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The Structure of Hexagonal Mercury(II)oxide

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The crystal structure of hexagonal mercury(II)oxide has been determined by means of X-ray and neutron diffraction methods. The symmetry is $P3_121$ (No. 152) or the enantiomorphous symmetry $P3_221$ (No. 154). The structure is built up of infinite spiral chains $(-\mathrm{O}-\mathrm{Hg}-)_n$ running parallel to the c axis of the hexagonal unit cell. Within the chains, the Hg-O distance is 2.03 ± 0.02 Å and the angles O−Hg−O and Hg−O−Hg are 176° ± 3° and 108° ± 2°, respectively. The structure is analogous to that of hexagonal mercury (II) sulphide (cinnabar).

In addition to the well-known orthorhombic modification of mercury(II) oxide, the structure of which was reported in a previous article [1], another form of hexagonal symmetry was recently described by Laruelle [2]. The crystal structure of the latter has now been determined by means of X-ray and neutron diffraction methods.

PREPARATION AND ANALYSIS

The hexagonal modification of mercury(II)oxide was synthesized according to Laruelle[2] by adding sodium hydroxide to a solution of K_2HgI_4, containing an excess of KI. The experimental conditions, such as concentrations and temperature, were varied within wide limits. The best method for preparing a pure sample of hexagonal mercury(II) oxide was to mix one part of 0.1 M K_2HgI_4, containing an excess of 0.025 M KI, with two parts of 5.5 M NaOH or KOH at about 50°C and to keep the solution at this temperature for about 100 h. The purity of the sample was checked by means of X-ray powder photographs. Identical preparations were also obtained by substituting rubidium or caesium for the potassium or sodium ions. It was, however, not possible to prepare hexagonal HgO from a solution of Li_2HgI_4, LiI and LiOH, probably because of the relatively low solubility of LiOH. The hexagonal modification mostly crystallized in spherical conglomerates of extremely small red crystals but sometimes it sedimented as a yellow powder. The preparations were not always pure but were sometimes mixed with orthorhombic mercury(II)oxide or with other phases probably containing alkali. Occasionally, red transparent plates appeared. They were always found to be built up of both hexagonal and orthorhombic mercury(II)oxide.

The pure sample described above was analysed for Hg, Na, K, I and H_2O and was found to contain neither alkali, iodine nor water. The result of the mercury analysis performed using electrolysis was 92.1 % in fair agreement with the value of 92.6 % calculated for HgO.

CELL DIMENSIONS AND SYMMETRY

The powder photographs were taken in a Guinier focussing camera of 80 mm diameter using monochromatic Cu$K\alpha_1$ radiation and potassium chloride (a = 6.2930 Å)[3] as an internal standard. The powder pattern is given in Table 1. Amply exposed photographs (3 h) did not show any lines that were not visible in normally exposed ones (1 h). The powder pattern could be interpreted by means of a hexagonal unit cell with the cell dimensions:

Table 1. Powder photograph of HgO. Cu$K\alpha_1$ radiation.

hkl	$\sin^2\Theta_{\rm obs}$	$\sin^2\Theta_{\rm calc}$	$I_{\rm obs}$
100	0.0618	0.0618	m
101	0.0697	0.0697	vst
003	0.0708	0.0709	m+
102	0.0934	0.0933	vst
103	0.1327	0.1327	w
110	0.1854	0.1855	m
104	0.1879	0.1878	m
111	0.1932	0.1934	m
112	0.2169	0.2170	w
200	0.2475	0.2473	vvw
201	0.2564	0.2552	st
113		0.2563	
105	0.2588	0.2587	m
202	0.2788	0.2788	m
006	0.2833	0.2834	w
114	0.3115	0.3115	vw
203	0.3181	0.3182	vw
106	0.3454	0.3453	vvw
204	0.3733	0.3733	w
115	0.3823	0.3823	vw
210	0.4330	0.4328	w+
211	0.4408	0.4407	vw
205	0.4441	0.4441	vw

$$a = 3.577 \text{ Å} \qquad c = 8.681 \text{ Å} \qquad V = 96.2 \text{ Å}^3$$

The observed density 11.0 indicates a cell content of 3 formula units of HgO (calculated density 11.2).

The only crystals that were large enough for single crystal studies with the equipment available were obtained from samples containing both forms of the oxide. Several crystals were investigated and found to be composed of individuals of both modifications. However, a Weissenberg photograph was finally taken, registering both the reflexions $h0l$ of hexagonal HgO and $hk0$ of orthorhombic HgO.

