On the Crystal Structure of Cinnabar

KARIN LUNDBORG AURIVILLIUS

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

PREVIOUS WORK ON MERCURY (II) HALIDES AND MERCURY (II) CHALCOGENIDES

In connection with an X ray investigation of mercury (II) oxyhalides it seemed of interest to review what is known about the type of bond between bivalent mercury and metalloids of group VII b (halogens) and VI b (chalcogens). As seen from the following retrospect much work has been done on the halogen compounds HgX_2 but relatively meagre data are available on the mercury compounds containing O, S, Se and Te.

From powder photographs of crystalline HgF_2 Ebert and Woitinek[1] concluded that this compound is isomorphous with CaF_2. The F atoms, however, contribute very sparsely to the intensities, so their positions can not be regarded as proved. With the structure of Ebert and Woitinek every Hg atom is surrounded by 8 F atoms in a cubical arrangement and every F tetrahedrically by 4 Hg atoms in the distance 2.4_0 kX and thus the structure probably is built up from Hg^{2+} and F^- ions. If this is so, HgF_2 forms an exception from the other mercury (II) halides, where mercury is coordinated with two and in one case with four X atoms.

By X ray methods crystalline $HgCl_2$ and $HgBr_2$ have been found to be molecular compounds; each molecule HgX_2 can be regarded as linear ($HgCl_2$: Braekken and Harang[2], Nieuwenkamp and Bijvoet[3], Braekken and Scholten[4]. $HgBr_2$: Verweel and Bijvoet[5]).

The distance Hg → Cl is 2.25 kX (Braekken and Scholten[4]) and Hg → Br 2.48 kX (*Strukturbericht 1928—1932*, p. 19).

Yellow HgI_2, which is stable above 127° (Smits[6]) is isomorphous with $HgBr_2$ (Verweel and Bijvoet[5], Gorskiï[7]). The distance Hg → I has been calculated to be 2.62 kX (Gorskiï).

In the vapour state the compounds HgX_2 are also found to be linear or nearly linear. The following distances are found from electron interference studies on HgX_2 (gas):

$Hg \rightarrow Cl$ 2.2_8 kX, $Hg \rightarrow Br$ 2.3_8 kX, $Hg \rightarrow I$ 2.5_5 kX (Braune and Knoke [8])
$Hg \rightarrow Cl$ 2.3_4 kX, $Hg \rightarrow Br$ 2.4_4 kX $Hg \rightarrow I$ 2.6_1 kX (Gregg *et al.*[9]).

In red HgI_2, stable at ordinary temperature, a new type of coordination occurs. Thus every Hg atom is surrounded tetrahedrically by 4 I (Havighurst [10], Bijvoet, Classen and Karssen [11], Classen [12], Huggins and Magill [13]). The distance $Hg \rightarrow I$ is 2.78 kX (*Strukturbericht 1913—1928*, p. 180).

According to Wells [14], [p. 514] the colinear bonds (in $HgCl_2$ (s), $HgBr_2$ (s), yellow HgI_2 (s) and the gaseous molecules) are sp bonds, whereas the tetrahedral bonds in red HgI_2 are sp [3] bonds.

The mercury (II) oxide can be prepared with two colours, yellow and red. It has been discussed by several authors if the yellow and the red oxides are identical or not (Gay-Lussac [15], Ostwald [16], [17], Varet [18], Cohen [19], Hulett [20], Schick [21], Fuseya [22], Levi [23], [24], Goldschmidt [25], Fricke [26], Zachariasen [27], Kolkmeijer [28], [29]).

The conclusion is that the oxides are identical compounds; they give the same powder photographs and differ only in the grain size. The division of the yellow oxide is, however, finer than of the red one.

The structure of HgO is orthorhombic. Zachariasen [27] has approximately fixed the positions of the Hg atoms ($x_{Hg} \approx \frac{1}{4}$) and discussed a few possibilities for the positions of the O atoms.

Of the mercury (II) sulphide two modifications are known; the red cinnabar and the black metacinnabar.

Metacinnabar is cubic. The structure is of the B 3 type, thus isomorphous with ZnS (blende) (Kolkmeijer, Bijvoet and Karssen [30], Lehmann [31], v. Olshausen [32], Buckley and Vernon [33], Hartwig [34], Goldschmidt [25], [35]).

The Hg atoms, therefore, are tetrahedrically surrounded by S atoms; the distance $Hg \rightarrow S$ is 2.52_5 kX ($a\frac{\sqrt{3}}{4}$) since $a = 5.83_2$ kX (Goldschmidt [35]).

HgSe and HgTe are isomorphous with metacinnabar and have the cell edges $a_{HgSe} = 6.06_8$ kX and $a_{HgTe} = 6.44_0$ kX. The distance $Hg \rightarrow Se$ is 2.62_8 kX and $Hg \rightarrow Te$ 2.78_9 kX (*Strukturbericht 1913—1928*, p. 77) (Zachariasen [36], Hartwig [34], Goldschmidt [25], [35], de Jong [37]).

The four tetrahedral bonds the mercury atom forms in HgS (metacinnabar), HgSe and HgTe are probably sp [3] bonds as in red HgI_2.

In the mercaptides $Hg(SC_2H_5)_2$, $Hg(SC_4H_9)_2$ and $Hg(SC_8H_{17})_2$ the bonds S-Hg-S form straight or almost straight lines and are thus probably sp bonds. The distance Hg → S was calculated to be 2.5_0 kX from a Fourier projection, assuming the S-Hg-S bonds to be exactly colinear (Wells [38]).

The other form of HgS, cinnabar, is hexagonal. By various authors, values for a have been reported from 4.12 to 4.16 kX and for c from 9.43 to 9.54 kX. A structure has been proposed which is denoted by *Strukturbericht* as B 9 (Mauguin [39], v. Olshausen [32]).

The space groups proposed are D_3^4 or D_3^6, which give left handed or right handed spirals (Buckley and Vernon [33], de Jong and Willems [40]).

With D_3^4 the point positions are:

$$3 \text{ Hg in } 3 \text{ (a): } x_1 \ 0 \ \tfrac{1}{3}, \ 0 \ x_1 \ \tfrac{2}{3}, \ \bar{x}_1 \ \bar{x}_1 \ 0 \text{ and}$$
$$3 \text{ S } \text{ in } 3 \text{ (b): } x_2 \ 0 \ \tfrac{5}{6}, \ 0 \cdot x_2 \ \tfrac{1}{6}, \ \bar{x}_2 \ \bar{x}_2 \ \tfrac{1}{2}$$

For cinnabar no direct determination of the distances Hg → S has hitherto been made. The positions of the S atoms have been fixed by assuming the same distance Hg → S as found for metacinnabar. This distance is about the same as the sum of the atomic radii for covalent tetrahedral structures according to Pauling [41] (Hg = 1.48 kX, S = 1.04 kX).

From intensity calculations based on powder photographs Buckley and Vernon [33] found the value $x_1 \approx \tfrac{1}{3}$. With $x_2 = 0.21$ for the S parameter the same distance Hg → S was obtained as found in metacinnabar. This x_2 value also seemed to suit the intensities best.

From powder photographs de Jong and Willems [40] could conclude that x_1 is in one of the ranges 0.25—0.40 or 0.60—0.75 but could draw no conclusion as to the value of x_2. They found that with a coordination Hg → 6S or Hg → 4S, the Hg → S distances would be unbelievably long. They thus assumed that each Hg has 2 nearest S neighbours and that the distance Hg → S is 2.52 kX (the sum of the *tetrahedral* atomic radii!). They finally arrived at the values $x_1 = 0.72_5$ and $x_2 = 0.55$.

In the present work the author has tried to redetermine the positions of Hg and S in cinnabar with the aid of intensity calculations only, and without any previous assumption about distances and coordination. Work on HgO and Hg oxyhalides is in progress.

MATERIALS

For the X ray measurements of this investigation native cinnabar was used, which was kindly supplied by Professor S. Gavelin of the Mineralogical Institute, University of Stockholm.

For getting single crystals, suitable for X ray investigation, the native cinnabar crystal conglomerate was crushed. A number of fragments were picked out and examined by Laue photographs before two acceptable single crystals were found.

Reflexions, which should have the same intensities according to the Laue symmetry, showed different values because of the fact that the shape of the crystals (flat needles) did not show the same symmetry as the reciprocal lattice, and therefore the observed absorption shows a lower symmetry, too.

