Structural and Dynamic Behaviour of Cadmium(II) and Mercury(II) Complexes of 1,4,8,11-Tetra-azacyclotetradecane and 1,4,8,11-Tetramethyl-1,4,8,11-tetra-azacyclotetradecane

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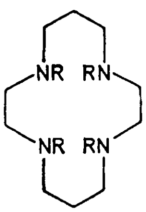
The macrocyclic ligand 1,4,8,11-tetra-azacyclotetradecane (L_a) gives a complex with cadmium(II) which is a mixture of two isomers in solution. The isomers are observed in the ^{13}C n.m.r. spectra at low temperatures, and are postulated to involve square and dynamically folded trigonal-bipyramidal (t.b.p.) co-ordination of the macrocycle, with different configurations at the co-ordinated nitrogen donors (square, *R, S, S, R*; t.b.p., *R, S, R, S*). These two isomers are found to interconvert on the n.m.r. timescale at elevated temperatures, a process which requires double nitrogen-atom inversions. The complex of L_a with mercury(II) has a ^{13}C n.m.r. spectrum consistent with a stable '*trans*' co-ordination of the macrocycle which may only be achieved by the adoption of a geometry, unique for L_a with *R, S, R, S* donor-atom configurations. This geometry is confirmed by an *X*-ray analysis of the complex $[Hg(L_a)Cl]_2[HgCl_4]$ where the conformation of the macrocycle forces distorted square-pyramidal five-co-ordination upon the mercury(II) ion. The complex crystallises in the monoclinic space group *C*2/*c*, *Z* = 4, with *a* = 15.686(9), *b* = 15.058(8), *c* = 14.979(6) Å, and β = 103.03(4)° (*T* = 153 K). 2 226 Reflections with $I/\sigma(I) \geqslant 3.0$ have been recorded by a four-circle diffractometer and least-squares refinement has produced a final *R* of 0.037. Both cadmium(II) and mercury(II) ions form complexes with 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (L_b) which are best envisaged as five-co-ordinate with macrocyclic configurations *R, S, R, S*. These complexes are found to undergo Berry-type dynamic rearrangements between equivalent trigonal bipyramids as found previously for the analogous complexes of zinc(II) ion. The behaviours of the complexes are compared and discussed in relation to metal-ion size and macrocycle configurations.

THE co-ordinative properties of 14-membered macrocyclic ligands to metal ions have been shown to be determined by a combination of effects.[1,2] The most obvious is that of metal-donor bond length in relation to the hole size of the macrocycle. For simple 14-membered tetra-aza macrocycles such as L_a and L_b it has been calculated that square-planar co-ordination of the macrocycle requires an optimum M–N distance of 2.07 Å.[3] Such a distance corresponds to a metal with an ionic radius of *ca.* 0.65—0.7 Å. Small deviations in radius either side of this optimum value may, however, be accommodated by the flexibility of the ring, and it is generally found that first-row transition-metal ions produce planar co-ordination of L_a, with nitrogen configurations *R, S, S, R* [Figure 1(*a*)]. This apparently simple situation with L_a becomes somewhat more complicated when one considers complexes of L_b. In this case the tertiary amine donors are almost always found to adopt configurations *R, S, R, S* [Figure 1(*b*)]; this still contains a planar set of donor atoms, but the macrocycle conformation effectively blocks one of the two remaining octahedral sites of the central metal [Figure 1(*b*)]. The resulting five-co-ordinate geometry, with the metal ion displaced from the nitrogen-donor plane towards the fifth unidentate ligand, has been identified in two crystallographic studies[4,5] and is presumed to arise from kinetic control in the formation of the complex.[6] The geometry of the five-co-ordinated products also depends on the physical state. In the crystal with zinc(II)[4] and nickel(II),[5] the complexes are square pyramidal [Figure 1(*b*)], whereas in solution[7,8] they appear to be trigonal bipyramidal [Figure 1(*c*)].



L_a R = H
L_b R = Me

The effects described above apply to metal ions of ionic radius <0.75 Å. However, we have been interested in the co-ordination of the larger metal ions, Cd^{II} (0.97 Å), Hg^{II} (1.10 Å), and Pb^{II} (1.20 Å), of a prohibitive size for accommodation within the plane of the four amine donors of L_a or L_b. Recent work with lead(II)[2] has indicated that this extremely large ion is the only example of a labile metal which is capable of forcing L_a to adopt a folded conformation in which the complex is *cis* octahedral. In addition, the complex with L_b, while apparently square pyramidal, is very unstable in solution. These results have led us to consider Cd^{II} and Hg^{II}, of intermediate size, in an effort to understand how the macrocycles L_a and L_b adjust their

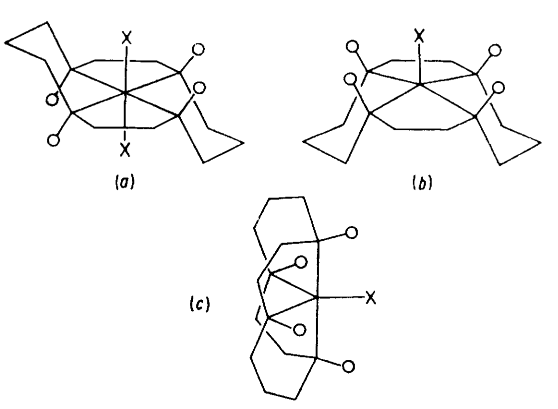


FIGURE 1 Three of the possible geometries for 14-membered macrocycle complexes

co-ordinative preferences in order to accommodate these ions.

