

Comparison of the Different Modes of Bonding of the Macrocycle in μ -(1,4,8,11-Tetrathiacyclotetradecane- $S^1S^4;S^8S^{11}$)-bis[dichloromercury(II)] and Aqua(1,4,8,11-tetrathiacyclotetradecane)mercury(II) Perchlorate by X-Ray Structural Analysis

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The crystal structures of the title complexes $[(HgCl_2)_2L]$ (1) and $[HgL(OH_2)](ClO_4)_2$ (2) have been determined by X-ray diffraction. Complex (1) crystallises in the monoclinic space group $P2_1/n$, $Z = 2$, with $a = 8.080(2)$, $b = 11.389(2)$, $c = 10.706(2)$ Å, and $\beta = 92.15(1)^\circ$, and (2) crystallises in the orthorhombic space group $Pn2_1a$, $Z = 4$, $a = 16.583(2)$, $b = 13.986(3)$, and $c = 8.932(2)$ Å. Intensities [1 675 and 1 695 with $I/\sigma(I) \geq 3.0$ for (1) and (2)] have been recorded on a four-circle diffractometer, and the structures refined by the least-squares method to yield final R values of 0.030 and 0.116 for (1) and (2) respectively. The two structures differ markedly; Hg^{II} adopts approximately tetrahedral co-ordination in (1) and a square-pyramidal geometry in (2), indicating both the flexibility of the ligand (L) and the marked influence of the co-ordinative ability of the anions present. With the co-ordinating chloride anions, L adopts a doubly bidentate bridging conformation, while with the non-co-ordinating perchlorate ion L is quadridentate, imposing a square-pyramidal geometry at mercury, the fifth site being occupied by solvent water.

RECENT structural studies on the co-ordination chemistry of the potentially quadridentate macrocycle 1,4,8,11-tetrathiacyclotetradecane (L) have shown the ligand to have remarkable versatility in adopting several different modes of bonding. In a given complex the bonding mode appears to be controlled by a combination of several factors including metal-ion size (as related to the central cavity of the macrocycle) and the presence of other competing ligands. The smaller transition metals form *endo*-type complexes [Figure 1(a)] such as $[NiL][BF_4]_2$ ¹ and $[CuL](ClO_4)_2$ ² where the macrocycle is quadridentate and the complexes are respectively centrosymmetric square planar and tetragonal. With the larger ions Co^{III} and Rh^{III} the ligand remains *endo*-quadridentate, but folds to give a *cis* geometry in complexes of the type *cis*- $[MLX_2]Y$ (X = halide ion, Y = univalent counter ion).³ This folding was assumed to be due to the larger size of those ions which prevents

¹ P. H. Davis, L. K. White, and R. L. Belford, *Inorg. Chem.*, 1975, **14**, 1753.

² M. D. Glick, D. P. Gavel, L. L. Diddario, and D. B. Rorbacher, *Inorg. Chem.*, 1976, **15**, 1190.

them from sitting in the plane of the macrocycle, but more recently Lemke *et al.*⁴ have prepared a pseudo-square-planar complex of Rh^I (an even larger cation) as

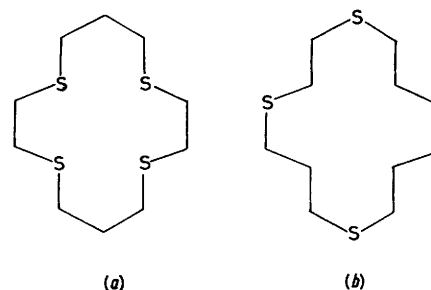


FIGURE 1 Representations of (a) the *endo* and (b) the *exo* conformations of the ligand L

well as several *trans*-octahedral rhodium(III) complexes. It is clear, therefore, that metal-ion size, although important, is not the only factor to be considered. This

³ K. E. Travis and D. H. Busch, *Inorg. Chem.*, 1974, **13**, 2591.

⁴ W. D. Lemke, K. E. Travis, N. E. Takvoryan, and D. H. Busch, *Adv. Chem. Ser.*, 1976, **150**, 358.

point is emphasised by the structure of $[(\text{NbCl}_5)_2\text{L}]$ which contains two NbCl_5 units bridged by a bis-unidentate ligand in the *exo* conformation [Figure 1(b)].⁵ In this case it seems that the availability of co-ordination sites on the central metal is more important than metal size, since the vacant octahedral site of the NbCl_5 units is occupied by a sulphur atom of the macrocycle.

