Synthesis, Protonation and Co-ordination Abilities of the Open-chain Polyamine 4,8,11,15-Tetraazaoctadecane-1,18-diamine *

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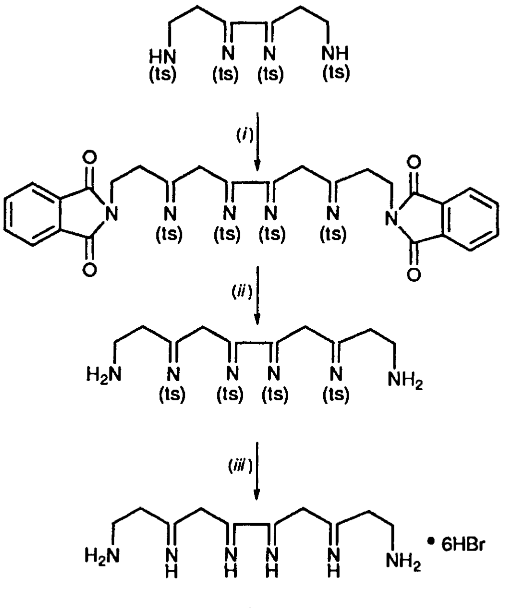
The new open-chain polyamine 4,8,11,15-tetraazaoctadecane-1,18-diamine has been synthesised and characterized. The acid–base behaviour and the co-ordination abilities towards Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} have been studied by potentiometry at 298.1 K in 0.15 mol dm^{-3} $NaClO_4$, as well as by ^1H and ^{13}C NMR spectroscopy. The protonation pattern shows the effects produced by the presence of primary and secondary nitrogen atoms as well as ethylenic and propylenic hydrocarbon chains within the molecule. The stability and spectroscopic data show that at most four of the six nitrogens present are involved in co-ordination to the different metal ions. The contrast to other hexaamines, this compound is able to form binuclear species with all the metal ions studied. Formation of predominant binuclear hydroxo species has been detected in a number of systems.

In the last few years[1] much effort has been devoted to the synthesis and characterization of large cyclic saturated polyamines able to enclose more than one metal ion within their macrocyclic framework as well as to strongly interact when protonated with anionic substrates. Among these, macrocycles of the [3*k*]aneN$_k$ (k = 5–12) series have been extensively investigated.[2] One conclusion derived from such studies concerned the great flexibility of the ligands which can rearrange themselves around the different metal ions better to match their stereochemical requirements.[3–5] Recently, some of us[6–8] reported that open-chain polyamines containing similar numbers and type of nitrogen donors yielded very similar metal co-ordination chemistry, both in terms of the equilibrium speciation and of the stabilities of the different complexes formed.

Despite these findings, the literature describing the co-ordination characteristics of long-chain polyamines is much scarcer than that of their cyclic analogues. Therefore, to get further insight into the chemistry of long open-chain polyamines we have synthesised the compound 4,8,11,15-tetraazaoctadecane-1,18-diamine (L^1) which contains a symmetrical array of four propylenic and one central ethylenic chain connecting the set of nitrogen atoms. We also report on its protonation behaviour and co-ordination tendencies towards the bivalent metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}.

Experimental

Synthesis of 4,8,11,15-*Tetraazaoctadecane*-1,18-*diamine* (L^1).—The synthesis of compound L^1 was carried out by the general synthetic route depicted in Scheme 1.



L^1• 6HBr

Scheme 1 (*i*) *N*-(3-Bromopropyl)phthalimide, K_2CO_3, tetrahydrofuran, reflux; (*ii*) N_2H_4, EtOH, reflux; (*iii*) HBr, acetic acid, reflux

N,*N*′,4,7-Tetrakis(*p*-tolylsulfonyl)-4,7-diazadecane-1,10-diamine was prepared as described in ref. 9.

1,18-*Phthalimido*-4,8,11,15-*tetrakis*(p-*tolylsulfonyl*)-4,8,11,15-*tetraazaoctadecane* **2**. The tosylated amine **1** (5 g, 6 mmol) and K_2CO_3 (3.5 g, 25 mmol) were suspended in refluxing MeCN (75 cm^3). To this mixture was added dropwise a solution of *N*-(3-bromopropyl)phthalimide (5.09 g, 1.9 mmol) in MeCN (50 cm^3). After the addition was complete, the suspension was

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* *Non-SI unit employed:* cal = 4.184 J.

refluxed for 3 d and then filtered. The solution was vacuum evaporated to dryness, and the residue suspended in refluxing ethanol to give **2** as a white solid (yield 60%), m.p. 173–175 °C; $\delta_H(CDCl_3)$ 1.84–1.85 (m, 8 H), 2.38 (2, 6 H), 2.39 (s, 6 H), 3.11–3.20 (m, 12 H), 3.30 (s, 4 H), 3.64 (t, J = 7 Hz, 4 H), 7.23–7.30 (m, 8 H) and 7.60–7.79 (m, 16 H); $\delta_C(CDCl_3)$ 21.5, 27.8, 28.7, 35.6, 46.4, 46.8, 48.1, 49.1, 123.2, 127.2, 127.3, 129.8, 129.9, 132.1, 133.9, 143.3, 143.5 and 168.2.

4,8,11,15-*Tetrakis*(p-*tolylsulfonyl*)-4,8,11,15-*tetraazaoctadecane*-1,18-*diamine* **3**. A mixture of compound **2** (5 g, 4.4 mmol) and hydrazine hydrate (85%, 3 cm^3, 60 mmol) in ethanol (20 cm^3) was refluxed for 24 h, then cooled and the resulting solid filtered off. The solution was vacuum evaporated to dryness and the solid recrystallized from hexane–ethyl acetate to give **3** (yield 50%), m.p. 121–122 °C; $\delta_H(CDCl_3)$ 1.64–1.69 (m, 4 H), 1.89–1.93 (m, 4 H), 2.24 (br, 4 H), 2.39 (s, 6 H), 2.41 (s, 6 H), 2.72 (t, J = 7 Hz, 4 H), 3.10–3.18 (m, 12 H), 3.31 (s, 4 H), 7.26–7.33 (m, 4 H) and 7.64–7.70 (m, 8 H); $\delta_C(CDCl_3)$ 21.4, 21.5, 28.7, 32.1, 38.9, 46.6, 46.7, 48.2, 49.2, 127.1, 127.3, 129.7, 129.9, 135.2, 136.0, 143.3 and 143.6.