Of course the asymmetrical absorption effects might be diminished by grinding the crystal to cylindrical form, but it seemed that the single crystals available were too tiny for such a procedure.

Attempts to synthesize HgS crystals, suitable for X ray analysis, were not successful. Only microcrystalline cinnabar was obtained.

This synthetical cinnabar gave powder photographs identical with those of native cinnabar.

UNIT CELL AND SPACE GROUP

The dimensions of the unit cell were determined accurately from the powder photographs with CrKα radiation and focussing cameras of the Phragmén-Westgren type (Table 1).

The powder photographs could be interpreted with a hexagonal unit cell with:

$$a = 4.137 \text{ kX} = 4.146 \text{ Å}$$
$$c = 9.477 \text{ kX} = 9.497 \text{ Å}$$
$$V = 140.4_6 \text{ kX}^3 = 141.3_6 \text{ Å}^3 \qquad \text{Accuracy about } 0.05 \text{ \%}$$

The cell dimensions according to de Jong and Willems (1926) are $a = 4.12$ kX $c = 9.43$ kX.

The density according to Allen and Crenshaw[42] is 8.176, thus allowing 3 formula units per unit cell (calculated density 8.19_8).

Laue photographs, rotation and Weissenberg photographs around (001) (zero layer and first layer) and (010) (zero layer) were taken. From the Laue photographs, (incident beam parallel to the threefold axis) the Laue symmetry was found to be D_{3d}—$\bar{3}m$. The only systematic extinction found was that 00l was absent for $l \neq 3n$, which is characteristic of the space groups D_3^{3-6}.

Because the unit cell contains 3 formula units and because cinnabar has a definite composition the only way to get an ordered structure was to assume the Hg atoms occupy one threefold point position. For each of the space

Table 1. Powder photographs of HgS (cinnabar). CrKα radiation.

hkl	$10^4\sin^2\Theta_{calc.}$	$10^4\sin^2\Theta_{obs.}$	$I_{obs.}$	hkl	$10^4\sin^2\Theta_{calc.}$	$10^4\sin^2\Theta_{obs.}$	$I_{obs.}$
100	0.1018	0.1007	w	006	0.5238	0.5247	w
101	.1163	.1150	vst	203	.5381	.5386	m
003	·.1310	(.1301)	(st)	106	.6256	—	—·
102	.1600	.1586	vst	204	.6399	.6400	st
103	.2327	.2320	vw	115	.6691	.6688	vvw
110	.3053	.3056	st	210	.7125	.7121	w
111	.3199	.3204	m	211	.7270	.7270	m
104	.3346	.3358	st	212	.7707⎫		
112	.3635	(.3624)	(m)	205	.7709⎭	.7707	m
200	.4071	—	—	107	.8147	.8149	w
201	.4217	.4221	st	116	.8291	.8302	w
113	.4363	.4368	st	213	.8434	· .8434	w
202	.4653⎫						
105	.4655⎭	.4655	st				

In the list of the powder photographs, the reflexions systematically absent and the β reflexions have been omitted. If a tabulated reflexion coincides with a β reflexion, the sin² $\Theta_{obs.}$ and the observed intensity of the resulting line are given in brackets. The observed intensities are indicated as follows: vst = very strong, st = strong, m = medium, w = weak, vw = very weak and vvw = very, very weak.

groups D_3^{3-6} two different sets of threefold point positions 3 (a) and 3 (b) are possible. However, on displacing the origin of the unit cell by $c/2$ the positions 3 (a) could be made identical with the positions 3 (b). It was thus arbitrarily assumed that the Hg atoms are situated in 3 (a) with the coordinates:

$$D_3^3: \quad x_1 \ \bar{x}_1 \ 0, \ x_1 \ 2x_1 \ \tfrac{1}{3}, \ 2\bar{x}_1 \ \bar{x}_1 \ \tfrac{2}{3}$$
$$D_3^5: \quad x_1 \ \bar{x}_1 \ 0, \ x_1 \ 2x_1 \ \tfrac{2}{3}, \ 2\bar{x}_1 \ \bar{x}_1 \ \tfrac{1}{3}$$
$$D_3^4: \quad x_1 \ 0 \ \tfrac{1}{3}, \ 0 \ \ x_1 \ \tfrac{2}{3}, \ \bar{x}_1 \ \bar{x}_1 \ 0$$
$$D_3^6: \quad x_1 \ 0 \ \tfrac{2}{3}, \ 0 \ \ x_1 \ \tfrac{1}{3}, \ \bar{x}_1 \ \bar{x}_1 \ 0$$

The space group D_3^3 or D_3^5 being assumed, maxima for the following x values are expected, according to the interatomic distances Hg → Hg and Hg → S in the Patterson projections $P(xpz)$; $z = \tfrac{1}{6}$, $\tfrac{1}{3}$ and $\tfrac{1}{2}$ (Table 2).

Thus if the Hg atoms are arranged according to space groups D_3^3 or D_3^5, the Patterson projections $P(xpz)$ (Table 2) would be symmetrical curves. However, such symmetrical projections can only be expected if $I_{h0l} = I_{\bar{h}0\bar{l}}$

Table 2. *Expected maxima, due to interatomic distances* $Hg \rightarrow Hg$ *and* $Hg \rightarrow S$ *in* $P (xpz)$, *space groups* D_3^3 *and* D_3^5 *being assumed.* x_1 *is the Hg parameter and* x_2 *is the S parameter.*

Projection	Expected x value for the maxima	
	$Hg \rightarrow Hg$	$Hg \rightarrow S$
$P\ (xp\,\frac{1}{6})$		$\pm\ (x_1 - x_2)$ $\pm\ (x_1 + 2x_2)$ $\pm\ (2x_1 + x_2)$
$P\ (xp\,\frac{1}{3})$	$\pm\ 3x_1$ 0	
$P\ (xp\,\frac{1}{2})$		$\pm\ (x_1 - x_2)$ $\pm\ 2(x_1 - x_2)$

and $I_{h0l} = I_{h0\bar{l}}$. Actually, $I_{h0l} \neq I_{h0\bar{l}}$, as seen from the reflexions $h0l$. Therefore D_3^3 and D_3^5 can be excluded.

The point positions in D_3^4 are mirror images of those in D_3^6 (Fig. 1). On calculating the intensities from the structure factors A and B (*International tables* [43]), D_3^4 and D_3^6 give the same result if the signs of the parameters are reverted ($x\ y\ z$ in D_3^4 correspond to $\bar{x}\ \bar{y}\ \bar{z}$ in D_3^6).

As seen from Fig. 1, with the threefold point positions of D_3^4 the atoms will be coiled into lefthanded spirals and with those of D_3^6 into right handed spirals, if the xyz axes form a right coordinate system (as in the *International tables*).
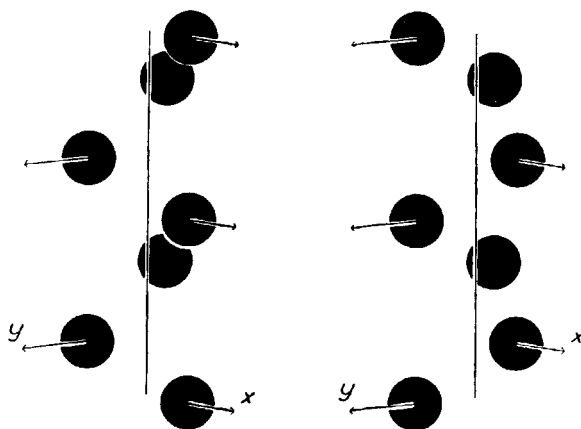

Figure 1. *Spiral chains of the mercury atoms of HgS (cinnabar). The Hg atoms are arranged according to space groups* D_3^4 *(left) and* D_3^6 *(right). The arrows point in the direction of the x and y axes.*

The optical rotating power of cinnabar crystals has been investigated by several authors (des Cloizeaux[44], Wyrouboff[45], Tschermak[46], Melville and Lindgren[47], Becquerel[48], Rose[49]).

According to these authors both dextrorotary and laevorotary cinnabar crystals exist. By the X ray methods it is not possible to distinguish between D_3^4 and D_3^6, nor to decide which of the dextrorotary crystal and the laevorotary crystal crystallizes with the symmetry D_3^4 and which with D_3^6.

As mentioned above the same structure factors are obtained for D_3^6 as for D_3^4. Therefore only the space group D_3^4 is considered in the following.

