Crystal Structure and Spectroscopic Properties of Mercury(II) Halide Complexes. Part II.[1] The Dimethyl Sulphoxide–Mercury(II) Chloride (2/3) Adduct

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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 8·5% for 1986 observed reflections. Crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions: $a = 6{\cdot}672(7)$, $b = 9{\cdot}286(8)$, $c = 8{\cdot}764(8)$ Å, $\alpha = 60{\cdot}0(1)$, $\beta = 95{\cdot}5(1)$, $\gamma = 90{\cdot}1(2)°$, $Z = 1$. In the asymmetric unit there are two crystallographically independent mercury atoms. One of them bonds covalently to two chlorine atoms at 2·306 Å, and four other chlorine atoms with long contacts (3·004 and 3·081 Å). The co-ordination around the other mercury involves two dimethyl sulphoxide molecules *via* the oxygen atom at 2·52 and 2·56 Å, two close chlorine atoms at 2·309 and 2·320 Å, and two chlorine atoms of neighbouring molecules at 3·302 and 3·372 Å. The sulphoxide groups are bonded to two mercury atoms so that a bridging centrosymmetric structure is reached. I.r. spectroscopic data are consistent with the presence of two types of nearly linear $HgCl_2$ moieties. The large frequency shift between ν(S–O) of the free sulphoxide and that of the adducts is ascribed to the bonding of the oxygen atom to two mercury atoms.

CRYSTAL structures of several adducts between mercury(II) chloride and ligands with donors such as oxygen atoms, showed the possibility of the mercury atom attaining a tetrahedral or a distorted octahedral co-ordination, according to the nature of the ligand. In the structure of $Ph_2SO,HgCl_2$ [1] one phenyl ring of the aromatic sulphoxide completes the octahedral co-ordination around the mercury atom. Thus, it appeared of interest to investigate an adduct between mercury(II) chloride and an aliphatic sulphoxide. The compound $2Me_2SO,3HgCl_2$ was chosen since the structure of adducts of mercury(II) chloride with this mole ratio has never been reported previously. In addition this study aims to assess the presence of O–Hg bonds as well as the existence in the crystal structure of two types of differently co-ordinated mercury atoms, as suggested by the spectral behaviour of this and analogous adducts of sulphoxides and mercury(II) chloride with mole ratios 2 : 3.[2]

EXPERIMENTAL

Preparation.—The compound was obtained as previously described [2a] and crystallized from absolute ethanol as thick tablets.

Crystal Data.—$2Me_2SO,3HgCl_2$, $M = 970{\cdot}8$, Triclinic, $a = 6{\cdot}672(7)$, $b = 9{\cdot}286(8)$, $c = 8{\cdot}764(8)$ Å, $\alpha = 60{\cdot}0(1)$, $\beta = 95{\cdot}5(1)$, $\gamma = 90{\cdot}1(2)°$, $U = 467{\cdot}5$ Å^3, $D_m = 3{\cdot}25$, $Z = 1$, $D_c = 3{\cdot}45$, $F(000) = 426$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 261·3 cm^{-1}. Space group $P\bar{1}$ (from structure determination).

Cell dimensions were determined from rotation and Weissenberg photographs (Cu-K_α radiation, $\bar{\lambda} = 1{\cdot}5418$ Å) and refined from θ, φ, and χ measurements on an on-line Siemens AED single-crystal diffractometer for 16 reflections in the range $9° < \theta < 22°$.

Data Collection.—A thick tablet, mean cross-section radius 0·13 mm, was sealed in a thin-walled glass capillary, owing to its instability to air, and mounted with its c axis coincident with the φ axis of the instrument. All 2451 independent reflections with $\theta < 29°$ were recorded; 465 reflections, having $I < 2\sigma(I)$, and three low-angle ($\theta < 3{\cdot}0°$) reflections were discarded; Zr-filtered Mo-K_α radiation and the ω—2θ scan technique was used. A reference reflection, monitored every twenty reflections, showed a 4—5% decrease in intensity during data collection. This is consistent with a slight decomposition of the sample rather than with fluctuations in the primary beam. A correction for this slight crystal decay was applied by means a computer program using the intensity of the standard reflection for an internal scaling of the data set. After corrections for Lorentz and polarization effects, the structure amplitudes were put on absolute scale first by Wilson's method and then by com-

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[1] Part I, P. Biscarini, L. Fusina, G. D. Nivellini, A. Mangia, and G. Pelizzi, *J.C.S. Dalton*, 1973, 159.

