Selection of Metal Ions by Geometric Isomers of a Polyamine Macrocycle with Pendant Donors†

Peter G. Lye,[a] Geoffrey A. Lawrance,*[,a] Marcel Maeder,[a] Brian W. Skelton,[b] Huo Wen[b] and Allan H. White[b]
[a] *Department of Chemistry, The University of Newcastle, Callaghan, New South Wales 2308, Australia*
[b] *Department of Chemistry, The University of Western Australia, Nedlands, Western Australia 6009, Australia*

The *syn* and *anti* isomers of 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (L^1 and L^2 respectively) have distinctly different shapes for binding metal ions. This is reflected in part in the stability constants for complexation (log *K*, 25 °C, 1:1 complex), which have been determined for the d^{10} metal ions Zn^{2+} (*syn*, 16.1; *anti*, 14.9), Cd^{2+} (*syn*, 12.1; *anti*, 10.6), Hg^{2+} (*syn*, 12.2; *anti*, 10.5), and Pb^{2+}(*syn*, 11.8; *anti*, 10.8), none of which involves ligand-field stabilization contributions to the stability of complexes. The *syn* isomer, with its sterically undemanding 'nest' shape, displays higher *K* values than the *anti* isomer irrespective of metal ion size. Selection of the small zinc(II) ion compared to the larger cadmium(II) ion by both isomers is significant (Δ log *K* *syn* 4.0, *anti* 4.6). The *syn* isomer accommodates the large lead(II) ion, the $[PbL^1(H_2O)][ClO_4]_2$ complex crystallizing in the monoclinic $P2_1/c$ space group, $Z = 4$, $a = 8.774(3)$, $b = 17.794(6)$, $c = 15.738(5)$ Å, $\beta = 109.67(3)°$. The lead(II) ion is co-ordinated by all six amines [Pb–N range 2.505(5)–2.809(7) Å], the water molecule [Pb–O 3.098(6) Å] and weakly chelated by a perchlorate ion [Pb–O 3.24(1), 3.298(9) Å]. By contrast, the slightly smaller mercury(II) ion is not accommodated in the cavity of the *anti* isomer, the isolated complex $[(H_2L^2)(HgCl_3)_2][L^2(HgCl_2)_2]\cdot2H_2O$ crystallizing in the triclinic $P\bar{1}$ space group, $Z = 1$, $a = 14.321(4)$, $b = 10.317(2)$, $c = 8.246(2)$ Å, $\alpha = 95.19(2)$, $\beta = 96.24(2)$, $\gamma = 97.68(2)°$. Two separate molecular units co-exist in equal amounts in the structure, the first with mercury(II) ions bound to each pendant amine in a unidentate manner, whereas the second has two mercury ions chelated at opposite sides of the macrocycle to, in each case, the pendant amine and one secondary amine. In each unit, chloride ions complete the tetrahedral environment for the metal ion, with variable Hg–N [range 2.279(7)–2.364(7) Å] and Hg–Cl [range 2.370(3)–2.535(2) Å] distances.

The potentially sexidentate polyamine 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine exists as two geometric isomers, *syn* (L^1) and *anti* (L^2), which differ in terms of the dispositions of the primary amines and methyl groups which are pendant to the central carbon of the two propane links of the 1,4,8,11-tetraazacyclotetradecane framework.[1,2] When all six amines are employed as donors to a metal ion, the shape of the resultant complexes is effectively defined by the location of the pendant primary amines. For the *anti* isomer, co-ordination requires a metal ion to be encapsulated in the plane of the four secondary amine donors of the macrocycle, with the two pendant occupying axial sites on opposite sides of this plane.[3] For the *syn* isomer, the two pendants lie on the same side of the plane and, for all six amines to co-ordinate, the molecule must adopt a 'nest' or folded configuration with the metal lying above the four secondary amines and below the two primary amine pendants.[2] Considering only these six donors, a distorted trigonal-prismatic geometry is an appropriate description in the latter case,[2] as distinct from a distorted octahedral geometry defined for the *anti* isomer,[3] although co-ordination numbers greater than six may apply in the case of the *syn* isomer.

Molecular mechanics examination of L^1 and L^2 for six-co-ordination defined a relatively deep and sharp minimum in the relationship between total strain energy and M–N distance for the *anti* isomer, whereas for the *syn* isomer a very shallow relationship between strain energy and M–N distance was predicted.[4] Further, for L^2, the minimum in the strain energy is consistent with a preference for small metal ions. This prediction can be understood partly in terms of the shapes of the two types of complexes. The two *trans*-disposed amine 'caps' in complexes of L^2 will, as the M–N distance is increased, be pulled away from the axis perpendicular to the macrocycle plane as a consequence of attachment of the primary amine to the central carbon of the bound macrocyclic –N–C–C–C–N– framework, which cannot readily distort. In the extreme, this will lead to bond rupture and reduction of the number of co-ordinated amines for the ligand to four. At the same time, large ions may not be readily accommodated in the macrocycle plane, but distortion of the macrocycle does not significantly reduce this strain until the metal ion is displaced above the secondary nitrogen donor plane, where at best it can be bound by five nitrogen donors. For L^1, accommodating a larger ion with a preference for longer M–N bonds is readily achieved by extension of bonds, since the metal ion is not required to occupy the same plane as the four secondary amines in any case, and 'pulling' the metal ion further away from the secondary amines can occur along with expansion of the bonds to the two primary amines, so that a large ion can be readily accommodated by adjustments to all six rather than just dominantly two M–N bonds. The preferred configurations of the secondary nitrogen donors in the *anti* isomer is *RRSS*, whereas with the *syn* isomer *RRRR* is preferred.

