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Synthesis, solution studies and structural characterisation of complexes of a mixed oxa–aza macrocycle bearing pendant amino arms

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A new mixed oxa–aza macrocycle having ethylamino pendant arms on the secondary nitrogens, namely 7,10,13-tris(2-aminoethyl)-1,4-dioxa-7,10,13-triazacyclopentadecane (L), has been synthesized. The co-ordination chemistry of L towards Zn^{II}, Cu^{II}, Cd^{II}, Pb^{II} and Ba^{II} has been studied by X-ray crystallography, potentiometry and NMR spectroscopy. The single crystal structures of $[Zn(L)][ClO_4]_2$ and $[Cu(L)][ClO_4]_2$ confirm that the complexes are isostructural with the metal ion bound to the three pendant arm N-donors and to two N-donors of the macrocyclic core to give a slightly distorted square-pyramidal geometry. The remaining three donors, a tertiary amine and the two oxygens of the ring, remain unco-ordinated leaving one part of the macrocyclic cavity open with the metal ion bound *exo* to the macrocyclic cavity. The single crystal structures of $[Pb(L)][ClO_4]_2$ and $[Ba(L)][ClO_4]_2$ show the metal ion co-ordinated to all the donor atoms of the ligand, with Ba^{II} co-ordinated additionally to a ClO_4^- anion in a bidentate fashion to give a 10-co-ordinate metal centre. The binding of L to Zn^{II}, Cu^{II}, Cd^{II} and Pb^{II} was investigated by potentiometric measurements in aqueous solutions. These metals form only mononuclear complexes with unusually low stability constants compared with those found for other hexaamine macrocycles. All the complexes show a marked tendency to protonation. These observations suggest the presence of unco-ordinated or weakly co-ordinated N-donors also in aqueous solution. NMR spectroscopic studies on the complexes of Zn^{II}, Cd^{II}, Ba^{II} and Pb^{II} of L reveal a rigidity which is lost on increasing temperature.

Introduction

The co-ordination chemistry of aza and mixed oxa–aza macrocycles containing different pendant arms attached to the aza centres has attracted the attention of many researchers over the past twenty years.[1,2] These ligands can exhibit remarkable metal ion selectivity and show specific complexation behaviour forming metal complexes with unusual structures.[2,3] While carboxylate or phosphonate pendant arm derivatives have widely been studied for the application of their lanthanide complexes as contrast agents in magnetic resonance imaging,[3] and ligands with hydroxyalkyl or ether pendant groups exhibit good selectivity between large and small metal ions,[2] there have been far fewer reports on attachment of amine pendant arms.

Primary aminoalkyl pendant arms have been attached to simple macrocyclic ligands such as $[9]aneN_3$,[4–6] $[12]aneN_3$,[7] and $[14]aneN_4$,[8–10] and solution data and crystal structure determinations have been reported. In complexes of functionalised $[14]aneN_4$ the metal ions are normally held within the macrocycle, but examples of exocyclic complexes with two metal centres not incorporated into the ring have also been reported, for example with *N*,*N′*,*N″*,*N‴*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane.[9] Less work has been reported on mixed oxa–aza macrocycles bearing primary aminoalkyl pendant arms. Hosseini and Lehn have reported[11] the synthesis of the macrocycle $[24]aneN_6O_2$ with six aminoethyl pendant arms, McAuley and co-workers[12] the preparation of $[9]aneN_2O$ with two propylamino groups, while Zinic *et al.* have described[13] the synthesis of various oxa–aza macrocycles such as $[15]aneNO_4$, $[18]aneNO_5$ and $[18]aneN_2O_4$ with aminoethyl pendant arms. However, in none of these studies has the co-ordination chemistry of these ligands been reported. Pendant arms with O-donor groups such as alcohols, ethers, amides and carboxylic acids have also been attached to oxa–aza macrocycles.[2,14–16] These ligands have been studied in solution to determine potential metal ion selectivity, for example for the large Pb^{II} over the small Zn^{II},[2,14,15] or for the complexation of Gd^{III} for use as contrast agents.[3,15]

In this work we focus on the co-ordination properties of the ligand 7,10,13-tris(2-aminoethyl)-1,4-dioxa-7,10,13-triazacyclopentadecane (L), which has an asymmetric disposition of donor atoms as well as the potential for simultaneous co-ordination of O- and N-donors. Solution and structural studies have been reported on the macrocyclic precursor $[15]aneN_3O_2$;[14,17] the synthesis of its derivative with hydroxyalkyl pendant arms and the stability constants of its complexes with Cu^{II}, Ni^{II}, Zn^{II}, Cd^{II} and Pb^{II} have also been studied by Hancock *et al.*[14] Other derivatives of $[15]aneN_3O_2$ have been reported,[13,18] but their co-ordination chemistry has not been investigated. We report herein the synthesis of the new ligand L, the single crystal structure determination of its complexes with Zn^{II}, Cu^{II}, Pb^{II} and Ba^{II}, and solution studies on both the ligand and complexes. Studies on the protonation of L and its stability constants with Cu^{II}, Zn^{II}, Cd^{II} and Pb^{II} and NMR spectroscopic studies of complexes of Zn^{II}, Cd^{II}, Ba^{II} and Pb^{II} are also reported.

Results and discussion

The synthesis of 7,10,13-tris(2-aminoethyl)-1,4-dioxa-7,10,13-triazacyclopentadecane (L) is summarised in Scheme 1. The procedure starting from 1,4-dioxa-7,10,13-cyclopentadecane ($[15]aneN_3O_2$; **1** in Scheme 1) is similar to that reported

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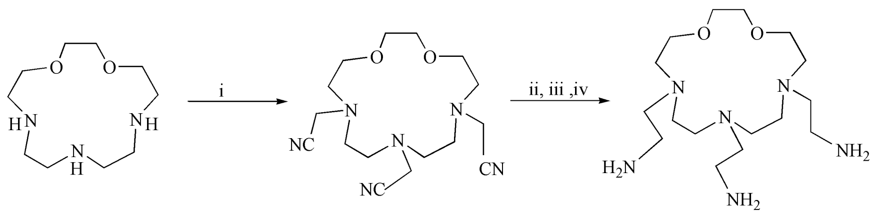
Table 1 Crystal data and X-ray experimental details for $[Zn(L)][ClO_4]_2$ **3**, $[Cu(L)][ClO_4]_2$ **4**, $[Pb(L)][ClO_4]_2$ **5** and $[Ba(L)][ClO_4]_2$ **6**

Formula	$C_{16}H_{38}N_6O_2Zn{\cdot}2ClO_4$	$C_{16}H_{38}CuN_6O_2{\cdot}2ClO_4$	$C_{16}H_{38}N_6O_2Pb{\cdot}2ClO_4$	$C_{16}H_{38}BaN_6O_2{\cdot}2ClO_4$
M	610.79	608.96	752.61	682.76
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/Å	9.273(5)	9.2446(13)	10.816(8)	9.402(1)
b/Å	13.154(8)	13.129(2)	15.486(9)	14.365(2)
c/Å	20.692(13)	20.653(3)	15.844(10)	19.363(2)
V/Å^3	2476(2)	2459.7(6)	2624(3)	2598.5(9)
T/K	150(2)	150(2)	220(2)	150(2)
Z	4	4	4	4
μ/mm^{-1}	1.271	1.169	6.693	1.790
Unique data	3233	4313	5145	6259
Observed data	2103	3568	3729	3553
$R1$, $wR2$[a]	0.0755, 0.1552	0.0449, 0.1135	0.0659, 0.1895	0.0387, 0.0625

[a] SHELXL 97 $R1$ based on observed data with $I \geq 2\sigma(I)$, $wR2$ on all unique data.



(1) **(2)** **L**

Scheme 1 i $ClCH_2CN$, NEt_3, EtOH, 18 h; ii 1 M $BH_3{\cdot}THF$, 48 h; iii 6 M HCl, 24 h; iv Dowex 1 × 8-50.

previously for the introduction of three aminoethyl pendant arms to 1,4,7-triazacyclononane.[6] Compound **2** can be prepared in 56% yield by treatment of $[15]aneN_3O_2$ with three equivalents of chloroacetonitrile in the presence of an excess of Et_3N in EtOH. Conversion into the desired product L was achieved in 75% yield by reduction of **2** with 1 M BH_3 solution in THF followed by hydrolysis with concentrated HCl solution. The free amine is obtained by passing an aqueous solution of the hydrochloride salt of L through a Dowex 1 × 8-50 column. All products were characterised satisfactorily by ^1H and ^{13}C NMR spectroscopy, EI mass spectrometry and by elemental analysis.