There are no previous reports of complexes between L_b and either cadmium(II) or mercury(II) ions, but the analogous complexes with L_a have been the subjects of considerable speculation. The complex $[Cd(L_a)][ClO_4]_2$ was reported by Denning *et al.*[9] in 1976, but in 1977 other workers categorically stated that no complex between $Cd[NO_3]_2$ and L_a was formed during their aqueous polarographic studies.[10] The same two sets of workers also imply that the mercury(II) ion is too large to sit within the cavity of L_a and that the cation $[Hg(L_a)]^{2+}$ must, therefore, have a folded macrocycle conformation.[9,11] In addition, the thermodynamics of formation of the cation $[Hg(L_a)]^{2+}$ prove to be anomalous,[11] and these workers postulate that ' some, as yet unidentified, properties attached to the structure may be responsible.'

In order to clarify these points and to extend our own work on the co-ordination of heavy metal ions, we have prepared the cadmium(II) and mercury(II) complexes of L_a and L_b, and the results of our ^{13}C n.m.r. and *X*-ray crystallographic investigations are reported here.

EXPERIMENTAL

$[Cd(L_a)][NO_3]_2$.—This complex was prepared by mixing $Cd[NO_3]_2 \cdot 4H_2O$ (0.62 g) with L_a[12] (0.4 g) in methanol (5 cm^3). Evaporation of the solvent left a fine white powder which may be recrystallised from nitromethane. Yield 0.81 g (92%) {Found: C, 27.3; H, 5.50; Cd, 25.0; N, 19.1. Calc. for $[Cd(L_a)][NO_3]_2$: C, 27.5; H, 5.50; Cd, 25.7; N, 19.2%}. Conductivity of a 2×10^{-3} mol dm^{-3} solution in dry dimethyl sulphoxide (dmso) at 18.4 ± 0.2 °C is $(7.9 \pm 0.3) \times 10^{-2}$ ohm^{-1} m^2 mol^{-1}, consistent with a 2 : 1 electrolyte ($Na[ClO_4]$, reference conductivity = 3.1×10^{-2} ohm^{-1} m^2 mol^{-1}). The i.r. spectrum of the solid shows ν(NH) at 3 275, ν(NO_3) at 1 480—1 240, 1 020, 808, 742, and 720 cm^{-1} consistent with unidentate nitrate co-ordination.[13]

$[Hg(L_a)Cl]_2[HgCl_4]$.—The complex was prepared by mixing AnalaR $HgCl_2$ (0.28 g) with L_a (0.13 g)[12] in methanol (1 cm^3). Evaporation of the solvent left clear crystals of the complex which were washed with ice-cold methanol, chloroform, and diethyl ether. Yield 0.30 g (93%) {Found: C, 19.4; H, 4.10; N, 8.90. Calc. for $[Hg(L_a)Cl]_2[HgCl_4]$: C, 19.7; H, 3.95; N, 9.20%}. An identical procedure may be employed, using excess of $Hg[ClO_4]_2$ for the preparation (as a white solid) of the very much more soluble perchlorate complex, presumed to be $[Hg(L_a)][ClO_4]_2$. The purity of the latter was confirmed by ^{13}C n.m.r. spectroscopy.

The conductivities of 2×10^{-3} mol dm^{-3} solutions of each complex in dry dmso at 18.4 ± 0.2 °C are $(7.9 \pm 0.3) \times 10^{-2}$ ohm^{-1} m^2 mol^{-1} (chloro-complex) and $(7.6 \pm 0.3) \times 10^{-2}$ ohm^{-1} m^2 mol^{-1} (perchlorate), both consistent with 2 : 1 electrolytes. The i.r. spectrum of the chloro-complex shows ν(NH) at 3 210 and ν(HgCl) at *ca.* 260 cm^{-1}.

$[Cd(L_b)][NO_3]_2$.—The salt $Cd[NO_3]_2 \cdot 4H_2O$ (0.62 g) was mixed with L_b (0.51 g)[6] in methanol (5 cm^3). Stirring and heating for 30 min followed by evaporation to dryness gave a white crystalline complex which was washed with ice-cold methanol. Yield 0.87 g (92%) {Found: C, 33.4; H, 6.30; Cd, 22.7; N, 16.6. Calc. for $[Cd(L_b)][NO_3]_2$: C, 34.1; H, 6.50; Cd, 22.8; N, 17.1%}. The i.r. spectrum of the complex shows both free nitrate, ν(NO_3) at 1 380, 829, and 720 cm^{-1} and unidentate nitrate, ν(NO_3) at 1 460, 1 280, 1 029, 805, and 739 cm^{-1}.[13]

$[Hg(L_b)Cl]_2[HgCl_4]$.—AnalaR $HgCl_2$ (0.54 g) was mixed with L_b (0.34 g)[6] in methanol (5 cm^3). After a brief induction period, crystals of the complex began to precipitate. The product may be recrystallised from nitromethane as clear laths. Yield 0.72 g (81%) {Found: C, 25.3; H, 4.90; N, 8.40. Calc. for $[Hg(L_b)Cl]_2[HgCl_4]$: C, 25.3; H, 4.85; N, 8.50%}. The i.r. spectrum of the solid shows ν(HgCl) at *ca.* 250 cm^{-1}.

