14. Metal Complexes with Macrocyclic Ligands

Part XXXI[1])

Protonation Studies and Complexation Properties of Tetraazamacrocyclic Methylenephosphonates with Earth-Alkali Ions

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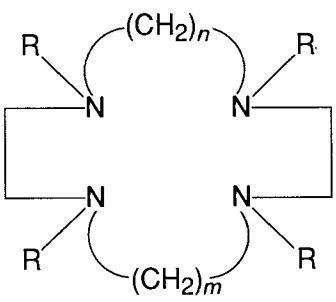
The three ligands 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrakis(methylenephosphonic acid) (**1**), 1,4,7,11-tetraazacyclotridecane-1,4,7,11-tetrakis(methylenephosphonic acid) (**2**), and 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetrakis(methylenephosphonic acid) (**3**) have been synthesized by condensation of the corresponding macrocycles with formaldehyde and phosphorous acid. The protonation and stability constants with the earth-alkali ions have been determined at 25° and $I = 0.1$M ($Me_4N(NO_3)$) by potentiometric titrations. Because of the high values of the first two protonation constants, ^{1}H-NMR measurements were necessary to determine them. Titrations in different supporting electrolytes ($NaNO_3$, KNO_3, $RbNO_3$, $CsNO_3$, and $Me_4N(NO_3)$) show that their choice is of paramount importance, as the above ligands can form complexes with alkali-metal ions. The potentiometric results for the earth-alkali ions show that beside mononuclear complexes of different degrees of protonation ($[MLH_n]$, $n = 0$–4), also binuclear species are formed ($[M_2LH_m]$, $m = 0$–2). It is interesting that **1** with the smallest macrocyclic ring has the greatest tendency to form binuclear complexes, which are so stable that they partially prevent the formation of the corresponding mononuclear species. For [ML], [MLH], $[M_2L]$, and $[M_2LH]$, the stability sequence is $Mg^{2+} < Ca^{2+} > Sr^{2+} > Ba^{2+}$, whereas for $[MLH_2]$, $[MLH_3]$, and $[MLH_4]$, the stability steadily decreases from Mg^{2+} to Ba^{2+}.

Introduction. – A large number of tetra-*N*-functionalized tetraazamacrocycles have been described in the literature [2–11]. Most of the tetracarboxylates **4**–**6** have been investigated through equilibria [2], calorimetric [3] and kinetical [4] studies, supplemented by spectral [5] and structural investigations [6]. The Gd^{3+} complex of **4** has been developed into a contrast agent for NMR imaging in medicine [7]. Synthetic work, equilibria measurements, and structural studies have been described for the tetrakisethanol derivatives **7** and **8** which are interesting for their fast rate of metal-ion incorporation [8]. Four aminoethyl groups have also been attached to give the 14-membered macrocycle **9**, and a large number of interesting structures of their metal complexes have been published [9]. A tetrakis(propanenitrile) derivative **10** has been prepared [10], and it has been shown that the coordinated metal ion can cleave off one of the side chains and/or hydrolyze the nitrile group [11]. Less, however, has been done with phosphonate derivatives [12–15], although aminophosphonates have interesting properties as chelating agents for metal ions, as

[1]) Part XXX: see [1].



1 $n = m = 2$, R = $CH_2PO_3H_2$
2 $n = 2$, $m = 3$, R = $CH_2PO_3H_2$
3 $n = m = 3$, R = $CH_2PO_3H_2$
4 $n = m = 2$, R = CH_2COOH
5 $n = 2$, $m = 3$, R = CH_2COOH
6 $n = m = 3$, R = CH_2COOH
7 $n = m = 2$, R = CH_2CH_2OH
8 $n = m = 3$, R = CH_2CH_2OH
9 $n = m = 3$, R = $CH_2CH_2NH_2$
10 $n = m = 3$, R = CH_2CH_2CN
11 $n = m = 2$, R = H
12 $n = 2$, $m = 3$, R = H
13 $n = m = 3$, R = H

shown by many papers on open-chain ligands of this type [16] [24]. Thus, we have prepared the tetrakis(methylenephosphonic acids) **1–3** and studied their protonation and complexation properties.

