ACTA CHEMICA SCANDINAVICA 18 (1964) 2375–2378

The Crystal Structures of $Bi_2O_2SO_4 \cdot H_2O$ and $BiOHSeO_4 \cdot H_2O$

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In the structures of $Bi_2O_2SO_4 \cdot H_2O$ and the isotypic compound $Bi_2O_2SeO_4 \cdot H_2O$ aggregates of the probable composition $Bi_2O(OH)^{3+}$, which take part of infinite double chains $Bi_2O(OH)_2^{2+}$, are found. Thus it seems likely that the formulae of the compounds should be written $Bi_2O(OH)_2SO_4$ and $Bi_2O(OH)_2SeO_4$. In the structures of the two isotypic compounds $BiOHSeO_4 \cdot H_2O$ and $BiOHSO_4 \cdot H_2O$ aggregates of the probable composition $Bi_2(OH)_2^{4+}$ exist. The dimensions of the groups $Bi_2O(OH)^{3+}$ and $Bi_2(OH)_2^{4+}$ are nearly the same as those found for $Bi_2(OH)_2^{4+}$ in the two modifications of $BiOHCrO_4$.[1,2] In the structure of $BiOHSeO_4 \cdot H_2O$ the bismuth atoms are coordinated by nine oxygen atoms in the form of a deformed square Archimedean antiprism with one oxygen atom outside one square face.

The investigation of the crystal structures of $Bi_2O_2SO_4 \cdot H_2O$, $BiOHSO_4 \cdot H_2O$ and the corresponding selenates is a part of a general study of the coordination of bismuth in compounds containing tetrahedral anions.

Single crystals of $Bi_2O_2SO_4 \cdot H_2O$, $BiOHSO_4 \cdot H_2O$ and the corresponding isotypic selenates were investigated by X-ray diffraction methods. The intensity materials of $Bi_2O_2SO_4 \cdot H_2O$ and $BiOHSeO_4 \cdot H_2O$ were made up of 753 and 1123 independent reflections, respectively. The intensities were in case of $BiOHSeO_4 \cdot H_2O$ corrected for absorption. The unit-cell dimensions were determined from X-ray Guinier diffractograms.

The following data are derived for the compounds $Bi_2O_2SO_4 \cdot H_2O$ and $Bi_2O_2SeO_4 \cdot H_2O$:

Space group: $P2_1/c$ (No.14).

4 Bi_1, 4 Bi_2, 4 S (Se), 4 O_1—4 O_7 in 4(*e*): $\pm (x,y,z;x,\frac{1}{2}-y,\frac{1}{2}+z)$.

Unit-cell dimensions:

$Bi_2O_2SO_4 \cdot H_2O$; $a = 7.641$ Å, $b = 13.857$ Å, $c = 5.694$ Å, $\beta = 108.8_2°$.

$Bi_2O_2SeO_4 \cdot H_2O$; $a = 7.803$ Å, $b = 14.05_0$ Å, $c = 5.793$ Å, $\beta = 108.3_7°$.

Cell contents: 4 formula units $Bi_2O_2SO_4 \cdot H_2O$ ($Bi_2O_2SeO_4 \cdot H_2O$). Final coordinates, isotropic temperature factors and standard deviations resulting from the least-squares refinement of the structure of $Bi_2O_2SO_4 \cdot H_2O$ are given in Table 1. $R = 18.8$ %, absent reflections not included.

Table 1.

