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## The Crystal Structure of Oxy-mercuric-mercurous Chloride, $2\text{HgO} \cdot \text{Hg}_2\text{Cl}_2$

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The crystal structure of the mercury oxychloride, known under the formula  $\text{HgO} \cdot \text{HgCl}$  and identical with the mineral terlinguaite, has been determined. It follows from the structure that  $2\text{HgO} \cdot \text{Hg}_2\text{Cl}_2$  is the correct formula.

The crystals are monoclinic holosymmetric with the space group  $C_{2h}^6-C2/c$ . The unit cell, of dimensions

$$a = 19.53, \quad b = 5.92, \quad c = 9.48 \text{ \AA}, \quad \beta = 144^\circ,$$

contains 4 formula units  $2\text{HgO} \cdot \text{Hg}_2\text{Cl}_2$ . The atomic co-ordinates have been obtained with the help of vector and electron-density projections along [001] and [010]. Diffraction effect of the mercury atoms did not allow the co-ordinates of the light atoms to be determined with greater accuracy than  $\pm 0.05 \text{ \AA}$ . The layer-type crystal structure is built up of mercuric oxide and mercurous chloride. The mercuric oxide forms zigzag chains  $\cdots \text{Hg}-\text{O}-\text{Hg}-\text{O}-\text{Hg} \cdots$  with the Hg-O distance  $2.03 \text{ \AA}$  and the bond angles at the mercury atoms  $180^\circ$  and  $168^\circ$  alternately and  $112^\circ$  at the oxygen atom. The mercurous chloride molecules are deformed with a deflection of  $19^\circ$  from linearity; the distances Hg-Hg and Hg-Cl are  $2.66$  and  $2.57 \text{ \AA}$  respectively.

### Introduction

In connexion with the earlier investigations of the mercury oxychlorides (Ščavničar & Grdenić, 1955; Ščavničar, 1955) an attempt was made to determine the crystal structure of the synthetic oxychloride known by formula  $\text{HgO} \cdot \text{HgCl}$ ; the mineral terlinguaite is a natural product of the same composition (Bird, 1932; Dana & Dana, 1951). This oxychloride contains mercury atoms in the mercuric and mercurous state. The aim of our investigation was to investigate the bonds between mercury and oxygen atoms and their crystallochemical and stereochemical relations, as it was indicated earlier (Grdenić & Ščavničar, 1953).

### Crystallographic data

The compound was prepared according to the known procedure (Fischer & v. Wartenberg, 1905). The homogeneous crystals were usually small (the average size was  $0.5 \times 0.3 \times 0.1 \text{ mm.}$ ) and of honey yellow colour. The crystals were monoclinic holosymmetric and flat-tened on {001}. The observed forms were: {100}, {001},  $\{\bar{1}01\}$ , {110},  $\{\bar{1}11\}$ . All data in this paper refer to an axis system which is different from that of Dana and the matrix  $\bar{1}02/0\bar{1}0/001$  serves for the transformation of our system to Dana's.

All the X-ray measurements were performed with Ni-filtered Cu K radiation. The dimensions of the unit

cell, as obtained from the oscillation photographs, were

$$a = 19.53, \quad b = 5.92, \quad c = 9.48 \text{ \AA}, \quad \beta = 144^\circ$$

and differed in average 2.2% from the Dana values for terlinguaite.

The pycnometrically determined density is  $9.27 \text{ g.cm.}^{-3}$  and the density calculated for 4 formula units  $2\text{HgO} \cdot \text{Hg}_2\text{Cl}_2$  is  $9.31 \text{ g.cm.}^{-3}$ . The systematically absent reflexions are  $hkl$  with  $h+k = 2n+1$ ,  $h0l$  with  $l$  odd, and  $0k0$  with  $k$  odd, so that the space group is  $C_{2h}^6-C2/c$ .

### Structure determination

The measurement of the relative intensities of the reflexions  $hk0$  and  $h0l$  and the corresponding corrections were performed in the manner described before (Ščavničar & Grdenić, 1955). In order to perform better correction for absorption ( $\mu = 1909 \text{ cm.}^{-1}$  for Cu K radiation) a suitable form was given to the specimen by grinding. The absorption corrections were made very carefully by using the formulae of the absorption factors for a single crystal of high absorbing power (Grdenić, 1952\*).

