

The Crystal Structure of Trimercuric Oxychloride, $\text{HgCl}_2 \cdot 2\text{HgO}$

BY S. ŠČAVNIČAR

Mineralogical and Petrological Institute, Faculty of Science, The University, Zagreb, Yugoslavia

(Received 3 February 1955 and in revised form 1 March 1955)

The application of the methods of X-ray analysis has shown that the crystal structure of the mercuric oxychloride known under the formula $\text{HgCl}_2 \cdot 2\text{HgO}$ is best interpreted by the formula $\text{Hg}(\text{OHgCl})_2$.

The crystals are monoclinic holosymmetric with the space group $C_{2h}^2-P2_1/c$. The unit cell of dimensions

$$a = 7.16, b = 6.87, c = 6.86 \text{ \AA}, \beta = 126^\circ 10',$$

contains two formula units. The parameters of all atoms were determined with the help of Patterson and Fourier-Bragg projections along [001] and [100].

It follows from the values of interatomic distances that the lattice is built up of mercury cations Hg^{++} located in special positions and polymeric anions $(\text{OHgCl})^-$, with all atoms in general positions. Each mercury atom in a general position is surrounded by three oxygen atoms and one chlorine atom in a distorted tetrahedron. These tetrahedra are linked together in layers in such a way that each chlorine atom belongs to only one mercury atom and each oxygen atom to three neighbouring mercury atoms, the distances within the layer being $\text{Hg-O} = 2.16 \text{ \AA}$ and $\text{Hg-Cl} = 2.66 \text{ \AA}$. Each mercury cation is surrounded by two oxygen and four chlorine atoms in a distorted octahedron at the distances of 2.49 and 2.94 \AA respectively.

Introduction

Trimercuric oxychloride has been repeatedly the object of crystallographic investigations. According to Blass (1879) the crystals are monoclinic holosymmetric with $a:b:c = 0.9178:1:0.9978$, $\beta = 114^\circ 30'$. Van Nest (1910) reinvestigated the crystals but obtained $a:b:c = 1.9782:1:1.0452$, $\beta = 125^\circ 57'$, which apparently differed from the values given by Blass. He explained this difference by assuming the occurrence of two different modifications.

At the beginning of the present investigation this alleged dimorphism had at first to be verified. In fact,

two kinds of crystals were found, but when the careful crystallographic measurements on many specimens had been accomplished it followed that the difference was only in crystal habit and no dimorphism could be observed. On the basis of the results of the morphological and X-ray study it seemed fully justified to index the crystal faces as shown in Fig. 1. The plate-shaped crystals (Fig. 1(a)) parallel to the first pinacoid were described and measured by Blass and the short prismatic crystals (Fig. 1(b)) were measured by van Nest. The face indices (HKL) according to Blass and those ($H'K'L'$) according to van Nest are to be transformed into the indices (hkl) used in the present paper by the equations:

$$\begin{aligned} h &= -(H+L); & k &= -K; & l &= L; \\ h &= L'; & k &= -K'; & l &= \frac{1}{2}H'. \end{aligned}$$

Experimental part

The crystals were prepared by leaving pieces of marble in 5% water solution of mercuric chloride at room temperature (Arctowski, 1895; Tarugi, 1901; Van Nest, 1910; Carozzi, 1926; Garret & Lemley, 1942). Under the same conditions, without any apparent reason, crystals of one habit were obtained in some vessels and of the other habit in other vessels. The crystals of both habits appear to be composed of stair-forming layers parallel to (100), but without any remarkable cleavage. The crystals are very bright and black, with a brown scratch.