The complexes $[M(L)][ClO_4]_2$ [M = Zn^{II}, Cu^{II}, Ba^{II} or Pb^{II}] and $[Cd(L)]Cl_2$ were prepared in good yields by treating L with one equivalent of $M(ClO_4)_2{\cdot}xH_2O$ or $CdCl_2{\cdot}2.5H_2O$ in MeOH at room temperature. Elemental analytical data and mass spectra for all the complexes are consistent with the formulation $[M(L)][ClO_4]_2$ and $[Cd(L)]Cl_2$. Single crystals suitable for X-ray diffraction studies were grown for all the complexes apart from $[Cd(L)]Cl_2$. $[Zn(L)][ClO_4]_2$ **3** and $[Cu(L)][ClO_4]_2$ **4** are isostructural (Table 1) with the five co-ordinated metal ion adopting a distorted square-based pyramidal geometry (Fig. 1a and 1b), *via* binding to three N-donors of the primary amines of the pendant arms and to two N-donors of the tertiary amine centres of the macrocycle. The metal centre is bound in an exocyclic manner and is situated outside the macrocyclic cavity. The two oxygens [O(10) and O(13)] and the remaining tertiary nitrogen [N(7)] from the macrocycle do not co-ordinate and are remote from the metal centre lying at 4.854(7), 5.114(7) and 3.492(8) Å, respectively, in **3** at 4.912(4), 5.052(3) and 3.627(3) Å, respectively, in **4**. The macrocyclic framework assumes a very similar conformation in **3** and **4** as indicated by the similar torsion angles within the macrocyclic backbones. The donor atoms forming the base of the pyramid are from two primary amines [N(3A) and N(3B)] from the pendant arms and two tertiary amines [N(1) and N(4)] from the macrocyclic framework. The r.m.s. deviation of the N atoms from the N_4 basal plane is 0.028 Å for the zinc(II) species and 0.010 Å for the copper(II) complex. The Zn^{II} ion lies 0.70 Å and the Cu^{II} 0.51 Å from their respective planes in the direction of the apical

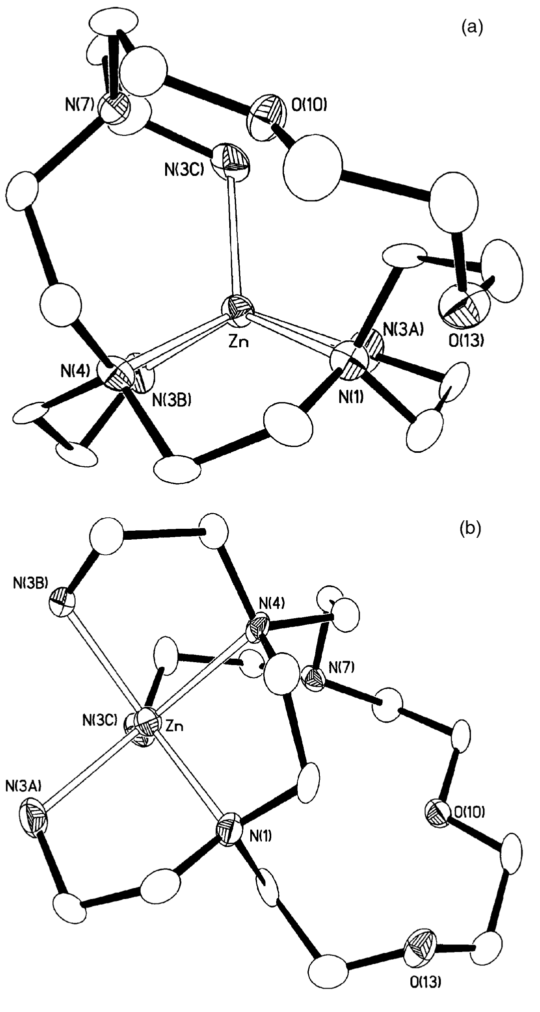


Fig. 1 (a) Crystal structure of the cation $[Zn(L)]^{2+}$ with numbering scheme adopted showing the square pyramidal co-ordination geometry. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at 50% probability. (b) Alternative view of the cation $[Zn(L)]^{2+}$ showing the unco-ordinated part of the macrocycle.

Table 2 Selected bond lengths (Å) and angles (°) for $[Zn(L)][ClO_4]_2$ **3** and $[Cu(L)][ClO_4]_2$ **4**

	$[Zn(L)][ClO_4]_2$	$[Cu(L)][ClO_4]_2$
M–N(1)	2.170(8)	2.068(3)
M–N(4)	2.211(8)	2.093(3)
M–N(3A)	2.181(9)	2.065(3)
M–N(3B)	2.128(8)	2.050(3)
M–N(3C)	2.039(9)	2.188(4)
N(1)–M–N(4)	81.9(3)	85.14(12)
N(1)–M–N(3A)	81.0(3)	84.12(13)
N(4)–M–N(3B)	81.6(3)	84.52(13)
N(3A)–M–N(3B)	91.9(3)	92.43(14)
N(1)–M–N(3B)	140.3(4)	150.70(14)
N(4)–M–N(3A)	144.1(3)	152.04(14)
N(3C)–M–N(1)	118.7(4)	112.71(13)
N(3C)–M–N(4)	117.4(3)	113.18(13)
N(3C)–M–N(3A)	98.4(4)	94.78(14)
N(3C)–M–N(3B)	100.9(4)	96.56(14)

Table 3 Selected bond lengths (Å) and angles (°) for $[Pb(L)][ClO_4]_2$ **5**

Pb–N(1)	2.853(10)	Pb–O(10)	3.048(15)
Pb–N(4)	2.587(11)	Pb–O(13)	3.083(14)
Pb–N(7)	2.802(10)	Pb–N(3A)′[a]	2.69(3)
Pb–N(3A)	2.65(2)	Pb–N(3B)′[a]	2.60(2)
Pb–N(3B)	2.51(2)	Pb–N(3C)′[a]	2.69(2)
Pb–N(3C)	2.60(3)		
O(10)–Pb–N(3A)	153.0(6)	N(3C)–Pb–N(7)	67.5(6)
O(10)–Pb–N(3B)	150.4(5)	O(13)–Pb–N(7)	109.9(4)
O(10)–Pb–N(3C)	107.7(7)	O(10)–Pb–N(7)	58.8(3)
O(10)–Pb–O(13)	53.3(4)	N(3A)–Pb–N(3B)	56.0(7)
O(13)–Pb–N(3A)	105.9(6)	N(3A)–Pb–N(3C)	81.0(7)
O(13)–Pb–N(3B)	134.9(6)	N(3B)–Pb–N(3C)	75.5(8)
O(13)–Pb–N(3C)	147.7(7)	N(1)–Pb–N(4)	68.8(3)
N(3B)–Pb–N(4)	62.81(8)	N(1)–Pb–N(7)	137.7(4)
N(3C)–Pb–N(4)	118.7(7)	N(3A)–Pb–N(1)	67.2(5)
O(10)–Pb–N(4)	85.9(4)	N(3B)–Pb–N(1)	78.9(5)
O(13)–Pb–N(4)	88.2(4)	N(3C)–Pb–N(1)	146.8(6)
N(3A)–Pb–N(7)	144.0(5)	N(4)–Pb–N(7)	62.06(9)
N(3B)–Pb–N(7)	98.1(5)	N(3A)–Pb–N(4)	88.39(10)

[a] Equally populated component of the disorder not described in the text.

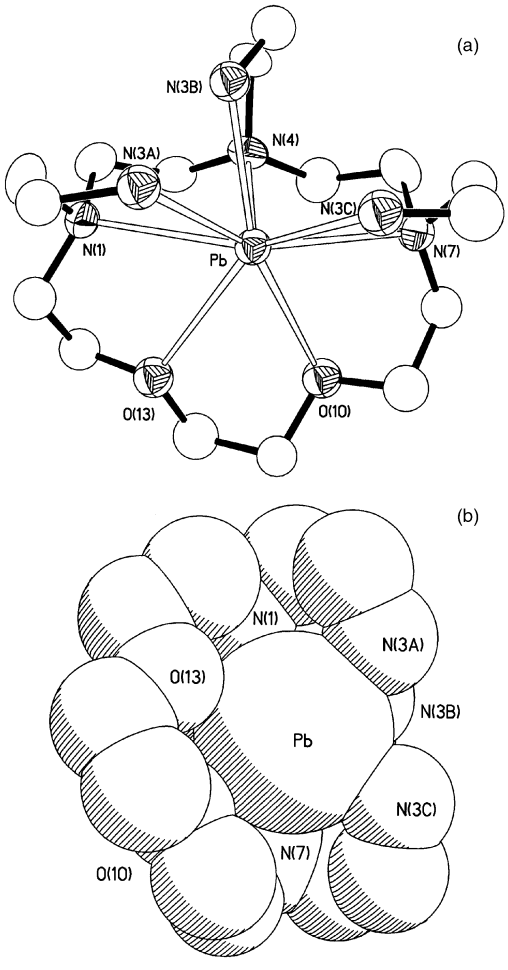


Fig. 2 (a) Crystal structure of the cation $[Pb(L)]^{2+}$ with numbering scheme adopted. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at 30% probability. (b) Space-filling model of the complex cation $[Pb(L)]^{2+}$ showing the co-ordination gap at the metal centre.