The ^1H-decoupled, natural abundance, ^{13}C (22.63-MHz) n.m.r. spectra were recorded in the temperature range 223—353 K with a Bruker WH90 Fourier transform spectrometer. Deuteriated solvents (99% [^2H]) were used as a lock signal and *ca.* 5% dioxan as an internal shift marker. Temperatures at which the spectra were recorded were held constant (±0.5 °C) with a standard Bruker control unit and measured (±0.5 °C) with a calibrated Comark copper–constantan thermocouple. Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer as Nujol mulls, using CsI windows, and conductivity measurements were performed with a Phillips PR 9500 conductivity bridge. Metal analyses were carried out with a Varian AAb atomic absorption spectrophotometer.

Crystals of the complex $[Hg(L_a)Cl]_2[HgCl_4]$, suitable for *X*-ray diffraction, were prepared by slow cooling and evaporation of a saturated methanol solution to give clear needles.

Crystal Data.—$C_{20}H_{48}Cl_6Hg_3N_8$, M = 1 215.2, Monoclinic, a = 15.686(9), b = 15.058(8), c = 14.979(6) Å, β = 103.03(4)°, U = 3 447(3) Å^3, T = 153(2) K, D_m = 2.40(5) g cm^{-3}, Z = 4, D_c = 2.34 g cm^{-3}, $F(000)$ = 2 264, space group $C2/c$, μ(Mo-K_α) = 138.19 cm^{-1}.

Data Collection.—A crystal, 0.04 × 0.28 × 0.21 mm, bounded by {100}{010}{101}{301} was examined with a Syntex $P2_1$ four-circle automated diffractometer. The temperature was held at −120 °C with the Syntex LT 1 attachment. The unit-cell dimensions and their estimated standard deviations (e.s.d.s) were obtained by a least-squares fit to 15 strong reflections with Mo-K_α graphite-monochromatised radiation (λ = 0.709 26 Å). Systematic absences, hkl with $h + k = 2n + 1$, $h0l$ with $l = 2n + 1$, indicate space groups CC or $C2/c$; the latter was confirmed by successful refinement. Intensity data in the range $3° \leqslant 2\theta \leqslant 55°$ were collected by the θ—2θ scan technique and three check reflections were monitored every 100 reflections. Some decrease in intensity during data collection was compensated for by re-scaling. 2 226 Reflections with $I \geqslant 3.0\sigma(I)$ were recorded and corrected for absorption by the method of Alcock[14] to give transmission factors in the range 0.193—0.544.

Structure Solution and Refinement.—The structure was solved by the heavy-atom method. All remaining non-hydrogen atoms were located in subsequent electron-density maps and all atoms were refined by minimising the function $\Sigma(|F_o| - |F_c|)$.[2] The cation, $[Hg(L_a)Cl]^+$, lies on a general position while the anion, $[HgCl_4]^{2-}$, is on special position e, of multiplicity 4, with crystallographic two-fold symmetry. Refinement by the least-squares method with anisotropic temperature factors for all atoms gave R = 0.037. Eight atoms showed large temperature factors and anomalous bond lengths and this is attributed to disorder, considered in detail below. Weights $w = XY$ were used, where $X = 1.0$ or $250/F$ for $F > 250$, $Y = 1.0$ or $[(\sin\theta)/\lambda]/0.36$ for $(\sin\theta)/\lambda < 0.36$. Scattering factors in the

TABLE 1

Atomic co-ordinates (× 10^4) with standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Hg(1)	2 918.3(5)	820.6(4)	4 587.4(5)
Hg(2)	5 000.0	3 261.3(6)	2 500.0
Cl(1)	3 849(3)	4 234(3)	2 894(3)
Cl(2)	4 518(3)	2 283(3)	1 129(3)
Cl(3)	3 742(4)	1 298(4)	6 108(4)
N(1)	3 296(8)	−733(7)	4 520(8)
N(2)	1 856(9)	1 700(8)	3 588(8)
N(3)	3 737(14)	947(18)	3 517(14)
N(4)	1 676(16)	254(25)	5 063(14)
C(1)	1 952(14)	1 729(13)	2 622(12)
C(2)	2 894(14)	1 878(14)	2 639(18)
C(3)	3 459(28)	857(32)	2 673(22)
C(4)	4 287(13)	−107(14)	3 559(19)
C(5)	3 700(15)	−880(16)	3 709(19)
C(6)	2 520(34)	−1 305(31)	4 501(35)
C(7)	822(26)	1 172(28)	4 482(33)
C(8)	1 091(26)	−158(31)	4 646(34)
C(9)	2 020(19)	−1 026(17)	5 218(18)
C(10)	902(14)	1 365(13)	3 530(16)

