The Crystal Structure of Hg₃O₂Cl₂, a Compound with Three-Coordinated Mercury(II)

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The structure of $Hg_3O_2Cl_2$ has been determined by Patterson and Fourier methods and refined to $R=0.059$ on the basis of 669 counter intensities. The crystals are monoclinic, space group $P2_1/c$, with $a=6.3100$ (7), $b=6.8657$ (5), $c=6.8579$ (5) Å, $\beta=114.366$ (6)° and $Z=2$. The mercury atoms are of two types, one [Hg(1)] linearly two-coordinated and the other [Hg(2)] three-coordinated with the mercury atom and its ligands in nearly the same plane. The mercury–oxygen distances are for Hg(1), 2.07 (2) Å ($2\times$) and for Hg(2), 2.17 (2), 2.32 (2) and 2.33 (2) Å. The shortest mercury–chlorine distance is 2.706 (5) Å. The mercury and oxygen atoms form a three-dimensional network with the chloride ions in its cavities. The oxygen and chlorine atoms are approximately hexagonally close-packed.

Introduction

The crystal chemistry of mercury oxide halides $nHgO.HgX_2$ ($n=\frac{1}{2},2,3,4$) has been the subject of several investigations (Aurivillius, 1954, 1965). There seemed to be reasons for a re-investigation of the compound with $n=2$ (Aurivillius, 1954; Ščavničar, 1955), as the positions of the light atoms must be considered as uncertain and thus the mode of coordination of the mercury atoms not clearly revealed.

Work is also in progress on an additional compound with $n=2$ but with the formula $Hg_6O_4Cl_4$.

Experimental

Single crystals of $Hg_3O_2Cl_2$ were prepared by a method given by Arctowski (1895). An approximately 0.2 *M* aqueous solution of $HgCl_2$ was hydrolysed by the weak basic action of pieces of marble. After some weeks black crystals of irregular form had grown out from the surface of the marble. Larger quantities of the compound in microcrystalline form were synthesized by boiling a dilute aqueous solution of $HgCl_2$ with a deficit of mercury(II) oxide. After some minutes a black precipitate was obtained which gave Guinier–Hägg powder photographs identical with those obtained for the crystals synthesized according to Arctowski (1895). The sample thus prepared was analysed for mercury, chlorine and water, giving a result in good agreement with the formula $Hg_3O_2Cl_2$. Weissenberg photographs showed systematic absences 0*k*0 for $k=2n+1$ and *h*0*l* for $l=2n+1$, except for two weak *h*0*l* reflexions. These two reflexions probably result from a small satellite on the crystal or a crystal defect. In spite of several attempts no other suitable single crystal could be picked out. Therefore the same crystal was used in the diffractometer work. The space group was assumed to be $P2_1/c$.

The density was determined from the loss of weight in benzene. Accurate cell dimensions were determined from a least-squares analysis of the θ values of 39 reflexions measured on a single-crystal diffractometer.

Crystal data

$Hg_3O_2Cl_2$, F.W. 704.68.
Monoclinic, $P2_1/c$, $a=6.3100(7)$, $b=6.8657(5)$, $c=6.8579(5)$ Å,
$\beta=114.366(6)°$,
$V=270.64$ Å³, $Z=2$.
$D_m=8.53$, $D_x=8.59$ g cm⁻³. μ(Mo $K\alpha$) = 869 cm⁻¹.

Intensities were collected for the single crystal of approximate dimensions $0.10 \times 0.10 \times 0.14$ mm on a computer-controlled diffractometer (CAD-4) with Mo $K\alpha$ ($\lambda=0.71069$ Å) radiation and a graphite monochromator.