position occupied by the remaining primary amine [N(3C)]. The Zn–N(3C) apical bond forms an angle of 13.7° with the normal to the basal plane, while the Cu–N(3C) bond forms an angle of 12.7°, being in both cases very near to perpendicular. In $[Cu(L)][ClO_4]_2$ the Cu–N (basal) bond lengths lie in the range 2.050(3)–2.093(3) Å and Cu–N (apical) is 2.188(4) Å. In $[Zn(L)][ClO_4]_2$ the corresponding bond lengths are 2.128(9)–2.211(8) and 2.039(9) Å (selected bond lengths and angles are in Table 2). The difference between the structures is that the apical donor is the closest to the metal centre in $[Zn(L)]^{2+}$, while in $[Cu(L)]^{2+}$ the shortest bond lengths are to the basal donors as expected in a d^9 Jahn–Teller distorted complex. The square base of the pyramid is quite regular with three five-membered chelate rings formed at the metal centre; these are very similar both in the angles at the metal centre {81.0(3)–81.9(3)° for $[Zn(L)]^{2+}$ and 84.1(1)–85.1(1)° for $[Cu(L)]^{2+}$} and in the distance between the N-donors [2.83(1)–2.87(1) Å for Zn^{II} and 2.769(4)–2.814(4) Å for Cu^{II}].

The major component of disorder on the macrocyclic backbone and one component of the disordered pendant arms for the crystal structure of $[Pb(L)][ClO_4]_2$ (Fig. 2a) are described in the Experimental section. Selected bond lengths and angles are reported in Table 3. The Pb^{II} is formally co-ordinated to all the eight donor atoms of the ligand, but some of these distances are extended (Table 3). Two types of the Pb–N interactions can be discerned in this structure: the three primary amines and N(4) of the ring are bound close to Pb^{II} with bond lengths [2.51(2)–2.65(2) Å] similar to those found in other N-macrocyclic complexes of Pb^{II}.[19,20] The lead(II) centre is co-ordinated further to two other tertiary nitrogens, N(1) and N(7), with bond lengths of 2.85(1) and 2.80(1) Å, respectively, and to two oxygens, O(10) and O(13), at 3.05(1) and 3.08(1) Å, respectively. We regard these $Pb\cdots O$ interactions as clearly long range since the sum of the ionic radius of Pb^{2+} with co-ordination number 8 and that of O^{2-} with co-ordination number 3 is 2.65 Å.[21]

The effect of the lone pair on Pb^{II} on the stability and geometry of its complexes has been discussed previously.[19,22,23] This lone pair can be either active or inactive, depending mostly on the nature of the donor atoms at Pb^{II}. In the structure of $[Pb(L)]^{2+}$ two effects of a stereochemically active lone pair can be envisaged: the shortening of some of the Pb–N bonds and the presence of a gap in the co-ordination sphere around the metal. When Pb^{II} has an active lone pair the apparent ionic radius decreases by about 0.3 Å, which may explain the strong co-ordination of the four nitrogens. Furthermore, the apparent occupation of a co-ordination site on Pb^{II} by the lone pair can be seen in Fig. 2(b) which shows the space-filling model for the $[Pb(L)]^{2+}$ complex cation. Given the very wide O(10)–Pb–N(3A) and O(13)–Pb–N(3C) angles of *ca.* 150°, it is not unreasonable to conclude that the lone pair resides between O(10) and O(13) and N(3A) and N(3C). In a recent study reported by Glusker and co-workers,[22] this co-ordination mode with a gap in the co-ordination sphere at the metal centre has been named hemi-directed. Hemi-directed structures with eight-co-ordinate Pb^{II}

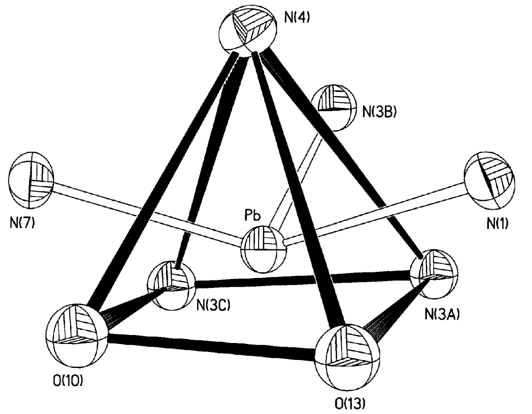


Fig. 3 Tricapped pyramidal co-ordination geometry about the lead(II) centre in complex **5**. Displacement ellipsoids are drawn at 30% probability.

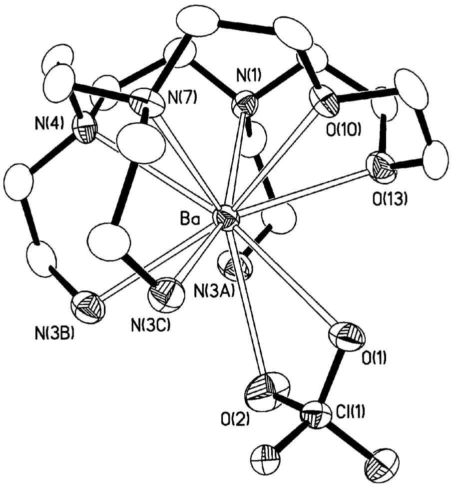


Fig. 4 Crystal structure of the cation $[Ba(L)(ClO_4)]^+$ with numbering scheme adopted. Hydrogen atoms have been omitted for clarity. Displacement ellipsoids are drawn at 50% probability.

have been found to be quire rare in comparison to structures with no stereochemically active lone pair at Pb^{II} (holodirected).[22]

The co-ordination sphere at Pb^{II} in $[Pb(L)]^{2+}$ can best be described as tricapped pyramidal (Fig. 3). The base of the pyramid is a rectangle formed by N(3A), N(3C), O(10) and O(13) with r.m.s. deviation from the basal plane of 0.085 Å. The long sides are N(3C)–O(10) and N(3A)–O(13) with distances of 4.57(3) and 4.58(3) Å, respectively, while the short sides are N(3A)–N(3C) and O(10)–O(13), 3.41(3) and 2.75(2) Å, respectively. The angles at the rectangular base are in the range 84.9(6)–94.7(5)°. N(1), N(7) and N(3B) cap three of the four triangular faces of the pyramid, while N(4) occupies the apical position.

The structure of the complex cation $[Ba(L)(ClO_4)]^+$ is shown in Fig. 4 and selected bond lengths and angles are reported in Table 4. The barium(II) centre is co-ordinated to all the donor atoms of the ligand plus two O-donors from one ClO_4^- anion, giving a co-ordination number of ten, as frequently found for the large Ba^{II} (the effective ionic radius of Ba^{2+} with co-ordination number 10 is 1.52 Å).[21] The metal ion is encapsulated by the three pendant arms and, in the side left open by the absence of pendant arms, the macrocycle is slightly bent to permit the two O-donors of the ClO_4^- anions to bind, thereby completing the co-ordination sphere. The Ba–N bond lengths are in the range 2.889(3)–2.996(3) Å, the three tertiary amines being a little more distant from the metal centre than the three primary ones. The bond lengths between Ba^{II} and the macrocyclic O-donors are in the range 2.846(3)–3.015(3) Å with the ClO_4^- O-donors [O(1) and O(2)] less strongly bound at 2.978(3) and 3.015(3) Å, respectively. All the distances are in the range found in the literature.[24]