Experimental. – The starting compounds 1,4,7,10-tetraazacyclododecane (**11**) [17], 1,4,7,11-tetraazacyclotridecane (**12**) [17], and 1,4,8,11-tetraazacyclotetradecane (**13**) [18] were prepared according to the literature.

1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetrakis(methylenephosphonic Acid) (**1**). In a typical experiment, **11**·4 HCl (3.5 g, 11 mmol) dissolved in 18% HCl soln. (40 ml) was mixed with crystalline H_3PO_3 (3.6 g, 44 mmol). After heating the soln. to reflux, 37% formaldehyde soln. (7.95 ml, 107 mmol) was added within 20 min. The soln. was kept for 4–5 h at reflux. Thereafter, the solvent was evaporated, and the brown oil, dissolved in 50 ml H_2O, was evaporated again to remove all formaldehyde. The residue, dissolved in H_2O (*ca.* 20 ml) at 70°, was slowly cooled to 4°: 2.38 g (37.1%) of **1**. From the mother liquor, an additional crop was collected by addition of EtOH. Anal. pure **1** was obtained by recrystallization from H_2O. M.p. 282–283°. ^{1}H-NMR (D_2O, pD 9.65): 3.03 (*d*, J(H,P) = 10.7, 4 NCH_2P); 3.35 (*s*, 8 CH_2N). Anal. calc. for $C_{12}H_{32}N_4O_{12}P_4 \cdot 0.15\ H_2O$ (551.00): C 26.16, H 5.94, N 10.17, P 22.49, H_2O 0.49; found: C 26.13, H 6.09, N 10.07, P 22.29, H_2O 0.49.

1,4,7,11-Tetraazacyclotridecane-1,4,7,11-tetrakis(methylenephosphonic Acid) (**2**). Compound **2** was prepared from **12**·4 HBr in a similar way as described for **1**, but it was recrystallized by suspending the residue in H_2O, adding so much 25% NH_3 soln. to dissolve it, filtering, and precipitating the product by addition of 36% HCl soln. Yield: 45.6%. M.p. 253–254°. ^{1}H-NMR (D_2O, pD 9.44): 2.03 (*quint.*, CH_2); 2.87 (*d*, J(H,P) = 10.7, 4 NCH_2P); 3.30 (*m*, 8 NCH_2). Anal. calc. for $C_{13}H_{34}N_4O_{12}P_4 \cdot H_2O$ (580.23): C 26.91, H 6.25, N 9.65, P 21.35; found: C 26.64, H 6.35, N 9.61, P 20.99.

1,4,8,11-Tetraazacyclotetradecane-1,4,8,11-tetrakis(methylenephosphonic Acid) (**3**). Compound **3** was prepared from **13** and recrystallized as described for **2**. Yield 53.4%. M.p. 271–273°. ^{1}H-NMR (D_2O, pD 9.36): 1.99 (*quint.*, 2 CH_2); 2.79 (*d*, J(H,P) = 11.0, 4 NCH_2P); 3.18 (*m*, 8 NCH_2). Anal. calc. for $C_{14}H_{36}N_4O_{12}P_4 \cdot H_2O$ (594.43): C 28.18, H 6.49, N 9.39, P 20.76, H_2O 3.03; found: C 28.00, H 6.49, N 9.57, P 20.66, H_2O 3.41.

The purity of the tetraphosphonates was checked by reversed-phase TLC (*Merck RP-8;* MeCN/H_2O).

Potentiometric Titrations. They were run on the automated titrator described previously [19] at 25° and I = 0.1M ($Me_4N(NO_3)$) under N_2. Typical concentrations were $5.5 \cdot 10^{-4}$ M or $2.2 \cdot 10^{-4}$ M ligand, with 0, 90, and 180% addition of metal ion as nitrate. To obtain solns. of **2** and **3**, the ligands were reacted with 1 equiv. of $Me_4N(OH)$, which was also used as titrating base. In the case of **1**, titrations in the presence of 0.1M alkali nitrates were also run to test the effect of the electrolyte on the $\log K_H$ values. The calculations of the protonation and stability constants were done with the program TITFIT [20] using $\alpha_H = 0.885$ and $pK_W = 13.94$, which were determined separately.

