Synthesis and Complexing Properties of Polyazamacrocycles with Pendant *N*-Methylenephosphinic Acid

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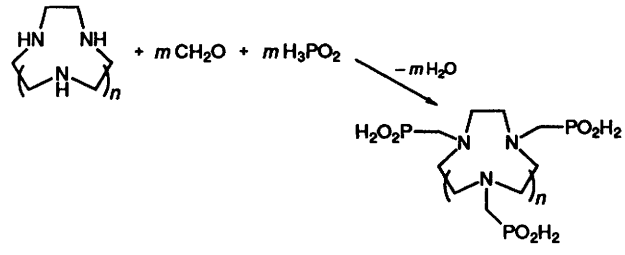
Two new polyazamacrocycles 1,4,7-triazacyclononane-1,4,7-triyltrimethylenetris(phosphinic acid) (H_3L^1) and 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayltetramethylenetetrakis(phosphinic acid) (H_4L^2) were synthesised and their acid–base and complexing properties with Mg^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} determined pH-metrically at 25 °C and at an ionic strength of 0.1 mol dm^{-3} (KNO_3). Both form 1:1 complexes over a wide pH range. The stability constants of H_3L^1 with transition metals lay in a narrow region and point to non-selectivity of the ligand; H_4L^2 forms more stable complexes with larger cations such as Cd^{2+} or Pb^{2+} than with the cations of the first transition row. This selectivity is much better than for analogous macrocycles bearing carboxymethyl or methylenephosphonic pendant groups.

During the past decade a number of studies have focused on polyazacycloalkanes with nitrogen atoms bearing carboxymethyl or alkylphosphonate as pendant groups. In contrast to open-chain ligands, the macrocyclic effect operating in the complexes of these compounds results in strongly variable thermodynamic and kinetic stability, thus offering a further opportunity for tuning properties crucial for biological applications such as paramagnetic contrast agents in magnetic resonance imaging (as lanthanide complexes),[1] therapeutic radiolabelled conjugates of tumour-localizing molecules (complexes with trivalent radionuclides),[2] and sequestering agents for toxic heavy metals such as lead, cadmium and mercury.[3] In addition several reports have dealt with the synthetic and co-ordination properties of polyazamacrocycles with pendant *N*-methylenephosphinic acids.[4–12] In comparison with analogous carboxylic and phosphonic acids, these compounds form complexes with lower stability constants but they have one very important intrinsic advantage: structural variation can readily be achieved within the $>NCH_2P(R)O_2H$ moiety by changing the R group allowing, for example, easy linkage to a protein or the control of ligand and complex lipophilicity. Also, variation of the R group should contribute to improvement of the ion selectivity of the macrocyclic compound.

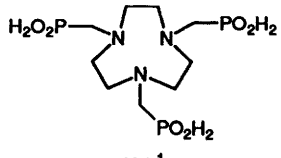
Here we report the synthesis, acid–base and complexing properties of two new fully *N*-substituted polyazamacrocyclic methylenephosphinic acids; 1,4,7-triazacyclononane-1,4,7-triyltrimethylenetris(phosphinic acid) H_3L^1 and 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayltetramethylenetetrakis(phosphinic acid) H_4L^2 as the second part of our work dealing with azacyclic aminomethylenephosphinic acids.[13]

Results and Discussion

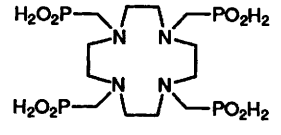
Synthesis.—Compounds H_3L^1 and H_4L^2 were synthesised by Mannich reaction of the macrocyclic amines 1,4,7-triazacyclononane trihydrobromide (tacn·3HBr) and 1,4,7,10-tetraazacyclododecane tetrahydrochloride (tacd·4HCl) with paraformaldehyde and H_3PO_2 in aqueous solution at 40 °C in the absence of HCl (Scheme 1). When the reaction was carried out at 100 °C and in the presence of HCl, it led to a mixture of products (TLC) which was not separated, and under conditions similar to those under which simple cyclic aminomethylenephosphinic ligands have been synthesised (0–20 °C) no conversion was observed. However, we found that at temperatures above