4,8,11,15-*Tetraazaoctadecane*-1,18-*diamine hexa*(*hydrobromide*) $L^1\cdot6HBr$. The tetratosylated amine **3** (3.76 g, 4 mmol) and phenol (5.9 g, 60 mmol) were suspended in HBr–acetic acid (33%, 114 cm^3). The mixture was stirred at 90 °C for 48 h and then cooled; the resulting solid was filtered off and washed several times with CH_2Cl_2 to give **4** (yield 90%), m.p. 292–294 °C; $\delta_H(D_2O)$ 1.95–2.12 (m, 8 H), 3.02 (t, J = 7.9 Hz, 4 H), 3.07–3.21 (m, 12 H) and 3.42 (s, 4 H). $\delta_C(D_2O)$ 23.5, 24.5, 37.4, 43.9, 45.3, 45.6 and 45.9 (Found: C, 21.7; H, 5.2; N, 10.9. Calc. for $C_{14}H_{42}Br_6N_6$: C, 21.80; H, 5.20; N, 10.90%).

Electromotive Force Measurements.—The potentiometric titrations were carried out, in 0.15 mol dm^{-3} $NaClO_4$ at 298.1 ± 0.1 K, by using the experimental procedure (burette, potentiometer, cell, stirrer, microcomputer, *etc.*) fully described elsewhere.[10] The acquisition of the e.m.f. data was performed with the computer program PASAT.[11] The reference electrode was an Ag–AgCl electrode in saturated KCl solution. The glass electrode was calibrated as an hydrogen-ion concentration probe by titration of well known amounts of HCl with CO_2-free NaOH solutions and determining the equivalence point by Gran's method,[12] which gives the standard potential, $E^{\circ\prime}$, and the ionic product of water [pK_w = 13.73(1)]. The concentrations of the different metal ions employed were determined gravimetrically by standard methods.

The computer program SUPERQUAD[13] was used to calculate the protonation and stability constants. The titration curves for each system (*ca.* 200 experimental points corresponding to at least three measurements, pH range investigated 2–10, concentration of metals and L′ ranging from 1×10^{-3} to 5×10^{-3} mol dm^{-3}) were treated either as a single set or as separate curves without significant variations in the values of the stability constants. Finally, the sets of data were merged and treated simultaneously to give the stability constants.

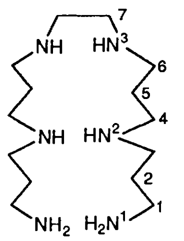
Microcalorimetry.—The enthalpies of protonation of the amines were determined in 0.15 mol dm^{-3} $NaClO_4$ at 298.1 K by means of an automated system comprising a Thermometric AB thermal-activity monitor (model 2277) equipped with a perfusion/titration device and a Hamilton pump (model Microlab M) coupled with a gas-tight Hamilton syringe (250 cm^3) (model 1750 LT). The microcalorimeter was checked by determining the enthalpy of reaction of a strong base (NaOH) with a strong acid (HCl). The value obtained, −13.55(5) kcal mol^{-1}, was in agreement with literature values.[14] Further checks were performed by determining the enthalpies of protonation of ethylenediamine. In a typical experiment a NaOH (0.15 mol dm^{-3}, addition volumes of 15 µl) solution was added to 1.5 cm^3 solutions of the free amine (0.01–5×10^{-3} mol dm^{-3}). Corrections for the heat of dilution were applied. Under the reaction conditions and employing the determined equilibrium constants, the concentrations of each species present in solution before and after each addition were calculated and the corresponding enthalpies of reaction determined from the calorimetric data by means of the KK88 program.[15] At least three titrations were performed. The titration curves for each system were treated either as a single set or as separate entities without significant variations in the values of the enthalpy changes.

Spectroscopy.—The ^1H and ^{13}C NMR spectra were recorded on Varian UNITY 300 and 400 spectrometers, operating at 299.95 and 399.95 MHz for ^1H and at 75.43 and 100.58 MHz for ^{13}C, at room temperature in D_2O or $CDCl_3$ solutions. For the ^{13}C NMR spectra dioxane was used as a reference (δ 67.4) and for the ^1H spectra the solvent signal. The ^{113}Cd NMR spectra were recorded on a Varian UNITY 300 spectrometer at 88.73 MHz using $Cd(ClO_4)_2\cdot4H_2O$ as external reference, UV/VIS with a Perkin Elmer Lambda 9 spectrophotometer and X-band ESR spectra of frozen solutions at 130 K with a Bruker ER 2000D spectrometer.

