Interaction of Long Polyazaalkanes with Zinc(II) and Cadmium(II) Ions. A Thermodynamic and ^{13}C Nuclear Magnetic Resonance Study *

Juan Aragó,[a] Andrea Bencini,[b] Antonio Bianchi,[b] Enrique Garcia-España,[a] Mauro Micheloni,[c] Piero Paoletti,[b] Jose A. Ramirez[a] and Agustín Rodriguez[b]
[a] *Department of Inorganic Chemistry, University of Valencia, C/Dr. Moliner 50, 46100 Burjassot (Valencia), Spain*
[b] *Department of Chemistry, University of Florence, Via Maragliano 75/77, 50144 Florence, Italy*
[c] *Institute of Chemical Sciences, University of Urbino, Urbino, Italy*

The interaction of Zn^{2+} and Cd^{2+} ions with a series of terminally methylated open-chain polyazaalkanes $CH_3NHCH_2CH_2NH[CH_2CH_2NH]_nCH_2CH_2NHCH_2CH_2NHCH_3$ (n = 1–5, L^1–L^5) has been studied by potentiometry and direct microcalorimetry at 298 K in 0.15 mol dm^{-3} $NaClO_4$, as well as by ^1H and ^{13}C NMR techniques. All these ligands form mononuclear complexes with Zn^{2+} and Cd^{2+}. The stability constants and the enthalpy of formation of the species $[ML]^{2+}$ for both metal ions are roughly constant along the series. The ^{13}C NMR spectra of the complexes $[ZnL^1]^{2+}$ and $[CdL^1]^{2+}$ indicate the presence of a C_2 symmetry axis. All the experimental evidence suggests five-co-ordination for the zinc complexes and six-co-ordination for the cadmium complexes. The great upfield shifts experienced by the methyl carbons at both ends of the chain suggest the involvement of the terminal nitrogens in the co-ordination to the metals. The three largest ligands form binuclear zinc and cadmium complexes, the stability of which increases with the number of nitrogen donors. Comparison with analogous polyazacycloalkanes shows that a macrocyclic effect is observed only for the zinc mononuclear complexes of the shortest ligand L^1 and for the cadmium complexes of L^1 and L^2. For all the other complexes, mono- or binuclear, a higher stability of the complexes of the open-chain ligands is observed. On the other hand, ^{13}C NMR spectra of the ligands L^3–L^5 allow a general protonation pattern to be established based on minimization of repulsive interactions between same-sign charges.

Although the chemistry of large polyazacycloalkanes has been widely studied in the last few years,[1–4] and many of its characteristics attributed to the cyclic topologies of the ligands, a comparison with adequate open-chain polyamines had not been performed. Recently, we have reported on the synthesis and co-ordination ability towards Cu^{2+} ion of the series of terminally methylated open-chain polyamines containing ethylenic chains 1,14-bis(methylamino)-3,6,9,12-tetraazatetradecane (L^1), 1,17-bis(methylamino)-3,6,9,12,15-pentaazaheptadecane(L^2), 1,20-bis(methylamino)-3,6,9,12,15,18-hexaazaicosane (L^3), 1,23-bis(methylamino)-3,6,9,12,15,18,21-heptaazatricosane (L^4) and 1,26-bis(methylamino)-3,6,9,12,15,18,21,24-octaazahexacosane (L^5).[5] The protonation and copper(II) co-ordination chemistry showed many analogies with the chemistry exhibited by their cyclic counterparts of the series of macrocyclic ligands [3*k*]aneN$_k$.[1] However, in many instances the stability of the complexes of the open-chain ligands was higher than that found for the analogous complexes of the cyclic ligands. Therefore, we suggested that a sort of antimacrocyclic effect could exist for these ligands having high conformational freedom. For the binuclear copper complexes both the enthalpy and entropy terms contributed to the enhanced stability of the open-chain ligands.

To get further insight into the origins of these unusual stability trends, we report on the interaction of Zn^{2+} and Cd^{2+} with the ligands L^1–L^5.

Experimental

Materials.—The ligands L^1–L^5 were synthesised as described in ref. 5. Hydrochloride salts of the ligands were used in the potentiometric and NMR measurements. All the other products were Merck analytical grade.

$$CH_3NHCH_2CH_2NH\left[CH_2CH_2NH\right]_nCH_2CH_2NHCH_2CH_2NHCH_3$$

	n
L^1	2
L^2	3
L^3	4
L^4	5
L^5	6

Electromotive Force Measurements.—The potentiometric titrations were carried out in 0.15 mol dm^{-3} $NaClO_4$ at 298.15 K, by using the equipment already described.[6] The acquisition of the data was performed by means of the computer program PASAT.[7] The reference electrode was an Ag–AgCl electrode in saturated KCl solution. The glass electrode was calibrated as a hydrogen-concentration probe by titrating well known amounts of HCl with CO_2-free NaOH solutions and determining the equivalence point by Gran's method[8] which gives the standard potential E° and the ionic product of water. The computer program SUPERQUAD[9] was used to calculate the stability constants. The concentrations of the standard solutions of Zn^{2+} and Cd^{2+} were determined gravimetrically by the usual methods. The titration curves for each system were treated either as a single set or as separated entities without significant variations in the values of the stability constants.