Table 4 Selected bond lengths (Å) and angles (°) for $[Ba(L)][ClO_4]_2$ **6**

Ba–N(1)	2.939(3)	Ba–N(3C)	2.902(3)
Ba–N(4)	2.949(3)	Ba–O(10)	2.846(3)
Ba–N(7)	2.996(3)	Ba–O(13)	2.911(3)
Ba–N(3A)	2.889(3)	Ba–O(1)	2.978(3)
Ba–N(3B)	2.889(3)	Ba–O(2)	3.015(3)
N(4)–Ba–N(7)	62.06(9)	O(10)–Ba–N(3C)	87.57(9)
N(3A)–Ba–N(4)	88.39(10)	O(10)–Ba–O(13)	57.58(8)
N(3B)–Ba–N(4)	62.81(8)	O(10)–Ba–O(1)	79.19(8)
N(3C)–Ba–N(4)	99.02(9)	O(10)–Ba–O(2)	123.90(8)
O(10)–Ba–N(4)	104.28(8)	O(13)–Ba–N(3A)	76.97(9)
O(13)–Ba–N(4)	122.24(8)	O(13)–Ba–N(3B)	147.26(9)
N(4)–Ba–O(1)	163.76(8)	O(13)–Ba–N(3C)	129.89(9)
N(4)–Ba–O(2)	131.31(8)	O(13)–Ba–O(1)	73.22(8)
N(3A)–Ba–N(7)	150.01(10)	O(13)–Ba–O(2)	92.10(9)
N(3B)–Ba–N(7)	97.64(9)	N(3A)–Ba–O(1)	100.94(9)
N(3C)–Ba–N(7)	60.04(9)	N(3A)–Ba–O(2)	65.16(9)
N(1)–Ba–N(4)	64.29(9)	O(13)–Ba–N(7)	113.30(8)
N(3B)–Ba–O(1)	107.56(8)	N(1)–Ba–N(7)	98.88(9)
O(10)–Ba–N(7)	57.83(8)	N(3B)–Ba–O(2)	69.87(9)
N(3A)–Ba–N(1)	60.71(9)	O(1)–Ba–N(7)	108.97(8)
N(3C)–Ba–O(1)	65.05(9)	N(3B)–Ba–N(1)	106.57(9)
O(2)–Ba–N(7)	138.15(9)	N(3C)–Ba–O(2)	78.12(9)
N(3C)–Ba–N(1)	158.46(9)	N(3A)–Ba–N(3B)	70.71(10)
O(1)–Ba–O(2)	45.50(7)	O(10)–Ba–N(1)	83.92(8)
N(3A)–Ba–N(3C)	135.92(10)	O(13)–Ba–N(1)	59.79(9)
N(3B)–Ba–N(3C)	74.45(10)	O(1)–Ba–N(1)	131.90(8)
O(10)–Ba–N(3A)	132.74(9)	O(2)–Ba–N(1)	122.88(9)
O(10)–Ba–N(3B)	155.00(9)		

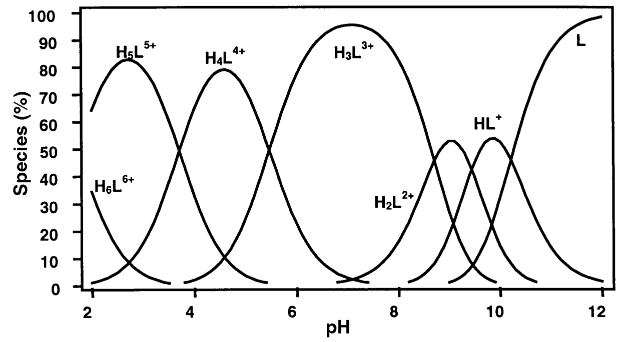


Fig. 5 Distribution diagram of the protonated species of L as a function of pH (0.1 M Me_4NCl, 298.1 K).

Protonation of L

The protonation equilibria of L have been studied in 0.1 mol dm^{-3} Me_4NCl aqueous solution at 298.1 ± 0.1 K by means of potentiometric pH ($-\log[H^+]$) measurements and the results are reported in Table 5, while a distribution diagram for the species present in solution as a function of pH for the system L/H^+ is reported in Fig. 5. Ligand L can bind up to six protons in the pH range investigated. The most interesting finding in Table 5 is the sharp decrease in basicity observed between the third and the fourth protonation steps. In fact the first three protonation constants range between 10.22 and 8.71 logarithmic units with a difference between the first and the third protonation constants of only 1.5 units, while the difference between the third and the fourth is *ca.* 3.4 logarithmic units. This behaviour can be rationalised taking into account the different nature of the N-donors of L, which contains three primary and three tertiary amine groups.[25] We suggest that the first three protonation steps will involve the NH_2 groups of the pendant arms. This affords the species $[H_3L]^{3+}$ in which the three acidic protons are located as far apart from one another thus minimising the electrostatic repulsion between the positive charges gathered on the ligand. This species $[H_3L]^{3+}$ is prevalent in

Table 5 Protonation constants of L (log *K*) determined by means of potentiometric measurements in 0.1 M $\mathrm{Me_4NCl}$ at 298.1 K

Equilibrium	Log *K*
$\mathrm{L + H^+ \rightleftharpoons [HL]^+}$	10.22(1)[a]
$\mathrm{[HL]^+ + H^+ \rightleftharpoons [H_2L]^{2+}}$	9.45(1)
$\mathrm{[H_2L]^{2+} + H^+ \rightleftharpoons [H_3L]^{3+}}$	8.71(1)
$\mathrm{[H_3L]^{3+} + H^+ \rightleftharpoons [H_4L]^{4+}}$	5.36(1)
$\mathrm{[H_4L]^{4+} + H^+ \rightleftharpoons [H_5L]^{5+}}$	3.70(1)
$\mathrm{[H_5L]^{5+} + H^+ \rightleftharpoons [H_6L]^{6+}}$	2.97(1)

[a] Values in parentheses are standard deviations on the last significant figure.

Table 6 Stability constants (log *K*) of the complexes of $\mathrm{Cu^{II}}$, $\mathrm{Zn^{II}}$, $\mathrm{Cd^{II}}$ and $\mathrm{Pb^{II}}$ with L (0.1 M $\mathrm{Me_4NCl}$, 298.1 K)

Equilibrium	log *K*
$\mathrm{Cu^{2+} + L \rightleftharpoons [Cu(L)]^{2+}}$	17.38(2)[a]
$\mathrm{[Cu(L)]^{2+} + H^+ \rightleftharpoons [Cu(HL)]^{3+}}$	9.26(2)
$\mathrm{[Cu(HL)]^{3+} + H^+ \rightleftharpoons [Cu(H_2L)]^{4+}}$	6.01(1)
$\mathrm{[Cu(H_3L)]^{4+} + H^+ \rightleftharpoons [Cu(H_3L)]^{5+}}$	2.98(2)
$\mathrm{Zn^{2+} + L \rightleftharpoons [Zn(L)]^{2+}}$	12.15(1)
$\mathrm{[Zn(L)]^{2+} + H^+ \rightleftharpoons [Zn(HL)]^{3+}}$	8.33(2)
$\mathrm{[Zn(HL)]^{3+} + H^+ \rightleftharpoons [Zn(H_2L)]^{4+}}$	5.81(1)
$\mathrm{[Zn(L)]^{2+} + OH^- \rightleftharpoons [Zn(L)(OH)]^+}$	2.44(6)
$\mathrm{Cd^{2+} + L \rightleftharpoons [Cd(L)]^{2+}}$	13.02(2)
$\mathrm{[Cd(L)]^{2+} + H^+ \rightleftharpoons [Cd(HL)]^{3+}}$	8.42(2)
$\mathrm{[Cd(HL)]^{3+} + H^+ \rightleftharpoons [Cd(H_2L)]^{4+}}$	6.35(1)
$\mathrm{Pb^{2+} + L \rightleftharpoons [Pb(L)]^{2+}}$	10.45(4)
$\mathrm{[Pb(L)]^{2+} + H^+ \rightleftharpoons [Pb(HL)]^{3+}}$	9.21(2)
$\mathrm{[Pb(HL)]^{3+} + H^+ \rightleftharpoons [Pb(H_2L)]^{4+}}$	5.98(1)

[a] Values in parentheses are standard deviations on the last significant figure.

aqueous solution over a wide pH range (5.5–9.0, Fig. 5). The subsequent protonation steps necessarily involve the sterically more protected tertiary N-donors of the macrocyclic ring, close to the already protonated primary amines. For these reasons the last thee protonation steps show much lower protonation constants (log $K < 5.5$) than the first ones.