All X-ray diffraction records were made with nickel-

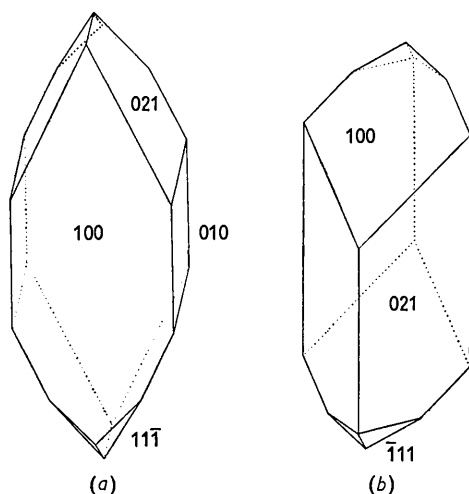


Fig. 1. Two different crystal habit of trimercuric oxychloride: (a) pinacoidal, (b) prismatic.

filtered Cu *K* radiation. The dimensions of the unit cell, as obtained from the oscillation photographs, are:

$$a = 7.16, b = 6.87, c = 6.86 \text{ \AA}, \beta = 126^\circ 10'.$$

The observed (Schoch, 1903) and calculated densities are 8.53 and 8.59 g.cm.⁻³ respectively, so that the unit cell contains two formula units Hg₃O₂Cl₂.

The systematically absent reflexions were only *0k0* with *k* odd and *h0l* with *l* odd so that the space group *C*_{2h}⁵-*P*2₁/*c* was unambiguously determined. It followed from the symmetry properties of this group that two mercury atoms had to be located in special positions (centres of symmetry) whereas the four remaining mercury atoms, as well as the four chlorine and four oxygen atoms, had to be located in general positions.

The above X-ray data are in agreement with those obtained previously by Gawrich (1938) and by Aurivilius (1954), provided that the appropriate axes are transformed, since these authors retained the axes chosen by Blass.

With the use of the Weissenberg goniometer the *hk0* and *0kl* reflexions were recorded. The determination of the relative intensities of the reflexions from the optical densities of the spots was performed by the procedure described by Grdenić (1952*a*). In order to apply the formulae for absorption correction (Grdenić, 1952*b*), a suitable form was given to the specimens by grinding. This correction had to be carried out very carefully, for the linear absorption coefficient is 1730 cm.⁻¹. For the *hk0* reflexions a crystal of the habit shown in Fig. 1(*a*) was used; the habit shown in Fig. 1(*b*) was used for the *0kl* reflexions. The corrections for polarization and Lorentz factors were made in the usual way.

Determination of the structure

The preliminary mercury atom co-ordinates:

$$\begin{aligned} x_{\text{I}} &= 0, & y_{\text{I}} &= 0, & z_{\text{I}} &= 0; \\ x_{\text{II}} &= 0.416, & y_{\text{II}} &= 0.363, & z_{\text{II}} &= 0.158; \end{aligned}$$

were obtained with the help of Patterson projection along [001] and [100] (see Fig. 2). The signs of the

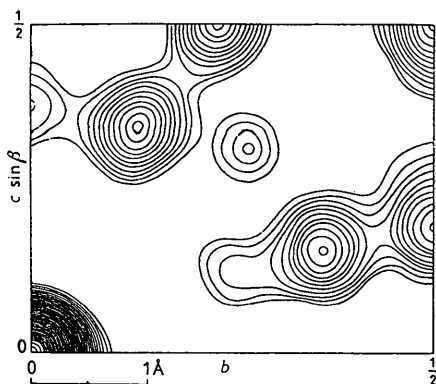


Fig. 2. The contour map of the Patterson projection along [100].

structure amplitudes *F*(*0kl*) and *F*(*hk0*) were then evaluated from the above mercury atom co-ordinates, neglecting the contributions of the chlorine and oxygen atoms, and Fourier projections along [100] and [001] (Figs. 3 and 4) were computed with use of Beever's &

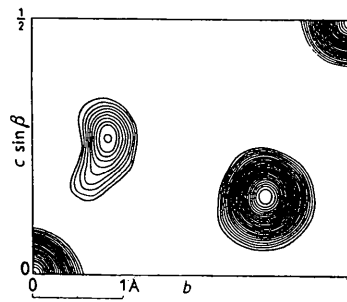


Fig. 3. The contour map of the electron-density projection along [100] of a fourth of the unit cell.