---

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

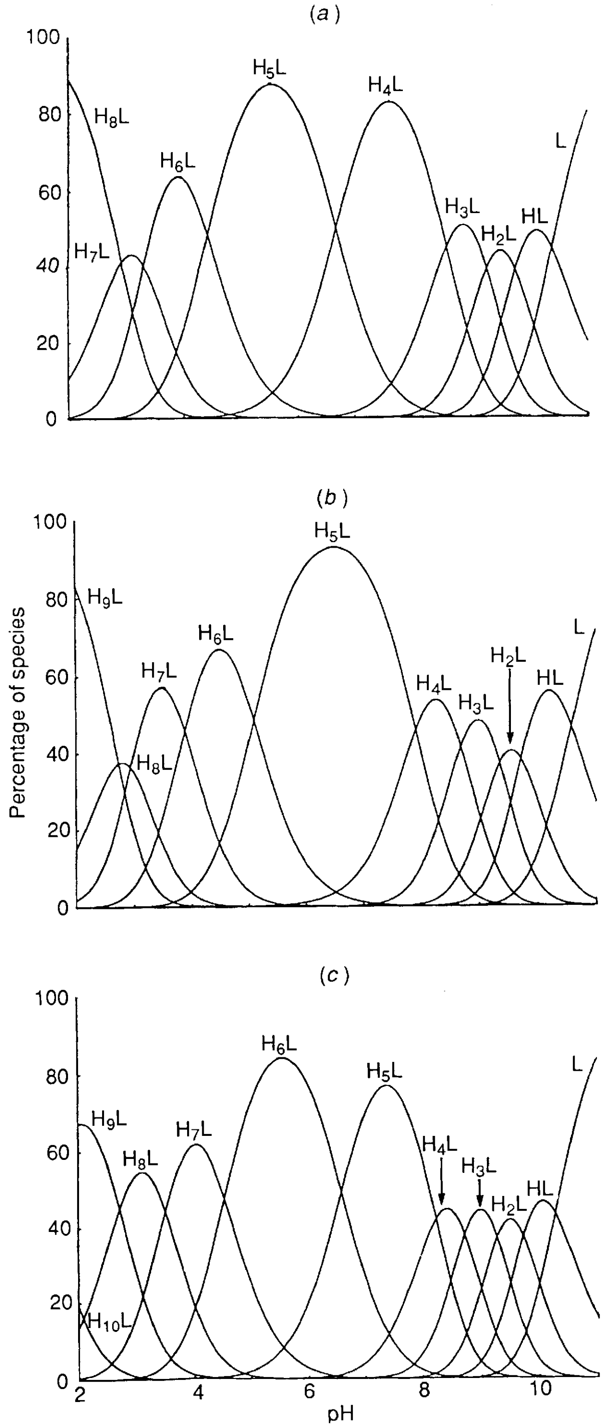


Fig. 1 Calculated distribution diagrams for the species existing in equilibria for the systems: (*a*) H^+–L^3, (*b*) H^+–L^4 and (*c*) H^+–L^5

Microcalorimetry.—The calorimetric measurements were performed by means of fully automatized equipment having a model 2277 (Termometric AB) Thermal Activity Monitor microcalorimeter as calorimetric unit. Solutions of the metal ions (0.1 mol dm^{-3}, addition volumes ranging from 20 to 30 μl) were added to solutions (2.0 cm^3) of the free ligands (0.001 mol dm^{-3}). Corrections for the heats of dilution of the reacting solutions were applied.

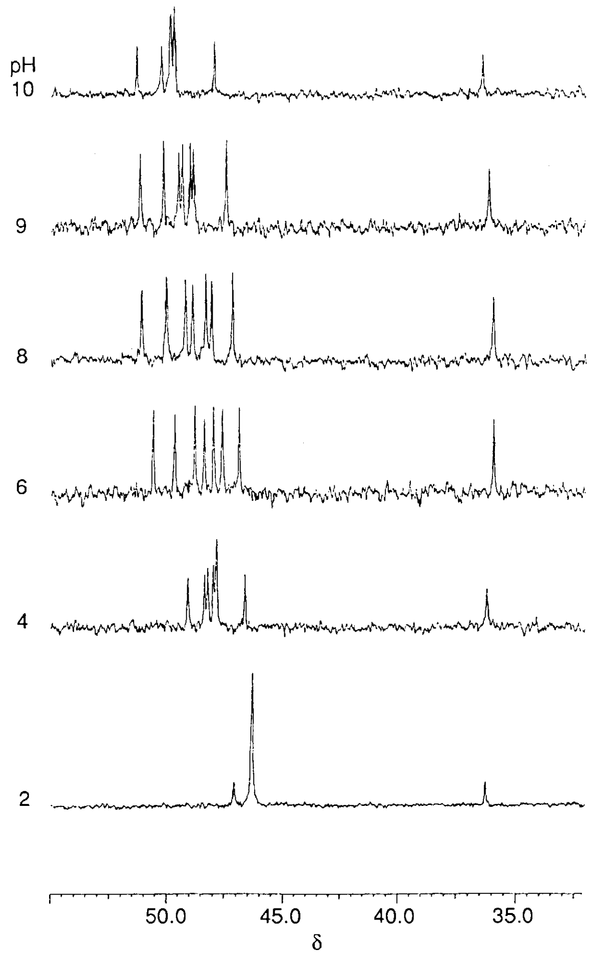


Fig. 2 Carbon NMR spectra at different pH for L^3

NMR Spectroscopy.—Proton (200.0 MHz) and ^{13}C (50.32 MHz) NMR spectra were recorded on Varian Gemini and Bruker AC-200 spectrometers in D_2O solutions with dioxane as reference standard (δ 67.4).

Results and Discussion

Protonation of the Ligands.—In a previous paper[5] we reported the protonation constants for all the studied ligands. From the protonation constants* and the ^1H and ^{13}C NMR spectra of the two shortest ligands of the series, L^1 and L^2, we concluded that an alternated protonation pattern minimizing electrostatic repulsions between same sign charges would satisfactorily fit the experimental data. The terminal nitrogens would be the first ones bearing protonation. In order to test if this, as proposed, would mean a general behaviour for all these ligands, we have extended our NMR studies to the other terms of the series, L^3–L^5.

In Fig. 1 the distribution diagrams for these polyamines are presented, and in Fig. 2 the ^{13}C NMR spectra of L^3 at different pH values. At pH 2, where the fully protonated species $[H_8L^3]^{8+}$ predominates in solution [see Fig. 1(*a*)], the ^{13}C NMR spectrum of the ligand consists of three non-equivalent signals integrating roughly 1:1:6, which can be attributed to the methyl carbons (C^1, δ 36.23), the carbon atoms in β position with respect to the methyl groups (C^2, δ 47.04) and to all the other carbon atoms which are magnetically equivalent (C^{3-8}, δ 46.26). When the pH is raised to 8 (Fig. 2), at which the tetraprotonated species $[H_4L^3]^{4+}$ predominates [see Fig. 1(*a*)], the number of non-equivalent signals is eight corresponding to

---

* Stepwise protonation constants for the ligands determined[5] in 0.15 mol dm^{-3} $NaClO_4$ at 298 K are: L^1, 10.28, 9.52, 8.84, 6.54, 3.80, 2.51; L^2, 10.22, 9.59, 8.94, 8.05, 4.75, 3.37, 2.45; L^3, 10.39, 9.77, 9.28, 8.61, 6.68, 4.44, 3.31, 2.93; L^4, 10.58, 9.72, 9.35, 8.70, 7.93, 5.10, 3.88, 2.94, 2.74; and L^5, 10.27, 9.72, 9.27, 8.72, 8.24, 6.58, 4.54, 3.50, 2.71, 1.46.

