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

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The structure of the title compound was solved from diffractometer data by the heavy-atom method and refined by least-squares techniques to R 0.109 for 1 134 observed reflections. Crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions: a = 20.710(10), b = 8.113(3), c = 8.090(4) Å, β = 94.74(5)°, and Z = 4. A distorted tetragonal-pyramidal co-ordination around the mercury atom involves the di-n-butyl sulphoxide molecule at the apex *via* the oxygen atom at 2.59 Å, two close chlorine atoms at 2.35 and 2.33 Å, and two chlorine atoms from neighbouring molecules at 3.13 and 3.16 Å at the base. The structural parameters of the title compound and of similar adducts have been correlated with their vibrational frequencies.

PREVIOUS crystal structure investigations evidenced that in the adducts between organic sulphoxides and mercury(II) chloride the oxygen atom of the ligand can be bonded to one metal atom, as in $Ph_2SO\cdot HgCl_2$ 1 : 1 adduct, or to two metal atoms, as in $Me_2SO\cdot HgCl_2$ 2 : 3 adduct, leading in this case to the formation of dimeric $(Me_2SO\cdot HgCl_2)_2$ units with oxygen bridges.[1] Moreover, in the former compound a phenyl ring occupies one of the six co-ordination positions around the metal atom (Hg–Ph 3.51 Å), so that a weak interaction between mercury and the π-electron cloud has been suggested. Since this interaction should affect the bonding geometry in the mercury environment and the vibrational frequencies of the Hg–O and Cl–Hg–Cl groups, it seemed interesting to compare the molecular parameters and the spectroscopic behaviour of $Ph_2SO\cdot HgCl_2$ with those of an adduct between an aliphatic sulphoxide and mercury(II) chloride having the same ligand–mercury mol ratio.

We have determined the crystal structure of the di-n-butyl sulphoxide–mercury(II) chloride (1/1) adduct, $Bu^n{}_2SO\cdot HgCl_2$, and investigated the effects on the structure of the possible interactions between the alkyl chains and the halogen atoms bonded to the mercury.[2,3]

EXPERIMENTAL

Preparation.—The compound was obtained by oxidation of $Bu^n{}_2S\cdot 2HgCl_2$ (8.8 mmol) with H_2O_2 (8.8 mmol) in 95% ethanol, as previously described.[4] By the slow evaporation of the solution, white crystals of di-n-butyl sulphoxide–mercury(II) chloride were obtained.

Crystal Data.—$C_8H_{18}Cl_2HgOS$, M = 433.79, Monoclinic, a = 20.710(10), b = 8.113(3), c = 8.090(4) Å; β = 94.74(5)°; U = 1 355(1) Å^3, D_m = 2.15 g cm^{-3}, Z = 4, D_c = 2.127 g cm^{-3}, $F(000)$ = 816, Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 118.8 cm^{-1}.

The space group $P2_1/c$ was deduced from systematic absences. The cell dimensions were refined by a least-squares procedure of 16 reflections measured by single-crystal diffractometry.

Data Collection.—Intensity data were collected on an on-line Siemens AED single-crystal diffractometer from a colourless, tabular shaped crystal (0.146 × 0.456 × 0.424 mm along a, b, and c respectively) aligned with its b axis (this being the extinction direction within the crystal) parallel to the ϕ axis of the instrument, by use of niobium-filtered Mo-K_α radiation at a takeoff angle of 4°. The moving counter–moving crystal scan technique was used, with a drive speed related to the number of counts on the peak. For intensities and background the 'five-points' technique was used.[5] A total of 3 287 reflections were measured in the range $5.0 < 2\theta < 48.0^\circ$; after systematic absences were deleted and equivalent reflections were averaged, the number of unique data was 2 134, of which 1 325 having $I \geqslant 2\sigma(I)$ were used in the structure determination. The (7 2 1) reflection was periodically measured every twenty reflections to monitor crystal and instrument stability. A scaling procedure was used to normalise the raw data based on the slight systematic decrease of the intensity of the reference reflection. Lorentz, polarisation, and absorption corrections were applied to the data which were scaled by a Wilson's plot.

Structure Determination and Refinement.—The heavy-atom method was used to solve the structure, with the Patterson map revealing the position of the mercury atom. A least-squares refinement of the Hg co-ordinates led to a conventional R index of 0.287. The remaining non-hydrogen atoms were located on a subsequent difference-Fourier synthesis, based upon the phases assigned from this refinement. Two cycles of full-matrix refinement with isotropic models for all atoms lowered R to 0.205, while with the introduction of anisotropic thermal parameters the index dropped to 0.132. At this stage six reflections (4 0 0, 6 0 0, 1 1 0, 3 1 0, 0 2 0, and 0 4 0) were omitted from the data set due to bad background statistics. A scan of the observed reflections indicated that several reflections at the limit of observability had large values of $F_o - F_c$, so it seemed reasonable to adopt for the unobserved reflections the new criterion of $F_o < 3\sigma F_o$. If these reflections are also excluded from the last cycle of refinement, the R index becomes 0.109 (1 134 reflections, 118 parameters).