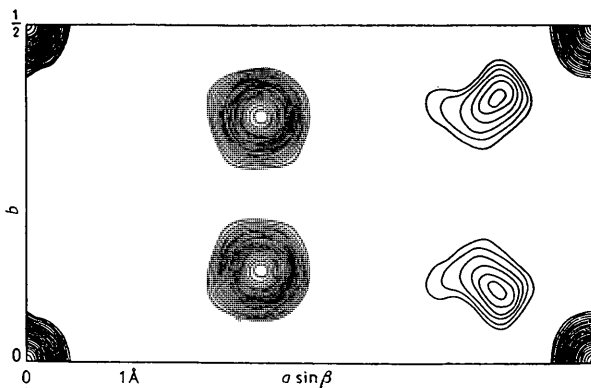


Fig. 4. The contour map of the electron-density projection along [001] of a half of the unit cell.

Lipson strips at 6° intervals. The chlorine atom peaks appeared neatly beside those of the mercury atoms, but there was no peak which could be attributed to the oxygen atom in either projection. Of course, some ghost peaks appeared in both projections, but they were so small and in such positions that there was no doubt they did not belong to the oxygen atoms.

Trusting in the experience previously gained in the analysis of mercury compounds (e.g. Grdenić & Ščavničar, 1953), it was assumed that the oxygen atom peaks should appear. Consequently, the next step in locating the oxygen atoms was made by assuming that in both projections the overlapping of the maxima might so occur that the oxygen atom peaks were concealed in the mercury or chlorine atom peaks. An improvised model of the structure was made and all probable oxygen atom positions were then considered with the allowance of the reasonable interionic and interatomic distances. This trial procedure was not very tedious since there was not much empty space in the structure so that there remained in reality only one possibility for locating the oxygen

Table 1. *Final atomic co-ordinates*

	<i>x</i>	<i>y</i>	<i>z</i>
Hg _I	0	0	0
Hg _{II}	0.412	0.365	0.151
Cl	0.185	0.620	0.233
O	0.397	0.115	0.331

atoms. It followed that the initial assumption about overlapping maxima was fully justified and that the oxygen atom should have such parameter values that the maximum belonging to it in the [100] projection coincided with the chlorine atom maximum and in the [001] projection with the mercury atom maximum. This result was proved by the broadening and the increase in height of the corresponding maxima which had been noticed in both projections.

The final atomic co-ordinates are given in Table 1. The mercury and chlorine atom co-ordinates were obtained from the Fourier projections along [100] and [001], those of the oxygen atom by the above trial procedure. For this reason the oxygen coordinates are less accurate. Their values were so chosen that the most probable Hg-O distances resulted. It followed from the geometrical consideration, as well as from the shape of the corresponding mercury and chlorine peaks in which the oxygen peak was hidden, that the oxygen atom position was determined with a maximum error of about ± 0.1 Å.

With the atomic parameters given in Table 1 the structure amplitudes $F_c(0kl)$ and $F_c(hk0)$ were calculated. The values of the atomic scattering factors were taken from the *Internationale Tabellen* without any correction for thermal motion. In Table 2 the comparison between the observed F_o and calculated F_c structure amplitudes is given. The agreement is quite satisfactory except for a few reflexions. These departures have two main sources: inaccuracy in density measurement of the diffraction spots and difficulty in the application of the absorption factor formulae owing to the smallness of the crystal specimens. The reliability index $R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$ has the values 0.18 and 0.19 for $F(hk0)$ and $F(0kl)$ respectively.

