Least-Squares Refinement of the Crystal Structures of Orthorhombic HgO and of Hg_2O_2NaI

KARIN AURIVILLIUS

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

Determinations of the crystal structures of orthorhombic mercury(II) oxide [1,2] and of Hg_2O_2NaI [3] have been previously reported by the author. Both structure determinations, performed by using Fourier methods, were based on X-ray single-crystal data, which in the case of HgO(o-rh) were combined with neutron single-crystal data and in the case of Hg_2O_2NaI with neutron powder data. Since the results of these investigations were published, the possibilities of using electronic computers for crystallographic work have been considerably increased at this laboratory, in particular by the preparation of several new programs, such as for the refinement of crystal structures by least-squares methods [4] and for absorption corrections.[5] The computing facilities thus available have been extensively used in the determination of the crystal structure of Hg_3OCl_4.[6,7] In this connection it was found worthwhile to under-take least-squares refinements of the crystal structures of HgO(o-rh) and Hg_2O_2NaI. The results thus obtained are briefly presented in this article. Full details are given elsewhere.[8]

Table 1. The structure of orthorhombic mercury(II)oxide. The coordinates given earlier [1] are in italics and below them are listed the values obtained from the present refinement.

Space group: *Pnma* (No. 62 in the *International Tables*).

Unit-cell dimensions: $a = 6.6129 \pm 0.0009$ Å, $b = 5.5208 \pm 0.0007$ Å, $c = 3.5219 \pm 0.0005$ Å.* Cell content: 4 formula units HgO
4 Hg in 4(*c*); $\pm(x,\frac{1}{4},z;\ \frac{1}{2}+x,\frac{1}{4},\frac{1}{2}-z)$
4 O in 4(*c*).

Atom	x	σ_x Å	y	z	σ_z Å	B Å^2	σ_B Å^2
Hg	*0.115* 0.1136	0.002	$\frac{1}{4}$	*0.245* 0.2456	0.001	1.20	0.04
O	*0.36*$_5$ 0.3592	0.029	$\frac{1}{4}$	*0.58*$_5$ 0.5955	0.027	1.47	0.49

* The standard deviations in the cell edges were calculated by means of the method of least squares.

Table 2. The crystal structure of Hg_2O_2NaI. The coordinates given earlier [3] are in italics and below them are listed the values obtained from the present refinement.
Space group: $P6_222$ (No. 180 in the *International Tables*). Unit-cell dimensions: $a = 6.667 \pm 0.001$ Å; $c = 10.054 \pm 0.002$ Å.* Cell content: 3 formula units Hg_2O_2NaI.
6 Hg in 6(*f*): $\frac{1}{2},0,\pm z;\ 0,\frac{1}{2},\frac{2}{3}\pm z;\ \frac{1}{2},\frac{1}{2},\frac{1}{3}\pm z$
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*): $0,0,\frac{1}{2};\ 0,0,\frac{5}{6};\ 0,0,\frac{1}{6}$
6 O in 6(*i*): $\pm(x,2x),0;\ \pm(2x,x),\frac{2}{3};\ \pm(x,\bar{x}),\frac{1}{3}$.

Atom	x	σ_x Å	y	σ_y Å	z	σ_z Å	B Å^2	σ_B Å^2
Hg	$\frac{1}{2}$		0		*0.333* 0.3333	0.003	0.17	0.05
I	$\frac{1}{2}$		0		0		0.43	0.09
Na	0		0		$\frac{1}{2}$		−0.76	0.52
O	*0.15* 0.1521	0.033	*0.30* 0.3042	0.033	0		0.12	0.82

* The standard deviations in the cell edges were calculated by means of the method of least squares.

For the refinement of the structure of HgO(o-rh), three-dimensional single-crystal X-ray data were collected using a synthetic crystal of accurately measured dimensions. The method of synthesis involved crystallization under hydrothermal conditions at 310°C and 3000 bars for a period of one week. For further details on the experimental work, *cf.* Ref.[8] The diffraction data thus obtained were carefully corrected for the heavy absorption.