Atom	$x \pm \sigma_x$	$y \pm \sigma_y$	$z \pm \sigma_z$	$B \pm \sigma_B$ Å^2
Bi_1	0.96534 ± 0.00056	0.15708 ± 0.00025	0.09608 ± 0.00067	0.905 ± 0.056
Bi_2	0.30993 ± 0.00061	0.13398 ± 0.00028	0.78571 ± 0.00074	1.252 ± 0.060
S	0.37732 ± 0.00555	0.63496 ± 0.00246	0.11861 ± 0.00669	2.600 ± 0.588
O_1	0.5990 ± 0.0106	0.0425 ± 0.0047	0.1999 ± 0.0129	0.86 ± 1.14
O_2	0.6742 ± 0.0083	0.0821 ± 0.0039	0.6108 ± 0.0106	−0.27 ± 0.90
O_3	0.4422 ± 0.0088	0.1925 ± 0.0039	0.3533 ± 0.0108	0.19 ± 0.90
O_4	0.7758 ± 0.0120	0.1961 ± 0.0057	0.3665 ± 0.0148	1.85 ± 1.41
O_5	0.1139 ± 0.0114	0.2255 ± 0.0053	0.8541 ± 0.0141	1.62 ± 1.27
O_6	0.1154 ± 0.0112	0.0605 ± 0.0052	0.4710 ± 0.0135	0.83 ± 1.20
O_7	0.1537 ± 0.0107	0.0547 ± 0.0050	0.9809 ± 0.0131	1.09 ± 1.20

THE STRUCTURE OF $Bi_2O_2SO_4 \cdot H_2O$

Aggregates of the probable composition $Bi_2O(OH)^{3+}$ may be visualized in the structure. The bismuth-bismuth distance in the groups is 3.667 ± 0.006 Å and the bismuth-oxygen distances range from 2.10 ± 0.09 Å to 2.28 ± 0.09 Å. These complexes are part of infinite double chains of the probable formula $Bi_2O(OH)_2^{2+}$. The formula of the compound should therefore rather be written $BiO(OH)_2SO_4$ than $Bi_2O_2SO_4 \cdot H_2O$. The arrangement of the square aggregates

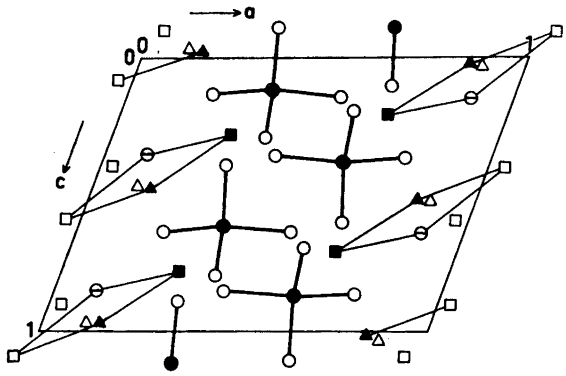

Fig. 1. Projection of the structure of $Bi_2O_2SO_4 \cdot H_2O$ on the *ac* plane. All atoms are shown. Heavy lines show the SO_4^{2-} tetrahedra. The atoms of the $Bi_2O(OH)^{3+}$ aggregates are connected by thin lines. Notations: Bi_1 □; Bi_2 ■; S ●; O_1—O_4 ○; O_5 ⊖; O_6 △; O_7 ▲.

and the sulphate tetrahedra in the compound is shown in Fig. 1, where a projection of the structure is drawn on the *ac* plane. The distances between the sulphur atom and the oxygen atoms in the SO_4^{2-} ion range from 1.43 ± 0.07 Å to 1.64 ± 0.09 Å and the corresponding angles O-S-O from 96° ± 2° to 115° ± 2°. The shortest distance between the oxygen atoms outside the tetrahedron is 2.45 ± 0.11 Å.

Table 2.

Atom	$x \pm \sigma_x$	$y \pm \sigma_y$	$z \pm \sigma_z$	$B \pm \sigma_B$ Å^2
Bi	0.58904 ± 0.00022	0.11853 ± 0.00010	0.15131 ± 0.00024	1.870 ± 0.024
Se	0.09182 ± 0.00062	0.16493 ± 0.00031	0.17416 ± 0.00071	2.079 ± 0.064
O_1	0.30333 ± 0.00429	0.09642 ± 0.00190	0.33641 ± 0.00466	1.598 ± 0.396
O_2	0.88107 ± 0.00499	0.08426 ± 0.00225	0.06972 ± 0.00533	2.434 ± 0.494
O_3	0.02130 ± 0.00577	0.24413 ± 0.00257	0.32340 ± 0.00614	3.325 ± 0.614
O_4	0.14392 ± 0.00541	0.20625 ± 0.00239	0.96628 ± 0.00590	2.877 ± 0.545
$O_5(H_2O)$	0.84541 ± 0.00554	0.08567 ± 0.00249	0.55479 ± 0.00595	2.913 ± 0.552
$O_6(OH)$	0.59604 ± 0.00426	0.95916 ± 0.00198	0.19998 ± 0.00489	1.822 ± 0.424

