Structure and Thermodynamic Properties of Aminopolyphosphonate Complexes of the Alkaline-earth Metal Ions

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The formation equilibria and thermodynamic properties of the alkaline-earth metal ($M = Mg^{2+}, Ca^{2+}, Sr^{2+}$ or Ba^{2+}) complexes of nitrilotris(methylenephosphonic acid) (H_6ntmp) and ethylenediaminetetrakis(methylenephosphonic acid) (H_8edtmp) have been studied by means of potentiometry, NMR spectroscopy and calorimetry at 25.0 °C and at an ionic strength of 0.1 mol dm^{-3} (KNO_3). The complex formation constants and the protonation constants of the complexes were determined from the potentiometric titration data. Thermodynamic parameters of the protonation of the ligand, and the formation and protonation of the metal complexes of ntmp and edtmp were evaluated from the calorimetric titration data. The first protonation on the nitrogen atom of ntmp is significantly exothermic and it is followed by the endothermic protonation on phosphonate O^-. The protonations of edtmp are exothermic up to the third step. The formation of magnesium complexes of ntmp and edtmp is endothermic and entropy driven, whereas that of the complexes of Ca^{2+}, Sr^{2+} and Ba^{2+} is weakly exothermic. This behaviour is analogous to that of aminopolycarboxylate complexes. The results of calorimetric measurements of ntmp complexes support the structure of protonated alkaline-earth metal–ntmp complexes predicted from the stability and NMR data, *i.e.* the first protonation of the metal complexes occurs on the nitrogen atom of the ligand, rupturing the M–N bond. The thermodynamic behaviour of the edtmp complexes is considerably complicated. In the analysis of the pH dependence of the ^{31}P NMR signals, the chemical shift of each species of ligand and its metal complexes was evaluated by using the formation constants obtained by potentiometry. The change in the chemical shift of the complexes upon protonation supports the structures of the alkaline-earth metal complexes predicted from the thermodynamic parameters.

Aminopolyphosphonates, which are analogues of aminopolycarboxylates, have been widely used for industrial purposes, *e.g.* as scale inhibitors. Nevertheless, their solution chemistry is not so well understood as that of aminopolycarboxylates. A main interest is the measurement of the formation constants of metal complexes[1-6] of aminopolycarboxylates upon partial or total replacement of carboxylate by phosphonate groups.[7] Comparisons of formation constants have been made in terms of the charge on the phosphonate group relative to the carboxylate group. It was suggested[1] that the formation of metal complexes with ligands bearing two or more phosphonate groups is subject to mutual repulsion between binegative phosphonate groups. The higher hydration number in the transition-metal complexes of ethylenediaminetetrakis(methylenephosphonic acid) (H_8edtmp) compared with that of the corresponding carboxylate complexes has been reported,[8] and this has been attributed to the additional strain within the complex arising from increased charge repulsion.

Thermodynamic properties have been studied for a variety of aminopolycarboxylate complexes[9-12] and structures of these complexes in solution have been discussed in detail.[13] On the other hand, thermodynamic parameters for chelate complexes of aminopolyphosphonates have not been reported. Relative to complexes with aminopolycarboxylates, aminopolyphosphonates form complexes incorporating larger numbers of protons, and so provide ideal examples to enable a study of the thermodynamic consequences of the protonation of chelate complexes to be made. In previous papers, we studied the complex formation and NMR behaviour of a series of alkaline-earth metal[14] and divalent transition-metal[15] complexes of nitrilotris(methylenephosphonic acid) (H_6ntmp) and the protonation equilibria of the rare-earth metal complexes[16] of ntmp and edtmp. These studies revealed that the first protonation of the alkaline-earth and rare-earth metal complexes occurs on the nitrogen atom of the ligand with rupture of the M–N bond, whereas protonation of divalent transition-metal complexes occurs simply on the phosphonate O^-.

In the present paper, the formation of edtmp–alkaline-earth metal complexes has been studied by potentiometry and ^{31}P NMR spectroscopy and the thermodynamic parameters of the formation and protonation of alkaline-earth metal complexes of ntmp and edtmp obtained by calorimetric titrations. The thermodynamic properties and structures of the alkaline-earth metal complexes are discussed.

Experimental

Reagents.—Nitrilotris(methylenephosphonic acid) (H_6ntmp) and ethylenediaminetetrakis(methylenephosphonic acid) (H_8edtmp) (Dojin pure chemicals) were purified by a method described elsewhere.[15,16] Alkaline-earth metal nitrates (Reagent grade, Wako pure chemicals) were recrystallized from water and the concentrations of the stock solutions were determined by a titration with ethylenediaminetetraacetate. All solutions were prepared with distilled and deionized water (Organo, Puric Z).

Potentiometric Measurements.—The pH titrations were carried out with a Corning model 130 pH meter. The glass electrode was calibrated by titration with nitric acid or potassium hydroxide ($I = 0.1$ mol dm^{-3} KNO_3, $pK_w = 13.82$). The pH, the logarithm of the reciprocal of the hydrogen

Table 1 Thermodynamic parameters of protonation of ntmp and edtmp[a]

		$-\Delta G$	$-\Delta H$	$T\Delta S$
ntmp	log K^b	kJ mol^{-1}		
$L + H \rightleftharpoons HL$	12.7(2)	72.5(9)	38.8(6)	33.7(11)
$HL + H \rightleftharpoons H_2L$	7.15(2)	40.8(1)	−6.4(8)	47.2(8)
$H_2L + H \rightleftharpoons H_3L$	5.89(2)	33.6(1)	−6.8(3)	40.4(3)
$H_3L + H \rightleftharpoons H_4L$	4.63(2)	26.4(1)	−4.8(5)	31.2(5)
$H_4L + H \rightleftharpoons H_5L$	1.4(1)	8(1)	−10(3)	18(3)
edtmp				
$L + H \rightleftharpoons HL$	13.0(2)	74.2(8)	44.5(6)	29.7(10)
$HL + H \rightleftharpoons H_2L$	9.85(1)	56.2(1)	3.8(5)	52.4(5)
$H_2L + H \rightleftharpoons H_3L$	7.87(1)	44.9(1)	6.5(3)	38.4(3)
$H_3L + H \rightleftharpoons H_4L$	6.40(1)	36.5(1)	−7.5(3)	44.0(3)
$H_4L + H \rightleftharpoons H_5L$	5.12(2)	29.2(1)	−7.1(4)	36.3(4)
$H_5L + H \rightleftharpoons H_6L$	2.96(3)	16.9(2)	−9(4)	26(4)

[a] Ionic strength = 0.1 mol dm^{-3} (KNO_3), 25.0 °C. Errors for the last digit (σ) are given in parentheses. [b] Log K of ntmp is cited from ref. 14.