The Weissenberg X-ray data used in the previous study of the compound Hg_2O_2NaI were considered less influenced by absorption than were those of HgO. The refinement of Hg_2O_2NaI was therefore carried out on the basis of the intensity data given in a previous paper,[3] disregarding the influence of absorption. It is fully realized that using appropriate absorption corrections a more accurate structure might have been obtained.

The refinement of the two structures were performed using the electronic computer FACIT EDB and the programs mentioned above.[4,5] When in the case of HgO the shifts in the coordinates of Hg and O were 0.0 % and 0.2 % of their standard deviations the refinement was considered to be complete. In the case of Hg_2O_2NaI the corresponding shifts were 6 % and 13 %. The weight analyses in the last cycles were considered acceptable. The individual isotropic temperature factors are of the same magnitude for both atomic species in HgO. The factors of all atoms in Hg_2O_2NaI lie close to zero and are not especially divergent. The low values of the factors obtained in the latter case probably reflect the fact that the intensities were not corrected for absorption. The final discrepancy factors of the structures are 8.9 % and 10.4 %, absent reflections included. The structural parameters are given in Tables 1 and 2, which also contain in italics the data obtained in the previous studies.

Table 3. Interatomic distances and angles in the structure of orthorhombic mercury(II) oxide.

Distances within the chain -O-Hg-O-	*Ref.1*	*Present investigation*
Hg-O	2.03±0.10 Å	2.067±0.028 Å
Hg-O	2.03±0.10 Å	2.039±0.028 Å
Hg-Hg	3.30 Å	3.307±0.003 Å
∠Hg-O-Hg	109°±1°	107.3°±1.3°
∠O-Hg-O	179°±3°	179.5°±1.1°
Closest distances between the chains -O-Hg-O-		
Hg-2O	2.82 Å	2.814±0.005 Å
Hg-O	2.82 Å	2.827±0.028 Å
Hg-O	2.82 Å	2.846±0.028 Å
Hg-Hg	3.59 Å	3.587±0.001 Å
O-O	3.39 Å	3.360±0.023 Å

Table 4. Interatomic distances and angles in the structure of Hg_2O_2NaI.

	Ref. 3	*Present investigation*
Hg-O	2.03 Å	2.014 ± 0.019 Å
Na-O	2.41 Å	2.427 ± 0.014 Å
I-O	3.76 Å	3.768 ± 0.020 Å
O-O	3.46 Å	3.513 ± 0.029 Å
O-O	3.77 Å	3.784 ± 0.009 Å
Hg-Hg	3.33 Å	3.334 ± 0.001 Å
∠O-Hg-O	180°±3°	180.0° ± 1.3°
∠Hg-O-Hg	110°±1°	111.7° ± 1.5°

The interatomic distances and angles corresponding to the refined parameters are given in Tables 3 and 4 together with the values previuosly obtained. The results of the refinements of the two structures are in very close agreement with the structural data previously reported by the author. This implies that the description and discussion of the two structures given earlier[1-3] still apply.

The neutron single-crystal intensities of HgO collected before [1] were also refined by the method of least squares, though the number of reflections was very small. The resulting z parameter of the oxygen atom lies within the values $z_0 \pm \sigma_0$ as determined from the X-ray investigation.

This study has been performed within a research program financially supported by the *Swedish Natural Science Research Council.*

1. Aurivillius, K. *Acta Chem. Scand.* **10** (1956) 852.
2. Aurivillius, K. *Acta Cryst.* **9** (1956) 685.
3. Aurivillius, K. *Acta Chem. Scand.* **14** (1960) 2196.
4. Åsbrink, S. and Brändén, C.-I. *Program No. 6023, World List of Crystallographic Computer Programs*, 1st ed., Sept. 1962.
5. Werner, P. E. *Program No. 6019. Ibid.*
6. Aurivillius, K. *Arkiv Kemi* **22** (1964) 517.
7. Aurivillius, K. *Arkiv Kemi* **22** (1964) 537.
8. Aurivillius, K. *Univ. Stockholm, Inorg. Chem., DIS* No. 6 (1964).

Received June 10, 1964.