Crystal and Molecular Structure of the 1 : 1 Adduct between Diphenyl Sulphoxide and Mercury(II) Chloride

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The structure of the title compound was solved from diffractometer data by Patterson and Fourier methods and refined by least-squares techniques to R 5·0% for 2967 observed reflections. Crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions: a = 8·354(8), b = 8·304(7), c = 11·115(8) Å, α = 108·2(1), β = 100·3(1), γ = 102·3(1)°, Z = 2. The co-ordination around mercury involves the diphenyl sulphoxide molecule *via* the oxygen atom at 2·58 Å, two close chlorine atoms at 2·291 and 2·289 Å, and two chlorine atoms of neighbouring molecules at 3·230 and 3·284 Å. A sixth position is occupied by a phenyl ring at 3·51 Å.

THE co-ordination properties of sulphoxides are currently attracting much attention, particularly for their donor abilities towards a variety of acceptors. An i.r. and Raman investigation of adducts between sulphoxides and mercury(II) chloride showed that the Cl–Hg–Cl stretching frequencies have relatively high values and yielded a spectral pattern consistent both with the presence of nearly linear $HgCl_2$ units and strong Hg–Cl bonds.[1] Because of the high dissociation of these adducts in ethanol solution it is not possible to establish the existence of strong bridging bonds.[2]

In the 1 : 1 adduct between diphenyl sulphoxide and mercury(II) chloride, $Ph_2SO,HgCl_2$, the metal–ligand bond (S–Hg or O–Hg) was at first suggested to be through sulphur,[3] although a more recent reinvestigation of the i.r. spectrum indicated that bonding occurs *via* oxygen.[2]

$Ph_2SO,HgCl_2$ has now been investigated by X-ray crystallographic methods in order to define unequivocally the type of ligand–metal bond, to establish the bonding geometry in the mercury environment and to obtain information valuable for correlating the spectroscopic data with the structure.

EXPERIMENTAL

Preparation.—The compound was obtained as previously described [2] and crystallized from ligroin as thick tablets. Unit-cell parameters were determined from the least-squares fit to the $(\theta,\chi,\phi)_{hkl}$ values of 19 reflections measured on a diffractometer.

Crystal Data.—$C_{12}H_{10}Cl_2HgOS$, M = 478·8, Triclinic, a = 8·354(8), b = 8·304(7), c = 11·115(8) Å, α = 108·2(1), β = 100·3(1), γ = 102·3(1)°, U = 690·7 Å^3, D_m = 2·4, Z = 2, D_c = 2·28, $F(000)$ = 440, Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 118·8 cm^{-1}. Space group $P\bar{1}$, from structural analysis.

Intensity Data Collection.—Since the crystals were unstable in air, the sample was enclosed in a Lindeman capillary; nevertheless it slowly decomposed in the X-ray beam as shown by the decrease in the intensity of the standard reflection measured systematically every 20 reflections.

Intensity data were collected on a Siemens single-crystal automated diffractometer, with Mo-K_α radiation up to θ = 29°, by use of the ω—2θ scan technique; of 3693 independent reflections, 2967 having $I > 2\sigma(I)$ were considered observed and were used in the analysis. No correction for absorption effects was made (μr = 1·1). After correction for Lorentz and polarization factors, the structure amplitudes were put on absolute scale first by Wilson's method and later by correlation of the observed and calculated values.

Structure Determination and Refinement.—The structure was solved by the heavy-atom method assuming the space group $P\bar{1}$ and the co-ordinates of mercury deduced from the three-dimensional Patterson map. The refinement was carried out down to R 5·0% by means of block-diagonal least-squares, with anisotropic thermal parameters, the quantity minimized being $\Sigma w(\Delta F)^2$ (weighting function $w = 1/(A + B|F_o|)^2$ with A = 0·450 and B = 0·057).

Final positional and thermal parameters, with their estimated standard deviations, are quoted in Table 1; observed and calculated structure factors are listed in Supplementary Publication No. SUP 20543 (16 pp., 1 microfiche).*

Atomic scattering factors were taken from ref. 4 for mercury(II) and from ref. 5 for chloride ion, sulphur, oxygen, and carbon.

All calculations were performed on the CDC 6600 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, with the programs of Immirzi.[6]

RESULTS AND DISCUSSION

The molecular structure of the adduct is depicted in Figure 1 which shows a clinographic projection; the most significant distances and angles are listed in Table 2. Two chlorine atoms are covalently bonded to mercury (Hg–Cl 2·291 and 2·289 Å) in a nearly linear arrangement (Cl–Hg–Cl 172·4°) and a third weaker bond to the metal involves the oxygen atom of the sulphoxide group (Hg–O 2·58 Å); this last interaction is almost perpendicular to the linear Cl–Hg–Cl system, a situation which is similar to that observed in the 1 : 1 adduct between dibromopyridine oxide and mercury(II) chloride.[7] Mercury is also loosely bonded to two chlorine atoms from two

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[1] P. Biscarini, L. Fusina, and G. D. Nivellini, *J.C.S. Dalton*, 1972, 1003.