[2] P. Biscarini, L. Fusina, and G. D. Nivellini, (*a*) *J. Chem. Soc.* (*A*), 1971, 1128; (*b*) *J.C.S. Dalton*, 1972, 1003.

parison with the calculated values. No absorption corrections were made.

Structure Determination and Refinement.—The structure was solved by the heavy-atom technique; a Patterson map was valuable for locating the mercury atoms, arranged in a centrosymmetric array. Hence, the space group $P\bar{1}$ was assumed with one Hg situated on a centre of symmetry. The co-ordinates of the two independent mercury atoms were used to phase a Fourier synthesis in which all non-hydrogen atoms were recognized, although many extraneous peaks were present, in particular around the heavy atoms. Co-ordinates and thermal parameters were refined in a block-diagonal least-squares procedure minimizing the function $\Sigma w(\Delta F)^2$ and their final values are given in Table 1. At the end of the refinement R was 0·085. At this stage a difference Fourier map was computed, which showed some maxima of 6—7 eÅ^{-3} (on a relatively high background of 1—1·5 eÅ^{-3}) in regions near to the heavy atom positions at distances varying from 0·8 to 1·2 Å to the mercury atoms and a number of maxima of 1·0—1·5 eÅ^{-3} in the neighbourhood of the methyl carbon atoms. None of these last could however be unambiguously interpreted as hydrogen atoms. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21018 (12 pp., 1 microfiche).*

TABLE 1

Atomic co-ordinates and thermal parameters * (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(1)	0	0	0	1·95(3)	2·38(3)	3·24(3)	−0·82(2)	0·44(2)	−1·18(2)
Hg(2)	0·5291(1)	−0·0178(1)	0·2840(1)	2·17(2)	2·01(2)	2·94(2)	−0·47(1)	0·40(2)	−1·27(2)
Cl(1)	0·2374(5)	0·1990(5)	−0·0934(5)	2·3(1)	2·6(1)	3·4(1)	−1·2(1)	0·9(1)	−1·5(1)
Cl(2)	0·2837(6)	−0·2067(4)	0·3293(5)	2·7(1)	2·2(1)	3·2(1)	−0·8(1)	0·1(1)	−0·8(1)
Cl(3)	0·7942(6)	0·1568(5)	0·1865(5)	3·1(1)	2·5(1)	3·6(1)	−1·0(1)	1·1(1)	−1·7(1)
S	0·2586(6)	0·3290(4)	0·2537(5)	3·1(1)	1·9(1)	2·7(1)	0·3(1)	−0·2(1)	−1·2(1)
O	0·351(2)	0·153(1)	0·385(1)	3·5(5)	2·0(4)	2·5(4)	0·3(3)	0·0(3)	−1·3(3)
C(1)	0·453(3)	0·469(2)	0·228(2)	4·3(7)	2·2(5)	3·9(7)	−1·3(5)	1·6(6)	−1·4(5)
C(2)	0·099(3)	0·377(2)	0·375(3)	4·4(8)	3·6(8)	4·7(9)	0·1(7)	2·0(7)	−2·7(7)

* Anisotropic thermal parameters are expressed in the form: $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