Scheme 1 $n = 1$ or 2; $m = 3$ for $n = 1$, 4 for $n = 2$

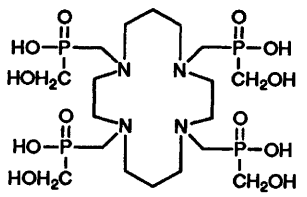


H_3L^1



H_4L^2

30 °C and in the absence of HCl, the required compounds are formed. The optimum temperature was about 40 °C at which the macrocyclic aminomethylenephosphinic compounds were the main products and could be isolated from the reaction mixture. The other by-products have not been isolated. The combination of column chromatography with silica gel and Dowex was very efficient for the separation and purification of both products, and no impurity peaks were found by NMR spectral analysis. This type of reaction was studied by Mollier *et al.*[14] Reaction of 1,4,8,11-tetraazacyclotetradecane (cyclam) with CH_2O and H_3PO_2 at 100 °C led to the formation of a fully *N*-substituted macrocyclic compound 1,4,8,11-tetraazacyclotetradecane-1,4,8,11-tetrayltetramethylenetetrakis(*P*-hydroxymethylphosphinic acid) H_4L^3. The reaction was studied kinetically and a mechanism was proposed. According to this mechanism, H_3PO_2 reacts with formaldehyde and forms



H_4L^3

Table 1 Protonation constants of macrocycles H_3L^1 and H_4L^2 and stability constants of their complexes at 25 °C and I = 0.1 mol dm^{-3}, $\beta_{pqr} = [M_pH_qL_r]/[M]^p[H]^q[L]^r$

				$\log \beta_{pqr}$	
	p	r	q	H_3L^1	H_4L^2
H^+	0	1	1	10.157(7)	10.413(6)
	0	1	2	13.29(1)	17.24(1)
	0	1	3	14.40(2)	19.21(1)
Mg^{2+}	1	1	0	5.32(6)	3.50(5)
	1	1	−1	3.52(1)	
Ca^{2+}	1	1	0	4.29(3)	9.458(6)
	1	1	1		13.4(2)
	1	1	−1	−7.41(6)	−3.6(1)
Co^{2+}	1	1	0	12.97(2)	15.55(2)
	1	1	1		16.9(2)
	1	1	−1		3.16(7)
Ni^{2+}	1	1	0	13.40(2)	15.91(2)
	1	1	1		17.93(9)
Cu^{2+}	1	1	0	13.43(1)	18.03(1)
Zn^{2+}	1	1	0	13.04(1)	14.60(1)
	1	1	1		17.22(2)
Cd^{2+}	1	1	0	12.521(4)	17.34(1)
	1	1	1		18.92(4)
Pb^{2+}	1	1	0	12.519(5)	16.99(1)
	1	1	1		18.95(3)

hydroxymethyl phosphinic acid which subsequently reacts with cyclam and formaldehyde to form H_4L^3. At the same time, a competitive reaction of cyclam with CH_2O and H_3PO_2 takes place and, analogously to H_3L^1 and H_4L^2, H_4L^3 is formed. At 100 °C H_4L^3 reacts rapidly with another CH_2O molecule to form hydroxymethyl phosphinic acid. Thus, H_4L^3 is only an intermediate in this reaction. If we suppose that Mollier's reaction scheme is valid under our conditions, then we can assume that, at high temperatures, analogous *P*-hydroxymethyl-substituted compounds are formed while, at lower temperatures, the competitive reaction which leads to the formation of H_3L^1 and H_4L^2 is preferred and at these temperatures they do not subsequently react to form the *P*-hydroxymethyl compounds. The observed lack of conversion at lower temperatures (0–20 °C) is probably due to the steric hindrance in this reaction so we can affirm that the optimum temperature region is 30–40 °C.

Acid–Base and Complexing Properties.—The calculated values of the protonation and stability constants of H_3L^1 and H_4L^2 are given in Table 1. Typical distribution diagrams for the systems Cu^{2+}–H_3L^1, Ca^{2+}–H_4L^2 and Co^{2+}–H_4L^2, are shown in Figs. 1–3. The variation of δ_P for the macrocycles with the pH is shown in Fig. 4.

