The Crystal Structure of Mercuric Oxychloride: $2HgCl_2 . HgO$

(A Preliminary X-Ray Examination)*

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The single crystals of the compound $2HgCl_2 . HgO$ were studied by the use of the X-ray methods. The dimensions of the unit cell quoted in the literature were confirmed. The crystals are cubic, the space group being T^4—$P2_13$. The twodimensional Patterson synthesis allowed the preliminary x, y coordinates of mercury atoms to be determined.

The complete X-ray analysis of this compound as well as of the other mercury oxyhalides is in progress.

Two different procedures for the preparation of mercuric oxychloride $2HgCl_2 . HgO$ had been hitherto reported. The first one is based on the slow action of the sublimate ($HgCl_2$) solution on the yellow mercuric oxide[1]. By the second, more intersting procedure, this oxychloride is prepared by leaving pieces of marble for several days in a sublimate solution at room temperature[2]. The latter method is especially convenient for preparing well developed single crystals since they grow freely on the raw marble faces or one the walls of the vessel.

It may also be of some interest to study the formation of this compound itself. After Lamure[3] it contains a molecule of water or mercuric hydroxide instead of mercuric oxide. It may therefore be a hydroxy-chloride.

From X-ray powder photographs Gawrych[4] allready determined that the crystals must be cubic with the cell edge $a = 9{\cdot}211$ Å. There is no report on other more detailed crystallographic or X-ray investigations.

Our goniometric measurements were in complete agreement with the cubic symmetry assumed by Gawrych. The crystal habit is cubic. The crystals are mainly regular rhombdodecahedrons, but the combinations with tetrahedral faces were also obserbed. Occasionally some crystals were slightly elongated in the axis direction. From the oscillation photographs about each crystallographic axis we obtained the same value: $a = b = c = 9{\cdot}22 \pm 0{\cdot}01$ Å for the lattice periodes. We used the nickel filtered CuK radiation (wave length taken as $\lambda = 1{\cdot}54$ Å). The density determined picnometrically was $6{\cdot}42$ g.cm^{-3}. The unit cell contains therefore 4 stoichiometric units of the formula Hg_3Cl_4O (the calculated density amounts to $6{\cdot}45$ g.cm^{-3}). The possible presence of water molecules may change the result by no more than 2%.

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The sysematic absence was observed only in the case of reflexions $h00$, $0k0$ and $00l$ with odd indices. The Bravais lattice is therefore primitive and from the space groups of cubic symmetry only T^4-$P2_13$ or O^2-$P4_232$ may occur. These groups can be well distinguished on the Laue photographs thanks to the different Laue symmetry groups to which they belong. Since on the Laue photographs taken along the crystallographic axis no diagonal symmetry planes had appeared, only the T^4 remains as the only possible cubic space group.

The total number of the equivalent points for the space group T^4 is 12 in the case of general positions and 4 in the case of special positions. To locate the 12 mercury atoms in the unit cell of this space group we have therefore two possibilities:

a) All mercury atoms in the general positions. Since in T^4 group there are triad axis as the only point group symmetry operators there should be four eqiuvalent groups of three mercury atoms, each group having a trigonal symmetry.

b) All mercury atoms located on the triad axis. In this case there should be four equivalent sets each of three independent mercury atoms in special positions.

It followed that no information about the structure elements of this oxychloride could be obtained from the unit cell and symmetry data only.

For evaluating the Patterson projection $P(x, y, 0)$ we recorded all possible reflexions of the [001] zone using a Weissenberg goniometer. The relative intensities were determined from the optical densities measured at the centre of each spot using a microphotometer (except those for very weak reflexions which were estimated visually) and with the help of the characteristic curves of the film. Because of the large apsorption power ($\mu = 124\ mm^{-1}$) an accurate absorption correction was obligatory. It was effected by means of the absorption factor formulae for prismatic crystals with the large linear absorption coefficient[5]. The prismatic form was given to the specimen by the method already described by one of the present authors[6]. For this purpose the chosen single crystal had been orientated on the object slide in the molten Canada balsam and was ground parallel to the [001] on each of the four rhombdodecahedron faces. In this way we succeded to obtain the specimen with the prismatic shape, the equatorial cross section of which was about 0·25 mm square.