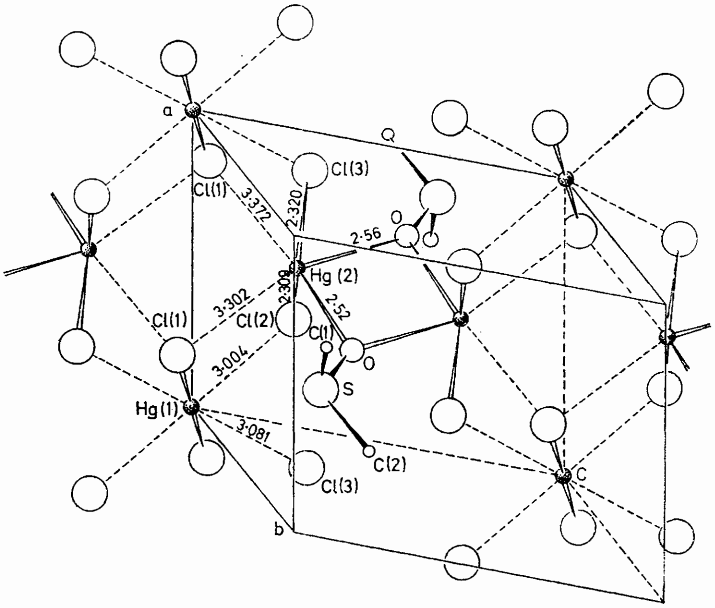

FIGURE 1 Clinographic projection of the structure with distances in the two mercury co-ordination polyhedra

The atomic scattering factors employed in the calculations were taken from ref. 3 for Hg^{2+} and from ref. 4 for other atoms. Calculations were performed on a CDC 6600 computer, with programs written by Immirzi.[5]

RESULTS AND DISCUSSION

The crystal structure (Figure 1) is composed of $HgCl_2$ molecules and dimeric $[Me_2SO,HgCl_2]_2$ groups with oxygen bridges. Table 2 lists the most significant distances and angles. Two types of Hg atoms, whose geometry differs significantly, are present: Hg(1), situated on a centre of symmetry, shows a two-co-ordinated linear structure [Hg(1)–Cl(1) 2·306 Å, Cl–Hg–Cl 180° for symmetry requirements]. Two pairs of chlorine atoms at 3·0 Å, belonging to adjacent dimeric groups, complete the co-ordination to oblate octahedral. This kind of co-ordination with four long and two short contacts, corresponding to covalent bonds, is typical of mercury(II)

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, **1973**, Index issue.

[3] D. T. Cromer and J. T. Waber, *Acta Cryst.*, **1965**, **18**, 104.

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

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

compounds.[6] Hg(2) Is in a general position and is covalently co-ordinated by two chlorine atoms (Hg–Cl 2·309, 2·320 Å, Cl–Hg–Cl 166·0°) and, more weakly, by two oxygen atoms (Hg–O 2·52 and 2·56 Å) of sulphoxide groups. These ligands are arranged in a highly distorted tetrahedral configuration with angles ranging from 75·3 to 166·0°. If two chlorine atoms from two adjacent $HgCl_2$ molecules are regarded as being part of the Hg(2) environment, the configuration may be described as a highly distorted octahedron. The values of these Hg $\cdots$ Cl distances (3·302 and 3·372 Å) are very close to the sum of the van der Waals radii (3·30 Å).[6]

The presence of two types of Hg atoms explains the two strong i.r. bands at **345** and **339** cm^{-1}, attributed to antisymmetric stretching ν(Cl–Hg–Cl) vibrations.[2b] These frequencies are only slightly lower than ν(Cl–Hg–Cl) of the free mercury(II) chloride (378—372 cm^{-1}) [7] and of $Ph_2SO,HgCl_2$ (362 cm^{-1}),[2b] and are consistent with both the nearly linear structure of the $HgCl_2$ groups and the mercury–chlorine distances: 2·26 in $HgCl_2$,[6] 2·29 in $Ph_2SO,HgCl_2$,[1] and 2·30—2·32 Å in $2Me_2SO,3HgCl_2$. The vibrations involving Hg–Cl bonds in mercury(II) chloride adducts seem to depend both on the mercury–chlorine distances, and on the distortion induced by the ligand on the linear $HgCl_2$ molecule. Their frequencies can be taken as an indication of the ligand–mercury interaction. The change from the linear co-ordination of $HgCl_2$ to the trigonal $HgCl_3^-$ or the tetrahedral $HgCl_4^{2-}$, lowers the stretching vibration ν(Hg–Cl) from 376 to 287 or 276 cm^{-1} respectively.[8] Adducts between $HgCl_2$ and ligands with donors such as sulphur or oxygen atoms, $Et_2S,2HgCl_2$,[9a] $C_4H_8S,HgCl_2$,[9b] $C_3H_6S_3,HgCl_2$,[10] and $Ph_3AsO,HgCl_2$,[9c] with highly distorted tetrahedral co-ordination around the mercury atom, exhibit ν(Cl–Hg–Cl) in the range 250—310 cm^{-1}.[7,11,12] Nearly linear $HgCl_2$ in adducts with ligands co-ordinated through oxygen atoms, *e.g.* dioxan [13] or diphenyl sulphoxide,[1] and the unsubstituted $HgCl_2$ molecule in $Et_2S,2HgCl_2$,[9a] exhibit the stretching mode at 348,[14] 362,[2b] and 341 cm^{-1} (ref. 7), respectively.

