X-Ray Investigation of Some Mercuric Sulphates

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Proceeding with the X-ray investigations on mercuric sulphates[1], we have studied the crystal structures of $HgSO_4$, $HgSO_4 \cdot 2HgO$ and $2HgSO_4 \cdot HgO \cdot 2H_2O$.

Meanwhile, the compounds $HgSO_4$ and $HgSO_4 \cdot 2HgO$ have been investigated by other authors[2,3],* who reported only the dimensions of the unit cells and the space groups of these crystals. The results reported in this note differ from those already published only in the space group of $HgSO_4$. In addition, the results of the Patterson analysis of these substances are given here, and some new conclusions are drawn from the present X-ray examination on $HgSO_4 \cdot HgO \cdot 2H_2O$.

The crystallographic data are given in Table I. For $HgSO_4$ the listed cell dimensions are in agreement with the results recently reported by Kokkoros and Rentzeperis[2] and by Aurivillius and Malmros[3]. However, the shape of the crystals suggests the hemihedral group. We therefore examined the crystals piezoelectrically and found a pronounced piezoelectric effect. We concluded that the $P2_1mn$ is the most probable space group, and not $Pmmn$ as reported by Kokkoros and Rentzeperis. The coordinates of mercury and sulphur atoms with the origin placed halfway between two mercury atoms have been obtained

TABLE I

Crystallographic data

Compound	a (Å) b (Å) c (Å)	β	Cell con- tent	Systematically absent spectra	Probable space group
$HgSO_4$	4.82 6.58 4.78 ($D_l = 6.47$, $D_x = 6.49$)		2	hko:h+k=2n+1	$P2_1mn$ (No. 31)
$HgSO_4 \cdot 2HgO$	7.05 — 10.02 ($D_l = 6.44$, $D_x = 8.42$)		3	00l:l≠3n	$P3_121$ (No. 152)
$2 HgSO_4 \cdot HgO \cdot 2 H_2O$	7.13 8.94 14.55 $D_m = 6.10$, $D_x = 6.14$	99°30'	4	hkl:h+k=2n+1 hol:l=2n+1	C 2/c (No. 15)

D_m = measured density (in g. cm^{-3}) D_x = calculated density (in g. cm^{-3})
D_l = density (in g. cm^{-3}) quoted in the literature[4]

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* Since the present paper was submitted for publication the crystal structure of $HgSO_4 \cdot 2HgO$ was published by G. N a g o r s e n, S. L u n g, Alarich W e i s s, and Armin W e i s s in *Angew. Chem.* **74** (1962) 119. Our results are in accord with theirs within the experimental error.

from the Patterson projections (Table II). Both mercury and sulphur atoms are linked in pairs across the centre of symmetry. However, we could not place the oxygen atoms centrosymmetrically, in such a way as to obtain reasonable interatomic distances and angles.

In the case of $HgSO_4 \cdot 2HgO$, the same cell edges and space group as those recently reported by Aurivillius and Malmros[3] were found. For a unit cell of three formula units the calculated density is 8.42 g. cm^{-3}. This value is in agreement with the results of Aurivillius and Malmros, being considerably different from 6.44 g. cm^{-3}, as given in the literature[4]. The coordinates of mercury atoms were found from the Patterson projections (Table II).

<div align="center">TABLE II</div>

Compound	Atom	Position	Atomic coordinates		
			x	y	z
$HgSO_4$	Hg		1/4	1/4	0.175
	S		—1/4	1/4	—0.262
$HgSO_4 \cdot 2HgO$	Hg	c	0.70	0.50	0.35
		a	0.70	0	1/3
$2HgSO_4 \cdot HgO \cdot 2H_2O$	Hg	c	1/4	1/4	0
		f	0.253	0.936	0.146
	S	f	0.208	0.623	0.099

The crystal structure of the compound $2HgSO_4 \cdot HgO \cdot 2H_2O$ has not been studied so far. The unit cell contains four formula units. We have found that four mercury and four oxygen atoms occupy special positions, other atoms being in general positions. Each mercury atom lies in the centre of a distorted octahedron of oxygen atoms. The coordinates of the mercury and of the sulphur atoms are included in Table II.

Further structure determinations are in progress and the results will be published elsewhere.

<div align="center">EXPERIMENTAL</div>

Single crystals of $HgSO_4$ and $2HgSO_4 \cdot HgO \cdot 2H_2O$ were prepared by slow evaporation of a solution of mercuric sulphate in dilute sulphuric acid. Single crystals of $HgSO_4 \cdot 2HgO$ were obtained by heating a mixture of mercuric nitrate, sodium sulphate and nitric acid in a sealed glass tube at 250°C. X-ray data were obtained from oscillation and Weissenberg diagrams taken with nickel-filtered CuK radiation. In order to facilitate the absorption correction, the specimens were made cylindrical by grinding. Corrections for Lorentz and polarization factors were made in the usual way. The densities were determined pycnometrically.

<div align="center">REFERENCES</div>

1. A. Bonefačić, Acta Cryst. 14 (1961) 116.
2. P.A. Kokkoros and P. J. Rentzeperis, Acta Cryst. 14 (1961) 329.
3. K. Aurivillius and B. Malmros, Acta Chem. Scand. 15 (1961) 1932.
4. Handbook of Chemistry and Physics, edited by C. D. Hodgman, Chemical Rubber Publ. Co., Cleveland 1958, 40th ed., p. 608.

IZVOD

Rendgenografska ispitivanja nekih merkurisulfata

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Metodom rendgenske strukturne analize određene su veličine elementarnih ćelija i prostorne grupe ovih merkurisulfata: $HgSO_4$, $HgSO_4 \cdot 2HgO$ i $2HgSO_4 \cdot HgO \cdot 2H_2O$. (Tablica I)

Koordinate atoma žive i sumpora određene su iz Pattersonovih projekcija. (Tablica II)

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