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The Crystal Structure of Trichlormercury Oxonium Chloride

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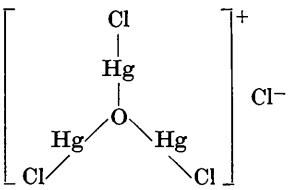
The crystal structure of the so-called trimercuric oxytetrachloride, $2HgCl_2.HgO$, has been analysed by X-ray methods. It follows from the positions of all atoms derived by means of the electron-density projection, and from the symmetry relations, that the lattice consists of $(ClHg)_3O$ cations and Cl anions. This compound is therefore a trichlormercury oxonium chloride:



The crystals are cubic with the space group T^4–$P2_13$. The unit cell, of dimension $a = 9{\cdot}22$ Å, contains four formula units. The oxygen atoms are located on triad axes and the $(ClHg)_3O^+$ ion thus has trigonal symmetry. Moreover, it follows from the atomic coordinates that this ion is planar with oxygen, mercury and chlorine atoms very nearly in a straight line, the distances O–Hg and Hg–Cl being 2·03 Å and 2·28 Å respectively. Each oxonium ion has three neighbouring chlorine ions located between two mercury atoms with Hg · · · Cl^- distances of 2·94 Å and 3·13 Å respectively.

Introduction

The mercuric oxychlorides of the general formula $mHgCl_2.nHgO$ are of special crystallochemical interest owing to the unknown role of the oxygen atoms in their crystal structure. In order to establish this role and to determine also the Hg–O bond length we have undertaken the crystal-structure investigation of this class of compounds.

At first we succeeded in establishing the crystal structure of $2HgCl_2.HgO$, as already announced in our preliminary reports (Grdenić & Šćavničar, 1953*a*, *b*) as well as in a note by Bezjak (1953). In our second report we published briefly the results of the complete structure analysis with all final interatomic and interionic distances, but afterwards we did not do any further work. We have shown that this compound is a trichlormercury oxonium chloride with the formula $[(HgCl)_3O]Cl$.

Meanwhile, independently of us, Weiss, Nagorsen & Weiss (1953*a*, *b*) had investigated the structure of the same compound by the X-ray methods and came to the same results. The structure proposed and described by these authors differs slightly from the present one only in the values of interatomic distances. We are, therefore, of opinion that publishing our paper, however late, would not be superfluous, but on the contrary it would enable comparison between two independent analyses of the same compound by different authors.

Crystallographic and X-ray data

The crystals were prepared according to the procedure described by Carozzi (1926), i.e. by leaving pieces of marble for several days in a mercuric chloride solution at room temperature. The crystals are very bright and colourless, or sometimes pale yellowish, with the average size of 1 mm.

The statement that the crystals are cubic, which was previously given by Gawrich (1938) on the basis of the powder diffraction photograph, was confirmed by our crystallographic measurements. The always well developed faces are the rhombododecahedron and the tetrahedron, but sometimes the small hexahedron faces were also observed. When both tetrahedra occurred simultaneously, they differed in magnitude. From these data it was assumed that the T or T_d was the highest possible symmetry class; the former was later confirmed by the X-ray diffraction pattern.

All X-ray diffraction data were obtained from oscillation, Laue and Weissenberg photographs. Nickel-filtered copper K radiation was used throughout the work. The cubic unit cell has the edge

$$a = 9{\cdot}22 \text{ Å}$$

(in agreement with the value $a = 9{\cdot}21$ Å reported previously by Gawrich, 1938) and contains 4 formula units Hg_3Cl_4O. (Calculated density, 6·45 g.cm.$^{-3}$; observed, 6·42 g.cm.$^{-3}$.)

The only systematically absent reflections were $h00$ with h odd. This extinction rule is satisfied in the cubic system only in the case of the space groups $P2_13$ or $P4_23$, but the crystal and Laue symmetry indicated $P2_13$ as the only possible space group. It followed from all these data that the oxygen atoms (4 atoms) had to be in the special positions on the triad axes, the chlorine atoms (16 atoms) in the general (12 atoms) and special (4 atoms) positions, and that the most probable positions for mercury atoms (12 atoms) were the general positions.

