

## The Crystal Structure of $\text{Hg}_2\text{O}_2\text{NaI}$ Studied by X-Ray and Neutron Diffraction Methods

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The crystal structure of  $\text{Hg}_2\text{O}_2\text{NaI}$  has been studied by X-ray (single crystal) and neutron (powder) diffraction methods. The crystals are hexagonal (space group  $P6_322$  ( $P6_322$ )) with the cell edges  $a = 6.667 \text{ \AA}$  and  $c = 10.054 \text{ \AA}$ . The unit cell contains three formula units. The mercury and oxygen atoms form infinite planar chains,  $-\text{Hg}-\text{O}-\text{Hg}-\text{O}-$ , lying perpendicularly to the  $c$  axis of the unit cell. The Hg-O distance is  $2.03 \text{ \AA}$  and the angles O-Hg-O and Hg-O-Hg are  $180^\circ$  and  $110^\circ$ , respectively.

As earlier reported<sup>1,2</sup>, the structures of the orthorhombic and hexagonal modifications of mercury(II)oxide are built up of infinite chains  $-\text{O}-\text{Hg}-\text{O}-$  which, in the orthorhombic modification, are of planar zig-zag type and, in the hexagonal modification, of spiral type. Every mercury atom is thus coordinated to two oxygen atoms and every oxygen atom to two mercury atoms. The aim of the present investigation was to find whether such chains  $-\text{O}-\text{Hg}-\text{O}-$  are fundamental constituents of other mercury(II)salts containing oxygen and whether this arrangement is independent of the other kinds of atoms occurring in the structure.

### PREPARATION AND ANALYSIS

In connection with the preparation of the hexagonal modification of mercury(II)oxide, the complex compound  $\text{Hg}_2\text{O}_2\text{NaI}$ , earlier reported by Laruelle<sup>3</sup>, was synthesized. The best way for preparing  $\text{Hg}_2\text{O}_2\text{NaI}$  is to mix one part of a cold solution of  $0.1 \text{ M K}_2\text{HgI}_4$  containing an excess of KI with two parts of  $10 \text{ M NaOH}$  at about  $0^\circ\text{C}$  and to keep the solution at this temperature for about 100 h. The temperature was then slowly increased to room temperature and the substance obtained, which consisted of beautiful yellow pencil-shaped crystals, was then filtered off. Another way of preparing this compound is to heat equivalent quantities of mercury(II)oxide and sodium

iodide in a fused glass tube to 130°C for about 100 h. This method, however, did not give a pure sample.

Attempts were made to replace the sodium atoms in the compound with lithium, potassium, rubidium and caesium. However, these efforts have not yet been successful.

The compound  $\text{Hg}_2\text{O}_2\text{NaI}$  decomposes into orthorhombic  $\text{HgO}$  and  $\text{NaI}$  when heated in open air to higher temperatures. Thus, a powder diagram of the residue, after the substance had been heated to 200°C for 14 days, did not show any lines characteristic for  $\text{Hg}_2\text{O}_2\text{NaI}$ .

The compound is not stable if treated with water — it decomposes into other, not yet identified, phases. Upon exposure to light, the yellow crystals of the substance become dark green. To investigate this phenomenon more closely, a sample of  $\text{Hg}_2\text{O}_2\text{NaI}$  was exposed to U.V. light for a long time. X-Ray diagrams of the green substance showed only lines characteristic for  $\text{Hg}_2\text{O}_2\text{NaI}$ . A microscopic examination revealed, however, the presence of small drops of mercury.

The pure sample was analysed for Hg, Na, K, I and  $\text{H}_2\text{O}$  and was found to contain neither potassium nor water. The mercury analysis was performed using electrolysis<sup>4</sup>, the sodium and potassium analyses flame spectrophotometrically using a Beckman D.U. spectrophotometer<sup>5</sup> and the iodine analysis by iodometric titration<sup>6</sup> after the sample had been brought into solution by melting with sodium hydroxide in a gold crucible. The water analysis was performed according to Penfield<sup>7</sup>. The results of the analyses are in fair agreement with the values calculated for  $\text{Hg}_2\text{O}_2\text{NaI}$  (Found %: Hg 67.9; Na 3.8; I 20.9. Calc. Hg 68.8; Na 3.9; I 21.8).

#### CELL DIMENSIONS AND SYMMETRY

The powder photographs were taken in a Guinier focusing camera of 80 mm diameter using  $\text{CuK}\alpha_1$  radiation and potassium chloride ( $a = 6.2930 \text{ \AA}^{(8)}$ ) as an internal standard. The powder pattern is given in Table 1. Heavily exposed photographs did not show any lines that were not visible in normally exposed ones. The powder pattern could be interpreted by means of a hexagonal unit cell with the following cell dimensions:

$$a = 6.667 \text{ \AA} \quad c = 10.054 \text{ \AA} \quad V = 387.0 \text{ \AA}^3$$

The observed density,  $7.0 \text{ gcm}^{-3}$ , indicates a cell content of three formula units  $\text{Hg}_2\text{O}_2\text{NaI}$  (calculated density  $7.5 \text{ gcm}^{-3}$ ). For the single crystal photographs,  $\text{CuK}$  and  $\text{MoK}$  radiations were used. Rotation diagrams were taken around the  $a$  and  $c$  axes and Weissenberg photographs were used to register the reflexions  $h0l$ - $h3l$  and  $hk0$ - $hk5$ .

Since  $|F(hk0)|^2$  was found throughout to be equal to  $|F(hk3)|^2$ ,  $|F(hk1)|^2$  equal to  $|F(hk4)|^2$  and  $|F(hk2)|^2$  equal to  $|F(hk5)|^2$  within the limits of experimental error, the heavy atoms of the structure must be situated at the planes normal to the  $c$  axis of the unit cell at the  $z$  values 0 and  $\pm \frac{1}{3}$  or  $\frac{1}{2}$  and  $\pm \frac{1}{6}$ . The coefficients

$$\sum_{l=-\infty}^{l=+\infty} |F(hkl)|^2$$

were thus approximated by the expressions

Table 1. Powder diagram (Guinier focusing camera) and powder diffractogram (Geiger Mueller diffractometer) of  $\text{Hg}_2\text{O}_2\text{NaI}$ .  $I_{\text{calc}}$  is normalized so as to give the best agreement with  $I_{\text{obs}}$ .

$hkl$	$10^4 \sin^2 \theta_{\text{obs}}$ Guinier	$10^4 \sin^2 \theta_{\text{calc}}$	$I_{\text{obs}}$ Guinier	$I_{\text{calc}}$ Guinier	$I_{\text{obs}}$ Diffr.	$I_{\text{calc}}$ Diffr.
1 0 0	178	178	st	540	218	236
1 0 1	237	237	m	165	52	59
1 0 2	413	413	w	105	35	31
0 0 3	529	528	vst	1072	} 376	415
1 1 0	534	534	m	276		
1 1 1	—	593	—	11	—	0
1 0 3	707	706	m	518	} 909	824
2 0 0	713	712	vst	2009		
1 1 2	769	769	vvw	8	} —	3
2 0 1	—	771	—	0		
2 0 2	—	947	—	0	—	0
1 1 3	1062	1062	m	360	149	112
1 0 4	—	1117	—	26	—	8
2 0 3	1240	1240	vst	1587	} 569	530
2 1 0	1245	1246	m	158		
2 1 1	1304	1305	w	47	—	14
1 1 4	—	1473	—	5	} —	13
2 1 2	1480	1481	w	41		
3 0 0	1601	1602	w	65	20	18
1 0 5	} 1648	1645	} vw	17	—	6
2 0 4		1651				
3 0 1	—	1660	—	5	—	—
2 1 3	1774	1774	st	346	100	93
3 0 2	—	1837	—	5	—	1
1 1 5	—	2001	—	4	—	1
0 0 6	2112	2113	m	196	} 258	227
3 0 3	—	2130	—	147		
2 2 0	2136	2136	m	553	—	—
2 0 5	—	2179	—	0	} —	6
2 1 4	—	2185	—	25		
2 2 1	—	2194	—	0	—	—
1 0 6	2291	2291	w	63	} 34	32
3 1 0	2313	2314	w	64		
2 2 2	} 2370	2370	} vvw	0	—	0
3 1 1		2372				
3 0 4	} 2544	2541	} vvw	3	—	1
3 1 2		2548				
1 1 6	—	2647	—	71	} 188	178
2 2 3	2663	2664	st	748		
2 1 5	—	2713	—	19	—	4
2 0 6	2825	2825	st	759	} 275	269
3 1 3	—	2842	—	196		
4 0 0	2847	2848	st	426	—	—
4 0 1	—	2906	—	0	} —	—
1 0 7	—	3054	—	8		
3 0 5	—	3069	—	3	} —	—
2 2 4	—	3075	—	0		
4 0 2	—	3082	—	0	} —	3
3 1 4	—	3253	—	16		
2 1 6	—	3359	—	109	—	—
4 0 3	3377	3376	st	575	} 120	125
3 2 0	—	3381	—	45		