^{1}H-NMR Titrations. The first two $\log K_H$ values, being too high to be measured by potentiometry, were determined by ^{1}H-NMR titrations without control of the ionic strength. The spectra were obtained on a *Jeol-JNM-100-PFT* instrument equipped with a *Jeol-980A* computer. D_2O solns. of the ligands (0.01M) were adjusted with DCl or KOD (CO_2-free) to the desired pD value which was measured with a radiometer *PHM 63* equipped with a microelectrode *Ingold 405-M3*. The electrode was calibrated with buffer solns. pH 4 and 7 *(Merck)*. The final pH value was calculated from pH = pD – 0.4 [21]. Chemical shifts were referenced to sodium 3-(trimethylsilyl)-propane-1-sulfonate *(Aldrich)* as internal standard. $\log K_{H,1}$ and $\log K_{H,2}$ values were obtained by fitting the

observed chemical shift $\delta_{obs.}$ *vs.* pH as described in [22], using a computer program based on the *Marquardt* non-linear regression algorithm.

Results and Discussion. – The synthesis of the phosphonates using the condensation of formaldehyde and phosphorous acid [23] is straightforward, but the purification is relatively difficult and must be carefully followed by TLC (reversed-phase).

The potentiometric titrations of ligand **1** with different supporting electrolytes show that its nature has a strong influence on the $\log K_H$ values, indicating that the 12-membered derivative can complex alkali ions. We, therefore, have used $Me_4N(OH)$ as base and $Me_4N(NO_3)$ as supporting electrolyte to avoid problems of complexation with the cation. The titrations with $Me_4N(OH)$ clearly show that $\log K_{H,1}$ and $\log K_{H,2}$ are too high to be determined by potentiometric methods. Thus, for the determination of these values, we run ^{1}H-NMR titrations. The fitting of the chemical shift of the NMR signals as a function of pH was done using two different models. For the 12- and 13-membered rings **1** and **2**, a stepwise two-protons addition *(Eqn. 1)* was used, whereas for the 14-membered ring **3** a two protons in one-step procedure *(Eqn. 2)* was the best model to fit the data. $\delta_{obs.}$ is the observed chemical shift of the non-labile protons at the particular pH, whereas $\delta(LH_2)$, $\delta(LH)$, and $\delta(L)$ are the chemical shifts for the three forms of the ligand LH_2, LH, and L, respectively (*Figs. 1* and *2*). The values obtained by the NMR-titration

