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Structure of Dichloro(1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane-*S*,*S*′)mercury(II)–Mercury Dichloride

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Abstract. $[Hg(C_{12}H_{24}O_4S_2)Cl_2].HgCl_2$, $M_r = 839{\cdot}3$, triclinic, $P\bar{1}$, $a = 8{\cdot}410\,(2)$, $b = 11{\cdot}351\,(9)$, $c = 12{\cdot}347\,(6)$ Å, $\alpha = 92{\cdot}48\,(5)$, $\beta = 94{\cdot}52\,(3)$, $\gamma = 105{\cdot}66\,(5)°$, $V = 1128{\cdot}8\,(11)$ Å^3, $Z = 2$, $D_o = 2{\cdot}43$, $D_c = 2{\cdot}46$ Mg m^{-3}. $R = 0{\cdot}058$, $R_w = 0{\cdot}063$ for 2113 independent data. The crystal structure consists of one $HgCl_2$ unit coordinated to a bidentate macrocyclic ligand and a second $HgCl_2$ unit which does not interact with an organic ligand. Only the S atoms of the organic ligand interact with the $HgCl_2$ unit resulting in a distorted tetrahedral geometry.

Introduction. The complex was prepared by mixing an aqueous solution of the ligand with a large excess of HgO dissolved in concentrated HCl. Chemical analysis of the resulting crystals indicated that there was more than one Hg for each ligand. The crystallographic study was initiated to determine the chemical composition, stoichiometry and coordination of the material. A small, nearly spherical crystal with an average diameter of 0·17 mm was mounted on a Syntex $P\bar{1}$ autodiffractometer. The lattice parameters given in the *Abstract* were determined by a least-squares refinement of 13 2θ values. Intensity statistics and the fact that $Z = 2$ suggested that the space group was $P\bar{1}$. This choice of space group was confirmed by the subsequent solution of the structure. Intensity data were collected using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71073$ Å). The data were recorded with a scintillation counter. Five check reflections which were measured every 95 reflections showed no significant change. A total of 2113 independent data points were recorded for $2\theta \leq 40°$ ($\sin\theta/\lambda = 0{\cdot}482$ Å^{-1}). These data included 321 reflections which were considered unobserved as $I < 2\sigma_I$; σ_I was based on counting statistics. Absorption corrections for a spherical crystal were applied to the data ($\mu = 15{\cdot}6$ mm^{-1}); the correction factor ranged from 1·04 to 1·10.

The trial structure was obtained by the heavy-atom technique. Positions for the H atoms were calculated from geometrical considerations; the C–H bond length was assumed to be 1·04 Å. The structure was refined using *ORFLS* (Busing, Martin & Levy, 1962), a full-matrix least-squares procedure. Positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. No attempt was made to refine H parameters. The refinement was considered complete when all change/error ratios were less than 0·05. At that point the R value was 0·058 and the weighted R value using unit weights was 0·063. The goodness-of-fit term was 2·5 with $m = 2113$ and $n = 217$. All data were included in the refinement. The final positional parameters are listed in Table 1.* Scattering-factor

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* Contribution No. 247.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36199 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional coordinates* ($\times 10^4$, *for* Hg $\times 10^5$) *and equivalent isotropic thermal parameters* ($\times 10^3$, *for* Hg $\times 10^4$), *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	U_{eq} (Å^2)
Hg(2)	14248 (12)	16894 (10)	44303 (8)	535 (4)
Hg(1)	62191 (14)	36476 (9)	45179 (7)	552 (5)
Cl(3)	2375 (8)	1659 (6)	2723 (5)	63 (3)
Cl(4)	−32 (8)	1360 (7)	5953 (5)	62 (3)
Cl(1)	4663 (7)	2102 (6)	5619 (5)	53 (2)
Cl(2)	7683 (9)	5516 (6)	5656 (5)	65 (3)
S(1)	5683 (8)	4321 (6)	2636 (5)	48 (2)
C(2)	6592 (33)	3351 (19)	1837 (17)	54 (10)
C(3)	8238 (30)	3203 (20)	2359 (19)	52 (10)
S(4)	8152 (7)	2442 (6)	3606 (5)	49 (2)
C(5)	6749 (30)	939 (22)	3279 (18)	55 (10)
C(6)	7278 (32)	166 (22)	2448 (21)	63 (11)
O(7)	6995 (22)	595 (16)	1392 (13)	66 (8)
C(8)	7934 (43)	171 (30)	607 (25)	96 (17)
C(9)	7359 (43)	553 (29)	−474 (22)	87 (16)
O(10)	7896 (23)	1833 (18)	−538 (13)	70 (8)
C(11)	7266 (36)	2222 (33)	−1521 (20)	77 (14)
C(12)	8027 (35)	3506 (32)	−1636 (20)	74 (14)
O(13)	7355 (21)	4218 (18)	−889 (13)	68 (8)
C(14)	8199 (34)	5464 (27)	−921 (19)	65 (12)
C(15)	7475 (33)	6207 (25)	−171 (19)	67 (12)
O(16)	7739 (20)	5833 (15)	903 (12)	58 (7)
C(17)	7110 (31)	6480 (22)	1713 (21)	60 (11)
C(18)	7191 (31)	5819 (20)	2752 (18)	54 (10)

