $\log K_{\text{MHL}}$; □, $\log K_{\text{MH}_2\text{L}}$.

phosphonate groups, r . Thus, the increase in complex stability with r is explained by the increase in basicity, but the increase in the negative charge of the phosphonate groups around the metal ions in the complex ML reduces or cancels the increase in the stability of the complexes.

The first protonation constants of the alkaline-earth metal complexes, K_{MHL} , are much larger than $K_{\text{H}_2\text{L}}$. If the first protonation takes place on the oxygen atoms of the phosphonate groups, K_{MHL} would be smaller than $K_{\text{H}_2\text{L}}$, the protonation constant of the phosphonate group of the “free” ligand. Consequently, this suggests that protonation occurs at the nitrogen atom, rupturing the M–N bond in the same manner as that of



ntmp complexes.²¹ The unprotonated and monoprotonated complexes are shown in Structures **I** and **II**. The order of the first protonation constant ($K_{\text{MgHL}} > K_{\text{CaHL}} > K_{\text{SrHL}} < K_{\text{BaHL}}$)

Table 3 The ^{31}P NMR chemical shifts ($\delta_{\text{H,L}}$ /ppm) of ligands

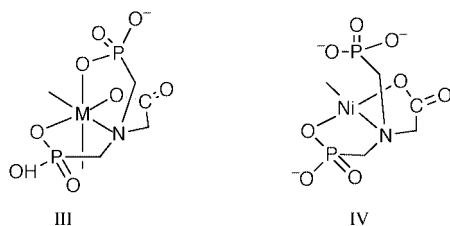
	ndamp	nadmp	ntmp ^a
δ_{L}	16.25 ± 0.03	16.96 ± 0.03	18.03
δ_{HL}	5.80 ± 0.03	6.23 ± 0.03	6.66
$\delta_{\text{H}_2\text{L}}$	7.33 ± 0.05	6.59 ± 0.03	6.73
$\delta_{\text{H}_3\text{L}}$	7.01 ± 0.05	7.29 ± 0.05	8.50
$\delta_{\text{H}_4\text{L}}$	7.0 ± 0.1	6.87 ± 0.05	7.15
$\delta_{\text{H}_5\text{L}}$		7.8 ± 0.1	7.3

^a Ref. 17.

(Fig. 3) is just the reverse of that of complex formation ($K_{\text{MgL}} < K_{\text{CaL}} > K_{\text{SrL}} > K_{\text{BaL}}$). That the first protonation of the complex becomes unfavorable with increase in M–L bond strength supports the protonation on the nitrogen atom of the complex. On the other hand, the second protonation constants of the complexes are much smaller than the first and hardly change among the metal ions. This indicates that the second protonation takes place on the free oxygen atoms of phosphonate groups.

Transition metal complexes. The formation constants of the transition metal complexes follow the so-called Irving–Williams series ($K_{\text{MnL}} < K_{\text{FeL}} < K_{\text{CoL}} < K_{\text{NiL}} < K_{\text{CuL}} > K_{\text{ZnL}} > K_{\text{CdL}}$) except for nickel complexes of nadmp and ntmp (Fig. 2). Although the formation constants increase with increasing number of phosphonate groups from nta to ntmp except for nickel complexes, the increments of those constants depend on the metal ions. The change of the formation constants of manganese and iron complexes is quite small between ndamp and nadmp, whereas that of the copper, zinc and cadmium complexes is small between nadmp and ntmp. In the case of nickel complexes the formation constants decrease with increase in the number of phosphonate groups ($K_{\text{Ni(ndamp)}} > K_{\text{Ni(nadmp)}} > K_{\text{Ni(ntmp)}}$), contrary to the order of the other metal complexes.