TABLE 2

Distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Distances			
Hg(1)–Cl(1)	2·306(6)	Hg(2)–O^{II}	2·56(1)
Hg(1) $\cdots$ Cl(2)	3·004(5)	Hg(2) $\cdots$ Cl(1)	3·302(6)
Hg(1) $\cdots$ Cl(3^{I})	3·081(6)	Hg(2) $\cdots$ Cl(1^{III})	3·372(7)
Hg(2)–Cl(2)	2·309(6)	O–S	1·54(1)
Hg(2)–Cl(3)	2·320(6)	S–C(1)	1·78(2)
Hg(2)–O	2·52(1)	S–C(2)	1·78(2)
(*b*) Angles			
Cl(1)–Hg(1) $\cdots$ Cl(2)	87·9(1)	O–Hg(2)–O^{II}	75·3(4)
Cl(1)–Hg(1) $\cdots$ Cl(3^{I})	92·1(1)	O–Hg(2) $\cdots$ Cl(1)	85·6(3)
Cl(2) $\cdots$ Hg(1) $\cdots$ Cl(3^{I})	90·4(1)	O–Hg(2) $\cdots$ Cl(1^{III})	172·1(3)
Cl(2)–Hg(2)–Cl(3)	166·0(2)	O^{II}–Hg(2) $\cdots$ Cl(1)	159·1(3)
Cl(2)–Hg(2)–O	97·6(3)	O^{II}–Hg(2) $\cdots$ Cl(1^{III})	111·6(3)
Cl(2)–Hg(2)–O^{II}	93·1(3)	Cl(1) $\cdots$ Hg(2) $\cdots$ Cl(1^{III})	88·1(1)
Cl(2)–Hg(2) $\cdots$ Cl(1)	81·0(1)	Hg(2)–O–S	121·9(6)
Cl(2)–Hg(2) $\cdots$ Cl(1^{III})	86·0(1)	Hg(2^{II})–O–S	130·2(7)
Cl(3)–Hg(2)–O	94·8(3)	Hg(2)–O–Hg(2^{II})	104·7(4)
Cl(3)–Hg(2)–O^{II}	96·2(3)	O–S–C(1)	106·5(8)
Cl(3)–Hg(2) $\cdots$ Cl(1)	93·7(1)	O–S–C(2)	105·5(9)
Cl(3)–Hg(2) $\cdots$ Cl(1^{III})	80·9(1)	C(1)–S–C(2)	99·9(10)

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

I $x - 1, y, z$ II $1 - x, \bar{y}, 1 - z$ III $1 - x, \bar{y}, \bar{z}$

The oxygen atom is involved in two acceptor–donor bonds to Hg(2) giving rise to a bridging situation like that found previously in the 2 : 1 adduct between *cis*-4-*p*-chlorophenylthian 1-oxide and mercury(II) chloride,[15] where the bridging Hg–O distances are 2·48 and 2·97 Å, and Cl–Hg–Cl 164·0°. Oxygen bridges are observed also in the 1 : 1 tetrahedral adduct between triphenylarsine oxide and mercury(II) chloride, where the Hg–O distance is 2·47 Å and the departure from linearity in the Cl–Hg–Cl angle is larger (147°).[9c]

The oxygen of a sulphoxide group connects two adjacent Hg(2) atoms, related by a centre of symmetry. As can be seen from the data of Table 3, which lists the bond distances of free and complexed dimethyl sulphoxides, co-ordination to metals *via* oxygen does not seem to influence appreciably the ligand dimensions. For comparison the S–O bond length in Me_2SO, 1·531 Å, has been used. This value was obtained at a temperature close to that used in the present work.