The consequences of the above is that it is the shape of the dipendant macrocycle, particularly the location of the two pendant primary amine groups, which may have a role to play in defining metal ion selection. For d^{10} metal ions with no ligand-field stabilization influences, one may expect L^1 to be relatively insensitive to metal ion size in terms of its metal ion selection, whereas for L^2 there should be a preference for small metal ions. This prospect is examined in this paper, along with a structural study of a complex of each isomer with a metal ion of relatively large ionic radius.

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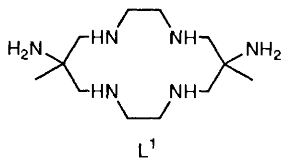
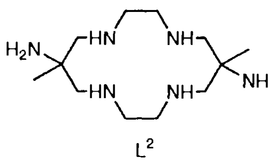
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



L^1



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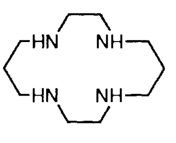

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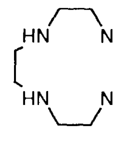

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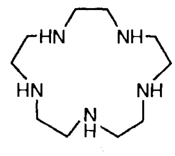
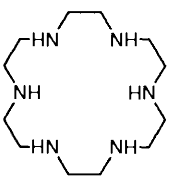
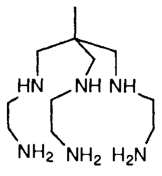


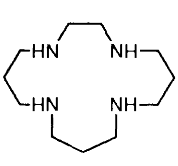
L^5



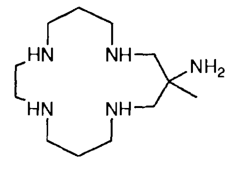
L^6



L^7



L^8



L^9

Experimental

Syntheses.—The *syn* (L^1) and *anti* (L^2) isomers of 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine as hexachloride salts L^1·6HCl·3H$_2$O and L^2·6HCl·2.5H$_2$O were prepared essentially as described previously,[1,2] and were characterized by microanalysis, NMR and IR spectroscopy.

Aqua(syn-6,13-*dimethyl*-1,4,8,11-*tetraazacyclotetradecane*-6,13-*diamine*)*lead*(II) *perchlorate*, [PbL^1(H$_2$O)][ClO$_4$]$_2$. A solution of L^1·6HCl·3H$_2$O (0.1 g), lead(II) nitrate (0.055 g) and sodium perchlorate monohydrate (1.4 g) in water (20 cm^3) was prepared and the pH raised to *ca.* 6 with sodium hydroxide solution. Colourless crystals suitable for X-ray work formed upon slow evaporation (weeks) of the solution at room temperature. The product was collected by filtration and air dried (Found: C, 21.2; H, 4.9; N, 12.2. Calc. for $C_{12}H_{32}Cl_2N_6O_9Pb$: C, 21.1; H, 4.7; N, 12.3%).

[(H$_2$L^2)(HgCl$_3$)$_2$][L^2(HgCl$_2$)$_2$]·2H$_2$O. To a solution of L^2·6HCl·2.5H$_2$O (0.4 g) in water (20 cm^3) was added mercury(II) chloride (0.23 g) and sodium perchlorate monohydrate (2.33 g). The pH of the solution was raised to *ca.* 6 with sodium hydroxide solution. Colourless crystals suitable for X-ray analysis formed after several weeks, and were collected by filtration and air dried (Found: C, 17.1; H, 3.9: N, 9.9. Calc. for $C_{12}H_{31}Cl_5Hg_2N_6$: C, 17.2; H, 3.7; N, 10.0%).

Physical Methods.—NMR spectra were recorded on a JEOL FX90Q Fourier transform spectrometer, using sodium trimethylsilyl [^{2}H$_4$] propionate and 1,4-dioxane as internal standards for ^{1}H and ^{13}C spectra respectively, and infrared spectra were recorded using a Bio-Rad FTS-7 spectrophotometer with compounds being dispersed in potassium bromide discs. Potentiometric titrations were performed with a Metrohm 665 digital burette and a Metrohm combined glass electrode, interfaced with an IBM clone computer *via* a high-impedance amplifier and AD board, as previously described.[5] All measurements were performed at 298 K and an ionic strength of 0.5 mol dm^{-3} KCl (or KNO$_3$) under nitrogen. Solutions (25 cm^3) of 1.5×10^{-5} mol dm^{-3} L^1·6HCl or L^2·6HCl alone and in the presence of 0.9 and 1.5 equivalents of metal(II) ion were titrated with 98 increments of 4×10^{-6} dm^3 using 0.4 mol dm^{-3} sodium hydroxide solution. Data reduction was performed using a TURBO BASIC version of the program TITFIT.[6]

Structure Determination.—*Crystal data*. [(H$_2$L^2)(HgCl$_3$)$_2$][L^2(HgCl$_2$)$_2$]·2H$_2$O(2 × $C_{12}H_{33}Cl_5Hg_2N_6O$), M = 869.9, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 14.321(4), b = 10.317(2), c = 8.246(2) Å, α = 95.19(2), β = 96.24(2), γ = 97.68(2)°, U = 1193 Å^3, $D_c(Z = 1)$ = 2.38 g cm^{-3}, $F(000)$ = 816, μ_{Mo} = 128 cm^{-1}. Specimen: colourless plate, 0.34 × 0.20 × 0.04 mm. $A^*_{min,max}$ 1.67, 8.41; $2\theta_{max}$ = 50°, N = 3940, N_o = 3321, R = 0.035, R' = 0.042.