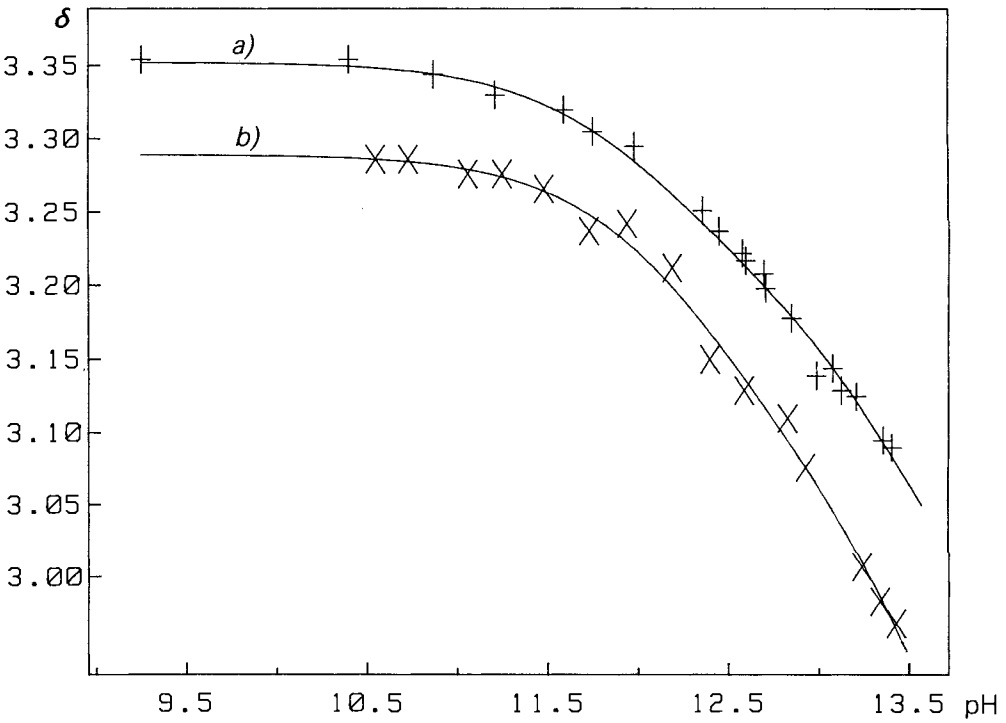


Fig. 1. *Chemical shift* (δ[ppm]) *of the* NCH_2P *protons* vs. *pH for* a) **1** *and* b) **2**. Experimental points (+, ×) and calculated curves (–) with *Eqn. 1* using $\delta(LH_2)$, $\delta(LH)$, and δ values of 3.352, 3.194, and 2.856 ppm for **1** and 3.289, 3.078, and 2.632 ppm for **2**, respectively.

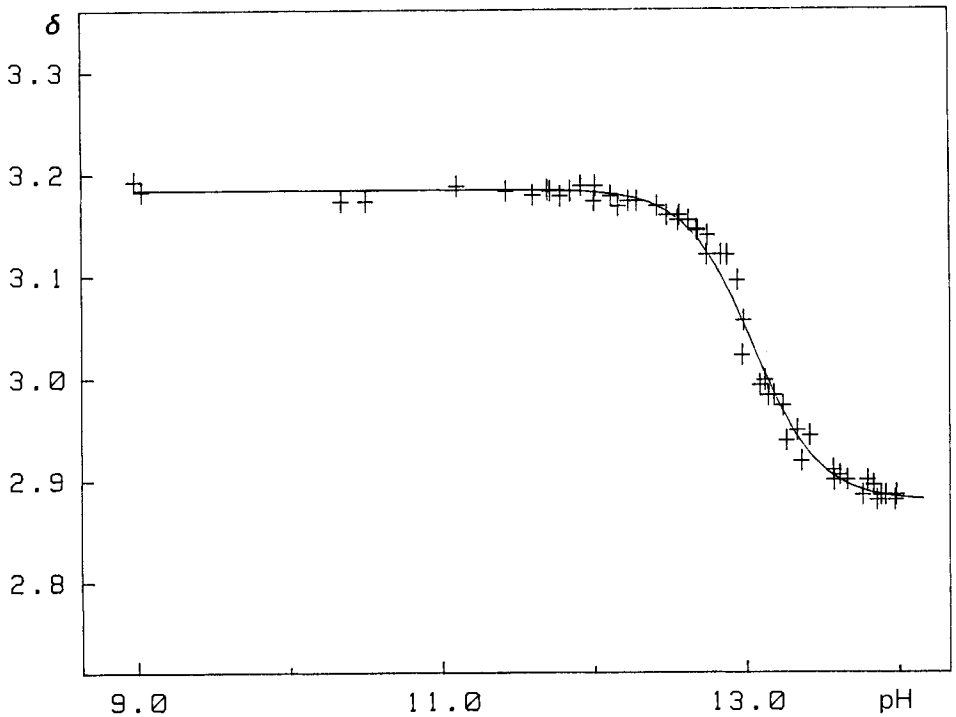


Fig. 2. *Chemical shift* (δ[ppm]) *of the* NCH_2P *protons* vs. *pH for* **3**. Experimental points (+) and calculated curve (−) with *Eqn. 2* using $\delta(LH_2) = 3.184$ and $\delta(L) = 2.879$ ppm.