Intensities

The $hk0$ reflexions were recorded on Weissenberg double-film photographs. The intensities of the reflexions were determined from the optical densities which were measured on the centre of each but a few weakest spots, using a microphotometer. The recorded optical densities were converted into relative intensities by means of the characteristic curve. The intensities of the weakest reflexions were estimated visually.

The absorption correction had to be applied very precisely since the linear absorption coefficient is $\mu = 1247$ cm.$^{-1}$. For this purpose the crystal specimen was prepared by grinding the natural rhombododecahedron faces by the usual method, i.e. sticking the crystal on a slide with Canada balsam and grinding it on a plane glass plate, using abrasive and saturated mercuric chloride solution. In this way we obtained a prism-shaped specimen with the cross section of 0·42×0·42 mm. which gave good diffraction photographs. The absorption factor was calculated applying the formulae previously suggested (Grdenić, 1952).

The corrections for polarization and Lorentz factors were made in the usual way. The secondary extinction was not taken into account.

Structure determination

The (001) projection of the unit cell of space group $P2_13$ possesses a symmetry centre at $x = 0$, $y = \frac{1}{4}$ (the origin is taken as in *International Tables* (1952)). Obviously, all calculations and Fourier summations were carried out with the reference to the symmetry centre as origin, but all parameter data given in the present paper are referred to the *International Tables* origin.

The Patterson synthesis on the (001), evaluated by the use of Beevers & Lipson strips at 6° intervals, is shown in Fig. 1. The positions of the large maxima belonging to the Hg–Hg vectors exclude the possibility of locating the mercury atoms in special position on triad axes since no one maximum appeared on the diagonals. There are also many overlappings of the maxima, as is evident from their relative sizes. The Patterson projection was interpreted by Bezjak's modification (1953) of the vector algebraic method described by Lindqvist (1952), taking into account the

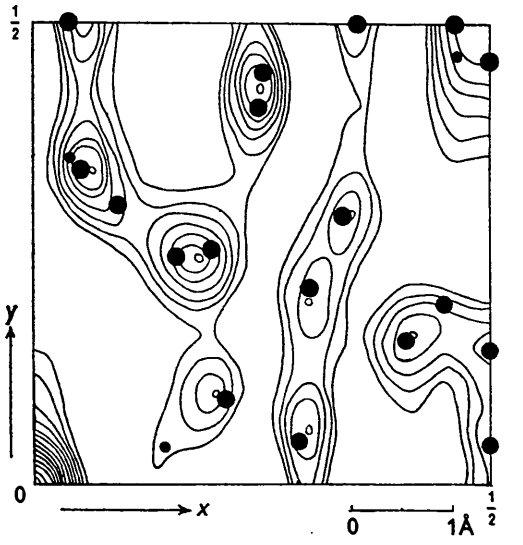


Fig. 1. Patterson (x, y) projection as interpreted by mercury–mercury peaks alone. Doubly weighted and singly weighted maxima are indicated by large and small dots respectively.

Hg–Hg maxima only. The preliminary mercury atom coordinates obtained in this way are given in Table 1.

Table 1. *Preliminary mercury co-ordinates*

	x	y
Hg_I	0·272	0·497
Hg_{II}	0·537	0·280
Hg_{III}	0·469	0·575

The condition $x_I = y_{II}$, $x_{II} = y_{III}$, $x_{III} = y_I$ required for the space group $P2_13$ was therefore fulfilled approximately. The signs of the observed structure amplitudes $F(hk0)$ were then determined with the help only of the above mercury atom coordinates, neglecting the contribution of the chlorine and oxygen atoms, and the two-dimensional electron-density map on (001) was computed. The parameters of all atoms were then refined by computing the second electron-density map, the signs having been recalculated by also taking the light atom contributions into account. This final electron-density map is shown in Fig. 2(*a*).

The maxima of all atoms are well resolved. The diffraction rings around the mercury atom maximum influenced notably the position of only one chlorine atom maximum, for this chlorine atom fell in the projection very near to the mercury atom. For this reason the parameters of this chlorine atom were obtained by symmetry relations from the parameters of the corresponding chlorine atoms. Also, for the same reason, oxygen atom peak appeared distorted and lengthened.

