as $2Nb^{4+}Nb^{5+}I^-6(Se_2)^{2-}$. Thus, the tantalum derivative may be formulated as $Ta^{4+}Ta^{5+}I^-4(Se_2)^{2-}$. The only difference between the two compounds is the metal–metal bond sequence. Nb_3ISe_{12} exhibits one short (3·061 Å) and two long (3·252 Å) intermetallic distances, whereas no difference is observed with Ta_2ISe_8. The sequence of long and short bonds in the metal–metal chain plays an essential role concerning the semi-conducting properties of these materials (Gressier, Meerschaut, Guemas, Rouxel & Monceau, 1982). More structural investigations are needed in this series of MY_xX_4 compounds (M = Nb, Ta; Y = Cl, Br, I; X = S, Se). These derivatives may provide a complete set of compounds to support a critical discussion in the scope of a bond-density wave theory (Whangbo, 1982).

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Di-μ-hydroxo-bis[aquasulfatobismuth(III)]

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Abstract. $[Bi_2(H_2O)_2(SO_4)_2(OH)_2]$, monoclinic, $P2_1/n$, $a = 6·021$ (1), $b = 13·363$ (2), $c = 6·495$ (1) Å, $\beta = 112·94$ (1)°, $D_m = 4·62$, $D_x = 4·69$ Mg m^{-3}, $Z = 2$; $R = 0·063$ for 853 observed diffractometer data. The structure consists of molecules in which an O atom of an SO_4^{2-} anion and a water molecule are bonded at relatively short distances to each Bi atom of a planar $Bi_2(OH)_2^{4+}$ unit. The coordination sphere around the Bi atom is completed by two more O atoms of two different SO_4^{2-} anions at longer distances. The coordination polyhedron is a distorted octahedron with the stereochemically active electron lone pair. The molecules form a three-dimensional network.

Introduction. The systematic investigation of the hydrolysis of bismuth(III) nitrate (Lazarini, 1981) has been extended to study the chemical behavior and structure of bismuth basic sulfates. There are two compounds important in the scheme of the hydrolysis of bismuth(III) sulfate. The title compound seems to be the first solid product of the hydrolysis at pH below 1·1. Its formula is usually quoted in the literature as $(BiOH)SO_4.H_2O$. The crystal structure of an isomorphous selenium compound has been determined by Aurivillius (1964). The title compound reconverts in the suspension at pH above 1·1 after a few hours into the second product of the hydrolysis, $[Bi_2O(OH)_2]SO_4$.

The crystal structure of this compound has also been published by Aurivillius (1964). We decided to reinvestigate the crystal structures of both compounds to enable a precise comparison between the structures of bismuth basic nitrates and sulfates to be made. This paper concerns the crystal-structure analysis of the first product of hydrolysis, $[Bi_2(H_2O)_2(SO_4)_2(OH)_2]$, while the results of the crystal-structure analysis of the second product of the hydrolysis are given in the following paper (Golič, Graunar & Lazarini, 1982).

The crystals of the title compound were obtained by slow diffusion of water into an acid-saturated solution of bismuth(III) sulfate using a method described by Ozols (1950). A well developed crystal, selected for the diffraction measurements, was characterized by the following planes (in parentheses are the distances from the crystal faces to an arbitrary origin inside the crystal): ±(110) (0·045 mm), ±($\bar{1}$10) (0·050 mm), ($\bar{1}$20) (0·068 mm), ($12\bar{1}$) (0·205 mm), ($12\bar{1}$) (0·180 mm) and ±(001) (0·240 mm).

The intensity data were collected at 293 (1) K with an Enraf–Nonius CAD-4 diffractometer. Experimental conditions were: graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0·71069$ Å), ω–2θ scan, $\theta_{min} = 1°$, $\theta_{max} = 25°$, 2θ scan width = $(1·0 + 0·6 \tan \theta)°$, aperture = $(2·5 + 0·9 \tan \theta)$ mm, maximum scan time 40 s, background = $\frac{1}{4}$ of the scan time at each of the

scan limits. 2304 reflexions were recorded. After symmetry-related reflexions were averaged (agreement factor 0·071) and the reflexions having $I < 3\sigma(I)$ (calculations based on counting statistics) were rejected, only 853 reflexions remained for the structural analysis. Corrections were applied for absorption [μ(Mo $K\alpha$) = 35·63 mm^{-1}]. The transmission factors, calculated with the measured crystal dimensions (3072 grid points, crystal volume 0·0063 mm^3), range from 0·019 to 0·129. The unit-cell parameters were obtained from a least-squares fit of the θ values of 45 reflexions measured on the diffractometer.