In a preliminary communication we reported X-ray work on a complex between mercury(II) chloride and L.⁶ In order to relate the contributions of metal size and of co-ordinating anions to the conformation adopted by the macrocycle, the structure of a second complex, that between Hg^{II} and L containing non-co-ordinating perchlorate anions, was determined, and both are reported here.

EXPERIMENTAL

(a) *Synthesis and Study of μ -(1,4,8,11-Tetrathiacyclotetradecane-S¹S⁴;S⁸S¹¹)-bis[dichloromercury(II)], $[(\text{HgCl}_2)_2\text{L}]$ (1).*—Solutions of HgCl_2 (0.27 g) and L (0.134 g)³ were mixed in boiling nitromethane (10 cm³). The white precipitate was collected and washed with chloroform and water to leave a dry powder. Recrystallisation by slow evaporation of a dilute nitromethane solution yielded clear lath crystals [Found: C, 15.2; H, 2.55; Hg, 48.8. Calc. for (1): C, 14.9; H, 2.50; Hg, 49.3%]. Crystal data are summarised in Table 1. Systematic absences, $0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$, were observed in the preliminary data collection, indicating the monoclinic space group $P2_1/n$ (a non-standard setting of $P2_1/c$). The crystal density was measured by flotation in bromoform–chloroform and

$0.05 \times 0.05 \times 0.30$ mm bounded by $\{011\}$ and $\{100\}$ was mounted and aligned on a Syntex $P2_1$ four-circle diffractometer. Intensity data were collected in the range $3 \leq 2\theta \leq 55^\circ$ by the θ – 2θ scan technique. Three check reflections monitored after every 100 reflections measured showed no significant variation. A total of 1 675 observed reflections [$I/\sigma(I) \geq 3.0$] were measured and corrected for absorption by the method of Alcock,⁷ giving transmission factors in the range 0.401–0.500. A weighting analysis on the corrected data indicated that unit weights were satisfactory.

(b) *Synthesis and Study of Aqua(1,4,8,11-tetrathiacyclotetradecane)mercury(II) Perchlorate, $[\text{HgL}(\text{OH}_2)](\text{ClO}_4)_2$ (2).*—The complex was prepared by mixing solutions of hydrated mercury(II) perchlorate (excess) and L (0.134 g) in aqueous methanol (10 cm³). The white powder which immediately precipitated was filtered off and washed with water and chloroform. Recrystallisation was accomplished by slow evaporation of an extremely dilute solution (0.1 g in 500 cm³) of the powder in 80% aqueous methanol. Small poorly formed fragments of crystalline material were obtained [Found: C, 17.8; H, 3.15; Hg, 28.2. Calc. for (2): C, 17.5; H, 3.20; Hg, 29.2%]. The crystal data are summarised in Table 1, the unit-cell parameters and crystal density being measured as in (a). Systematic absences, $hk0$ for $h = 2n + 1$ and $0kl$ for $k + l = 2n + 1$, indicated an orthorhombic space group $Pn2_1a$ or $Pnma$, and density measurements indicated $Z = 4$ molecules per unit cell. A small crystal of dimensions $0.05 \times 0.18 \times 0.13$ mm bounded by planes $\{100\}$, $\{010\}$, and $\{001\}$ was selected and centred on a Syntex $P2_1$ automatic diffractometer. Intensity data in the range $3 \leq 2\theta \leq 50^\circ$ were collected by the θ – 2θ scan technique and three check reflections were monitored throughout the data collection as in (a). 1 695 Observed reflections were collected and corrected for absorption, giving transmission factors in the range 0.25–0.60. Unit weights were again used.

Structure Solution.—The structures were solved using the heavy-atom method which employed a three-dimensional Patterson synthesis to locate the position of the mercury atoms. The remaining atoms were located in subsequent electron-density maps and all the atoms were refined by minimising the function $\Sigma(|F_o| - |F_c|)^2$. For (1), final refinement with anisotropic temperature factors for Hg, Cl, and S atoms gave R 0.030. For (2), initial refinement in the centric space group $Pnma$ produced a chemically inconsistent structure which would not refine below R 0.20. Conversion into the non-centric group $Pn2_1a$ (a non-standard setting of $Pna2_1$) allowed refinement to give a reasonable overall view of the chemical structure with R 0.116. Refinement to a higher accuracy proved impossible; this is probably due to: (i) an irregular crystal, leading to uncertain absorption corrections; (ii) disorder of the oxygen atoms of the two perchlorate groups; and (iii) disorder of the carbon backbone of the ligand L as shown by the high temperature factors associated with certain of the backbone atoms. (Although alternative positions of these carbons were tried, they provided no improvement.) It is clear that (2) is an adequate description of the molecular structure of this complex but also that the bond lengths and angles are less reliable than for structure (1).