TABLE 2

Bond lengths (Å) and angles (°) with standard deviations in parentheses

(*a*) Lengths

Hg(1)–N(1)	2.42(1)	N(3)–C(6)	1.56(3)
Hg(1)–N(2)	2.28(4)	N(4)–C(7)	1.98(6) *
Hg(1)–N(3)	2.38(4)	N(4)–C(8)	1.16(5) *
Hg(1)–N(4)	2.38(4)	N(4)–C(9)	2.00(5) *
Hg(1)–Cl(1)	2.46(5)	C(1)–C(2)	1.53(3)
Hg(2)–Cl(2)	2.50(2)	C(2)–C(3)	2.19(6) *
Hg(2)–Cl(3)	2.50(3)	C(3)–C(4)	1.77(5) *
N(1)–C(1)	1.51(4)	C(4)–C(5)	1.49(3)
N(1)–C(10)	1.49(5)	C(6)–C(7)	1.49(6)
N(2)–C(2)	1.80(3) *	C(7)–C(8)	2.05(6) *
N(2)–C(3)	1.25(4) *	C(8)–C(9)	2.00(6) *
N(2)–C(4)	2.16(4) *	C(9)–C(10)	1.52(7)
N(3)–C(5)	1.49(2)		

(*b*) Angles

Cl(1)–Hg(1)–N(1)	103.8(3)	Hg(1)–N(4)–C(7)	98(2)
Cl(1)–Hg(1)–N(2)	111.4(5)	Hg(1)–N(4)–C(8)	129(3)
Cl(1)–Hg(1)–N(3)	124.6(3)	Hg(1)–N(4)–C(9)	99(1)
Cl(1)–Hg(1)–N(4)	97.0(5)	C(7)–N(4)–C(8)	76(13)
N(1)–Hg(1)–N(2)	82.5(8)	C(7)–N(4)–C(9)	149(2)
N(1)–Hg(1)–N(3)	131.0(4)	C(8)–N(4)–C(9)	73(3)
N(1)–Hg(1)–N(4)	83.7(9)	N(1)–C(1)–C(2)	112(2)
N(2)–Hg(1)–N(3)	86.4(7)	C(1)–C(2)–N(2)	112(2)
N(2)–Hg(1)–N(4)	150.6(8)	C(1)–C(2)–C(3)	107(2)
N(3)–Hg(1)–N(4)	83.3(8)	C(2)–C(3)–C(4)	145(2)
Cl(2)–Hg(2)–Cl(2)	108.2(2)	C(2)–C(3)–N(2)	55(2)
Cl(2)–Hg(2)–Cl(3)	116.0(1)	N(2)–C(3)–C(4)	90(3)
Cl(3)–Hg(2)–Cl(3)	107.8(2)	C(3)–C(4)–C(5)	111(2)
Hg(1)–N(1)–C(1)	109(1)	N(2)–C(4)–C(5)	112(2)
Hg(1)–N(1)–C(10)	111(2)	C(4)–C(5)–N(3)	108(2)
C(1)–N(1)–C(10)	113(2)	N(3)–C(6)–C(7)	107(2)
Hg(1)–N(2)–C(2)	104(1)	C(6)–C(7)–N(4)	111(3)
Hg(1)–N(2)–C(3)	125(3)	C(6)–C(7)–C(8)	104(3)
Hg(1)–N(2)–C(4)	97(1)	C(7)–C(8)–C(9)	143(3)
C(2)–N(2)–C(3)	90(3)	N(4)–C(8)–C(9)	73(3)
C(2)–N(2)–C(4)	145(2)	C(7)–C(8)–N(4)	70(3)
C(3)–N(2)–C(4)	55(2)	C(8)–C(9)–C(10)	109(3)
Hg(1)–N(3)–C(5)	115(1)	N(4)–C(9)–C(10)	111(2)
Hg(1)–N(3)–C(6)	112(1)	C(9)–C(10)–N(1)	112(3)
C(5)–N(3)–C(6)	105(1)		

* Affected by disorder.

analytical form and anomalous dispersion factors [15] were used, and all computing was performed with a Burroughs B6700 computer, using the '*X*-ray '76' programs.[16] Atomic co-ordinates are in Table 1. Structure factors and temperature factors are listed in Supplementary Publication No. 22608 (15 pp.).* Bond lengths and angles are included in Table 2(*a*) and (*b*) respectively.