tables for C, O and S were taken from Cromer & Waber (1965); tables for H, Hg and Cl as well as the real and imaginary dispersion corrections for Hg, Cl and S were taken from *International Tables for X-ray Crystallography* (1968).

Discussion. The structure consists of a 1:1 $HgCl_2$–thiaether complex and a $HgCl_2$ molecule of crystallization. The conformation of the complex and its relationship to the $HgCl_2$ unit is illustrated in Fig. 1, which also shows the atom labels used.

Atom Hg(1), which is complexed by the bidentate thiaether, has a distorted tetrahedral coordination; the two S atoms of the ligand occupy two positions and two Cl atoms occupy the other two positions. The distortion is caused by the geometry of the S—C—C—S fragment of the ligand which does not allow the S—Hg—S angle to open to 109·5°. The S—Hg—S angle is nearly 25° less than the expected tetrahedral angle and while one Hg—S bond length is within the expected range for such bonds (see Table 2 of Grdenić, 1965) the other Hg—S bond is about 0·15 Å longer than expected. The bond lengths and angles involving the Hg atoms are given in Table 2.

The second Hg atom, Hg(2), has a nearly linear coordination with the Hg—Cl bond lengths (Table 2) being within the range of divalent Hg—Cl bond lengths reported in other studies. For example, Subramanian & Seff (1980) report Hg—Cl bond lengths of 2·284 (12) and 2·301 (14) Å in a redetermination of the structure of $HgCl_2$. Brotherton & White (1973), in a study of the $HgCl_2$–thiourea complex which contains a $HgCl_2$ unit, report a Hg—Cl bond distance of 2·32 (2) Å. In a neutron diffraction study of $HgCl_2.2KCl.H_2O$ Aurivillius & Stålhandske (1976) report a slightly longer Hg—Cl bond distance of 2·383 (1) Å. This longer bond distance can be explained by the environment of the Hg which, in addition to these Hg—Cl bonds, includes two intermediate Hg—Cl interatomic distances of 2·797 (1) Å and two much longer Hg—Cl distances of 3·251 (1) Å. The deviation of the Cl(3)—Hg(2)—Cl(4) angle from the expected 180° and the Hg(2)···Cl(1) contact of 2·900 (6) Å, which is 0·4 Å shorter than the sum of the van der Waals radii (Grdenić, 1965; Pauling, 1960) are evidence for an interaction of Cl(1) with Hg(2). The Hg(2)—Cl(1) vector bisects the obtuse Cl(3)—Hg(2)—Cl(4) angle.

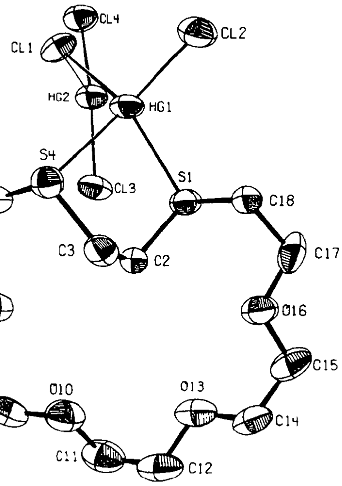

Fig. 1. An *ORTEP* (Johnson, 1965) drawing showing the relationship of the Hg–thiaether complex to the $HgCl_2$ unit as well as the atom labels.