<i>h k l</i>	10 <sup>4</sup> sin <sup>2</sup> Θ <sub>obs</sub> Guinier	10 <sup>4</sup> sin <sup>2</sup> Θ <sub>calc</sub>	<i>I</i> <sub>obs</sub> Guinier	<i>I</i> <sub>calc</sub> <sup>*</sup> Guinier	<i>I</i> <sub>obs</sub> Diffr.	<i>I</i> <sub>calc</sub> <sup>**</sup> Diffr.
1 1 7	—	3410	—	3	—	3
3 2 1	—	3440	—	14		
2 0 7	—	3588	—	0	—	2
2 2 5	—	3603	—	0		
3 2 2	—	3616	—	14	—	18
3 0 6	3713	3715	vwv	61		
4 1 0	3737	3737	vwv	60	—	3
3 1 5	—	3781	—	16		
4 0 4	—	3787	—	0	—	3
4 1 1	—	3796	—	7		
3 2 3	3911	3910	m <sup>-</sup>	160	8	24
1 0 8	—	3935	—	8		
4 1 2	—	3972	—	7	—	—
2 1 7	—	4122	—	19		
2 2 6	4249	4249	st	844	89	116
4 1 3	4268	4266	m	215		
1 1 8	—	4291	—	4	—	2
4 0 5	—	4315	—	0		
3 2 4	—	4321	—	16	—	12
3 1 6	4426	4427	w	119		

$$I_{\text{calc}}^* = 10^{-4} p \varphi(\Theta) F^2; \quad \varphi(\Theta) = \frac{1 + \cos 2a \cos^2 2\Theta}{\sin \Theta (1 + \cos 2a) \cos^2 (2\Theta - \beta) \sin 2\Theta} \quad (\text{cf. Ref. 9}).$$

$$I_{\text{calc}}^{**} = 10^{-4} p \frac{1 + \cos^2 \Theta}{\sin^2 \Theta \cos \Theta} F^2$$

$$|F(hk0)|^2 + |F(hk3)|^2 + |F(hk1)|^2 + |F(hk4)|^2 + |F(hk2)|^2 + |F(hk5)|^2.$$

The Laue symmetry found from the Weissenberg photographs was  $6/mmm$ . In the powder and Weissenberg photographs, the following spectra were systematically missing:  $h = 0, k = 0, l \neq 3n$  and  $h, k$  even,  $l \neq 3n$  ( $n$  is an integer). This is characteristic for the enantiomorphous space groups<sup>10</sup>  $P6_222$  (No. 180) and  $P6_422$  (No. 181). Possible space groups are:  $P6/mmm$  (No. 191),  $P6_2m$  (No. 189),  $P6_3m2$  (No. 187),  $P6mm$  (No. 183) and  $P622$  (No. 177).

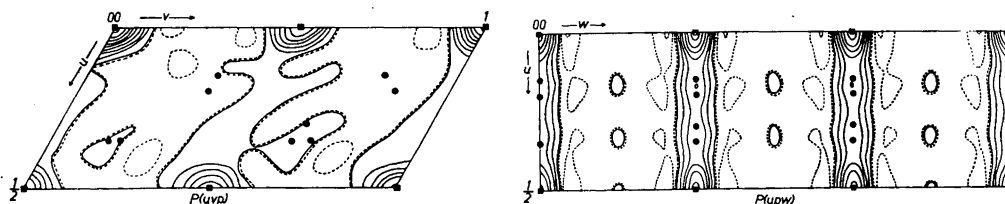


Fig. 1. The Patterson functions  $P(uvp)$  and  $P(upw)$ . The vectors Hg—Hg ( $\square$ ), Hg—I ( $\Delta$ ) and Hg—O ( $\bullet$ ) for the final structure are indicated. Dashed lines indicate negative values.

## THE POSITIONS OF THE MERCURY ATOMS

To locate the heavy metal atoms in the unit cell, the Patterson projections  $P(uvp)$  and  $P(upw)$  (Fig. 1) were calculated using  $F^2$  values derived from the visually estimated intensities of the Weissenberg photographs.

Now in space group  $P6_322$  (No. 180) and analogously for the enantiomorphous space group  $\bar{P}6_422$  (No. 181), it is possible for the six mercury atoms to occupy one of the sixfold point positions  $6(j)$ ,  $6(i)$ ,  $6(h)$ ,  $6(g)$ ,  $6(f)$  and  $6(e)$  or a combination of two threefold point positions  $3(d)$ ,  $3(c)$ ,  $3(b)$  and  $3(a)$ . Since it is not possible to distinguish between the two characteristic space groups, one of them, *viz.*  $P6_322$ , is chosen arbitrarily.

$P6_322$ :	$6(j)$ : $\pm(x, 2x), \frac{1}{2}$ ; $\pm(2x, x), \frac{1}{2}$ ; $\pm(x, \bar{x}), \frac{5}{6}$
	$6(i)$ : $\pm(x, 2x), 0$ ; $\pm(2x, x), \frac{5}{6}$ ; $\pm(x, \bar{x}), \frac{1}{3}$
	$6(h)$ : $\pm x, 0, \frac{1}{2}$ ; $0, \pm x, \frac{1}{2}$ ; $\pm(x, x), \frac{5}{6}$
	$6(g)$ : $\pm x, 0, 0$ ; $0, \pm x, \frac{1}{2}$ ; $\pm(x, x), \frac{1}{3}$
	$6(f)$ : $\frac{1}{2}, 0, \pm z$ ; $0, \frac{1}{2}, \frac{1}{2} \pm z$ ; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm z$
	$6(e)$ : $0, 0, \pm z$ ; $0, 0, \frac{1}{2} \pm z$ ; $0, 0, \frac{1}{2} \pm z$
	$3(d)$ : $\frac{1}{2}, 0, \frac{1}{2}$ ; $0, \frac{1}{2}, \frac{1}{2}$ ; $\frac{1}{2}, \frac{1}{2}, \frac{5}{6}$
	$3(c)$ : $\frac{1}{2}, 0, 0$ ; $0, \frac{1}{2}, \frac{1}{2}$ ; $\frac{1}{2}, \frac{1}{2}, \frac{1}{3}$
	$3(b)$ : $0, 0, \frac{1}{2}$ ; $0, 0, \frac{1}{2}$ ; $0, 0, \frac{1}{2}$
	$3(a)$ : $0, 0, 0$ ; $0, 0, \frac{1}{2}$ ; $0, 0, \frac{1}{2}$

The possible combinations of the threefold point positions are:

$3(a) + 3(b)$ ;  $3(a) + 3(c)$ ;  $3(a) + 3(d)$ ;  $3(b) + 3(c)$ ;  $3(b) + 3(d)$  and  $3(c) + 3(d)$ .

On displacing the origin of the unit cell by  $\frac{c}{2}$ , however, the point position

$6(j)$  becomes identical to  $6(i)$ ,  $6(h)$  to  $6(g)$ ,  $3(a) + 3(b)$  to  $3(c) + 3(d)$ ,  $3(a) + 3(c)$  to  $3(b) + 3(d)$  and  $3(a) + 3(d)$  to  $3(b) + 3(c)$ .

The Hg-Hg vectors  $u, v, w$ , required by these possibilities are given in Table 2. This table should be compared with Fig. 1.

The major maxima of the two Patterson projections should be mainly due to mercury-mercury vectors. The point positions  $6(e)$  and  $3(a) + 3(d)$  cannot explain the high maxima at

$u = \frac{1}{2}, v = 0$ ;  $u = 0, v = \frac{1}{2}$  and  $u = \frac{1}{2}, v = \frac{1}{2}$  in  $P(uvp)$  and can thus be excluded. Since there do not exist any heavy maxima at  $u = \frac{1}{2}, v = \frac{1}{3}$  or  $u = 0, v = \frac{1}{3}$  in  $P(uvp)$ , the combination  $3(a) + 3(b)$  can also be ruled out.