Compounds H_3L^1 and H_4L^2 are less basic than the analogous carboxylic[15,16] and phosphonic[17] acids. The values obtained for the protonation constants are in good agreement with literature values for analogous systems.[7,9] The order of the basicities of various aminomethylenephosphinic acids is influenced by the inductive effect of their phosphorus substituents. The present compounds having an H atom as

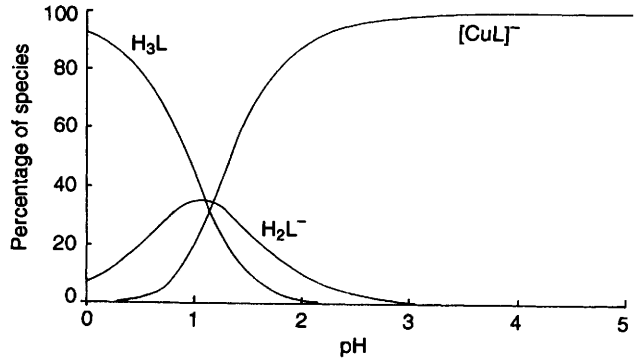


Fig. 1 Distribution diagram of H_3L^1 with Cu^{2+} at 25 °C and I = 0.1 mol dm^{-3} (KNO_3) (c_L = 0.005 and c_{Cu} = 0.005 mol dm^{-3})

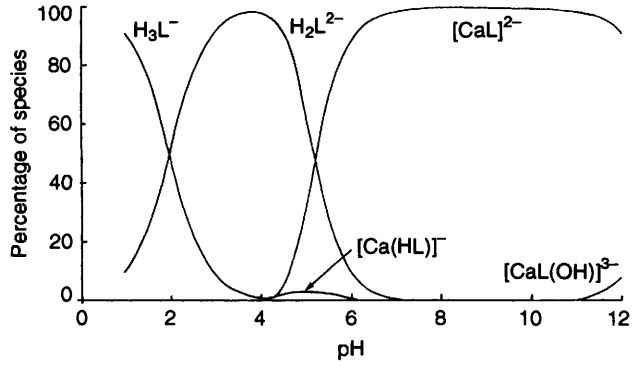


Fig. 2 Distribution diagram of H_4L^2 with Ca^{2+} at 25 °C and I = 0.1 mol dm^{-3} (KNO_3) (c_L = 0.005 and c_{Cu} = 0.005 mol dm^{-3})

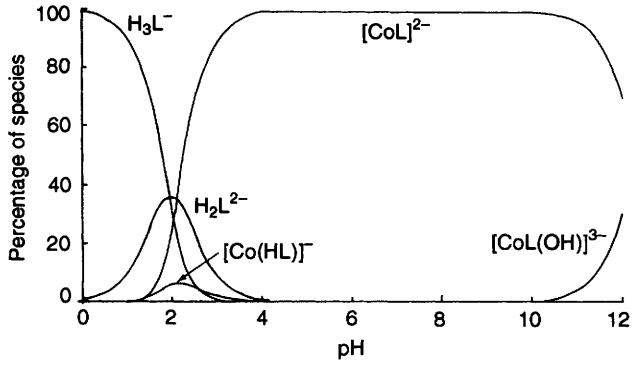


Fig. 3 Distribution diagram of H_4L^2 with Co^{2+} at 25 °C and I = 0.1 mol dm^{-3} (KNO_3) (c_L = 0.005 and c_{Co} = 0.005 mol dm^{-3})

substituent are less basic than all the macrocyclic aminomethylenephosphinic ligands studied so far.[7,9]

Only three dissociation constants of H_3L^1 have been calculated. The potentiometric results correspond to the pH *vs.* δ_P variation (Fig.4). The downfield shift of δ_P in the region pH 3–11 indicates that the first two observed protonations occur on N atoms, which is common in all the studied *N*-substituted carboxylic[18] or phosphonic[19] triazacyclononane systems. In the region pH 1–2.5 where, according to the potentiometric titration curves, the third protonation occurs, an upfield δ_P shift is observed. An analogous upfield shift in the ^{31}P NMR titration curves of phosphonic[19] or phosphinic[20] acids is interpreted as protonation at the phosphonic or phosphinic group, respectively. Thus, we assumed that at least the third protonation involves a phosphinic group. The decrease in the basicity in comparison to the analogous phosphinic acid *P*-substituted with phenyl[7] and with methyl[7] is from one to three pK_a units from pK_3 to pK_1 and corresponds with the phosphinic analogue of glycine.[21] The stability constants of H_3L^1 are the