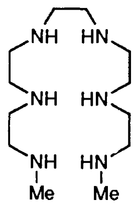
Results and Discussion

Protonation.—The behaviour of L^1 towards protonation has been studied in 0.15 mol dm^{-3} $NaClO_4$ solution at 298.1 ± 0.1 K. In Table 1 are presented the basicity constants of L^1 together with those of the open-chain hexamines *N*,*N*′-dimethyl-3,6,9,12-tetraazatetradecane-1,14-diamine (L^2)[6] and 4,8,12,16,19-pentaazanonadecane-1,19-diamine (L^3)[16] and the cyclic ones 1,5,9,13,17,21-hexaazacyclotetracosane (L^4)[16] and 1,4,7,10,13,16-hexaazacyclooctadecane (L^5).[17]

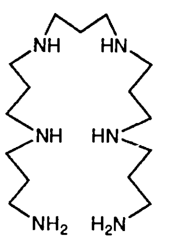
Several general comments can be made. First, as is generally observed, the presence of propylenic spacers between the nitrogen atoms yields higher basicity than that of ethylenic ones because of the reduced repulsions between polyammonium



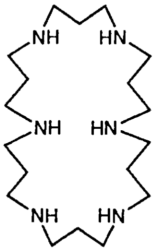
L^1



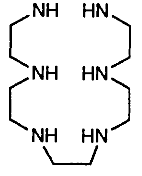
L^2



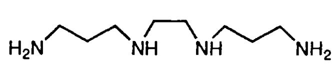
L^3



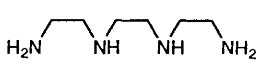
L^4



L^5



L^6



L^7

Table 1 Logarithms of the protonation constants

Reaction	log K L^1	L^2	L^3	L^4	L^5	L^6
$L + H \rightleftharpoons HL$	10.83(4)[b]	10.28[c]	10.10[d]	10.50[d]	10.15[e]	10.53[f]
$HL + H \rightleftharpoons H_2L$	10.15(5)	9.52	10.10	10.20	9.48	9.77
$H_2L + H \rightleftharpoons H_3L$	9.30(4)	8.84	9.30	9.25	8.89	8.30
$H_3L + H \rightleftharpoons H_4L$	8.45(5)	6.54	8.70	8.00	4.27	5.59
$H_4L + H \rightleftharpoons H_5L$	7.30(5)	3.80	7.70	7.05	2.21	
$H_5L + H \rightleftharpoons H_6L$	4.98(6)	2.51	7.00	6.40	1.0	

[a] Charges have been omitted for clarity. [b] This work. Values determined at 298.1 K in 0.15 mol dm^{-3} NaClO$_4$. [c] Values taken from ref. 6; 298.1 K, 0.15 mol dm^{-3} NaClO$_4$. [d] Values taken from ref. 16; 298.1 K, 0.1 mol dm^{-3} sodium toluene-*p*-sulfonate. [e] Values taken from ref. 17; 298.1 K, 0.15 mol dm^{-3} NaClO$_4$. [f] Taken from ref. 18, 298 K, 0.1 mol dm^{-3}.

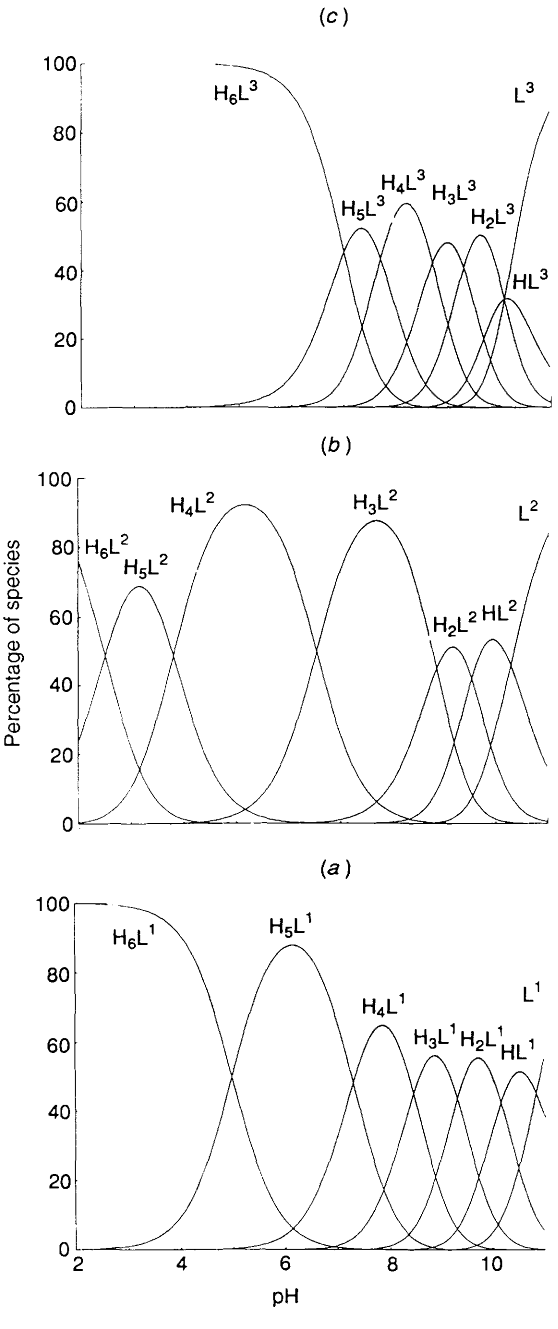


Fig. 1 Distribution diagrams for the species in equilibria as a function of pH in the systems (*a*) L^1–H^+, (*b*) L^2–H^+ and (*c*) L^3–H^+. Amine concentration 1 × 10^{-3} mol dm^{-3}

sites (see for instance the basicity constants for L^1–L^3).[16,19,20] The first five protonation constants of L^1 are high and compare well with those reported for the analogous open-chain polyamine with just propylenic chains, L^3. The sixth protonation constant of L^1 is, however, appreciably lower than that of L^3. This can be ascribed to the fact that the last protonation of L^1 should take place on one of the central ethylenic nitrogens which are separated from the adjacent polyammonium groups by an ethylenic and a propylenic chain. A similar event is observed in the last protonation step of the tetraamine 4,7-diazadecane-1,10-diamine (L^6)[18] which displays a symmetrical arrangement of two propylenic and one ethylenic chains between the nitrogens. The effects of the charge repulsions on the basicity constants of the polyamines is reflected in the distribution diagrams for L^1–L^3 (Fig. 1); while the fully protonated species of L^1, $[H_6L^1]^{6+}$, predominates at pH 3, L^2 is just in its pentaprotonated form and L^3 containing all propylenic spacers, would be already fully protonated around pH 6.