[PbL^1(H$_2$O)][ClO$_4$]$_2$, $C_{12}H_{32}Cl_2N_6O_9Pb$, M = 682.5, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), a = 8.774(3), b = 17.794(6), c = 15.738(5) Å, β = 109.67(3)°, U = 2314(1) Å^3, $D_c(Z = 4)$ = 1.96 g cm^{-3}, $F(000)$ = 1336, μ_{Mo} = 69.8 cm^{-1}. Specimen: colourless prism, 0.48 × 0.20 × 0.20 mm. $A^*_{min,max}$ 2.83, 4.47; $2\theta_{max}$ = 65°, N = 8293, N_o = 4042, R = 0.040, R' = 0.034.

Unique diffractometer data sets were measured at *ca.* 295 K to the specified $2\theta_{max}$ limits [2θ–θ scan mode; monochromatic Mo-Kα radiation (λ = 0.7107$_3$ Å)]. N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after analytical absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values, those for the protonated nitrogen atoms and inferred water molecules being included on the basis of stoichiometry, difference map residues and interspecies contacts. Residuals at convergence on $|F|$ are conventional R, R'; statistical reflection weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ were used. Neutral atom complex scattering factors were employed,[7] the program system being XTAL 3.0 implemented by Hall.[8] Pertinent results are given in the Figures and Tables. The atomic nomenclature is defined in Figs. 1 and 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The two geometric isomers of 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine present six potential nitrogen donor atoms to metal ions. For the *anti* isomer (L^2) with the two pendants on opposite sides of the macrocyclic tetraamine ring, complexes with metal ions of varying size and charge have been closely examined by crystal-structure analysis, with the steric demands of the ligand in this arrangement commonly leading to shorter than usual metal-nitrogen bond distances.[9–14] On the other hand, the *syn* isomer (L^1), with both primary amines pendant on the same side of the macrocyclic ring, has been defined in only two crystal structures,[2,15] although it appears that there may be a preference towards a distorted trigonal-bipyramidal geometry with relatively long metal–nitrogen distances.

Consequences of the two different geometries have been examined by molecular mechanics, where it is predicted that stability of complexes for each isomer will vary with metal–nitrogen distance (and metal-ion size), but that selection on the basis of ion size will be more clearly defined for the *anti* isomer.[4] This is related to the necessity imposed by sexidentate coordination by the latter isomer for the metal ion to lie in the macrocycle donor plane and in addition to bind to the two pendant amines, a task not readily accomplished as the ion size increases. Metal ions accommodated to date with L^2 in distorted octahedral geometry include Ni^{II},[9] Zn^{II},[10] Co^{III},[11] Rh^{III},[12] Cr^{III},[13] Fe^{III},[14] and possibly Pt^{IV},[16] all within a restricted range of ionic radii (0.63–0.74 Å). As ion size and preferred bond distances increase, sexidentate co-ordination remains more likely with the *syn* rather than *anti* isomer. The difference between the two isomers is exemplified by consideration of Zn^{II} (0.74 Å) and Cd^{II} (0.95 Å); the former but not the latter metal ion exhibits sexidentate co-ordination with the *anti* isomer,[10] although the latter ion exhibits sexidentate co-ordination with the *syn* isomer.[2] This shape-directed variation in co-ordination accommodation is not clearly reflected in complex formation constants, nevertheless.

The potentiometric titrations of the ligands L^1 and L^2 identified five of the six successive amine protonation constants, and these are given in Table 1. The first deprotonation steps for both L^1 and L^2 cannot be determined potentiometrically (pK_a < 1.3). The values determined for the *anti* isomer L^2 are in excellent agreement with those found previously,[10] with the pK_a values at 5.5 and 6.2 being assigned to deprotonations of the pendant primary amines and the remaining values to deprotonations of the secondary ring nitrogens. The protonation constants for L^1 are very close but not identical to those of L^2, as would be expected. The largest difference is found with the process $H_4L^{4+} + H^+ \rightleftharpoons H_5L^{5+}$; perhaps with the highly protonated ligands, variations in repulsions between like-charged protonated amines arising as a result of the differing ligand shapes are magnified and reflected in protonation constants.

The formation constants of 1:1 complexes have been determined for the d^{10} metal ions Zn^{II}, Cd^{II}, Hg^{II} and Pb^{II} from the titration of acidic solutions of the metal salts and L^1 or L^2 with base. The stability constants for the complexes formed were calculated and are included in Table 1. None of the metal ions studied involves any ligand-field stabilization contributions to the stability of the complexes formed, hence variation in stability constants between complexes of each isomer must be more closely defined by shape restrictions imposed by the isomer under examination.

For most of the complexation titrations, two protonated species, which can be assigned to protonation of the pendant primary amines, were observed. Mono- and di-protonated species can involve at best quinque- and quadri-dentate co-ordination to metal ions respectively, although sexidentate co-ordination is possible for the metal ion interacting with the unprotonated ligand, though this is not necessarily a requirement. The differences between the stability data for the isomers L^1 and L^2 with each metal ion are not marked, despite a range of ionic radii from 0.74 to 1.20 Å. The smallest d^{10} ion Zn^{II} examined is still slightly larger than most first-row transition metal ions encapsulated by the *anti* isomer, and exhibits quite long M–N distances. Although sexidentate co-ordination has been observed in the solid state with Zn^{II}, alternate quadridentate binding in the macrocycle plane by the secondary amines alone is possible in solution with both unprotonated L^1 and L^2, and may account for the similar complex formation constants. Sexidentate co-ordination has not been established for the other larger metal ions examined here with L^2 and consequently selection of the small zinc(II) ion compared to the larger cadmium(II) ion by the *anti* isomer is significant ($\Delta \log K_1$ 4.6), and may relate to the size restriction imposed by the shape adopted by the *anti* isomer for sexidentate co-ordination. The selection of Zn^{II} over Cd^{II} is comparable with or better than reported values for most ligand systems.[17,18] As one might anticipate, the $\log K_1$ value with Zn^{II} and L^2 or L^1 is similar to the value reported with the unsubstituted cyclam (1,4,8,11-tetraazacyclotetradecane, L^3) of 15.5,[19,20] since the basic macrocycle ring is identical in each case and the Zn^{II} ion is bound in the same macrocyclic plane in each case.