The only systematic extinction found in the powder and Weissenberg diagrams of hexagonal HgO was $00l$ absent for $l \neq 3n$, which is characteristic of the space groups $P3_112$ (No. 151), $P3_121$ (No. 152), $P3_212$ (No. 153) and $P3_221$ (No. 154). Because the unit cell contains 3 formula units of HgO, both the mercury and oxygen atoms must occupy threefold point positions 3(a) and/or 3(b). Since the (a) and (b) point positions only differ with respect

Table 2. Observed X-ray intensities *hkl* from the powder sample of HgO examined with a Geiger-Mueller diffractometer. The intensities are calculated: I) for the mercury atoms only, neglecting the influence of the oxygen atoms; II) for both the mercury and oxygen atoms. In each case, I_{calc} was normalized so as to give the best agreement with I_{obs}. A correction factor for each reflexion was taken from a curve where log I_{obs}/I_{calc} was plotted against $\sin^2\Theta$.

hkl	I_{obs}	$(I_{calc})_I$	$(I_{calc})_{II}$
100	29	41	33
101 $10\bar{1}$ 003	395	350	376
102 $10\bar{2}$	157	202	204
103 $10\bar{3}$	25	25	28
110 104 $10\bar{4}$ 111	127	131	129
112	13	21	18
200 201 $20\bar{1}$ 113 105 $10\bar{5}$	110	114	106
202 $20\bar{2}$ 006	57	37	36
114 203 $20\bar{3}$	15	15	15
106 $10\bar{6}$	3	4	3
204 $20\bar{4}$ 115	14	21	20
210 211 $21\bar{1}$ 205 $20\bar{5}$ 107 $10\bar{7}$	58	43	42
212 $21\bar{2}$ 116	18	21	19
213	15	18	16
300 214 $21\bar{4}$ 301 $30\bar{1}$ 108 $10\bar{8}$ 117	31	23	21

to the choice of origin, 3(*a*) was arbitrarily chosen as the site of the mercury atoms. For these point positions, the two groups with enantiomorphous symmetry ($P3_121$ and $P3_221$) and ($P3_112$ and $P3_212$) differ with respect to the structure amplitudes of the reflexions $h0l$ and $h0\bar{l}$, which are different for the former but assume identical values for the latter space-groups. Actually the intensities I_{h0l} differed from $I_{h0\bar{l}}$, as judged from the Weissenberg diagram, which suggested the symmetry to be $P3_121$ (or $P3_221$) in accordance with the data given by Laruelle [2]. Due to the composite character of the crystal, which was likely to give rise to serious absorption effects, this observation could not be considered conclusive. By means of neutron diffraction data (*v. infra*), however, it was possible to confirm the symmetry.

THE POSITIONS OF THE MERCURY ATOMS

Accurate values for the intensities of the X-ray powder reflexions were obtained by means of a Hilger Y 115 G.M. diffractometer, using Cu$K\alpha$ radiation. The sample was carefully ground and mounted in a cavity in an aluminium holder and the specimen was adjusted to the reflexion position. The intensities of the diffraction peaks were measured at counter intervals of 1°/60 scattering angle. The observed intensities obtained by measuring the areas under the peaks are given in Table 2. For overlapping reflexions, the sum of the intensities is given.

In the following the structure will be discussed in terms of the symmetry $P3_121$. The parameter value x for the mercury atoms in 3(a) was derived by trial and error, the best accordance between calculated and observed intensities being obtained for $x = 0.745$ (*cf.* Table 2).

THE POSITIONS OF THE OXYGEN ATOMS

The difference between mercury and oxygen in their scattering power for X-rays is considerable and this made it impossible to locate the latter from the observed intensity data. The relative scattering powers of the two elements for neutrons are much more favourable.

Scattering amplitude[4] *(10^{-12} cm)*

	Neutron	X-ray ($\Theta = 0°$)
Hg	1.31	22.5
O	0.58	2.25

The amplitude values for neutrons are independent of the scattering angle, while those for X-rays decrease with Θ and relatively more so for oxygen than for mercury.

The neutron diffraction work was carried out on a powder sample in a flat aluminium container. The reactor was run at a level of 450 kW. The diffracted intensity was measured at intervals of 0.2° scattering angle, counts being taken during the time necessary for accumulating 200 000 neutron counts from the monitor in the incident monochromator neutron beam. The appearance of the curve obtained by plotting the counts against the angles is given in Fig. 1. The observed intensities, obtained by measuring the areas under the peaks with a planimeter and corrected for the small contribution of the intensities of the aluminium reflexions 111 and 200 from the container, are given in Table 3. Due to serious overlapping, the intensities of reflexions at higher Θ angles could not be evaluated.