Scattering factors and anomalous-dispersion corrections

⁷ N. W. Alcock, 'Crystallographic Computing,' ed. F. Ahmed, Munksgaard, Copenhagen, 1970, p. 271.

TABLE 1
Crystal data
 $[(\text{HgCl}_2)_2\text{L}]$ (1) $[\text{HgL}(\text{OH}_2)](\text{ClO}_4)_2$ (2)

Colour	White	White
Habit	Needle	Irregular
Crystal system	Monoclinic	Orthorhombic
$a/\text{\AA}$	8.080(2)	16.583(2)
$b/\text{\AA}$	11.389(2)	13.986(3)
$c/\text{\AA}$	10.706(2)	8.932(2)
$\beta/^\circ$	92.15(1)	90.0(1)
$U/\text{\AA}^3$	984.5(3)	2 075.2(5)
$\theta_c/^\circ\text{C}$	18(2)	18(2)
Space group	$P2_1/n$	$Pn2_1a$
Equivalent positions	$\pm x, y, z; \frac{1}{2} + x,$ $\frac{1}{2} - y, \frac{1}{2} + z$	$x, y, z; -x, \frac{1}{2} + y,$ $-z; \frac{1}{2} - x, \frac{1}{2} + y,$ $\frac{1}{2} + z; \frac{1}{2} + x, y,$ $\frac{1}{2} - z$
μ/cm^{-1}	164.4	84.5
Relative molecular mass	810.9	685.6
$D_m/\text{g cm}^{-3}$	2.80(5)	2.24(5)
$D_c/\text{g cm}^{-3}$	2.736	2.195
Z	2	4
$N(3\sigma)$	1 675	1 695
$F(000)$	744	1 328

indicated two molecules per unit cell, each therefore lying on a special position of symmetry $\bar{1}$. The unit-cell dimensions and their estimated standard deviation were obtained by a least-squares fit to 15 strong reflections using $\text{Mo-K}\alpha$ radiation (λ 0.710 69 \AA). A crystal of dimensions *ca.*

⁵ R. E. DeSimone and M. D. Glick, *J. Co-ordination Chem.*, 1976, **5**, 181.

⁶ N. W. Alcock, N. Herron, and P. Moore, *J.C.S. Chem. Comm.*, 1976, 886.

TABLE 2
Fractional atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses

Atom	X	Y	Z	Atom	X	Y	Z
(a) Complex (1)							
Hg	1 617.9(4)	190.7(3)	1 668.2(3)	C(1)	5 188(10)	-1 509(7)	2 132(7)
S(1)	3 072(2)	-1 821(2)	1 541(2)	C(2)	5 237(11)	-711(7)	3 287(8)
S(2)	4 307(3)	748(2)	3 118(2)	C(3)	5 744(10)	1 613(7)	2 216(8)
Cl(1)	1 147(3)	1 567(2)	-15(2)	C(4)	5 908(11)	1 228(8)	865(8)
Cl(2)	-413(3)	113(2)	3 270(2)	C(5)	6 635(10)	2 237(7)	87(8)
(b) Complex (2)							
Hg	1 368(1)	2 500	2 113(3)	C(7)	1 089(39)	4 465(50)	10 079(72)
C(8)	5 098(80)	3 428(104)	6 316(131)	C(9)	5 247(52)	2 000(64)	6 486(87)
C(1)	1 396(56)	70(68)	934(93)	C(10)	797(49)	1 220(60)	8 910(85)
S(1)	699(23)	1 027(30)	890(25)	Cl(1)	2 673(10)	2 382(20)	6 676(17)
S(2)	2 356(31)	1 169(34)	2 530(39)	O(1)	2 430(23)	3 134(33)	7 651(54)
S(3)	2 387(40)	3 902(31)	2 407(45)	O(2)	1 977(17)	1 888(30)	6 143(43)
S(4)	421(27)	3 597(24)	333(34)	O(3)	3 104(29)	2 771(41)	5 441(36)
O(11)	568(25)	2 391(44)	4 282(45)	O(4)	3 178(28)	1 733(32)	7 470(61)
C(2)	2 311(44)	562(58)	915(83)	Cl(2)	-53(19)	4 955(22)	5 229(23)
C(3)	3 525(51)	1 729(65)	2 310(98)	O(5)	621(31)	4 780(50)	4 278(59)
C(4)	3 422(38)	3 791(47)	1 276(72)	O(6)	-612(31)	5 564(33)	4 481(62)
C(5)	3 197(69)	3 732(84)	1 482(123)	O(7)	-434(34)	4 073(26)	5 587(54)
C(6)	1 616(40)	4 886(49)	1 147(75)	O(8)	217(37)	5 406(35)	6 570(35)