With its sterically undemanding 'nest' shape, irregular metal–donor bond dispositions may be more readily accommodated with the *syn* isomer L^1 than in the case with the *anti* isomer, and consistently higher $\log K$ values with all metal ions fit with this concept. However, the *syn* isomer shows a selection profile for metal ions similar to that of the *anti* isomer, an outcome not expected from molecular mechanics analysis.[4] The molecular mechanics analysis assumed sexidentate co-ordination, and the profile observed suggests that sexidentate co-ordination of the unprotonated hexaamine is not necessarily occurring in solution with each metal ion.

Table 1 The logarithms of the protonation and formation constants for L^1 and L^2 with various d^{10} metal ions; some comparative values for L^3 are also included (charges are omitted for clarity)[a]

M	Complex	L^1	L^2	L^3
H^+	$H + L \rightleftharpoons HL$	10.6	11.0	11.6
	$HL + H \rightleftharpoons H_2L$	9.7	10.0	10.6
	$H_2L + H \rightleftharpoons H_3L$	6.3	6.2	—
	$H_3L + H \rightleftharpoons H_4L$	5.4	5.5	—
	$H_4L + H \rightleftharpoons H_5L$	2.7[b]	1.5[b]	1.6[d]
Zn^{2+}	$M + L \rightleftharpoons ML$	16.1	14.9	15.5
	$ML + H \rightleftharpoons MLH$	5.8	6.8	
	$MLH + H \rightleftharpoons MLH_2$	5.2	6.0	
	$ML \rightleftharpoons MLH_{-1} + H$	9.6	10.5	
Cd^{2+}	$M + L \rightleftharpoons ML$	12.1	10.6	11.3
	$ML + H \rightleftharpoons MLH$	5.9	7.5	
	$MLH + H \rightleftharpoons MLH_2$	—	5.7	
	$ML \rightleftharpoons MLH_{-1} + H$	7.4	—	
Hg^{2+}	$M + L \rightleftharpoons ML$	12.2	10.5 (21.4)[c]	23.0
	$ML + H \rightleftharpoons MLH$	6.8	7.5 (7.2)	
	$MLH + H \rightleftharpoons MLH_2$	6.8	5.7 (3.9)	
	$ML \rightleftharpoons MLH_{-1} + H$	8.0	— (11.4)	
	$M_2 + L \rightleftharpoons M_2L$		11.2	
	$M_2L + H \rightleftharpoons M_2LH$		9.1	
	$M_2L \rightleftharpoons M_2LH_{-1} + H$		7.7	
Pb^{2+}	$M + L \rightleftharpoons ML$	11.8	10.8	10.8
	$ML + H \rightleftharpoons MLH$	6.0	7.5	
	$MLH + H \rightleftharpoons MLH_2$	—	4.1	
	$ML \rightleftharpoons MLH_{-1} + H$	7.7	—	

[a] Standard errors are 0.1 log units; 25 °C, I = 0.5 mol dm^{-3} KCl. [b] Approximate only. [c] Values in parentheses determined in 0.5 mol dm^{-3} KNO_3. [d] Third protonation.

From the complexation titrations, protonated species were defined with each metal ion investigated, with the protonation sites assigned to the pendant amines. Co-ordination of the pendant arms appears weak in these systems, as their deprotonation is not significantly favoured by complexation to the metal ion. A deprotonated species for these systems is assigned to deprotonation of a co-ordinated water molecule in either a complex with quadri- or quinque-dentate co-ordination of the ligand and an axial water group or an overall seven-co-ordinate geometry with a co-ordinated water molecule as defined in the crystal structure of the lead(II) ion below.

Comparative values for formation of the 1:1 complexes with a range of dominantly cyclic polyamines are collected in Table 2.[19–24] With the exception of L^1, L^2 and L^3, there is no appreciable selectivity for Zn^{II} over Cd^{II} for the variety of polyamines reported despite the *ca.* 0.2 Å difference in ionic radius; this is a common observation with other polyamines also.[17] The subtleties of metal ion selection are emphasised by the observation that moving to either smaller or larger macrocycles does not enhance selectivity. With the ion Pb^{II}, which is *ca.* 0.2 Å larger than Cd^{II}, stabilities are higher with macrocycles both smaller and larger than the fourteen-membered L^3.[17]

Data which deserve some comment are the clear difference in $\log K_1$ with Hg^{II} determined in our studies and values reported in other studies. There is no strong reason, in terms of donor preferences, why Hg^{II} should bind nitrogen donors significantly better than Pb^{II}, and these ions are also similar in ionic radii. Our determinations of the stability constants for Hg^{II} and Pb^{II}

Table 2 log K_1 values for metal ions with various polyamines L^n [a]