METHOD OF ATTACK

An attempt was first made to determine the parameters by the method of trial and error. This proved to be very laborious, due to the complicated form of the structure factors A and B. Moreover, on account of the asymmetrical absorption it was difficult to compare the calculated values of I with those observed. It seemed that the best way of attacking the structure problem was to use Patterson and Fourier analysis.

If several different projections are used for the determination of the parameters, the intensities of quite a large number of reflexions will be considered. Errors in visually estimated intensities will cause a spread of the values of the parameters obtained from these different projections. In the average value of the parameters, it may be hoped that the errors, caused by the intensities, have partially cancelled out.

The following Patterson projections were computed: $P(xpz)$ with $z = \frac{1}{6}$, $\frac{1}{3}$ and $\frac{1}{2}$, based on the reflexions $h0l$ and $P(x0p)$ and $P(2xxp)$, based on the reflexions $hk0$.

The Patterson projections were calculated using both values of I and "F^2" (see p. 1420). From the Patterson projection $P(xp\frac{1}{3})$ (Table 5) a preliminary value of the Hg parameter was obtained and, with the aid of this value, the signs of the amplitudes of the reflexions could be calculated.

Then Fourier analyses were computed, based on "F" ($\sqrt{\text{"}F^2\text{"}}$) values for the reflexions equivalent to $h00$, $h\bar{h}0$ etc. and for $h0,3L$ ($l = 3L$, $L =$ whole number) and on the obtained signs of the amplitudes. If only these reflexions are considered, the Fourier analysis will give a density function ϱ_3 which can be referred to a hypothetical unit cell with a centre of symmetry in the projection ϱ_3 $(xp\bar{Z})$ (p. 1421—24).

The zero level is unknown in the curves obtained from the Patterson and Fourier projections, and false maxima may be introduced because of the limited number of reflexions used. However, the highest maxima in the curves

will probably give rather accurate values for the positions of the Hg atoms and it seems that the minor peaks might give information on the positions of the S atoms. If the maxima of different projections give the same values for the parameters of Hg and S, this will add to the probability of these values.

With the aid of mean values of x_1 and x_2, calculated from all these projections the value of the phase angle α_{h0l} for every reflexion $h0l$ was computed. Then it was possible to calculate a Fourier synthesis based on all reflexions $h0l$ and to obtain more accurate values for the parameters of Hg and S (p. 1426—28).

INTENSITIES

The values of I_{h0l} and I_{hk0} were estimated visually from the Weissenberg photographs.

In order to reduce the errors introduced by the absorption effects, average values of I were used for reflexions which should have the same intensities because of the Laue symmetry $D_{3d}\text{-}\bar{3}m$ (Table 3).

"F^2" for each reflexion was calculated from "F^2" $= I/f$, where I is the estimated value of the intensity, $f = 1 + \cos^2 2\Theta/\sin 2\Theta$ and Θ is the glancing angle. For each reflexion, f was taken from a curve where $1 + \cos^2 2\Theta/\sin 2\Theta$ had been plotted against $\sin^2\Theta$. $\sin^2\Theta$ was calculated from $\sin^2\Theta = k_1 \ (h^2 + k^2 + hk) + k_2 l^2$, where $k_1 = \lambda^2/3a^2$ and $k_2 = \lambda^2/4c^2$. a and c were obtained from the powder photographs.

Table 3. *Estimated intensities and mean values of I for some reflexions h0l and hk0 from Weissenberg photographs of HgS. CuKα radiation.*

hkl	I estimated	I mean value	hkl	I estimated	I mean value
20$\bar{8}$	30		210	50	
20$\bar{2}$	83	45	120	40	36
204	35		$\bar{1}$30	30	
20 10	30		$\bar{2}$30	25	
30$\bar{9}$	80		310	15	
30$\bar{3}$	75	79	130	10	10
303	80		$\bar{1}$40	9	
309	80		$\bar{3}$40	4	
40$\bar{2}$	15	11	110	60	62
404	7		$\bar{1}$20	65	
			$\bar{2}$10	60	
101	15	9	220	35	28
107	3		$\bar{2}$40	20	

In these "F^2" values no correction was thus made for thermal movement, nor for absorption.

The mean values of I and "F^2" for $hk0$ are given in Table 4 a, for $h0l$ in Table 4 b. Values of "F" for the reflexions $h00$ are given in Table 4 c and values of "F" for the reflexions $h0,3L$ in Table 4 d.

Since the values for I, "F^2" and "F" are given in an arbitrary scale, the Patterson function and the electron density ϱ obtained in the following are also expressed on a relative scale.

ON THE FUNCTION ϱ_3

The complex structure factor of hkl can be expressed by

$$F_{hkl} = \int\limits_0^1 \int\limits_0^1 \int\limits_0^1 e^{-2\pi i\,(hx + ky + lz)}\; \varrho\;(xyz)\;dxdydz$$

where ϱ is the electron density, thus $\varrho\,(xyz)\,dxdydz$ is the average number of electrons in the volume element $dxdydz$.

Table 4 a. Mean values of I and "F^2" from $hk0$ from Weissenberg photograph of HgS. CuKα radiation.

k	I						"F^2"					
	0k0	1k0	2k0	3k0	4k0	5k0	0k0	1k0	2k0	3k0	4k0	5k0
$\bar{5}$		34	46	46	34			7	20	20	7	
$\bar{4}$	62	10	28	10	62	34	44	10	28	10	44	7
$\bar{3}$	35	32	32	35	10	46	35	27	27	35	10	20
$\bar{2}$	4	62	4	32	28	46	2	28	2	27	28	20
$\bar{1}$	13	13	62	32	10	34	3	3	28	27	10	7
0		13	4	35	62			3	2	35	44	
1	13	62	32	10	34		3	28	27	10	7	
2	4	32	28	46			2	27	28	20		
3	35	10	46				35	10	20			
4	62	34					44	7				

Table 4 b. Mean values of I and "F²" from h0l from Weissenberg photograph of HgS. CuKα radiation.

l		I					"F^2"			
	00l	10l	20l	30l	40l	00l	10l	20l	30l	40l
± 12										
± 6	60	10	3	47	78	41	3	2	45	28
0										
7										
1		9	116	36	12		4	72	34	5
$\bar{5}$										
$\bar{11}$										
8										
2		60	23	5	31		27	15	5	19
$\bar{4}$										
$\bar{10}$										
± 3	47	6	12	79	38	16	2	8	48	23
± 9										
10										
4		0	45	75	11		0	31	64	7
$\bar{2}$										
$\bar{8}$										
11										
5		50	27	25	28		20	17	23	14
$\bar{1}$										
$\bar{7}$										

Table 4 c. Values for "F" of the reflexions h00, calculated from the average "F²" of h00, 0h0 and h$\bar{h}$0 in the Weissenberg photograph hk0.

hkl	100	200	300	400
	1.7	$\overline{1.4}$	5.9	6.6

Table 4 d. Values of "F" of the reflexions h0,3L, calculated from "F²" in the Weissenberg photograph h0l.

l	00l	10l	20l	30l	40l
± 12					
± 6	6.4	1.6	$\overline{1.4}$	6.7	5.3
0					
± 9					
± 3	3.9	1.4	$\overline{2.9}$	7.0	4.7

$$F_{h0l} = \int\limits_0^1\int\limits_0^1 e^{-2\pi i\ (hx+lz)}\ dxdz \int\limits_0^1 \varrho\ (xyz)dy = \int\limits_0^1\int\limits_0^1 e^{-2\pi i\ (hx+lz)}\ \varrho\ (xpz)\ dxdz$$

where $\varrho\ (xpz)$ is the projection of the electron density $\varrho\ (xyz)$ on the xz plane.
For the reflexions $h0,3L$

$$F_{h0,3L} = \int\limits_0^1\int\limits_0^1 e^{-2\pi i\ (hx+3Lz)}\ \varrho\ (xpz)\ dxdz \qquad (1)$$