Table 2 Thermodynamic parameters of formation and protonation of edtmp complexes *

			$-\Delta G$	$-\Delta H$	$T\Delta S$
		log K	kJ mol^{-1}		
Mg^{2+}	$M + L \rightleftharpoons ML$	8.35(3)	47.6(2)	−16.5(7)	64.1(7)
	$ML + H \rightleftharpoons MHL$	10.07(1)	57.5(1)	25.7(3)	31.8(3)
	$MHL + H \rightleftharpoons MH_2L$	8.73(2)	49.8(1)	20.7(3)	29.1(3)
	$MH_2L + H \rightleftharpoons MH_3L$	6.86(2)	39.1(1)	−0.3(4)	39.4(4)
	$MH_3L + H \rightleftharpoons MH_4L$	5.35(6)	30.5(3)	−0.6(5)	31.1(6)
Ca^{2+}	$M + L \rightleftharpoons ML$	9.29(3)	53.0(2)	5.7(6)	47.3(6)
	$ML + H \rightleftharpoons MHL$	9.45(1)	53.9(1)	8.1(4)	45.8(4)
	$MHL + H \rightleftharpoons MH_2L$	8.24(1)	47.0(1)	7.9(4)	39.1(4)
	$MH_2L + H \rightleftharpoons MH_3L$	6.74(4)	38.5(2)	7.7(3)	30.8(4)
	$MH_3L + H \rightleftharpoons MH_4L$	5.49(10)	31.3(6)	1.8(5)	29.5(8)
Sr^{2+}	$M + L \rightleftharpoons ML$	7.56(3)	43.1(2)	1.2(7)	41.9(7)
	$ML + H \rightleftharpoons MHL$	10.08(2)	57.5(1)	17.5(4)	40.0(4)
	$MHL + H \rightleftharpoons MH_2L$	8.50(2)	48.5(1)	7.5(5)	41.0(5)
	$MH_2L + H \rightleftharpoons MH_3L$	6.91(3)	39.4(2)	12.5(3)	26.9(4)
	$MH_3L + H \rightleftharpoons MH_4L$	5.82(8)	33.2(4)	−0.8(5)	34.0(6)
Ba^{2+}	$M + L \rightleftharpoons ML$	7.10(3)	40.5(2)	2.8(7)	37.7(7)
	$ML + H \rightleftharpoons MHL$	10.26(2)	58.5(1)	20.3(3)	38.2(3)
	$MHL + H \rightleftharpoons MH_2L$	8.54(3)	48.7(2)	8.6(4)	40.1(4)
	$MH_2L + H \rightleftharpoons MH_3L$	7.05(4)	40.2(2)	9.4(4)	30.8(4)
	$MH_3L + H \rightleftharpoons MH_4L$	5.78(7)	33.0(4)	−2.4(5)	35.4(6)

* Ionic strength = 0.1 mol dm^{-3} (KNO_3), 25.0 °C. Errors for the last digit (σ) are given in parentheses.

concentration, was evaluated from the electromotive force by using the calibration curve. A solution of 5 mmol dm^{-3} H_8edtmp (30 cm^3) containing an equimolar amount of alkaline-earth metal ion 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.—Phosphorus-31 NMR spectra of the ligand and ligand–metal solutions ($c_M = c_L = 0.01$ mol dm^{-3}) were measured in aqueous solution with a JEOL-FT 90Q NMR spectrometer (36.23 MHz for ^{31}P) with a 10 mm diameter sample tube at 25 °C. The NMR spectrometer was locked on the signal of D_2O, which served as an external standard in a 5 mm diameter concentric tube. The downfield shift is denoted by a positive sign of the chemical shift. The ^{31}P NMR spectra, measured under the same conditions as in the potentiometric measurements, were recorded against the external standard of 0.5% H_3PO_4 in D_2O and the chemical shifts are reported as the values converted to the aqueous 85% H_3PO_4 reference. The ^{13}C-{^1H} (22.49 MHz) and ^1H (89.55 MHz) spectra were recorded by using [$^2H_5$]trimethylsilylpropionate as an external standard.

Calorimetric Measurements.—A quantity [40 cm^3 (ntmp) or 200 cm^3 (edtmp)] of ligand or ligand–alkaline-earth metal ion solution [$c_L = c_M = 5$ mmol dm^{-3} (ntmp) or $c_M = 3.7$, $c_L = 3.4$ mmol dm^{-3} (edtmp)] neutralized [5 (ntmp) or 7 equivalents (edtmp)] with a known amount of KOH was titrated with HNO_3 at an ionic strength of 0.01 mol dm^{-3} (KNO_3). The heat of neutralization, $H^+ + OH^- = H_2O$, ΔH_w was found to be −56.9 kJ mol^{-1}. To avoid errors arising from the neutralization of OH^-, the last deprotonation was measured separately by titration of a KOH solution. In the case of the ntmp system, the heat evolved by titration was measured directly with a Rhesca CM-502 twin-type conduction calorimeter at 25.0 °C.[17] The titration of the edtmp system was carried out by a twin-type adiabatic calorimeter.[18] The temperature difference between the sample and reference cells was detected by a thermistor.

Results

Formation Constants of edtmp Complexes.—The mean number of protons bound to the ligand, $\bar{n}$, is obtained from the pH of the solution by using equation (1). The calculated value of

$$\bar{n}_{obs} = (8c_L - c_{OH} - [H^+] + [OH^-])/c_L \qquad (1)$$

the mean number of protons bound to edtmp, $\bar{n}_{calc}$, is obtained from equation (2) by using the protonation constant of ligand,

$$\bar{n}_{calc} = \Sigma n[H_nL]/c_L = \Sigma n\beta_n[H]^n/(1 + \Sigma\beta_n[H]^n) \qquad (2)$$

$K_n = [H_nL]/[H][H_{n-1}L]$, where $\beta_n = \Pi K_n$. The charges of chemical species are omitted for simplicity. The values of K_{H_nL} were evaluated with our original computer program.[14–16] A set of K_{H_nL} giving a minimum sum of squares of deviations [$= \Sigma(\bar{n}_{obs} - \bar{n}_{calc})^2$] was obtained by non-linear regression. The values of the protonation constants thus obtained are listed in Table 1 together with the values for ntmp.[14] The errors given to the protonation constants in parentheses (1σ) were estimated from triplicated titrations of 40–45 data points.