Metal ion	Ionic radius (Å)		L^1	L^2	L^3	L^4	L^5	L^6	L^7	L^8	L^9
		Ring size [b]	14	14	14	12	15	18	*c*	15	15
		No. of N-donors [d]	6	6	4	4	5	6	6	4	5
Zn^{II}	0.74		16.1	15.0	15.5	16.2	17.9	18.7	17.0	15.0	15.6
Cd^{II}	0.95		12.1	10.6	11.3	14.3	18.1	18.8	13.4	12.1	—
Hg^{II}	1.10		12.2	10.5 [e]	23.0	25.5	27.4	29.1	—	23.7	—
Pb^{II}	1.18		11.8	10.8	10.8	15.9	14.3	14.1	9.2	10.1	10.2

[a] L^1 and L^2, this work; other data from refs. 5, 17, 19–24; usually determined in 0.5 mol dm^{-3} KCl. [b] Macrocycle ring size. [c] Acyclic. [d] Number of potential amine donors in the ligand. [e] log K_1 = 21.4, determined in 0.5 mol dm^{-3} KNO_3.

Table 3 Non-hydrogen atom coordinates for $[PbL^1(H_2O)][ClO_4]_2$

Atom	*x*	*y*	*z*
Pb	0.131 70(3)	0.357 29(2)	0.591 56(2)
C(1)	0.135(1)	0.165 5(4)	0.590 0(6)
N(1)	0.065 1(8)	0.214 5(4)	0.511 6(4)
C(11)	0.104(1)	0.081 9(5)	0.569 1(6)
C(2a)	0.052 7(9)	0.185 0(4)	0.659 5(5)
N(3a)	0.096 7(7)	0.260 4(3)	0.701 2(4)
C(4a)	−0.017 5(9)	0.288 7(4)	0.743 9(5)
C(2b)	0.318(1)	0.178 8(4)	0.627 5(6)
N(3b)	0.364 4(7)	0.258 5(3)	0.624 3(4)
C(4b)	0.505 6(9)	0.280 5(4)	0.699 2(6)
C(1′)	0.235 3(9)	0.522 1(4)	0.706 4(5)
N(1′)	0.138 6(7)	0.513 2(3)	0.608 9(4)
C(11′)	0.267(1)	0.604 9(4)	0.731 8(6)
C(2a′)	0.137 8(9)	0.487 8(4)	0.761 5(5)
N(3a′)	0.052 0(7)	0.418 4(3)	0.721 6(4)
C(4a′)	0.033 5(8)	0.364 1(5)	0.786 8(5)
C(2b′)	0.395 9(8)	0.482 5(4)	0.721 8(5)
N(3b′)	0.381 4(6)	0.400 1(3)	0.714 7(4)
C(4b′)	0.527 3(8)	0.364 1(4)	0.705 6(5)
Cl(1)	0.303 9(3)	0.404 4(1)	0.402 3(1)
O(11)	0.384(1)	0.412 6(6)	0.494 2(5)
O(12)	0.170(1)	0.357 3(5)	0.390 2(5)
O(13)	0.408(1)	0.375 1(5)	0.362 7(7)
O(14)	0.250(1)	0.471 1(5)	0.360 0(8)
Cl(2)	0.591 4(3)	0.331 5(2)	0.962 2(2)
O(21)	0.620(1)	0.293 0(8)	1.038 8(6)
O(22)	0.429 3(9)	0.328 5(6)	0.909 4(5)
O(23)	0.687(1)	0.302(1)	0.918 7(6)
O(24)	0.641(2)	0.399 3(7)	0.981(2)
O	−0.240 0(7)	0.376 3(4)	0.536 1(4)

with L^2 involving KCl as the electrolyte produced comparable log K_1 values, but these are, for the former, less than half those reported for a range of polyamines with Hg^{II}.[17] Repeating the determination with KNO_3 as electrolyte yielded a stability constant > 20 and comparable to others reported earlier.[17] Even with the macrobicyclic encapsulating hexaamine 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane, log K_1 for complexation of Hg^{II} is estimated to be near 20,[25] so very high values for other polyamines are surprising. Possible competition between Hg^{2+} and $HgCl^+$ (or higher halide) species presumably has a role to play in complicating the analyses when using KCl as electrolyte, as implied from the form of species crystallized from dilute chloride ion solution described below. Nevertheless, despite suggestions for the source of the high log *K* values for Hg^{2+},[17] there remains some source of concern about results with this metal ion.

Structural characterization of the cadmium(II) complex of L^1 has been reported recently.[4] We were interested in examining binding of the even larger metal ion Pb^{II} with this ligand, and the structure of the complex $[PbL^1(H_2O)][ClO_4]_2$ is reported here. Non-hydrogen positional parameters appear in Table 3, with the metal environment described in Table 5 and ring torsion angles in Table 6. Views of the complex cation appear in Fig. 1.