The positions of the Bi and S atoms were taken from the Patterson map, while the O atoms were located from a difference Fourier map. The structure was refined by the full-matrix least-squares technique with anisotropic thermal parameters for Bi and S atoms, isotropic for O atoms and with anomalous-dispersion correction for all atoms. The weighting function applied in the final cycle was $w = 34\cdot4/[\sigma(F_o)^2 + 0\cdot00061\ F_c^2]$. An empirical extinction parameter was also included in the final stage of the refinement; its value in the final cycle was 6·8 (5) × 10^{-3}. Final R values are: $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0\cdot063$ and $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0\cdot068$ for 45 parameters and 853 reflexions. The final difference Fourier map was featureless.
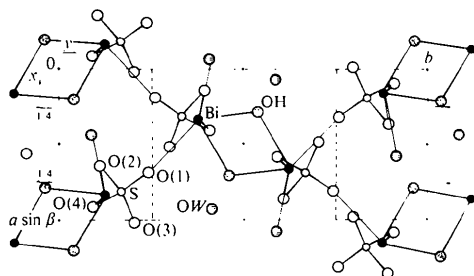

Fig. 1. Projection of the structure of |Bi$_2$(H$_2$O)$_2$(SO$_4$)$_2$(OH)$_2$| along **c**.

Table 1. *Final positional parameters* (×10^4) *and isotropic thermal parameters* (Å^2 ×10^3) *with e.s.d.'s in parentheses*

For Bi and S atoms the equivalent isotropic thermal parameter is given [calculated as $U_{eq} = (U_{11}.U_{22}.U_{33})^{1/3}$], for O atoms the isotropic thermal parameter is given.

	x	y	z	U_{eq}/U
Bi	3460 (2)	3791 (1)	4124 (2)	6 (1)
S	8229 (12)	1660 (5)	4085 (12)	6 (3)
O(1)	6932 (59)	2428 (17)	4673 (49)	21 (6)
O(2)	6515 (42)	1083 (14)	2027 (41)	17 (5)
O(3)	10232 (47)	2044 (16)	3608 (42)	19 (5)
O(4)	9165 (42)	913 (15)	5962 (40)	18 (5)
OH	2942 (41)	5420 (14)	4041 (35)	12 (4)
OW	9379 (43)	4146 (15)	1470 (41)	21 (5)

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Bi–OH	2·20 (2)	S–O(1)	1·43 (3)
Bi–OH^i	2·28 (2)	S–O(2)	1·54 (2)
Bi–O(4^{ii})	2·29 (3)	S–O(3)	1·45 (3)
Bi–OW^{iii}	2·44 (2)	S–O(4)	1·50 (2)
Bi–O(2^{iv})	2·58 (3)	OH–O(2^v)	2·65 (3)
Bi–O(1)	2·69 (3)		

Bi–OH–Bi^i	110·4 (9)	OW^{iii}–Bi–O(2^{iv})	83·4 (8)
OH–Bi–OH^i	69·6 (7)	OW^{iii}–Bi–O(4^{ii})	79·6 (9)
OH–Bi–O(1)	140·3 (9)	OH^i–Bi–O(2^{iv})	101·3 (8)
OH–Bi–OW^{iii}	72·3 (7)	OH^i–Bi–O(4^{ii})	85·3 (8)
OH–Bi–O(2^{iv})	81·5 (8)	O(2^{iv})–Bi–O(4^{ii})	159·9 (7)
OH–Bi–O(4^{ii})	83·2 (9)	O(1)–S–O(2)	110 (1)
O(1)–Bi–OW^{iii}	138·0 (8)	O(1)–S–O(3)	113 (2)
O(1)–Bi–OH^i	73·3 (8)	O(1)–S–O(4)	109 (2)
O(1)–Bi–O(2^{iv})	119·8 (9)	O(2)–S–O(3)	109 (2)
O(1)–Bi–O(4^{ii})	80·2 (9)	O(2)–S–O(4)	106 (1)
OW^{iii}–Bi–OH^i	140·3 (7)	O(3)–S–O(4)	109 (1)

Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$; (ii) $-\frac{1}{2} + x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$; (iii) $-1 + x, y, z$; (iv) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

The calculations were performed on the DEC-10 computer at the University Edvard Kardelj of Ljubljana with *SHELX* 76 (Sheldrick, 1976). Atomic scattering factors for neutral atoms tabulated by Cromer & Mann (1968) and the values of f' and f'' for the anomalous-dispersion correction of Cromer & Liberman (1970) were applied.