\* It has been noticed that in this communication one of the formulae was misprinted. In the denominator of the formula  $A(4)$  the sine fraction should be  $\sin \varphi_2 / \sin \psi_2$  instead of  $\sin \psi_2 / \sin \varphi_2$ . For all corrections previously done the correct formula was applied from a manuscript copy used in the laboratory.

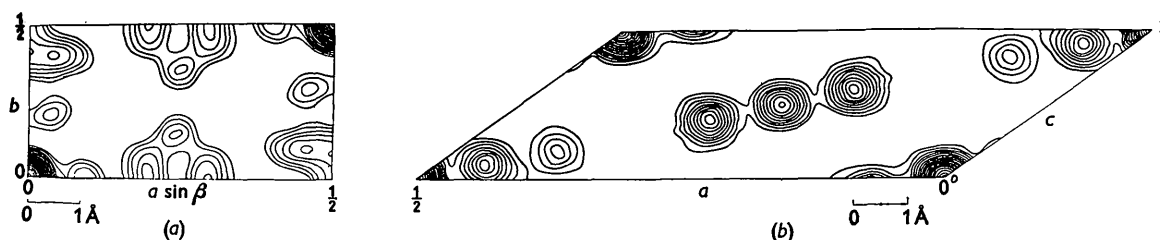


Fig. 1. Contour map of the Patterson projection: (a) along [001], (b) along [010].

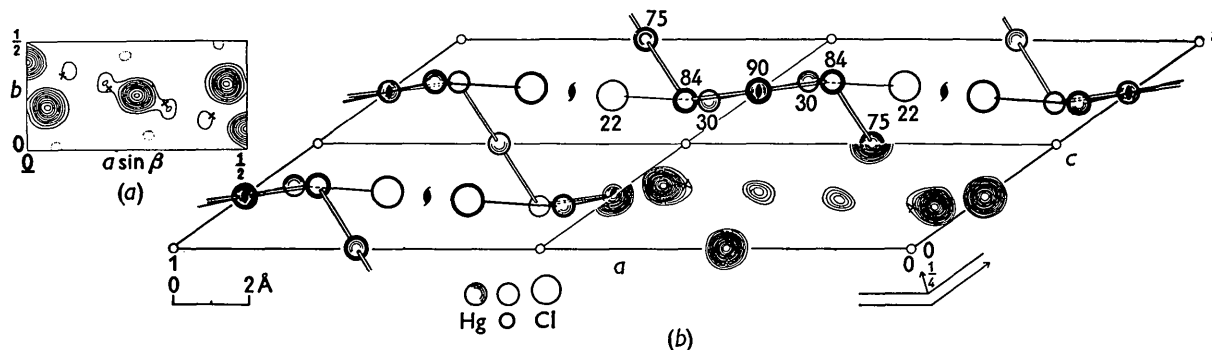


Fig. 2. (a) Contour map of the electron-density projection along [001] of a fourth of the unit cell. The positions of oxygen and chlorine atoms are marked with crosses.

(b) Contour map of the electron-density projection along [010] of a fourth of the unit cell, with a schematic representation of the rest of the unit cell. The atoms belonging to the calomel molecules are connected with single lines and those from mercuric oxide chains with double lines. Numbers give the height of each atom expressed as a percentage of the  $b$  translation.

The Patterson projections  $P(x, y)$  and  $P(x, z)$  are given in Fig. 1. The preliminary co-ordinates for mercury atoms, obtained from these projections, are:  $\text{Hg}_I(\frac{1}{4}, \frac{1}{4}, 0)$ ,  $\text{Hg}_{II}(0, y, \frac{1}{4})$  with  $y = 0.60$  and  $\text{Hg}_{III}(x, y, z)$  with  $x = 0.05$ ,  $y = 0.20$ ,  $z = 0.20$ . The signs of the structure amplitudes  $F(hk0)$  and  $F(h0l)$  were evaluated taking into account only the contribution of mercury atoms.

The Fourier electron-density projections along [001] and [010] are given in Fig. 2. In the projection along [001] (Fig. 2(a)) the chlorine atoms are projected very close to the mercury atom,  $\text{Hg}_I$ , and those of oxygen in the neighbourhood of the  $\text{Hg}_{II}$  and  $\text{Hg}_{III}$  atoms, so that their maxima are smaller than expected. In the [010] projection the chlorine atom maxima are well resolved; the oxygen atom maxima, however, coincide with those of  $\text{Hg}_{III}$  as is clearly seen from the broadening of the  $\text{Hg}_{III}$  maxima. The  $x$  co-ordinate for the oxygen atom at this position corresponds to that from [001] projection. For this reason it was impossible to determine the positions of the oxygen and chlorine atoms directly from the projections, but those values were taken for the light-atom co-ordinates which gave the best agreement for the interatomic contacts. So the final positions of the oxygen and chlorine atoms do not coincide exactly with the peaks in the projections, as it is noticed in Fig. 2.