Table 2. *Final atomic co-ordinates*

	x	y	z
Hg	0·269	0·480	0·573
O	0·443	0·443	0·443
Cl	0·075	0·533	0·717
Cl^-	0·315	0·185	0·685

In Table 2 the final atomic co-ordinates are given. The chlorine atom in the special position is referred to as Cl^-, to distinguish it from the chlorine atom located in the general position. The former is bound ionically, the latter covalently, as it will be explained below.

In Table 3 the comparison between F_o and F_c is given. For evaluating F_c the corresponding atomic scattering factors from *Internationale Tabellen* (1935) were used by applying an average temperature factor $\exp[-B(\sin\theta/\lambda)^2]$ with $B = 2$ Å^2. The observed structure amplitudes were put on the absolute scale by being multiplied by an appropriate factor. The agreement is quite good with the exception of about ten reflexions which were not observed because of the great absorption. The reliability index $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$ has the value of $R = 0{\cdot}18$. If the calculated structure factors for the non-observable reflexions are omitted, R becomes 0·16.

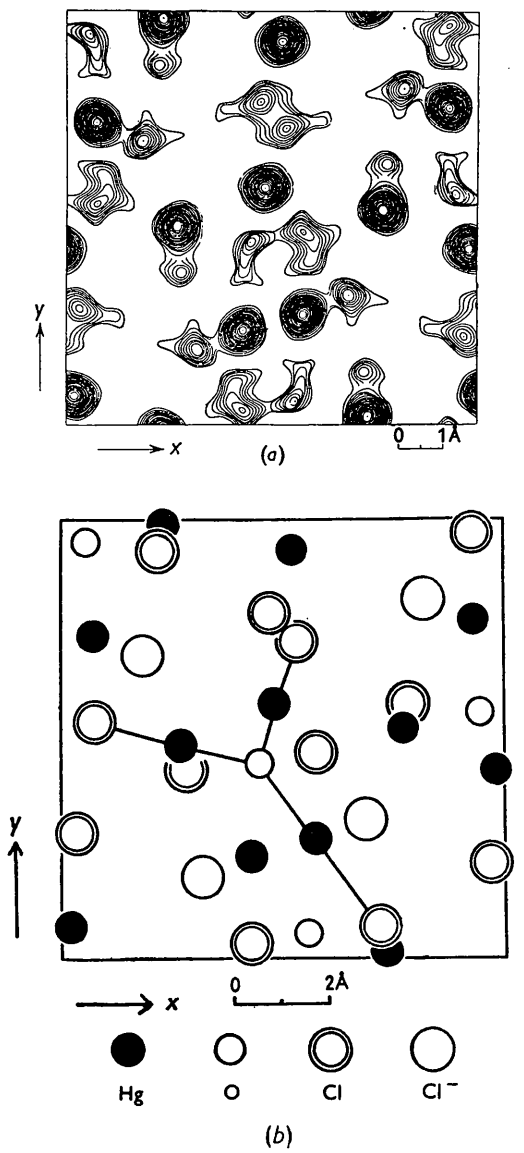


Fig. 2. Projection of the unit cell on (001). (*a*) Electron-density projection with contours drawn at equal intervals on an arbitrary scale. (*b*) Schematic projection of the structure. One oxonium ion $(ClHg)_3O$ is drawn in full lines.

Description of the structure

It follows from the space group and symmetry relations that three-quarters of all the chlorine atoms have to be of one kind and the remainder, one-quarter, of the other kind. It was therefore fully justified to suggest $(OHg_3Cl_3)Cl$ as the rational chemical formula and to suppose that the chlorine atoms are not only crystallographically different but also that they differ in chemical function and physical state in the structure. On the basis of the electron-density map this assumption was shown to be correct. Fortunately, owing to the symmetry relations in group $P2_13$, only one electron-density map was fully sufficient for the determination of all three parameters of each atom in the cell. Moreover, the oxygen atom peaks neatly appeared on the map so that it was possible to establish unambiguously the position of the oxygen atom and its relation to the neighbouring mercury atoms. It followed that every three mercury atoms in general positions were grouped round an oxygen atom with obvious trigonal symmetry, the Hg–O distance amounting to 2·03 Å (Table 4). To each mercury atom a