The positional and thermal parameters are listed in Table 1. Equivalent isotropic thermal parameters are given for Bi and S atoms and isotropic thermal parameters for O atoms.* A projection of the structure along **c** and the atom-numbering system used are shown in Fig. 1. The interatomic distances and angles are given in Table 2.

Discussion. The main feature of the structure of the title compound seems to be the presence of a rhomboidal planar [Bi$_2$(OH)$_2$]$^{4+}$ group. A group with similar geometry can be observed as a fragment of the polycations existing in bismuth basic nitrates (Lazarini, 1978, 1979a,b) and perchlorates (Sundvall, 1979). The BiOH^{2+} cation has also been postulated beside BiO$^+$ and Bi(OH)$_2^+$ species on the basis of conductimetric measurements in nitrate solutions (Quartaroli, 1913) and in small amounts beside the |Bi$_6$O$_n$(OH)$_{12-2n}$|$^{6+}$ polycations on the basis of e.m.f. measurements in perchlorate solutions (Olin, 1957). Aurivillius (1964) concluded from the crystal-structure analysis of (BiOH)SeO$_4$.H$_2$O, which is isomorphous with the title compound, that the [Bi$_2$(OH)$_2$]$^{4+}$ cations are fairly

isolated in the structure. The crystal-structure determination of the title compound yields some additional structural details.

To each Bi atom of the $[Bi_2(OH)_2]^{4+}$ group [with Bi—OH distances 2·20 (2) and 2·28 (2) Å] one O atom of the SO_4^{2-} anion and a water molecule are bonded relatively strongly [distances 2·29 (3) and 2·44 (2) Å respectively]. The coordination sphere around each Bi atom is completed by two more O atoms of two different SO_4^{2-} anions at longer distances [2·58 (3) and 2·69 (3) Å]. The coordination polyhedron is a distorted octahedron with the stereochemically active lone electron pair. The molecules, interlinked by O atoms of different SO_4^{2-} anions, form a three-dimensional network. A hydrogen bond is also present [OH—O(2^v) distance 2·65 (3) Å].

The Bi—OH distances are somewhat shorter than those of the $[Bi_6O_4(OH)_4]^{6+}$ groups, present in nitrates (mean Bi—OH distance 2·40 Å; Lazarini, 1979a,b), probably because each OH group of these polycations is bonded pyramidally to three Bi atoms. It should be mentioned that in one of the bismuth basic nitrates, $[Bi_6(H_2O)(NO_3)O_4(OH)_4](NO_3)_5$ (Lazarini, 1979b), the water molecule and one O atom of an NO_3^- anion are bonded to two neighboring Bi atoms of the polycation at fairly longer distances [2·64 (3) and 2·62 (3) Å

respectively] than the water molecule and the O atom of the SO_4^{2-} anion in the title compound [2·44 (2) and 2·29 (3) Å respectively]. The bond distances and angles within the SO_4^{2-} anion are similar to those found in other sulfates.

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catena-Di-μ-hydroxo-μ_3-oxo-dibismuth(III) Sulfate

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Abstract. $[Bi_2O(OH)_2]SO_4$, monoclinic, $P2_1/c$, $a = 7·692$ (3), $b = 13·87$ (1), $c = 5·688$ (2) Å, $\beta = 109·01$ (3)°, $D_m = 6·5$ (1), $D_x = 6·53$ Mg m^{-3}, $Z = 4$; $R = 0·039$ for 1356 observed diffractometer data. The structure consists of sulfate anions and $[Bi_2O(OH)_2^{2+}]_n$ infinite double chains in which two $[Bi(OH)^{2+}]_n$ chains are interconnected through O atoms. One of the two Bi atoms of the asymmetric unit is coordinated pyramidally by one O atom and two OH groups, the second Bi atom is coordinated pyramidally by two O atoms and two OH groups. Each OH group interconnects two Bi atoms, each O atom three Bi atoms.

Introduction. This work is part of the investigation of chemical behavior and structure of bismuth basic

sulfates (see the preceding paper, Graunar & Lazarini, 1982). The title compound is a product of further hydrolysis of $[Bi_2(H_2O)_2(SO_4)_2(OH)_2]$ at pH above 1·1. The formula of the title compound is usually given in the literature as $(BiO)_2SO_4 \cdot H_2O$. The crystal structure of this compound has already been determined by Aurivillius (1964). We decided to reinvestigate this crystal structure in order to obtain results of the same accuracy as those of the crystal structures of other bismuth basic salts determined recently.

Crystals of suitable dimensions for X-ray structural analysis were obtained by slow diffusion of a saturated acid solution of bismuth(III) sulfate into water, using a method described by Ozols (1950). A well developed crystal, selected for the diffraction measurements, was