It follows from the geometrical consideration that the positional accuracy of the light atoms is about  $\pm 0.05$  Å. The Cruickshank (1949) formulae were used

for evaluating the accuracy of the mercury atom co-ordinates. The value  $\sigma_{(y)} = \pm 0.006$  Å was obtained as a standard deviation for the  $\text{Hg}_{II}$  atom. In order to obtain a reliable value for the standard deviation of the  $\text{Hg}_{III}$  atom, the electron-density function was recalculated at intervals of  $a/120$  and  $c/120$ , and the values so obtained were:  $\sigma_{(x)} = \sigma_{(z)} = \pm 0.003$  Å. The final atomic co-ordinates are given in Table 1.

Table 1. Final atomic co-ordinates

	$x$	$y$	$z$
$\text{Hg}_I$	0.25	0.25	0
$\text{Hg}_{II}$	0	0.594	0.25
$\text{Hg}_{III}$	0.047	0.197	0.200
Cl	0.188	0.282	0.230
O	0.082	0.656	0.200

We can get a certain estimate of the correctness of the structure by a comparison (Table 2) of observed and calculated structure amplitudes  $F(hk0)$  and  $F(h0l)$ .

The reliability index  $R = \sum ||F_o| - |F_c|| \div \sum |F_o|$  is 0.14 and 0.08 for  $hk0$  and  $h0l$  reflexions respectively. The values of the atomic scattering factors were taken from *Internationale Tabellen* with the application of an average temperature factor with  $B = 1.76$  Å<sup>2</sup>. This value for  $B$  was obtained graphically by plotting  $\ln(F_o/F_c)$  against  $(\sin \theta/\lambda)^2$ .

### Description of the structure

The mercury atoms differing in their chemical function also occupy crystallographically different positions

Table 2. Observed and calculated structure amplitudes

<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub>/8</i>	<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub>/8</i>	<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub>/8</i>
200	51	+54	12,4,0	0	-2	18,0,4	17	+19
400	84	+85	150	52	+50	20,0,4	36	+34
600	16	-9	350	40	+42	206	29	-27
800	0	+4	550	13	+13	206	0	0
10,0,0	31	-29	750	0	+1	406	37	+34
12,0,0	4	+4	950	8	-7	606	0	-7
14,0,0	11	-13	11,5,0	9	-12	806	21	+21
020	79	-83	260	13	+14	10,0,6	68	-67
040	18	+19	460	22	-21	12,0,6	26	-28
060	13	-15	660	0	-3	14,0,6	78	-80
002	65	-67	860	32	-26	16,0,6	32	-36
004	65	+63	170	6	-8	18,0,6	39	-42
006	0	+5	370	0	-7	20,0,6	0	-2
110	0	-12*	570	10	+8	22,0,6	10	-9
310	0	-11*	202	112	-108	208	17	-22
510	26	-22	402	36	-36	408	5	+6
710	32	-25	602	55	-53	608	12	-10
910	30	-27	802	16	+16	808	32	+35
11,1,0	23	-24	10,0,2	16	-8	10,0,8	29	+29
13,1,0	15	-14	202	84	-83	12,0,8	66	+64
220	0	+9*	402	22	+22	14,0,8	29	+32
420	34	-33	602	16	-16	16,0,8	52	+53
620	39	+37	802	68	+67	18,0,8	0	-7
820	17	+16	10,0,2	15	-16	20,0,8	15	+18
10,2,0	44	+43	12,0,2	17	+17	22,0,8	23	-24
12,2,0	8	+10	14,0,2	33	-33	24,0,8	0	-1
14,2,0	23	+23	16,0,2	16	-19	8,0,10	7	-13
130	46	-34	18,0,2	33	-34	10,0,10	48	-45
330	28	-27	204	23	+29	12,0,10	16	-16
530	0	+3	404	55	+55	14,0,10	36	-37
730	17	+16	604	16	+22	16,0,10	0	+2
930	29	+26	204	23	-25	18,0,10	0	-6
11,3,0	28	+27	404	14	+13	20,0,10	20	+19
13,3,0	9	+14	604	61	-59	22,0,10	0	0
240	29	-34	804	0	+3	24,0,10	12	+13
440	10	+10	10,0,4	9	-10	18,0,12	21	-20
640	32	-28	12,0,4	50	+53	20,0,12	5	+5
840	0	-3	14,0,4	24	+25	22,0,12	13	-13
10,4,0	31	-25	16,0,4	62	+67			