The first protonation constants (K_{MHL}) of the complexes are almost the same or smaller than the second protonation constants ($K_{\text{H}_2\text{L}}$) of the corresponding ligands (Fig. 3). This indicates that the first protonation takes place on the free oxygen atoms of the phosphonate groups of the complex (Structure III). The formation behavior and the protonation constants of



nickel complexes are quite different from those of other metal complexes. This might be explained by the square planar structure of the nadmp and ntmp complexes. The difference in the bond angles between the phosphonate, PO_3^{2-} (tetrahedral), and the carboxylate, CO_2^- (triangular), co-ordination, might have a large effect on the stability of chelate rings. If we assume the structure for the nadmp complex is as in IV, i.e. the co-ordination of one phosphonate and one carboxylate in the equatorial plane is the most suitable combination, the results are reasonably explained. In the case of ndamp, the axial carboxylate is co-ordinated to Ni^{2+} ion, thus the ndamp complex is the most stable among the nickel complexes. Since both of the co-ordinating groups of the ntmp are phosphonate the ntmp complex is less stable than the nadmp complex. The first protonation of nadmp and ntmp complexes occurs on the free axial phosphonate group or nitrogen atom.

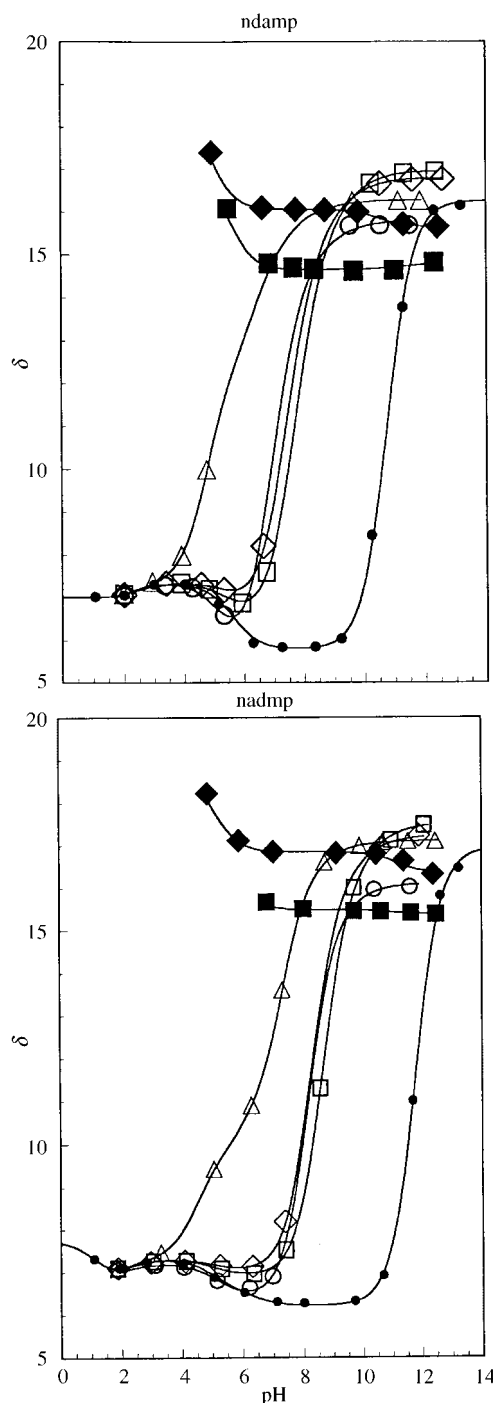


Fig. 4 Plots of ^{31}P NMR chemical shifts of ligand or metal–ligand solution as a function of pH. ●, Ligand; ○, Mg^{2+} ; △, Ca^{2+} ; ◇, Sr^{2+} ; □, Ba^{2+} ; ◆, Zn^{2+} ; ■, Cd^{2+} .

Phosphorus-31 NMR spectroscopy

The proton decoupled ^{31}P NMR spectra show one single sharp signal the chemical shift of which changes with the pH (Fig. 4). Thus, the ligand protonation equilibria are fast and the chemical shifts are given by a linear combination of those for each species, H_nL , $\delta_{\text{calc}} = \sum \delta_{\text{H}_n\text{L}} X_{\text{H}_n\text{L}}$, where $X_{\text{H}_n\text{L}}$ refers to the proportion of H_nL and is calculated using the protonation constants, $K_{\text{H}_n\text{L}}$. A set of chemical shifts for each species, $\delta_{\text{H}_n\text{L}}$, minimizing the square sum of the deviations, $\sum (\delta_{\text{obs}} - \delta_{\text{calc}})^2$, was evaluated by a non-linear regression.^{17,19} In the case of nadmp the value of $\log K_{\text{HL}}$ determined by the ^{31}P NMR chemical shift is listed, because the experimental error of the pH titration is much larger than that of spectroscopy (NMR) in the higher pH region.¹⁷ The chemical shifts of ndamp and nadmp ($\delta_{\text{H,L}}$) are listed in Table 3 together with results for