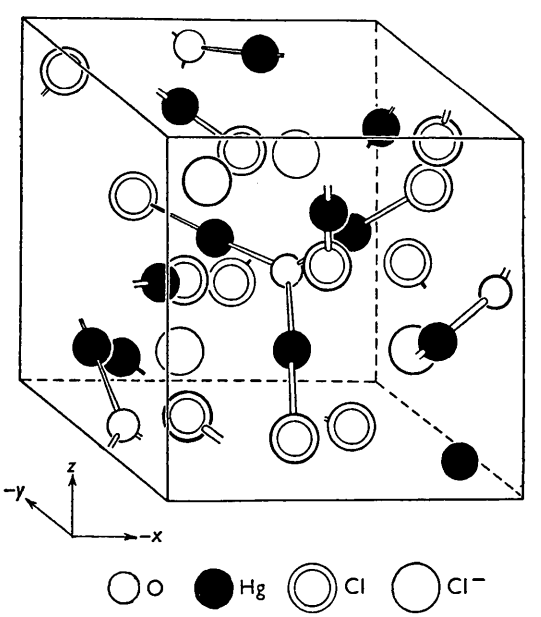


Fig. 3. View of the unit cell of trichlormercury oxonium chloride along $3\bar{1}0$ planes.

Table 3. *Observed and calculated structure amplitudes*

*hk*0	F_o	$\frac{1}{4}F_c$	*hk*0	F_o	$\frac{1}{4}F_c$	*hk*0	F_o	$\frac{1}{4}F_c$
200	47	+48	2,10,0	21	+16	570	26	+28
400	87	+99	2,11,0	18	−18	580	36	+35
600	61	−47	310	40	+37	590	18	−12
800	0	+ 4	320	48	+51	5,10,0	13	−11
10,0,0	4	− 6	330	53	−65	610	60	+56
020	42	−48	340	37	−35	620	17	−12
040	89	+98	350	35	+34	630	36	−41
060	62	+47	360	55	+59	640	56	−66
080	0	− 4	370	19	−14	650	15	−18
0,10,0	3	+ 6	380	0	0	660	0	+13
110	24	−33	390	29	−22	670	0	0
120	0*	+ 5	3,10,0	32	+31	680	40	−38
130	72	−93	3,11,0	9	+ 9	690	10	−14
140	44	+44	410	23	−16	6,10,0	0	− 4
150	0*	− 8	420	75	−88	710	74	+58
160	0*	+13	430	11	+ 8	720	28	+30
170	0*	− 7	440	15	+16	730	11	−10
180	41	+33	450	48	−50	740	31	−33
190	40	−40	460	0*	+ 5	750	52	+60
1,10,0	15	−11	470	0*	+ 4	760	17	+18
1,11,0	13	+16	480	13	−15	770	0	− 1
210	0*	−19	490	41	−35	780	12	− 8
220	49	+64	4,10,0	8	− 7	790	10	+10
230	42	−37	4,11,0	17	−13	810	0	+ 2
240	23	−29	510	52	+44	820	51	−54
250	33	−35	520	0*	−12	830	18	+16
260	90	+87	530	0*	+ 7	840	15	−13
270	25	−17	540	0*	− 3	850	20	−24
280	33	−26	550	41	+37	860	12	−11
290	21	−20	560	0	+ 4	870	35	+29
						880	13	− 8

* Not observed because of the great absorption.