The electron density $\varrho\ (xpz)$ is the same for $z,\ z+1,\ z+2$ — — — — —
but the term $e^{-2\pi i\ (hx+3Lz)}$ has the same value for $z,\ z+\frac{1}{3},\ z+\frac{2}{3}$ — — — — —.
Thus the z period is 1 for $\varrho\ (xpz)$ and $\frac{1}{3}$ for $e^{-2\pi i\ (hx+3Lz)}$. The xz plane can
therefore be divided into 3 parts, corresponding points of which give the
same value for the complex term $e^{-2\pi i\ (hx+3Lz)}$.
We replace z in (1) by a parameter

$$Z = 3\ z \qquad (2)$$

and find

$$F_{h0,3L} = \int\limits_0^1\int\limits_0^1 e^{-2\pi i\ (hx+LZ)}\ \varrho_3(xpZ)\ dxdZ \qquad (3)$$

where ϱ_3 is defined by

$$\varrho\ (x,\ y,\ z) + \varrho\ (x,\ y,\ z+\tfrac{1}{3}) + \varrho\ (x,\ y,\ z+\tfrac{2}{3}) = 3\ \varrho_3\ (x,\ y,\ Z) \qquad (4)$$

The Z period of $\varrho_3\ (xyZ)$ and its projection $\varrho_3\ (xpZ)$ is 1.
By reversal of (3) we find

$$\varrho_3\ (xpZ) = \sum_h\sum_L F_{h0,3L}\ e^{-2\pi i\ (hx+LZ)} = \sum_h\sum_L F_{h0,3L}\ \cos\ 2\pi\ (hx+LZ) \qquad (5)$$

The general point position xyz [6 (c)] of D_3^4, if transferred to the projection
$\varrho_3(xpZ)$ will give points at $\pm\ (xpZ,\ \bar{y}pZ,\ (y\text{-}x)\ pZ)$. Since the projection
has thus a centre of symmetry, $F_{h0,3L} = F_{\bar{h}0,3\bar{L}}$ and the sine terms cancel
out in (5).

In a hypothetical cell with the electron density $\varrho_3\ (xyZ)$ each atomic posi-
tion 3 (a) in the ordinary cell (p. 1415) will correspond to 3 maxima of electron
density at $x00,0x0$ and $\bar{x}\bar{x}0$. The projection $\varrho_3\ (xpZ)$ from the reflexions $h0,3L$
has maxima in $xp0,0p0$ and $\bar{x}p0$ and the cut $\varrho_3\ (xp0)$ has maxima at $x,\ 0$ and $\bar{x}$.

In the same manner an atomic position 3 (b) (p. 1415) gives in the projec-
tion $\varrho_3(xpZ)$ maxima of electron density at $xp\frac{1}{2},\ 0p\frac{1}{2}$ and $\bar{x}p\frac{1}{2}$. The cut
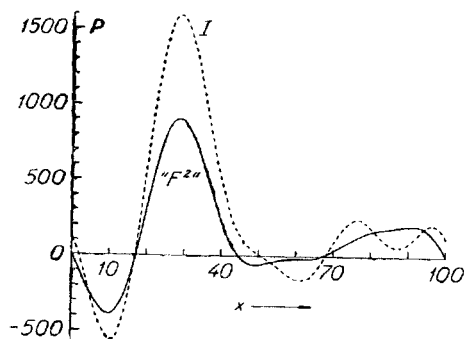$\varrho_3(xp\frac{1}{2})$ gives maxima at $x,\ 0$ and $\bar{x}$.

Figure 2. Patterson function $P(xp\frac{1}{3})$ of HgS (cinnabar).

Full curve: $\sum_{h}{}^{"}F^{2"}{}_{h0l}\cos2\pi(hx + \frac{1}{3})$

Dotted   » $\sum_{h} I_{h0l}\cos2\pi(hx + \frac{1}{3})$

For the two cuts desired, equation (5) gives:

$$\varrho_3(xp0) = \sum_{h}\sum_{L}F_{h0,3L}\cos2\pi hx = \sum_{h}\cos2\pi hx\left[\sum_{\substack{L\\ \text{even}}}F_{h0,3L} + \sum_{\substack{L\\ \text{odd}}}F_{h0,3L}\right] \quad (6)$$

$$\varrho_3(xp\tfrac{1}{2}) = \sum_{h}\sum_{L}F_{h0,3L}\cos2\pi(hx + \tfrac{1}{2}) = \sum_{h}\cos2\pi hx\left[\sum_{\substack{L\\ \text{even}}}F_{h0,3L} - \sum_{\substack{L\\ \text{odd}}}F_{h0,3L}\right] \quad (7)$$

These functions will be used in the calculations which follow.

PRELIMINARY DETERMINATION OF THE PARAMETERS

The highest maximum of the Patterson projections is found in $P(xp\frac{1}{3})$ at $x = 0.29$ (Fig. 2). This must be due to the distance Hg → Hg, which should give a maximum of weight 2 at $\bar{x}_1$ (Table 5). From this follows $x_1 = 0.71$.

In order to secure more information on the positions of the Hg atoms and especially on the positions of the S atoms the Fourier sums $\varrho_3(xp0)$ and $\varrho_3(xp\tfrac{1}{2})$ were calculated from (6) and (7), using solely the reflexions $h0,3L$. The signs of the amplitudes (Table 4 d) were determined using the approximate parameter $x_1 = 0.71$ and neglecting the influence of the S atoms.

Atoms in the point position 3 (a) (levels 0, $\frac{1}{3}$ and $\frac{2}{3}$) should give maxima at 0, x and $\bar{x}$ in the function $\varrho_3(xp0)$. In the same way atoms in the point position 3 (b) (levels $\frac{1}{6}$, $\frac{1}{2}$ and $\frac{5}{6}$) should give maxima at 0, x and $\bar{x}$ in $\varrho_3(xp\tfrac{1}{2})$. Now in each of the two cuts there is one such group of maxima (Fig. 3). The high maxima in $\varrho_3(xp0)$ are due to Hg atoms, which occupy 3 (a) according to our arbitrary assumption in calculating the signs. From the much lower maximum in $\varrho_3(xp\tfrac{1}{2})$ it was concluded that the S atoms occupy the point position 3 (b).

Figure 3. Fourier sums of HgS (cinnabar).

Full curve: $\varrho_3(xp0)$
Dotted » $\varrho_3(xp\frac{1}{2})$
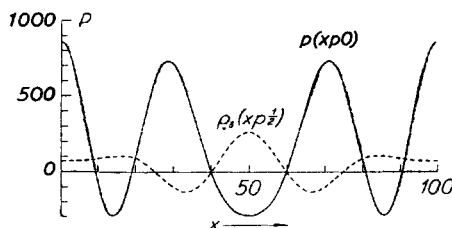
The cut $\varrho_3(xp0)$ gives the value $x_1 = 0.71$ for the Hg parameter and $\varrho_3(xp\frac{1}{2})$ the value $x_2 \approx 0.50$ for the S parameter (Fig. 3, Table 6).

If we consider separately the sums $\sum_h \sum_{\substack{L \\ even}} "F"_{h0,3L} \cos 2\pi hx$ and $\sum_h \sum_{\substack{L \\ odd}} "F"_{h0,3L} \cos 2\pi hx$, which were used for calculating $\varrho_3(xp0)$ and $\varrho_3(xp\frac{1}{2})$, we find the values $x_1 = 0.72$ and $x_1 = 0.71$ (Fig. 4).

Since it seemed definite that Hg occupies 3 (a) and S 3 (b), Tables 5 and 6 were made giving the expected positions of maxima in various Patterson and Fourier cuts, the positions observed, and the derived values for x_1 and x_2.

The Fourier sum ϱ $(xp0)$ was computed, using the reflexions $h00$ and equivalents from the photograph $hk0$.

From this projection a value $x_1 = 0.73$ was obtained for the Hg parameter (Fig. 5, Table 6). Since the cut ϱ $(xp0)$ is based on only a few reflexions, less weight should be ascribed to this value $x_1 = 0.73$ than to the other values for x_1, which seem to be of greater accuracy.

From the Fourier projections (Table 6) and the Patterson projection $P(xp\frac{1}{3})$ (Fig. 2, Table 5) the average value 0.72 ± 0.01 was assumed for the Hg parameter on calculating the S parameter x_2.

As seen from Table 5 the projections based on values of I and those based on values of $"F^2"$ gave somewhat different values for x_2.

The value $x_2 = 0.50$ from the cut $\varrho_3(xp\frac{1}{2})$ (Table 6) is not very accurate since the maximum at 0.50 (Fig. 3) may also consist of two overlapping maxima.

The average value of the S parameter was assumed to be 0.48 ± 0.02.

Figure 4. Fourier sums of HgS (cinnabar).