The function minimised was $\Sigma w(F_o - F_c)^2$, where the weight for each reflection was unity at first, while in the

TABLE 1

Fractional atomic co-ordinates, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Hg	0.251 7(1)	0.226 4(2)	0.292 8(2)
Cl(1)	0.338 1(8)	0.276 3(19)	0.493 2(15)
Cl(2)	0.164 0(9)	0.242 0(17)	0.093 3(17)
S	0.251 0(8)	−0.173 4(13)	0.159 1(10)
O	0.253(1)	−0.092(4)	0.321(3)
C(1)	1.184(5)	—0.319(7)	0.166(6)
C(2)	0.122(4)	−0.219(7)	0.165(8)
C(3)	0.064(6)	−0.336(11)	0.160(9)
C(4)	−0.003(4)	−0.250(8)	0.172(10)
C(5)	0.313(4)	−0.333(7)	0.199(5)
C(6)	0.380(4)	−0.245(7)	0.198(8)
C(7)	0.434(6)	−0.381(8)	0.209(9)
C(8)	0.502(5)	−0.311(11)	0.210(11)

last cycles the weighting scheme $w = [\sigma^2(F_o) + 0.005F_o^2]^{-1}$ based on counting statistics was employed. The largest peak on a final ΔF map was of height 2.4 e Å^{-3} and was close to the mercury atom.

Neutral-atom scattering factors were taken from Cromer and Mann.[6] Final atomic co-ordinates are listed in Table 1. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22980 (8 pp.).*

All computations were performed, using the 'SHELX '76'[7] system of programs, on the Cyber 76 Computer of Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Casalecchio, Bologna), with the financial support from the University of Parma.

RESULTS AND DISCUSSION

Table 2 lists selected bond lengths and angles; the Figure shows the molecular structure and illustrates the atom-numbering scheme.

TABLE 2

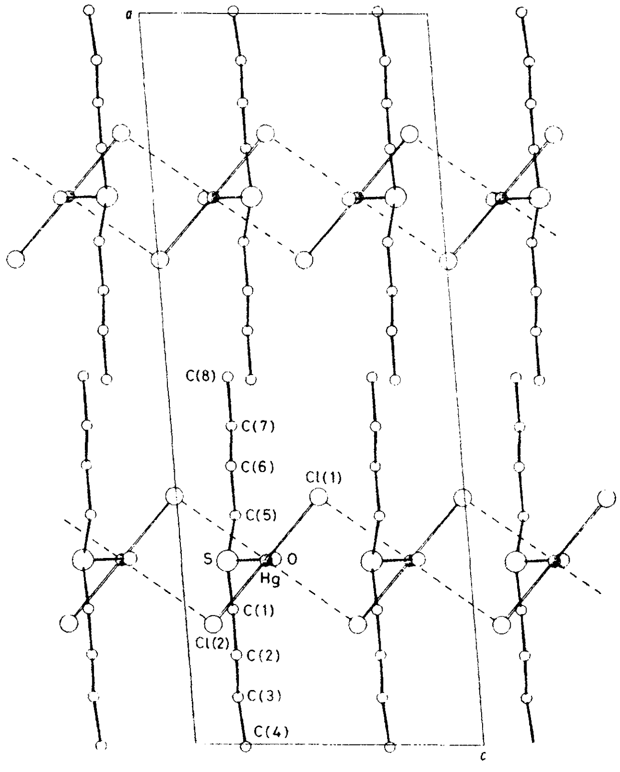
Selected distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Distances			
Hg–Cl(1)	2.35(1)	Hg–Cl(2^{II})	3.16(2)
Hg–Cl(2)	2.33(1)	S–O	1.47(3)
Hg–O	2.59(3)	S–C(1)	1.82(8)
Hg–Cl(1^{I})	3.13(1)	S–C(5)	1.83(7)
(*b*) Angles			
Cl(1)–Hg–Cl(2)	167.0(5)	Hg–O–S	112(1)
Cl(1)–Hg–O	96.1(7)	O–S–C(1)	104(2)
Cl(2)–Hg–O	96.9(7)	O–S–C(5)	101(2)
Cl(1^{I})–Hg–Cl(2^{II})	175.7(6)	C(1)–S–C(5)	93(3)