Table 4 The ^{31}P NMR chemical shifts of the metal complexes^a

	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺	Zn ²⁺	Cd ²⁺
ndamp						
δ_{ML}	15.79	16.27	16.79	16.96	16.05	14.65
δ_{MHL}	5.61	15.65	8.12	7.48	19.4	17.7
$\delta_{\text{MH}_2\text{L}}$	8.0	7.3	7.5	7.5		
$\delta_{\text{M(OH)L}}$					15.64	14.80
nadmp						
δ_{ML}	16.11	17.12	17.25	17.53	16.86	15.48
δ_{MHL}	6.43	11.85	7.55	7.40	18.31	16.4
$\delta_{\text{MH}_2\text{L}}$	7.10	12.41	8.15	7.99	20.8	
$\delta_{\text{MH}_3\text{L}}$	6.2	7.3	7.1	7.5		
$\delta_{\text{M(OH)L}}$					16.36	15.38
ntmp ^b						
δ_{ML}	17.44	18.25	18.09	18.06	17.61	16.43
δ_{MHL}	6.23	7.26	7.22	7.18	18.50	16.34
$\delta_{\text{MH}_2\text{L}}$	6.58	8.96	8.48	9.24	19.63	16.31
$\delta_{\text{MH}_3\text{L}}$	5.7	15.6	7.6	8.0	23.2	20.2

^a Errors of chemical shifts were estimated as ± 0.03 for δ_{ML} (M–ndamp and M–nadmp), δ_{MHL} (A.E.–nadmp) and $\delta_{\text{M(OH)L}}$ (T.M.–ndamp and T.M.–nadmp); ± 0.05 for δ_{MHL} (A.E.–ndamp and Zn–nadmp) and $\delta_{\text{MH}_2\text{L}}$ (A.E.–nadmp); ± 0.1 for δ_{MHL} (T.M.–ndamp and Cd–nadmp), $\delta_{\text{MH}_2\text{L}}$ (A.E.–ndamp and Zn–nadmp) and $\delta_{\text{MH}_3\text{L}}$ (A.E.–nadmp). ^b Refs. 21, 22.