Full curve: $\sum_h \sum_{\substack{L \\ odd}} "F"_{h0,3L} \cos 2\pi hx$

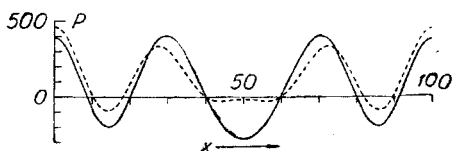Dotted » $\sum_h \sum_{\substack{L \\ even}} "F"_{h0,3L} \cos 2\pi hx$

7

Table 5. Patterson projections

x_1 is the Hg parameter and x_2 the S parameter.

Projection	x value expected distance		x value observed distance				x value calc.		rel. weight in units		rel. weight observed
	Hg → Hg	Hg → S	Hg → Hg "F2"	I	Hg → S "F2"	I	Hg	S	(Hg)²	HgS	
$P\ (xp\frac{1}{2})$ Fig. 6		$\pm (x_1-x_2)$ 0			± 0.23	± 0.23		0.49		2 1	high —
$P\ (xp\frac{1}{3})$ Fig. 2	$\bar{x}_1$ $2\,x_1$		0.29	0.29			0.71		2 1		high
$P\ (xp\frac{1}{6})$ Fig. 7		x_1			0.81	0.80				2	high, broad
		$-(x_1+x_2)$								2	
		x_2			0.45	0.47		0.45 0.47		2	high
$P\ (x0p)$ Fig. 8		$x_1 - x_2$			0.26	0.23		0.46 0.49			small
$P\ (2\,xxp)$ Fig. 9		$x_1 - x_2$			0.26						small

FINAL FOURIER CUTS

Finally the Fourier sums $\varrho\ (xp0)$ and $\varrho\ (xp\frac{1}{2})$ were computed using all reflexions $h0l$.

$$\varrho(xpz) = \sum_h \sum_l e^{-2\pi i(hx+lz)}\ F_{h0l} = \sum_h \sum_l e^{-2\pi i(hx+lz)}\ (A_{h0l} + iB_{h0l}) =$$

$$= \sum_h \sum_l \left[A_{h0l}\ \cos 2\pi(hx + lz) - B_{h0l}\ \sin 2\pi(hx + lz) \right]$$

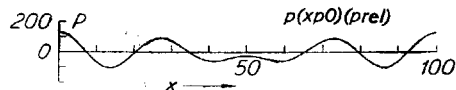since the imaginary terms cancel out.

Table 6. Fourier sums.

x_1 is the Hg parameter and x_2 the S parameter.

cut	x value expected	x value observed	x calculated Hg	S
$\varrho_3\ (xp0)$	$0,\ \pm x_1$	0.29,　0.71	0.71	
$\varrho_3\ (xp\frac{1}{2})$	$0,\ \pm x_2$	0.50		≈ 0.50
$\varrho\ (xp0)$ (prel.)	$0,\ \pm x_1$	0.27,　0.73	0.73	
$\varrho\ (xp0)$ (final)	x_1	0.720	0.720	
$\varrho\ (xp\frac{1}{2})$ (final)	x_2	0.48_5		0.48_5

Figure 5. Fourier sum $\sum_{h}$ *"F"$_{h00}$cos2πhx of HgS (cinnabar).*

The cut $\varrho(xp0)$ was calculated to study the Hg parameter and the cut $\varrho(xp\frac{1}{2})$ to study the S parameter.

$$\varrho(xp0) = \sum_{h}\sum_{l} A_{h0l}\cos2\pi hx - \sum_{h}\sum_{l} B_{h0l}\sin2\pi hx$$

$$\varrho(xp\tfrac{1}{2}) = \left[\sum_{h}\sum_{l} A_{h0l}\cos2\pi hx - \sum_{h}\sum_{l} B_{h0l}\sin2\pi hx\right]_{l\text{ even}} -$$

$$-\left[\sum_{h}\sum_{l} A_{h0l}\cos2\pi hx - \sum_{h}\sum_{l} B_{h0l}\sin2\pi hx\right]_{l\text{ odd}}$$

The values of A_{h0l} and B_{h0l} that were used for these projections were calculated from $A_{h0l} = \left|\text{"F"}_{h0l}\right|\cos\alpha_{h0l}$, $B_{h0l} = \left|\text{"F"}_{h0l}\right|\sin\alpha_{h0l}$. $\alpha_{h0l} = $ phase angle.

For each reflexion $h0l$, A_{h0l} and B_{h0l} were also computed according to the appropriate terms of the structure factors in the *International tables* and with the aid of the values $x_1 = 0.72$, $x_2 = 0.48$ and α_{h0l} calculated from

$$\alpha_{h0l} = \text{arctg}\,\frac{B_{h0l}}{A_{h0l}}.$$

"F" was calculated from the visually estimated values of I of the reflexions $h0l$ (p. 1420).

In Table 7 are given the values for $\left|\text{"F"}_{h0l}\right|\sin\alpha_{h0l}$ and in 8 the values for $\left|\text{"F"}_{h0l}\right|\cos\alpha_{h0l}$.

The projections $\varrho(xp0)$ and $\varrho(xp\frac{1}{2})$ are given in Fig. 11. The cut $\varrho(xp0)$ has a very high and well defined maximum at 0.720, from which the Hg para-

Table 7.

$$\left|\text{"F"}_{h0l}\right|\sin\alpha_{h0l} = B_{h0l}$$

hl → 0	1	2	3	4	5
0	0			0		
1	0	1.6_{25}	4.5_{00}	0	$\overline{0}$	3.9_{00}
2	0	$\overline{7.3}_{58}$	3.3_{70}	0	$\overline{4.8}_{58}$	3.5_{51}
3	0	$\overline{5.0}_{45}$	1.9_{28}	0	6.9_{27}	4.1_{60}
4	0	1.9_{23}	3.7_{17}	0	2.2_{88}	3.2_{65}

Table 8.

$$\left|\text{"F"}_{h0l}\right|\cos\alpha_{h0l} = A_{h0l}$$

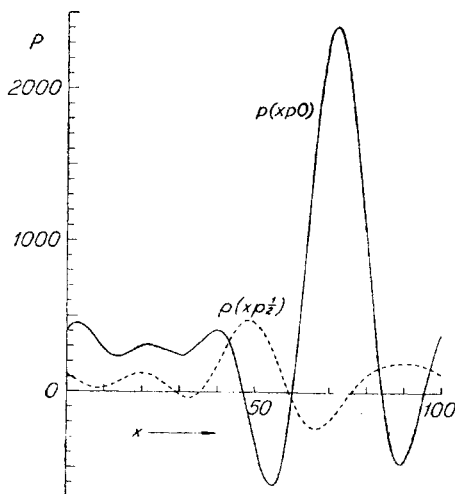| hl → 0	1	2	3	4	5
0	6.4_{03}			3.9_{37}		
1	1.5_{81}	0.9_{26}	$\overline{2.6}_{06}$	1.4_{14}	0	$\overline{2.2}_{66}$
2	1.4_{14}	$\overline{4.2}_{55}$	1.9_{82}	2.8_{81}	$\overline{2.7}_{85}$	2.0_{29}
3	6.6_{86}	2.9_{23}	1.1_{39}	6.9_{50}	$\overline{4.0}_{01}$	2.3_{94}
4	5.3_{20}	1.1_{48}	$\overline{2.1}_{62}$	4.7_{43}	1.3_{37}	$\overline{1.8}_{42}$

Figure 11. Fourier sums of HgS (cinnabar).

Full curve: $\varrho\,(xp0)$
Dotted   » $\varrho\,(xp\tfrac{1}{2})$

meter was fixed at 0.720 ± 0.003. The sulphur parameter was fixed at $0.48_5 \pm 0.01$ from $\varrho(xp\tfrac{1}{2})$.

There seemed to be no point in trying to obtain greater accuracy with the experimental data available.

DETAILED DISCUSSION OF THE PATTERSON PROJECTIONS

$P(xp\tfrac{1}{3})$: (Fig. 2)

The projection has its highest maximum at $x = 0.29$ due to the distance Hg → Hg of weight 2 at $\bar{x}_1 \cdot A$ Hg → Hg maximum of weight 1 would be expected at $x \approx 0.40$. However, it seems probable that the maximum at ≈ 0.40 is concealed by the maximum at 0.29. Maxima are also expected from interatomic distances S → S in this projection. However, they are too small to stand out among the false maxima.