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

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

ΠK_{MH_mL}. The constants K_{ML} and K_{MH_mL} giving a minimum sum of squares of deviations for $\bar{n}$ were calculated and the results for the edtmp complexes are listed in Table 2. The errors given to the constants in parentheses (1σ) were evaluated from duplicated titrations of 30–40 data points. The formation of hydroxo complexes such as M(OH)L or polynuclear complexes such as M_2L, was not observed under these experimental conditions.

The protonation constants of edtmp have been evaluated by many investigators by means of potentiometry, see Table 3. As pointed out by Martell and co-workers,[1b] the values reported before 1976 may contain a considerable degree of inaccuracy because of an impure reagent or an imperfect analysis of data. Particularly, the failure of evaluation of the first protonation constant (log $K_1 \approx 10$)[2a,4,19] causes serious errors for the successive protonation constants. The values reported by Martell and co-workers[1b] agree with our results within an error of ± 0.1. As will be shown below, the value of log K_1 determined here is in good agreement with the value evaluated by ^{31}P NMR

Table 3 Reported values of protonation constants of edtmp*

	Ref. 2(*a*)	Ref. 3	Ref. 19	Ref. 1(*b*)	Ref. 4	This work
log K_1	10.6	12.10	10.68	12.99	10.60	13.07
log K_2	9.22	10.18	9.21	9.78	10.48	9.85
log K_3	7.43	8.08	7.66	7.94	9.27	7.87
log K_4	6.63	6.54	6.59	6.42	7.39	6.40
log K_5	6.18	5.23	5.64	5.17	5.63	5.12
log K_6	5.05	3.00	3.72	3.02	3.80	2.96
log K_7	2.72		1.50	1.33	2.73	
log K_8	1.46				2.43	

* $K_n = [H_nL]/[H_{n-1}L][H]$. Ionic strength = 0.1 mol dm^{-3} (KNO_3), 25 °C.

measurements. The spectroscopic methods are suitable for the determination of equilibrium constants at high or low pH compared with potentiometry. The value of log K_1 = 13.0 for edtmp is reasonably close to that of ntmp[14] or other aminopolyphosphonates.[20] The formation and protonation constants of edtmp complexes with alkaline-earth metal ions were reported by Martell and co-workers[1b] for Mg^{2+} and Ca^{2+} and by Rizkalla and Zaki,[4] for Mg^{2+}, Ca^{2+} and Ba^{2+}. The former values agree with our data within an error of ± 0.1, but the latter values show quite large discrepancies from our data of up to 3 units. The protonation constants of ntmp and complex formation constants with alkaline-earth metal ions reported by Carter *et al.*[21] and Nikitina *et al.*[22] agree reasonably well with our results.

NMR Spectra.—The ^{31}P NMR spectra of edtmp solutions show triplet peaks with an intensity ratio of 1:2:1 arising from coupling with the two protons of the adjacent methylene group. The resonance line becomes a singlet upon complete proton decoupling. In spite of the presence of many kinds of protonated species H_nL, only one sharp singlet peak is observed in the ^{31}P-{^{1}H} NMR spectra over the whole range of pH studied. This observation indicates that the proton exchange of edtmp is very fast. Thus, the four phosphorus atoms of edtmp are averaged and the chemical shift is given by $\delta_{calc} = \Sigma\delta_n X_{H_nL}$ where δ_n and X_{H_nL} are the chemical shift and the proportion of each protonated or unprotonated species, H_nL, respectively. By using the protonation constants K_n, the individual chemical shift, δ_n, minimizing the sum of squares of deviations $[=\Sigma(\delta_{obs} - \delta_{calc})^2]$ was evaluated by a non-linear regression. Values of δ_n thus obtained are plotted as a function of the number of protons bound to the ligand, *n*, in Fig. 1 together with the results for ntmp.[14] The first protonation constant K_1 evaluated from these NMR chemical shift data (log K_1 = 12.9 ± 0.1) agrees with the value obtained by potentiometry within experimental error.

The 1:1 alkaline-earth metal ion–edtmp solution has the same ^{31}P NMR pattern as that of the ligand. Although the singlet peak of the ^{31}P-{^{1}H} spectrum is very sharp in acidic or alkaline regions, it is broad at neutral pH. The chemical shift is written by a linear combination of the chemical shifts of each species present in the solution as $\delta_{calc} = \Sigma\delta_n X_{H_nL} + \Sigma\delta_m X_{MH_mL}$ where δ_m and X_{MH_mL} are the chemical shift and proportion of protonated or unprotonated complex, MH_mL. The values of δ_m minimizing the sum of squares of deviations for the observed and calculated chemical shifts were evaluated by a non-linear regression. The chemical shifts of complexes MH_mL, δ_m, thus obtained are plotted in Fig. 1 as a function of the number of protons bound to the complex MH_mL, *m*, together with the results for ntmp and Sr–ntmp.[14]

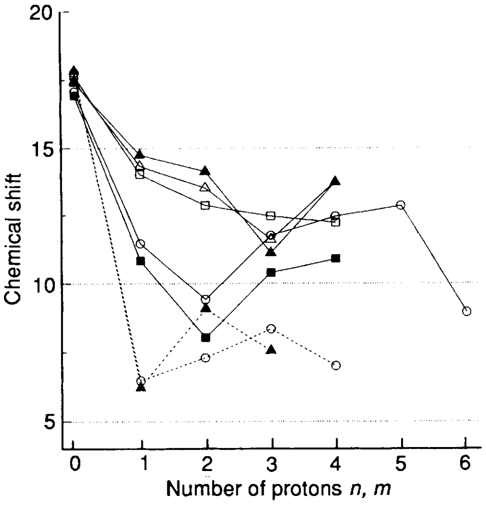


Fig. 1 Plots of the ^{31}P chemical shifts of the aminopolyphosphonate ligands and their complexes with alkaline-earth metals as a function of the number of protons bound to the ligand (H_nL), *n*, or complex (MH_mL), *m*. ○, ligand; ■, Mg; □, Ca; ▲, Sr; △, Ba. Ligands: —— edtmp, ···· ntmp

The ^{31}P-{^{1}H} NMR at various ratios of $c_M:c_L$ was measured at pH 7.2 and 11.5. The patterns of the spectra are shown in Fig. 2, where the width of the symbol of a triangle refers to the broadness of the peak. The chemical shifts corresponding to the uncomplexed ligand, L′, and the complexes, ML′, were calculated by $\delta_{L'} = \Sigma\delta_n X_{H_nL}$ and $\delta_{ML'} = \Sigma\delta_m X_{MH_mL}$ at the given pH. Although the signals of the 1:1 solutions at pH 11.5 are very sharp, those of the solutions containing an excess of ligand ($c_M/c_L < 1$) are quite broad. The signals of the Mg^{2+} and Ca^{2+} solutions split into two broad peaks corresponding to the ligand $\delta_{L'}$ and the complex $\delta_{ML'}$. On the other hand, the signals of the 1:1 solutions at pH 7.2 show broad peaks except for that of magnesium complex. Upon decreasing the ratio of $c_M:c_L$, the linewidth decreases and the value of the chemical shift of the solution approaches that of the free ligand, $\delta_{L'}$.