Table 2 Cation selectivity of macrocyclic ligands

Ligand	$\log(\beta_{Cd}/\beta_{Zn})$	$\log(\beta_{Pb}/\beta_{Zn})$
H_3L^1	−0.48	−0.48
H_4L^2	2.74	2.39
tacd[25]	−2.0	−0.4
a[15]	−2.3	−1.7
b[17]	−5.2	−2.8
c[17]	−1.9	−1.5
d[9]	0.85	—
e[4]	4.0	1.6

[a] 1,4,7-Triazacyclononane-1,4,7-triacetic acid. [b] 1,4,7-Triazacyclononane-1,4,7-triyltrimethylenetris(phosphonic acid). [c] 1,4,7,10-Tetraazacyclododecane 1,4,7,10-tetrayltetramethylenetetrakis(phosphonic acid). [d] Tetraethyl 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrayltetramethylenetetrakis(phosphinate). [e] 1,4,7,10-Tetrakis(2-hydroxypropyl)-1,4,7,10-tetraazacyclododecane.

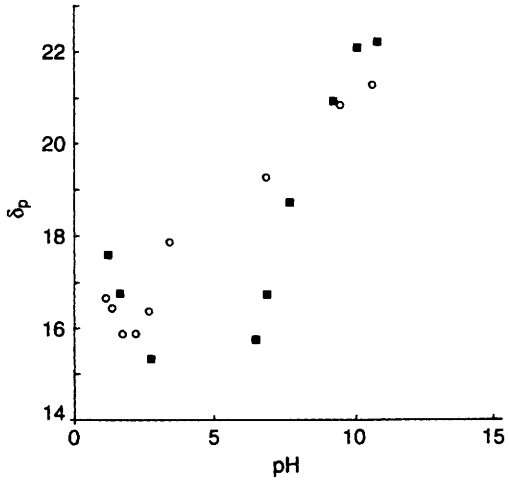


Fig. 4 Variation with pH of δ_P of the methylenephosphinic group for solutions of H_3L^1 (o) and H_4L^2 (■)

first reported for triazacyclononanes with a methylenephosphinic pendant group. This compound forms only 1 : 1 complexes. Complexes with the non-protonated macrocycles were observed for all the metal ions studied but not with the protonated macrocycles. On the other hand, the formation of hydroxo-complexes with Mg^{2+} and Ca^{2+} was observed. The values of log β_{pqr} with the transition metals lay in a narrow range and point to non-selectivity of the ligand. Similar to other triazacyclononane systems,[15] H_3L^1 forms more stable complexes with Mg^{2+} than with Ca^{2+} as a result of the size-match selectivity. The stability constants with Mg^{2+} and Ca^{2+} are very similar to those of the trimethyl 1,4,7-triazacyclononane-1,4,7-triyltris(methylenephosphonate).[22] With Mg^{2+}, Co^{2+} and Ni^{2+} slow complex-formation kinetics has been observed. Such behaviour is common for other triazacyclononane systems.[23]

A comparison of the log β_{110} values of H_3L^1 with the log β_{130} values of the model ligand piperidinomethylphosphinic acid[12] (for systems with Co^{2+} and Ni^{2+}) shows that these values are similar. This could indicate an N_3O_3 co-ordination of H_3L^1. This means of co-ordination has been demonstrated in the crystal structures of complexes of two macrocyclic aminomethylenephosphinic acids.[7,8] As for H_3L^1, only three protonation constants have been calculated for H_4L^2 (Table 1). The fourth protonation constant is too small to be determined by potentiometric titration. There is an increase in basicity from H_4L^2 to the *P*-ethyl substituted derivative: H_4L^1 < *P*-Ph[7] < *P*-Me[7] < *P*-Et derivative.[9]

The ^{31}P NMR titration curve of H_4L^2 has a similar shape to that of the *P*-methyl substituted compound.[4] The upfield shift of δ_P in the region pH 1–3 indicates that, for the same reasons as for H_3L^1, the third and fourth protonations probably involve phosphinic groups and the downfield δ_P shift at higher pH values indicates that the first two protons are also localised on nitrogen atoms.