from ref. 8 were used, and all the computing was carried out with the 'X-Ray '76' programs⁹ on a Burroughs B6700 computer. Final co-ordinates are in Table 2. Structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22191 (33 pp.).* Bond lengths and angles are in Tables 3 and 4 respectively.

TABLE 3
Bond lengths (Å) with standard deviations in parentheses

Bond	Complex	
	(1)	(2)
Hg-Cl(1)	2.407(3)	
Hg-Cl(2)	2.419(3)	
Hg-S(1)	2.580(2)	2.58(4)
Hg-S(2)	2.699(2)	2.51(5)
Hg-S(3)		2.60(5)
Hg-S(4)		2.71(4)
Hg-O(11)		2.35(4)
S(1)-C(1)	1.838(8)	1.77(10)
S(1)-C(10)		1.80(8)
S(2)-C(2)	1.827(9)	1.68(8)
S(2)-C(3)	1.827(9)	2.10(10)
S(3)-C(5)		1.60(13)
S(3)-C(6)		2.19(8)
S(4)-C(7)		1.66(8)
S(4)-C(8)		1.58(12)
C(1)-C(2)	1.53(1)	1.67(13)
C(3)-C(4)	1.52(1)	1.76(11)
C(4)-C(5)	1.55(1)	1.38(13)
C(5)-C(7)		1.42(9)
C(8)-C(9)		2.00(17)
C(9)-C(10)		1.47(12)

RESULTS AND DISCUSSION

The molecular structure of $[(\text{HgCl}_2)_2\text{L}]$ (Figure 2) may be described in terms of the ligand L being simultaneously bidentate to two distinct HgCl_2 moieties, and therefore bridging in a symmetrical *exo*-dentate manner [Figure 1(b)] between them. The co-ordinated chloride ions therefore impose a distorted tetrahedral geometry on the metal. This geometry is relatively common for Hg^{II} ,¹⁰ although the conformation adopted by the ligand is, as yet, unique. This conformation displays several

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

⁸ 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3.

TABLE 4
Bond angles ($^\circ$) with standard deviations in parentheses

Angle	Complex	
	(1)	(2)
Cl(1)-Hg-Cl(2)	117.54(9)	
Cl(1)-Hg-Cl(1)	126.71(8)	
Cl(1)-Hg-S(2)	112.19(8)	
Cl(2)-Hg-S(1)	109.11(8)	
Cl(2)-Hg-S(2)	98.88(7)	
S(1)-Hg-S(2)	83.15(6)	76(1)
S(1)-Hg-S(3)		157(1)
S(1)-Hg-S(4)		87(1)
S(1)-Hg-O(11)		93(1)
S(2)-Hg-S(3)		97(2)
S(2)-Hg-S(4)		152(1)
S(2)-Hg-O(11)		101(2)
S(3)-Hg-S(4)		90(1)
S(3)-Hg-O(11)		109(2)
S(4)-Hg-O(11)		101(1)
C(1)-S(1)-C(10)	103.2(4)	94(4)
C(1)-S(1)-Hg	103.3(3)	108(3)
C(10)-S(1)-Hg	110.9(3)	105(3)
C(2)-S(2)-C(3)	106.0(4)	98(4)
C(2)-S(2)-Hg	99.2(3)	103(3)
C(3)-S(2)-Hg	109.8(3)	108(3)
C(5)-S(3)-C(6)		109(5)
C(5)-S(3)-Hg		112(5)
C(6)-S(3)-Hg		92(3)
C(7)-S(4)-C(8)		102(6)
C(7)-S(4)-Hg		96(3)
C(8)-S(4)-Hg		131(5)
S(1)-C(1)-C(2)	112.6(6)	106(6)
C(1)-C(2)-S(2)	117.8(6)	104(5)
S(2)-C(3)-C(4)	115.2(6)	106(5)
C(3)-C(4)-C(5)	110.2(7)	140(7)
C(4)-C(5)-S(3)	112.6(6)	116(8)
S(3)-C(6)-C(7)		116(5)
C(6)-C(7)-S(4)		128(5)
S(4)-C(8)-C(9)		100(7)
C(8)-C(9)-C(10)		143(7)
C(9)-C(10)-S(1)		107(6)

