The Structure of the Mercuric Chloride Adduct of *cis*-4-*p*-Chlorophenylthian 1-Oxide

By R. S. McEWEN*
(*Bell Telephone Laboratories, Murray Hill, New Jersey*)

and G. A. SIM
(*The Chemical Laboratory, University of Sussex*)

and C. R. JOHNSON
(*Department of Chemistry, Wayne State University, Detroit, Michigan*)

Two distinct aspects of sulphoxide chemistry are currently attracting attention: (i) the configurations of dialkyl sulphoxides,[1,2] and (ii) the co-ordination properties of dimethyl sulphoxide.[3,4] We report here results which are pertinent to both areas of enquiry.

The *cis*- and *trans*-isomers of 4-*p*-chlorophenylthian 1-oxid were distinguished by Johnson[2] on the basis of dipole moment measurements, which were interpreted by assuming that the thian ring adopts a chair conformation. The earlier and unexpected conclusion "that a six-membered-ring sulphoxide is more stable with the oxide in the axial position"[2] imparts particular importance to unequivocal structural determination in this series, and we therefore considered a crystallographic study desirable.

The isomer which was assigned the *cis*-configuration forms a 2 : 1 adduct with mercuric chloride, and crystals of the complex are monoclinic, space group $P2_1/c$, with four units of $(ClC_6H_4{\cdot}C_5H_9SO)_2,HgCl_2$ in a cell of dimensions $a = 15{\cdot}40$, $b = 9{\cdot}37$, $c = 22{\cdot}50$ Å, $\beta = 128°0'$. After Fourier and least-squares adjustment of the atomic co-ordinates, the value of R is 11·2% over 2274 independent reflexions. From the X-ray analysis we find that each thian ring of the two distinct 4-*p*-chlorophenylthian 1-oxide molecules in the complex assumes a chair conformation with the S–O group axial and the *p*-chlorophenyl substituent equatorial, thus confirming the previous assignment of *cis*-stereochemistry.

The thian sulphoxide molecules are co-ordinated with the Hg^{II} cation through the oxygen atoms (see the Figure). Dimethyl sulphoxide co-ordinates through oxygen in $[Fe(Me_2SO)_4Cl_2][FeCl_4]$,[3] but through sulphur in *trans*-$PdCl_2(Me_2SO)_2$[3] and $(C_{15}H_{13}O)Cl_2Ir(Me_2SO)_2$.[4] The average S–O bond length of 1·56 ± 0·03 Å in the $HgCl_2$ adduct is close to the distance of 1·54 Å in the dimethyl sulphoxide–Fe^{III} complex, whereas the S–O distances in the Pd^{II} and Ir^{III} complexes are 1·47 and 1·46 Å, in excellent agreement with the value in dimethyl sulphoxide, 1·47 Å.[5]

The complex has the centrosymmetric dimeric structure (I) with bridging Hg–O distances of 2·48 and 2·97 Å, and terminal Hg–O distance of 2·70 Å (standard deviation, 0·02 Å). The Hg–Cl distances are 2·284 and 2·295 Å (±0·01 Å), and the angle Cl–Hg–Cl is 164·0 ± 0·3°. The distorted octahedral environment of the mercury atom is completed, *trans* to the short Hg–O bond, by the chlorine atom of a *p*-chlorophenyl group of a neighbouring molecule, but the Hg–Cl distance of 3·88 Å is very long and the interaction between these atoms must be extremely tenuous.

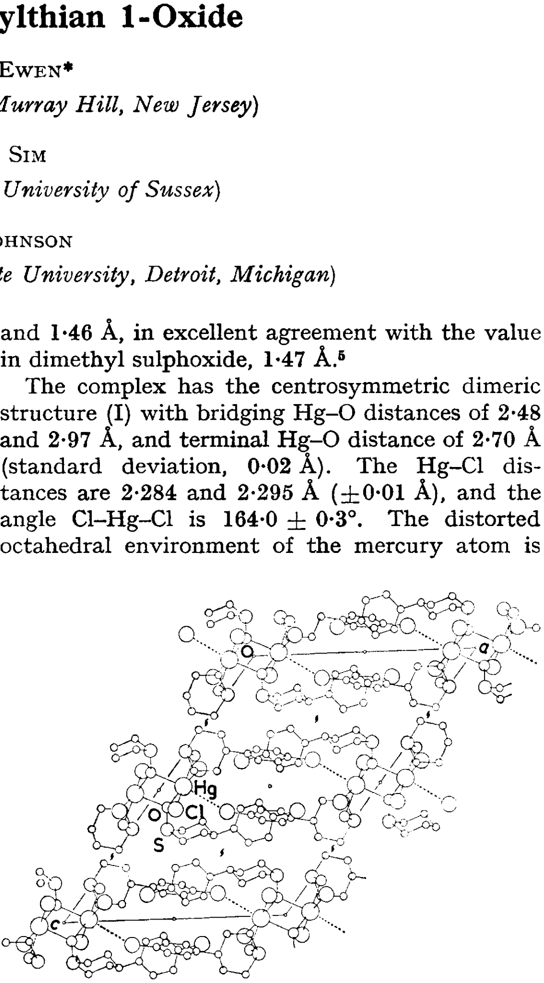
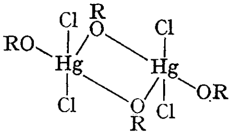
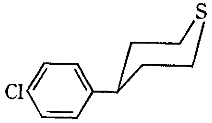


FIGURE. *The crystal structure, viewed in projection along the* b *axis.*



(I)

R=


In the 1 : 1 and 1 : 2 adducts of mercuric chloride and triphenylarsine oxide, the mercury atoms display distorted tetrahedral co-ordination with Cl–Hg–Cl angles of 147° and 145°, respectively,[6] and the Hg–Cl bonds are slightly longer, and the Hg–O bonds shorter, than the bonds in the $HgCl_2$–thian sulphoxide complex. In the mercuric chloride adducts of azoxyanisole and quinoline *N*-oxide, on the other hand, the mercury atoms are octahedrally co-ordinated, and less distorted $HgCl_2$ molecules can be recognized with Cl–Hg–Cl angles of 175° and 174°, respectively.[7] These results suggest that in donor ability the sulphoxide S–O group falls between the As-oxide and N-oxide groups.[8]

(*Received, July 4th,* 1967; *Com.* 693.)

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