\* Not observed because of the great absorption.

in the structure. The mercuric atoms are placed in the special positions

- (1)  $Hg_I (\frac{1}{4}, \frac{1}{4}, 0)$  and  
 (2)  $Hg_{II} (0, y, \frac{1}{4})$

and the mercurous atoms in the general positions. The chlorine and oxygen atoms also occupy general positions.

The interatomic distances and the bond angles are given in Table 3.

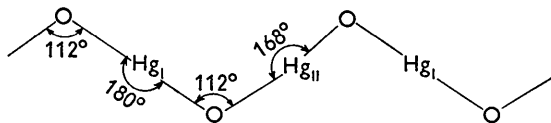
$Hg_I-O$  and  $Hg_{II}-O$  distances are equal, 2.03 Å. This

Table 3. Interatomic distances and bond-angles

$Hg_I-O$	2.03 Å	$O-Hg_I-O$	180°
$Hg_{II}-O$	2.03	$O-Hg_{II}-O$	168
		$Hg_I-O-Hg_{II}$	112
$Hg_{III}-Hg_{III}$	2.66	$Hg_{III}-Hg_{III}-Cl$	161
$Hg_{III}-Cl$	2.57	$Cl-Hg_{III}-O$	77.5
		$Hg_{III}-Hg_{III}-O$	114
$Hg_{II} \dots O$	2.46		
	2.80		
$Hg_{III} \dots Hg_{II}$	2.70		
$Hg_{II} \dots Cl$	2.80		
$Hg_I \dots Cl$	3.25		
$Cl \dots O$	2.88		

value for the  $Hg-O$  bond length was found earlier in the structure of trichloromercury oxonium chloride (Ščavničar & Grdenić, 1955) and it is a little smaller than the sum of the covalent radii for mercury (1.48 Å) and oxygen (0.66 Å) atoms.

The mercuric and oxygen atoms are linked in the zigzag chains



stretching through the whole crystal, so that the mercury atoms lie in the planes parallel to  $(\bar{1}01)$ , on both sides of which the oxygen atoms are alternately placed at a distance of 1.1 Å from the plane. The good  $(\bar{1}01)$  cleavage of terlinguaite (Dana & Dana, 1951) can be explained in this way.

Each mercury atom in the general position,  $Hg_{III}$ , is surrounded by three atoms, one of which is mercury at a distance of 2.66 Å and the others chlorine and oxygen at distances of 2.57 and 2.46 Å respectively.

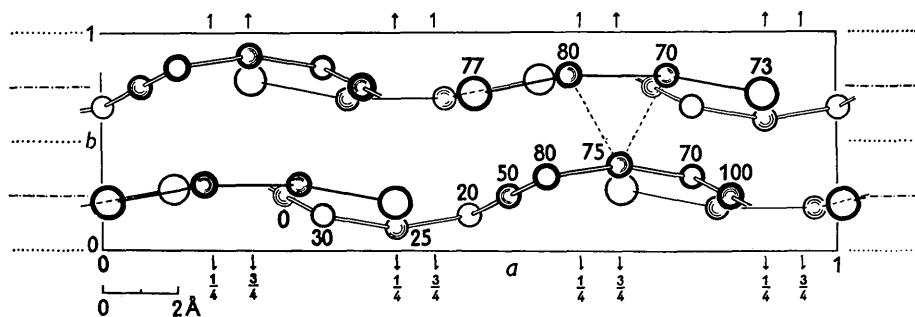


Fig. 3. Projection of the structure on the (001) plane (schematic). Key as in Fig. 2(b), except that the numbers refer to the  $c$  translation. One of the  $\text{Hg}_{\text{III}}\text{-Hg}_{\text{II}}\text{-Hg}_{\text{III}}$  triangles is indicated with broken lines.