Metal binding properties in aqueous solution

The formation of complexes of $\mathrm{Cu^{II}}$, $\mathrm{Zn^{II}}$, $\mathrm{Cd^{II}}$ and $\mathrm{Pb^{II}}$ with L has been studied by potentiometric measurements in aqueous solution (0.1 M $\mathrm{Me_4NCl}$, 298.1 K). The stability constants are reported in Table 6, while distribution diagrams are shown in Fig. 6. No interaction between L and $\mathrm{Ba^{II}}$ was monitored by potentiometry under these conditions. With these metal ions L forms only mononuclear complexes, all of which show a marked tendency to protonate. As shown in Fig. 6, all complexes easily form mono- and di-protonated species under alkaline to slightly acidic conditions and, in the case of $\mathrm{Cu^{II}}$, a triprotonated species is also formed below pH 4. The stability constants of the complexes of L are unusually low compared to those found for macrocyclic hexaamine ligands.[26] For example, they are much lower than those found for the corresponding complexes with 1,4,7,10,13,16-hexaazacyclooctadecane ([18]-ane$\mathrm{N_6}$) and also lower than those with 1,4,7,13-tetramethyl-1,4,7,10,13,16-hexaazacyclooctadecane ($\mathrm{Me_4}$[18]ane$\mathrm{N_6}$),[26] which contains two secondary and four tertiary nitrogen donors. The stability constants of the complexes of $\mathrm{Cu^{II}}$ and $\mathrm{Zn^{II}}$ with [18]ane$\mathrm{N_6}$ are 24.40 and 18.70 logarithmic units, respectively, and those with $\mathrm{Me_4}$[18]ane$\mathrm{N_6}$ 20.49 and 13.29, respectively, significantly higher than those found for the corresponding complexes with L (17.38 and 12.15 logarithmic units, respectively, see Table 6). Furthermore, the complexes of $\mathrm{Zn^{II}}$, $\mathrm{Cd^{II}}$ and $\mathrm{Pb^{II}}$ with these hexaazamacrocycles, in which the metals are six-co-ordinated, do not show any tendency to protonate. Only the copper(II) complexes with $\mathrm{Me_4}$[18]ane$\mathrm{N_6}$ and [18]ane$\mathrm{N_6}$ bind two protons at acidic pH with very low protonation constants (log $K < 3.5$ log units for the equilibria $\mathrm{[Cu(L)]^{2+} + H^+ \rightleftharpoons [Cu(HL)]^{3+}}$ or $\mathrm{[Cu(HL)]^{3+} + H^+ \rightleftharpoons [Cu(H_2L)]^{4+}}$ respectively.

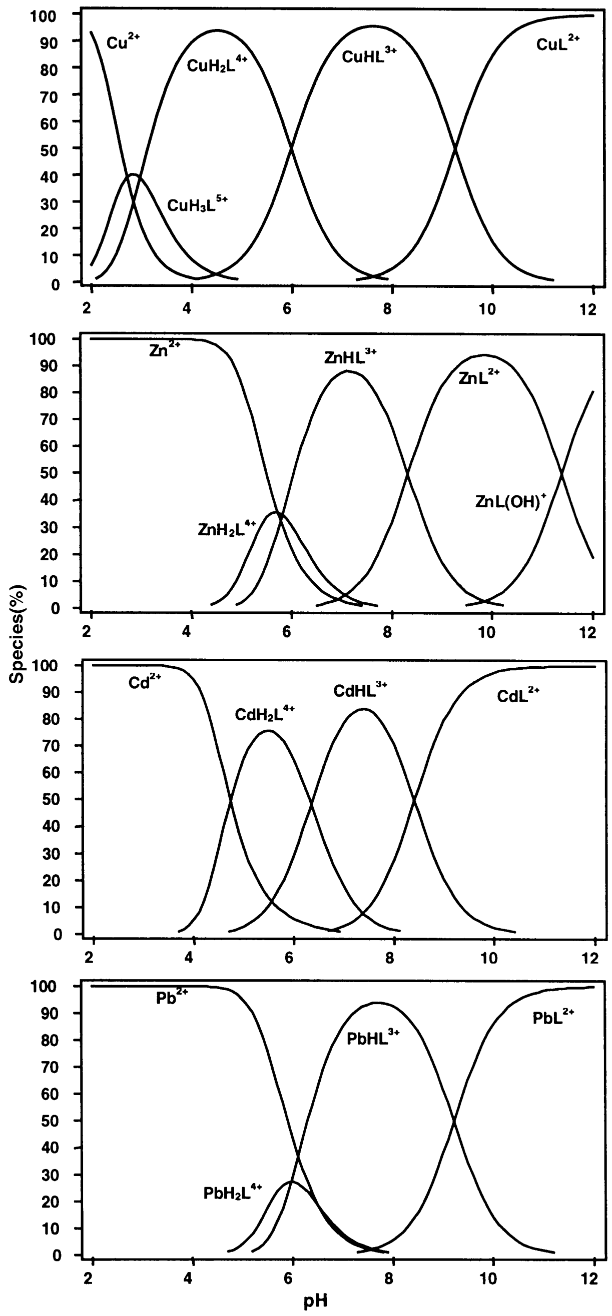


Fig. 6 Distribution diagrams for the L/$\mathrm{M^{II}}$ systems ([L] = [$\mathrm{M^{II}}$] = 1×10^{-3} M, 0.1 M $\mathrm{Me_4NCl}$, 298.1 K).

Among macrocyclic ligands bearing aminoalkyl pendant arms, the octaamine *N*,*N*′,*N*″,*N*‴-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (TAEC) has been investigated by Wainwright and co-workers, with particular attention to the stability of its metal complexes in aqueous solution.[10] This ligand contains four primary and four tertiary amine groups and shows a marked tendency to give binuclear complexes due to the large number of N-donors available for metal co-ordination. Only $\mathrm{Cu^{II}}$ and $\mathrm{Cd^{II}}$ give mononuclear complexes $\mathrm{[M(TAEC)]^{2+}}$ in aqueous solutions, with similar or somewhat higher stability than that of complexes of L (19.9 and 13.4 logarithmic units, respectively).

It should also be noted that only extensive protonation of L inhibits the formation of metal complexes. In fact, as can be seen from Table 6 and Fig. 6, all the metal ions under investigation form complexes with protonated species of L. In particular, the equilibrium constants for the addition of the first H^+ to the complexes $[M(L)]^{2+}$ are quite high, only 1–2 log units lower than the first protonation constant of the "free" ligand, suggesting that protonation occurs on an N-centre uninvolved, or only weakly involved, in metal co-ordination. This observation can partially explain the lower stability of the present metal complexes with respect to those formed with other macrocyclic hexaamines.[26] Furthermore, L contains three tertiary amine groups, which usually show lower binding ability than primary or secondary ones. In fact tertiary N-centres can be poorer σ donors than primary or secondary amines, since N-functionalisation prevents the formation of hydrogen bonds between water and amine groups which contribute, *via* the $H_2O \cdots H–N$ interaction, to the σ-donating ability of amine groups in aqueous solution.[25]

These observations are supported by the crystal structure analyses. In the four crystal structures reported not all the nitrogen centres are strongly involved in metal co-ordination; in particular, the crystal structures of $[Cu(L)]^{2+}$ and $[Zn(L)]^{2+}$ confirm that a tertiary amine is not bound to the metal ion. The metal centre in these complexes is situated outside the macrocyclic cavity and, therefore, a large part of the macrocyclic framework, containing an amine donor, is not involved in co-ordination. Although conclusions about co-ordination properties of ligands in solution derived from solid state data may sometimes be misleading, these observations can reasonably explain the low values of the stability constants for these copper(II) and zinc(II) complexes compared to those of complexes formed with other hexaamine ligands,[26] as well as the high values of equilibrium constants for addition of the first proton to the complexes $[M(L)]^{2+}$.

Comparing the stability of the different metal complexes, it should be noted that $[Cd(L)]^{2+}$ shows a higher thermodynamic stability than $[Zn(L)]^{2+}$, suggesting involvement of the oxygen donors in the cadmium co-ordination sphere. Finally, looking at the stability of the lead(II) complex of L, it has been observed previously that adding pendant arms to a macrocycle does not significantly increase the stability constants of lead(II) complexes if a stereochemically active lone pair is present on the lead.[23] For example, the stability constants of lead(II) complexes decrease upon addition of hydroxyalkyl groups to $[12]aneN_4$ and $[12]aneN_3O$ (0.83 and 0.63 logarithmic units, respectively).[23] In the case described here, there is only a small increase in stability (0.38 logarithmic units) between the lead(II) complex with $[15]aneN_3O_2$ and $[Pb(L)]^{2+}$ (Table 6). Plots of the stability constants (Table 7) against ionic radius are shown in Fig. 7 for the complexes of Cu^{II}, Zn^{II}, Cd^{II} and Pb^{II} of L, of the macrocyclic precursor $[15]aneN_3O_2$ and of the ligand obtained by adding hydroxyalkyl arms to the macrocycle (THP-$[15]aneN_3O_2$).[14] Apart from the lead(II) complexes, the other complexes show an increase in stability upon attachment of pendant arms containing strong donors such as primary amines. On the other hand, the attachment of weaker donor groups such as hydroxyalkyl groups (which do not co-ordinate) to $[15]aneN_3O_2$ causes a decrease in stability in all the complexes studied because the N-donor atoms are now all tertiary amines rather than the secondary amines present in the precursor $[15]aneN_3O_2$.