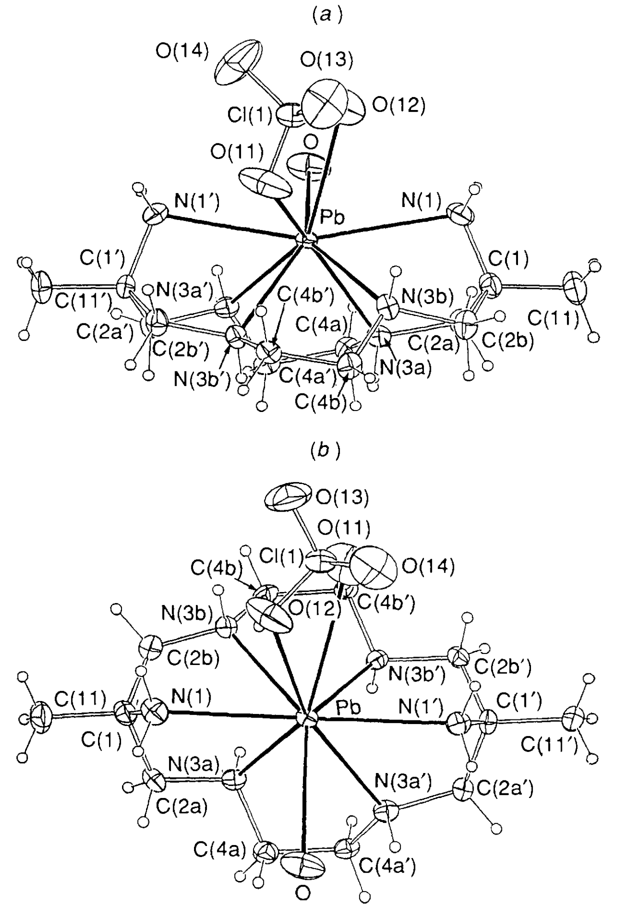


Fig. 1 Projections of the cation $[PbL^1(H_2O)]^{2+}$ at (*a*) 90° and (*b*) normal to the plane of the secondary amines; hydrogen atoms have arbitrary radii of 0.1 Å

The structure consists of a cation containing the Pb^{II} coordinated to all six nitrogen donors of L^1 as well as to a water molecule and weakly chelated to two oxygen atoms of one perchlorate ion, with the other perchlorate counter ion at a general position, the totality comprising the asymmetric unit. Ignoring the oxygen donors, there is an approximate two-fold axis in the cation including pendant methyl and amine groups and the lead ion [Fig. 1(*b*)]. Distances involving the amines are in the range 2.505(5)–2.611(6) Å for the secondary amines and significantly longer at 2.787(6) and 2.809(7) Å for the primary amines. The Pb–OH_2 length [3.098(6) Å] is significantly shorter than the perchlorate Pb–O distances [3.24(1), 3.298(9) Å]. If the two chelated perchlorate oxygens are averaged to one site, the structure can be visualized as a distorted square antiprism with the four secondary amines of the macrocycle occupying an approximate plane on one side of the lead atom and the two primary amines and two oxygens (one the average chelated perchlorate oxygens) occupying a very distorted plane at longer distances on the opposite side of the metal atom. The Pb lies 1.551(1) Å above the averaged secondary amine plane. One clear consequence of introducing the larger Pb^{II} ion rather than the Cd^{II} ion into the structure is that there has been a switch over from the M–N(secondary) distances being longer than the M–N(primary) distances with cadmium (average 2.41_8, 2.30_0 Å respectively) to the opposite behaviour with Pb (average 2.56_7, 2.79_8 Å respectively). As the average bond distance increases with the larger ion there is an 'opening out' of the 'nest', seen as a flattening of each six-membered chelate ring carrying the amine pendant (reflected in the average increase in the M–N–C angle involving this ring from 106.1 to 114.8° from Cd to Pb, and in torsion angles) and a concomitant increase in the distance of the pendant primary amine from the metal centre. The more 'open' structure may permit co-ordination of both a water molecule and a chelate perchlorate in the case of Hg (pseudo-nine-co-ordinate), whereas with Cd (pseudo-eight-co-ordinate) only bonds to two oxygens of unidentate perchlorate ions [2.947(3), 3.059(5) Å] are present. The ability of the *syn* isomer L^1 to maintain sexidentate co-ordination despite the increase in ion size is notable, and confirms molecular mechanics predictions.

Table 4 Non-hydrogen atom coordinates for $[(H_2L^2)(HgCl_3)_2][L^2(HgCl_2)_2]{\cdot}2H_2O$

Atom	*x*	*y*	*z*
Hg(1)	0.295 02(3)	0.889 68(4)	0.403 69(5)
Hg(2)	0.814 64(3)	0.537 18(4)	0.423 43(4)
Cl(11)	0.287 7(2)	0.983 4(3)	0.674 4(3)
Cl(12)	0.178 6(2)	0.932 9(2)	0.167 3(3)
Cl(21)	0.782 1(2)	0.714 2(3)	0.609 7(3)
Cl(22)	0.662 9(2)	0.409 1(3)	0.277 0(3)
Cl(23)	0.891 2(2)	0.377 8(3)	0.581 7(4)
O	0.205 9(5)	0.652 3(7)	−0.003 9(8)
C(1)	0.434 3(6)	0.694 3(8)	0.285 (1)
N(1)	0.336 1(5)	0.685 7(7)	0.332 8(9)
C(11)	0.444 9(8)	0.573(1)	0.176(1)
C(2a)	0.505 2(6)	0.706 0(9)	0.442(1)
N(3a)	0.493 2(4)	0.810 4(7)	0.566 7(8)
C(4a)	0.568 4(6)	0.828 9(9)	0.706(1)
C(2b)	0.451 0(6)	0.814 3(9)	0.191(1)
N(3b)	0.435 5(4)	0.936 7(7)	0.280 6(8)
C(4b)	0.442 6(6)	1.050 3(9)	0.186(1)
C(1′)	0.887 9(5)	0.706 3(8)	0.126(1)
N(1′)	0.896 5(5)	0.583 6(7)	0.208 7(8)
C(11′)	0.783 2(6)	0.704 4(9)	0.063(1)
C(2a′)	0.927 0(6)	0.821 9(8)	0.253(1)
N(3a′)	0.924 9(5)	0.949 1(7)	0.183 1(8)
C(4a′)	0.967 4(6)	1.059 4(9)	0.304(1)
C(2b′)	0.950 1(6)	0.697 2(8)	−0.015(1)
N(3b′)	0.953 5(5)	0.812 4(7)	−0.110 0(8)
C(4b′)	1.025 7(6)	0.812 1(8)	−0.229(1)