Nor was it possible to find an  $x$  parameter for the vectors  $u, v, w$ , of the point positions  $6(j)$  and  $6(h)$  which could satisfy the Patterson projections  $P(uvp)$  and  $P(upw)$ . Thus the remaining possibilities for the positions of the six mercury atoms in  $P6_322$  (No. 180) are:  $6(f)$  with  $z = 0.333$  or  $3(a) + 3(c)$ .

By calculating the values of the structure factors  $|F_{hkl}| = \sqrt{A^2 + B^2}$  for the two geometrically different arrangements of the six mercury atoms, it was found that they gave the same values. Thus, by evaluating the Patterson projections  $P(uvp)$  and  $P(upw)$  above, a homometric pair of arrangements for the mercury atoms was found. These two homometric mercury atom positions gave rise to six possible point positions for the three iodine atoms. The Patterson projections  $P(uvp)$  and  $P(upw)$  were then examined for these different possibilities.

Table 2. Required vectors Hg-Hg in the Patterson functions.

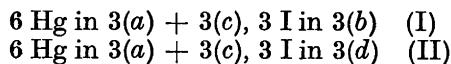
$6(j)$ :	$u$	$v$	$w$	Relative weight
	$\pm(3x$ ,	$3x)$	$\pm\frac{1}{3}$	4
	$\pm(x$ ,	$\bar{x})$	$\pm\frac{1}{3}$	4
	0	$\pm 3x$	$\pm\frac{1}{3}$	4
	$\pm 3x$	0	$\pm\frac{1}{3}$	4
	$\pm(2x$ ,	$x)$	$\pm\frac{1}{3}$	4
	$\pm(x$ ,	$2x)$	$\pm\frac{1}{3}$	4
	$\pm(4x$ ,	$2x)$	0	2
	$\pm(2x$ ,	$4x)$	0	2
	$\pm(2x$ ,	$2\bar{x})$	0	2
$6(h)$ :	$\pm(x$ ,	$\bar{x})$	$\pm\frac{1}{3}$	4
	$\pm(x$ ,	$x)$	$\pm\frac{1}{3}$	4
	$\pm(x$ ,	$2x)$	$\pm\frac{1}{3}$	4
	$\pm(2x$ ,	$x)$	$\pm\frac{1}{3}$	4
	0	$\pm x$	$\pm\frac{1}{3}$	4
	$\pm x$	0	$\pm\frac{1}{3}$	4
	$\pm 2x$	0	0	2
	0	$\pm 2x$	0	2
	$\pm(2x$ ,	$2x)$	0	2
$6(f)$ :	$\frac{1}{2}$	0	$\pm\frac{1}{3}$	4
	0	$\frac{1}{2}$	$\pm\frac{1}{3}$	4
	$\frac{1}{2}$	$\frac{1}{2}$	$\pm\frac{1}{3}$	4
	0	0	$\pm 2z$	6
	$\frac{1}{2}$	0	$\pm(2z \pm \frac{1}{3})$	4
	0	$\frac{1}{2}$	$\pm(2z \pm \frac{1}{3})$	4
	$\frac{1}{2}$	$\frac{1}{2}$	$\pm 2(z \pm \frac{1}{3})$	4
$6(e)$ :	0	0	$\pm\frac{1}{3}$	12
	0	0	$\pm 2z$	6
	0	0	$\pm(2z \pm \frac{1}{3})$	8
	0	0	$\pm(2z \pm \frac{2}{3})$	4
$3(a) + 3(b)$ :	$\frac{1}{2}$	0	$\pm\frac{1}{3}$	4
	$\frac{1}{2}$	0	$\pm\frac{1}{3}$	4
	0	$\frac{1}{2}$	$\pm\frac{1}{3}$	4
	0	$\frac{1}{2}$	$\pm\frac{1}{3}$	4
	$\frac{1}{2}$	$\frac{1}{2}$	$\pm\frac{1}{3}$	4
	$\frac{1}{2}$	$\frac{1}{2}$	$\pm\frac{1}{3}$	4
$3(a) + 3(c)$ :	0	0	$\pm\frac{1}{3}$	6
	$\frac{1}{2}$	0	$\pm\frac{1}{3}$	6
	0	$\frac{1}{2}$	$\pm\frac{1}{3}$	6
	$\frac{1}{2}$	$\frac{1}{2}$	$\pm\frac{1}{3}$	6
	$\frac{1}{2}$	0	0	2
	0	$\frac{1}{2}$	0	2
	$\frac{1}{2}$	$\frac{1}{2}$	0	2
$3(a) + 3(d)$ :	0	0	$\pm\frac{1}{3}$	12
	0	0	$\pm\frac{1}{3}$	12
	0	0	$\pm\frac{1}{3}$	6

Thus, if the mercury atoms occupy the combination of threefold point positions  $3(a)$  and  $3(c)$ , the only possible point positions left for the three iodine atoms are  $3(b)$  and  $3(d)$  since a statistical distribution over a sixfold point

Table 3. Required and observed vectors Hg-Hg and Hg-I in the Patterson projection  $P(uvw)$ . The structure possibility: 6 Hg in  $3(a) + 3(c)$ . The calculated relative weights of the maxima due to the Hg-Hg and Hg-I vectors were calculated using the expression  $v \sum_{h,i} f_i f_j$  where  $v$  denotes the frequency of the vector and  $f_i, f_j$  the scattering factors of the atoms.

$u$	$w$	Vectors Hg-Hg 6 Hg in $3(a) + 3(c)$	Vectors Hg-I 3 I in $3(b)$	Vectors Hg-I 3 I in $3(d)$	calc. I	calc. II	obs.
0	$\frac{1}{2}$		4	2	75	37	$\overline{200}$
0	$\frac{1}{3}$	6			178	178	400
0	$\frac{1}{3}$		4	4	75	75	$\overline{200}$
$\frac{1}{3}$	0	2			59	59	310
$\frac{1}{3}$	$\frac{1}{3}$		2	4	37	75	20
$\frac{1}{3}$	$\frac{1}{3}$	6			178	178	310
$\frac{1}{3}$	$\frac{1}{3}$		2	2	37	37	0

position is very improbable. Now, in Table 3, there are listed the required vectors mercury-mercury and mercury-iodine ( $u, w$ ) for the combinations:



From the calculated and observed heights of the maxima in this table, it is clearly seen that the possibilities I and II are inconsistent with the experimental data.

The arrangements I and II seem to be impossible also from space considerations. Case I gives a very short distance Hg-I of only 1.7 Å and case II offers 3 (b) as the only possible position for the three sodium atoms which results in the very short distance Hg-Na of 1.7 Å.

However, if the mercury atoms occupy the point position 6(f), then a point position for the iodine atoms can be found. This is explained in the following section.

The contribution of the iodine atoms to the X-ray intensities is relatively large and thus the observed Laue symmetry  $6/mmm$  must be valid also for the iodine atoms. Attempts have been made to find a mercury arrangement equivalent to  $3(a) + 3(c)$  in  $P6_222$  and to derive possible iodine arrangements, satisfying the observed heights of the maxima of the Patterson projection  $P(uvw)$ , in the possible space groups  $P6/mmm$  (No. 191),  $P\bar{6}2m$  (No. 189),  $P\bar{6}m2$  (No. 187),  $P6mm$  (No. 183) and  $P622$  (No. 177). The results of these calculations were in no case satisfactory.

Thus, X-ray data were alone sufficient to make a decision between the two homometric mercury atom positions. The only possibility was, namely, the point position 6(f) in  $P6_222$  (No. 180).

Table 4. Required vectors Hg-I in the Patterson functions.  
6 Hg in 6(*f*) + 3 I in 3(*a*), 3(*b*), 3(*c*) or 3(*d*).