Table 7 Stability constants of complexes of Cu^{II}, Zn^{II}, Cd^{II} and Pb^{II} with the ligand L compared to those with $[15]aneN_3O_2$ and THP-$[15]aneN_3O_2$

	$[15]aneN_3O_2$ 1[a]	L[b]	THP-$[15]ane$-N_3O_2[a]
$Cu^{2+} + L \rightleftharpoons [Cu(L)]^{2+}$	15.27(1)	17.38(2)	12.68(2)
$Zn^{2+} + L \rightleftharpoons [Zn(L)]^{2+}$	8.85(1)	12.15(1)	7.21(1)
$Cd^{2+} + L \rightleftharpoons [Cd(L)]^{2+}$	10.05(1)	13.02(2)	9.15(2)
$Pb^{2+} + L \rightleftharpoons [Pb(L)]^{2+}$	10.07(1)	10.45(4)	9.09(2)

[a] In 0.1 M $NaNO_3$ at 298 K. [b] In 0.1 M Me_4NCl, at 298.1 K.

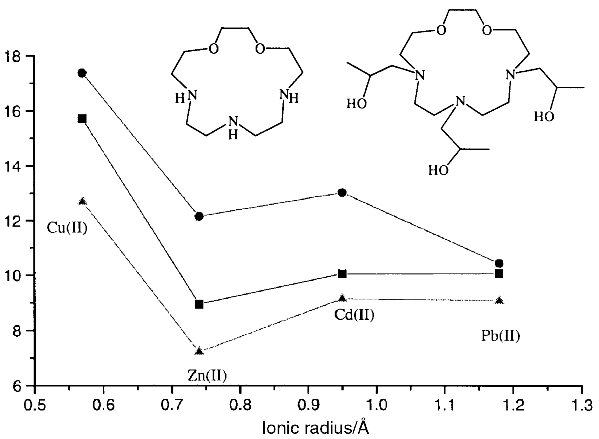


Fig. 7 Plot of the stability constants (log *K*) of complexes of Cu^{II}, Zn^{II}, Cd^{II} and Pb^{II} with the ligand L and the ligands shown above the graph against the ionic radius (Å): ■ $[15]aneN_3O_2$; ● L; ▲ THP-$[15]aneN_3O_2$.

NMR spectroscopic studies

In order to investigate further the structural features of the complexes in solution, ^1H NMR spectra in CD_3CN were recorded at various temperatures. The proton NMR spectra of all the complexes recorded at 300 MHz at room temperature show a complicated splitting pattern. A complex series of multiplets due to all the protons adjacent to the amines is observed between δ 2.2 and 3.1 in the case of $[Zn(L)]^{2+}$ and $[Cd(L)]^{2+}$, at δ 2.1–2.9 for $[Ba(L)]^{2+}$, and at δ 2.5–3.4 for $[Pb(L)]^{2+}$. The resonances due to protons adjacent to oxygen are observed in the region between δ 3.5 and 3.9. In all the spectra a triplet of doublets and a doublet of doublets due to the axial and equatorial protons of the methylene group next to oxygen (OCH_2CH_2N) can be discerned quite clearly, although for $[Zn(L)]^{2+}$ and $[Cd(L)]^{2+}$ these peaks overlap slightly. This splitting pattern is the result of coupling with the axial and equatorial protons of the methylene group next to nitrogen. In this region of the spectra another multiplet can be assigned as the other methylene group adjacent to the oxygen (OCH_2). The resonances of these two methylene groups are shifted slightly downfield with respect to the resonance observed for the "free" ligand recorded under the same conditions. The shift is more evident for the complexes of Ba^{II} ($\Delta\delta = 0.18$ ppm), Cd^{II} (0.11 ppm) and Pb^{II} (0.10 ppm) than for the zinc(II) species ($\Delta\delta = 0.04$ ppm). This difference, although very small, can be explained by the fact that in $[Zn(L)]^{2+}$ there is no interaction between the metal ion and the macrocyclic oxygen centres, while in the other complexes the O-donors are co-ordinated.

The presence of a splitting pattern where axial and equatorial protons can be detected and the resonances assigned suggests that the complexes are quite rigid at room temperature. Variable-temperature experiments have been carried out to determine fluxionality and differences between the complexes. Upon increasing the temperature all the peaks broaden and those due to axial and equatorial protons tend to collapse into a single broad peak. This can be explained by a loss of rigidity of the complexes and with enhanced fluxionality of the macrocycle. The complex $[Zn(L)]^{2+}$ loses its rigidity by 40 °C, while resonances in the spectra of $[Ba(L)]^{2+}$ and $[Pb(L)]^{2+}$ broaden only at 55 and 70 °C, respectively. We rationalise this in terms of the barium(II) and lead(II) centres interacting with all the donor atoms of the ligand and thereby enhancing their stereochemical and co-ordinative rigidity. Interestingly, the complex $[Cd(L)]^{2+}$ shows the onset of fluxionality at 40 °C, thus behaving more like the zinc(II) complex rather than the analogous barium(II) or lead(II) complexes.

Experimental

Spectra were recorded on a Bruker DPX 300 (^{1}H and ^{13}C NMR), on a Perkin-Elmer System 2000 FT-IR Spectrometer fitted with an i-Series FT-IR microscope (FTIR on single crystal) and a Perkin-Elmer 1600 spectrometer (FTIR, KBr discs). Elemental analytical data were obtained by the Microanalytical Service (Perkin-Elmer 240B analyser) at the University of Nottingham and EI (electron impact) mass spectra were measured using a V6 Autospec V67070E spectrometer. FAB (Fast Atom Bombardment) mass spectra were obtained by the EPSRC National Mass Spectrometery Service at the University of Swansea. 1,4-Dioxa-7,10,13-triazacyclopentadecane ([15]aneN_3O_2; **1** in Scheme 1) was prepared as described in the literature.[14] All starting materials were obtained from Aldrich Chemical Co. and used without further purification.

Syntheses

7,10,13-Tris(cyanomethyl)-1,4-dioxa-7,10,13-triazacyclopentadecane 2. [15]aneN_3O_2 (0.22 g, 1.01 mmol), chloroacetonitrile (0.25 g, 3.33 mmol), and Et_3N (10 g, 0.099 mol) in EtOH (50 cm^3) were refluxed under N_2 for 18 h. After cooling, the solvent was removed by rotary evaporation to yield a red oil which was dissolved in $CHCl_3$ (50 cm^3) and washed with water (3 × 30 cm^3). The organic phase was collected and dried ($MgSO_4$). The yellow oil obtained after evaporation of the solvent was dried *in vacuo* (0.19 g, 0.568 mmol). Yield: 56%. ^{1}H NMR ($CDCl_3$): δ 3.63 (OCH_2, 4 H, s), 3.63, 2.81 ($\mathrm{OC}H_2\mathrm{C}H_2\mathrm{N}$, 8 H, tt), 2.78 ($NCH_2$, 8 H, t), 3.66 (4 H, s, NCH_2CN) and 3.71 (2 H, s, $\mathrm{NC}H_2\mathrm{CN}$). ^{13}C NMR ($CDCl_3$): δ 70.4 (OCH_2), 69.0 ($\mathrm{O}C\mathrm{H_2CH_2N}$), 54.4 ($\mathrm{OCH_2}C\mathrm{H_2N}$), 51.9 ($\mathrm{N}C\mathrm{H_2CH_2N}$), 51.4 ($\mathrm{NCH_2}C\mathrm{H_2N}$). 43.7 ($\mathrm{N}C\mathrm{H_2CN}$), 43.5 ($\mathrm{N}C\mathrm{H_2CN}$) and 115.4 (CN). EI mass spectrum: *m*/*z* found 334.2, 308.2, 267.1 for 334.4 [M^+], 308.4 [$M^+ - CN$] and 268.4 [$M^+ - CH_2CN - CN$] respectively. Found: C, 57.2; H, 7.6; N, 24.8. Calc. for $C_8H_{13}N_3O$: C, 57.5; H, 7.8; N, 25.1%.