$$\delta_{obs.} = \frac{K_{H,1} \cdot K_{H,2} \cdot [H^+]^2 \cdot \delta(LH_2) + K_{H,1} \cdot [H^+] \cdot \delta(LH) + \delta(L)}{K_{H,1} \cdot K_{H,2} \cdot [H^+]^2 + K_{H,1} \cdot [H^+] + 1} \quad (1)$$

$$\delta_{obs.} = \frac{K_{H,1} \cdot K_{H,2} \cdot [H^+]^2 \cdot \delta(LH_2) + \delta(L)}{K_{H,1} \cdot K_{H,2} \cdot [H^+]^2 + 1} \quad (2)$$

procedure *(Table 1)* are of course not so accurate, because the ionic strength could not be controlled, and pH measurements with a glass electrode above pH 12 are biased by the relatively high alkaline error. NMR measurements are practically the only technique for obtaining such high $\log K_H$ values, besides calorimetric methods. The other protonation constants, determined by fitting the potentiometric titration curves with the program TITFIT [20] *(Table 1)*, have the usual high precision of this kind of measurements. The lower $\log K_H$ values could not be determined due to the unsolubility of the ligands at low pH.

In *Table 1*, we also have reported the values published by *Kabachnik et al.* [14] which were obtained under somewhat different conditions than ours (I = 1M KNO_3) and those of *Geraldes et al.* [15] which, although measured under identical conditions as ours, disagree. It seems as if the authors have not realized that there is an additional very basic proton. Indeed, if one shifts all $\log K_H$ values by one proton, the agreement between our

Table 1. *Protonation Constants of the Macrocyclic Tetrakis(methylenephosphonates)* **1–3**. $T = 25°$.

	Electrolyte ($I = 0.1$)	$\log K_{H,1}$	$\log K_{H,2}$	$\log K_{H,3}$	$\log K_{H,4}$	$\log K_{H,5}$	$\log K_{H,6}$	Ref.
1	$Me_4N(NO_3)$	13.7(1)[a]	12.2(1)[a]	9.28(1)	8.09(1)	6.12(1)	5.22(1)	
	Me_4NCl	12.6	9.3	8.0	6.0	5.2	–	[15]
	$NaNO_3$	–	11.44(2)	8.90(1)	7.71(1)	5.96(1)	5.10(1)	
	NaCl	10.9	9.2	8.1	6.3	5.4	1.8	[15]
	KNO_3	–	–	9.03(1)	7.81(1)	6.03(1)	5.13(1)	
	$RbNO_3$	–	–	9.06(1)	7.83(1)	6.03(1)	5.13(1)	
	$CsNO_3$	–	–	9.07(1)	7.82(1)	6.02(1)	5.15(1)	
	[c]	12.12	11.52	8.46	7.29	5.73	4.88	[14]
2	$Me_4N(NO_3)$	13.8(1)[a]	12.4(1)[a]	9.02(1)	7.54(1)	6.22(1)	5.09(1)	
3	$Me_4N(NO_3)$	13.4(1)[a][b]	12.8(1)[a][b]	8.82(1)	7.75(1)	6.25(1)	5.42(1)	

[a] Determined by ^{1}H-NMR titration.

[b] Only $\log\beta_{012} = 26.1$ could be determined, so $\log K_{H,1}$ and $\log K_{H,2}$ were calculated assuming a statistical factor of 4.

[c] $I = 1$ (KNO_3).

and their values is good for 0.1M $Me_4N(NO_3)$ as electrolyte. For 0.1M NaCl, however, the values of *Geraldes et al.* are in general higher than ours, and in some cases even higher than those measured by them in 0.1M Me_4NCl which indicates a systematic error.

The high values of $\log K_{H,1}$ and $\log K_{H,2}$ for the three ligands **1–3** compared to those of the tetraacetates **4–6** are a consequence of an increase of electron density on the N-atoms caused by the high negative charges of the phosphonate groups [16] [24]. Acetate substitution has a similar but smaller effect [2]. The differences between subsequent $\log K_{H,n}$ values with $n > 3$ indicate that the stepwise protonation of each phosphonate group has only little effect on the next one.

The lowering of $\log K_H$ in the presence of alkali nitrates as compared to those with $Me_4N(NO_3)$ is an indication that there is an interaction between these ions and the macrocycles[2]). Indeed, these titration curves can be fitted ($\sigma_{ml} = 0.0012$–0.0016 ml) by assuming a series of protonated 1:1 complexes $[ML H_n]$, the stability of which are given in *Table 2*. The assumption of only 1:1 alkali complexes is the simplest model, which fits the data.