As expected, the configuration of the sulphoxide group is pyramidal. The distance from sulphur to the O,C(1),C(2) plane is 0·70 Å. The whole structure of the adduct is built up of layers of chlorine octahedra held

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[6] D. Grdenić, *Quart. Rev.*, 1965, **19**, 303.

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[9] C. I. Brändén, *Arkiv Kemi*, 1964, **22**, (*a*) p. 83; (*b*) p. 495; (*c*) p. 485.

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[14] Y. Mikawa, R. J. Jakobsen, and J. W. Brasch, *J. Chem. Phys.*, 1966, **45**, 4528.

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together by bridging dimethyl sulphoxide molecules (Figure 2).

TABLE 3

S–O and S–C distances (Å) in dimethyl sulphoxide groups in various compounds

Complex	S–O	S–C
Me_2SO (5 °C) [a]	1·531	1·775, 1·821
Me_2SO (−60 °C) [b]	1·471	1·801 (mean)
$[Ir(C_{15}H_{13}O)Cl_2(Me_2SO)_2]$ [c]	1·44, 1·46 *	1·80, 1·80, 1·82, 1·85
$PdCl_2(Me_2SO)_2$ [d]	1·47 *	1·79 (mean)
$[(Me_2SO)(NH_3)_5Ru^{II}](PF_6)_2$ [e]	1·527 *	1·834, 1·846
$FeCl_3(Me_2SO)_2$ [f]	1·541 †	1·795, 1·804
$CuCl_2(Me_2SO)_2$ [g]	1·531 †	1·765, 1·771
$Cl_2(Me_2SO)_2Me_2Sn^{IV}$ [h]	1·51, 1·61 †	1·75, 1·85, 1·78, 1·84
$La(NO_3)_3(Me_2SO)_4$ [i]	1·48, 1·53 †	1·75, 1·82, 1·77, 1·80
$2Me_2SO,3HgCl_2$ [j]	1·54 †	1·78, 1·78

* Co-ordinated through sulphur. † Co-ordinated through oxygen.

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It is of interest to compare the structures of $2Me_2SO,3HgCl_2$ and $Ph_2SO,HgCl_2$, especially to discuss their spectral behaviour. The oxygen atom of the diphenyl sulphoxide is bonded to only one mercury atom (Hg–O 2·58 Å) and weak bridging bonds to chlorine are also present.[1] The structural differences between the two adducts do not seem to affect ν(Hg–O) since $2Me_2SO,3HgCl_2$ shows only one intense i.r. band at 403 cm^{-1}, which occurs at a frequency slightly higher than that observed for the diphenyl sulphoxide adduct (398 cm^{-1}).[2b] However, the ν(S–O) stretching mode seems to be more sensitive to these differences. For the Me_2SO adduct it is shifted to lower frequencies (*ca.* 60 cm^{-1}) relative to that for the free sulphoxide, while the analogous shift for the diphenyl sulphoxide compound is only 30 cm^{-1}.[2a] These shifts cannot be rationalized on the basis of a lengthening of the S–O bond in adducts of methyl and phenyl sulphoxide, thus being 0·01 and 0·04 Å respectively.

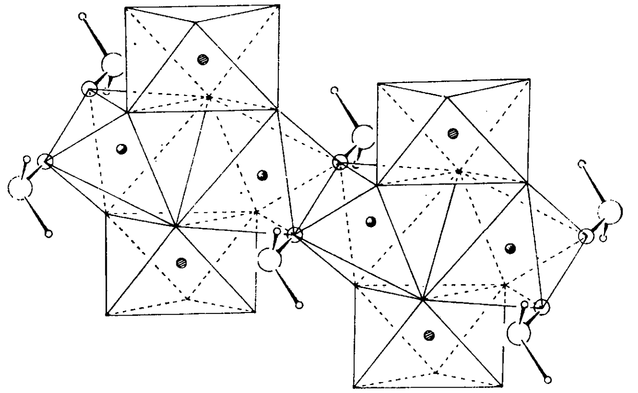

FIGURE 2 Diagrammatic view of co-ordination octahedra. Chlorine atoms at the vertices of the octahedra are not shown; Hg(1) is shown hatched, Hg(2) is partially black

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