[2] P. Biscarini, L. Fusina, and G. D. Nivellini, *J. Chem. Soc.* (*A*), 1971, 1128.

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[5] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[6] A. Immirzi, *Ricerca Sci.*, 1967, **37**, 743.

[7] F. Genet and J. C. Leguen, *Acta Cryst.*, 1969, **B25**, 2029.

Table 1

Fractional atomic co-ordinates ($\times 10^4$) and temperature factors ($\times 10^2$ Å^2) * with estimated standard deviations in parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg	−96(1)	2492(1)	137(1)	503(1)	480(1)	377(1)	219(1)	135(1)	176(1)
Cl(1)	2112(3)	1677(4)	1083(3)	575(12)	587(12)	452(10)	270(10)	73(9)	197(9)
Cl(2)	−2099(3)	3355(4)	−1003(3)	467(10)	554(11)	528(11)	197(9)	75(9)	226(9)
S	−3067(4)	1236(3)	2014(2)	628(12)	494(10)	345(8)	234(9)	163(8)	168(7)
O	−1541(11)	2585(9)	2010(7)	954(50)	474(30)	552(35)	299(32)	419(35)	274(27)
C(1)	−2271(12)	−466(11)	2351(8)	560(43)	358(32)	380(33)	139(30)	219(31)	116(26)
C(2)	−631(15)	−40(13)	3120(10)	668(54)	451(42)	506(44)	207(39)	183(40)	186(35)
C(3)	−45(18)	−1400(17)	3326(13)	820(71)	650(59)	654(60)	349(53)	259(54)	341(50)
C(4)	−1043(17)	−3116(15)	2789(13)	881(72)	572(53)	761(65)	382(51)	511(59)	339(48)
C(5)	−2653(17)	−3530(14)	2039(13)	892(73)	389(41)	743(65)	140(44)	497(59)	135(41)
C(6)	−3318(14)	−2180(14)	1780(12)	606(51)	465(44)	628(53)	122(38)	338(45)	91(38)
C(7)	−3504(11)	2213(11)	3558(8)	462(36)	433(35)	344(30)	206(29)	120(27)	187(26)
C(8)	−2352(13)	3758(13)	4468(10)	479(42)	497(42)	457(40)	130(34)	133(33)	140(33)
C(9)	−2700(14)	4517(15)	5668(10)	563(48)	579(49)	441(40)	219(40)	160(36)	151(36)
C(10)	−4171(13)	3712(14)	5931(10)	575(46)	596(48)	452(40)	312(40)	199(36)	228(36)
C(11)	−5310(13)	2182(15)	5010(11)	509(46)	648(56)	583(52)	221(42)	253(43)	229(45)
C(12)	−4990(13)	1389(14)	3786(10)	499(43)	537(46)	492(43)	179(36)	131(35)	201(36)

* The B_{ij} values refer to the formula: $\exp -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)$ in which $b_{11} = \frac{1}{4}a^{*2}B_{11}$, $b_{12} = \frac{1}{2}a^{*}b^{*}B_{12} \ldots$

adjacent molecules (Hg–Cl 3·284 and 3·230 Å), so the metal atom lies at the centre of a distorted tetragonal pyramid with the four chlorine atoms at the base and the oxygen atom at the apex. In addition there is a long contact directed towards the centre of the phenyl ring (perpendicular distance, Hg–Ph 3·51 Å; angle with the mean plane running through the four chlorine atoms, 86·0°) and *trans* with respect to the Hg–O bond. This particular situation can be explained as a consequence of packing requirements as it corresponds to the best packing of the 'tails' of the ligand (Figure 2) and it is possible also that there is a weak interaction between mercury and a π electron cloud of the phenyl group. This makes the environment of the metal octahedral; a similar situation has been recently found in $HgCl_2$,-PhHgCl [8] in which the octahedral co-ordination around mercury involves two phenyl groups at *ca.* 3·40 Å from the metal.