	<i>u</i>	<i>v</i>	<i>w</i>	Relative weight
6( <i>f</i> ), 3( <i>a</i> ):	0	$\frac{1}{2}$	0	2
	0	$\frac{1}{2}$	$\pm \frac{1}{3}$	4
	$\frac{1}{2}$	0	0	2
	$\frac{1}{2}$	0	$\pm \frac{1}{3}$	4
	$\frac{1}{2}$	$\frac{1}{2}$	0	2
	$\frac{1}{2}$	$\frac{1}{2}$	$\pm \frac{1}{3}$	4
6( <i>f</i> ), 3( <i>b</i> ):	0	$\frac{1}{2}$	$\pm \frac{1}{3}$	4
	0	$\frac{1}{2}$	$\frac{1}{3}$	2
	$\frac{1}{2}$	0	$\pm \frac{1}{3}$	4
	$\frac{1}{2}$	0	$\frac{1}{3}$	2
	$\frac{1}{2}$	$\frac{1}{2}$	$\pm \frac{1}{3}$	4
	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{3}$	2
6( <i>f</i> ), 3( <i>c</i> ):	0	0	$\pm \frac{1}{3}$	6
	0	$\frac{1}{2}$	0	2
	0	$\frac{1}{2}$	$\pm \frac{1}{3}$	2
	$\frac{1}{2}$	0	0	2
	$\frac{1}{2}$	0	$\pm \frac{1}{3}$	2
	$\frac{1}{2}$	$\frac{1}{2}$	0	2
6( <i>f</i> ), 3( <i>d</i> ):	0	0	$\pm \frac{1}{3}$	6
	0	$\frac{1}{2}$	$\pm \frac{1}{3}$	2
	0	$\frac{1}{2}$	$\frac{1}{3}$	2
	$\frac{1}{2}$	0	$\pm \frac{1}{3}$	2
	$\frac{1}{2}$	0	$\frac{1}{3}$	2
	$\frac{1}{2}$	$\frac{1}{2}$	$\pm \frac{1}{3}$	2

#### THE POSITIONS OF THE IODINE ATOMS

Since the six mercury atoms occupy the point position 6(*f*) with  $z = 0.333$ , it is thus possible for the three iodine atoms to occupy one of the threefold point positions 3(*a*), 3(*b*), 3(*c*) or 3(*d*). The required mercury-iodine vectors  $u$ ,  $v$ ,  $w$  for the four different cases are listed in Table 4. From the Patterson projection  $P(upw)$  (Fig. 1), it is seen that it is impossible for the relatively heavy iodine atoms to occupy one of the threefold point positions 3(*b*) or 3(*d*) because the projection does not show any maxima at  $u = 0$ ,  $w = \pm \frac{1}{3}$  or  $u = 0$ ,  $w = \frac{1}{2}$ . On the other hand it is seen that the expected vectors Hg-I for the remaining possibilities for the iodine atoms 3(*a*) and 3(*c*) correspond to the calculated projection. However, the maximum of the projection  $P(upw)$  at  $u = 0$ ,  $w = \frac{1}{3}$  is about 30 % higher than that at  $u = \frac{1}{2}$ ,  $w = \frac{1}{3}$ . This can only be explained if the iodine atoms are situated in the point position 3(*c*) (Table 5).

To confirm that 3(*c*) is the actual point position for the iodine atoms, three-dimensional electron density calculations were performed using 860 reflexions (not independent) obtained with  $\text{CuK}$  radiation. Theoretically, the Fourier projection  $\rho(xyp)$  should differentiate between the possibilities 3(*a*) and



Table 5. Required and observed vectors Hg-Hg and Hg-I in the Patterson projection  $P(uvw)$ . The structure possibility: 6 Hg in 6(*f*). The calculations were performed as in Table 3.

$u$	$w$	Vectors Hg-Hg 6 Hg in 6( <i>f</i> )	Vectors Hg-I 3 I in 3( <i>a</i> )	Vectors Hg-I 3 I in 3( <i>c</i> )	Rel. weight calc. 3( <i>a</i> ), 6( <i>f</i> )	Rel. weight calc. 3( <i>c</i> ), 6( <i>f</i> )	Rel. weight obs.
0	$\frac{1}{3}$	6	2	4	332	395	400
$\frac{1}{2}$	0	4	4	4	298	298	310
$\frac{1}{2}$	$\frac{1}{3}$	6	4	2	395	332	310

3(*c*) but, as it is based on only a few reflexions, its exactness is much less than that of the sections of the three-dimensional electron density space. Hence, the electron density sections  $\rho(xy z)$  at  $z = 0, \frac{1}{6}, \frac{1}{3}, \frac{1}{2}$  and  $\frac{2}{3}$  were computed. The calculations were at first based on  $F$  values derived in the usual way from the visually estimated intensities of the reflexions and on the signs and values of the phase angles  $\alpha_{hkl} = \arctg \left( \frac{B}{A} \right)_{hkl}$  determined from the mercury contributions for all reflexions except 54 of the weakest.

The sections show high maxima at  $0\frac{1}{2}0, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{3}, 0\frac{1}{2}\frac{1}{3}, \frac{1}{2}0\frac{2}{3}$  and  $\frac{1}{2}\frac{1}{2}\frac{2}{3}$  which is expected for mercury atoms occupying the point position 6(*f*) that was assumed when calculating the values of the phase angles. Moreover, maxima with a height correct for an iodine atom appear at  $\frac{1}{2}00, \frac{1}{2}\frac{1}{2}\frac{1}{3}$  and  $0\frac{1}{2}\frac{2}{3}$ , indicating that the iodine atoms are situated in the point position 3(*c*). Apart from these maxima, there are only small maxima in the sections  $\rho(xy0), \rho(xy\frac{1}{3})$  and  $\rho(xy\frac{2}{3})$  and they can be ascribed to diffraction effects from the mercury and iodine atoms and to sodium and oxygen atoms. The sections  $\rho(xy\frac{1}{6})$  and  $\rho(xy\frac{1}{2})$  show small peaks at  $x = 0, y = 0$  (Fig. 2). Otherwise, these sections do not show any peaks with a height differing from the general background by more than that expected for diffraction effects from the heavy atoms. Using calculated  $F$  values (the contributions of the mercury atoms only being taken into account) and the same phase angles as above, the electron density sections  $\rho(xy0)$  and  $\rho(xy\frac{1}{3})$  were also computed. These sections did not show any maxima at  $\frac{1}{2}00$  and  $\frac{1}{2}\frac{1}{2}\frac{1}{3}$  — only the high maxima at  $0\frac{1}{2}0, \frac{1}{2}\frac{1}{2}0, \frac{1}{2}0\frac{1}{3}$  and  $0\frac{1}{2}\frac{1}{3}$ . This further confirms that the point position of the iodine atoms is 3(*c*).

The electron density sections  $\rho(xy0), \rho(xy\frac{1}{3})$  (Fig. 2) and  $\rho(xy\frac{2}{3})$  were then recalculated using the observed  $F$  values and the signs and values of the phase angles determined from the contributions of the mercury and iodine atoms for all observed reflexions. There was no difference worth mentioning between these sections and those obtained by the previous calculations. To obtain further proof concerning the positions of the iodine atoms and if possible to get some information on the positions of the sodium and the oxygen atoms, first the mercury atoms and then both the mercury and iodine atoms (Fig. 2) were subtracted from  $\rho(xy0)$  and  $\rho(xy\frac{1}{3})$ . In this way, most of the diffraction