Description and discussion of the structure

Of the six mercury atoms in the unit cell two are located in the special positions

$$\text{Hg}_I (0, 0, 0; 0, \frac{1}{2}, \frac{1}{2})$$

and four in the general positions

$$\text{Hg}_{II} (x, y, z; \bar{x}, \frac{1}{2}+y, \frac{1}{2}-z; x, \frac{1}{2}-y, \frac{1}{2}+z; \bar{x}, \bar{y}, \bar{z}).$$

It followed from the values of atomic co-ordinates of chlorine and oxygen that mercury atoms differ not only crystallographically but also in their chemical

Table 2. *Observed and calculated structure amplitudes*

<i>hkl</i>	F_o	$\frac{1}{2}F_c$	<i>hkl</i>	F_o	$\frac{1}{2}F_c$	<i>hkl</i>	F_o	$\frac{1}{2}F_c$
100	26	-28	350	59	+43	022	34	+33
200	47	+59	360	26	+24	032	32	-28
300	42	+29	370	16	+18	042	56	+54
400	0	-9	380	15	+17	052	39	+40
500	65	+78	410	30	+27	062	17	+19
600	0	-16	420	40	+30	072	6	+11
700	35	+48	430	17	+17	082	0	+2
020	25	+28	440	62	+54	013	67	+72
040	38	-40	450	28	-27	023	25	+26
060	36	+40	460	12	+12	033	11	-19
080	51	+64	470	0	-7	043	0	-1
002	0	-2	510	15	-15	053	0	-1
004	0	-5	520	25	+18	063	17	-19
006	47	+50	530	13	-12	073	44	+60
110	26	-25	540	20	-26	083	3	+5
120	43	+41	550	13	+15	014	20	+19
130	19	-14	560	29	+32	024	30	+31
140	65	+75	610	0	-4	034	13	+10
150	19	+20	620	32	+27	044	42	+53
160	0	+9	630	0	-2	054	17	-21
170	0	+4	640	43	+55	064	3	+8
180	7	-9	650	0	+4	074	3	-5
210	51	+54	710	16	+25	015	22	+19
220	30	+28	720	19	+16	025	42	-50
230	40	+38	730	12	+20	035	15	+26
240	12	+9	011	0	+4	045	8	+11
250	44	-45	021	42	+38	055	18	+24
260	35	+31	031	72	+63	065	29	+41
270	15	-19	041	13	-13	016	16	+21
280	23	+32	051	35	+42	026	14	+17
310	55	-49	061	22	-26	036	7	+16
320	33	+22	071	0	-2	046	0	-8
330	42	-35	081	14	+18	017	0	-1
340	33	+27	012	50	-43			

function. The chemical formula of trimercuric oxychloride, $\text{HgCl}_2 \cdot 2\text{HgO}$, is to be written, therefore, $\text{Hg}(\text{OHgCl})_2$.

This formula is best understood by considering the interatomic distances and co-ordination polyhedra. As it is evident from Table 3, there are two kinds of Hg-O

Table 3. *Interatomic distances and bond-angles*

Mercury atom (Hg_I) in octahedral co-ordination

Hg-O	2.49 Å	O-Hg-O	180°
Hg-Cl	2.94	Cl-Hg-Cl	180
O...Cl	3.62	O-Hg-Cl	83
	3.78		88
	3.91		92
	4.07		97
Cl...Cl	3.86	Cl-Hg-Cl	82
	4.41		98

Mercury atom (Hg_{II}) in tetrahedral co-ordination

Hg-O	2.16 Å	O-Hg-O	70°
Hg-Cl	2.66		129
O...O	2.48		147
	3.90		147
	4.14		147
O...Cl	3.27	O-Hg-Cl	85
	3.69		99½
	4.18		120

and Hg-Cl distances. The longer ones belong to the mercury atoms Hg_I , the shorter ones to the mercury atoms Hg_{II} ; the difference amounts to about 0.3 Å. The Hg-Cl distance (2.94 Å) is in good agreement with the sum of the ionic radii, as is the Hg-O distance (2.49 Å) (the values 1.10 Å for Hg^{++} , 1.81 Å for Cl⁻ and 1.40 Å for O⁻ have been used; Pauling, 1940). The octahedral co-ordination around Hg_I also argues for the ionic nature of the Hg_I atom in the structure, each Hg_I atom being surrounded by two oxygen and four chlorine atoms in a distorted octahedron (Fig. 5).