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

I $x, \frac{1}{2} - y, z - \frac{1}{2}$ II $x, \frac{1}{2} - y, \frac{1}{2} + z$

The mercury atom is strongly bonded to two chlorine atoms [Hg–Cl(1) 2.35(1), Hg–Cl(2) 2.33(1) Å] and its so-called 'characteristic' co-ordination number is two.[8] The oxygen atom from the $Bu^n{}_2SO$ group at 2.59(3) Å and two chlorine atoms belonging to adjacent molecules at 3.13(1) and 3.16(2) Å form weaker bonds to Hg, so that the whole co-ordination polyhedron appears as a distorted square pyramid with the four chlorine atoms at the base and the oxygen atom at the apex. The four chlorines are not strictly coplanar, but slightly tetrahedrally distorted, lying within 0.08 Å of the mean least-squares plane. The mercury atom is displaced by 0.19 Å below this plane. This effective co-ordination is quite unusual since generally the most common distorted octahedral co-ordination around the mercury atom is observed.[8,9] Moreover, when mercury is five-co-ordinated the preferred co-ordination polyhedron is a distorted trigonal bipyramid, with two atoms strongly bonded in axial positions and three weaker bonds in the equatorial plane, as found in di-μ-chloro-bis[chloro(1-methylcytosine-*O*,*N*^{3})mercury(II)],[10] or with three strong bonds forming a trigonal plane and two more atoms one above and one below this plane as found in dithiocyanato(triphenylarsine)mercury(II),[11] and in diacetato[tris(t-butyl)phosphine]mercury(II).[12] A distorted tetragonal pyramid is observed only in the crystal structure of mercury methyl sulphide, $Hg(SMe)_2$.[13] Also in the structure of $Ph_2SO{\cdot}HgCl_2$, which is very similar to that of our compound, a distorted octahedral co-ordination is attained if we consider the long contact, *trans* to the O–Hg bond, from the mercury towards the centre of a phenyl ring of a nearby molecule.[1a] If this structural situation reflected the formation of a weak interaction between mercury and the π-electron cloud of the phenyl group, a Hg–O bond weaker in this than in the aliphatic compound would be expected. However, even if we don't take into account this interaction, we will be forced to the same conclusion considering the lower basicity of Ph_2SO compared to $Bu^n{}_2SO$. Experimental data show that the values of ν(Hg–O) are only



Projection of the structure along [0 1 0]

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

TABLE 3

Distances and angles within the complexes and ligands, and associated i.r. (and Raman) frequencies

Compound	S–O/ Å	ν(S–O)[a]/ cm^{-1}	Hg–Cl/ Å	Cl–Hg–Cl/°	ν(Cl–Hg–Cl)[b]/cm^{-1}		Hg···Cl/ Å	Hg–O/ Å	ν(Hg–O)[b]/ cm^{-1}
					asym	sym			
$Bu^{n}_{2}SO$		1 034							
$Bu^{n}_{2}SO \cdot HgCl_2$	1.47(3)	975	2.33(1) 2.35(1)	167.0(5)	348	304 (298)	3.13(1) 3.16(2)	2.59(3)	403
Ph_2SO[c]	1.47	1 037							
$Ph_2SO \cdot HgCl_2$[c]	1.51(1)	1 008	2.291(4) 2.289(4)	172.4(1)	362	311 (308)	3.284(5) 3.230(6)	2.58(1)	398
Me_2SO[d]	1.53	1 057							
$2Me_2SO \cdot 3HgCl_2$[d]	1.54(1)	994	2.309(6) 2.320(6)	166.0(2)	345, 339	291 (288)	3.302(6) 3.372(7)	2.56(1) 2.52(1)	403
$HgCl_2$[e]			2.26	180	378, 372 (380)	329, 310 (313)			

[a] From ref. 4. [b] Ref. 14. [c] Ref. 1(*a*). [d] Ref. 1(*b*). [e] Ref. 8.

slightly different (403 and 398 cm^{-1}) and the Hg–O lengths are identical within experimental error [2.59(3) and 2.58(1) Å] for $Bu^{n}_{2}SO$ and Ph_2SO respectively.[1,14] These distances are longer than those in $[Hg(OSMe_2)_6][ClO_4]_2$ (2.317—2.376 Å),[9a] and than the terminal Hg–O bonds in $4Me_2SO \cdot Hg[ClO_4]_2$ (2.13—2.40 Å),[9b] and are similar to the bridging Hg–O distances in the latter compound (2.37—2.54 Å) and in $2Me_2SO \cdot 3HgCl_2$ (2.52—2.56 Å).