With the *anti* isomer L^2, extensive structural studies with a range of metal ions have shown that axial elongation of the pendant primary amines increases more markedly than do increases in secondary amine distances with increasing metal ion size.[9–14] Further, the N(secondary)–M–N(pendant) bite angle becomes increasingly acute as the metal ion becomes larger, to the point where this concomitant elongation and lateral displacement prohibit pendant co-ordination, limiting sexidentate co-ordination to relatively small metal ions. Attempts to produce sexidentate complexation of cadmium(II) with L^2 have not been successful,[10] so it was not surprising to find the same applies with mercury(II). Crystallization of a mercury(II) complex with L^2 from aqueous solution containing

Table 5 The metal environments for (*a*) $[PbL^1(H_2O)][ClO_4]_2$ and (*b*) $[(H_2L^2)(HgCl_3)_2][L^2(HgCl_2)_2]{\cdot}2H_2O$ [interatomic distances (Å) and angles (°)]

(*a*) $[PbL^1(H_2O)][ClO_4]_2$

Atom	*r*	N(3a)	N(3b)	N(1′)	N(3a′)	N(3b′)	O(11)	O(12)	O
N(1)	2.809(7)	68.5(2)	60.7(2)	159.9(2)	131.1(2)	128.2(2)	97.8(2)	69.1(2)	86.1(2)
N(3a)	2.530(6)		70.9(2)	128.0(2)	67.9(2)	87.4(2)	142.1(2)	136.9(2)	84.8(2)
N(3b)	2.611(6)			131.4(2)	121.6(2)	68.3(2)	71.6(2)	82.2(2)	143.9(2)
N(1′)	2.787(6)				60.8(2)	68.7(2)	75.4(2)	95.1(2)	84.6(2)
N(3a′)	2.611(6)					70.3(2)	130.5(2)	153.4(2)	69.0(2)
N(3b′)	2.505(5)						73.4(2)	113.4(2)	138.4(2)
O(11)	3.24(1)							40.4(2)	130.9(2)
O(12)	3.298(9)								99.7(2)
O	3.098(6)								

(*b*) $[(H_2L^1)(HgCl_3)_2][L^1(HgCl_2)_2]{\cdot}2H_2O$

Unprimed ligand: Hg(1)

Atom	*r*	Cl(2)	N(1)	N(3b)
Cl(1)	2.370(3)	120.6(1)	125.7(2)	119.7(2)
Cl(2)	2.535(2)		106.0(2)	97.7(2)
N(1)	2.303(8)			76.1(2)
N(3b)	2.364(7)			

Primed ligand: Hg(2)

Atom	*r*	Cl(2)	Cl(3)	N(1′)
Cl(1)	2.406(3)	110.59(9)	109.4(1)	119.6(2)
Cl(2)	2.510(2)		105.26(9)	101.3(2)
Cl(3)	2.484(3)			109.6(2)
N(1′)	2.279(7)			

r/Å is the metal-ligand atom distance. Other entries are the angles (°) subtended by the relevant atoms at the head of the row and column.

Table 6 Ring torsion angles (°), ring atoms denoted by number only, nitrogen italicized

(*a*) The macrocycle

	Lead complex				Mercury complex			
Section	*a*	*b*	*a′*	*b′*	*a*	*b*	*a′*	*b′*
2–1–2–*3*	50.3(8)	−80.4(9)	−79.0(7)	48.7(8)	66.7(9)	−63.6(9)	64.4(9)	−63.1(9)
1–2–*3*–4	161.5(6)	145.7(8)	148.5(6)	164.8(8)	−173.1(7)	−174.5(6)	−177.1(7)	171.1(6)
2–*3*–4–4	178.8(5)	−167.3(7)	−166.2(6)	179.7(6)	172.1(7)	−176.4(7)	174.3(7)	−173.1(6)
3–4–4–*3*	56.2(7)	57.8(9)	—	—	−59.3(9)	—	−68.5(8)	—

(*b*) The mercurial ring of the mercury complex: torsion angles in the bonds Hg–N(1), N(1)–C(1), C(1)–C(2), C(2)–N(3), N(3)–Hg are, respectively 12.0(5), −37.0(7), 55.3(8), −43.3(7), 16.0(5)

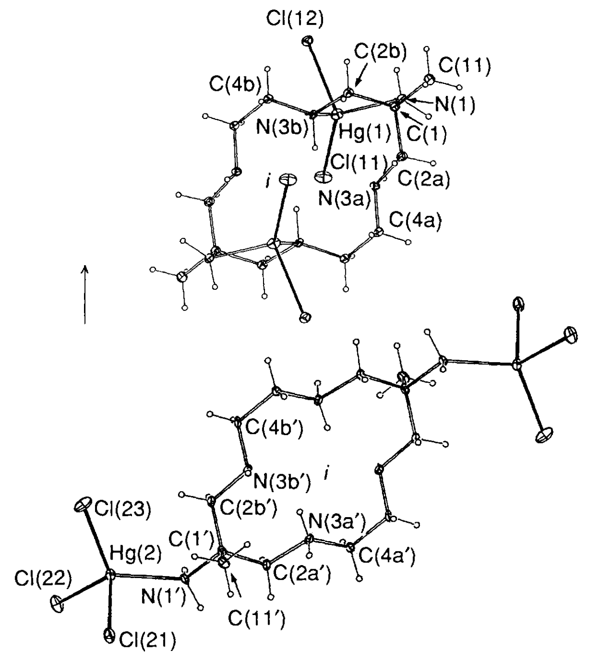


Fig. 2 Projections of the two complex units in $[(H_2L^2)(HgCl_3)_2]$-$[L^2(HgCl_2)_2]\cdot 2H_2O$, normal to the approximate plane of the secondary amines; hydrogen atoms have arbitrary radii of 0.1 Å