$P(xp\tfrac{1}{2})$: (Fig. 6)

The cut based on the values of I has a small maximum at $x = 0.50$ which could not be found in the cut "F^2". The projection of "F^2" sums probably gives more accurate values than that of I sums. The Hg → S maximum of weight 1 expected at 0 is not observed.
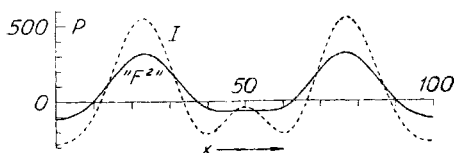

Figure 6. Patterson function $P\,(xp\tfrac{1}{2})$ of HgS (cinnabar).

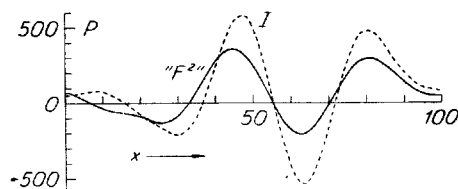Full curve: $\sum\limits_{h}\text{``}F^2\text{''}_{h0l}\cos 2\pi\,(hx + \tfrac{1}{2})$

Dotted   » $\sum\limits_{h} I_{h0l}\cos 2\pi\,(hx + \tfrac{1}{2})$

Figure 7. Patterson function $P(xp\frac{1}{6})$ of HgS (cinnabar).

Full curve: $\sum_h "F^2"_{h0l}\cos2\pi(hx+\frac{1}{6})$
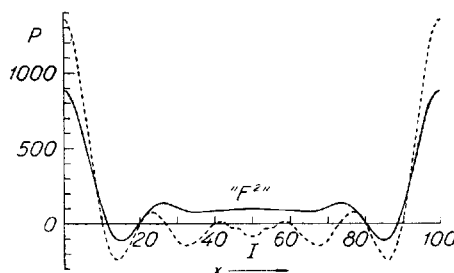
Dotted » $\sum_h I_{h0l}\cos2\pi(hx+\frac{1}{6})$

$P(xp\frac{1}{6})$: (Fig. 7)

The maximum at $x=0.80-0.81$ is not of the same height but much broader than the Hg → S maximum found at 0.45 ("F^2" sum) and 0.47 (I sum). This maximum (0.80—0.81) is probably due to overlapping of a Hg → S maximum expected at 0.72 and a Hg → S maximum, expected at 0.80.

Figure 8. Patterson function $P(x0p)$ of HgS (cinnabar).
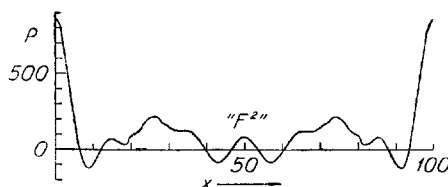
Full curve: $\sum_h "F^2"_{hk0}\cos2\pi hx$

Dotted » $\sum_h I_{hk0}\cos2\pi hx$

$P(x0p)$: (Fig. 8)

In the cut $P(x0p)$ maxima depending on the distance Hg → S are expected. The cut I gives its highest maximum at x = 0.23 and a smaller one at $x = 0.42$. In the cut "F^2" there is only one maximum at $x = 0.26$. No significance could be ascribed to the maximum at $x = 0.42$ (cut I).

Figure 9. Patterson function $P(2xxp) = \sum_h "F^2"\cos2\pi(2h+k)x$ of HgS (cinnabar).

$P(2xxp)$: (Fig. 9)

In the cut $P(2xxp)$ are expected maxima, resulting from the interaction between maxima depending on the distance Hg → Hg and maxima depending on the distance Hg → S (Fig. 10). The projection has a much too complicated appearance to give a clear understanding about the parameters of Hg and S.
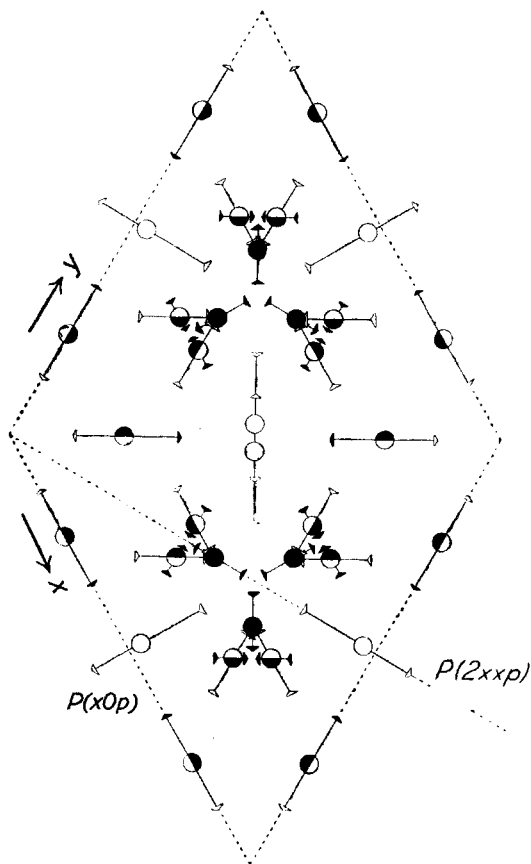
Figure 10. Expected maxima in the Patterson functions. The centres of the spheres are situated in the points calculated with the aid of the parameter values $x_{Hg} = 0.720$ and $x_S = 0.48_5$. Expected $Hg \rightarrow Hg$ maxima are marked out with black spheres, $S \rightarrow S$ maxima with white spheres and $Hg \rightarrow S$ maxima with spheres, half black. The black arrows indicate the displacements of the $Hg \rightarrow Hg$ and $Hg \rightarrow S$ maxima which would follow from altering the Hg parameter. The white ones show the displacements of the $S \rightarrow S$ and $Hg \rightarrow S$ maxima, following from an alteration of the S parameter. x_{Hg} is assumed to be in the range $0.68 - 0.75$ and $x_S = 0.40 - 0.55$. The arrows point in the direction of increasing parameter values.

FINAL STRUCTURE PROPOSITION

Now that the positions of the sulphur and the mercury atoms have been determined, the intensities of the reflexions $hk0$ and $h0l$ of the Weissenberg photographs were calculated, considering the scattering power of both the Hg and the S atoms.

In Tables 9 and 10 the calculated values of I are compared with the observed intensities of the reflexions in the Weissenberg photographs $hk0$ and $h0l$. They agree as closely as can be expected, bearing in mind that the "observed intensities" are mean values of the estimated intensities, which sometimes differ considerably because of asymmetrical absorption (see again Table 3).

Thus the following structure is proposed for HgS (cinnabar):
Hexagonal, $a = 4.146$ Å, $c = 9.497$ Å, 3 HgS per unit cell.

Table 9. Calculated and observed intensities of hk0 from Weissenberg photograph of HgS. CuKα radiation. The calculated intensity is given on the left of each column and the intensity estimated on the right.

$$I_{calc.} = \tfrac{2}{3} (F/2f_{Hg})^2 \, 10^3$$

k	$\bar{5}$		$\bar{4}$		$\bar{3}$		$\bar{2}$		$\bar{1}$		0		1		2		3		4	
	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
0k0			55	44	23	35	1	2	1	3			1	3	1	2	23	35	55	44
1k0	10	7	8	10	18	27	45	28	1	3	1	3	45	28	18	27	8	10	10	7
2k0	30	20	15	28	18	27	1	2	45	28	1	2	18	27	15	28	30	20		
3k0	30	20	8	10	23	35	18	27	18	27	23	35	8	10	30	20				
4k0	10	7	55	44	8	10	15	28	8	10	55	44	10	7						
5k0			10	7	48	20	48	20	10	7										

Table 10. Calculated and observed intensities of h0l from Weissenberg photograph of HgS. CuKα radiation. The calculated intensity is given on the left of each column and the intensity estimated on the right.

$$I_{calc.} = \tfrac{5}{9} (F/f_{Hg})^2 \, 10^3$$

l	00l		10l		20l		30l		40l	
	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
0 ± 12, ± 6	69	41	1	3	1	2	21	45	49	28
1, 7 $\bar{5}$, $\overline{11}$			4	4	39	72	12	34	3	5
2, 8 $\bar{4}$, $\overline{10}$			57	27	11	15	3	5	15	19
± 3 ± 9	34	16	3	2	11	8	28	48	21	23
4, 10 $\bar{2}$, $\bar{8}$			0	0	35	31	32	64	6	7
5, 11 $\bar{1}$, $\bar{7}$			37	20	8	17	8	23	9	14

Space group $D_3^4 - C3_12$

3 Hg in 3 (a): x 0 $\frac{1}{3}$, 0 x $\frac{2}{3}$, $\bar{x}$ $\bar{x}$ 0 $x = 0.720 \pm 0.003$

3 S in 3 (b): x 0 $\frac{5}{6}$, 0 x $\frac{1}{6}$, $\bar{x}$ $\bar{x}$ $\frac{1}{2}$ $x = 0.48_5 \pm 0.01$

DISCUSSION OF THE STRUCTURE

If S — Hg — S are to lie on a straight line, x_1 and x_2 must satisfy the equation: $x_1 = 1 - \frac{1}{2} x_2$. The Hg parameter $x_1 = 0.720 \pm 0.003$ is determined with greater accuracy than the S parameter $x_2 = 0.48_5 \pm 0.01$. If the value 0.720 for x_1 is inserted in the above equation the value $x_2 = 0.56$ is obtained and differs too greatly from the experimental value $x_2 = 0.48_5$. Thus S — Hg — S do not lie on a straight line.