From space considerations, it was found that both mercury and oxygen atoms cannot occupy the same point position (3(a)) since this would give mercury-oxygen distances shorter than $a/2 \sim 1.8$ Å. The only point position left for the oxygen atoms is thus 3(b). Systematic variation of the parameter for the oxygen atom position gave the best agreement between observed and calculated intensities when x_0 was equal to 0.46 (Table 3). The neutron intensities of the reflexions were calculated according to Bacon[4], the temperature factor, however, being neglected. (The R index for the data given in Table 3 was found to be 0.7 %. This means, of course, that the agreement is good

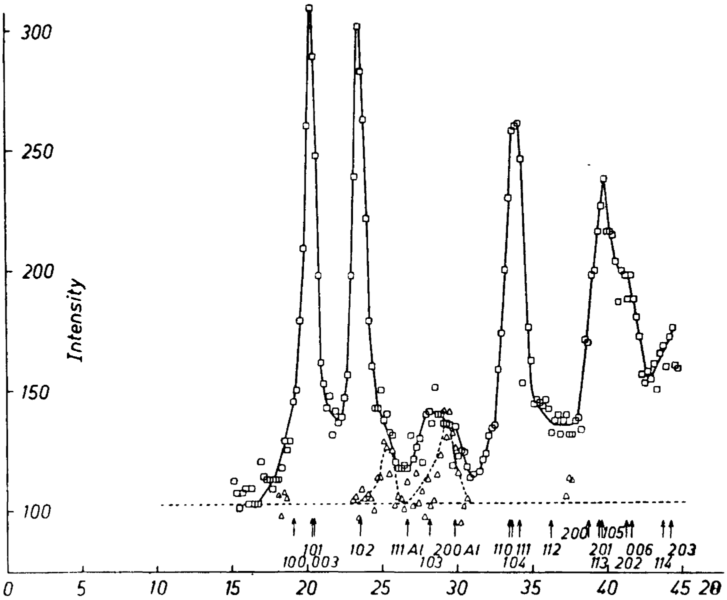

Fig. 1. Neutron diffraction powder diagram of a sample of hexagonal mercury(II) oxide in an aluminium container.

Table 3. Observed neutron intensities from a powdered sample of HgO in a flat aluminium container. The reflexions 102 and 103 are corrected for the small contributions of the aluminium reflexions 111 and 200. The calculations are made according to Bacon [4]. No correction was made for thermal vibrations. The value μt was found by measurement to be 1.23. The intensities are calculated: I) for the mercury atoms only, neglecting the influence of the oxygen atoms; II) for both the mercury and oxygen atoms. In each case I_{calc} was normalized so as to give the best agreement with I_{obs}.

hkl	I_{obs}	$(I_{\text{calc}})_{\text{I}}$	$(I_{\text{calc}})_{\text{II}}$
100 101 $10\bar{1}$ 003	324	497	321
102 $10\bar{2}$	331	251	334
103 $10\bar{3}$	74	39	73
110 104 $10\bar{4}$ 111 112	375	318	374

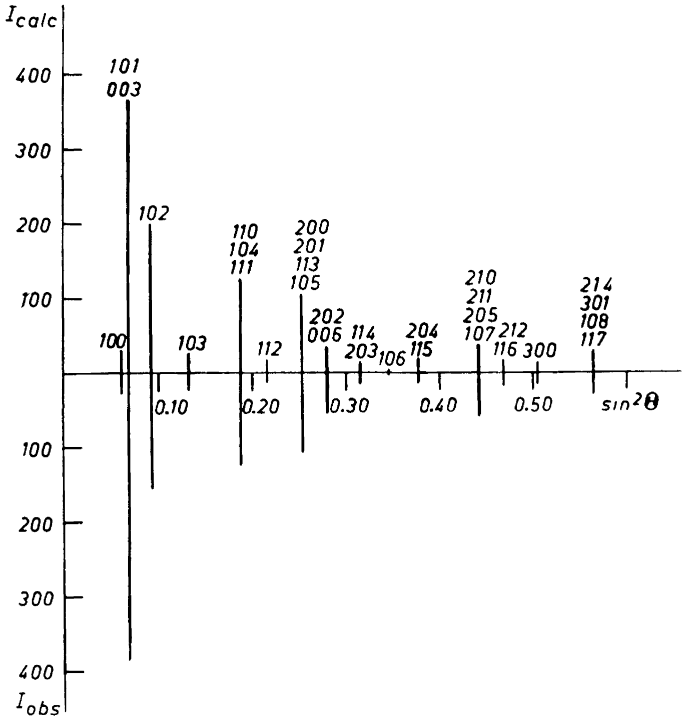

Fig. 2. Comparison between observed and calculated X-ray intensities of the reflexions *hkl* registered in a powder diffractogram of hexagonal mercury(II) oxide.

but the small number of reflexions implies that the *R* index is lacking in statistical significance.)