Table 2

Distances (Å) and angles (deg.); see Figure 1 for key

(*a*) Distances

a	2·291(4)	*i*	1·36(2)	*q*	1·41(2)
b	2·289(4)	*j*	1·43(2)	*r*	1·39(1)
c	2·58(1)	*k*	1·38(1)	*s*	3·230(6)
d	1·51(1)	*l*	1·79(1)	*t*	3·284(5)
e	1·80(1)	*m*	1·38(1)	*u*	3·51(1)
f	1·39(1)	*n*	1·40(2)	*v*	4·094(4)
g	1·39(2)	*o*	1·39(2)	*w*	4·242(4)
h	1·37(2)	*p*	1·38(1)		

(*b*) Angles

a,b	172·4(1)	*f,g*	118(1)	*o,p*	121(1)
a,c	93·3(2)	*g,h*	121(1)	*p,q*	120(1)
b,c	94·3(2)	*h,i*	120(1)	*q,r*	118(1)
c,d	128·1(4)	*i,j*	121(1)	*a,s*	85·8(1)
d,e	105·6(5)	*j,k*	117(1)	*a,t*	94·7(1)
d,l	104·7(4)	*l,m*	118·6(7)	*b,s*	96·0(1)
e,l	98·7(4)	*l,r*	118·6(7)	*b,t*	82·5(1)
e,f	119·8(8)	*m,r*	122·8(9)	*c,s*	85·2(2)
e,k	117·7(8)	*m,n*	118(1)	*c,t*	102·5(2)
f,k	122(1)	*n,o*	120(1)	*s,t*	172·3(7)
c,u	172(1)				

The sulphoxide group co-ordinates through the oxygen atom as we have previously suggested [2] and its configuration is pyramidal with sulphur out of the O,C(1),C(7) plane by 0·67 Å. The effect of co-ordination on the S–O bond in dimethyl sulphoxide complexes has been discussed by Cotton *et al.*,[9] who found that the S–O distances in the sulphur-bonded complexes are significantly shorter than those in the oxygen-bonded complexes

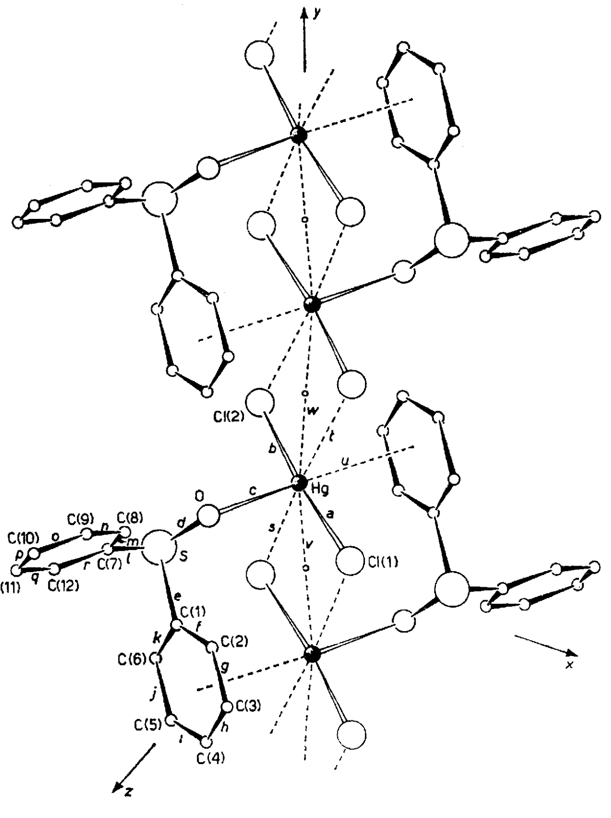

Figure 1 Clinographic projection of the structure

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[8] M. Colapietro and A. Domenicano, Abstracts 5th Associazione Italiana di Cristallografia Meeting, Bari, October 1971.

[9] M. J. Bennett, F. A. Cotton, and D. L. Weaver, *Nature*, 1966, **212**, 286.

and of the same order of magnitude as the distance in the ligand itself. The line corresponding to the S–O stretching mode in $Ph_2SO,HgCl_2$ is shifted to lower frequencies (*ca.* 30 cm^{-1}) with respect to that given by the free diphenyl sulphoxide.[2] This could be correlated with the difference in S–O distance which is slightly longer (1·51 Å) than that found in the free ligand (1·47 Å),* even if the difference is not strictly significant. The two S–C distances (1·79 and 1·80 Å) are typical of single-bond contacts. The two benzene rings are planar, with no unexpected geometry. Their orientation, with respect to the S–O bond, is defined by the rotation angles of +30·6 and −8·5° around C(1)–S and C(7)–S respectively; the corresponding angles in the free diphenyl sulphoxide are +16 and −6°.