Table 2. *Stability Constants of the Macrocyclic Tetrakis(methylenephosphonate)* **1** *with Alkali Ions.* $T = 25°$, $I = 0.1$.

M^+	$\log\beta_{mlh}$			
	111[a]	112[a]	113[a]	114[a]
Na^+	16.72(8)	27.93(3)	36.67(2)	44.10(3)
K^+	15.98(5)	27.49(3)	36.36(2)	43.79(3)
Rb^+	–	27.35(2)	36.28(2)	43.72(3)
Cs^+	–	27.16(3)	36.22(3)	43.65(5)

[a] m, l, and h for $\log\beta_{mlh} = [M_m L_l H_h]/([M]^m \cdot [L]^l \cdot a_H^h)$.

[2] The difference in $\log K_H$ obtained in different inert-salt solutions (0.1M MNO_3) could also be due to the fact that the diffusion potentials between different inert salts and the solution of the inert salt of the reference electrode are not equal.

The complexation with the earth-alkali ions was studied in more detail, using different total concentrations and metal-to-ligand ratios. Since these phosphonates have eight potential donor groups and so many negative charges, a large number of complexes is conceivable: a series of 1:1 species [MLH_n] with a variable number of protons n, then 2:1 species [M_2LH_m] which also could carry a variable number of protons m, and finally even polynuclear species could be formed.

Since it was not possible to test all the permutations and combinations of those species, we have proceeded in the following way. First we introduced the 1:1 species [MLH_n] with different protonation degree to fit the 90% curve. Then, we checked whether the 180% curve could also be fitted with the same model or whether inclusion of additional species was needed, for example 2:1 complexes [M_2LH_m]. If this was necessary, we went back to the 90% curve keeping the stability constants of the 2:1 species constant and those of the 1:1 species variable, until a rough fit was obtained. Finally, the calculations were run using all titration curves in a batch with the consequence that sometimes species previously introduced had to be removed or additional species had to be included. The final model *(Table 3)*, additionally checked by introducing complexes which looked

Table 3. *Stability Constants of the Macrocyclic Tetrakis(methylenephosphonates)* **1–3** *with Earth-Alkali Ions.* $T = 25°, I = 0.1$.

	M^{2+}	$\log\beta_{mlh}$							
		110[a])	111[a])	112[a])	113[a])	114[a])	210[a])	211[a])	212[a])
1	Mg^{2+}	9.38(5)	20.57(8)	30.60(2)	39.53(2)	46.09(3)	15.75(2)	24.78(2)	
	[b])	7.3	18.12	26.84	35.2	41.59			
	Ca^{2+}	11.12(7)				45.65(4)	18.67(2)	28.32(2)	36.03(2)
	[b])	10.3	19.82	28.34	35.2				
	Sr^{2+}	10.95(2)				45.34(6)	18.35(2)	27.35(2)	34.68(2)
	[b])	9.8	19.32	27.44					
	Ba^{2+}	10.65(2)			38.13(2)		17.12(2)	25.78(2)	
	[b])	8.8	18.22	25.54					
2	Mg^{2+}		19.34(2)	30.42(2)	38.86(2)	45.43(3)	11.38(4)		
	Ca^{2+}			30.23(3)	38.72(3)	45.26(5)	15.90(2)	24.74(3)	
	Sr^{2+}		19.39(5)	28.72(5)	37.33(6)		12.95(2)	22.76(4)	
	Ba^{2+}		19.24(4)	28.94(5)			12.61(2)		
3	Mg^{2+}		19.07(3)	30.35(3)	38.48(2)	45.43(5)			
	Ca^{2+}		19.33(2)	30.18(2)	38.32(2)	45.18(2)			
	Sr^{2+}		18.61(3)	29.64(2)	37.86(2)	45.10(4)			
	Ba^{2+}		18.75(2)	29.64(2)	37.90(2)	45.43(5)			

[a]) For the definition of m, l, and h, see *Table 2, Footnote a.*

[b]) Taken from [14], $I = 1$M (KNO_3).