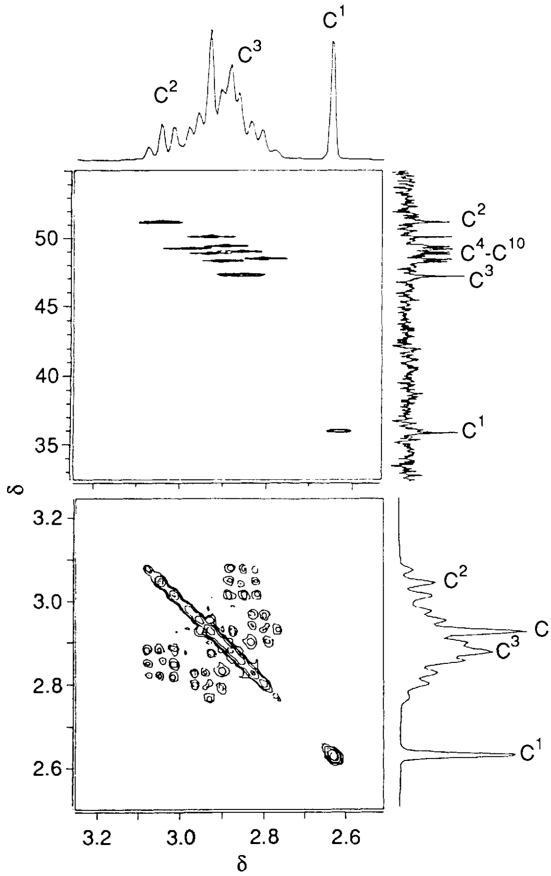


Fig. 3 Correlated ^1H–^1H and ^1H–^{13}C NMR spectra for L^5 at pH 7

half of the overall number of carbons present in the molecule indicating, therefore, at least C_2 time-averaged symmetry. If the pH is further increased, although shifted downfield the carbon atoms recover their magnetic equivalence, and for instance, at pH 10 where $[H_2L^3]^{2+}$ predominates, the number of signals found in the ^{13}C NMR spectrum is reduced to six. The ligands L^4 and L^5 present similar behaviour but the maximum number of signals found for intermediate protonation degrees is nine ($[H_4L^4]^{4+}$ and $[H_5L^4]^{5+}$) and 10 ($[H_5L^5]^{5+}$ and $[H_6L^5]^{6+}$). The spectra of the free amines, recorded in $CDCl_3$ due to their low water solubility, all consist of four resonances at δ 37.4 (C^1), 53.0 (C^2), 50.7 (C^3) and the signal corresponding to all the other carbons at δ 51.0.

By means of the empirical formula of Reilley and co-workers[10] for aliphatic amines, we have obtained the theoretical chemical shifts for a variety of supposed protonation patterns for both ligands L^3 and L^4. Due to the small differences in chemical shifts for the carbon atoms placed in central positions in the chains, it is rather difficult to establish unequivocal assignments for such atoms. However, on the basis of the fitting between experimental and theoretical values of chemical shift, and by recording ^1H–^1H and ^1H–^{13}C two-dimensional spectra (see Fig. 3), the signals of some carbon atoms very sensitive towards protonation can be unambiguously identified and the main features of the protonation patterns deduced.

Thus, it is interesting to analyse the variations in the chemical shift experienced by some particular carbon atoms (see Fig. 4 and Scheme 1). First, the methyl carbon (C^1) and the carbon atom β with respect to the terminal nitrogen atom (C^3) do not present relevant upfield shifts between pH 2 and 10. This would agree with protonation of these terminal nitrogens taking place at pH > 10. Therefore, in accord with the distribution diagram (Fig. 1), these would be the first nitrogens bearing protonation. For the shortest ligands of the series, L^1 and L^2, a similar feature was also observed.[6]

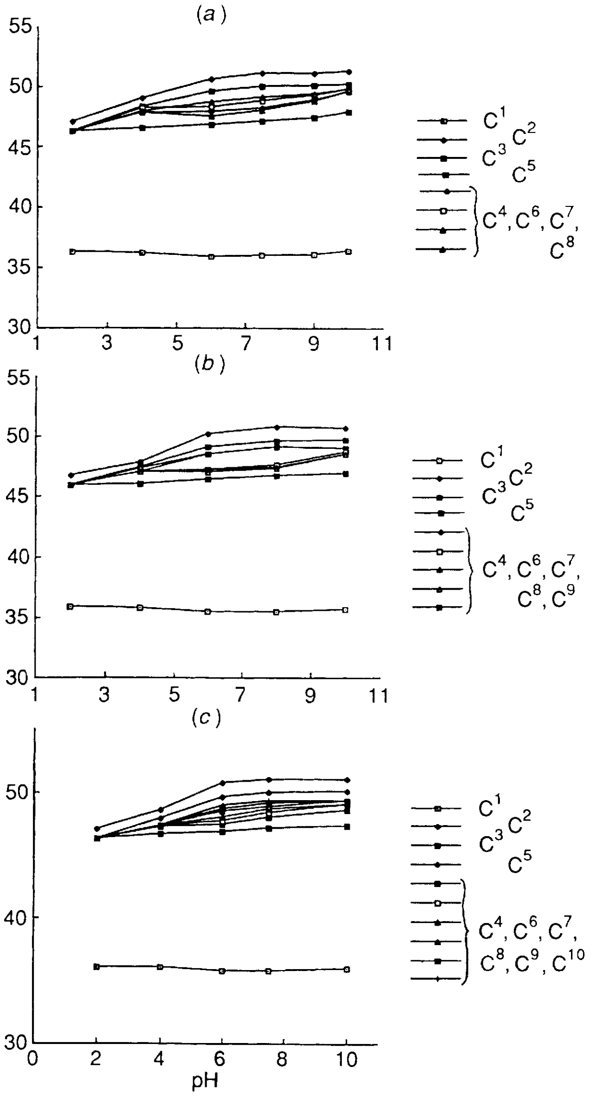
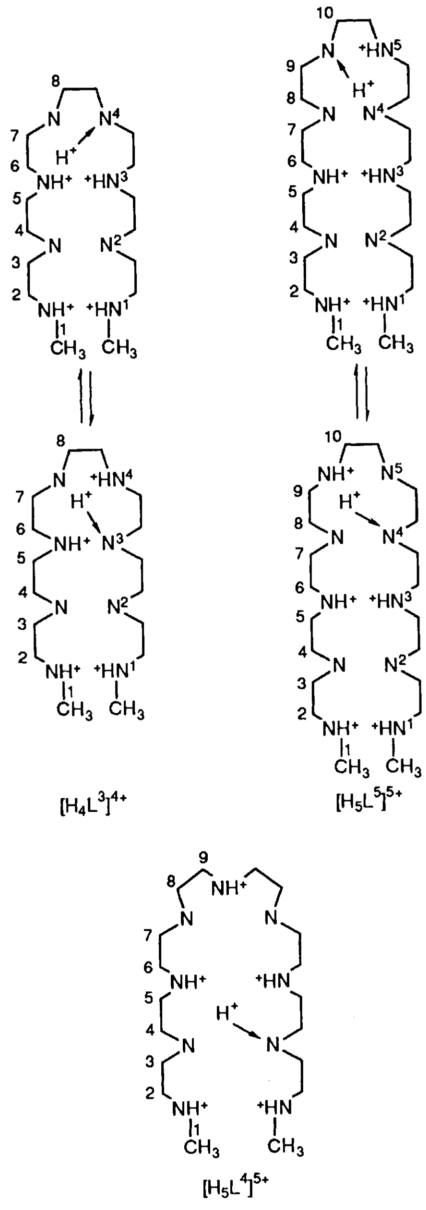