The high positive charge L^1 can accumulate around neutral pH makes it, on the other hand, a promising potential receptor for anionic species in aqueous solution. We are carrying out studies on this aspect.

A further comment can be made on the basicities of open-chain and cyclic polyamines. When the open-chain polyamines L^1 and L^3 are compared with the cyclic one L^4 it can be noticed that, in these large ligands with propylenic chains, the cyclic topology does not produce significantly higher charge accumulations in the cyclic ligands with respect to the analogous open-chain ones. Therefore, the basicity displayed by both types of ligand is similar. The effect of the charge accumulation induced by the cyclic topology is much larger in the case of the ligands with just ethylenic chains as can be seen when comparing the data for L^2 and L^5.

In Table 2 are shown the stepwise enthalpies for the protonation of L^1 as determined by direct microcalorimetry, as well as the calculated entropic contributions. For comparison, also given are the enthalpy and entropy terms reported for the tetraamine L^6 and for 3,6-diazaoctane-1,8-diamine (L^7) containing all ethylenic chains.[18] In the case of L^1 all the protonation steps are mainly enthalpy driven, the entropy terms being slightly favourable for the first three protonation steps, close to zero for the fourth and increasingly unfavourable for the last two. Of note is the decrease in exothermicity of 1.6 kcal mol^{-1} between the fifth and sixth protonation stages which, again, may reflect the higher electrostatic repulsion between polyammonium sites occurring when the last proton is attached to the amine. This decrease in the enthalpy term can be compared with that reported for the third and fourth protonation steps of L^6. The enthalpy term for the last protonation of L^7, in which the entering proton should be placed between two already protonated nitrogens separated by ethylenic chains and therefore yielding shorter-range electrostatic interactions, is much lower ($\Delta H° = -6.8$ kcal mol^{-1}).[18]

Table 2 Enthalpy and entropy terms (kcal mol^{-1}) for the stepwise protonation of L^1 and related polyamines

	$-\Delta H^\circ$			$T\Delta S^\circ$		
Reaction[a]	L	L^5	L^6	L	L^5	L^6
$L + H \rightleftharpoons HL$	13.11(6)[b]	12.35[c]	11.0[c]	1.7(1)	2.0	2.4
$HL + H \rightleftharpoons H_2L$	11.93(6)	12.38	11.3	1.9(1)	1.0	1.2
$H_2L + H \rightleftharpoons H_3L$	11.63(6)	12.8	9.5	1.1(1)	1.0	−0.6
$H_3L + H \rightleftharpoons H_4L$	11.97(8)	10.3	6.8	−0.4(1)	−0.5	−2.4
$H_4L + H \rightleftharpoons H_5L$	11.1(1)			−1.1(2)		
$H_5L + H \rightleftharpoons H_6L$	9.5(1)			−2.7(2)		

[a] Charges have been omitted for clarity. [b] Values in parentheses are standard deviations in the last significant figure. [c] Values taken from ref. 18; 0.1 mol dm^{-3}, 298.1 K.

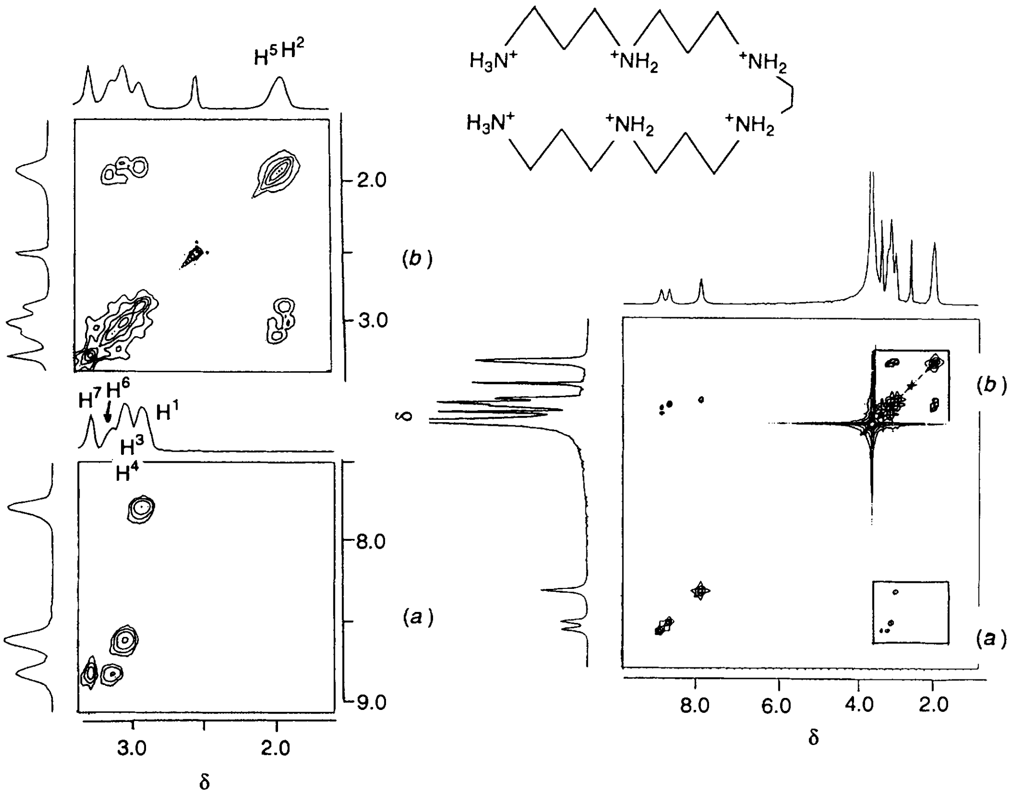


Fig. 2 The ^1H–^1H two-dimensional NMR homonuclear correlation spectrum of the fully protonated ligand (L^1) at pH 3 in dmso