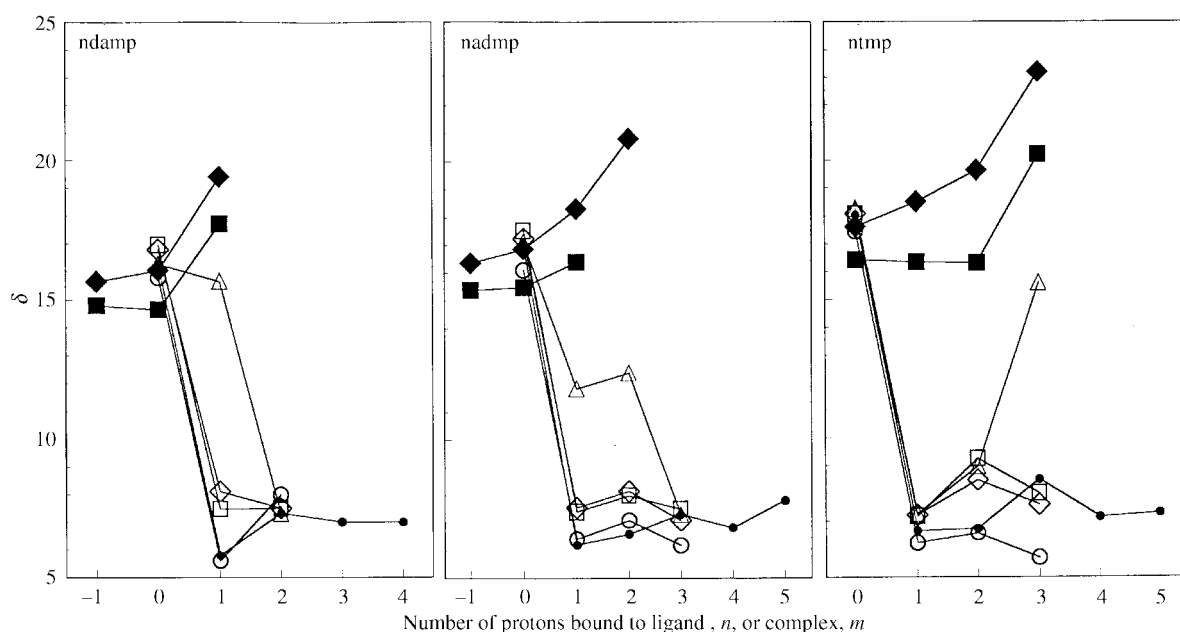


Fig. 5 Plots of ^{31}P NMR chemical shifts of each species of ligand (H_nL) and complex (MH_mL) as a function of the number of protons bound to the ligand, n and complex, m . Symbols: see Fig. 4.

ntmp.¹⁷ The 1:1 metal–ligand solution also shows a single ^{31}P - $\{^1\text{H}\}$ NMR signal. Its chemical shift change with pH (Fig. 4) was analyzed in the same manner as that of the ligand and a set of chemical shifts for each complex, $\delta_{\text{MH}_m\text{L}}$, giving a minimum sum of the square of the deviations between δ_{obs} and δ_{calc} ($= \sum \delta_{\text{H}_n\text{L}}^2 X_{\text{H}_n\text{L}} + \sum \delta_{\text{MH}_m\text{L}}^2 X_{\text{MH}_m\text{L}}$) was evaluated. The results are listed in Table 4 together with the results for ntmp.^{21,22} Calculated curves of the chemical shift obtained by using these values are shown by solid lines in Fig. 4. The chemical shifts of the ligands ($\delta_{\text{H}_n\text{L}}$) and complexes ($\delta_{\text{MH}_m\text{L}}$) are plotted in Fig. 5 as a function of the number of protons attached to ligand (n) or complex (m).

The chemical shifts of unprotonated ligand species are almost the same among the different ligands (δ_{L} 16–18) and do not show a significant change upon complex formation for any metal ions. Upon protonation of the nitrilo nitrogen atom of the ligands the chemical shifts show a steep upfield shift ($\delta_{\text{HL}} \approx 6$).¹⁷ Higher protonation ($n \geq 2$), *i.e.* protonation at the

phosphonate or carboxylate groups, does not result in any significant change in the chemical shift.

In the case of the alkaline-earth metal complexes the chemical shift shows a large upfield shift upon the first protonation in the same manner as that of the ligands except for calcium complexes of ndamp and nadmp. These results support that the first protonation of the complex takes place on the nitrogen atom of the ligand (Structure II). The small changes of the chemical shifts from second to third protonation indicate that the higher protonations take place on the oxygen atoms of phosphonate groups. The chemical shift changes of the Ca–ndamp and Ca–nadmp complexes are considerably different from those of other alkaline-earth metal complexes. That of Ca–ndamp hardly changes upon the first protonation and shows a large upfield change at the second step. These results indicate that the first protonation occurs on an oxygen atom of the phosphonate group (Structure III) followed by the protonation on the nitrogen atom. In the case of the Ca–nadmp complex, the values of

the chemical shifts of the monoprotinated and diprotinated complex are between those of unprotonated and triprotonated complexes. Thus, the monoprotinated and diprotinated complexes might be in equilibrium with species protonated at the oxygen of a phosphonate group and the nitrilo nitrogen atom. That K_{CaHL} of ndamp and nadmp is comparable to $K_{\text{H}_2\text{L}}$ is consistent with the structures of these complexes, CaHL .

In the case of the Zn^{2+} and Cd^{2+} complexes, no upfield shifts are observed at any step of protonation. This result supports the conclusion that the protonation of the transition metal complexes occurs on a free oxygen atom of a phosphonate group (Structure III).

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