chemically reasonable or removing species which were present in low concentrations, is the simplest one giving a satisfactory fit as shown by the σ_{ml} value of 0.0015–0.0018 ml for batches of three curves. The results of *Table 3* are mean values of two batches calculated with three curves each. Included also in *Table 3* are the results of *Kabachnik et al.* [14] which differ from ours because of the different supporting electrolytes, but also because of the different models used to explain the measurements. To fit our titration curves, we had to introduce 2:1 species which are completely missing in the model of *Kabatchnik et al.*

A first glance at *Table 3* gives a somewhat unexpected result. The 12-membered macrocycle **1** gives the most stable 2:1 species (*Figs. 3* and *4*), the 13-membered compound **2** still gives a few 2:1 complexes, whereas the 14-membered derivative **3** forms no species of this type at all. An explanation of this is difficult as long as structures are not available. Comparison with the analogous tetraacetates [6] suggests possible reasons. The fact that ligand **1** is prone to give 2:1 species could be due to the inability of the ring to encompass the metal ion within four N-atoms of the macrocycle. Alternatively, the formation of a 2:1 species allows the negative charges of the phosphonate groups to be kept further away and thus to minimize electrostatic repulsions.

Another point taken from *Table 3* is the fact that the stronger the 2:1 species, the less 1:1 species are found. So for **1**, only in the case of Mg^{2+} a series of protonated 1:1 species are found, whereas for **2** and **3**, the 1:1 protonated species predominate over the binuclear ones. The observation that in some cases complex [ML] has not been found is due to the high value of the deprotonation of [MLH] which we could not determine by potentiometric titrations.

A third point to note is the sequence of stability in the series of the earth-alkali ions. For the species [ML], [MLH], $[M_2L]$, and $[M_2LH]$, there is an increase in stability going from Mg^{2+} to Ca^{2+}, followed by a decrease to Sr^{2+} and Ba^{2+}. This trend, however, is not found for the other species such as $[MLH_2]$, $[MLH_3]$, and $[MLH_4]$ for which the highest stability is observed for Mg^{2+} with a steadily decrease in the order Ca^{2+}, Sr^{2+}, and Ba^{2+}. It

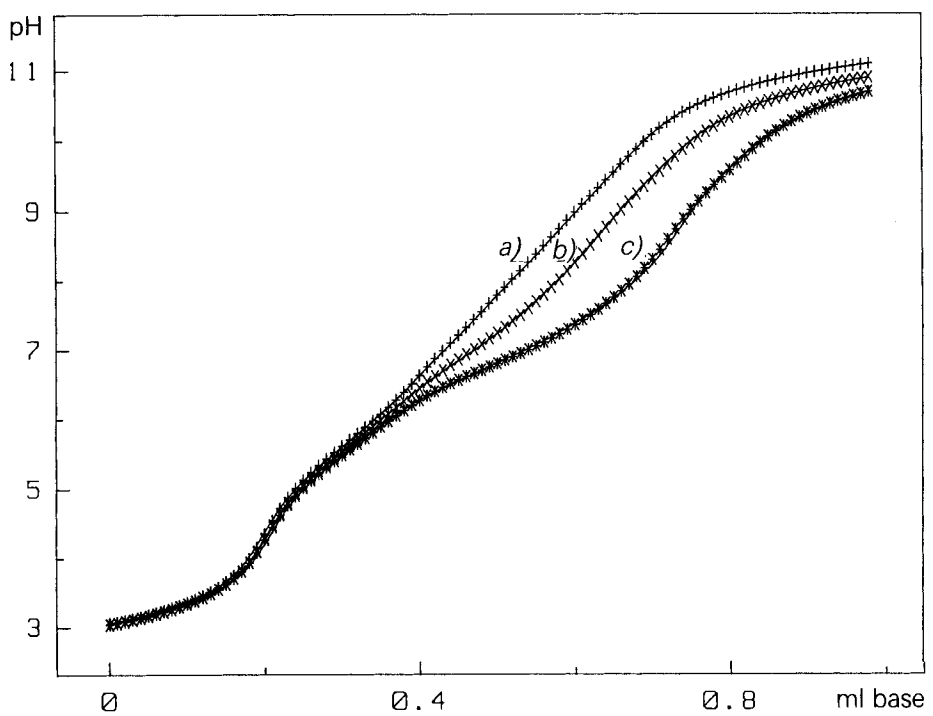


Fig. 3. *Potentiometric titration curves of* **1** ($5.5 \cdot 10^{-4}$ M) *with* a) *45%*, b) *90%, and* c) *180% Ca^{2+} in 0.1 M $Me_4N(NO_3)$ at 25°*. Titrating base, 0.1 M $Me_4N(OH)$.