To perform a more thorough analysis of the protonation of L^1 we recorded its ^1H and ^{13}C NMR spectra at different pH values. At pH 3, where $[H_6L^1]^{6+}$ predominates, the propylenic chain protons present two different $A_2B_2C_2$ [J_{AB} = 7.5, J_{BC} = 8.0 Hz) spin systems and the protons of the ethylenic chain (H^7) appear as a singlet (A4) as a consequence of the equivalence of the hydrogens on each carbon atom. The spectral features indicate the presence of a binary element of symmetry in the molecule. The singlet of the ethylenic protons may serve as starting point fully to assign the different signals. The spectrum of L^1·6HBr in dimethyl sulfoxide (dmso) is practically the same as that obtained in D_2O at pH 3, and is of great help for fully identifying all the signals. Since the exchange of the amine hydrogens in dmso is very slow within the NMR time-scale, it is possible to observe, in addition to the resonances of the aliphatic protons, three signals for these amine protons at δ 7.79, 8.59 and 8.79 integrating as 6:4:4. From ^1H–^1H two-dimensional experiments (Fig. 2) the latter signals can be correlated to the resonances of the methylenic and propylenic protons. For instance, the signal at δ 8.79 presents cross-peaks with the singlet of the ethylenic chain protons (H^7) and with another signal belonging to the propylenic chains (H^6); the signal at δ 7.79 presents just one correlation with that of H^1. The ^{13}C NMR spectrum in D_2O consists, at this pH, of seven different signals corresponding to half of the carbon atoms present in the molecule. From the ^1H–^1H and ^1H–^{13}C two-dimensional correlations, all these signals can be unequivocally assigned (Fig. 3) throughout the pH range and a detailed analysis of the variations of the chemical shifts allows one to establish a protonation sequence (see Fig. 4).

When the pH is increased the proton chemical shifts move upfield and the carbon ones downfield but the proton NMR pattern as well as the number of ^{13}C signals are the same independently of pH. In the range pH 3–6, where the first proton leaves the molecule, only slight variations in the chemical shifts of H^6 and H^7 occur, but between pH 6 and 8, corresponding to loss of the second proton, more pronounced variations in the chemical shifts are observed for hydrogens such as H^6 and H^7, in α position with respect to the central nitrogens (N^3), and for carbons C^5 and C^7 located in β position to these nitrogens. These variations would account for these last two protonation steps mainly affecting both central nitrogens of L^1, in such a way that while loss of the first proton still leaves the second one exchanging between both equivalent ethylenic

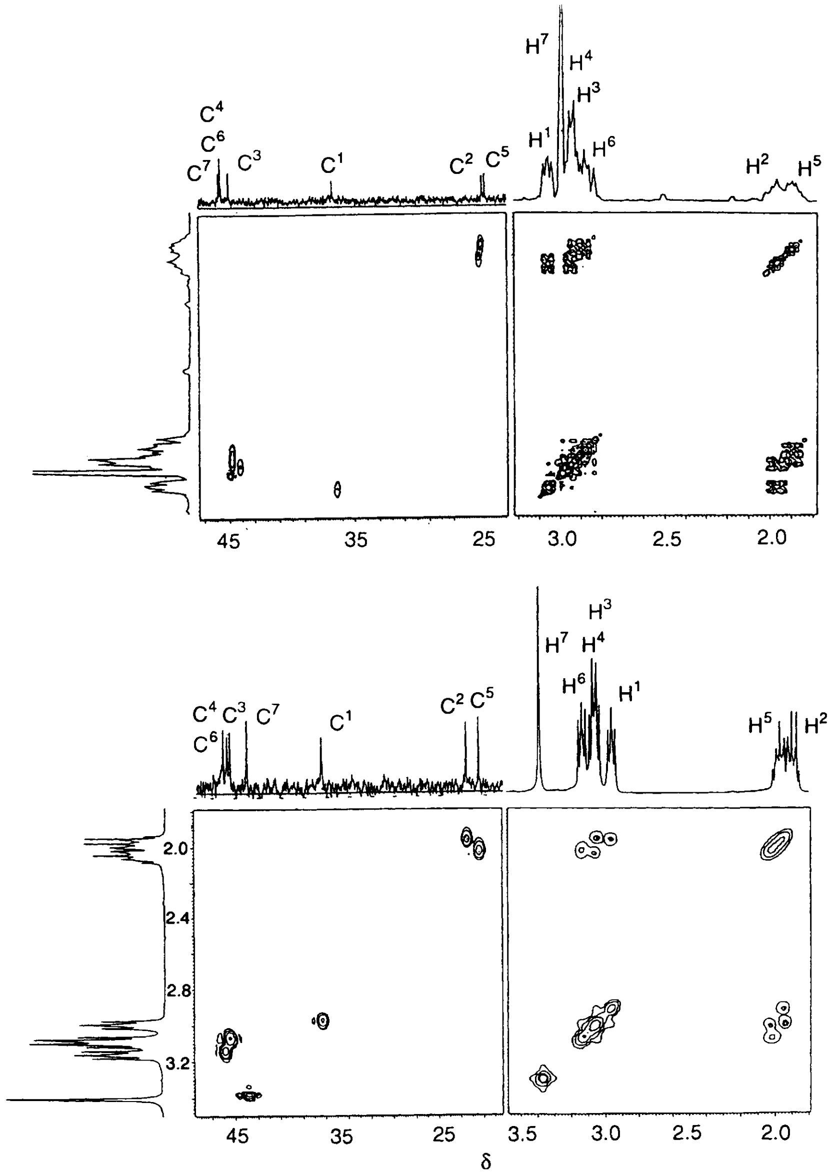


Fig. 3 The $^1H-^1H$ and $^1H-^{13}C$ two-dimensional NMR correlation spectra of $[H_6L^1]^{6+}$ (pH 3, lower) and $[H_3L^1]^{3+}$ (pH 9.5, upper) in D_2O

nitrogens (N^3), the removal of the second proton results in a more drastic reduction of the positive charge on both central nitrogens.