RESULTS AND DISCUSSION

$[Cd(L_a)][NO_3]_2$.—Contrary to a recent report,[10] this complex is readily produced in many different solvents, including water. The ^{13}C n.m.r. spectra of the complex in a 1 : 1 D_2O–[$^2H_6$]dmso mixture are shown in Figure 2. Conductivity studies indicate that the complex is a 2 : 1 electrolyte in this medium, and that dissociation of the nitrate ions is complete in solution. The spectra show a very complicated variable-temperature profile; at 253 K (10% methanol added to prevent freezing) the spectrum contains eight resonances which may readily be assigned to two distinct species A and B (see Figure 2). On elevating the temperature, the five-line species B undergoes a dynamic process which causes a collapse to three lines at 303 K (dynamic process 1). Continued warming eventually causes the exchange of the two species A and B such that the two sets of three lines collapse to give just three lines at 373 K (dynamic process 2).

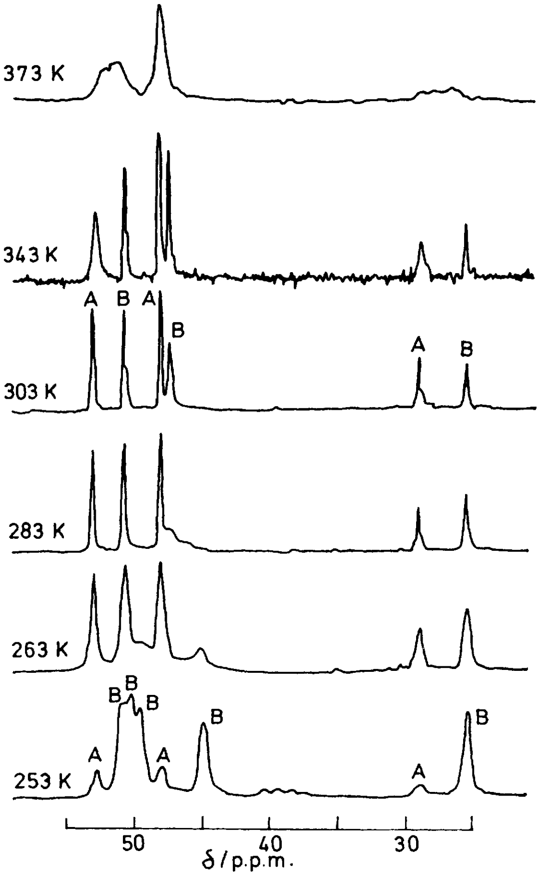


FIGURE 2 Variable-temperature ^{13}C n.m.r. spectra of $[Cd(L_a)][NO_3]_2$ in 1 : 1 D_2O–[$^2H_6$]dmso (chemical shifts relative to internal dioxan, δ = 67.3 p.p.m.)

Addition of free macrocycle L_a to these solutions produces three new resonances in the spectra over the entire temperature range studied, proving that neither species A nor B is attributable to, or is in fast exchange

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 3

Ratio of species A and B for $[Cd(L_a)][NO_3]_2$ in various solvents (based on integrals of ^{13}C n.m.r. spectra)

Solvent	Ratio A : B at 303 K
D_2O	1.43
$[^2H_4]$Methanol	2.63
$[^2H_3]$Nitromethane	1.57
$[^2H_6]$dmso	0.34

with, free ligand. The two species A and B are, therefore, both interpreted as being 'cadmium–macrocycle' complexes which are in equilibrium and are kinetically inert to macrocycle substitution. The equilibrium between A and B is sharply solvent dependent as shown in Table 3, perhaps indicating some solvent involvement in the equilibrium.

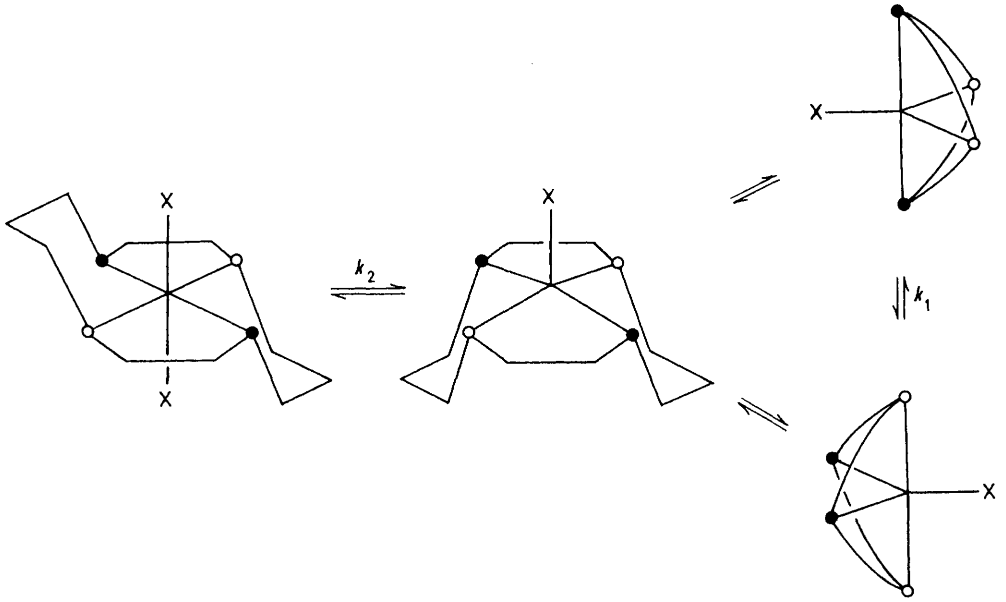

FIGURE 3 Schematic illustration of the proposed dynamic processes observed in the ^{13}C n.m.r. spectra of $[Cd(L_a)][NO_3]_2$