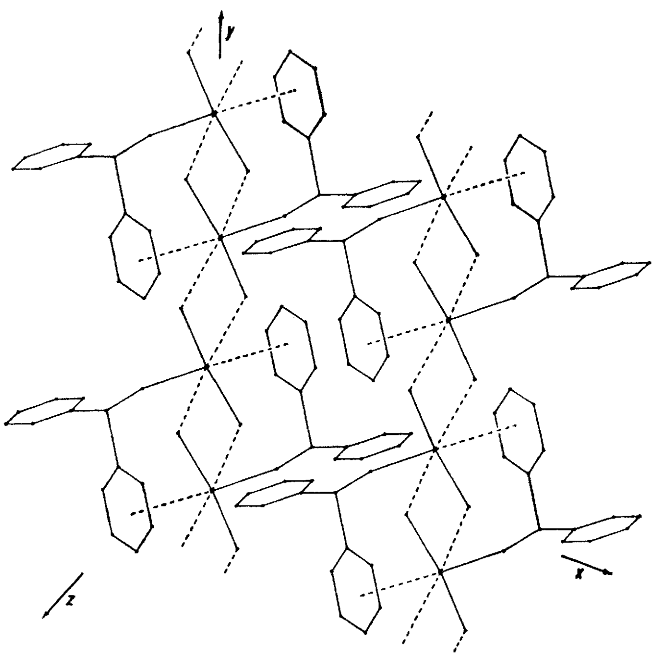

FIGURE 2 Clinographic view of two chains in $Ph_2SO,HgCl_2$

Each chlorine atom is shared by two adjacent mercury atoms, related by a centre of symmetry, so zig-zag chains running along [010] are formed. Along these chains the Hg · · · Hg distances are 4·094 and 4·242 Å. The most significant van der Waals interactions are listed in Table 3.

TABLE 3

Intermolecular contacts (Å)

Hg · · · C(3^{I})	3·70(1)	Cl(2) · · · C(4^{I})	3·56(2)
Hg · · · C(4^{I})	3·70(1)	Cl(2) · · · C(6^{III})	3·61(1)
Cl(1) · · · Cl(1^{I})	3·822(8)	Cl(2) · · · C(10^{IV})	3·67(1)
Cl(1) · · · C(1^{I})	3·67(1)	O · · · C(4^{V})	3·31(2)
Cl(1) · · · C(6^{I})	3·62(1)	O · · · C(5^{V})	3·53(2)
Cl(2) · · · Cl(2^{II})	3·750(8)	C(12) · · · Cl(1^{VI})	3·61(1)
Cl(2) · · · C(3^{I})	3·58(2)		

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $\bar{x}, \bar{y}, \bar{z}$
II $\bar{x}, 1 - y, \bar{z}$
III $\bar{x} - 1, \bar{y}, \bar{z}$
IV $x, y, z - 1$
V $x, y + 1, z$
VI $x - 1, y, z$

The presence of a nearly linear $HgCl_2$ unit, the weak bonds of bridging chlorine, and the values of the bond lengths Hg–Cl and Hg–O make the $Ph_2SO,HgCl_2$ structure similar to that of the 1 : 1 adduct between quinoline *N*-oxide and mercury(II) chloride,[11] but different from that of the 2 : 1 adduct between *cis*-4-*p*-chlorophenylthian 1-oxide and mercury(II) chloride,[12] where the mercury atom exhibits a more distorted $HgCl_2$ unit with Cl–Hg–Cl 164°, a shorter Hg–O bond (2·48 Å), and bridging oxygen bonds. The present data indicate that the S–O group in Ph_2SO has lower electron-donor abilities than in *cis*-4-*p*-chlorophenylthian 1-oxide [12] and are consistent with the i.r. and Raman results which show antisymmetric and symmetric Cl–Hg–Cl stretching vibrations at 362 and 308 cm^{-1} similar to those of free mercury(II) chloride.[1] In the present complex the sulphoxide group does not substitute the halogen, in contrast with the behaviour observed in adducts between sulphides and mercury(II) chloride, where one of the chlorine atoms in $HgCl_2$ is partially displaced (2·62, 2·70 Å) by the entering sulphide molecule with the consequence that the Cl–Hg–Cl group is no longer linear (Cl–Hg–Cl 110·0 and 106·1°).[13]

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* The structure of diphenyl sulphoxide given by Abrahams [10] was refined by us using least-squares methods on the data of ref. 10. This refinement improved *R* from 17·4 down to 13·4%; no further improvement was achieved, probably because the set of data was incomplete. The distances and angles used in the comparison are those calculated after this refinement.

[10] S. C. Abrahams, *Acta Cryst.*, 1957, **10**, 417.

[11] A. T. McPhail and G. A. Sim, *Chem. Comm.*, 1966, 21.

[12] R. S. McEwen, G. A. Sim, and C. R. Johnson, *Chem. Comm.*, 1967, 885.

[13] C. I. Brändén, *Arkiv. Kemi*, 1964, **22**, pp. 83, 495, 501.