interesting features including the preferential formation of five-membered chelate rings as opposed to the more flexible six-membered rings. Thus, while constraining the S(1)-Hg-S(2) angle to 83° and imposing considerable strain, as shown by the lengthening of the S(2)-Hg bond relative to S(1)-Hg, this allows the ligand to adopt a

⁹ J. M. Stewart, University of Maryland, Technical Report TR-446, 1976.

¹⁰ S. L. Lawton, *Inorg. Chem.*, 1971, **10**, 328.

more extended conformation enabling a greater separation of the bulky HgCl_2 groups. It therefore seems likely that the structure of the molecule is a result of several effects. (i) A greater bond strength between

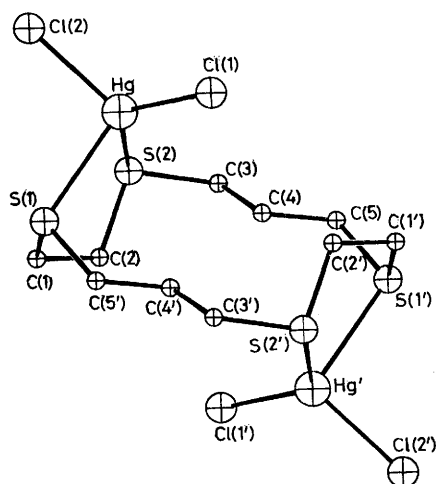


FIGURE 2 Molecular structure of complex (1)

Hg^{II} and chloride ion than between Hg^{II} and the sulphur in a thioether. This prevents all four sulphur atoms from co-ordinating to the same mercury ion, and therefore forces tetrahedral geometry on the metal. (ii) The large size of the HgCl_2 moieties which force the ligand to adopt a 'strung-out' conformation so as to keep these bulky groups well separated.

It is clear that the co-ordinating anions have a marked effect on the conformation that the ligand adopts, and this is emphasized by consideration of the structure of $[\text{HgL}(\text{OH}_2)][\text{ClO}_4]_2$ (Figure 3). In this case the four

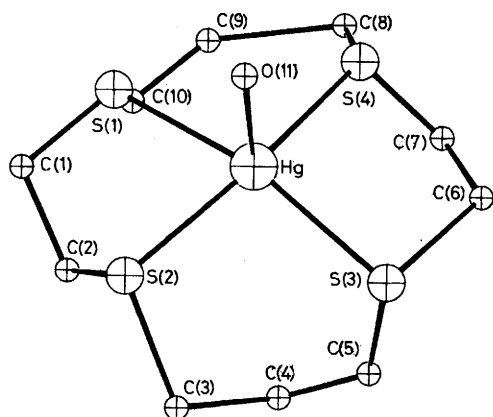


FIGURE 3 Molecular structure of the $[\text{HgL}(\text{OH}_2)]^{2+}$ cation

sulphur atoms occupy co-ordination sites on the same mercury atom and impose a tetragonal-pyramidal environment upon it. The sulphur atoms S(1), S(2), S(3), and S(4) occupy the basal plane of the pyramid and lie approximately in a plane ($\pm 0.15 \text{ \AA}$). The $\text{Hg}-\text{O}(11)$ vector is nearly perpendicular to this plane at an angle of 82° , while the mercury atom is 0.48 \AA above the plane.

The ligand itself is apparently sufficiently flexible to adopt either configuration without substantial conform-

ational strain. This is shown by the dihedral angles (Table 5). The values for C(1)-C(2) and C(6)-C(7)

TABLE 5

Dihedral angles ($^\circ$) with standard deviations in parentheses

About bond	Complex	
	(1)	(2)
C(1)-C(2)	60(1)	64(6)
C(3)-C(4)	160(1)	80(10)
C(4)-C(5)	151(2)	47(14)
C(6)-C(7)	60(1)	95(3)
C(8)-C(9)	160(1)	50(2)
C(9)-C(10)	151(2)	88(4)

correspond to those required for chelation with a twisted five-membered chelate ring (ideally 60°), although the large value for C(6)-C(7) in (2) is slightly unexpected. The remaining values are close to the ideal 180° in the extended chain of (1), and to the 60° values expected for a six-membered chelate ring in (2), although there are some minor deviations. In (2) these may be due to the size of Hg, preventing the two S-C bonds from being parallel, while in (1) they are possibly due to compression caused by packing forces.