A comparison between $Ph_2SO \cdot HgCl_2$ and $2Me_2SO \cdot 3HgCl_2$ pointed out that the stretching frequency of the S–O bond is a more sensitive parameter than the Hg–O length and ν(Hg–O) to differences in the oxygen-mercury interaction (see Table 3).[1] In $Bu^{n}_{2}SO \cdot HgCl_2$, ν(S–O) is shifted to lower wavenumbers by 59 cm^{-1} and in $Ph_2SO \cdot HgCl_2$ by 29 cm^{-1} relative to the values in the free sulphoxides, thus suggesting a weaker S–O bond and stronger O–Hg interaction in the aliphatic adduct.[4] In the case of the aromatic compound this shift corresponds to a lengthening of the S–O distance by 0.04 Å upon complexation.[1a] The S–O distance in $Bu^{n}_{2}SO \cdot HgCl_2$ [1.47(3) Å] is shorter than in $Ph_2SO \cdot HgCl_2$ [1.51(1) Å] but it is not possible to compare this value with that of the free sulphoxide for which no experimental data are available.

Other parameters that can be taken as an indication of the strength of the ligand–metal interaction are the Cl–Hg–Cl stretching frequencies and the structural modifications induced in the $HgCl_2$ molecule. In fact the higher charge density on the mercury atom due to the attack of the sulphoxide group weakens the Hg–Cl bonds, thus producing a shift of ν(Cl–Hg–Cl) towards lower wavenumber and a lengthening of the Hg–Cl distance, generally accompanied by a departure from linearity. The behaviour of $Bu^{n}_{2}SO \cdot HgCl_2$ is consistent with this expectation; the Hg–Cl mean distance is 2.34 Å compared to the value of 2.26 Å in free $HgCl_2$, the i.r. and Raman Cl–Hg–Cl stretching frequencies are 348 and 304 cm^{-1} compared to 378—372 and 329—310 cm^{-1}, respectively, and Cl–Hg–Cl is 167.0(5)° instead of 180°.[8]

If we compare the structure of the $HgCl_2$ molecule in $Bu^{n}_{2}SO \cdot HgCl_2$ and in $Ph_2SO \cdot HgCl_2$, we will observe that in the former adduct the Hg–Cl distances are 0.05 Å longer, and that the deviation from linearity is greater [Cl–Hg–Cl 167.0(5)° compared to 172.4(1)°]. Moreover, these structural differences in the two compounds are consistent with the i.r. (and Raman) stretching frequencies of the Cl–Hg–Cl groups which are observed at lower wavenumbers in the aliphatic adduct: $\nu(Cl\text{–}Hg\text{–}Cl)_{asym}$ 348 compared to 362 cm^{-1}, $\nu(Cl\text{–}Hg\text{–}Cl)_{sym}$ 304 (Raman, 298) *versus* 311 (308) cm^{-1}. We can then conclude that the Hg–Cl bonds are weaker in the $Bu^{n}_{2}SO$ than in the Ph_2SO adduct as a consequence of the stronger interaction between the mercury and the aliphatic sulphoxide, in accordance with the above discussion on the ν(S–O) shifts. On the basis of these results it is not possible to confirm the existence in $Ph_2SO \cdot HgCl_2$ of an interaction between the mercury atom and the π-electron cloud of a nearby molecule, even if we cannot definitely exclude it. Since this interaction could be clearly demonstrated, only if the structural and spectroscopic data showed weaker Hg–Cl bonds in the Ph_2SO than in the $Bu^{n}_{2}SO$ adduct, we can only say that, if present, its effects are certainly weaker than those due to the higher basicity of the aliphatic compared to that of the aromatic sulphoxide.

The intra- or inter-molecular interactions between the chlorine atoms and the alkyl chains of the ligand can also contribute to the lengthening of the Hg–Cl bonds and to the departure from linearity of the $HgCl_2$ molecule by lowering the charge density on the halogen atoms. A mechanism involving an intramolecular C–H ··· Cl interaction was hypothesised to explain the thermal decomposition of the di-t-butyl sulphide–mercury(II) chloride (1/1) adduct and of a 1 : 1 mixture of Me_2SO and $HgCl_2$.[2,3] To support this hypothesis in the present compound there is a C(1) ··· Cl(2) ($x, y - 1, z$) intermolecular interaction of 3.63(6) Å, with the hydrogen atom, whose position has been theoretically calculated at 2.95 Å from Cl(2), giving a H ··· Cl distance slightly smaller than the sum of the van der Waals radii (3.0 Å).

The two butyl chains are planar within experimental error and nearly parallel to each other (dihedral angle 5°) and to the *a* axis as illustrated in the Figure. As usually found in similar cases, the butyl groups caused some difficulties related to the large thermal motion rather than to disordering which probably account for the relatively unsatisfactory *R* value.

There are no non-bonded approaches smaller than the sums of the corresponding van der Waals radii, the closest intermolecular distance being 3.3 Å between the oxygen atom and a carbon atom belonging to an adjacent Bu^n_2SO group.

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