If one considers the ^{13}C n.m.r. spectra from 303 to 373 K, their appearance and the dynamic process displayed (process 2) are seen to be qualitatively very similar to those observed for the complex (1,4,8,11-tetrathiacyclotetradecane)nickel(II).[17] In this case, the two species were assigned with their sulphur atoms in a plane with configurations *R, S, S, R* and *R, S, R, S* [Figure 1(*a*) and 1(*b*) respectively] and interconversion of the two three-line species was postulated to proceed *via* double sulphur inversion. It seems reasonable, therefore, to make a similar assignment in this instance, the two species having a planar set of nitrogen donors of configurations *R, S, S, R* and *R, S, R, S*. Such an interpretation implies that the cadmium(II) ion (r = 0.97 Å) is slightly too large to fit comfortably within the plane of the four nitrogen donors of L_a. This will then cause an equilibrium between the two isomers, *R, S, S, R* [Figure 1(*a*)] (which is thermodynamically most stable [6] for the macrocycle itself, but requires cadmium to be in-plane) and *R, S, R, S* [Figure 1(*b*)] (which allows the cadmium ion to sit above the plane) with the balance between the two being finely poised. Such a hypothesis seems reasonable in view of the following facts: (*a*) the slightly smaller silver(II) ion (r = 0.89 Å) is still capable of being accommodated within the 14-membered ring in a perfect *R, S, S, R* type geometry [18] [Figure 1(*a*)]; (*b*) the slightly larger mercury(II) (r = 1.10 Å) is too large to adopt an *R, S, S, R* structure and so prefers an *R, S, R, S* [Figure 1(*b*)] geometry (see below).

A complete lineshape analysis [19] of the ^{13}C n.m.r. spectra involving dynamic process 2 (interpreted as double nitrogen configurational inversion) gives the activation parameters shown in Table 4. The parameters derived are very similar to those for the (1,4,8,11-tetrathiacyclotetradecane)nickel(II) cation which confirms a similar interpretation for both systems.

If this interpretation of process 2 is correct, then the dynamic process 1 at low temperature which causes one of the three-line species to split to five lines must be interpreted as folding of one of the species away from a planar array of nitrogen donors. In view of other work,[4] on $[Zn(L_b)X]^+$ ions and on an analogous copper(II) complex,[20] the process is best interpreted as folding of the isomer with *R, S, R, S* nitrogen configurations [Figure 1(*b*)] to a trigonal-bipyramidal geometry with identical configurations [Figure 1(*c*)]. A complete lineshape analysis [19] of process 1 gives the activation parameters in Table 4.

The whole system is summarised in Figure 3. Process

TABLE 4

Rate and activation parameters at 298 K for the two dynamic processes in the ^{13}C n.m.r. spectra of $[Cd(L_a)][NO_3]_2$ in D_2O–$[^2H_6]$dmso (1 : 1)

Process	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	Rate constant/s^{-1}
1	8.8 ± 1.3	−169 ± 15	$k_1 = 285$
2	78 ± 14	−11 ± 20	$k_2 = 0.049$

1 (rate constant k_1) is seen to involve an interconversion of axial and equatorial nitrogen atoms of a trigonal-bipyramid by passage through a 'square-pyramidal' intermediate or transition state (solid and open circles represent pairs of equivalent donor atoms). This interconversion, when rapid, will produce the observed collapse of five resonances to three for species B (Figure 2). The activation parameters for the process (Table 4) show that the bond rotation about the cadmium atom is a low-energy process (which is reasonable) whilst the large negative entropy of activation indicates significantly increased solvation of the square-pyramidal intermediate or transition state. This may well be due to the greater accessibility of the sixth octahedral site in the transition state, allowing the co-ordination of a second solvent molecule in the position which was blocked by the folded macrocycle in the trigonal bipyramid. Exchange process 2 (rate constant k_2) involves two nitrogen configurational inversions and the relatively high energy of the process (Table 4) supports this hypothesis. The small entropy of activation is also reasonable if one assumes that both species are octahedrally solvated and that such amine inversions are not accompanied by any great solvation effects.

The $[Hg(L_a)]^{2+}$ *Cation.*—The extremely soluble perchlorate salt was used for the solution studies of this cation in methanol–dmso (1 : 4). Variable-temperature ^{13}C n.m.r. spectra in this medium show only three resonances [δ = 53.47, 46.76, and 29.37 p.p.m., intensity ratio 2 : 2 : 1, reference dioxan (δ = 67.26 p.p.m.)] over the temperature range 233—273 K with no significant broadening other than that due to viscosity effects.