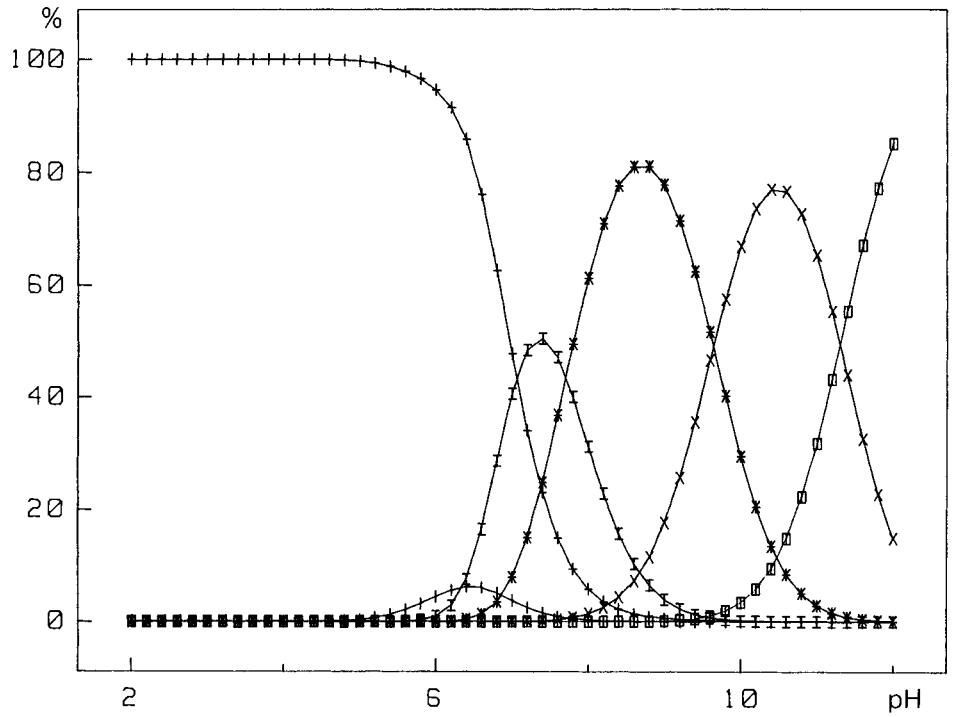


Fig. 4. *Species distribution for* $5.5 \cdot 10^{-4}$ M **1** *and* $4.95 \cdot 10^{-4}$ M Ca^{2+} *calculated with the stability constants of* Table 3. Ca^{2+} (+), $[CaLH_4]^{2-}$ (|), $[Ca_2LH_2]^{2-}$ (I), $[Ca_2LH]^{3-}$ (*), $[Ca_2L]^{4-}$ (×), $[CaL]^{6-}$ (ϕ).

is difficult to state at the moment, whether this is caused by structural differences in the complexes or different donor groups being involved in the coordination of the metal ion [24].

When we compare the complexation behavior of the tetrakis(methylenephosphonates) **1–3** and of the tetraacetates **4–6** [2] with earth-alkali ions, we find that the stabilities of the phosphonates are lower than those of the acetates although the basicity of the former is higher. Similar observations of this type were made by other authors studying analogous open-chain ligands [16]. In addition, the tetraacetates are more selective than the tetraphosphonates. The differences in stability between the different ions are more pronounced for the tetraacetates [2] than for the tetraphosphonates. Finally, the tendency to form 2:1 complexes is relatively strong for the smallest macrocyclic tetraphosphonate, whereas 2:1 species were only observed for the larger rings of the tetraacetates [2].

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