The intensities were recorded at a take-off angle of 5°. The ω–2θ scan technique was used with a scan interval of $(0.9+0.5 \tan \theta)°$. The background was measured for $\frac{1}{4}$ of the scan time at each end of the interval. A fast pre-scan was used to calculate the scan speed at which a minimum net count of 2000 was attained within a maximum measuring time of 4 min. To test the systematic absences all reflexions with $3°<\theta<30°$ were measured in two octants of reciprocal space. Of the 920 reflexions collected 70 were of type *h*0*l* with $l=2n+1$ or 0*k*0 with $k=2n+1$. Only four of these gave net intensities $I>3\sigma(I)$, where $\sigma(I)$ is based on counting statistics. Two of them, $\bar{1}03$ and $\bar{3}09$, gave $I>5\sigma(I)$ and were also observed in the Weissenberg photographs. These reflexions were rejected in the structure determination, assuming space group $P2_1/c$ as correct. The intensities of two standard reflexions, 004 and $\bar{3}31$, were measured at regular intervals to check the stability of the crystal and the electronics. No systematic variation was detected. All reflexions with $I<3\sigma(I)$ were rejected. The remaining 669 independent reflexions were corrected for Lorentz, polarization and absorption effects. Transmission factors, evaluated by the numerical method, varied from 0.007 to 0.039.

Structure determination and refinement

The structure was solved by the heavy-atom method. From a vector map the six mercury atoms were found to occupy one fourfold and one twofold point position. A least-squares refinement of these positions, followed by difference syntheses, revealed the positions of the chlorine and oxygen atoms. A full-matrix least-squares calculation was then performed refining the atomic coordinates, isotropic temperature factors, and a scale factor. The resulting R was 0·10, where $R = \sum[|F_o| - |F_c|]/\sum|F_o|$. The function $\sum w_i(|F_o| - |F_c|)^2$ was minimized with the weights w_i calculated from the expression $w_i^{-1} = \sigma^2(F_o^2)/4F_o^2 + aF_o^2 + b$. When anisotropic temperature factors were used for all atoms R fell to 0·07. A final refinement, including an isotropic extinction coefficient, converged to $R = 0.059$, $R_w = 0.073$ and $g = 0.26(3) \times 10^4$ where $R_w = [\sum w_i(|F_o| - |F_c|)^2/\sum w_i|F_o|^2]^{1/2}$ and g is the extinction parameter.

In the last cycle all parameter shifts were less than 0·05 of the estimated standard deviations. The parameters a and b were 0·002 and 2·0, respectively. $S = [\sum w_i(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where m and n are the number of observations and parameters varied, was 1·43. A final difference map was featureless.

The scattering factors were those of Doyle & Turner (1968), for neutral mercury, chlorine and oxygen. An anomalous dispersion correction for mercury (Cromer & Liberman, 1970) was also included.

The final positional parameters are given in Table 1 and the thermal parameters in Table 2. Observed and calculated structure amplitudes are presented in Table 3. In Table 4 selected interatomic distances and angles are given.

Table 1. *Fractional coordinates obtained in the final least-squares refinement*

Estimated standard deviations are given in parentheses.

$P2_1/c$; 2 Hg(1) in 2(a); 4 Hg(2), 4 Cl, 4 O in 4(e).

	x	y	z
Hg(1)	0	0	0
Hg(2)	0·4116 (1)	0·3635 (1)	0·2633 (1)
Cl	0·7891 (9)	0·1246 (8)	0·5546 (8)
O	0·3261 (25)	0·1084 (20)	0·0600 (22)

All computations were made on the UNIVAC 1108 computer in Lund. A short account of the program system used is given by Stålhandske (1974).

Description and discussion of the structure

Šćavničar (1955) has described the structure of this compound as being built up of Hg^{2+} ions and polymeric ions $(OHgCl)_n^{n-}$, the study being based on rather few intensities. The present investigation gives a result that differs from the earlier one.