The compound H_4L^2 forms only 1 : 1 complexes in a wide pH region, for the transition metals from pH 1.5 to 12 (see Table 1). Except for Cu^{2+}, these involve the protonated ligand in the region pH 1–4. Formation of the hydroxo complex was found in the Co^{2+} system. In contrast, with Mg^{2+} and Ca^{2+} the abundance of $[ML]^{2-}$ is lower and its formation is shifted to a higher pH region. The formation of hydroxo complexes in both systems and of $[Ca(HL)]^-$ was also observed.

The pK_a value of the protonated ligand complexes of H_4L^2 with transition-metal ions is about 2, very similar to the ligand pK_2 value. On the basis of the ^{31}P NMR spectra we assumed that the third macrocycle protonation involves a phosphinic group. If this is true, then the similarity of the pK_a value of the $[M(HL)]^-$ to the pK_2 value of the ligand should indicate that the phosphinic group of the complex is protonated. The analogous well known macrocycle 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid forms complexes in which protonation of the carboxylic groups was confirmed by X-ray crystal-structure analysis.[24] For these complexes, an analogous similarity of the pK_a values of mono- and di-protonated ligand complexes to the pK_3 and pK_4 values of the macrocycle was also observed.[16]

According to the values found for log β, H_4L^2 is a stronger complexing agent than H_3L^1 due to its higher basicity and the higher number of donor atoms. The most important feature observed for this ligand is its selectivity for larger cations. It forms more stable complexes with Ca^{2+} and Cd^{2+} than its corresponding *P*-ethyl derivative. The macrocyclic hole size should not be influenced by a substituent at phosphorus, and so the smaller steric hindrance of the hydrogen atom bonded to phosphorus in comparison with the ethyl group should be the main reason. For the smaller cations, the situation is reversed and the factor which determines the stability of the complexes is the ligand basicity.

Hancock[3] has studied the complexing properties of some macrocyclic ligands in order to prepare compounds which could selectively bind larger toxic metal ions like Cd^{2+} and Pb^{2+} and consecutively sequester them from a patient's body. A comparison of complexes with toxic and non-toxic essential metal ions (*i.e.* Zn^{2+}) is important to show whether the ligands can selectively bind the toxic cations. In Table 2 this Cd/Zn and Pb/Zn selectivity (difference between log β of the two metal ions with various ligands) is shown. The selectivity of H_3L^1 and H_4L^2 is comparable with that of Hancock's model 1,4,7,10-tetrakis(2-hydroxypropyl)-1,4,7,10-tetraazacyclododecane[4] but it is probably worse than his 1,4,7,10-tetrakis(carbamoylmethyl)-1,4,7,10-tetraazacyclododecane.[26] As we can see, H_4L^2 exhibits somewhat worse Cd/Zn selectivity than the hydroxypropyl derivative but better Pb/Zn selectivity. The macrocyclic amine tacd prefers the smaller Zn^{2+} to Cd^{2+} or Pb^{2+}. After a systematic study, Hancock suggested that the number of five-membered chelate rings and the co-ordination of neutral oxygen-donor atoms are the main factors which determine the preference of the ligands for the larger metal ions.

Our measurements show that H_4L^2 forms more stable complexes with larger cations while H_3L^1 prefers small cations (probably for reasons of size matching). The former macrocycle does not possess any neutral groups with oxygen donor atoms but negatively charged ones; nonetheless, its selectivity for larger metal ions is comparable to those of Hancock's ligands. Thus, according to our experience we suggest that optimisation of the known three ligand parameters, the actual macrocyclic hole size influenced by pendant groups, the number of five-

membered chelate rings which the ligand can form and the electronic and steric properties of the pendant donor groups, is important for the development of good sequestering agents for heavy toxic metals. It seems that 1,4,7,10-tetraazacyclododecane aminomethylenephosphinic acids could have appropriate properties for use as sequestering agents and further study in this direction would be useful.