These results imply (*i*) a rigid planar array of nitrogen donor atoms, as in Figure 1(*a*) or 1(*b*), or (*ii*) a thermodynamically unstable complex where free and folded bound macrocycle are in very rapid exchange, producing an averaged three-line spectrum. This latter interpretation is readily dismissed by the presence of couplings [to ^{199}Hg (16%) with spin $\frac{1}{2}$] on all three peaks in the ^{13}C spectrum, proving that total macrocycle exchange is not rapid. $^2J(^{199}\text{Hg}-^{13}\text{C}) = 43.5$ Hz, $\delta = 29.4$ p.p.m.

The structure is, therefore, interpreted as being either as in 1(*a*) or 1(*b*) with nitrogen configurations *R*, *S*, *S*, *R* or *R*, *S*, *R*, *S* respectively. In view of the large size of the mercury(II) ion ($r = 1.10$ Å) a structure such as 1(*a*) where the mercury atom is constrained to lie in the donor-atom plane is very unlikely,[3] and therefore structure 1(*b*) with configurations *R*, *S*, *R*, *S* is more probable. Such a geometry, although also postulated for one of the $[Cd(L_a)]^{2+}$ species above, would be unique for the macrocycle L_a, and would be predicted to favour five-co-ordination at the metal atom [Figure 1(*b*)] exactly as is observed for equivalent complexes of L_b.[4,6] The stoicheiometry of the chloro-complex, $(HgCl_2)_3(L_a)_2$, indicated that five-co-ordination was, indeed, probable, and in order to confirm the geometry (*R*, *S*, *R*, *S*) a crystal-structure analysis of this complex was performed.

The cation $[Hg(L_a)Cl]^+$ is shown in Figure 4 and is seen to be essentially square pyramidal with all four nitrogen donors in a plane (±0.23 Å) and with the central mercury atom [Hg(1)] displaced from this plane by 0.80 Å towards the apical chlorine atom, Cl(1). The Hg(1)–Cl(1) vector makes an angle of 77.4° with this plane. There is considerable disorder within the macrocycle. Two nitrogen atoms [N(1), N(3)] have unique positions, but moving in either direction from them there may be either two or three carbon atoms before the next nitrogen atom is reached. The bond and dihedral angles are such that these [N(2), N(4)] are in almost the same place in either case, and they and the carbon atoms could not be seen in different positions, but only as elongated areas of electron density; all bond lengths measured from the centre of these areas are therefore abnormally long. In Figure 4 one linkage (N–C–C–N–C–C–C–N) is shown with solid bonds, and the alternative with open bonds. The macrocycle is seen to confirm the n.m.r. data, showing an *R*, *S*, *R*, *S* set of nitrogen configurations and imposing square-pyramidal five-co-ordination upon the mercury atom. The geometry is very similar to that found for an analogous mercury complex of 1,4,8,11-tetrathiacyclotetradecane,[1] and both structures tend to confirm the postulate that the *R*, *S*, *R*, *S* set of configurations is preferred by 14-membered macrocycles which are forced to encompass metal ions too large for their cavity.

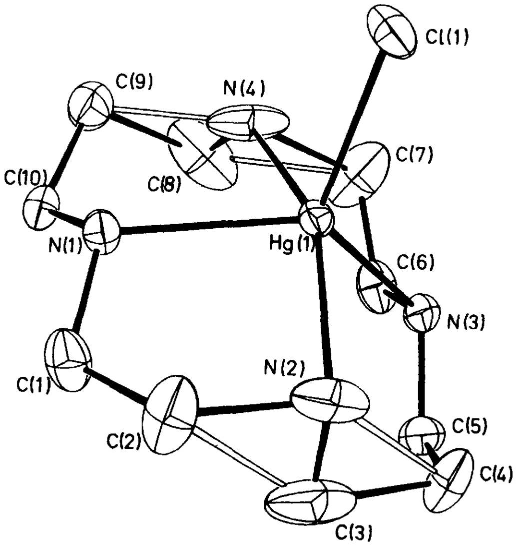

FIGURE 4 Molecular structure of the $[Hg(L_a)Cl]^+$ cation, showing atomic numbering

The crystal-packing diagram (Figure 5) shows that the isolated cations are flanked by non-co-ordinated $[HgCl_4]^{2-}$ anions on special positions of two-fold symmetry. The crystal forces between the ions must be mainly electrostatic.

The identification of this geometry for $[Hg(L_a)Cl]^+$ may help to interpret the electrochemical, e.s.r., and anomalous thermodynamic [11] data obtained by other workers on this compound, in terms of its structure. Figure 4 also shows the very close structural relationship between the trigonal-bipyramidal and square-pyramidal geometries for complexes of L_a or L_b. It requires little