The following data are derived for the compounds $BiOHSeO_4 \cdot H_2O$ and $BiOHSO_4 \cdot H_2O$:
Space group: $P2_1/n$ (No. 14, with other orientation than that given in the International Tables.)
4 Bi, 4 Se (S), 4 O_1—4 O_6 in 4(*e*): $\pm (x,y,z;\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z)$.
Unit-cell dimensions:
$BiOHSeO_4 \cdot H_2O$; $a = 6.500$ Å, $b = 13.36_9$ Å, $c = 6.094$ Å, $\beta = 112.9_2°$.
$BiOHSO_4 \cdot H_2O$; $a = 6.719$ Å, $b = 13.57_8$ Å, $c = 6.106$ Å, $\beta = 114.3_6°$.
Cell content: 4 formula units $BiOHSeO_4 \cdot H_2O$ ($BiOHSO_4 \cdot H_2O$). Final coordinates, isotropic temperature factors and standard deviations resulting from the least-squares refinement of the structure of $BiOHSeO_4 \cdot H_2O$ are given in Table 2. $R = 11.2$ %, absent reflections not included and 14.0 %, absent reflections included.

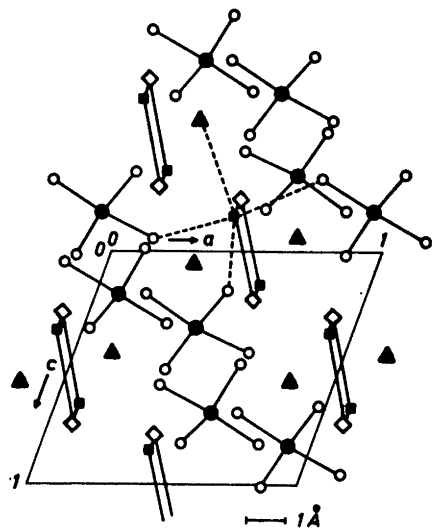

Fig. 2. Projection of the structure of $BiOHSeO_4 \cdot H_2O$ on the *ac* plane. The bismuth atoms are indicated by ■; the selenium atoms by ●; the oxygen atoms in the ions SeO_4^{2-} by O; the ions OH^- by ◇; and H_2O by ▲. Dashed lines connect one bismuth atom with its nearest oxygen atoms. The aggregates $Bi_2(OH)_2^{4+}$ and the SeO_4^{2-} groups are shown by full lines.

THE STRUCTURE OF $BiOHSeO_4 \cdot H_2O$

The shortest distances between bismuth atoms in the structure are 3.664 ± 0.003 Å and 4.998 ± 0.002 Å. The bismuth atoms lying at a distance of 3.664 Å are joined by a double hydroxide bridge. Aggregates $Bi_2(OH)_2^{4+}$ may be visualized as in the structure of the two modifications of $BiOHCrO_4$.[1,2] The arrangement of the aggregates and of the ions SeO_4^{2-} are given in Fig. 2, showing a projection of the structure on the *ac* plane. The selenium-oxygen distances in the ion SeO_4^{2-} range from 1.56 ± 0.04 Å to 1.70 ± 0.04 Å and the corresponding angles from 103.9° ± 2.1° to 114.3° ± 2.1°. The shortest oxygen-oxygen distance outside the tetrahedra is 2.51 ± 0.06 Å.

Each bismuth atom in the structure is coordinated by nine oxygen atoms forming a fairly irregular polyhedron. The latter, similar to the coordination polyhedra in the two forms of $BiOHCrO_4$,[1,2] can be derived from a square Archimedean antiprism with one extra oxygen atom outside one square face.

A full account of the present work will appear in a forthcoming article.

These studies form part of a research program on bismuth oxide salts, financially supported by the *Swedish Natural Science Research Council.*

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Received July 25, 1964.