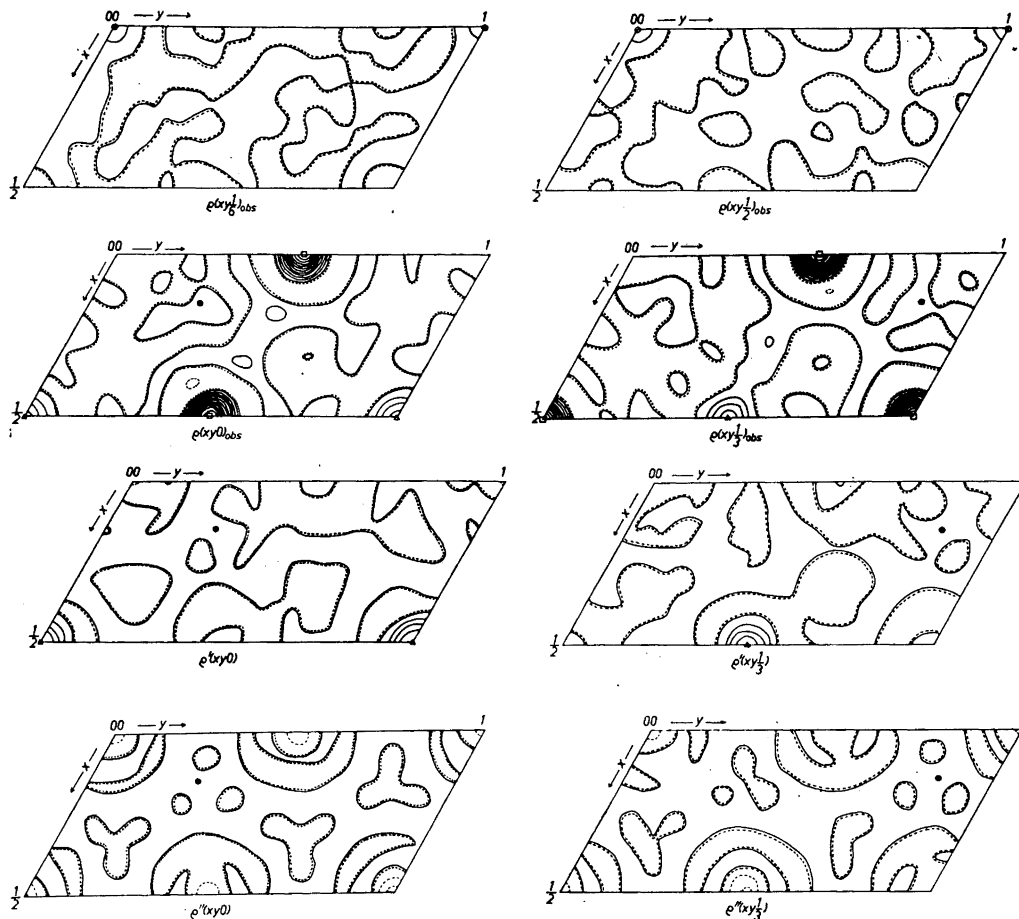


Fig. 2. The observed electron density sections  $\rho(xy\frac{1}{2})$ ,  $\rho(xy\frac{1}{2})$ ,  $\rho(xy0)$  and  $\rho(xy\frac{1}{2})$ , the electron density sections  $\rho'(xy0)$  and  $\rho''(xy\frac{1}{2})$ , where the contributions of the mercury atoms are subtracted from  $\rho(xy0)$  and  $\rho(xy\frac{1}{2})$ , and the electron density sections  $\rho''(xy0)$  and  $\rho''(xy\frac{1}{2})$ , where the contributions of the mercury and of the iodine atoms have been subtracted from  $\rho(xy0)$  and  $\rho(xy\frac{1}{2})$ . The final mercury ( $\square$ ), iodine ( $\triangle$ ), oxygen ( $\bullet$ ) and sodium ( $\circ$ ) atom positions are indicated. Dashed lines indicate negative values.

effects<sup>4</sup> from the heavy atoms should disappear and only maxima indicating the iodine atoms and possibly small maxima indicating the sodium and oxygen atoms (Fig. 2) should be obtained. As expected, these calculations show clearly that the point position of the three iodine atoms is 3(c).

The temperature factor that should have been introduced in these calculations was found to be negligible when calculated by the ordinary procedure. Probably, it approximately cancels out with the absorption effects.

The positions for the sodium and oxygen atoms which could possibly be obtained from these sections would doubtless be rather uncertain. One reason is that the Fourier series has in fact been broken at  $l = 5$ , another one is the dominant scattering power for X-rays of the heavy atoms. No attempt was therefore made to utilize the information obtainable from these small maxima for the determination of the positions of the light atoms.

### THE POSITIONS OF THE LIGHT ATOMS

The above discussion has shown that the six mercury atoms occupy the point position  $6(f)$  and the three iodine atoms the point position  $3(c)$  in the space group  $P6_222$  (No. 180). Consequently the holes between these atoms must also possess the symmetry  $P6_222$ . It is therefore probable that the sodium and the oxygen atoms have the same symmetry — it will be seen later on that this is supported by the results of a neutron diffraction investigation. Now, in  $P6_222$ , the only positions left for the three sodium atoms are  $3(a)$ ,  $3(b)$  and  $3(d)$  (see p. 2200). The position  $3(d)$  would result in a very short distance Hg-Na of only 1.7 Å and can therefore be excluded. The remaining positions  $3(a)$  and  $3(b)$  are, with regard to the distances Hg-Na and I-Na, equally probable for the sodium atoms. In the unit cell, there are in addition six oxygen atoms. The positions left for them are therefore:  $6(i)$ ,  $6(j)$ ,  $6(h)$ ,  $6(g)$ ,  $6(f)$ ,  $6(e)$ , the combinations of the threefold point positions  $3(a) + 3(d)$  and  $3(b) + 3(d)$  and the less probable arrangement of a statistical distribution over  $12(k)$ . The possibilities  $3(a) + 3(d)$ ,  $3(b) + 3(d)$ ,  $6(e)$  and  $6(f)$  would give a very short distance of 1.7 Å between Hg-O, O-O or I-O and can thus be ruled out. Hence, the possibilities for the oxygen atoms are limited to  $6(j)$ ,  $6(i)$ ,  $6(h)$  and  $6(g)$ . To find the arrangement of the light atoms according to the possible point positions, it is necessary to consider the geometry of the holes in the structure. The following distances from the mercury, sodium and iodine atoms to the oxygen atoms were assumed when drawing  $xy$ -sections of the unit cell at different  $z$  values:

$$\text{Hg-O} \geq 2.0 \text{ \AA}, \quad \text{Na-O} \geq 2.3 \text{ \AA}, \quad \text{I-O} \geq 3.0 \text{ \AA}.$$

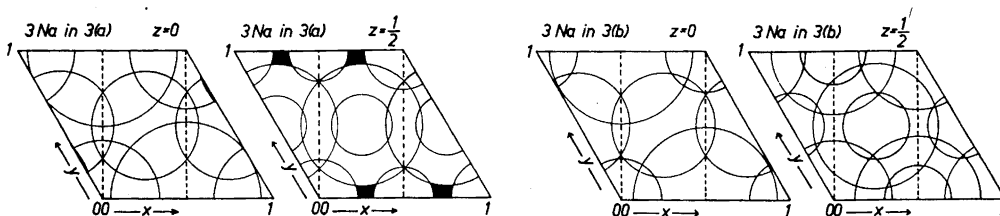


Fig. 3. Survey over the space which is free (black areas) for the oxygen atoms in the planes  $z = 0$  and  $z = 0.50$ . The point position of the sodium atoms is assumed to be  $3(a)$  and  $3(b)$ . The function  $y = 2x$  is drawn with dashed lines.

The results are given in Fig. 3. From these figures, it can be concluded that the possible positions for the sodium and oxygen atoms are:

- A: 3 Na in 3(*a*), 6 O in 6(*j*) with  $x \sim 0.40$ .  
 B: 3 Na in 3(*a*), 6 O in 6(*h*) with  $0.30 \geq x \geq 0.20$ .  
 C: 3 Na in 3(*b*), 6 O in 6(*i*) with  $x \sim 0.15$ .

The combinations A and B give rise to an arrangement for the mercury and the oxygen atoms which seems very unusual. Each mercury atom is coordinated to two oxygen atoms and each oxygen atom to two mercury atoms, giving an arrangement of isolated rhombs of the composition  $\text{Hg}_2\text{O}_2$ . The distances from the mercury and sodium atoms to the oxygen atoms are:

- A:  $x_0 = 0.40$ , Hg-O = 2.6 Å, Na-O = 2.1 Å.  
 B:  $x_0 = 0.25$ , Hg-O = 2.4 Å, Na-O = 2.4 Å.

With the combination C, the arrangement of the mercury and oxygen atoms is made up of planar zig-zag chains -Hg-O-Hg- with all distances Hg-O equal to 2.0 Å, the oxygen parameter being 0.15. The structure of orthorhombic mercury(II)oxide described earlier<sup>1</sup> is built up of such chains with the same distance Hg-O and the same values for the angles O-Hg-O and Hg-O-Hg as given here for the possibility C. It seems therefore very probable that the combination C is the most applicable one for this structure problem.

In order to make possible an objective decision between the three geometrically possible structures, the investigation was supplemented by a neutron diffraction study.