Table 2. *Bond distances* (Å) *and angles* (°) *about the* Hg *atoms*

1	2	3	1–2	1–2–3
Cl(1)	Hg(1)	Cl(2)	2·427 (6)	110·6 (2)
S(1)	Hg(1)	Cl(1)	2·522 (6)	134·19 (19)
S(4)	Hg(1)	Cl(1)	2·672 (7)	101·3 (2)
Cl(2)	Hg(1)	S(1)	2·460 (6)	106·4 (2)
Cl(2)	Hg(1)	S(4)		115·7 (2)
S(1)	Hg(1)	S(4)		85·8 (2)
Hg(2)	Cl(1)	Hg(1)	2·900 (6)	98·1 (2)
Cl(3)	Hg(2)	Cl(4)	2·315 (7)	166·8 (2)
Cl(3)	Hg(2)	Cl(1)		95·2 (2)
Cl(4)	Hg(2)	Cl(1)	2·313 (7)	95·1 (2)
Hg(1)	S(1)	C(2)		100·7 (8)
Hg(1)	S(1)	C(18)		99·4 (8)
Hg(1)	S(4)	C(3)		95·7 (9)
Hg(1)	S(4)	C(5)		102·3 (9)

Table 3. *Bond distances* (Å) *and bond and torsion angles* (°) *in the organic ligand*

1	2	3	4	1–2	1–2–3	1–2–3–4
S(1)	C(2)	C(3)	S(4)	1·80 (3)	114·5 (15)	64·7 (19)
C(2)	C(3)	S(4)	C(5)	1·53 (4)	116·5 (17)	60 (2)
C(3)	S(4)	C(5)	C(6)	1·79 (2)	105·6 (10)	62 (2)
S(4)	C(5)	C(6)	O(7)	1·80 (2)	115·1 (17)	−76 (2)
C(5)	C(6)	O(7)	C(8)	1·49 (4)	109 (2)	161·7 (19)
C(6)	O(7)	C(8)	C(9)	1·44 (3)	112 (2)	173·2 (19)
O(7)	C(8)	C(9)	O(10)	1·44 (4)	106 (3)	70 (3)
C(8)	C(9)	O(10)	C(11)	1·51 (4)	112 (2)	−176 (3)
C(9)	O(10)	C(11)	C(12)	1·41 (4)	113 (2)	−172 (3)
O(10)	C(11)	C(12)	O(13)	1·42 (3)	111 (2)	−74 (3)
C(11)	C(12)	O(13)	C(14)	1·44 (5)	109 (2)	175 (2)
C(12)	O(13)	C(14)	C(15)	1·45 (4)	109 (2)	179 (2)
O(13)	C(14)	C(15)	O(16)	1·40 (3)	109 (2)	62 (2)
C(14)	C(15)	O(16)	C(17)	1·50 (4)	107 (2)	179·7 (17)
C(15)	O(16)	C(17)	C(18)	1·43 (3)	113 (2)	169·5 (17)
O(16)	C(17)	C(18)	S(1)	1·43 (3)	106 (2)	−70 (2)
C(17)	C(18)	S(1)	C(2)	1·52 (3)	111·2 (15)	78 (2)
C(18)	S(1)	C(2)	C(3)	1·82 (2)	105·0 (11)	61·9 (18)

While Hg(2) interacts with three Cl atoms it does not possess a regular trigonal coordination. Hg(2)—Cl(3) and Hg(2)—Cl(4) are clearly covalent bonds but the much longer Hg(2)···Cl(1) interaction is weak. Trigonal Hg compounds are not common, but a few exist. In a study of $(\mathrm{Me}_4\mathrm{N})\mathrm{HgBr}_3$, White (1963) reports a structure that contains two HgBr_3 units. The Hg—Br bond lengths in the two units vary from 2·48 to 2·56 Å and the Hg atoms deviate from the Br planes by 0·32 and 0·31 Å respectively. A fourth Br atom interacts much more weakly with each Hg; the Hg—Br distances are 2·92 and 2·94 Å respectively. This interaction causes the deviation from planarity in $(\mathrm{Me}_4\mathrm{N})\mathrm{HgBr}_3$, just as the weak Hg—Cl interaction causes the deviation from linearity in the title compound.

Bond lengths and angles and torsion angles of the organic ligand are listed in Table 3. The conformation of the macrocyclic ligand is very similar to that of the uncomplexed ligand (Dalley, Larson, Matheson, Smith, Izatt & Christensen, 1981). The average difference between corresponding torsion angles of the non-complexed and complexed molecules is about 5°. In both the non-complexed and the complexed molecules the S—C—C—S torsion angle is about 60° with the C—C bridge joining the S atoms directed into the interior of the macrocycle. The average bond lengths for C—C, C—O and C—S are 1·498 (31), 1·427 (15), and 1·804 (10) Å, respectively, which agree well with the results of studies of other thiaethers (Dalley *et al.*, 1981).

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