7,10,13-Tris(2-aminoethyl)-1,4-dioxa-7,10,13-triazacyclopentadecane L. Compound **2** (0.440 g, 1.31 mmol) and BH_3·THF (40 cm^3, 1 M solution in THF) were refluxed under N_2 for 48 h. After cooling, the excess of borane was destroyed by adding water (5 cm^3), and the solution dried *in vacuo*. The white solid obtained was dissolved in 6 M HCl (50 cm^3) and heated under reflux for 24 h. After cooling, the solution was dried *in vacuo* to yield a white solid. The solid was dissolved in the minimum amount of water and the solution obtained passed through a Dowex 1 × 8-50 column (10 g) activated with a solution of 1 M sodium hydroxide. The solvent was removed under reduced pressure to yield a colourless oil (0.340 g, 0.98 mmol). Yield: 75%. ^{1}H NMR ($CDCl_3$): δ 3.59 (OCH_2, 4 H, s), 3.58, 2.61 ($\mathrm{OC}H_2\mathrm{C}H_2\mathrm{N}$, 8 H, tt), 2.51 ($NCH_2$, 8 H, t), 2.70, 2.67 (12 H, tt, $\mathrm{C}H_2\mathrm{C}H_2\mathrm{N}$) and 1.5 (6 H, broad, NH_2). ^{13}C NMR ($CDCl_3$): δ 70.9 (OCH_2), 70.6 ($\mathrm{O}C\mathrm{H_2CH_2N}$), 54.3 ($\mathrm{OCH_2}C\mathrm{H_2N}$), 53.5 ($\mathrm{N}C\mathrm{H_2CH_2N}$), 53.3 ($\mathrm{NCH_2}C\mathrm{H_2N}$), 58.7 ($\mathrm{N}C\mathrm{H_2CH_2NH_2}$) and 39.8 ($\mathrm{NCH_2}C\mathrm{H_2NH_2}$). EI mass spectrum: *m*/*z* found 330.2, 303.2, 286.2 and 259.2 for 330.5 [$M^+ - NH_2$], 302.4 [$M^+ - CH_2CH_2NH_2$], 286.4 [$M^+ - CH_2CH_2NH_2 - NH_2$] and 258.4 [$M^+ - 2CH_2CH_2NH_2$] respectively. Found: C, 53.0; H, 11.2; N, 23.4. Calc. for $C_{16}H_{38}N_6O_2 \cdot H_2O$: C, 52.7; H, 11.1; N, 23.1%.

L·3HCl·H_2O. The hydrochloride salt was obtained in quantitative yield by adding diluted HCl (1 : 1 in EtOH) to an ethanolic solution containing the free amine until precipitation of a white solid which was filtered off and washed with EtOH. Found: C, 40.3; H, 9.2; N, 17.5. Calc. for $C_{16}H_{43}Cl_3N_6O_3$: C, 40.6; H, 9.2; N, 17.7%.

CAUTION: transition metal perchlorates are potentially explosive. These materials should be made in small quantities and handled with extreme caution.

General synthesis of [M(L)][ClO_4]$_2$. The metal salt was dissolved in MeOH (20 cm^3) and a solution of L in MeOH (20 cm^3) added dropwise. The solution was stirred for 3 h at room temperature and subsequent addition of Et_2O afforded the desired product.

[Zn(L)][ClO$_4$]$_2$ **3**. From $Zn(ClO_4)_2 \cdot 6H_2O$ (26.8 mg, 0.072 mmol) and L (25 mg, 0.072 mmol). White product, yield = 34.2 mg, 0.056 mmol, 77.8%. Single crystals suitable for X-ray structural analysis were obtained by diffusion of Et_2O into a solution of the complex in MeOH at room temperature. FAB mass spectrum (glycerol–MeOH–water matrix): *m*/*z* 511 for $[C_{16}H_{38}N_6O_2Zn \cdot ClO_4]^+$. IR (single crystal): 3337.5, 3290.5 (s, NH_2 stretch), 2937.0, 2899.0 (s, CH_2 stretch), 1592.6, 1561.7 (s, NH_2 bend) and 1090.8 cm^{-1} (s, ClO_4^-). Found: C, 31.8; H, 5.9; N, 13.6. Calc. for $C_{16}H_{38}Cl_2N_6O_{10}Zn$: C, 31.5; H, 6.3; N, 13.8%.

[Cu(L)][ClO$_4$]$_2$ **4**. From $Cu(ClO_4)_2 \cdot 6H_2O$ (21.5 mg, 0.058 mmol) and L (20 mg, 0.058 mmol). Blue product, yield = 29.9 mg, 0.049 mmol, 84.5%. Single crystals suitable for X-ray structural analysis were obtained by diffusion of Et_2O into a solution of the complex in MeCN at room temperature. FAB mass spectrum (3-nitrobenzyl alcohol matrix): *m*/*z* 510 for $[C_{16}H_{38}N_6O_2Cu \cdot ClO_4]^+$. IR (single crystal): 3334.7, 3286.4 (s, NH_2 stretch), 2934.2, 2895.8 (s, CH_2 stretch), 1590.6, 1560.2 (s, NH_2 bend) and 1091.3 cm^{-1} (s, ClO_4^-). Found: C, 32.0; H, 5.9; N, 13.7. Calc. for $C_{16}H_{38}Cl_2CuN_6O_{10}$: C, 31.6; H, 6.3; N, 13.8%.

[Pb(L)][ClO$_4$]$_2$ **5**. From $Pb(ClO_4)_2 \cdot 3H_2O$ (33.1 mg, 0.072 mmol) and L (25 mg, 0.072 mmol). White product, yield = 45.2 mg, 0.06 mmol, 83.3%. Single crystals obtained as for **4**. FAB mass spectrum (3-nitrobenzyl alcohol matrix): *m*/*z* 653 for $[C_{16}H_{38}N_6O_2Pb \cdot ClO_4]^+$. IR (KBr disc): 2876w, 1513w, 1384w, 1121s, 1090s and 626m cm^{-1}. Found: C, 25.2; H, 4.9; N, 10.8. Calc. for $C_{16}H_{38}Cl_2N_6O_{10}Pb \cdot H_2O$: C, 24.9; H, 5.2; N, 10.9%.

[Ba(L)][ClO$_4$]$_2$ **6**. From $Ba(ClO_4)_2$ (19.5 mg, 0.058 mmol) and L (20 mg, 0.058 mmol). White solid, yield = 30.7 mg, 0.045 mmol, 77.6%. Single crystals obtained as for **4**. FAB mass spectrum (3-nitrobenzyl alcohol matrix): *m*/*z* 583 for $[C_{16}H_{38}N_6O_2Ba \cdot ClO_4]^+$. IR (KBr disc): 2865w, 1498w, 1383w, 1091s and 628m cm^{-1}. Found: C, 28.0; H, 5.8; N, 12.4. Calc. for $C_{16}H_{38}BaCl_2N_6O_{10}$: C, 28.2; H, 5.6; N, 12.3%.

[Cd(L)]Cl$_2$ **7**. $CdCl_2 \cdot 2.5H_2O$ (13.2 mg, 0.058 mmol) was dissolved in MeOH (15 cm^3) and a solution of L (20 mg, 0.058 mmol) in MeOH (15 cm^3) added dropwise. The solution was stirred for 3 h at room temperature. Addition of Et_2O yielded a white solid (21.1 mg, 0.047 mmol). Yield 81.0%. FAB mass spectrum (3-nitrobenzyl alcohol matrix): *m*/*z* 494 for $[C_{16}H_{38}N_6O_2Cd \cdot Cl]^+$. IR (KBr disc): 2878w, 1493w, 1378w, 1091s and 628m cm^{-1}. Found: C, 36.8; H, 7.4; N, 15.9. Calc. for $C_{16}H_{38}CdCl_2N_6O_2$: C, 36.3; H, 7.2; N, 15.9%.

Crystal structure determinations

Crystal data, data collection and refinement parameters for compounds [ML^1][ClO_4]$_2$ [M = Zn^{II} **3**, Cu^{II} **4**, Pb^{II} **5** or Ba^{II} **6**] are given in Table 1. Data for structures **3**, **4** and **5** were collected on a Stoe Stadi-4 four-circle diffractometer equipped with a low temperature device, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Numerical absorption corrections based on face indexing were applied to the data for these compounds. The data for **6** were collected at low temperature using a Bruker SMART CCD area detector diffractometer and graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Multi-scan absorption corrections were applied.

All the structures were solved by direct methods[27] and completed by iterative cycles of full-matrix least squares refinement and ΔF syntheses. All non-H atoms, except for those in disordered groups, were refined anisotropically. All the H atoms were placed in calculated positions and refined using a riding model,[28] except that in the zinc(II) and copper(II) structures the hydrogens on the primary amines were located from difference maps and the N–H distances restrained to 0.90 Å during refinement.

The perchlorate anions were found to exhibit disorder in all four compounds, and this was modelled using partial occupancy models over either two or three sites. In **3** the occupancy factor is 0.70 for the three oxygens of one perchlorate (O1, O3 and O4) found disordered over two sites (and 0.30 for O1′, O3′ and O4′). In **4** and **6** the oxygens were equally disordered over three sites. In the structure of $[Pb(L)][ClO_4]_2$ **5** disorder was identified in part of the macrocyclic backbone and in parts of the amine arms and was modelled using partial occupancy over two sites for all the disordered atoms. The occupancy factor is 0.70 for the atoms from C8 to C15 and 0.30 for C8′ to C15′, while the disordered atoms within the arms have occupancies of 0.5. Moreover, all the perchlorate oxygen atoms are disordered, each equally over two sites, and were modelled using the same method as described above. Appropriate restraints were applied to all bond distances involving disordered atoms.

CCDC reference number 186/2144.

See http://www.rsc.org/suppdata/dt/b0/b003352i/ for crystallographic files in .cif format.