The ^{13}C-{^{1}H} NMR spectrum of edtmp at pH 9.1 is shown in Fig. 3. The resonance of the methylene carbon of the methylenephosphonate group, C^A, splits into a doublet by coupling with an adjacent phosphorus P^A ($^1J_{C-P}$ = 130.9 Hz) and splits further into a doublet by three-bond coupling with phosphorus $P^{A'}$ ($^3J_{C-P}$ = 4.4 Hz). The resonance of the methylene carbon of the ethylene group, C^B, splits into a triplet by three-bond coupling with two phosphorus atoms P^A and $P^{A'}$ ($^3J_{C-P}$ = 4.4 Hz). The ^{13}C signal shows an upfield shift upon protonation of edtmp^{8-}. The ^{13}C NMR of the ligand–metal ion solution shows a similar pattern and shift of signals as that of the ligand. The signals at neutral pH are quite broad in the same manner as those of the ^{31}P. The ^{1}H spectrum of edtmp shows a doublet for the methylene protons of methylenephosphonate and a singlet for the ethylene protons. The signals shift steeply downfield upon the first protonation of edtmp^{8-}. The shifts of the signals are very similar to those of ntmp.[14]

Calorimetry.—By using the enthalpy changes of the successive protonations of ntmp, ΔH_n, the total heat change of the protonation of ntmp corrected for the neutralization of OH^- or H^+, Q^N, is given by equation (4) where ΔH_n^T is the

$$Q^N = \Sigma\Delta H_n^T \Delta m_{H_nL} \quad (4)$$

overall enthalpy change $(=\Sigma\Delta H_n)$ and Δm_{H_nL} is the change in moles of each species H_nL. The enthalpy changes of the protonation of ntmp, ΔH_n, giving a minimum sum of squares of deviations $[=\Sigma(Q^N{}_{obs} - Q^N{}_{calc})^2]$ were calculated by using the protonation constant with the aid of a computer.[17,23] The values of the thermodynamic parameters thus obtained are listed in Table 1.

The total heat change of the metal–ntmp solution is given by equation (5) where $\Delta H^T_{MH_mL} = \Delta H_{ML} + \Sigma\Delta H_{MH_mL}$. The

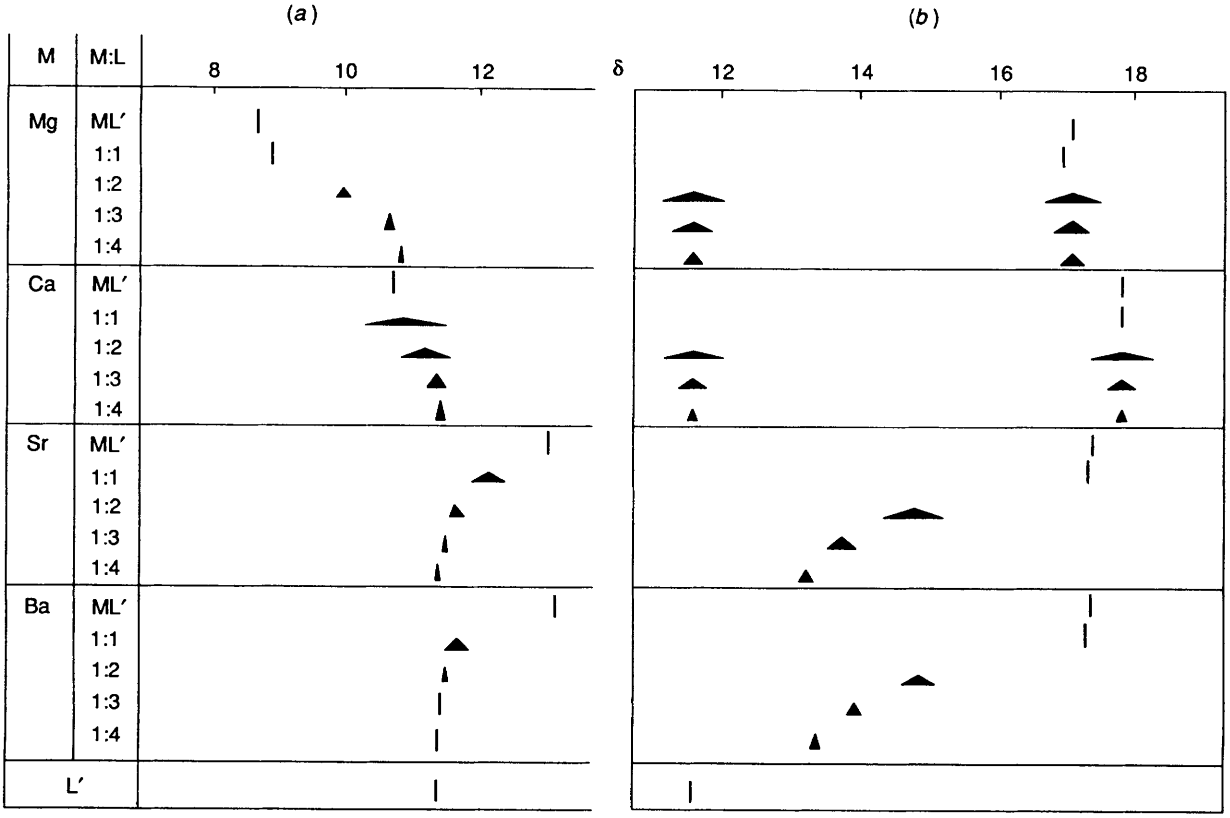


Fig. 2 The ^{31}P-{^{1}H} NMR spectral pattern of alkaline-earth metal–edtmp solutions at various metal to ligand ratios at pH 7.2 (*a*) and 11.5 (*b*); $c_L = 10^{-2}$ mol dm^{-3}