#### NEUTRON DIFFRACTION STUDIES

The coherent scattering amplitudes of mercury, iodine, sodium and oxygen for neutrons and X-rays are given in the following table:

	Scattering amplitude ( $10^{-12}$ cm), Ref. <sup>11</sup>	
	Neutron	X-ray ( $\theta = 0^\circ$ )
Hg	1.31	22.5
I	0.52	15.0
Na	0.35	3.09
O	0.58	2.25

The amplitude values for neutrons are independent of the scattering angle while those for X-rays decrease with  $\theta$  and relatively more so for sodium and oxygen than for mercury and iodine. Therefore, it seems rather unlikely that one can locate these light atoms from the observed X-ray data but it is evident that neutron diffraction work would provide much better possibilities for the determination of the sites. Since it was impossible to get a crystal large enough for single crystal investigations with the apparatus available, the neutron diffraction work was carried out on a powder sample in a flat aluminium container. Since the cross section for true absorption is very large

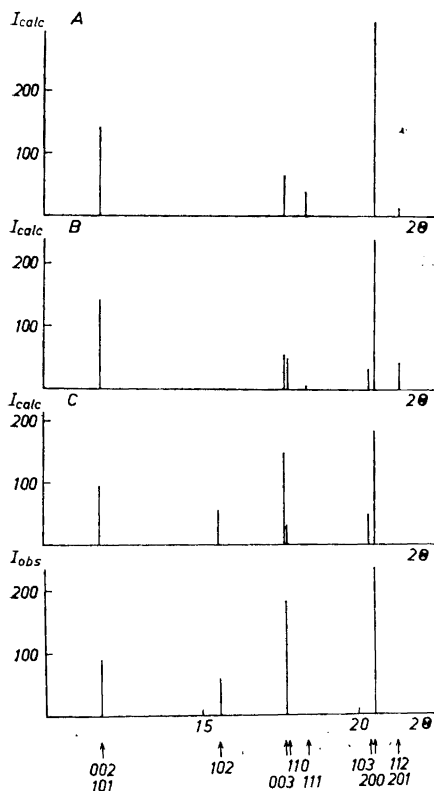
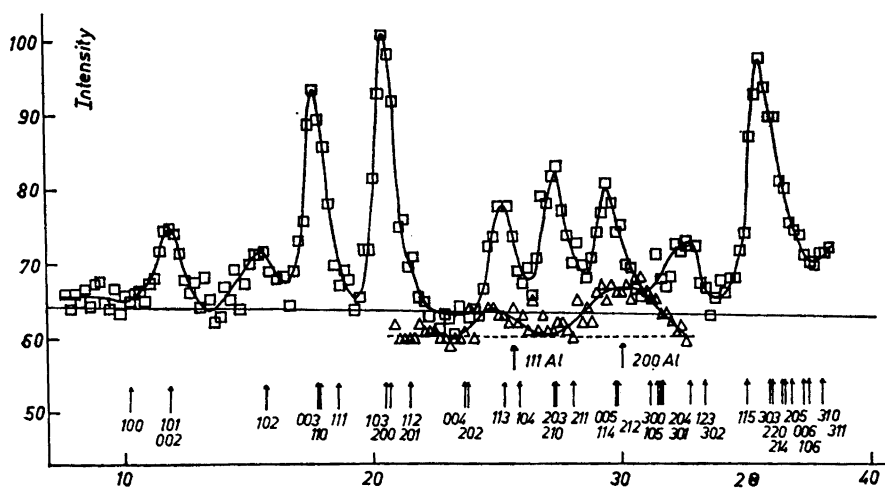


Fig. 4. Neutron diffraction powder diagram of  $\text{Hg}_2\text{O}_2\text{NaI}$  in an aluminium container. The curve for the aluminium reflections 111 and 200 is shown underneath. The diagrams at the left show observed neutron intensities and intensities calculated for the cases A, B and C. Only reflections of angles up to  $2\theta = 21.5^\circ$  are given.

Table 6. Observed neutron intensities from a powdered sample of  $\text{Hg}_2\text{O}_2\text{NaI}$ . The intensities of the coinciding reflexions 113 and 104, from 005 to 212 and from 300 to 302 were corrected for the contributions of the aluminium reflexions 111 and 200. The intensities were calculated for the case C (3(b), 6(i)): I. neglecting the influence of the oxygen atoms and II. taking the influence of the oxygen atoms into account.  $I_{\text{calc I}}$  and  $I_{\text{calc II}}$  are normalized so as to give the best agreement with  $I_{\text{obs}}$ .

<i>hkl</i>	$I_{\text{obs}}$	$I_{\text{calc I}}$	$I_{\text{calc II}}$	<i>hkl</i>	$I_{\text{obs}}$	$I_{\text{calc I}}$	$I_{\text{calc II}}$
101	89	40	93	005			
002				114	66	20	39
				212			
102	59	23	54				
003				300			
110	182	116	176	204			
111				105			
				301	128	102	103
103				123			
200	235	404	227	302			
112							
201				115			
004	—	0	1	303			
202				220			
				221			
113	84	73	106	214			
104				205	290	206	300
203				006			
210	143	293	178	106			
211				310			
				222			
				311			

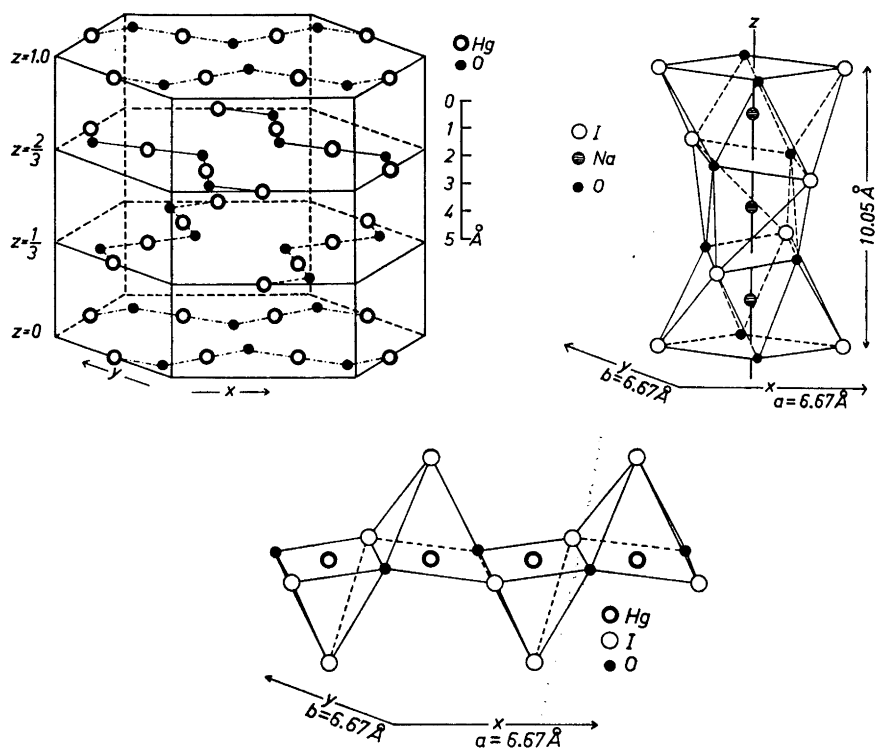
for mercury, the powder sample had to be thin and the observed neutron intensities were therefore low. The aluminium holder was chosen so that  $\mu \cdot t = 0.439$  where  $\mu$  is the linear absorption coefficient of the compound.

Table 7. Observed neutron intensities from a powdered sample of  $\text{Hg}_2\text{O}_2\text{NaI}$  and intensities calculated for the structure possibility C. The parameter for the oxygen atom position was varied within the limits  $0.10 \leq x_{\text{O}} \leq 0.20$ .

<i>hkl</i>	$I_{\text{obs}}$	$I_{\text{calc}}$				
		$x_{\text{O}} = 0.10$	$x_{\text{O}} = 0.13$	$x_{\text{O}} = 0.15$	$x_{\text{O}} = 0.17$	$x_{\text{O}} = 0.20$
101 } 002 }	89	69	83	96	92	101
102 } 003 }	59	40	48	55	53	58
110 } 111 }	182	166	197	180	203	152
103 } 200 }	235	290	237	233	217	254
112 } 201 }						

Table 8. Calculated and observed structure factors  $hkl$  for  $\text{Hg}_2\text{O}_2\text{NaI}$ .