In the range pH 8–10 where the main species in solution are $[H_4L^1]^{4+}$, $[H_3L^1]^{3+}$ and $[H_2L^1]^{2+}$ the significant downfield shift of the C^2 and C^5 resonances in the ^{13}C NMR spectra as well as the upfield shifts of the H^3 and H^4 signals in the ^1H NMR spectra indicate an involvement of N^2, located between the propylenic chains, in these protonation steps. Finally, from pH 10 to 12, the most significant feature is the clear downfield shift experienced by C^2 which confirms that the terminal primary nitrogens are the atoms mainly involved in the first two protonation steps.

Therefore, although it has to be pointed out that these are time-averaged situations and the protons seem not to be so fixed on individual nitrogens as was observed for compounds with only ethylenic chains, on summarizing all these data the following protonation model may be advanced: (*i*) the first two protonations of L^1 mainly occur at the terminal primary nitrogens; (*ii*) the next two protons will bind the nitrogens in the middle of the propylenic chains (N^2); and (*iii*) the last two protons bind to the ethylenic chain nitrogens.

Metal Co-ordination.—In Tables 3 and 4 we report the stability constants for the formation of mono- and bi-nuclear complexes of L^1 with the bivalent metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}. Compound L^1 forms both mono- and bi-nuclear complexes with all the metal ions studied, however, the low solubility in water of the binuclear species with Pb^{2+} prevented determination of their stability constants. As shown in Fig. 5 the stability constants of the $[ML^1]^{2+}$, $[M(HL^1)]^{3+}$ and $[M(H_2L^1)]^{4+}$ species follow the order $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+} > Cd^{2+} > Pb^{2+}$ in accord with the general Irving–Williams order. The magnitude of the stability constants for the formation of the non-protonated $[ML^1]^{2+}$ species is low when compared with the corresponding complexes of the hexaamine L^2. Decreases in stability of 4.4, 6.0, 2.0, 2.8 and 5.8 logarithm units are found for the complexes of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} respectively. Although L^1 and L^2 are not strictly comparable since they present different sets of hydrocarbon chains and therefore different sequences of chelate rings, these data probably suggest that the number of bound nitrogens in L^1 is lower than in L^2. The number of protonated complexes and the values for the stepwise protonation constants of $[ML^1]^{2+}$ give some indication of the co-

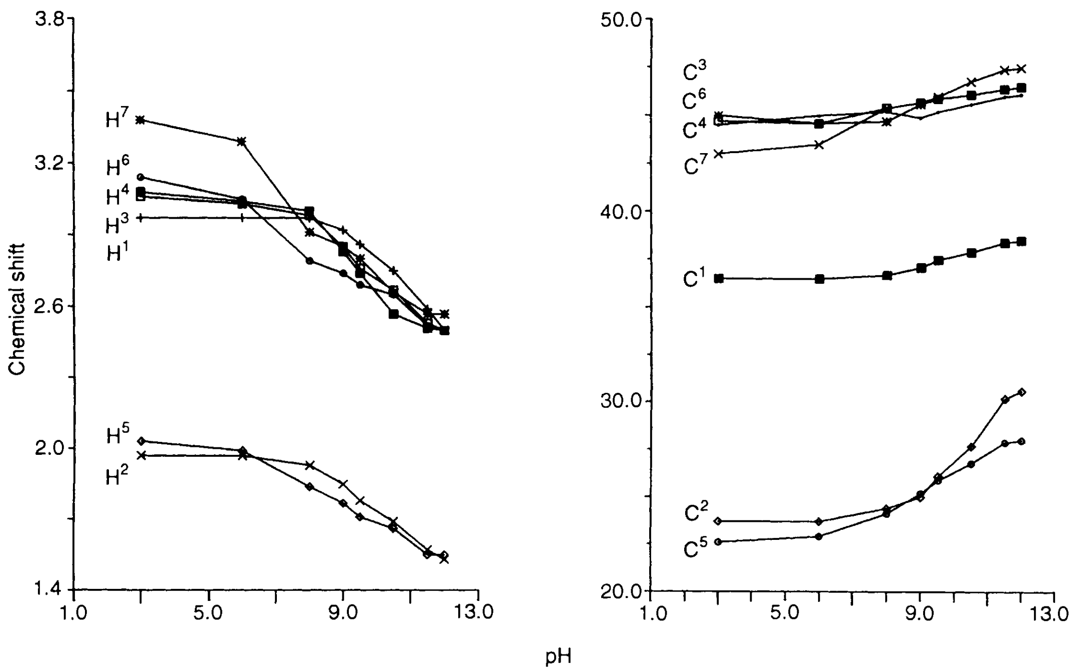


Fig. 4 Plots of the ^{1}H NMR chemical shifts (left) and ^{13}C NMR chemical shifts (right) of the amine L^1 *vs.* pH