The distances from the mercury atoms Hg_{II} in

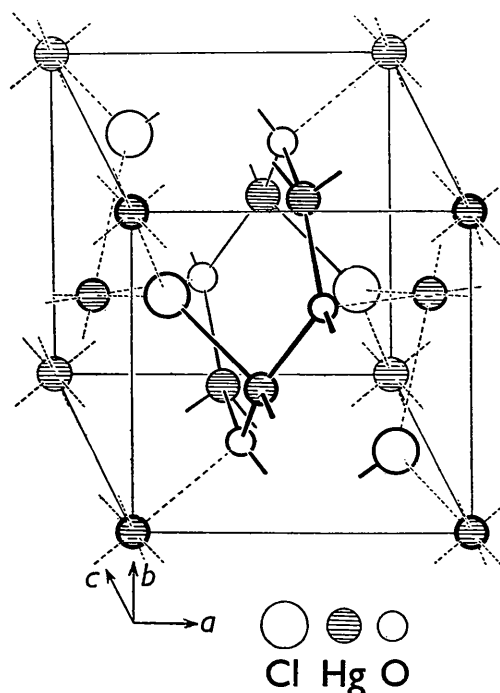


Fig. 5. A view of the structure model of $\text{Hg}(\text{OHgCl})_2$. The unit cell is shown.

general positions to oxygen (2.16 Å) and to chlorine (2.66 Å) are nearly equal to the sum of corresponding covalent radii (the values 1.48 Å for Hg, 0.66 Å for O and 0.99 Å for Cl have been used; Pauling, 1940). Three oxygen atoms and one chlorine atom are located around each Hg_{II} atom at the corners of a distorted tetrahedron. Each chlorine atom belongs to only one tetrahedron and each oxygen atom to three tetrahedra. Consequently, the OHgCl tetrahedra are linked to-

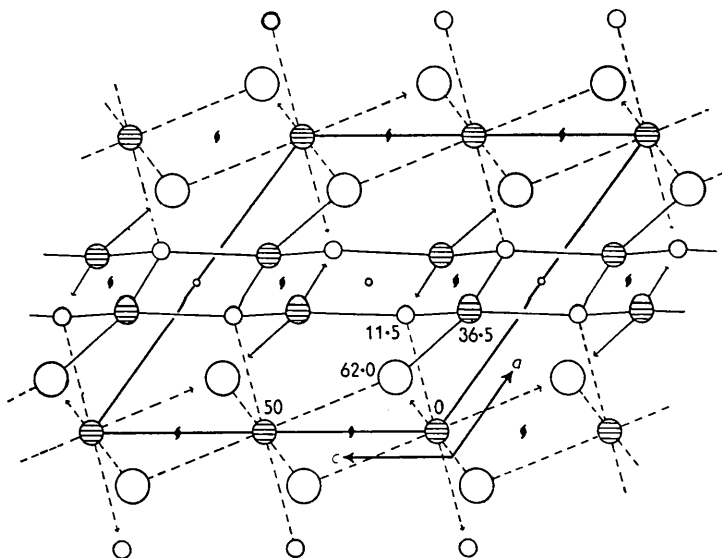


Fig. 6. Projection of the structure along [010] (schematic). The O-Hg-Cl tetrahedra are traced by full lines and the octahedra by broken lines. Numbers give the height of each atom expressed as a percentage of the b translation. Key as in Fig. 5.

gether into one infinite layer through the oxygen atoms parallel to (100). In addition, each oxygen atom belongs to one Hg_I octahedron, and each chlorine atom to two such octahedra. It follows that the structure is built up of alternating layers of Hg_I^{++} cations and polymeric $(\text{OHgCl})^-$ anions. These layers can be best realized from the projection on (010) plane in (Fig. 6). The Hg_{II} tetrahedron is far more distorted than the Hg_I octahedron, as may be seen from Table 3. This distortion is partly caused by the polarization action of the mercuric ion (Hg_{II}) and partly by the packing conditions dictated by the largest Cl ions. The O-O approaches in the same tetrahedron are 4.14, 3.90 and 2.48 Å. The last value belongs to the common edge of two linked tetrahedra, since each tetrahedron shares one of its O-O edges with its neighbour. That is the shortest distance between the non-bonded atoms.