The X-ray intensities of the reflexions *hkl* were now recalculated, the influence of the oxygen atoms being also taken into account (*cf.* Table 2 and Fig. 2). In this way the agreement between calculated and observed intensities was improved. (The *R* index for the data given in Table 2 was thus found to decrease from 16.3 % to 13.0 %.)

DESCRIPTION OF THE STRUCTURE

The following structure for the hexagonal modification of mercury(II) oxide has been arrived at:

Cell content: 3 HgO.
Symmetry: $P3_121$, No. 152 or $P3_221$, No. 154.
Space-group $P3_121$; 3 Hg in 3(*a*): $x0\frac{1}{3}$; $0x\frac{2}{3}$; $\bar{x}\bar{x}0$ $x = 0.745$
3 O in 3(*b*): $x0\frac{5}{6}$; $0x\frac{1}{6}$; $\bar{x}\bar{x}\frac{1}{2}$ $x = 0.46$

The structure is built up of infinite spiral chains, $(\text{—O—Hg—})_n$, running parallel to the *c* axis of the hexagonal unit cell (*cf.* Figs. 3 and 4).

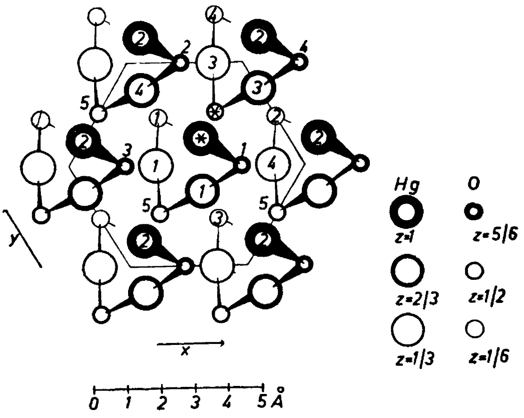

Fig. 3. Projection parallel to [00*l*] of the structure of hexagonal mercury(II) oxide. The diagram shows the coordination of the atoms. The large circles indicate mercury atoms and the smaller ones oxygen atoms.

Every mercury atom (*e.g.* Hg *, $(\bar{x}\bar{x}0)$ in Fig. 3) is surrounded by:

2	O	(1)	at	2.03 ± 0.02 Å
2	O	(2)		2.79 ± 0.02 Å
2	O	(3)		2.90 ± 0.03 Å
2	Hg	(1)		3.30 ± 0.02 Å
6	Hg	(2)		3.58 Å = *a*
4	Hg	(3,4)		3.72 ± 0.02 Å

The oxygen atoms around each mercury form a greatly distorted octahedron. Every oxygen atom (*e.g.* O *, $(\overline{xx}\frac{1}{2})$ in Fig. 3) is surrounded by:

2	Hg	(3)	at	2.03 ± 0.02 Å
2	Hg	(4)		2.79 ± 0.02 Å
2	Hg	(1)		2.90 ± 0.02 Å
2	O	(4)		4.06 ± 0.04 Å
6	O	(5)		3.58 Å = *a*
4	O	(1,2)		3.41 ± 0.02 Å

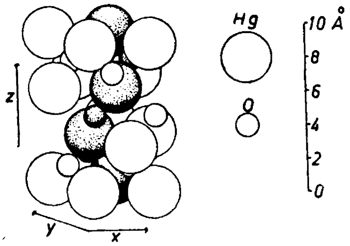

Fig. 4. Diagram showing the spiral chain $(-\mathrm{Hg}-\mathrm{O}-)_n$ which extends parallel to the *c* axis of hexagonal mercury(II)oxide.

The angles within the chains are:

Hg — O — Hg 108° ± 2°
O — Hg — O 176° ± 3°

The Hg—O distance found within the chain and the bond angles are nearly the same as those found in the planar zig-zag chain of orthorhombic mercury(II) oxide [1]. Thus, for the hexagonal modification, it can also be suggested that the bond between the Hg and O atoms within the chain is mainly homopolar. The forces between the chains are far weaker since the interatomic distances are considerably larger than those within the chains. It is probable that the chains support each other by means of these Hg—O contacts.

A comparison between the structures of hexagonal mercury(II)oxide and hexagonal mercury(II)sulphide (cinnabar [5]) indicates that these compounds are isostructural.

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