Experimental

Synthesis.—Salts of the cyclic amines tacn·4HBr and tacd·4HCl were synthesised using known procedures.[27]

H_3L^1. To a stirred aqueous solution (5 cm^3) of tacn·3HBr (1 g, 2.09 mmol) and H_3PO_2 (1.06 g, 16.14 mmol) was added paraformaldehyde (484 mg, 16.14 mmol) over 1 h at 40 °C. After the paraformaldehyde had dissolved, the reaction mixture was stirred for 3 h at the same temperature. Then the reaction mixture was evaporated (bath temperature 30–40 °C) and codistilled three times with water. The colourless oil was dissolved in water (3 cm^3) and purified by chromatography on a Dowex 50 column (2 × 20 cm) in the H^+ form. The mixture was eluted with water. Fractions containing HBr, H_3PO_2 and a mixture in which H_3L^1 was the main component were gradually eluted. The fractions containing H_3L^1 were combined and water was removed by rotary evaporation. The colourless oil obtained was dissolved in 25% NH_4OH–EtOH (1 : 2, 5 cm^3) and this solution was passed through a silica gel column (7 × 7 cm). The macrocycle was eluted with the same mixture. Fractions containing TLC-pure macrocycle in an ammonium salt form were combined and the solution was evaporated to a colourless oil. This was then dissolved in water (2 cm^3) and passed through a Dowex column in the H^+ form. Pure H_3L^1 was eluted with water. The aqueous solution was evaporated to a colourless oil which was then dissolved in MeOH–EtOH (1 : 1, 10 cm^3). From this solution a white solid was precipitated after standing overnight at 0 °C. The solid was filtered off and dried over P_2O_5. All the reaction and purification steps were monitored by TLC on silica gel using NH_4OH–EtOH (1 : 6) as the mobile phase. Yield 245 mg (25%). B.p. 210 °C [Found (Calc.): C, 28.50 (28.85); H, 6.65 (6.35%)]. NMR (D_2O): ^1H, δ 3.32 (NCH_2P), 3.59 (NCH_2CH_2N) and 7.628 (PH); ^{31}P, δ 15.7 at pD 2.0.

H_4L^2. To a stirred aqueous solution (5 cm^3) of tacd·4HCl (1 g, 3.143 mmol) and H_3PO_2 (1.66 g, 25.15 mmol) was added paraformaldehyde (0.77 g, 25.15 mmol) over 1 h at 40 °C. After the paraformaldehyde had dissolved the solution was maintained at 40 °C for 3 h. The compound H_4L^2 was purified in the same way as H_3L^2 (Dowex, silica gel). The reaction and purification steps were monitored by TLC on silica gel using 25% NH_4OH–EtOH (1 : 2) as the mobile phase. Pure H_4L^2 was isolated by precipitation from its aqueous solution by acetone. The white microcrystalline solid was filtered off and dried over P_2O_5. Yield 440 mg (29%). B.p. 232–234 °C [Found (Calc.): C, 29.25 (29.75); H, 6.60 (6.65)%]. NMR (D_2O): ^1H, δ 3.284 (NCH_2P), 3.429 (NCH_2CH_2N) and 7.625 (PH); ^{31}P, δ 15.2 at pD 2.5.

Chemicals, Stock Solutions for the Potentiometric Titrations.—The stock solutions of the individual metal cations were acidified solutions (pH ≈ 2) of the appropriate nitrates recrystallised from aqueous solutions. Nitric acid was prepared by passing potassium nitrate through a Dowex 50W column in the H^+ form because of traces of NO and NO_2 in the concentrated acid. The metal content in the solutions was determined by titration with ethylenediaminetetraacetate solution and excess of nitric acid was determined by pH-metric acid–base titration.

Potentiometric Titrations.—Potentiometric measurements were carried out using a PHM 84 pH-meter, ABU 80 autoburette and a GK 2401 B combination electrode (Radiometer) in a glass vessel (10 cm^3) thermostatted at 25 ± 0.1 °C at an ionic strength of $I(KNO_3)$ = 0.1 mol dm^{-3}. An inert atmosphere was ensured by constant passage of argon saturated with the solvent vapour. The initial solution volume was 5 cm^{-3} and the macrocycle concentration was 0.005 mol dm^{-3}. In the determination of the stability constants of the transition-metal complexes, the metal : macrocycle concentration ratio was mostly 1 : 1, and incidentally 1 : 2 to confirm stoichiometry. The total number of data points was more than 200. After calibration using two buffers, precision calibration was carried out by titration of 0.015 mol dm^{-3} HNO_3 with 0.2 mol dm^{-3} KOH in 0.1 mol dm^{-3} KNO_3 in the region pH 1.8–12.0, with the pH-meter yielding E values. The relation between E and $-\log[H^+]$ is expressed by equation (1)