$hkl$	$ F_{\text{calc}} $	$ F_{\text{obs}} $	$hkl$	$ F_{\text{calc}} $	$ F_{\text{obs}} $
0 1 0	160	149	1 6 2	34	36
0 2 0	556	502	2 2 2	2	—
0 3 0	147	192	2 3 2	42	38
0 4 0	430	418	2 4 2	5	—
0 5 0	117	122	2 5 2	29	33
0 6 0	369	355	2 6 2	6	—
0 7 0	84	124	3 3 2	28	33
1 1 0	173	236	3 4 2	39	38
1 2 0	146	195	3 5 2	34	36
1 3 0	122	162	4 4 2	3	—
1 4 0	119	154	0 0 3	579	619
1 5 0	108	99	0 1 3	198	195
1 6 0	93	83	0 2 3	463	325
2 2 0	490	418	0 3 3	179	215
2 3 0	106	112	0 4 3	379	401
2 4 0	380	388	0 5 3	144	163
2 5 0	106	83	0 6 3	336	329
2 6 0	315	281	0 7 3	103	117
3 3 0	110	145	1 1 3	206	178
3 4 0	107	107	1 2 3	179	183
3 5 0	95	83	1 3 3	155	195
4 4 0	335	289	1 4 3	148	185
0 1 1	66	64	1 5 3	133	149
0 2 1	5	—	1 6 3	113	124
0 3 1	29	30	2 2 3	427	274
0 4 1	8	—	2 3 3	136	135
0 5 1	43	46	2 4 3	342	383
0 6 1	2	—	2 5 3	128	144
0 7 1	32	33	2 6 3	290	282
1 1 1	26	13	3 3 3	137	167
1 2 1	58	58	3 4 3	129	134
1 3 1	49	46	3 5 3	113	109
1 4 1	29	33	4 4 3	308	291
1 5 1	41	51	0 1 4	58	54
1 6 1	34	45	0 2 4	2	—
2 2 1	1	—	0 3 4	29	31
2 3 1	42	40	0 4 4	6	—
2 4 1	6	—	0 5 4	41	48
2 5 1	29	26	0 6 4	0	—
2 6 1	7	—	0 7 4	32	28
3 3 1	28	38	1 1 4	27	25
3 4 1	39	45	1 2 4	52	45
3 5 1	34	41	1 3 4	45	46
4 4 1	3	—	1 4 4	28	30
0 1 2	64	51	1 5 4	39	46
0 2 2	5	—	1 6 4	33	33
0 3 2	29	26	2 2 4	2	—
0 4 2	7	—	2 3 4	40	46
0 5 2	42	41	2 4 4	4	—
0 6 2	2	—	2 5 4	29	25
0 7 2	32	46	3 3 4	27	36
1 1 2	26	31	3 4 4	38	46
1 2 2	57	61	3 5 4	33	33
1 3 2	48	56	4 4 4	2	—
1 4 2	29	33			
1 5 2	41	50			



*Fig. 5.* Schematic drawings showing the infinite planar chains  $-\text{O}-\text{Hg}-\text{O}-\text{Hg}-$ , lying perpendicularly to the  $c$  axis at the heights  $z = 0, \frac{1}{3}$  and  $\frac{2}{3}$ , showing a chain of deformed Archimedean square antiprisms, running parallel to the  $c$  axis and showing a chain of pyramids, lying perpendicularly to the  $c$  axis. Each Archimedean antiprism is made up of four iodine and four oxygen atoms with one sodium atom in its centre. Each pyramid is made up of three iodine and two oxygen atoms with one mercury atom in the centre of its base plane.

and  $t$  the length of the sample. The reactor was run at a level of 450 kW. The diffracted intensity was measured at intervals of  $0.2^\circ$  scattering angle, counts being taken during the time necessary for accumulating 500 000 neutron counts in the monitor for the incident neutron beam. The curve that was obtained by plotting the counts against the angles is given in Fig. 4. The observed intensities, obtained by measuring the areas under the peaks with a planimeter and correcting for the contribution of the aluminium reflexions 111 and 200 from the container, are given in Table 6. Due to serious overlapping, only the intensities of the reflexions at low  $\theta$  could be evaluated with accuracy. The neutron intensities of the observed reflexions were calculated for the structure possibilities A, B and C assuming the parameter values given above and were compared with the observed intensities in a neutron diffraction diagram. The result is given in Fig. 4, from which it is



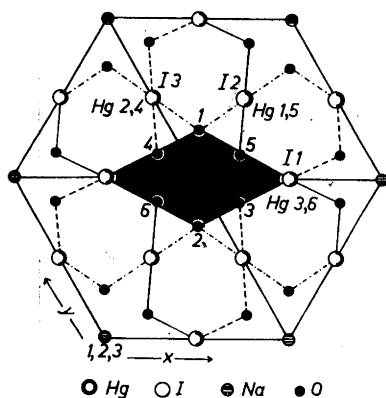


Fig. 6: The  $xy$  projection of the structure of  $\text{Hg}_2\text{O}_2\text{NaI}$  showing the coordination of the atoms. The infinite planar chain  $-\text{O}-\text{Hg}-\text{O}-$  at  $z = 0$  is indicated by a dashed-dotted line, that at  $z = 0.33$  by a dotted line and that at  $z = 0.67$  by a full line. The base plane of the deformed Archimedean antiprism at  $z = 0$  is indicated by the black area.

Na 1	$z = 1/6$ ;	Hg 1,2	$z = 0$ ;	I 1	$z = 0$ ;	O 1,2	$z = 0$
Na 2	$z = 1/2$ ;	Hg 3,4	$z = 1/3$ ;	I 2	$z = 1/3$ ;	O 3,4	$z = 1/3$
Na 3	$z = 5/6$ ;	Hg 5,6	$z = 2/3$ ;	I 3	$z = 2/3$ ;	O 5,6	$z = 2/3$

clearly seen that the possibility C is the only one that is consistent with the experimental data. For the case C, a systematic variation of the parameter for the oxygen atom position gave the best agreement between observed and calculated intensities when  $x_0 = 0.15$  (Table 7). The neutron intensities of the reflexions were calculated according to Bacon<sup>12</sup>, the influence of the temperature factor being, however, neglected.

#### CORRELATION OF X-RAY AND NEUTRON DIFFRACTION INTENSITIES

The point positions and parameters of the atoms having been determined, the X-ray structure factors of the reflexions  $hkl$  were then calculated and compared with the observed ones (*cf.* Table 8). The influence of the temperature factor was, however, neglected. The agreement between observed and calculated values was found to be good. To obtain a criterion of the correspondence, the reliability factor  $R = \frac{\sum ||F_{\text{obs}}| - |F_{\text{calc}}||}{\sum |F_{\text{obs}}|}$  was calculated according to Booth<sup>13</sup> and found to be 13.7 % (absent reflexions included) or 13.0 % (absent reflexions not included), showing that the structure should be essentially correct as regards the heavy atoms.

To reduce the influence of orientation effects observed in the Guinier photogram (*e.g.* the reflexion 303), accurate values for the intensities of the X-ray powder reflexions were measured for a sample mixed with gum arabic (1 : 3) using a Geiger-Mueller diffractometer. The observed intensities obtained by measuring the areas under the peaks are given in Table 1. For overlapping reflexions, the sum of the intensities are given. As seen, the agreement between observed and calculated intensities is good (Table 1).

The calculated and observed neutron intensities for all reflexions that could be evaluated are given in Table 6. The accuracy of the observed reflexions

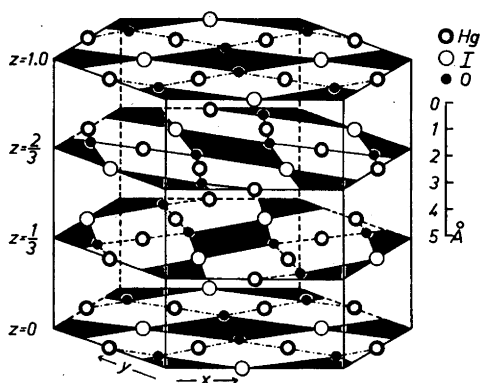


Fig. 7. A schematic drawing showing the connection between the infinite planar chains  $-\text{O}-\text{Hg}-\text{O}-$  and the base planes of the Archimedean antiprisms. The base planes are indicated by black areas.