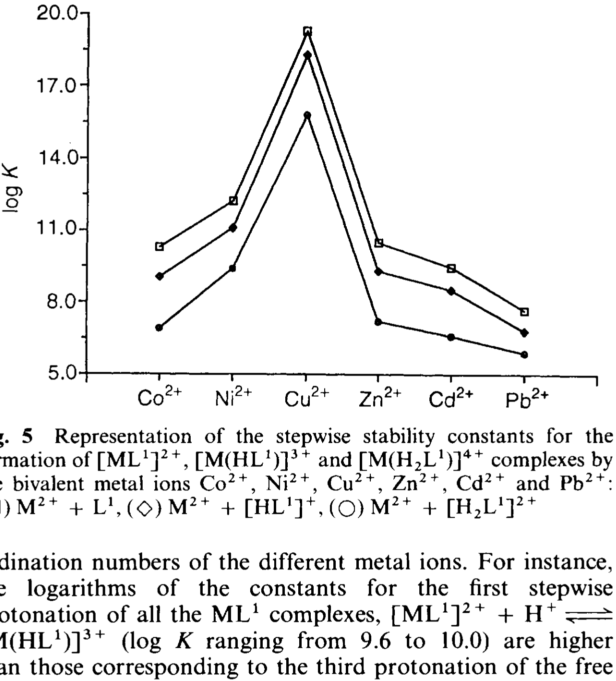


Fig. 5 Representation of the stepwise stability constants for the formation of $[ML^1]^{2+}$, $[M(HL^1)]^{3+}$ and $[M(H_2L^1)]^{4+}$ complexes by the bivalent metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}: (□) $M^{2+} + L^1$, (◇) $M^{2+} + [HL^1]^+$, (○) $M^{2+} + [H_2L^1]^{2+}$

ordination numbers of the different metal ions. For instance, the logarithms of the constants for the first stepwise protonation of all the ML^1 complexes, $[ML^1]^{2+} + H^+ \rightleftharpoons [M(HL^1)]^{3+}$ (log *K* ranging from 9.6 to 10.0) are higher than those corresponding to the third protonation of the free amine, $[H_2L^1]^{2+} + H^+ \rightleftharpoons [H_3L^1]^{3+}$ (log $K = 9.30$). A similar feature is observed for the second stepwise protonation reactions, $[M(HL^1)]^{3+} + H^+ \rightleftharpoons [M(H_2L^1)]^{4+}$, with logarithms of the protonation constant also high and close to the constant for the fourth protonation of the free ligand, $[H_3L^1]^{3+} + H^+ \rightleftharpoons [H_4L^1]^{4+}$ (log $K = 8.45$). For L^2 with which co-ordination numbers of five for Cu^{2+} and Zn^{2+} and six for Co^{2+}, Ni^{2+} and Cd^{2+} were ascertained the situation was rather different (see Table 3).[6–8] For this amine, the $[ML^2]^{2+}$ complexes of the first two metal ions had first protonation constants close to that for the third protonation of the free amine L^2, while the constants for the second successive protonation of the complexes were much lower than those of the fourth protonation step of the free amine. For Ni^{2+}, Co^{2+} and Zn^{2+} the first protonation constants of the complexes were small and much lower than those of the third protonation of the free amine accounting for cleavage of one M–N bond upon protonation. All these considerations seem to point out that at least two of the nitrogens of L^1 remain unco-ordinated in all the $[ML^1]^{2+}$ complexes. The UV/VIS and ESR spectra of the complexes of Cu^{2+} support this. The electronic spectra of solutions where the species $[Cu(H_2L^1)]^{4+}$, $[Cu(HL^1)]^{3+}$ and $[CuL^1]^{2+}$ predominate are equivalent, consisting of a broad signal centred at 575 nm ($\varepsilon = 165$ dm^3 mol^{-1} cm^{-1}). The ESR spectra are also equivalent for these species and in accord with a distorted tetragonal structure ($g_\parallel = 2.21$, $g_\perp = 2.07$, $A_\parallel = 190 \times 10^{-4}$ cm^{-1}).

If we focus our attention on the post-transition cations, Zn^{2+}, Cd^{2+} and Pb^{2+}, some further hypotheses may be advanced. First, the higher constant found for the formation of $[ZnL^1]^{2+}$ than for $[CdL^1]^{2+}$ seems to be in agreement with the literature values for polyamine complexes of Zn^{2+} and Cd^{2+} displaying the same co-ordination number. With L^2 for which co-ordination numbers of five and six were established for Zn^{2+} and Cd^{2+}, respectively, the stability constants for Cd^{2+} were slightly higher than for Zn^{2+}. Finally, the constant for the third stepwide protonation of $[PbL^1]^{2+}$, $[Pb(H_2L^1)]^{4+} + H^+ \rightleftharpoons [Pb(H_3L^1)]^{5+}$, is still very high (log $K = 8.1$). Additionally, the value for the formation constant of $[PbL^2]^{2+}$, log $K = 10.0$, which was presumably four-co-ordinate was definitely higher than that for $[PbL^1]^{2+}$ (log $K = 7.66$).[21] These data could imply that just three out of the six nitrogen donors of L^1 participate in the co-ordination to Pb^{2+}. Nevertheless, it has to be stressed that information on co-ordination numbers obtained just on the basis of the free-energy terms can often be misleading. The NMR spectra of the complexes may give additional information on the co-ordination. At room temperature the ^{1}H and ^{13}C NMR spectra for solutions of L^1 and Zn^{2+} or Cd^{2+} at pH 9 show very broad signals which may be indicative of some exchange process. In fact, when the temperature is raised, the spectra appear more resolved and the proton NMR pattern resembles that of the free amine with a singlet and two $A_2B_2C_2$ spin systems in agreement with the presence of a binary element of symmetry. The most distinctive feature with respect to the spectra of the free amine is the upfield shift experienced by the singlet resonance corresponding to the hydrogen of the central ethylenic chain (H^7) which demonstrates the involvement of the ethylenic nitrogens in the co-ordination. The low co-ordination of these metal complexes is also reflected in the ^{113}Cd NMR spectra, which show at room

Table 3 Logarithms of the stability constants for the formation of mononuclear complexes of L^1 determined at 298.1 K in 0.15 mol dm^{-3} $NaClO_4$. Some values for the related polyamine L^2 have also been included