Thus, when no competing anion is present it seems that L can become quadridentate although its limited 'hole size' prevents the large mercury(II) ion from sitting completely inside the ring. In this case, therefore, metal-ion size is another factor contributing to the conformation adopted by L. The fact that the mercury(II) ion is forced out of the basal plane probably dictates the remainder of the co-ordination in that the ion then has one open face which is occupied by a solvent water molecule. The vacant site in a *trans* position to this water molecule is then obstructed by the carbon backbone of the macrocycle which prevents co-ordination of a sixth ligand. This illustrates another important property of this type of ligand, namely the ability to confer unusual geometries upon metals due to overcrowding.

The crystal-packing diagrams show that the molecules in structure (1) (Figure 4) lie in chains with $\text{Cl} \cdots \text{Cl}$ as the dominant contacts between molecules in the chain. Between chains, $\text{H} \cdots \text{H}$ contacts are the major packing forces. In structure (2) (Figure 5) the isolated cations are surrounded by perchlorate anions, and the crystal forces must be mainly the electrostatic interactions between these.

It is interesting to note that the ligand conformation in (2) is the first found for L in which all the four sulphur atoms have their lone pairs of electrons on the same side of the plane defined by the sulphur atoms [Figure 6(a)]. This is in contrast to the crystal structures of $[\text{NiL}][\text{BF}_4]_2$ ¹ and $[\text{CuL}][\text{ClO}_4]_2$ ² where L adopts the more common centrosymmetric geometry [Figure 6(b)] with opposite pairs of sulphur atoms having their lone pairs on opposite sides of the plane. [Figure 6(a) and 6(b) are two of the five structures which are possible for complexes of L and the related ligand 1,4,8,11-tetra-azacyclotetradecane.¹¹] This can be rationalised since

¹¹ B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, 4, 1102.

geometry 6(b) with Hg would require either short Hg...C contacts and overcrowding of the macrocycle, or else a movement of the mercury atom into the plane

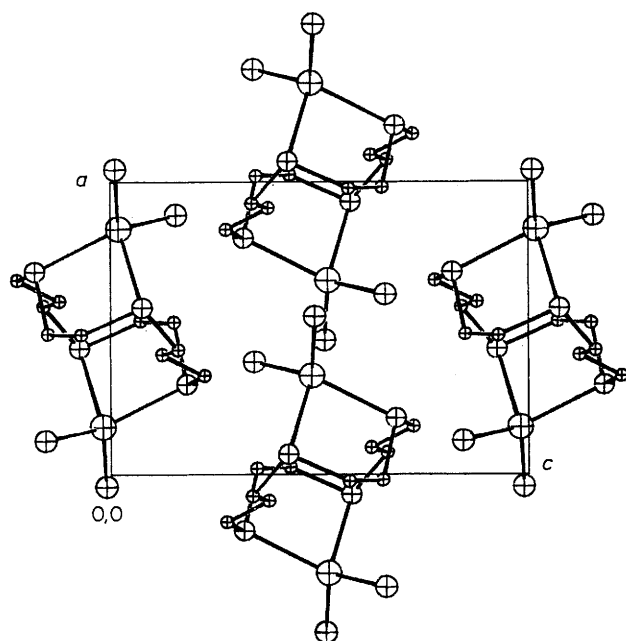


FIGURE 4 Crystal-packing diagram for structure (1) viewed along the *b* axis

of the four sulphur atoms which is disfavoured on grounds of metal-ion size. Geometry 6(a) has previously been postulated from ^{13}C n.m.r. work. Solutions of