Fig. 4 Experimental ^{13}C NMR chemical shifts as a function of pH for: (*a*) L^3, (*b*) L^4 and (*c*) L^5

The next protons until intermediate protonation degrees bind the ligand in an alternated manner in order to minimize electrostatic repulsions. Such a pattern for $[H_4L^3]^{4+}$, $[H_5L^4]^{5+}$ and $[H_5L^5]^{5+}$ is depicted in Scheme 1. The carbon chemical shifts would not disagree, in principle, with such a scheme. Obviously, proton exchanges between similar sites are to be expected and Scheme 1 represents average situations; for instance in L^3 the third and fourth protons could be at any one of the four nitrogens at the middle of the chain as long as there is at least one unprotonated nitrogen between them. The fifth proton for L^3, and more generally the $(k/2)+1$th proton for ligands with even number of nitrogens (where k represents the overall number of nitrogens in the ligand), has to be necessarily placed in a position adjacent to one protonated nitrogen (one-side repulsions). Thus, in L^3 it could attach either to the contiguous nitrogen to that labelled as N^3 (N^4), or to that contiguous to the terminal ones labelled as N^1 (N^2). The signals of the carbon atoms placed β to N^2, namely C^2 and C^5, do not experience significant upfield shifts until pH *ca.* 6 (see Fig. 4). At this pH value not the fifth but the sixth proton is attached to the ligand [see Fig. 1(*a*)]. Therefore, the fifth proton should bind to N^4 and not to N^2. Thus it seems that at this protonation stage the presence of two unprotonated nitrogens in the central part of the chain favours the binding of the $(k/2)+1$th proton for ligands with even numbers of nitrogens. This proton will be shared at both unprotonated positions. Correspondingly for L^5



Scheme 1

such a situation will arise with the binding of the sixth proton (see Scheme 1), and in this case the greater upfield shifts of carbon atoms C^2 and C^5 occur for the binding of the seventh proton [see Figs. 4 and 1(*c*)].

For L^4 which presents an odd number of nitrogens, the first five protons can be placed in alternate positions without great repulsions between same-sign charges. The sixth proton has to bind necessarily between two polyammonium sites (two-side repulsions) (see Scheme 1), and in this case the greater upfield shifts of C^2 and C^5 are observed between pH 4 and 6 corresponding precisely to the attachment of this sixth proton. All these results suggest that one-side repulsions are preferred in the central part of the molecule and two-side repulsions at the nitrogen next to the terminal ones.

The general features that can therefore be deduced from the NMR analysis are as follows: (*i*) for all the ligands of the series, the first two nitrogens bearing protonation are the terminal ones; (*ii*) the next protons up to $k/2$ for ligands with even numbers of nitrogens and $(k + 1)/2$ for those with odd numbers attach in such a way that electrostatic repulsions are minimized (alternated protonation pattern); (*iii*) the $(k/2) + 1$th protonation for ligands with even numbers of nitrogens takes place in the central part of the chain (one-side repulsion); and (*iv*) the $[(k + 1)/2] + 1$th protonation for ligands with odd numbers of nitrogens takes place at the nitrogens contiguous to the terminal ones (two-side repulsion).

Zinc(II) *and Cadmium*(II) *Complexes*.—The formation constants of the zinc and cadmium complexes of the open-chain polyamines L^1–L^5 are presented in Tables 1 and 2, respectively. All these ligands form mononuclear $[ML]^{2+}$ species with both metal ions, with the only exception of L^5, for which the species $[ZnL^5]^{2+}$ has not been detected under the experimental conditions employed. The longer polyamines L^3–L^5 also form binuclear $[M_2L]^{4+}$ complexes. The stability of the $[ZnL]^{2+}$ and $[CdL]^{2+}$ species does not follow any clear tendency, remaining roughly constant along the series (Tables 1 and 2). For each ligand the stability of the $[CdL]^{2+}$ complex is somewhat higher than that of the corresponding $[ZnL]^{2+}$ species. Usually, polyamine ligands give rise to the formation of zinc complexes which are more stable than those of Cd^{2+}, when similar co-ordination geometries are presented by both metal complexes.[11] In order to gain further insight into this point we have also determined the enthalpy changes for the formation of these mononuclear species in solution. The thermodynamic data obtained are reported in Table 3. From these data two main features can be outlined: (*i*) for all the ligands studied the enthalpic contributions to the formation of zinc and cadmium complexes are the same within the experimental errors; (*ii*) the slightly greater stability of the cadmium complexes, with respect to those of Zn^{2+}, is due to a marked enhancement of the enthalpic term while $T\Delta S$ is more favourable for the formation of the zinc complexes. These results suggest that the co-ordination number of the zinc and cadmium complexes is the same for all the terms of the series, but in the cadmium complexes one more nitrogen is involved in the co-ordination than in the zinc complexes.