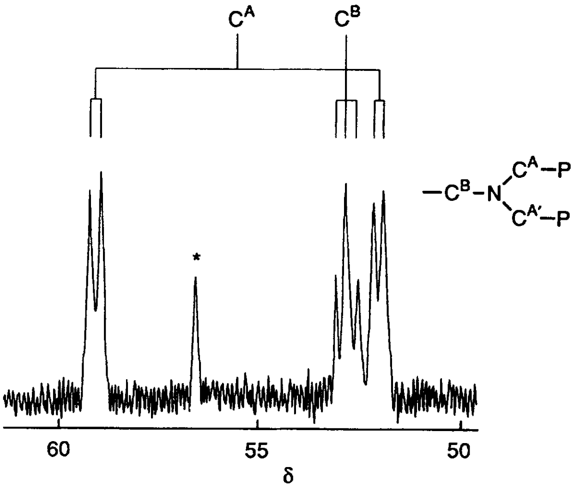


Fig. 3 The ^{13}C-{^{1}H} NMR spectrum of edtmp at pH 9.1; * signal of [^{2}H$_5$]trimethylsilylpropionate

Table 4 Thermodynamic parameters of formation and protonation of ntmp complexes[a]

			$-\Delta G$	$-\Delta H$	$T\Delta S$
		log K[b]	kJ mol^{-1}		
Mg^{2+}	$M + L \rightleftharpoons ML$	7.54(1)	42.9(1)	−25.8(8)	68.7(8)
	$ML + H \rightleftharpoons MHL$	9.42(1)	53.8(1)	48.6(4)	5.2(4)
	$MHL + H \rightleftharpoons MH_2L$	6.10(2)	34.8(1)	−8.8(4)	43.6(4)
Ca^{2+}	$M + L \rightleftharpoons ML$	7.86(2)	44.9(1)	0.6(6)	44.3(6)
	$ML + H \rightleftharpoons MHL$	8.80(1)	50.2(1)	19.7(4)	30.5(4)
	$MHL + H \rightleftharpoons MH_2L$	6.11(3)	34.9(2)	−5.0(5)	39.9(5)
Sr^{2+}	$M + L \rightleftharpoons ML$	6.52(2)	37 2(1)	6.5(6)	30.7(6)
	$ML + H \rightleftharpoons MHL$	9.41(1)	53.7(1)	21.2(3)	32.5(3)
	$MHL + H \rightleftharpoons MH_2L$	6.15(3)	35.1(2)	−15.6(4)	50.7(5)
Ba^{2+}	$M + L \rightleftharpoons ML$	6.34(2)	36.2(1)	8.2(7)	28.0(7)
	$ML + H \rightleftharpoons MHL$	9.72(1)	55.5(1)	22.5(3)	33.0(3)
	$MHL + H \rightleftharpoons MH_2L$	6.16(3)	35.2(2)	−12.4(6)	47.6(6)

[a] Ionic strength = 0.1 mol dm^{-3} (KNO$_3$), 25.0 °C. Errors for the last digit (σ) are given in parentheses. [b] Ref. 14.

$$Q^N = \Sigma\Delta H_n^T \Delta m_{H_nL} + \Sigma\Delta H^T_{MH_mL}\Delta m_{MH_mL} \qquad (5)$$

parameters ΔH_{ML} and ΔH_{MH_mL} correspond to the enthalpy change of complex formation and successive protonation of metal–ntmp complexes, respectively. The thermodynamic parameters of the metal complexes obtained by using their equilibrium constants are listed in Table 4.

$$\Delta T = \int\left(\frac{dQ^E}{dt}\frac{e^{\alpha t}}{C_0 + at}\right)dt\, e^{-\alpha t} \qquad (6)$$

The basic equation[24–26] of the thermometric titration of the edtmp system is the same as described elsewhere,[18] except for the correction of heat capacity of the solution and vessel, C, *i.e.*, $C = C_0 + at$ where C_0 is the initial heat capacity and at is a correction term for the increase of volume by the titrant. The temperature change, ΔT, at time t is obtained by the integration of equation (6), where Q^E is the heat evolution associated with the complex formation and neutralization of H^+ or OH^- and α is the Newtonian heat-leak constant of the titration vessel. The heat Q^E of the edtmp solution is given by equation (7) and for metal–edtmp solution by equation (8), where ΔH_w and Δm_{H_2O}

$$Q^E = \Sigma\Delta H_n^T \Delta m_{H_nL} + \Delta H_w \Delta m_{H_2O} \qquad (7)$$

$$Q^E = \Sigma\Delta H_n^T \Delta m_{H_nL} + \Sigma\Delta H^T_{MH_mL}\Delta m_{MH_mL} + \Delta H_w \Delta m_{H_2O} \qquad (8)$$

are the enthalpy of neutralization and number of moles of water formed by neutralization, respectively. The value of ΔT at each point of time t, ΔT_{calc}, was calculated by using the value of the

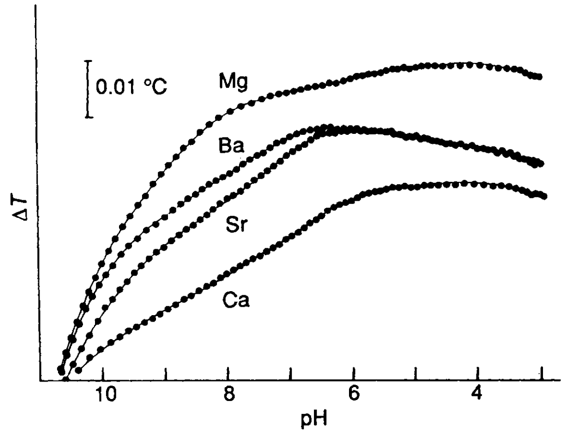


Fig. 4 Thermometric titration of alkaline-earth metal–edtmp complexes with HNO_3 at 25 °C; c_L = 3.4 mmol dm^{-3}, c_M = 3.7 mmol dm^{-3}. Solid lines are calculated curves (see text)