$$E = E_0 - S(-\log[H^+]) + j_a[H^+] + j_b(K_w/[H^+]) \quad (1)$$

where the additive term E_0 contains the standard potentials of the electrodes used and contributions of inert ions to the liquid-junction potential, S corresponds to the Nernstian slope the value of which should be close to the theoretical one and $j_a[H^+]$ and $j_b[OH^-]$ are contributions of the H^+ and OH^- ions to the liquid-junction potential. It is clear that j_a and j_b cause deviation from a linear dependence between E and $-\log[H^+]$ only in strong acid and strong base. The equation was manipulated with the program ESAB.[28] The values of E_0, S, j_a and j_b at pK_w = 13.75 were calculated for each calibration and then used to determine $-\log[H^+]$ values from the E titration values of each series of measurements.

The stability and protonation constants β_{pqr} are concentration constants defined as $\beta_{pqr} = [M_pH_qL_r]/[M]^p[H]^q[L]^r$. They were calculated using the MINIQUAD 82 program.[29] The complex-formation kinetics in systems Co^{2+}–H_3L^1, Ni^{2+}–H_3L^1, Mg^{2+}–H_3L^1 and Ni^{2+}–H_4L^2 was too slow to use the above-mentioned potentiometric method for the determination of the stability constants so an 'out-of-cell' potentiometric method was used. For each system three series of thirty solutions with a volume of 1 cm^3 were prepared in special glass tubes (5 cm^3). The ionic strength, metal and ligand concentrations were the same as in the previous potentiometric measurements. After the preparation of the solutions a different amount of 0.2 mol dm^{-3} KOH was added to each solution (under an argon atmosphere) and the E values measured with the electrode calibrated as described above. The same measurement was repeated at regular time intervals (6 h). According to the pH values found for each system, the Co^{2+}–H_3L^1 and Ni^{2+}–H_3L^1 systems reached equilibrium after 12 h the Co^{2+}–H_4L^2 system after 6 h and the Mg^{2+}–H_3L^1 system after 48 h. The stability constants were calculated as above.

NMR Spectra.—Spectra used for the characterisation of the macrocycles were measured using a Varian XL-200 instrument at 25 °C: ^1H at 200.057 MHz with sodium 4,4-dimethyl-4-silapentanesulfonate as the internal standard and ^{31}P at 80.53 MHz with 85% H_3PO_4 as the external standard. The measured solutions were about 10% (w/v) in D_2O. The ^{31}P NMR titration measurements were carried out using a Tesla 80 instrument at 32.35 MHz and with 85% H_3PO_4 as the external standard. Owing to the small quantities of the macrocycles only one solution (about 10% w/v in water) of each was prepared and the pH adjusted by the addition of 0.1 mol dm^{-3} KOH or HNO_3.