Both the free-energy change and the enthalpic contribution to the formation of $[CdL^1]^{2+}$ complex (Table 3) are more favourable than those, previously reported, for the cadmium complex of the pentaamino ligand tetraen (3,6,9-triazaundecane-1,11-diamine) ($\Delta G° = 19.09$, $\Delta H° = -12.8$ kcal mol^{-1}),[11] which has been shown to involve all its five donor atoms in the co-ordination. This suggests six-co-ordination of L^3 in the complex $[CdL^3]^{2+}$ in solution. As was shown by the molecular structure of the dinuclear complex $Na[Cd_2([30]aneN_{10})Cl_2][ClO_4]_3$, such six-co-ordination can be reached even at the expense of severe conformational constraints; in this complex one of the metal centres is six-co-ordinated by disposing the six contiguous nitrogen donors of the ligand at the vertices of a very distorted trigonal prism.[12] On the basis of the above considerations, a co-ordination number of five should be achieved by Zn^{2+} with these terminally methylated polyamines. The free energy and enthalpy changes for the formation of the complex $[ZnL^1]^{2+}$ (Table 3) are much closer to those for the zinc complex of tetraen ($\Delta G° = -20.59$, $\Delta H° = -13.4$ kcal mol^{-1})[11] than to those for the zinc complex of the tetradentate ligand trien (3,6-diazaoctane-1,8-diamine)[11] ($\Delta G° = -16.40$, $\Delta H° = -8.4$ kcal mol^{-1}). Furthermore the equilibrium constant for the protonation of $[ZnL^1]^{2+}$ to $[Zn(HL^1)]^{3+}$ is much greater (more than 2 logarithmic units) than the protonation constants of $[CdL^1]^{2+}$ and is similar to the protonation constant of $[CdL^2]^{2+}$ ($\log K = 8.74$) and to the third stepwise protonation constant ($\log K = 8.84$) of the free ligand. Therefore, taking into account all these considerations it can be confidently deduced that all the polyamines of the present series involve five and six nitrogen donor atoms in the co-ordination to Zn^{2+} and Cd^{2+} ions, respectively.

In Table 4 the ^{13}C NMR spectral features of the zinc and cadmium mononuclear complexes of the ligands L^1–L^3 are presented. First, it should be noted that in all the complexes the terminal methyl carbons present just one signal which is considerably upfield shifted with respect to those of the

Table 1 Formation constants of zinc(II) complexes of the polyazaalkanes L^1–L^5 in 0.15 mol dm^{-3} $NaClO_4$ aqueous solution at 298 K

Reaction[a]	L^1	L^2	L^3	L^4	L^5
$Zn + L \rightleftharpoons [ZnL]$	14.02(2)[b]	13.52(1)	15.18(6)	14.80(2)	—
$Zn + L + H \rightleftharpoons [Zn(HL)]$	21.96(1)	23.12(1)	24.49(3)	24.55(2)	23.21(2)
$Zn + L + 2H \rightleftharpoons [Zn(H_2L)]$	—	28.926(7)	31.58(1)	33.06(1)	32.22(2)
$Zn + L + 3H \rightleftharpoons [Zn(H_3L)]$	—	—	—	39.04(1)	39.90(1)
$Zn + L + 4H \rightleftharpoons [Zn(H_4L)]$	—	—	—	—	45.22(2)
$ZnL + H \rightleftharpoons [Zn(HL)]$	7.94	9.60	9.31	9.75	—
$[Zn(HL)] + H \rightleftharpoons [Zn(H_2L)]$	—	5.80	7.09	8.51	9.01
$[Zn(H_2L)] + H \rightleftharpoons [Zn(H_3L)]$	—	—	—	5.97	7.68
$[Zn(H_3L)] + H \rightleftharpoons [Zn(H_4L)]$	—	—	—	—	5.32
$Zn + HL \rightleftharpoons [Zn(HL)]$	11.68	12.92	14.10	13.97	12.94
$Zn + H_2L \rightleftharpoons [Zn(H_2L)]$	—	9.11	11.42	12.27	12.22
$Zn + H_3L \rightleftharpoons [Zn(H_3L)]$	—	—	—	9.39	10.63
$Zn + H_4L \rightleftharpoons [Zn(H_4L)]$	—	—	—	—	7.23
$2Zn + L \rightleftharpoons [Zn_2L]$	—	—	20.71(3)	23.79(1)	25.43(2)
$2Zn + L + H \rightleftharpoons [Zn_2(HL)]$	—	—	—	29.71(5)	31.63(3)
$2Zn + L + H_2O \rightleftharpoons [Zn_2L(OH)] + H$	—	—	12.88(3)	15.83(2)	14.71(3)
$2Zn + L + 2H_2O \rightleftharpoons [Zn_2L(OH)_2] + 2H$	—	—	3.89(6)	5.68(5)	—
$[Zn_2L] + H \rightleftharpoons [Zn_2(HL)]$	—	—	—	5.92	6.20
$[Zn_2L] + H_2O \rightleftharpoons [Zn_2L(OH)] + H$	—	—	−7.83	−7.96	−10.72
$[Zn_2L(OH)] + H_2O \rightleftharpoons [Zn_2L(OH)_2] + H$	—	—	−8.99	−10.15	—
$[Zn_2L] + OH \rightleftharpoons [Zn_2L(OH)]$	—	—	5.90	5.77	3.01
$[Zn_2L(OH)] + OH \rightleftharpoons [Zn_2L(OH)_2]$	—	—	4.74	3.58	—
$[ZnL] + Zn \rightleftharpoons [Zn_2L]$	—	—	5.53	8.99	—

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

Table 2 Formation constants of cadmium(II) complexes of the polyazaalkanes L^1–L^5 in 0.15 mol dm^{-3} $NaClO_4$ aqueous solution at 298 K