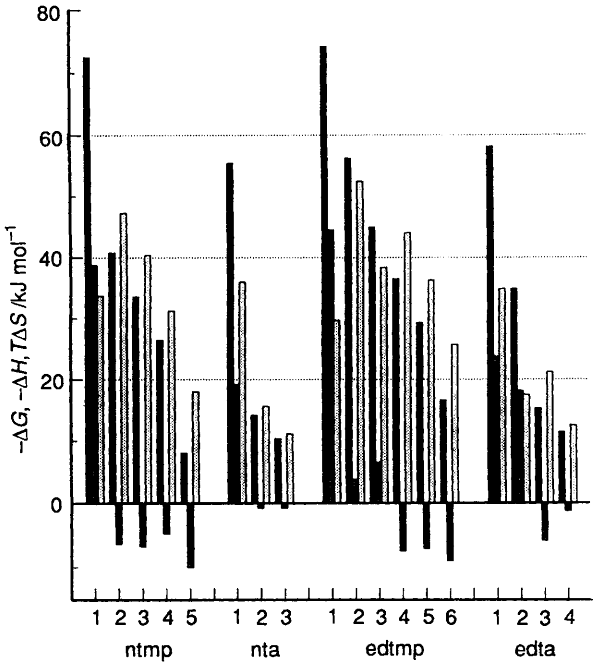


Fig. 5 Thermodynamic parameters (25 °C) for the successive protonation of aminopolyphosphonates (ntmp, edtmp) and aminopolycarboxylates (nta, edta), I = 0.1 mol dm^{-3} (KNO_3). ■, $-\Delta G$; ▩, $-\Delta H$; ▒, $T\Delta S$

pH of the solution at the point with the aid of the Newton–Cotes numerical quadrature.[18] The values of ΔH minimizing the sum of squares of deviations $[=\Sigma(\Delta T_{\text{obs}} - \Delta T_{\text{calc}})^2]$ were evaluated by non-linear regression. The values of the thermodynamic parameters obtained for edtmp and its complexes are shown in Tables 1 and 2. The temperature difference observed by the titration of the edtmp system is plotted as a function of pH in Fig. 4. Solid lines are the best-fit curves calculated by using the values of ΔH thus obtained and equilibrium constants K listed in Tables 1 and 2.

Discussion

Protonation of Ligands.—Thermodynamic parameters for the protonation of ntmp and edtmp are plotted as a function of the number of protons bound to the ligand in Fig. 5, where those of the corresponding aminopolycarboxylates, H_4edta (ethylenediaminetetraacetic acid)[27] and H_3nta (nitrilotriacetic acid),[28] are also depicted. The first protonation of ntmp is appreciably exothermic ($\Delta H_1 = -38.8$ kJ mol^{-1}), which indicates the addition of a proton to the nitrilo nitrogen atom.[29] The large negative value of ΔH_1 of ntmp contributes to ΔG_1 and leads to the high basicity of the nitrogen atom of ntmp. The successive replacement of a hydrogen atom of ammonia with an acetate group causes a decrease in exothermic enthalpy change and an increase in the entropy change for the protonation of the nitrogen atom of the substituted aminopolycarboxylate.[12] On the first protonation, the dehydration of the carboxylate group caused by electrostatic interaction and/or the hydrogen bond between NH^+ and CO_2^- plays an important part together with the formation of the N–H$^+$ bond. In addition to these interactions, the strengthening of the N–H$^+$ bond by an inductive effect of the binegative charge of the phosphonate group on the positive nitrogen atom would make the protonation of the nitrogen atom of ntmp more exothermic.

The endothermic enthalpy changes of the second and higher protonations ($\Delta H_n \approx 7$ kJ mol^{-1}, n = 2–5) of ntmp indicate that these protonations occur on the phosphonate groups. These values are larger than those of nta ($\Delta H_n \approx 0$ kJ mol^{-1}, n = 2 or 3) and the stronger basicity of ntmp compared with nta leads to larger entropy changes (Fig. 5). These observations are quite reasonable because the number of water molecules released upon protonation, which results in a decrease of negative charge, could be higher for the more negatively charged ntmp (PO_3^{2-}) than for nta (CO_2^-).

In the case of edtmp, the situation is relatively complicated compared with ntmp or edta. The exothermic enthalpy changes of the first and second protonations of edta (ΔH_1, $\Delta H_2 < 0$) indicate the successive protonations of two nitrogen atoms of edta (Fig. 5). The fact that the enthalpy changes of the third and fourth protonations, ΔH_3 and ΔH_4, are near to zero is explained by the successive protonations of carboxylate groups. These two types of protonation of edta have been confirmed by ^{1}H NMR spectral studies of the acetate methylene groups[30–32] and the IR spectra of the carboxyl groups.[33] A quite large enthalpy change of the first protonation of edtmp ($\Delta H_1 = -44.5$ kJ mol^{-1}) is evidence of protonation on the nitrogen atom similar to that of ntmp. In a similar manner as for edta,[33–35] the proton of monoprotonated edtmp might be shared between two nitrogen atoms and form intramolecular hydrogen bonds with phosphonate O^-. Both the second and third protonations of edtmp are weakly exothermic. Two types of protonation of the second step are considered, *i.e.*, protonation on the phosphonate O^- maintaining the structure of HL or on two nitrogen atoms of both sides of the ethylene chain. The enthalpy changes ΔH_2 and ΔH_3 cannot be explained by the addition of a proton to either phosphonate O^- or a single nitrogen atom. The proton affinity of the second nitrogen of HL^{7-} is lowered enough to be comparable with that of the phosphonate O^- by the protonation of the first nitrogen. Consequently, two microspecies (H_2edtmp^{6-}) should coexist in equilibrium. The same extent of endothermic enthalpy changes and the regular decrease in $T\Delta S$ for the protonations n = 4–6 indicate that both nitrogen atoms are completely protonated in the species H_3edtmp^{5-} and the subsequent protonations n = 4–6 occur on the phosphonate O^-.

The results of ^{31}P NMR spectroscopy support the sequence of the protonations of aminopolyphosphonates estimated by the thermodynamics. As shown in Fig. 1, the upfield shift of the protonated species of ntmp indicates the protonation of the nitrogen atom. The steep upfield shift of Hedtmp^{7-} corresponds to the protonation of the nitrogen atom and the relatively small change of chemical shift from Hedtmp^{7-} to H_2edtmp^{6-} indicates only partial protonation of the second nitrogen atom.