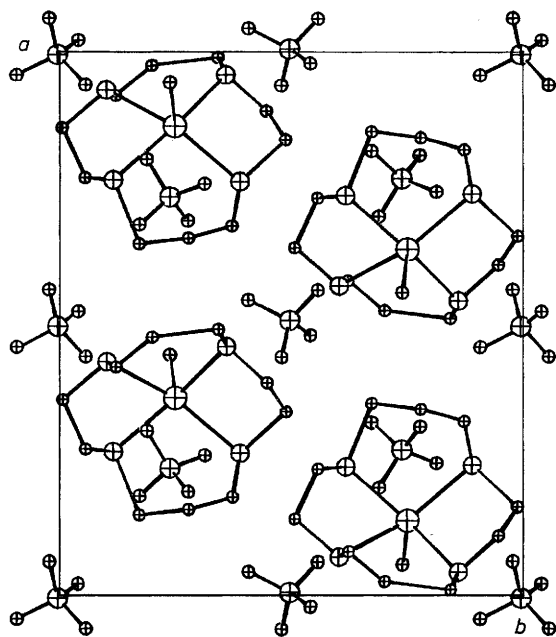


FIGURE 5 Crystal-packing diagram for structure (2) viewed along the *c* axis

$[\text{NiL}][\text{BF}_4]_2$ in nitromethane show two $[\text{NiL}]^{2+}$ species to be present,¹² one of which preferentially co-ordinates water to become paramagnetic. This observation is in

complete agreement with the structure of the $[\text{HgL}(\text{OH}_2)]^{2+}$ ion if we assume that the $[\text{NiL}]^{2+}$ ion with the same structure [6(a)] is the one which readily co-ordinates a water molecule.

Further evidence for the importance of macrocycle hole size in determining the geometry about a metal ion, and therefore its own conformation, is provided by the crystal structure of $[\text{HgL}'(\text{ClO}_4)_2]$ ¹³ ($\text{L}' = 1,5,9,13$ -tetrathiacyclohexadecane), a macrocycle similar to L except that it contains two extra carbon atoms in the ring thus expanding the ring hole size considerably. In this case the mercury atom is found to sit in the plane of the macrocycle and has co-ordinated perchlorate groups above and below this plane. The expansion of ring size has therefore allowed the mercury atom to adopt a more conventional 'octahedral' co-ordination geometry.

Complexes of L' with Cu^{II} are postulated to be directly analogous to those found in the present study.¹⁴

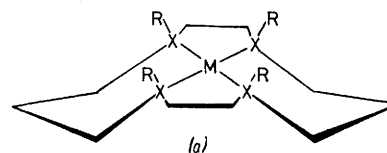
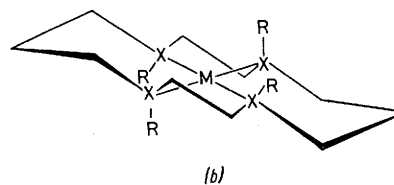


FIGURE 6 Two of the five possible conformations of $[\text{ML}]^{n+}$ ions (M = central metal, X = sulphur atom, and R = lone pair of electrons)

It is thought that, in the presence of co-ordinating ligands such as chloride ion, a bridged binuclear complex $[(\text{CuCl}_2)_2\text{L}']$ is produced with a structure identical to (1). If $[\text{ClO}_4]^-$ or $[\text{BF}_4]^-$ are the counter anions, they do not co-ordinate and a square-planar copper(II) complex is formed. Here we see that the factors important in determining the conformation of the macrocycle, namely metal-ion size and the presence of co-ordinating anions, are identical for Cu^{II} in complexes of L' as for complexes of Hg^{II} with L.

Finally, the structure of complex (2) indicates the possibility of using this type of quadridentate macrocycle as a complexing agent for the highly toxic methylmercury(II) cation. A similar structure may be formed

¹² N. Herron, O. W. Howarth, and P. Moore, *Inorg. Chim. Acta*, 1976, **20**, L43.

¹³ M. D. Glick, R. E. DeSimone, D. B. Rorabacher, D. Gavel, and T. Jones, *Abs. Amer. Chem. Soc. Meeting*, April 1975, INOR **104**.

¹⁴ B. V. Gorewit and W. K. Musker, *J. Co-ordination Chem.*, 1976, **5**, 67.

with this ion, but with the co-ordinated water replaced by the methyl group. This type of macrocyclic complex could therefore prove to be important in the medical treatment of methylmercury(II) and other heavy-metal poisoning, and ^{13}C n.m.r. investigations, using related macrocycles (*e.g.* *N*-donor quadridentates such as 1,4,8,11-tetra-azacyclotetradecane and its *N*-

alkyl derivatives), with Cd^{II} , Pb^{II} , Hg^{II} , and $[\text{HgMe}]^+$ are underway in this laboratory.

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