The bonding angle $S_1 - Hg^* - S_1$ (Θ_1) (Fig. 12) was calculated from the formula:

$$ \operatorname{tg} \frac{\Theta_1}{2} = \frac{\sqrt{0.75 x_2^2 + \left(\frac{c}{a}\right)^2 \frac{1}{36}}}{1 - x_1 - 0.50 x_2} $$

and the angle $Hg_1 - S_1 - Hg^*$ (Θ_2) (Fig. 12) was evaluated from:

$$ \operatorname{tg} \frac{\Theta_2}{2} = \frac{\sqrt{0.75 (1 - x_1)^2 + \left(\frac{c}{a}\right)^2 \frac{1}{36}}}{x_2 - 0.50 (1 - x_1)} $$

With $x_1 = 0.720 \pm 0.003$ and $x_2 = 0.48_5 \pm 0.01$ the value of Θ_1 and Θ_2 are: $\Theta_1 = 172°\cdot4 \pm 1°\cdot7$, $\Theta_2 = 105°\cdot2 \pm 2°\cdot0$.

As seen Θ_1, the angle between the mercury bonds is not far from 180°, which is the angle between the mercury bonds of the halogen compounds $HgCl_2$ (s), $HgBr_2$ (s), yellow HgJ_2 (s), the gaseous molecules HgX_2 and HgSR ($R = n$-alkyl group) (p. 1413). Θ_2, the angle between the bonds from a sulphur atom, lies close to the values found for molecules containing 2-covalent S [SCl_2 103°, S_2Cl_2 105° $\pm$ 5° (Wells [14, p. 306])].

By assuming $x_1 = 0.720$ and $x_2 = 0.48_5$ the following distances and coordination were obtained:

The neighbourhood of one mercury atom ($\bar{x}_1$ $\bar{x}_1$ 0) Hg * in Fig. 12:

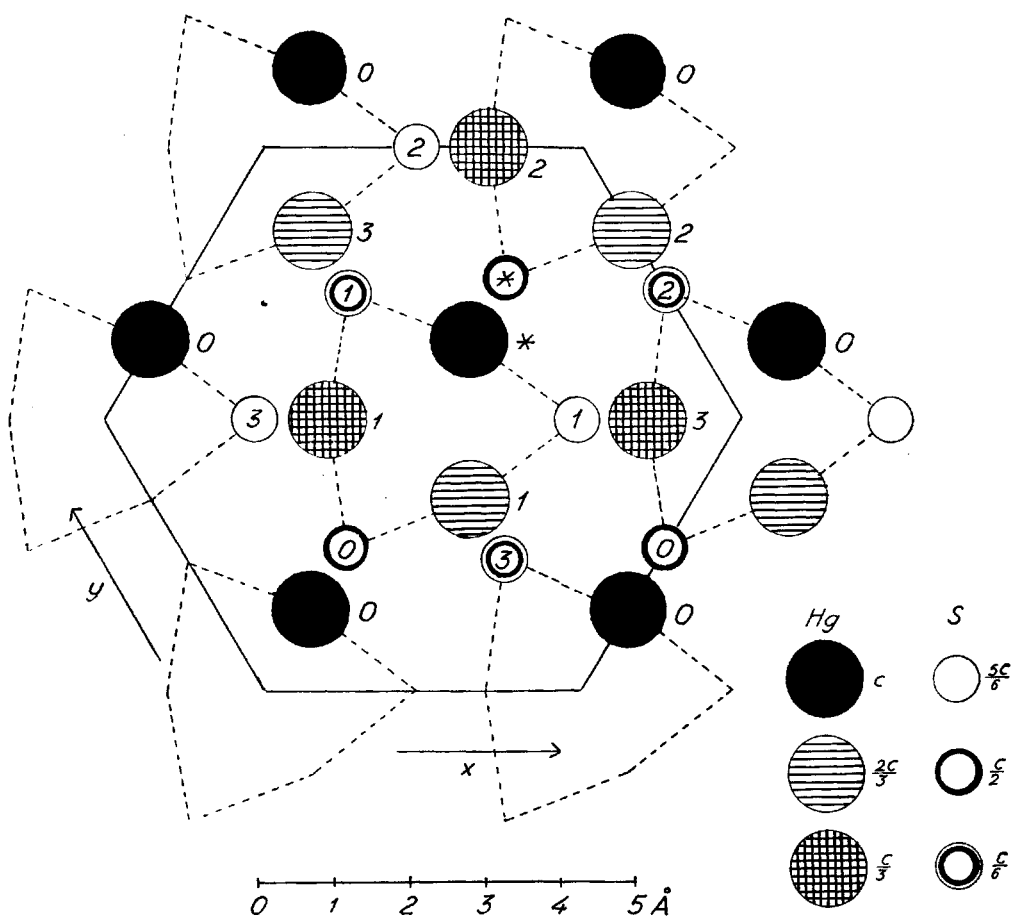|					
2 S at	2.3$_6$ Å	S_1	6 Hg at 4.1$_5$ Å		Hg_0
2 S	3.1$_0$	S_2	2 Hg	3.7$_5$	Hg_1
2 S	3.3$_0$	S_3	4 Hg	4.1$_0$	Hg_2, Hg_3

Figure 12. xy projection of the structure of cinnabar. The diagram shows the coordination of the atoms. The small circles ①, ②, ③ show the S atoms and the larger ones ◯₁, ◯₂, ◯₃ *the Hg atoms. The distances Hg→Hg, Hg→S and S→S are listed in the text. The dotted line unites the atoms of one spiral chain.*

The neighbourhood of one sulphur atom $(\bar{x}_2 \ x_2 \ \frac{1}{2})$ S * in figure 12:

2 Hg	at	2.3_6	Å	Hg_2	6 S	at 4.1_5 Å S_0
2 Hg		3.1_0		Hg_3	2 S	4.8_7 S_3
2 Hg		3.3_0		Hg_1	4 S	3.7_9 S_1, S_2

(The distance Hg * → S * is 4.8_5 Å.)
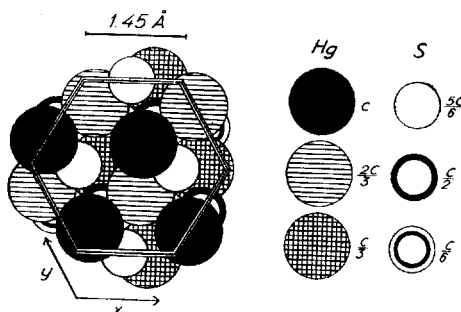
Figure 13. xy projection of the structure of cinnabar. The diagram shows the contents of one hexagon (3 hexagonal unit cells). The Hg atoms are situated at the levels $\frac{c}{3} \frac{2c}{3}$ and c and the S atoms at the levels $\frac{c}{6} \frac{c}{2}$ and $\frac{5c}{6}$. The distance $Hg \rightarrow S$ is $2.3_6 \mathring{A}$. The radii of the Hg and the S atoms are assumed to be $1.4_0 \mathring{A}$ and $0.9_6 \mathring{A}$.

If HgS were built up from Hg^{2+} and S^{2-} ions, the distance $Hg \rightarrow S$ would be 2.94 kX. (Hg^{2+} : $r = 1.10$ kX, S^{2-}: $r = 1.84$ kX, according to Pauling [41]). This value is much longer than that found, 2.3_6 Å. Also, the distance calculated from covalent tetrahedral radii, 2.52 Å, seems to differ too much from the obtained value.