Reaction[a]	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	Pb^{2+}
$M + L^1 \rightleftharpoons [ML^1]$	10.30(3)[b]	12.23(8)	19.35(4)	10.53(2)	9.46(3)	7.66(3)
$[ML^1] + H \rightleftharpoons [M(HL^1)]$	9.58(3)	9.7(1)	9.75(5)	9.56(1)	9.89(2)	9.97(4)
$[M(HL^1)] + H \rightleftharpoons [M(H_2L^1)]$	8.00(2)	8.46(5)	7.69(2)	8.16(2)	8.23(2)	9.22(3)
$[M(H_2L^1)] + H \rightleftharpoons M(H_3L^1)]$		6.2	4.06(2)			8.12(2)
$M + L^2 \rightleftharpoons [ML^2]$	14.8[c]	18.2[c]	21.6[d]	14.0[e]	15.4[e]	10.0[f]
$[ML^2] + H \rightleftharpoons [M(HL^2)]$	5.9	5.9	8.6	7.9	5.8	9.3
$[M(HL^2)] + H \rightleftharpoons [M(H_2L^2)]$	5.6	4.8	3.9			6.7

[a] Charges have been omitted for clarity. [b] Values in parentheses are standard deviations in the last significant figure. [c] Values taken from ref. 8; 0.15 mol dm^{-3} $NaClO_4$, 298.1 K. [d] Values taken from ref. 6; 0.15 mol dm^{-3} $NaClO_4$, 298.1 K. [e] Values taken from ref. 7; 0.15 mol dm^{-3} $NaClO_4$, 298.1 K. [f] Values taken from ref. 21; 0.15 mol dm^{-3} $NaClO_4$, 298.1 K.

Table 4 Logarithms of the stability constants for the formation of binuclear complexes of L^1 determined at 298.1 K in 0.15 mol dm^{-3} $NaClO_4$

Reaction[a]	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
$2M + L^1 \rightleftharpoons [M_2L^1]$			27.17(3)[b]		
$2M + L^1 + H_2O \rightleftharpoons [M_2L^1(OH)] + H$		7.83(5)	19.37(5)	7.55(3)	4.19(2)
$2M + L^1 + 2H_2O \rightleftharpoons [M_2L^1(OH)_2] + 2H$	−3.43(2)	−2.7(1)	10.0(1)	−1.98(8)	−5.51(3)
$[M_2L^1] + H_2O \rightleftharpoons [M_2L^1(OH)] + H$			−7.81(7)		
$[M_2L^1(OH)] + H_2O \rightleftharpoons [M_2L^1(OH)_2] + H$		−10.5(1)	−9.4(1)	−9.5(1)	−9.69(3)

[a] Charges have been omitted for clarity. [b] Values in parentheses are standard deviations in the last significant figure.

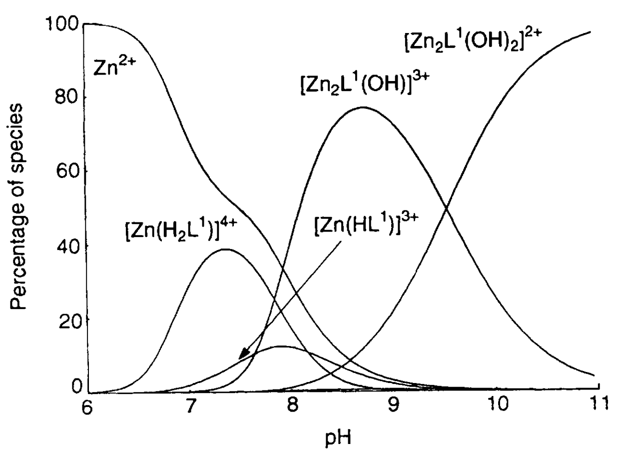


Fig. 6 Distribution diagram for the species existing in equilbria in the system Zn^{2+}–L^1: $[Zn^{2+}] = 2 \times 10^{-3}$, $[L^1] = 1 \times 10^{-3}$ mol dm^{-3}

temperature and pH 9 only one signal δ *ca.* 30 shifted downfield with respect to $Cd(ClO_4)_2$; this shift can be compared with the literature values for other polyamine complexes. However, the observed chemical shifts for ^{113}Cd are strongly dependent on the temperature and concentration due to the well known lability of cadmium complexes.[22,23]

For Zn^{2+}, Cd^{2+} and Pb^{2+} the formation of monohydroxo species has also been detected; the constants for the addition of OH^- to $[ML^1]^{2+}$ species vary from 3 to 4 logarithm units.

Perhaps the most noticeable feature of the co-ordination chemistry of L^1 is that it forms binuclear species with all the metal ions studied. This is in contrast to L^2, for which the formation of binuclear species was observed only in the case of Cu^{2+}. This fact, again, may reflect the low co-ordination numbers achieved by L^1 in its mononuclear complexes. This ligand is probably too long to arrange all its donor atoms around a single metal centre leaving, therefore, unco-ordinated nitrogen atoms which initially can attach to an additional metal ion inducing the necessary reorganization to yield the final conformation of the binuclear complexes. Another aspect of interest is that a non-protonated $[M_2L^1]^{4+}$ species has only been detected for Cu^{2+}. For Ni^{2+}, Zn^{2+} and Cd^{2+} the formation of mono- and di-hydroxo species and for Co^{2+} just a dihydroxo species was observed. In Fig. 6 the percentages of species present in equilibria are plotted as a function of pH for the system Zn^{2+}–L^1, in molar ratio M:L 2:1. It can be seen that the binuclear hydroxylated species are predominant from pH values around 7.5.

The low co-ordination L^1 achieves both in its mono- and bi-nuclear complexes may have important implications in the use of these complexes for catalytically assisting a variety of processes [acid–base ones for the complexes of Zn^{2+} and Cd^{2+} or redox for the copper(II) complexes] or in the activation and transport of small molecules.[24–26] We are exploring these reactions.

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