Reaction[a]	L^1	L^2	L^3	L^4	L^5
$Cd + L \rightleftharpoons [CdL]$	15.289(4)[b]	14.497(7)	15.81(1)	15.38(1)	15.23(2)
$Cd + L + H \rightleftharpoons [Cd(HL)]$	21.116(6)	23.240(3)	25.303(8)	25.21(1)	24.91(2)
$Cd + L + 2H \rightleftharpoons [Cd(H_2L)]$	—	28.48(1)	31.753(5)	33.198(5)	33.52(2)
$Cd + L + 3H \rightleftharpoons [Cd(H_3L)]$	—	—	36.757(2)	38.779(8)	40.112(8)
$Cd + L + 4H \rightleftharpoons [Cd(H_4L)]$	—	—	—	—	45.053(3)
$[CdL] + H \rightleftharpoons [Cd(HL)]$	5.83	8.74	9.49	9.83	9.68
$[Cd(HL)] + H \rightleftharpoons [Cd(H_2L)]$	—	5.24	6.45	7.99	8.61
$[Cd(H_2L)] + H \rightleftharpoons [Cd(H_3L)]$	—	—	5.00	5.58	6.59
$[Cd(H_3L)] + H \rightleftharpoons [Cd(H_4L)]$	—	—	—	—	4.94
$Cd + HL \rightleftharpoons [Cd(HL)]$	10.84	13.04	14.91	14.63	14.64
$Cd + H_2L \rightleftharpoons [Cd(H_2L)]$	—	8.66	11.59	12.90	13.52
$Cd + H_3L \rightleftharpoons [Cd(H_3L)]$	—	—	7.32	9.12	10.84
$Cd + H_4L \rightleftharpoons [Cd(H_4L)]$	—	—	—	—	7.06
$2Cd + L \rightleftharpoons [Cd_2L]$	—	—	20.55(2)	21.84(1)	23.48(2)
$2Cd + L + H \rightleftharpoons [Cd_2(HL)]$	—	—	28.20(3)	28.81(7)	30.38(3)
$[Cd_2L] + H \rightleftharpoons [Cd_2(HL)]$	—	—	7.65	6.97	6.90
$2Cd + HL \rightleftharpoons [Cd_2(HL)]$	—	—	17.81	18.23	20.10
$[CdL] + Cd \rightleftharpoons [Cd_2L]$	—	—	4.74	6.46	8.25

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

Table 3 Thermodynamic parameters (kcal mol^{-1}) for the formation of zinc and cadmium complexes of L^1–L^5 in 0.15 mol dm^{-3} $NaClO_4$ aqueous solution at 298 K

Reaction[a]	$-\Delta G^\circ$	$-\Delta H^\circ$	$T\Delta S^\circ$
$Zn^{a} + L^1$	19.12(3)[b]	11.8(5)	7.3(5)
$Zn + L^2$	18.44(1)	11.3(3)	7.1(3)
$Zn + L^2$	20.70(8)	11.6(2)	9.1(3)
$Zn + L^3$	20.18(3)	12.3(5)	7.9(5)
$Cd + L^1$	20.85(1)	15.5(4)	5.3(4)
$Cd + L^2$	19.77(1)	14.8(2)	5.0(2)
$Cd + L^3$	21.56(1)	15.3(3)	6.3(3)
$Cd + L^4$	20.97(1)	15.5(5)	5.5(8)
$Cd + L^5$	20.77(3)	14.0(5)	6.8(5)

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

corresponding free ligands, indicating an effective co-ordination of both terminal nitrogens to the metal ions. In Fig. 5 the spectrum of a solution containing Zn^{2+} and an excess of L^1, is presented. It can be seen that both the signals of the complex and of the free ligand appear. Two different signals for the methyl groups are present. Upon co-ordination to the metal ions the signals of the methyl groups are precisely those which shift the most. The other carbon atoms of the chain, probably due to opposite effects induced by the co-ordination to the metal, do not exhibit such significant variations in their chemical shifts. Another feature is that the ^{13}C NMR spectra of the complexes $[CdL^1]^{2+}$ and $[CdL^2]^{2+}$ consist of six and seven different signals respectively (see Fig. 5), corresponding to half of the overall number of carbon atoms present in the ligands and indicating the presence of a C_2 symmetry axis in the molecules. Taking into account all these considerations the structure depicted in Fig. 6 can be suggested for the complex $[CdL^1]^{2+}$. The nitrogens of the ligand would be placed in a very distorted trigonal-prismatic disposition with a C_2 axis.

As noted above, L^3–L^5 form both mono- and bi-nuclear species (Tables 2 and 3). The stability of the $[Zn_2L]^{4+}$ and $[Cd_2L]^{4+}$ complexes grows with the number of nitrogen

Table 4 Carbon-13 NMR chemical shifts (δ) for some cadmium and zinc complexes of the ligands L^1–L^3; 0.1 mol dm^{-3} solutions of metals and ligands

L^1 (pH 8.5)										
Cd^{2+}		39.2	52.9	48.4	48.9	49.2	49.5			
Zn^{2+}		38.1	51.1	48.5	49.0	49.7(2)*				
L^2 (pH 10)										
Cd^{2+}		38.6	52.0	48.6	48.9	49.2	49.3	49.5		
Zn^{2+}		38.2	52.3	49.0	49.3	49.5(2)	50.2			
L^3										
Cd^{2+}	pH 7.5	37.8	52.0	48.2	48.9	49.0(2)	49.2	50.1		
	pH 10	37.6	51.9	48.4(4)	48.7	49.6				
Zn^{2+}	pH 7.5	37.6	51.6	48.1	49.2	49.3(2)	49.5	50.2		
	pH 10	38.3	52.5	49.4	49.5	49.8	50.1	50.5	50.7	

* Relative intensities are given in parentheses

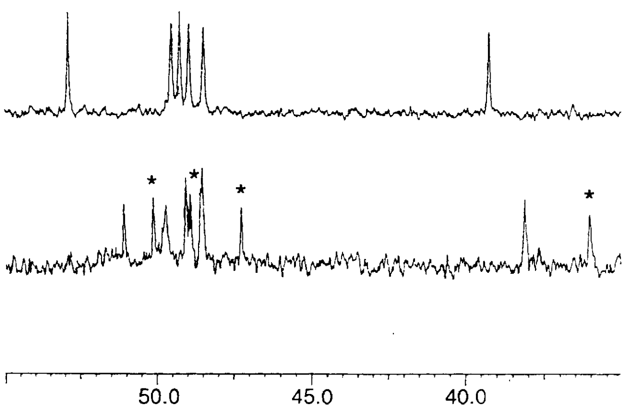


Fig. 5 Carbon-13 NMR spectra of solutions of $[L^1]:[Zn^{2+}] = 1.5:1$ (lower) and $[L^1]:[Cd^{2+}] = 1.0:1$ (upper) at pH 8.5. $[Zn^{2+}] = [Cd^{2+}] = 1 \times 10^{-2}$ mol dm^{-3}. The signals with an asterisk correspond to resonance of the free ligand