From the distances $Hg \rightarrow X$ in HgX_2 (gas) (Braune and Knoke [8], Gregg et al [9], see page 1414) and the normal covalent radii (Wells [18, p. 81]) the 2-covalent Hg radius was calculated to be $\approx 1.2_7$ Å. If the 2-covalent S radius is 1.04 Å (Wells [14, p. 81]), the distance $Hg \rightarrow S$ should be 2.3_2 Å, if the forces between the Hg and S atoms are exclusively homopolar.

The distance $Hg \rightarrow S$ actually found is 2.3_6 Å.

From this distance $Hg \rightarrow S$ 2.3_6 Å (2.3_5 kX) and the values of Θ_1 and Θ_2 the conclusion can be drawn that the bond between Hg and S is mainly homo-
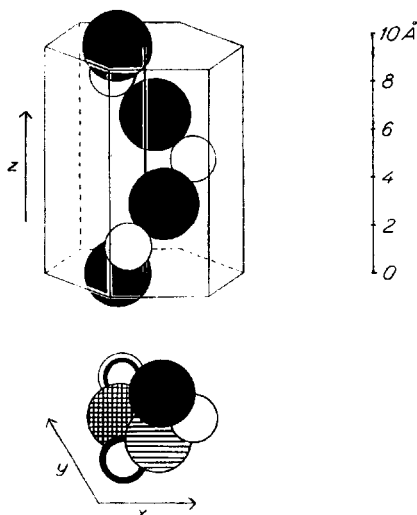

Figure 14. Diagrams from the side and above of one spiral chain $-S-Hg-S-$ of the structure of cinnabar. The spiral chain extends indefinitely through the crystal in the vertical direction.

The atoms in the projection are seen in the centre of Fig. 13.

polar (sp type) in spite of the deviation of the angle from the normal value, 180°, for sp bonds.

Thus the structure of HgS can be described as consisting of a series of infinite spiral chains -S-Hg-S-, running parallel to the c-axis of the hexagonal unit cell (Figs. 13 and 14).

Within the chain each atom is strongly bound, chiefly by homopolar forces, to its two immediate neighbours, but between the chains the forces are far less strong, and the interatomic distances are correspondingly considerably greater than within the chain. The chains probably support each other by means of the longer Hg → S contacts. It can be noted that the Hg atoms approximate a close-packed lattice.

SUMMARY

The crystal structure of native cinnabar has been investigated. The positions of the Hg and S atoms have been determined by means of Fourier synthesis. The cell edges are: $a = 4.14_6$ Å, $c = 9.49_7$ Å (accuracy 0.05 %). The following structure is proposed:

Space group: $D_3^4 - C\ 3_1\ 2$

3 Hg in the point position 3 (a): $x\ 0\ \frac{1}{3},\ 0\ x\ \frac{2}{3},\ \bar{x}\ \bar{x}\ 0,$

$$x = 0.720 \pm 0.003$$

3 S in the point position 3 (b): $x\ 0\ \frac{5}{6},\ 0\ x\ \frac{1}{6},\ \bar{x}\ \bar{x}\ \frac{1}{2}$

$$x = 0.48_5 \pm 0.01$$

The structure is built up of infinite spiral chains, $(-S-Hg-)_n$ running parallel to the c axis of the hexagonal unit cell.

The angle S-Hg-S is 172°.4 $\pm$ 1°.7 and the angle Hg-S-Hg 105°.2 $\pm$ 2°.0.

The distances Hg → S within the chain are 2.3_6 Å.

From the angles and distances the bonds seem to be mainly covalent sp bonds.

A 2-covalent Hg radius $\approx 1.2_7$ Å may be probable.

REFERENCES

1. Ebert, F., and Woitinek, H. *Z. anorg. Chem.* **210** (1933) 270.
2. Braekken, H., and Harang, L. *Z. Krist.* **68** (1928) 123.
3. Nieuwenkamp, W., and Bijvoet, J. M. *Z. Krist.* **84** (1932) 61.
4. Braekken, H., and Scholten, W. *Z. Krist.* **89** (1934) 448.
5. Verweel, H. J., and Bijvoet, J. M. *Z. Krist.* **77** (1931) 122.

6. Smits, A. *Z. physik. Chem.* **92** (1918) 345.
7. Gorskiǐ, W. *Physik. Z. Sowjetunion* **5** (1934) 367.
8. Braune, H., and Knoke, S. *Z. physik. Chem.* **B 23** (1933) 163.
9. Gregg, A. H., Hampson, G. C., Jenkins, G. J., Sutton, R. L. F., and Sutton, L. E. *Trans. Faraday Soc.* **33** (1937) 852.
10. Havighurst, R. J. *Am. J. Sci.* **10** (1925) 556.
11. Bijvoet, J. M., Classen, A., and Karssen, A. *Proc. Acad. Sci. Amsterdam* **29** (1926) 529.
12. Classen, A. Diss., Amsterdam (1926).
13. Huggins, M. L., and Magill, P. L. *J. Am. Chem. Soc.* **49** (1927) 2357.
14. Wells, A. F. *Structural inorganic chemistry*. Oxford (1945).
15. Gay-Lussac, J. L. *Compt. rend.* **16** (1843) 309.
16. Ostwald, W. *Z. physik. Chem.* **18** (1895) 159.
17. Ostwald, W. *Z. physik. Chem.* **34** (1900) 495.
18. Varet, R. *Compt. rend.* **120** (1895) 622.
19. Cohen, E. *Z. physik. Chem.* **34** (1900) 69.
20. Hulett, G. A. *Z. physik. Chem.* **37** (1901) 400.
21. Schick, K. *Z. physik. Chem.* **42** (1903) 155.
22. Fuseya, G. *J. Am. Chem. Soc.* **42** (1920) 368.
23. Levi, G. R. *Gazz. chim. ital.* **54** (1924) 709.
24. Levi, G. R. *Gazz. chim. ital.* **58** (1928) 417.
25. Goldschmidt, V. M. *G. V.* **VII** (1926).
26. Fricke, R. *Z. anorg. Chem.* **166** (1927) 255.
27. Zachariasen, W. H. *Z. physik. Chem.* **128** (1927) 421.
28. Kolkmeijer, N. H. *Z. physik. Chem.* **A 136** (1928) 45.
29. Kolkmeijer, N. H. *Z. physik. Chem.* **A 138** (1928) 311.
30. Kolkmeijer, N. H., Bijvoet, J. M., and Karssen, A. *Rec. trav. chim.* **43** (1924) 894.
31. Lehmann, W. *Z. Krist.* **60** (1924) 379.
32. v. Olshausen, S. *Z. Krist.* **61** (1925) 483.
33. Buckley, H. E., and Vernon, W. S. *Mineralog. Mag.* **20** (1925) 382.
34. Hartwig, W. *Sitz.ber. preuss. Akad. Wiss. Physik. math. Klasse* **10** (1926) 79.
35. Goldschmidt, V. M. *G. V.* **VIII** (1927).
36. Zachariasen, W. H. *Z. physik. Chem.* **124** (1926) 277, 436.
37. de Jong, W. F. *Z. Krist.* **63** (1926) 466.
38. Wells, A. F. *Z. Krist.* **96** (1937) 435.
39. Mauguin, C. *Compt. rend.* **176** (1923) 1483.
40. de Jong, W. F., and Willems, H. W. V. *Physica* **6** (1926) 129.
41. Pauling, L. *Z. Krist.* **87** (1934) 205.
42. Allen, E. T., and Crenshaw, J. L. *Z. anorg. Chem.* **79** (1913) 158.
43. *Internationale Tabellen zur Bestimmung von Kristallstrukturen.* Berlin (1935).
44. Des Cloizeaux, A. *Compt. rend.* **44** (1857) 876.
45. Wyrouboff, G. *Ann. chim. et phys.* **8** (1886) 340.
46. Tschermak, G. *Mineralog. u. petrog. Mitt. N. F.* **7** (1886) 362.
47. Melville, W. H., and Lindgren, W. *Bull. U. S. Geol. Survey* **61** (1890) 12.
48. Becquerel, J. *Compt. rend.* **147** (1908) 1281.
49. Rose, H. *N. Jahrb. Mineralog.* **29** (1910) 94.