The author wishes to express his sincere gratitude to Dr D. Grdenić (Laboratory for General and Inorganic Chemistry, Faculty of Science) for many valuable suggestions and helpful discussions and encouragement during the whole work. Thanks are due to Prof. M. Pačić at whose laboratory (Physical Institute, Fac-

ulty of Science) a part of the experimental work was performed. The investigation described in this paper was supported by the Institute Rudjer Bošković, Zagreb.

References

- ARCTOWSKI, H. (1895). *Z. anorg. Chem.* **9**, 178.
 AURIVILLIUS, K. (1954). *Acta Chem. Scand.* **8**, 523.
 BLASS, J. (1879). *Tscherm. Mitt.* **2**, 177.
 CAROZZI, E. (1926). *Gazz. chim. ital.* **56**, 175.
 GARRET, A. B. & LEMLEY, J. (1942). *J. Amer. Chem. Soc.* **64**, 2380.
 GAWRICH, S. (1938). *Roczn. Chem. (Ann. Soc. Chim. Polonorum)*, **18**, 107. (Quoted in *Chem. Zbl.* (1940), **1**, 3622.)
 GRDENIĆ, D. (1952a). *Acta Cryst.* **5**, 367.
 GRDENIĆ, D. (1952b). *Acta Cryst.* **5**, 238.
 GRDENIĆ, D. & ŠČAVNIČAR, S. (1953). *Nature, Lond.* **172**, 584.
Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Berlin: Borntraeger.
 NEST, J. S. v. (1910). *Z. Kristallogr.* **47**, 263.
 PAULING, L. (1940). *The Nature of the Chemical Bond*. Ithaca: Cornell University Press.
 SCHOCH, E. P. (1903). *Amer. Chem. J.* **29**, 319. (Quoted in *Chem. Zbl.* (1903), **1**, 1173.)
 TARUGI, N. (1901). *Gazz. chim. ital.* **31**, 313. (Quoted in *Chem. Zbl.* (1901), **2**, 1147.)

Acta Cryst. (1955). **8**, 383

The Probability Distribution of Intensities. VI. The Influence of Intensity Errors on the Statistical Tests

BY D. ROGERS, E. STANLEY* AND A. J. C. WILSON

Viriamu Jones Laboratory, University College, Cardiff, Wales

(Received 2 February 1955)

The statistical tests, three for centrosymmetry and one for planes of symmetry, have been examined to determine quantitatively their sensitivity to errors in the original intensity data. The errors considered are (i) random errors proportional to I , (ii) errors systematic in I of the form $I_0 = k\Sigma(1 - \exp(-I/k\Sigma))$, (iii) errors systematic in $\sin \theta$, and (iv) errors associated with the non-observance of very weak reflexions. Errors (i) and (ii) of ordinary magnitude produce no confusion. Errors (iii) can affect the tests only through errors in the determination of $\langle I \rangle$ as a function of $\sin^2 \theta$, and to these the tests are rather sensitive. Errors (iv) can also have marked effects, for which, however, allowances can be made. The tests are unequally affected by a given amount of error, but the results derived here permit the estimation in a given problem of likely outer limits for the result of each test. Results lying outside this limit may be regarded as significantly different and indicative of some structural peculiarity.

1. Introduction

1.1. Several authors have reported successful decisions for or against centrosymmetry using the statistical tests discussed in the preceding papers of this series, but results are sometimes obtained which do not agree well with the criteria which characterize the two ideal

intensity distributions, the centric and the acentric. The discrepancies may be attributed to:

(i) some violation of the assumptions underlying the derivation of the ideal distribution functions, e.g. too few atoms (for allowances see Wilson (1951), Hauptman & Karle (1953) and Karle & Hauptman (1953)), lack of generality in their positions, pseudosymmetry (for a possible example see Bragg, Howells

* Now at the National Research Council, Ottawa, Canada.