Complex Formation.—Thermodynamic parameters of the complex formation of alkaline-earth metals with ntmp and edtmp are shown in Fig. 6, where those with nta[36–38] and edta[28,39,40] complexes are also depicted. The order of the

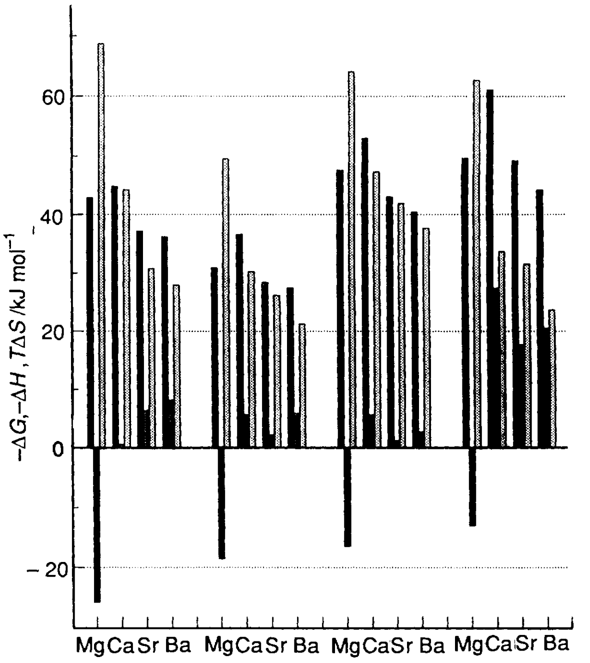


Fig. 6 Thermodynamic parameters (25.0 °C) of complex formation of alkaline-earth metal complexes of aminopolyphosphonates (ntmp, edtmp) and aminopolycarboxylates (nta, edta), $I = 0.1$ mol dm^{-3} (KNO_3). ■, $-\Delta G$; ▨, $-\Delta H$; ░, $T\Delta S$

values of the formation constants of the aminopolyphosphonate complexes ($-\Delta G_{MgL} < -\Delta G_{CaL} > -\Delta G_{SrL} > -\Delta G_{BaL}$) agrees with that of the aminopolycarboxylate complexes. The formation of the calcium, strontium and barium complexes is exothermic in each case and the decrease in the formation constant from the calcium to barium complexes is attributed to the decrease in the entropy term, $T\Delta S_{ML}$. Relatively large formation constants of ntmp complexes compared with those of nta are owed to the large entropy change upon formation of the ntmp complexes (Fig. 6). The stability of the complexes of Ca^{2+}, Sr^{2+} or Ba^{2+} with edtmp is rather low compared with that of the corresponding edta complex. The enthalpy change of the formation of the edta complex $-\Delta H_{M(edta)}$ is comparable to its entropy term $T\Delta S_{M(edta)}$. On the other hand, the enthalpy change of the formation of the edtmp complex, ΔH_{ML}, is close to zero and the formation is entropy driven. These observations indicate that the M–N bond of the edtmp complex is considerably weak and the co-ordination of edtmp to the metal is rather ionic. This nature might result from the mutual charge repulsion among the binegative phosphonate groups in the complex and/or a distortion of the chelate ring caused by the longer lengths of the P–O bonds compared with the C–O bonds of edta.

Similarly to the aminopolycarboxylate complexes, the formation of magnesium complexes of ntmp and edtmp is endothermic and entropy driven (Fig. 6). The quite large entropy change indicates that the magnesium ion having a small ion size releases a large number of water molecules upon formation of the complex. As distinct from complexes with Ca^{2+}, Sr^{2+} and Ba^{2+}, the values of $-\Delta H$ and $T\Delta S$ of the Mg–edtmp complex are similar to those of the Mg–edta complex, *i.e.*, there is no profit in the entropy term for the formation of Mg–edtmp. This observation suggests a very weak metal–nitrogen bond in the $Mg(edtmp)^{6-}$ complex.

The ^{31}P NMR chemical shifts of the unprotonated edtmp complexes (Fig. 1, $m = 0$) do not differ much from that of the unprotonated ligand $edtmp^{8-}$ as observed for the ntmp system. This observation supports the conclusion that the co-ordination of aminopolyphosphonate to metal ion is predominantly ionic and scarcely affects the electron density of phosphonate P.

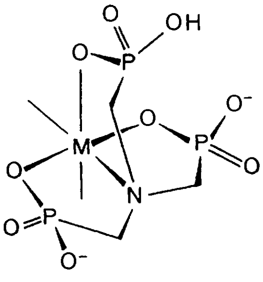
Protonation of Complexes.—As can be seen from Table 4, the first protonation of all the ntmp complexes is considerably exothermic. This exothermicity strongly supports the conclusion that the first protonation occurs on the nitrogen atom of ntmp in the complexes. That is, the monoprotonated complex of the alkaline-earth metals has the structure **II** as predicted from potentiometric and NMR spectroscopic studies.[14]

The first protonation of the magnesium complex [$\Delta H_{Mg(Hntmp)} = -48.6$ kJ mol^{-1}] is significantly exothermic and more negative than that of the free ligand ntmp ($\Delta H_{Hntmp} = -38.8$ kJ mol^{-1}). This high negative value of $\Delta H_{Mg(Hntmp)}$ reflects the very weak Mg–N bond. The complete cleavage of the magnesium–nitrogen bond by the protonation might result in the co-ordination of a water molecule to the magnesium ion and the co-ordination causes the additional enthalpy change. The quite small entropy change of the first protonation, $\Delta S_{Mg(HL)}$, indicates hydration of the complex upon the first protonation step. The entropy term of the first protonation, $T\Delta S_{M(Hntmp)}$, of the complexes with Ca^{2+}, Sr^{2+} and Ba^{2+} is almost the same as that of the ligand, $T\Delta S_{Hntmp}$, and the large values of the first protonation constants of the complexes compared with that of free ligand is due to the contribution of the ΔH term to ΔG. The enthalpy and entropy changes of the magnesium upon the formation of the monoprotonated complex from Mg^{2+} and $Hntmp^{5-}$ [$Mg^{2+} + Hntmp^{5-} \rightleftharpoons Mg(Hntmp)^{3-}$; $\Delta H^{HL}_{Mg(HL)} = 16.0$ kJ mol^{-1}, $T\Delta S^{HL}_{Mg(HL)} = 40.2$ kJ mol^{-1}] are comparable to those of the Ca^{2+}, Sr^{2+} and Ba^{2+} ions, respectively, *e.g.*, $\Delta H^{HL}_{Ca(HL)} = 18.5$ kJ mol^{-1} and $T\Delta S^{HL}_{Ca(HL)} = 41.1$ kJ mol^{-1}. The formation of $M(Hntmp)^{3-}$ from M^{2+} and $Hntmp^{5-}$ is endothermic and entropy driven for all the alkaline-earth metal cations. These observations corroborate that all the monoprotonated complexes of the alkaline-earth metals have the same structure, *i.e.* with protonation on the nitrogen atom.