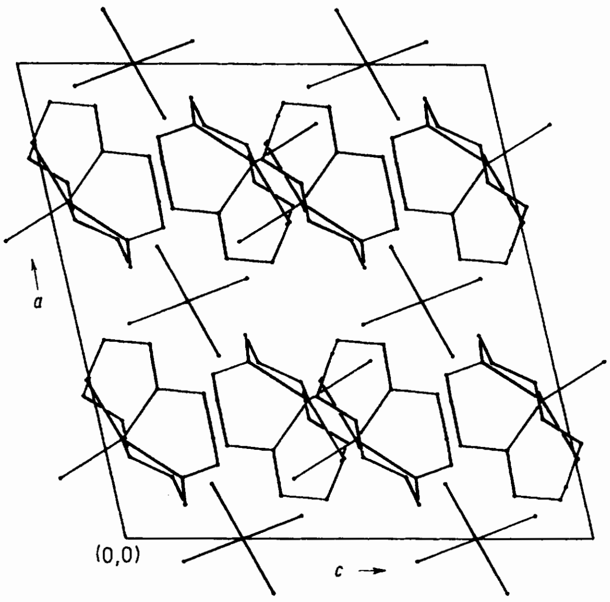

FIGURE 5 Crystal-packing diagram for $[Hg(L_a)Cl]_2[HgCl_4]$ viewed along the *b* axis

imagination to envisage a distortion of Figure 4 where atoms N(1) and N(3) are bent back until the structure becomes trigonal bipyramidal. Exactly this distortion was postulated for the complex with Cd^{II} (above) and for the complexes of L_b with Zn^{II} previously studied [4] and with Hg^{II} and Cd^{II} (below).

$[Cd(L_b)][NO_3]_2$ *and* $[Hg(L_b)Cl]_2[HgCl_4]$.—Both complexes dissolve in nitromethane to give very similar ^{13}C n.m.r. spectra, although the mercury complex is much less soluble. Variable-temperature spectra of the cadmium complex are shown in Figure 6. The behaviour observed, splitting of four room-temperature resonances to seven at low temperature, is identical to that already reported for equivalent complexes of the zinc(II) ion.[4] The interpretation of the latter as Berry-type rotation of a square-pyramidal structure [Figure 1(*b*)] to rapidly interconverting trigonal bipyramidal [Figure 1(*c*)] is therefore extended directly to the present systems.

A complete lineshape analysis [19] of the ^{13}C n.m.r. spectra obtained for the cadmium(II) complex in nitromethane gives activation parameters at 298 K of $\Delta H^{\ddagger} = 46 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = -14 \pm 10$ J K^{-1} mol^{-1}, and $k = 9\,100$ s^{-1}. A similar analysis of the mercury complex was not attempted due to its much lower solubility [$\delta = 23.0$, 43.2, 46.2, 56.5, 57.5, 60.3, and 65.9 p.p.m. at 233 K; reference dioxan ($\delta = 67.3$)]. The activation parameters are very similar to those obtained for the zinc(II) complexes [4] and add support to the conclusion that both the cadmium and mercury complexes have trigonal-bipyramidal stereochemistry [Figure 1(*c*)]. It is significant that this geometry was postulated above for one of the species present in solutions of $[Cd(L_a)][NO_3]_2$ and that the same dynamic process in that case gave very different activation parameters (process 1, Table 4).

The much higher value of $\Delta H^{\ddagger}$ for the present cadmium(II) complex is probably a manifestation of the steric requirements imposed by the N-methyl groups. These groups will tend to disfavour the exchange transition state [square pyramidal, Figure 1(*b*)] since in it they will be forced to approach each other and the fifth ligand more closely, so raising the enthalpic barrier to this motion relative to the equivalent complex with L_a. Similarly, the difference in the entropy of activation probably arises from the presence of the N-methyl groups. When they are absent (L_a) the square-pyramidal state is interpreted as being solvated in the sixth octahedral site, whereas when they are present (L_b) their interactions with the fifth ligand will tend to push the cadmium atom further out of plane towards the fifth ligand in order to reduce these contacts. If this occurs, then the macrocycle backbone continues to block the sixth octahedral site, preventing increased solvation of the transition state.

Conclusions.—With metal ions of radius slightly larger than the macrocycle cavity, both L_a and L_b adopt structures which are a compromise between the cavity overcrowding and the preferred ***trans*** geometry. Whereas the very large lead(II) ion forces L_a to adopt a *cis*-geometry,[6] the smaller mercury(II) and cadmium(II) ions tend towards a ***trans*** structure but with nitrogen configurations *R*, *S*, *R*, *S* instead of the more usual *R*, *S*, *S*, *R*. The former has the advantage that it allows the metal ion to sit above the plane of the macrocycle donors unconstricted by them. This geometry has

FIGURE 6 Variable-temperature ^{13}C n.m.r. spectra of $[Cd(L_b)][NO_3]_2$ in $[^2H_3]$nitromethane (chemical shifts relative to internal dioxan, $\delta = 67.3$ p.p.m.)

only been found, for L_a, in the complexes discussed here. With L_b, however, the *R*, *S*, *R*, *S* isomer is the most common, and is adopted by the complexes examined above, although, as previously reported,[4,7,8] these complexes appear to be trigonal bipyramidal in solution.

Much of the work on the macrocycle L_a discussed above, together with the complex with lead(II), has been supported by natural-abundance ^{15}N n.m.r. studies. In all cases, ^{15}N shifts and direct ^{1}J metal–nitrogen coupling constants have been observed and will be discussed and compared to those found for *trans*-1,2-diaminocyclohexane-*NNN'N'*-tetra-acetate complexes of these and other metals in a future publication.

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