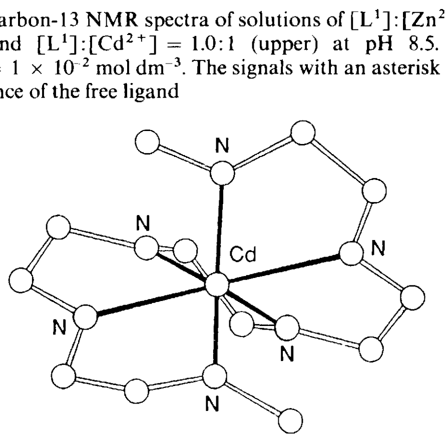


Fig. 6 Proposed structure for $[CdL^1]^{2+}$ calculated by means of the MMX program. Hydrogen atoms have been omitted for clarity

donors in the ligands in accord with the involvement of an increasing number of donor atoms in the co-ordination to the two metal ions. In spite of what has been observed for mononuclear complexes, the species $[Zn_2L]^{4+}$ are more stable than $[Cd_2L]^{4+}$, in agreement with the presence in the $[ZnL]^{2+}$ complex of one more unco-ordinated nitrogen, available for binding to a further Zn^{2+} ion, than in the $[CdL]^{2+}$ species to form $[Cd_2L]^{4+}$. This fact is also reflected in the constants corresponding to the addition of the second metal ion to the mononuclear complex, $[ML]^{2+} + M^{2+} \rightleftharpoons [M_2L]^{4+}$, which are higher for Zn^{2+} than for Cd^{2+}. It does not imply that in the resulting binuclear complexes the nitrogen donors of the ligand could not be shared as evenly as possible by the two metal centres.

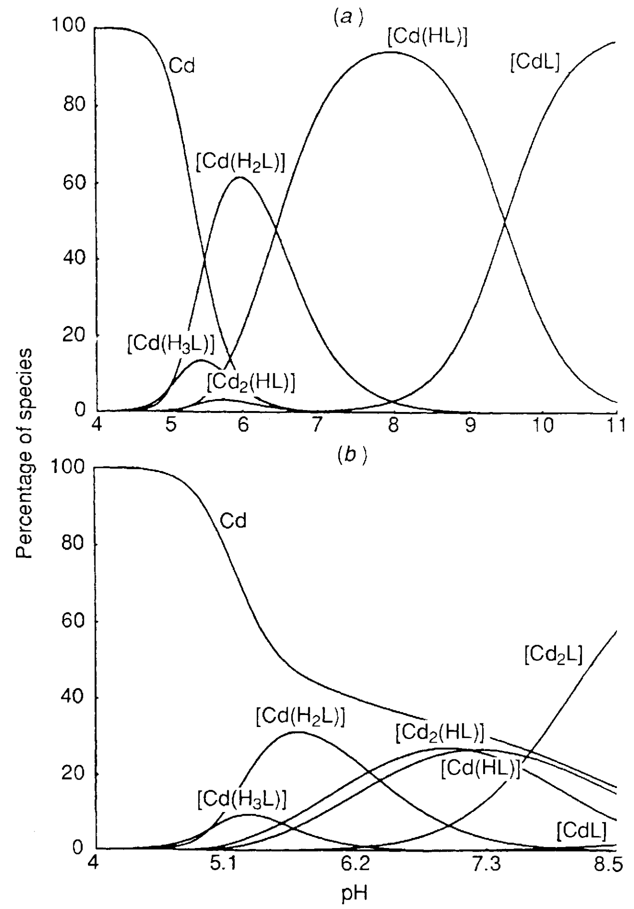


Fig. 7 Distribution diagram for the system Cd^{2+}–L^3. $[L^3] = 1 \times 10^{-3}$ mol dm^{-3}. (*a*) $[Cd^{2+}] = 1 \times 10^{-3}$ mol dm^{-3}, (*b*) 2×10^{-3} mol dm^{-3}

Fig. 7 shows the calculated distribution diagrams for the species formed in solution, as a function of pH, in the system Cd^{2+}–L^3, for 1:1 and 2:1 Cd^{2+}: L^3 molar ratios. At 1:1 molar ratio the mononuclear complexes are almost the unique species in solution [Fig. 7(*a*)], while at 2:1 the binuclear ones predominate [Fig. 7(*b*)]. However, the ability of L^3 to form dicadmium(II) complexes is relatively low, as indicated by the values of the stability constant for the addition of Cd^{2+} to $[CdL^3]^{2+}$ (log $K = 4.74$ in Table 2), so that some Cd^{2+} remains unco-ordinated [Fig. 7(*b*)] and the formation of cadmium hydroxide occurs at pH >8. For this reason the potentiometric measurements involving this system have been limited to pH <8. The tendency of L^4 and L^5 to form binuclear complexes as indicated before is greater and formation of cadmium hydroxide does not occur in these cases.

In all the systems forming zinc binuclear complexes the formation of hydroxo species has been detected. Although the tendency of these open-chain ligand binuclear complexes to form hydroxo-species is relatively high (see Table 1), it is not so great as that observed for the binuclear complexes of their macrocyclic counterparts.[13,14]

Conclusion

In a previous paper[15] we noted that the ligand L^1 forms a mononuclear copper(II) complex whose stability is lower than that of the analogous complex of its macrocyclic $[3k]aneN_k$ counterpart ($[18]aneN_6$). It was found that the greater stability of the macrocyclic complex is due to a large entropic contribution, although the enthalpic term favours the formation of the open-chain complex. With this exception, a macrocyclic effect was not observed for any other copper complex, mono- or bi-nuclear, of the $[3k]aneN_k$ ($k = 6$–10) macrocyclic series of

Table 5 Thermodynamic parameters for some zinc(II) and cadmium(II) complexes of the large polyazacycloalkanes of the series [3k]aneN$_k$ in 0.15 mol dm^{-3} NaClO$_4$ aqueous solution at 298 K *

log K

Reaction	[18]aneN$_6$	[21]aneN$_7$	[24]aneN$_8$	[27]aneN$_9$	[30]aneN$_{10}$
$Zn + L \rightleftharpoons [ZnL]$	18.70	13.33	13.49	—	—
$2Zn + L \rightleftharpoons [Zn_2L]$	—	—	—	20.55	22.51
$[Zn_2L] + OH \rightleftharpoons [Zn_2L(OH)]$	—	—	—	6.70	5.40
$[Zn_2L(OH)] + OH \rightleftharpoons [Zn_2L(OH)_2]$	—	—	4.10	4.90	2.70
$Cd + L \rightleftharpoons [CdL]$	18.80	18.10	14.5	—	—
$2Cd + L \rightleftharpoons [Cd_2L]$	—	—	18.2	20.75	23.21