These atoms lie nearly in the same plane (the departure amounts to approximately  $0.3 \text{ \AA}$ ), so that the central mercury atom is placed in a triangle at the corners of which are chlorine, oxygen and  $\text{Hg}_{\text{III}}$  atoms. The values of the bond angles are:

$$\begin{aligned} \text{Cl-Hg}_{\text{III}}\text{-Hg}_{\text{III}} &= 161^\circ, \quad \text{Cl-Hg}_{\text{III}}\text{-O} = 77.5^\circ, \\ \text{O-Hg}_{\text{III}}\text{-Hg}_{\text{III}} &= 114^\circ. \end{aligned}$$

The distance  $\text{Hg}_{\text{III}}\text{-Hg}_{\text{III}} = 2.66 \text{ \AA}$  is greater than the value  $2.53 \text{ \AA}$  for the  $\text{Hg-Hg}$  bond length found in calomel (Havighurst, 1926). This difference in the  $\text{Hg-Hg}$  distance shows that the  $\text{Hg-Hg}$  bond in  $2\text{HgO} \cdot \text{Hg}_2\text{Cl}_2$  is not the same as in calomel. This change of the bond nature can be explained (1) by the fact that in the  $2\text{HgO} \cdot \text{Hg}_2\text{Cl}_2$  structure the mercury atom,  $\text{Hg}_{\text{III}}$ , has a co-ordinately bonded oxygen atom, so that the bonds are approximately  $sp^2$  and not  $sp$  as in calomel, or (2) by the polarizing activity of the mercury atom which is extended to the chlorine and oxygen atoms and which together give a greater electronic cloud than is the case in calomel. For this reason the distance  $\text{Hg}_{\text{III}}\text{-Hg}_{\text{III}}$  in  $2\text{HgO} \cdot \text{Hg}_2\text{Cl}_2$  is approximately equal to that in  $\text{Hg}_2\text{I}_2$  ( $2.69 \text{ \AA}$ ) (Havighurst, 1926).

The idealized structure of this oxychloride can be described as a structure composed of mercuric oxide and calomel. In fact, there are deformations in the mercuric oxide chains as in the calomel molecules. They prove the existence of strong interaction between these two components on the basis of the polarizing forces of the mercury atoms. The  $\text{O-Hg-O}$  angle is  $180^\circ$  in the case of  $\text{Hg}_{\text{I}}$ . The distance  $3.25 \text{ \AA}$  between  $\text{Hg}_{\text{I}}$  and two neighbouring chlorine atoms is close to the sum of the van der Waals radii. The  $\text{Hg}_{\text{II}}$  atom, however, is remarkably closer to the chlorine atom ( $2.80 \text{ \AA}$ ) and it is also close to  $\text{Hg}_{\text{III}}$  ( $2.70 \text{ \AA}$ ); for this reason the  $\text{O-Hg}_{\text{II}}\text{-O}$  bond angle is  $168^\circ$ , and not  $180^\circ$  as would be expected. The  $\text{Hg}_2\text{Cl}_2$  molecules suffer very great deformations, as in the above mentioned increase of the bond lengths, so that in the considerable departure from the linearity the bond angle  $\text{Cl-Hg}_{\text{III}}\text{-Hg}_{\text{III}}$  is  $161^\circ$ .

The distance  $\text{Hg}_{\text{III}}\text{-Hg}_{\text{II}}$  of  $2.70 \text{ \AA}$  deserves some

more attention. This is the distance from the mercury atoms ( $\text{Hg}_{\text{III}}$ ) in the calomel molecules to the mercury atom ( $\text{Hg}_{\text{II}}$ ) in the oxide chain. It is nearly equal to the  $\text{Hg}_{\text{III}}\text{-Hg}_{\text{III}}$  distance ( $2.66 \text{ \AA}$ ) in calomel molecules, so that one  $\text{Hg}_{\text{II}}$  atom and two  $\text{Hg}_{\text{III}}$  atoms form a triangle. This triangle is clearly seen in the projection on (001) (Fig. 3). The present knowledge of the bond nature, distances and radii in mercurous compounds is still not sufficient, so that any explanation is to be postponed until more data are available. Accurate measurement of the  $\text{Hg-Hg}$  bond length in mercurous nitrate dihydrate (Grdenić, 1956) and mercurous fluoride (Grdenić & Djordjević, 1956) has been made already.

The layered nature of the structure can be seen from Fig. 3.

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