Table 9. Interatomic distances in the structure of  $\text{Hg}_3\text{O}_3\text{NaI}$ . The atoms are named as in the  $xy$  projection (Fig. 6).

$\text{Hg}_1-\text{O}_1, \text{O}_3$	2.03 Å	$\text{Hg}_1-\text{Hg}_2$	3.33 Å
$\text{Hg}_2-\text{O}_1, \text{O}_3$	2.03 Å	$\text{Hg}_1-\text{Hg}_5$	3.35 Å
$\text{Hg}_3-\text{O}_3, \text{O}_4$	2.03 Å	$\text{Hg}_2-\text{Hg}_4$	3.35 Å
$\text{Hg}_4-\text{O}_3, \text{O}_4$	2.03 Å	$\text{Hg}_3-\text{Hg}_4$	3.33 Å
$\text{Hg}_5-\text{O}_5, \text{O}_6$	2.03 Å	$\text{Hg}_3-\text{Hg}_6$	3.35 Å
$\text{Hg}_6-\text{O}_5, \text{O}_6$	2.03 Å	$\text{Hg}_5-\text{Hg}_6$	3.33 Å
$\text{Na}_1-\text{O}_1, \text{O}_3, \text{O}_5, \text{O}_6$	2.41 Å	$\text{Na}_1-\text{Na}_2$	3.35 Å
$\text{Na}_2-\text{O}_3, \text{O}_4, \text{O}_5, \text{O}_6$	2.41 Å	$\text{Na}_1-\text{Na}_3$	3.35 Å
$\text{Na}_3-\text{O}_1, \text{O}_2, \text{O}_5, \text{O}_6$	2.41 Å	$\text{Na}_2-\text{Na}_3$	3.35 Å
$\text{Na}_1-\text{I}_1, \text{I}_2$	3.73 Å	$\text{I}_1-\text{I}_2, \text{I}_3$	4.73 Å
$\text{Na}_2-\text{I}_2, \text{I}_3$	3.73 Å	$\text{I}_2-\text{I}_3$	4.73 Å
$\text{Na}_3-\text{I}_1, \text{I}_3$	3.73 Å		
$\text{I}_1-\text{Hg}_1, \text{Hg}_2$	3.33 Å	$\text{O}_1-\text{O}_2$	3.46 Å*, 4.06 Å**
$\text{I}_1-\text{Hg}_3, \text{Hg}_6$	3.35 Å	$\text{O}_1-\text{O}_4, \text{O}_5$	3.77 Å
$\text{I}_2-\text{Hg}_3, \text{Hg}_4$	3.33 Å	$\text{O}_1-\text{O}_3, \text{O}_6$	4.49 Å
$\text{I}_2-\text{Hg}_1, \text{Hg}_5$	3.35 Å	$\text{O}_2-\text{O}_3, \text{O}_6$	3.77 Å
$\text{I}_3-\text{Hg}_3, \text{Hg}_6$	3.33 Å	$\text{O}_2-\text{O}_4, \text{O}_5$	4.49 Å
$\text{I}_3-\text{Hg}_2, \text{Hg}_4$	3.35 Å	$\text{O}_3-\text{O}_4$	3.46 Å*, 4.06 Å**
		$\text{O}_3-\text{O}_5$	3.77 Å
$\text{I}_1-\text{O}_1, \text{O}_3$	3.76 Å	$\text{O}_3-\text{O}_6$	4.49 Å
$\text{I}_1-\text{O}_3, \text{O}_4, \text{O}_5, \text{O}_6$	3.92 Å	$\text{O}_4-\text{O}_5$	4.49 Å
$\text{I}_2-\text{O}_1, \text{O}_3, \text{O}_5, \text{O}_6$	3.92 Å	$\text{O}_4-\text{O}_6$	3.77 Å
$\text{I}_2-\text{O}_3, \text{O}_4$	3.76 Å	$\text{O}_5-\text{O}_6$	3.46 Å*, 4.06 Å**
$\text{I}_3-\text{O}_5, \text{O}_6$	3.76 Å		
$\text{I}_3-\text{O}_1, \text{O}_2, \text{O}_3, \text{O}_4$	3.92 Å		
$\text{Na}_1-\text{Hg}_1, \text{Hg}_2, \text{Hg}_3, \text{Hg}_4$	3.73 Å		
$\text{Na}_2-\text{Hg}_3, \text{Hg}_4, \text{Hg}_5, \text{Hg}_6$	3.73 Å		
$\text{Na}_3-\text{Hg}_1, \text{Hg}_2, \text{Hg}_5, \text{Hg}_6$	3.73 Å		

\* within a chain  $-\text{O}-\text{Hg}-\text{O}-$   
 \*\* between two chains  $-\text{O}-\text{Hg}-\text{O}-$

that had to be corrected for the contributions due to the aluminium reflexions is less than that of those peaks, at low  $2\theta$  values, which were not affected by these reflexions (Fig. 4). Taking this fact into consideration, it can be concluded that the agreement between calculated and observed intensities is satisfactory, thus showing that the structure should be principally correct also as regards the light atoms.

#### DESCRIPTION OF THE STRUCTURE

The following structure is therefore proposed for  $\text{Hg}_2\text{O}_2\text{NaI}$ :  
Cell content: 3  $\text{Hg}_2\text{O}_2\text{NaI}$

Space group:  $P6_22$  (No. 180)

6 Hg in 6(*f*):  $\frac{1}{2}, 0, \pm z$ ;  $0, \frac{1}{2}, \frac{2}{3} \pm z$ ;  $\frac{1}{2}, \frac{1}{2}, \frac{1}{3} \pm z$ ;  $z = 0.333$

3 I in 3(*c*):  $\frac{1}{2}, 0, 0$ ;  $0, \frac{1}{2}, \frac{2}{3}$ ;  $\frac{1}{2}, \frac{1}{2}, \frac{1}{3}$

3 Na in 3(*b*):  $0, 0, \frac{1}{2}$ ;  $0, 0, \frac{5}{8}$ ;  $0, 0, \frac{1}{8}$

6 O in 6(*i*):  $\pm(x, 2x), 0$ ;  $\pm(2x, x), \frac{2}{3}$ ;  $\pm(x, \bar{x}), \frac{1}{3}$ ;  $x = 0.15$

A fundamental constituent of the structure is the series of infinite planar zig-zag chains  $-\text{O}-\text{Hg}-\text{O}-$ , lying perpendicularly to the *c* axis at the heights  $z = 0, \frac{1}{3}$  and  $\frac{2}{3}$  (Fig. 5). The distances Hg-O within the chains are 2.03 Å (Table 9) and the angles O-Hg-O  $180^\circ \pm 3^\circ$  and Hg-O-Hg  $110^\circ \pm 1^\circ$ . This Hg-O distance and the values of the angles (*cf.* Refs.<sup>14,15</sup>) suggest that the bond between Hg and O within the chains is mainly homopolar. Since the interatomic distances are considerably larger between the chains, the forces between them are far weaker.

Each mercury atom is, in addition to the two oxygen atoms at the close distance of 2.03 Å, also surrounded by three iodine atoms at the distances  $\frac{a}{2} = 3.33$  Å and  $\frac{c}{3} = 3.35$  Å, the two oxygen and the three iodine atoms thus forming a pyramid with the mercury atom in the centre of its base plane (Fig. 5).

Each iodine atom is octahedrally surrounded by six mercury atoms at the distances 3.33 and 3.35 Å. The calculated sum of the ionic radii is 3.26 Å (Ref.<sup>16</sup>).

Each sodium atom in the structure is surrounded by four oxygen and four iodine atoms, forming a deformed square Archimedean antiprism. These coordination polyhedra share their base planes to form infinite chains running along the *c* axis of the unit cell (Fig. 5). The interatomic distances in the polyhedra and between the polyhedra and the chains are listed in Table 9 (Fig. 6). The distances Na-I seem to be relatively long but the Na-O distances are close to the sum of the ionic radii (Ref.<sup>16</sup>):

	obs.	calc.		obs.	calc.
Na-I, (Å)	3.73	3.11	Na-O, (Å)	2.41	2.36

The connection between the chains and the base planes of the Archimedean antiprism is shown clearly in Fig. 7.

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