	$-\Delta H^\circ$		$T\Delta S^\circ$	
	[18]aneN$_6$	[21]aneN$_7$	[18]aneN$_6$	[21]aneN$_7$
$Zn + L \rightleftharpoons [ZnL]$	14.0		11.5	
$Cd + L \rightleftharpoons [CdL]$	15.3	16.1	10.3	8.6

* Values for Zn^{2+} taken from refs. 13 and 14, values for Cd^{2+} taken from ref. 12; [18]aneN$_6$ = 1,4,7,10,13,16-hexaazacyclooctadecane, [21]aneN$_7$ = 1,4,7,10,13,16,19-heptaazacyclohenicosane, [24]aneN$_8$ = 1,4,7,10,13,16,19,22-octaazacyclotetracosane, [27]aneN$_9$ = 1,4,7,10,13,16,19,22,25-nonaazacycloheptacosane and [30]aneN$_{10}$ = 1,4,7,10,13,16,19,22,25,28-decaazacyclotriacontane.

ligands. In order to analyse the macrocyclic effect[16] for the zinc and cadmium complexes of this series, the metathetical reaction $[M_nL_{cyclic}] + L_{open\ chain} \longrightarrow [M_nL_{open\ chain}] + L_{cyclic}$ ($M = Zn^{2+}$ or Cd^{2+}; $n = 1$ or 2) has to be considered. The stability constants of the zinc and cadmium complexes of [3k]aneN$_k$ ($k = 6$–10) ligands are reported in Table 5. This reaction presents negative log K values, *i.e.* there is a macrocyclic effect only for the mononuclear zinc complexes of the ligands with six nitrogens ([18]aneN$_6$, L^1) and for the mononuclear cadmium complexes of the ligands with six and seven nitrogens ([18]aneN$_6$, L^1; [21]aneN$_7$, L^2). In all these cases, as it was observed for $[Cu([18]aneN_6)]^{2+}$, the greater stability of the macrocyclic complexes is mainly due to larger enthalpic contributions. The macrocyclic effect rapidly vanishes with longer ligands, for which an opposite effect is observed (Tables 3 and 5).

Acknowledgements

This work was partially supported by the Spanish Comisión de Ciencia y Tecnologia (Proyecto PB88-0490) and Progetto Finalizzato di Chimica Fine e Secondaria of the Italian Research Council (CNR). We are also indebted to the Italian-Spanish 'Acciones Integradas' for support. One of us (A. R.) thanks the 'Consejería de Educación del Gobierno Autónomo Canario' for a postdoctoral fellowship.

References

1 A. Bianchi, S. Mangani, M. Micheloni, V. Nanini, P. Orioli, P. Paoletti and B. Seghi, *Inorg. Chem.*, 1985, **24**, 1182; A. Bianchi, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1985, **24** 3702; A. Bencini, A. Bianchi, E. García-España, M. Giusti, M. Micheloni and P Paoletti, *Inorg. Chem.*, 1987, **26**, 681; A. Bencini, A. Bianchi, E. García-España, M. Giusti, S. Mangani, M. Micheloni, P. Orioli and P. Paoletti, *Inorg. Chem.*, 1987, **26**, 1243; A. Bencini, A. Bianchi, E. Garcia-España. M. Giusti, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1988, **27**, 176.

2 A. Bencini, A. Bianchi, E. García-España, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1989, **28**, 2480.

3 A. Bencini, A. Bianchi, P. Dapporto, E. García-España, V. Marcelino, M. Micheloni, P. Paoletti and P. Paoli, *Inorg. Chem.*, 1990, **29**, 1716.

4 A. Bencini, A. Bianchi, M. Castelló, P. Dapporto, J. Faus, E. García-España, M. Micheloni, P. Paoletti and P. Paoli, *Inorg. Chem.*, 1989, **28**, 3175.

5 J. Aragó, A. Bencini, A. Bianchi, E. García-España, M. Micheloni, P. Paoletti, J. A. Ramírez and P Paoli, *Inorg. Chem.*, 1991, **30**, 1843.

6 A. Bianchi, L. Bologni, P. Dapporto, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1984, **23**, 1201.

7 M. Fontanelli and M. Micheloni, *Proceedings of the I Spanish-Italian Congress on Thermodynamics of Metal Complexes*, Peñiscola, 3–6th June, 1990.

8 G. Gran, *Analyst* (*London*), 1952, **77**, 601; F. J. Rossotti and H. J. Rossotti, *J. Chem. Educ.*, 1965, **42**, 375.

9 P. Gans, A. Sabatini and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.

10 E. J. Sarnesky, H. L. Surprenant, F. K. Molen and C. N. Reilley, *Anal. Chem.*, 1975, **47**, 1126.

11 R. M. Smith and A. E. Martell, *Critical Stability Constants*, Plenum, New York, 1975, vol. 2.

12 A. Bencini, A. Bianchi, M. Castelló, M. Di Vaira, J. Faus, E. García-España, M. Micheloni, P. Paoletti and P. Paoli, *Inorg. Chem.*, 1989, **28**, 347.

13 A. Bencini, A. Bianchi, E. García-España, S. Mangani, M. Micheloni, P. Orioli and P. Paoletti, *Inorg. Chem.*, 1988, **27**, 1104.

14 A. Bencini, A. Bianchi, P. Dapporto, E. García-España, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1989, **28**, 1188.

15 A. Bencini, A. Bianchi, M. Micheloni, P. Paoletti, E. García-España and M. A. Niño, *J. Chem. Soc., Dalton Trans.*, 1991, 1171.

16 D. K. Cabiness and D. W. Margerum, *J. Am. Chem. Soc.*, 1969, **91**, 6540; F. P. Hinz and D. W. Margerum, *J. Chem. Soc., Dalton Trans.*, 1976, **13**, 2941; E. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1976, **116**, 2341; A. Anichini, L. Fabrizzi, P. Paoletti and R. M. Clay, *J. Chem. Soc., Chem. Commun.*, 1977, 244; R. M. Clay, S. Corr, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1985, **24**, 3330.

Received 22*nd March* 1991; *Paper* 1/01390D