The Patterson function

$$P(x, y, 0) = \sum_h \sum_k (F_{hk0})^2 \cos 2\pi(hx + ky)$$

was evaluated by the use of Beevers & Lipson strips at intervals of 1/60 of the cell edge. The contour map of its projection is given in Fig. 1. The origin is in the centre of symmetry i. e. y-coordinate differs from the one in the »Internationale Tabellen«* for 1/4. At first glance it is evident from the map that in the case of group T^4 mercury atoms cannot be located on the triad axis. If the opposite were true, the large mercury-mercury peaks would have appeared on the diagonals with the coordinates smaller then 1/2. For T^4 remains therefore only the possibility of locating the mercury atoms in general positions.

* Internationale Tabellen zur Bestimmung von Kristallstrukturen, Berlin 1935.

As the breadth of the peaks indicates, many overlappings of the maxima have occured. For this reason it was rather difficult to find the position even of the mercury atoms. At first we tried the method described by Lindqvist[7], but later the procedure devised by Bezjak[8] was successfully applied. The obtained x, y coordinates for mercury atoms are (origin as in »Internationale Tabellen«):

	x	y
Hg_1	0·575	0·280
Hg_2	0·469	0·579
Hg_3	0·272	0·479

In the case of the space group T^4 the relations: $x_1 = y_2$, $x_2 = y_3$, $x_3 = y_1$ must be satisfied. In the above set of coordinates this request is only approximately fulfilled. Since this coordinated had been obtained from Patterson synthesis, they are, of course, not very accurate. They will be used only as

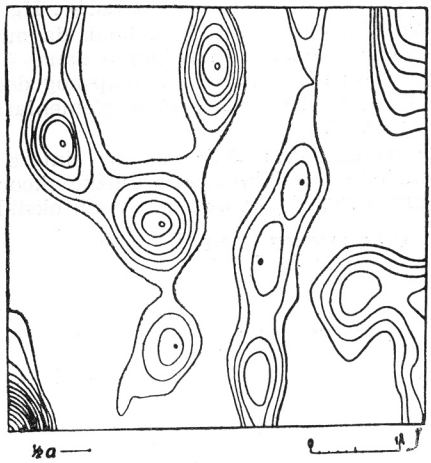

Fig. 1. Patterson projection on (001) plane. Contours are drawn at arbitrary intervals of 50.

preliminary parameters for evaluating the signs of the coefficients in the first Fourier synthesis. But, in this stage of analysis the pseudocubic symmetry is also to be supposed. The orthorhombic space group $D_4^2 - P2_12_12_1$ must be in this case taken into account for it satisfied the observed extinctions. It is to be noted that a Laue photograph taken afterwards along the direction [111] showed the triad axis symetry.

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IZVOD

Kristalna struktura živinog oksiklorida: $2HgCl_2 . HgO$ (Prethodno rentgenografsko istraživanje)

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Kristalna rešetka kao i struktura živinih oksiklorida, koji općenito imaju formulu $mHgCl_2 . nHgO$, do danas nije poznata. Te su rešetke od osobitog interesa u kristalokemijskom pogledu, jer su sastavljene od komponenata, koje same za sebe imaju temeljito različite kristalne rešetke. Kao prvi objekt naših istraživanja na tom području odabrali smo oksiklorid bruto-formule $2HgCl_2 . HgO$.

Monokristali toga oksiklorida priređeni su tako, da mramor stoji u zasićenoj otopini sublimata kod obične temperature nekoliko dana[1, 2]. To su bezbojni sjajni kristali kubičnog sustava[4], obično kombinacije rompskog dodekaedra i tetraedra, a pripadaju tetartoedrijskoj grupi $T^4 - P2_13$. Brid elementarne ćelije iznosi 9,22 Å, kako je to već i prije utvrđeno[4].

Interpretacija dvodimenzionalne Pattersonove sinteze provedena je pomoću »vektorsko algebarske metode«[8] i dobivene približne koordinate živinih atoma. Dalje istraživanje strukture ovoga kao i drugih živinih oksiklorida je u toku.

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