dilute chloride ion was achieved. However, the compound contains no encapsulation or co-ordination of mercury by the four macrocycle secondary amine donors. Instead, the crystallized complex contains two distinct macrocyclic units, one with unidentate co-ordination of $HgCl_3^-$ groups to each pendant primary amine, and the other with chelation of $HgCl_2$ groups to the primary amine and a secondary amine on opposite sides of the macrocyclic plane. The two separate centrosymmetric complex units are shown in Fig. 2. Non-hydrogen positional parameters appear in Table 4, with the metal environment for the complex units described in Table 5 and ring torsion angles in Table 6.

The unique Hg–N distance in the unidentate species [2.279(7) Å] is markedly shorter than those of the chelated species [2.303(8), 2.364(7) Å], possibly influenced by the differing number of chloride anions in each case. The Hg–Cl distances range between 2.370(3) and 2.535(2) Å, and are not noticeably different between the two complex units. The five-membered chelate ring formed adopts a conformation in which the methyl pendant on the macrocycle is in an equatorial configuration relative to the ring, as is the methylene attached to the secondary amine, the anticipated lowest energy conformation. Each Hg displays a distorted tetrahedral geometry. The N–Hg–N chelate angle [76.1(2)°] is significantly reduced from the standard tetrahedral angle, with some of the other angles [range 106.0(2)–125.7(2)°] opened significantly to compensate. Angles around the unidentate amine-bound tetrahedral Hg centre [range 101.3(2)–110.6(1)°] are far less distorted, indicating that in chelation the metal ion has had to accommodate the small 'bite' angle of the chelate.

The crystallization of halogenomercury complexes, even from aqueous solution relatively low in chloride concentration, reflects the propensity of Hg^{II} towards halide donors rather than nitrogen and oxygen, and further suggests that very high formation constants for Hg^{II} with polyamines may need further consideration. Further, the selective involvement of the pendant primary amines in both the unidentate and bidentate co-ordination of the metal ion may infer a route for complexation of metal ions by these types of ligands generally. Capture of a metal ion by the pendant as a unidentate may be followed by chelation involving one of the adjacent macrocyclic amines, the metal ion still remaining *exo* to the macrocyclic ring at this stage. For small metal ions, subsequent incorporation into the macrocyclic plane will occur, also retaining co-ordination of the pendant amines in some cases. Preliminary examination of formation kinetics of complexes with small labile metal ions suggests this model may be applicable.[24]

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References

1 P. Comba, N. F. Curtis, G. A. Lawrance, A. M. Sargeson, B. W. Skelton and A. H. White, *Inorg. Chem.*, 1986, **25**, 4260.
2 P. V. Bernhardt, P. Comba, T. W. Hambley, G. A. Lawrance and K. Varnagy, *J. Chem. Soc., Dalton Trans.*, 1992, 355.
3 P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297.
4 P. V. Bernhardt and P. Comba, *Helv. Chim. Acta*, 1991, **74**, 1834.
5 G. K. Hollingshed, G. A. Lawrance, M. Maeder and M. Rossignoli, *Polyhedron*, 1991, **10**, 409.
6 A. D. Zuberbuehler and T. A. Kaden, *Talanta*, 1982, **29**, 201.
7 J. A. Ibers and W. C. Hamilton (Editors), *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
8 S. R. Hall and J. M. Stewart (Editors), The XTAL System Version 3.0, Universities of Western Australia and Maryland, 1990.
9 N. F. Curtis, G. J. Gainsford, T. W. Hambley, G. A. Lawrance, K. R. Morgan and A. Siriwardena, *J. Chem. Soc., Chem. Commun.*, 1987, 295.
10 P. V. Bernhardt, G. A. Lawrance, M. Maeder, M. Rossignoli and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1991, 1167.
11 P. V. Bernhardt, G. A. Lawrance and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1989, 1059.
12 P. V. Bernhardt, G. A. Lawrance and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1990, 983.
13 P. V. Bernhardt, P. Comba, N. F. Curtis, T. W. Hambley, G. A. Lawrance, M. Maeder and A. Siriwardena, *Inorg. Chem.*, 1990, **29**, 3208.
14 P. V. Bernhardt, P. Comba, T. W. Hambley and G. A. Lawrance, *Inorg. Chem.*, 1991, **30**, 942.
15 P. V. Bernhardt, P. Comba and T. W. Hambley, *Inorg. Chem.*, 1993, **32**, 2804.
16 P. V. Bernhardt, Doctoral Dissertation, The University of Newcastle, Australia, 1989.
17 A. Bianchi, M. Micheloni and P. Paoletti, *Coord. Chem. Rev.*, 1991, **116**, 17.
18 R. D. Hancock and A. E. Martell, *Chem. Rev.*, 1989, **89**, 1875.
19 M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1977, 2269.
20 V. J. Thöm, G. D. Hosken and R. D. Hancock, *Inorg. Chem.*, 1985, **24**, 3378.
21 M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1976, 2335.
22 M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1978, 1081.
23 M. Kodama, E. Kimura and S. Yamaguchi, *J. Chem. Soc., Dalton Trans.*, 1980, 2536.
24 P. G. Lye and A. Bayada, unpublished work.
25 G. A. Lawrance and A. M. Sargeson, unpublished work.

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