The two unique mercury atoms Hg(1) and Hg(2) of the unit cell have different point symmetries, viz. Hg(1) $\bar{1}$ and Hg(2) 1. The atom Hg(1) is linearly coordinated to two oxygen atoms at 2·07(2) Å, whereas Hg(2) has a (1 + 2) coordination; to an oxygen atom at 2·17(2) Å and to two oxygen atoms at 2·32(2) and 2·33(2) Å. The linear coordination of Hg(1) is normal for a covalent sp bond of mercury, e.g. orthorhombic mercury(II) oxide (Aurivillius, 1956). The Hg(2)–O
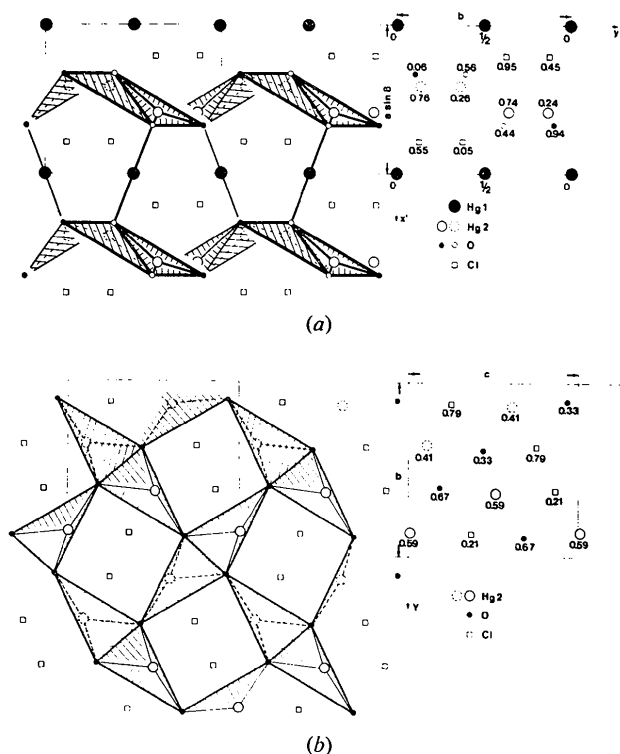

(a)

(b)

Fig. 1. (a) Projection of the structure along [001]. The oxygen atoms form the basal corners of the $Hg(2)O_3$ polyhedra, linked by Hg(1) atoms to form a three-dimensional network. The chloride ions are situated in cavities. (b) Projection of the structure on the yz plane. Hg(1) atoms are omitted.

Table 2. *Vibrational parameters for the atoms*

The anisotropic thermal parameters are based on the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The β_{ij} values are multiplied by 10^5 and the r.m.s. components (Å) by 10^3.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Hg(1)	76 (3)	65 (2)	85 (3)	−12 (2)	31 (2)	0 (1)	106 (3)	128 (2)	134 (2)
Hg(2)	162 (3)	55 (2)	71 (2)	−3 (1)	29 (2)	−19 (1)	97 (2)	133 (2)	175 (2)
Cl	158 (14)	83 (10)	97 (11)	−5 (9)	50 (10)	0 (8)	138 (8)	141 (9)	165 (7)
O	137 (37)	36 (23)	112 (35)	0 (24)	75 (30)	13 (21)	87 (31)	126 (23)	162 (21)

distances are in the same range as in $Hg(OHg)_4Br_2$, 2·25(5) Å (Aurivillius, 1968) for a tetrahedral mercury to oxygen coordination. The next nearest neighbour

Table 3. *Observed and calculated structure factor amplitudes*

The columns are l, $|F_o|$ and $|F_c|$.

[Dense multi-column table of structure factor amplitudes — numerical data not legibly reproducible.]

Table 4. *Selected interatomic distances (Å) and angles (°) with standard deviations in parentheses*

Within the mercury–oxygen network

Distances		Angles	
Hg(1)–2O	2·067 (14)	O–Hg(1)–O	180
Hg(2)– O	2·168 (14)	O–Hg(2)–O	81·7 (5)
Hg(2)– O	2·323 (14)	O–Hg(2)–O	123·1 (4)
Hg(2)– O	2·325 (14)	O–Hg(2)–O	149·1 (2)
Hg——Hg	≥3·516 (1)	Hg(1)–O–Hg(2)	106·3 (6)
O——O	≥3·039 (28)	Hg(1)–O–Hg(2)	112·6 (6)
		Hg(1)–O–Hg(2)	115·4 (6)
		Hg(2)–O–Hg(2)	98·3 (5)
		Hg(2)–O–Hg(2)	108·4 (6)
		Hg(2)–O–Hg(2)	114·3 (6)

To atoms outside the network

Distances	
Hg(1)–2Cl	2·918 (5)
Hg(1)–2Cl	2·996 (5)
Hg(2)– Cl	2·706 (5)
Hg(2)– Cl	2·909 (5)
Hg(2)– Cl	3·259 (5)
O –Cl	≥3·421 (15)
Cl—Cl	≥3·503 (10)

to Hg(2) is a chlorine atom at 2·706(5) Å, which is appreciably longer than the 2·50 Å corresponding to sp^3 hybridized mercury reported for the isolated $HgCl_4^{2-}$ anion in bis(perloline)-tetrachloromercurate(II) dihydrate (Ferguson, Jeffreys & Sim, 1966). In the present structure the bonding of the chlorine atom nearest to Hg(2) is probably predominantly of ionic character. The conclusion was thus drawn that the atoms Hg(2) are three-coordinated.

