Encircling of Mercury(II) by a Macrocyclic Ligand: X-Ray Crystal Structure of 1,5,9,13-Tetrathiacyclohexadecanemercury(II) Perchlorate

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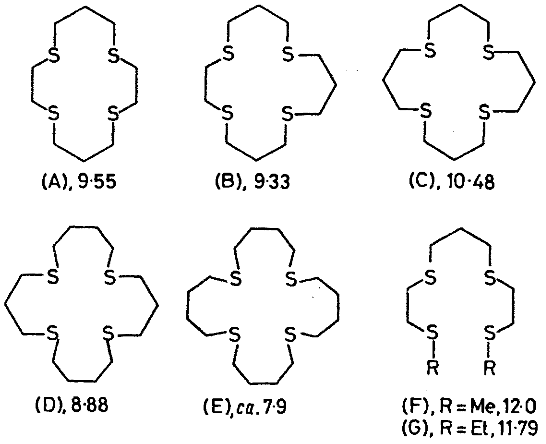
Summary The crystal structure of the most stable complex involving Hg^{II} co-ordinated to a macrocyclic tetrathia-ether (1,5,9,13-tetrathiacyclohexadecane) reveals that the Hg^{II} ion is situated almost in the centre of the four sulphur donor atoms, which themselves are twisted somewhat out of plane, with the inner co-ordination sphere being completed by two unequally bonded perchlorate ions situated along the z axis.



Logarithmic stability constants of Hg^{II}–tetrathia-ether complexes in $MeOH–H_2O$ (80:20) at 25 °C ($\mu = 0\cdot10$ M ClO_4^-).

RECENT thermodynamic studies on Hg^{II}–polyamine complexes by Kodama and Kimura[1] reveal that Hg^{II} exhibits no preference for macrocyclic ligands compared to their open-chain analogues. We have now measured the stability constants of complexes of Hg^{II} with a corresponding series of tetrathia-ether ligands (**A**—**G**) and, in fact, have found that the open-chain ligand complexes are at least one order of magnitude more stable than their macrocyclic counterparts.

This behaviour is in marked contrast to the 'macrocyclic effect' exhibited by lighter transition metal ions with the same series of ligands[2] and has raised the question as to whether Hg^{II} is actually circumscribed by the donor atoms in any of its complexes with flexible macrocyclic ligands. Although Moore and his co-workers have recently reported a structure of the Hg^{II} complex of the 14-membered macrocyclic tetrathiaether (**A**) in which the Hg^{II} ion is situated *ca.* 0·5 Å above the plane of the sulphur atoms,[3] no structural evidence appears to exist illustrating Hg^{II} centred within the cavity of a co-ordinated macrocycle.

We now report the crystal structure of the 1:1 complex of Hg^{II} with the sixteen-membered macrocyclic tetrathiaether, 1,5,9,13-tetrathiacyclohexadecane (**C**). This complex, which represents the most stable Hg^{II}-macrocyclic tetrathia-ether complex in solution, is found to involve a completely circumscribed, somewhat non-planar, ligand with the inner co-ordination sphere completed by two unequally bonded perchlorate ions along the z axis. The net structure resembles an elongated octahedral (*i.e.*, tetragonal) arrangement which is relatively rare for Hg^{II} compounds.[4]

Crystals of $[Hg^{II}–(\mathbf{C})](ClO_4)_2$, which were grown from methanol–water mixtures, are monoclinic, space group $P2_1$, $a = 13\cdot448(5)$, $b = 9\cdot538(4)$, $c = 8\cdot680(2)$ Å, $\beta = 95\cdot10(3)°$, $Z = 2$. The structure was solved by conventional heavy atom methods from data collected on a Syntex $P2_1$ diffractometer to $2\theta(Mo\text{-}K_\alpha) = 50°$. For the 1336 reflexions for which $I > 3\sigma(I)$, R is 0·039.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

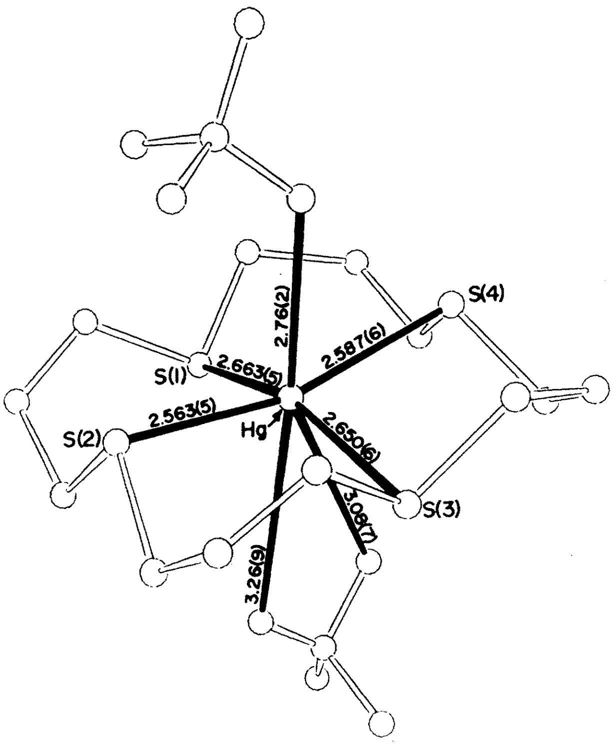

FIGURE. Molecular structure of $[Hg^{II}-(C)](ClO_4)_2$ showing co-ordinate bond distances.

The four sulphur atoms surround the mercury(II) ion at an average distance of 2·62 Å and are alternately displaced from their mean plane by ±0·42 Å while the Hg^{II} ion is almost exactly centred among these four donor atoms, being displaced only 0·04 Å from this mean plane. The four *cis* S–Hg–S angles are within the range 91·2—91·7° while the two *trans* S–Hg–S angles are 159·6 and 163·5°. The sum of the absolute deviations of these six angles from the square-planar values is 43°, in contrast to the sum of 126° from tetrahedral values.

The inner co-ordination sphere is completed by two unequally bonded perchlorate ions, one of these being attached in a monodentate fashion with a Hg–O bond distance of 2·76 Å while the second shows some disorder, appearing to be weakly bidentate (although perhaps representing a space-disordered monodentate ligand) with apparent proximal Hg–O distances of 3·08 and 3·26 Å. Thus the Hg^{II} ion appears to be seven-co-ordinate although the general morphology of the complex is that of an irregular tetragonally-elongated octahedron.

A comparison of this structure with that reported by Moore *et al.*[3] for $[Hg^{II}-(A)-(H_2O)](ClO_4)_2$ indicates that a 16-membered macrocyclic tetrathia-ether is required to provide a 'hole' large enough to accommodate the Hg^{II} ion. The relative lack of strain in the 16-membered ring complex is shown by the fact that the average deviation from the strain-free values of the torsion angles is only 6·7° as revealed by the present structural data. In view of this minimal strain, the increased stability of the complexes formed by Hg^{II} ion with the corresponding open-chain ligands (**F**) and (**G**) remains unexplained and suggests that previous explanations of the 'macrocyclic effect' are inadequate when applied to Hg^{II}.

We thank Dr. L. A. Ochrymowycz of the University of Wisconsin, Eau Claire, for providing the sample of (**C**) and the U.S. National Institutes of Health for support.

(*Received* 11*th September* 1978; *Com.* 987.)

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