The second protonation of the ntmp complexes is endothermic and the entropy change, $T\Delta S_{M(H_2ntmp)}$, is larger than that of the first protonation, $T\Delta S_{M(Hntmp)}$. The peculiar behaviour of the magnesium complex is no longer observed. These results support the addition of the second proton to the O^- of the phosphonate group (structure **III**). The protonation on the phosphonate O^- of the complex scarcely gives a change in the structure of the complex. Thus, the values of the enthalpy and entropy changes of the second protonation of the complex do not differ significantly from those of the second protonation of the ligand.

As can be seen from Table 2, the relative values of the protonation constants of the edtmp complexes among the alkaline-earth metal ions show a similar behaviour to those of the ntmp complexes. That is, the order of the first protonation constant of the edtmp complexes [$-\Delta G_{Mg(HL)} > -\Delta G_{Ca(HL)} < -G_{Sr(HL)} < -\Delta G_{Ba(HL)}$] is the reverse of that of the formation constants of the complexes ($-\Delta G_{MgL} < -\Delta G_{CaL} > -\Delta G_{SrL} > -\Delta G_{BaL}$) and the second and higher protonation constants of the edtmp complexes scarcely change with the metal ion. Nevertheless, the behaviour of the thermodynamic parameters upon protonation of the edtmp complexes is apparently different from that of the ntmp complexes and is quite complicated. The first and second protonations of the magnesium complex are exothermic and ΔH of the third and fourth protonations are almost zero, whereas the protonations of the other complexes are exothermic up to the third protonation. These results indicate that both of the microspecies with phosphonate O^- or nitrogen sites of the complex are involved in the first and second protonations of the complexes in the same manner as the protonations of the ligand edtmp ($n = 2$ or 3).

As shown in Fig. 1, the ^{31}P NMR chemical shifts of the protonated complexes show a corresponding behaviour with the thermodynamic parameters. The ligand ntmp and its complexes (the Sr–edtmp complex is depicted in Fig. 1 as an example) show a steep upfield shift upon addition of the first proton *i.e.*, protonation at nitrogen. For the edtmp system, the



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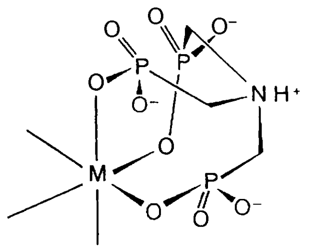
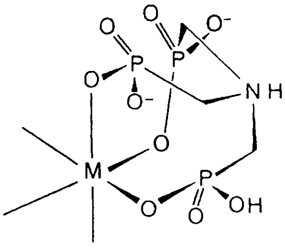


II



III

change in the chemical shift of the magnesium complexes upon protonation is parallel to that of the ligand, *i.e.*, it shows a steep upfield shift up to $Mg(H_2edtmp)^{4-}$. The chemical shifts of the protonated species of the magnesium(II) complex show a higher upfield shift compared with those of the corresponding protonated species of edtmp. This observation indicates that a significant portion of the nitrogen atoms of the complex may already be protonated by $Mg(H_2edtmp)^{4-}$ and corroborate the results of the calorimetry studies. On the other hand, the change in the chemical shifts of the complexes with Ca^{2+}, Sr^{2+} and Ba^{2+} show almost the same pattern irrespective of the metal ions and they shift gradually upfield upon successive protonations. The chemical shifts of $M(H_3edtmp)^{3-}$ and $M(H_4edtmp)^{2-}$ are very close to those of the protonated ligand species, H_3edtmp^{5-} and H_4edtmp^{4-}. The enthalpy changes of the fourth protonation of all the edtmp complexes are almost zero (Table 2). These observations indicate that the protonation of the two nitrogen atoms of edtmp in the complex has been accomplished at the triprotonated complex, $M(H_3edtmp)^{3-}$. It was reported for transition-metal–edtmp complexes[8] that the number of water molecules co-ordinating is larger than that for the edta complexes. This finding is explained by the fact that the nitrogen atom does not co-ordinate to the metal ion in the protonated edtmp complexes.

The linewidths of the NMR signals shown in Fig. 2 give information about the rate of complex formation and protonation of the complex. Since the dissociation of the complex is negligible at high pH even at a 1 : 1 metal–edtmp ratio and only an unprotonated species $M(edtmp)^{6-}$ is formed at pH 11.5, the $^{31}P-\{^1H\}$ NMR signal of the 1 : 1 mixture at pH 11.5 is a sharp single peak at the position close to the $\delta_{ML'}$ (Fig. 2). The NMR signal becomes quite broad under the conditions of $c_M : c_L < 1 : 1$. The signals of edtmp in solutions of Mg^{2+} or Ca^{2+} split into two peaks which appear at the positions of $\delta_{ML'}$ and $\delta_{L'}$. At this pH the predominant species are ML and HL. Thus, this line-broadening reflects ligand exchange [equation (9)].

$$ML + HL^* \rightleftharpoons ML^* + HL \qquad (9)$$

This situation is the same as that found for the ntmp system[14] but the extent of line broadening of the edtmp complexes is larger than that of the ntmp complexes and in the case of edtmp not only the signal of the magnesium(II) complex but also that of the calcium(II) complex split into two peaks. These results indicate that ligand exchange of edtmp (which has a more complicated structure) is slower than that of ntmp.

The signals of the $c_M : c_L$ 1 : 1 solutions of edtmp at pH = 7.5 are considerably broadened except for the magnesium(II) solution, whereas all the signals of the ntmp solution (pH = 7.8) are quite sharp.[14] For ntmp, the predominant complex species under these conditions is M(HL) in which the nitrogen atom of ntmp is protonated. Thus, the ligand co-ordinates to the metal ion only by the phosphonate groups (structure **II**) and the ligand exchange of the complex is very fast. On the other hand, the predominant complexed species of edtmp at this pH is the diprotonated complex $M(H_2edtmp)^{4-}$. As reported for the ntmp complex,[14] the ligand exchange of the chelate complex co-ordinated by nitrogen, ML (structure **I**), is considerably slower. Consequently, the slow ligand exchange of the $M(H_2edtmp)^{4-}$ complexes of Ca^{2+}, Sr^{2+} and Ba^{2+} corroborates the fact that the nitrogen atom is still co-ordinated to the metal ion. The rapid ligand exchange of the diprotonated complex of the magnesium complex supports the conclusion that both two nitrogen atoms are already protonated.

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