chlorine atom is linked at a distance of 2·28 Å, the line joining oxygen, mercury and chlorine atoms being straight. From these distances it may be concluded that the bonds Hg–O and Hg–Cl are covalent. The Hg–O bond length is nearly equal to the sum of the covalent radii, 0·66 Å and 1·48 Å being taken as the covalent radii for oxygen and mercury atoms respectively (Pauling, 1940). The Hg–Cl bond has the same length as in mercuric chloride (Braekken & Scholten, 1934; Grdenić, 1950). The third bond to the oxygen atom is a coordinate bond with the oxygen atom as a donor. The consequence is the formation of positively charged oxonium ions $(ClHg)_3O^+$ which are held together in the structure by the chlorine anions (Fig. 3). Oxonium ions of this type, wherein all three atoms bounded to oxygen are metal atoms, are hardly known (e.g. tri-trimethyl-stannic oxonium halides (Harada, 1940)) and have not yet been investigated by X-ray methods. Trichlormercury oxonium chloride is now the first better known compound of this class, so that no comparison and discussion on its stereochemistry can be given. Nevertheless, an interesting feature concerning the bond angles at the oxygen atom is to be stressed. The trichlormercury oxonium ion is planar, the Hg–O–Hg angles being 120°. This planarity has not been expected and may be explained only by the assumption that O–Hg bonds are not truly covalent. For, in the case of true covalency, the pyramidal configuration ought to be expected owing to the hybridized p^3 bonds. In any case, the further investigation of oxonium compounds by X-ray methods is of stereochemical and crystallochemical interest.

Table 4. *Interatomic distances* (Å)

	Present authors	Weiss, Nagorsen & Weiss (1953*b*)
Hg–O	2·03	2·06
Hg–Cl	2·28	2·39
Hg · · · Cl^-	2·94	2·94
	3·13	3·18
Hg · · · Cl	3·14	3·26
	3·32	3·26
	3·43	3·28
Cl · · · Cl	3·56	
	3·64	

The Cl–Hg–O angle (175°) is slightly smaller than 180°.

The distances of a given chlorine anion from two neighbouring mercury atoms differ quite appreciably, being 2·94 and 3·13 Å. The former value is smaller than the sum of the van der Waals radii (3·20 Å). The remaining chlorine–mercury van der Waals distances are normal, being 3·14 and 3·33 Å.

The structure investigation of the other mercury oxy-halides by X-ray methods is in progress in our laboratory and results will be published shortly.

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Polymorphism in One Dimension*

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An admissible set of structures is defined to contain all stackings of rigid hexagonal nets at constant vertical interval with the nodes of each net centered on the nodes of the net below. The immediate environment of each net is either cubic or hexagonal. If V is the difference in potential energy between layers in the two environments, the ratio of the number of nets h to the number c is given by $n_h/n_c = \exp[-V/kT]$ (the Boltzmann factor). Setting this equal to $(1-D)/D$, a distribution function D is defined equal to the probability that a given layer is in the state c. By discarding the one-dimensional approximation, V becomes proportional to D and the polymorphism is cooperational with a critical temperature. By assuming a difference in interaction energy between two layers depending on whether the layers are in the same or in different states, the long-period polymorphs are shown to represent potential minima. The 15 observed polymorphs of silicon carbide are characterized by maximum numbers of interaction contacts between layers in unlike states.

The phase transformation proceeds over a temperature range by infinitesimal steps so that density and probability distribution vary continuously across a critical temperature while derivatives of these are discontinuous. An anomalous heat capacity replaces latent heat. Intermediate phases appear at simple proportions of layer types, unaccompanied by discontinuities.

Introduction

Polymorphism in one dimension, or polytypism (Baumhauer, 1915) is here treated as a cooperational phenomenon after the manner of Bragg & Williams (1934, 1935), and Bethe (1935), in their treatment of order–disorder in binary alloys. Fifteen silicon carbide polymorphs in one dimension are known. Seven zinc sulfide structures have been observed with the same periodicities reported for the silicon carbides. The theory implies the existence of other modifications of substances such as AgI and Cu_3AsS_4 already known to crystallize with structures parallel to those of zinc sulfide.

A satisfactory explanation of polymorphism in one dimension must account for the relative energies of the various polymorphs. I have first restricted the problem under consideration to a particular admissible set of structures. This limited set of structures contains closest packings of spheres and also all geometrically similar structures satisfying the condition that they may be related to rigid hexagonal nets stacked at constant vertical interval with the nodes of every net directly above the centers of triangles of the net below. These are true nets of equivalent points until they are stacked together. They are thereafter considered as layers. Ewald & Hermann (1931) observed

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