Three-coordinated mercury seems to be rare in the solid state. It has, however, been found in $(CH_3)_4N$. $HgBr_3$ (White, 1963), $(CH_3)_3SHgI_3$ (Fenn, Oldham & Phillips, 1963) and $HgTiO_3$ (Sleight & Prewitt, 1973). In the oxide the mercury–oxygen distance is 2·20(4) Å (3 ×).

In the present compound each Hg(2) and its closest neighbours, the three oxygen atoms, are situated in nearly the same plane. The deviation of the mercury atom from the plane through the oxygen atoms is 0·29 Å. The bonding angles O–Hg–O of 82°, 123° and 149° (Table 4) deviate considerably from the ideal value 120° for sp^2 hybridization. If this hybridization exists, the distortion may be caused by ionic forces from the chloride ions.

The oxygen atoms have a tetrahedral $(1+1+2)$ coordination. It is known that the sulphur atoms in the hexagonal modification of HgS are two-coordinated (S–2Hg 2·378(2) Å) and in the cubic modification tetrahedrally four-coordinated (S–4Hg 2·534 Å) (Aurivillius 1972, 1964). The bonding of the oxygen atoms in $Hg_3O_2Cl_2$ may be intermediate between those of the sulphur atoms in the two mercury(II) sulphide modifications.

This structure can formally be described in terms of flat HgO_3 pyramids [Fig. 1(a),(b)] with the mercury atoms at their apices. Every oxygen atom is coordinated
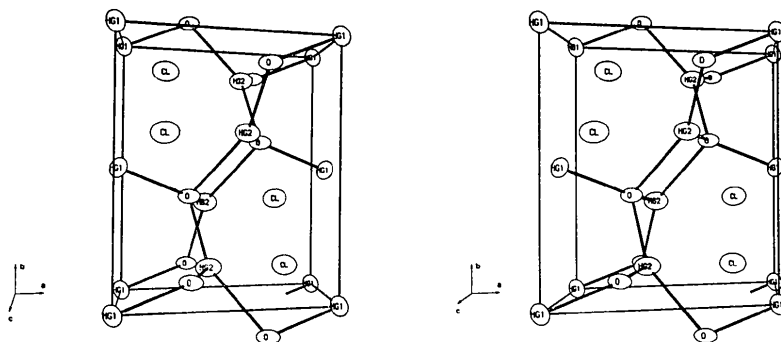
Fig. 2. A stereo view of the structure.

to three mercury atoms Hg(2) at 2·17, 2·32 and 2·33 Å. Each polyhedron thus shares its basal corners with three polyhedra and its basal edges with two polyhedra, building up infinite layers parallel to (100). Every oxygen atom is also bonded to an atom Hg(1) at 2·07 Å, completing the deformed tetrahedral coordination of oxygen. Thus every basal corner of the polyhedra in parallel layers is linked by the atoms Hg(1) to form a three-dimensional network of formula $(Hg_3O_2)_n^{2n+}$.

The mercury–chlorine distances are $\geq 2·706(5)$ Å (Table 4), indicating mainly ionic bonding. The chloride ions are situated in cavities in the three-dimensional network. A stereo view of the structure is given in Fig. 2.

From an *entirely geometrical* point of view the polyhedra around Hg(1) and Hg(2) can be described as follows:

Each Hg(1) atom is surrounded by two oxygen atoms at short distances (2·07 Å) and four chlorine atoms more distant (2·92–3·00 Å), the atoms forming a distorted octahedron with the chlorine atoms defining an equatorial plane. Hg(2) atoms are each surrounded by three oxygen atoms (2·17–2·33 Å) and a chlorine atom (2·71 Å), the atoms forming a deformed tetrahedron with the mercury atom drawn very near to one face. If the next nearest chlorine atom at 2·91 Å is also considered, the polyhedron is a deformed trigonal bipyramid.

The arrangement of the oxygen and chlorine atoms approximates hexagonal close-packing.

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