Potentiometric measurements

Equilibrium constants for protonation and complexation reactions with L were determined by pH-metric measurements ($pH = -\log[H^+]$) in 0.1 M Me_4NCl at 298.1 ± 0.1 K, by using potentiometric equipment that has been described.[29] The combined glass electrode was calibrated as a hydrogen concentration probe by titrating known amounts of HCl with CO_2-free NaOH solutions and determining the equivalence point by Gran's method[30] which allows one to determine the standard potential $E°$, and the ionic product of water ($pK_w = 13.83(1)$ at 298.1 K in 0.1 M Me_4NCl). Concentrations of 0.5×10^{-3}–1×10^{-3} M of ligands and metal ions were employed in the potentiometric measurements and three titration experiments were performed in the pH range 2–11, giving about 100 data points each. The computer program HYPERQUAD[31] was used to calculate equilibrium constants from emf data. All titrations were treated either as single sets or as separated entities, for each system, without significant variation in the values of the constants determined.

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References

1 K. P. Wainwright, *Coord. Chem. Rev.*, 1997, **166**, 35; P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297.

2 G. W. Gokel, *Chem. Soc. Rev.*, 1992, **21**, 39; R. D. Hancock, H. Maumela and A. S. de Sousa, *Coord. Chem. Rev.*, 1996, **148**, 315.

3 R. B. Laufer, *Chem. Rev.*, 1987, **87**, 901; D. Parker and J. A. G. Williams, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3613.

4 A. Hammershøi and A. M. Sargeson, *Inorg. Chem.*, 1983, **22**, 3554; S. G. Taylor, M. R. Snow and T. W. Hambley, *Aust. J. Chem.*, 1983, **36**, 2359.

5 D. G. Fortier and A. McAuley, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 101; D. G. Fortier and A. McAuley, *J. Am. Chem. Soc.*, 1990, **112**, 2640.

6 L. Tei, G. Baum, A. J. Blake, D. Fenske and M. Schröder, *J. Chem. Soc.*, *Dalton Trans.*, 2000, 2793 and references therein.

7 S. C. Rawle, A. J. Clarke, P. Moore and N. W. Alcock, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 2755.

8 K. P. Wainwright, *J. Chem. Soc.*, *Dalton Trans.*, 1983, 1149; I. Murase, M. Mikuriya, H. Sonoda, Y. Fukuda and S. Kida, *J. Chem. Soc.*, *Dalton Trans.*, 1986, 953; I. Murase, I. Ueda, M. Marubayashi, S. Kida, N. Mastumoto, M. Kudo, M. Toyohara, K. Hiate and M. Mikuriya, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 2763; H. Aneetha, Y.-H. Lai, S.-C. Lin, K. Panneerselvam, T.-H. Lu and C.-S. Chung, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 2885; P. S. Pallavicini, A. Perotti, A. Poggi, B. Seghi and L. Fabbrizzi, *J. Am. Chem. Soc.*, 1987, **109**, 5139.

9 I. Murase, M. Mikuriya, H. Sonoda and S. Kida, *J. Chem. Soc.*, *Chem. Commun.*, 1984, 692; A. Evers, R. D. Hancock and I. Murase, *Inorg. Chem.*, 1986, **25**, 2160.

10 L. H. Tan, M. R. Taylor, K. P. Wainwright and P. A. Duckworth, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 2921.

11 M. W. Hosseini and J.-M. Lehn, *J. Am. Chem. Soc.*, 1987, **109**, 7047.

12 K. A. Beveridge, A. McAuley and C. Xu, *Inorg. Chem.*, 1991, **30**, 2074.

13 M. Zinic, S. Alihodzic and V. Skaric, *J. Chem. Soc.*, *Perkin Trans. 1*, 1993, 21.

14 R. D. Hancock, R. Bhavan, P. W. Wade, J. C. A. Boeyens and S. M. Dobson, *Inorg. Chem.*, 1989, **28**, 187.

15 K. V. Damu, M. S. Shaikjee, J. P. Michael, A. S. Howard and R. D. Hancock, *Inorg. Chem.*, 1986, **25**, 3879; K. V. Damu, R. D. Hancock, P. W. Wade, J. C. A. Boeyens and S. M. Dobson, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 293; R. D. Hancock and A. E. Martell, *Chem. Rev.*, 1989, **89**, 1875.

16 C. J. Broan, J. P. L. Cox, A. S. Craig, R. Kataky, D. Parker, A. Harrison, A. M. Randall and G. Ferguson, *J. Chem. Soc.*, *Perkin Trans. 2*, 1991, **2**, 87; R. Delgado, Y. Sun, R. J. Motekaitis and A. E. Martell, *Inorg. Chem.*, 1993, **32**, 3320.

17 M. F. Cabral and R. Delgado, *Helv. Chim. Acta*, 1994, **77**, 515; C. Bazzicalupi, A. Bencini, A. Bianchi, F. Corana, V. Fusi, C. Giorgi, P. Paoli, P. Paoletti, B. Valtancoli and C. Zanchini, *Inorg. Chem.*, 1996, **35**, 5540.

18 N. A. Nedolya, N. P. Papsheva and B. A. Trofimov, *Russ. J. Org. Chem.*, 1997, **33**, 143; K. E. Krakowiak, J. S. Bradshaw and R. M. Izatt, *J. Org. Chem.*, 1990, **55**, 3364; K. E. Krakowiak, J. S. Bradshaw, N. K. Dalley, W. Jiang and R. M. Izatt, *Tetrahedron Lett.*, 1989, **30**, 2897; K. E. Krakowiak, J. S. Bradshaw and R. M. Izatt, *Tetrahedron Lett.*, 1989, **30**, 803.

19 K. Wieghardt, M. Kleine-Boymann, B. Nuber, J. Weiss and L. Zsolnai, *Inorg. Chem.*, 1986, **25**, 1647.

20 M. G. B. Drew and S. M. Nelson, *Acta Crystallogr.*, *Sect. B*, 1979, **35**, 1594; N. W. Alcock, E. H. Curzon and P. Moore, *J. Chem. Soc.*, *Dalton Trans.*, 1984, 2813; N. W. Alcock, E. H. Curzon and P. Moore, *J. Chem. Soc.*, *Dalton Trans.*, 1979, 1486; I. W. Nowell, *Acta Crystallogr.*, *Sect. B*, 1979, **35**, 1891; B. Metz and R. Weiss, *Acta Crystallogr.*, *Sect. B*, 1973, **29**, 1088; B. Metz and R. Weiss, *Inorg. Chem.*, 1974, **13**, 2094.

21 R. D. Shannon, *Acta Crystallogr.*, *Sect. A*, 1976, **32**, 751.

22 L. Shimoni-Livny, J. P. Glusker and C. W. Bock, *Inorg. Chem.*, 1998, **37**, 1853.

23 R. D. Hancock, M. S. Shaikjee, S. M. Dobson and J. C. A. Boeyens, *Inorg. Chim. Acta*, 1988, **154**, 229.

24 T. Tsabomura, T. Sato, K. Yasaku, K. Sakai, K. Kobayashi and M. Morita, *Chem. Lett.*, 1992, 731; H. Adams, N. A. Bailey, S. R. Collinson, D. E. Fenton, C. J. Harding and S. J. Kitchen, *Inorg. Chim. Acta*, 1996, **246**, 81; R. Bhavan, R. D. Hancock, P. W. Wade, J. C. A. Boeyens and S. M. Dobson, *Inorg. Chim. Acta*, 1990, **171**, 235; D. Esteban, D. Bañobre, R. Bastida, A. de Blas, A. Macias, A. Rodriguez, T. Rodriguez-Blas, D. E. Fenton, H. Adam and J. Mahia, *Inorg. Chem.*, 1999, **38**, 1937.

25 A. Bencini, A. Bianchi, E. Garcia-España, M. Micheloni and J. A. Ramirez, *Coord. Chem. Rev.*, 1999, **118**, 97.

26 A. Bencini, A. Bianchi, C. Giorgi, P. Paoletti, B. Valtancoli, V. Fusi, E. Garcia-España, J. M. Llinares and J. A. Ramirez, *Inorg. Chem.*, 1996, **35**, 1114; A. Bencini, A. Bianchi, P. Dapporto, V. Fusi, P. E. Garcia-España, M. Micheloni, P. Paoletti, P. Paoli, A. Rodriguez and B. Valtancoli, *Inorg. Chem.*, 1993, **32**, 2753.

27 G. M. Sheldrick, SHELXS 97, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 461.

28 G. M. Sheldrick, SHELXL 97, University of Göttingen, Germany, 1997.

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

30 G. Gran, *Analyst* (*London*), 1952, **77**, 661; F J Rossotti and H. Rossotti, *J. Chem. Educ.*, 1965, **42**, 375.

31 P. Gans, A. Sabatini and A. Vacca, *Talanta*, 1996, **43**, 1739.