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References

1 C. F. G. C. Geraldes, R. D. Brown III, W. P. Cacheris, S. H. Koenig, A. D. Sherry and M. Spiller, *Magn. Reson. Med.*, 1989, **9**, 84; R. B. Lauffer, *Chem. Rev.*, 1987, **87**, 90.
2 D. Parker, *Chem. Soc. Rev.*, 1990, 271; S. Jurrisson, D. Berning, W. Jia and D. Ma, *Chem. Rev.*, 1993, **93**, 1137; Y.-F. Liu and C. Wu, *Pure Appl. Chem.*, 1991, **63**, 427.
3 R. Hancock, in *Perspectives in Coordination Chemistry*, eds. A. F. Williams, C. Floriani and A. E. Nurbach, Verlag Helv. Chim. Acta, Basel, 1992, p. 129.
4 C. J. Broan, K. J. Jankowski, R. Kataky and D. Parker, *J. Chem. Soc., Chem. Commun.*, 1990, 1738.
5 K. P. Pulukkody, T. J. Norman, D. Parker, L. Royle and C. J. Broan, *J. Chem. Soc., Perkin Trans. 2*, 1993, 605.
6 D. Parker and M. A. W. Eaton, *Eur. Pat. Appl.*, 90 301 477.7, 1990.
7 E. Cole, D. Parker, G. Ferguson, J. F. Gallagher and B. Kaitner, *J. Chem. Soc., Chem. Commun.*, 1991, 1473.
8 E. Cole, R. C. B. Copley, J. A. K. Howard, D. Parker, G. Ferguson, J. F. Gallagher, B. Kaitner, A. Harrison and L. Royle, *J. Chem. Soc., Dalton Trans.*, 1994, 1619.
9 I. Lazar, A. D. Sherry, R. Ramasamy, E. Brucher and R. Kiraly, *Inorg. Chem.*, 1991, **30**, 5016.
10 C. J. Broan, K. J. Jankowski, R. Kataky, D. Parker, A. M. Randall and A. Harrison, *J. Chem. Soc., Chem. Commun.*, 1990, 1739.
11 C. J. Broan, E. Cole, K. J. Jankowski, D. Parker, K. Pulukkody, B. A. Boyce, N. R. A. Beeley, K. Millar and A. Millican, *Synthesis*, 1992, 63.
12 D. Parker, K. Pulukkody, T. J. Norman, A. Harrison, L. Royle and C. Walker, *J. Chem. Soc., Chem. Commun.*, 1992, 1441.
13 I. Lukeš, K. Bazakas, P. Hermann and P. Vojtíšek, *J. Chem. Soc., Dalton Trans.*, 1992, 939.
14 H. Mollier, M. Vincens, M. Vidal, R. Pasqualini and M. Duet, *Bull. Soc. Chim. Fr.*, 1991, **128**, 787.
15 A. E. Martell and E. T. Clarke, *Inorg. Chim. Acta*, 1991, **181**, 273
16 A. E. Martell and E. T. Clarke, *Inorg. Chim. Acta*, 1991, **190**, 2736.
17 M. I. Kabachnik, T. J. Medved, J. M. Polikarpov, B. K. Shcherbakov, F. I. Belskii, E. I. Matrosov and M. P. Pasechnik; *Izv. Akad. Nauk SSSR, Ser. Chim.*, 1984, 835; J. M. Polikarpov, F. I. Belskii, T. J. Medved, S. A. Pisareva and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Chim.*, 1989, 21125.
18 C. F. G. C. Geraldes, A. D. Sherry, M. P. M. Marques, M. C. Alpoim and S. Cortes, *J. Chem. Soc., Perkin Trans. 2*, 1991, 137.
19 C. F. G. C. Geraldes, A. D. Sherry and W. P. Cacheris, *Inorg. Chem.*, 1989, **28**, 3336.
20 I. Lukeš, P. Hermann and P. Pech, *Collect. Czech. Chem. Commun.*, 1989, **54**, 653.
21 I. Lukeš and J. Rohovec, unpublished work.
22 I. Lazar, R. Ramasamy, E. Brucher, C. F. G. C. Geraldes and A. D. Sherry, *Inorg. Chim. Acta*, 1992, **195**, 89.
23 S. Cortes, E. Brucher, C. F. G. C. Geraldes and A. D. Sherry, *Inorg. Chem.*, 1990, **29**, 55.
24 A. Riesen, M. Zehnder and T. A. Kaden, *Helv. Chim. Acta*, 1986, **69**, 2067.
25 A. E. Martell and R. M. Smith, *Critical Stability Constants*, Plenum, New York, 1974–1989, vols. 1–6.
26 L. Carlton, R. D. Hancock, H. Maumela and K. P. Wainwright, *J. Chem. Soc., Chem. Commun.*, 1994, 1007.
27 H. Koyama and T. Yoshino, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 481; W. D. White, B. A. Karcher, R. A. Jakobson and J. G. Verkade, *J. Am. Chem. Soc.*, 1979, **101**, 4921; E. Brucher, S. Cortes, F. Chavez and A. D. Sherry, *Inorg. Chem.*, 1991, **30**, 2092; D. W. Swinkels, J. P. M. Duynhoven, C. W. Hilbers and G. I. Tesser, *Recl. Trav. Chim. Pays-Bas*, 1991, **110**, 124.
28 G. Arena, E. Rizzarelli, S. Sammartano and C. Rigano, *Talanta*, 1979, **26**, 1; C. Rigano, M. Grasso and S. Sammartano, *Ann. Chim. (Rome)*, 1984, **74**, 537; C. De Stefano, P. Princi, C. Rigano and S. Sammartano, *Ann. Chim. (Rome)*, 1987, **77**, 643
29 A. Sabatini, A. Vacca and P. Gans, *Talanta*, 1974, **21**, 53.

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