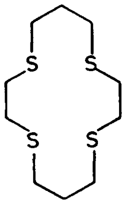
New Mode of Bonding for 1,4,8,11-Tetrathiacyclotetradecane (ttp): *X*-Ray Crystal Structure of $[(Cl_2Hg)_2(ttp)]$

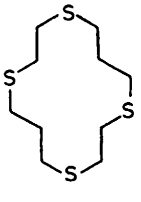
By NATHANIEL W. ALCOCK, NORMAN HERRON, and PETER MOORE*
(*Department of Molecular Sciences, University of Warwick, Coventry* CV4 7AL)

Summary *X*-Ray crystal structure determination reveals a new type of bonding for the ligand 1,4,8,11-tetrathiacyclotetradecane (ttp) in $[(Cl_2Hg)_2(ttp)]$.

RECENT crystal structure determinations have revealed different types of bonding for the potentially quadridentate macrocyclic ligand 1,4,8,11-tetrathiacyclotetradecane (ttp).[1-3] In $[Ni(ttp)](BF_4)_2$ and $[Cu(ttp)](ClO_4)_2$ the metal ions have square-planar[1] and tetragonal[2] geometries respectively, and the ligand ttp adopts the same *endo*-conformation (I) in each case. However, in the compound with niobium pentachloride,[3] $[(Cl_5Nb)_2(ttp)]$, ttp is turned 'inside-out' and adopts the *exo*-conformation (II), with two of the four sulphur atoms unco-ordinated and with two lone-pairs pointing towards the inside of the 14-membered macrocyclic ring, the other two sulphur atoms donating to separate $NbCl_5$ units in a unidentate-fashion. A folded quadridentate *endo*-conformation is also known for ttp in complexes of the type *cis*-$[M(ttp)X_2]Y$ (*e.g.*, M = Co^{III}, Rh^{III}; X = halide ion; Y = univalent counter-ion).[4] With larger metal ions, *endo*-conformations are unlikely because of the relatively small 'hole-size' in the centre of the macrocyclic ligand.



(I)



(II)

We report here a new type of *exo*-conformation for ttp in the binuclear complex with mercury(II) chloride, this being the first reported structure for a complex between ttp and a third row transition metal ion. Evidence for bonding between Hg^{II} and ttp was found in a recent solvent extraction study,[5] and crystals of $[(Cl_2Hg)_2(ttp)]$

were readily prepared by mixing 5 ml solutions of mercury(II) chloride (0·272 g) and ttp (0·134 g) in boiling nitromethane. The precipitate was collected, washed with chloroform and water, dried, and recrystallised from nitromethane. The crystals are monoclinic, space group $P2_1/n$, with $a = 8{\cdot}080(2)$, $b = 11{\cdot}389(2)$, $c = 10{\cdot}706(2)$ Å, $\beta = 92{\cdot}15(1)^\circ$, and $Z = 2$. 1675 reflections were collected with a Syntex $P2_1$ diffractometer, and the structure was solved by the heavy atom method and refined to an R value of 0·038 (absorption corrected, and atoms Hg, Cl, and S with anisotropic temperature factors). The structure analysis is summarised in the Figure, and shows that all four sulphur atoms are co-ordinated to mercury, ttp forming two five-membered chelate rings with an $HgCl_2$ unit. Each mercury atom is co-ordinated to two sulphur atoms and two chloride ions in an approximately tetrahedral arrangement.

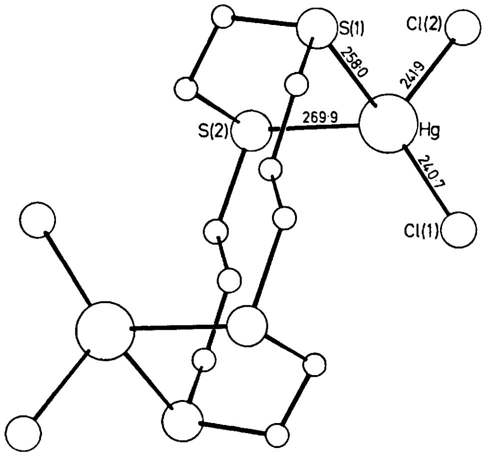


FIGURE. Molecular structure of $[(Cl_2Hg)_2(ttp)]$. Bond lengths are in pm. Bond angles are as follows: S(1)–Hg–Cl(1), 126·7; S(1)–Hg–Cl(2), 109·1; Cl(1)–Hg–Cl(2), 117·5; S(1)–Hg–S(2), 83·2; S(2)–Hg–Cl(1), 112·2; S(2)–Hg–Cl(2), 98·9°.

This is the second type of bonding found in complexes of ttp in which the ligand adopts an *exo*-conformation, and differs from all other conformations found so far in its co-ordination compounds.[1–4] Crystals of the various forms of the free ligand also have *exo*-conformations.[6] The versatility and remarkable flexibility of ttp contrasts with that observed in the analogous nitrogen-donor macrocyclic ligand 1,4,8,11-tetra-azacyclotetradecane (cyclam) where only *endo*-conformations have so far been found. This is presumably attributable in part to the larger size of the sulphur-donor atoms which might be expected to favour *exo*-conformations. The second lone-pair of electrons on each of the donor atoms of ttp would also favour *exo*-conformations more than in cyclam. A third major difference between these two ligands is the greater tendency for cyclam to form hydrogen-bonds with its basic nitrogen-donor atoms. In solution the importance of hydrogen-bonding, which enhances the macrocyclic effect for cyclam compared with thioethers has been stressed in a recent thermodynamic study.[7] Hydrogen-bonding is also an important factor in determining the conformations of unco-ordinated cyclam.[8]

The *exo*-conformation adopted by ttp in $[(Cl_2Hg)_2(ttp)]$ is also postulated for an analagous copper(II) complex of the more flexible 16-membered ring macrocyclic ligand 1,5,9,13-tetrathiacyclohexadecane (L) in $[(Cl_2Cu)_2L]$.[9] In the copper(II) complexes of L a switch from an *exo*- to an *endo*-conformation is indicated as the counterion is changed from one which co-ordinates (*e.g.* Cl^-) to one which does not co-ordinate (*e.g.* BF_4^-, ClO_4^-). It seems unlikely that a similar change of conformation will occur for mercury(II) complexes of ttp, because the tetragonal structures adopted by copper(II) will probably not be possible with the larger Hg^{II} ion. Further studies of mercury(II) complexes containing non-co-ordinating anions are under way to clarify this point.

Finally we point out that the solid-state structures found so far in metal complexes of ttp are not necessarily the only ones to be found in solutions of these complex ions. For example, although only one structure is evident from the crystal structure[1] and solution thermodynamic studies of $[Ni(ttp)](BF_4)_2$, a preliminary ^{13}C n.m.r. investigation of solutions of this complex in the non-co-ordinating solvent nitromethane reveals the presence of comparable amounts of at least two species in dynamic equilibrium.[10]

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