X-Ray Investigation of Some Mercuric Sulphates

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Proceeding with the X-ray investigations on mercuric sulphates, we have studied the crystal structures of \( \text{HgSO}_4 \), \( \text{HgSO}_4 \cdot 2\text{HgO} \) and \( 2\text{HgSO}_4 \cdot \text{HgO} \cdot 2\text{H}_2\text{O} \).

Meanwhile, the compounds \( \text{HgSO}_4 \) and \( \text{HgSO}_4 \cdot 2\text{HgO} \) have been investigated by other authors 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 \( \text{HgSO}_4 \). 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 \( 2\text{HgSO}_4 \cdot \text{HgO} \cdot 2\text{H}_2\text{O} \).

The crystallographic data are given in Table I. For \( \text{HgSO}_4 \) the listed cell dimensions are in agreement with the results recently reported by Kokkoros and Rentzeperis and by Aurivillius and Malmros. 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>
<thead>
<tr>
<th>Compound</th>
<th>( a(\text{Å}) )</th>
<th>( b(\text{Å}) )</th>
<th>( c(\text{Å}) )</th>
<th>( \beta )</th>
<th>Cell content</th>
<th>Systematically absent spectra</th>
<th>Probable space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HgSO}_4 )</td>
<td>4.82</td>
<td>6.58</td>
<td>4.78</td>
<td>2</td>
<td>hko:h+k=2n+1</td>
<td>( P2_1mn ) (No. 31)</td>
<td></td>
</tr>
<tr>
<td>( \text{HgSO}_4 \cdot 2\text{HgO} )</td>
<td>7.05</td>
<td>10.02</td>
<td>10.02</td>
<td>3</td>
<td>00l:l=3n</td>
<td>( P3_121 ) (No. 152)</td>
<td></td>
</tr>
<tr>
<td>( 2\text{HgSO}_4 \cdot \text{HgO} \cdot 2\text{H}_2\text{O} )</td>
<td>7.13</td>
<td>8.94</td>
<td>14.55</td>
<td>4</td>
<td>hkl:h+k=2n+1</td>
<td>C 2/c (No. 15)</td>
<td></td>
</tr>
</tbody>
</table>

\( D_m = \) 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

* Since the present paper was submitted for publication the crystal structure of \( \text{HgSO}_4 \cdot 2\text{HgO} \) was published by G. Nagoršen, S. Lung, Alarich Weiss, and Armin Weiss 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 $\text{HgSO}_4 \cdot 2\text{HgO}$, 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).

**TABLE II**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Atom</th>
<th>Position</th>
<th>Atomic coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>$\text{HgSO}_4$</td>
<td>Hg</td>
<td>1/4</td>
<td>1/4</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>-1/4</td>
<td>1/4</td>
</tr>
<tr>
<td>$\text{HgSO}_4 \cdot 2\text{HgO}$</td>
<td>Hg</td>
<td>c</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>a</td>
<td>0.70</td>
</tr>
<tr>
<td>$2\text{HgSO}_4 \cdot \text{HgO} \cdot 2\text{H}_2\text{O}$</td>
<td>Hg</td>
<td>c</td>
<td>1/4</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>f</td>
<td>0.253</td>
</tr>
</tbody>
</table>

The crystal structure of the compound $2\text{HgSO}_4 \cdot \text{HgO} \cdot 2\text{H}_2\text{O}$ 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.

**EXPERIMENTAL**

Single crystals of $\text{HgSO}_4$ and $2\text{HgSO}_4 \cdot \text{HgO} \cdot 2\text{H}_2\text{O}$ were prepared by slow evaporation of a solution of mercuric sulphate in dilute sulphuric acid. Single crystals of $\text{HgSO}_4 \cdot 2\text{HgO}$ 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.

**REFERENCES**

IZVOD

Rendgenografska ispitivanja nekih merkurisulfata

A. Bonefačić

Metodom rendgenske strukturne analize određene su veličine elementarnih čelija i prostorne grupe ovih merkurisulfata: HgSO₄, HgSO₄ · 2HgO i 2HgSO₄ · HgO · 2H₂O. (Tablica I)

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

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