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-μ3-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

characterized by the following planes (in parentheses are the distances from the crystal faces to an arbitrary origin inside the crystal): $\pm(101)$ (0·0375 mm), $\pm(40\bar{1})$ (0·0260 mm) and $\pm(\bar{6}01)$ (0·0450 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), $\omega$–$2\theta$ scan, $\theta_{min} = 1°$, $\theta_{max} = 25°$, $2\theta$ 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. 5768 reflexions were recorded. After symmetry-related reflexions were averaged (agreement factor was 0·068), and the reflexions having $I < 2·5\sigma(I)$ (calculations based on counting statistics) were rejected, 1356 reflexions remained for the structural analysis. Corrections were applied for absorption [$\mu$(Mo $K\alpha$) = 59·33 mm$^{-1}$]. The transmission factors, calculated with the measured crystal dimensions (3392 grid points, crystal volume 0·00077 mm$^3$), range from 0·021 to 0·135. The unit-cell parameters were obtained from a least-squares fit of the $\theta$ values of 30 reflexions measured on the diffractometer.

The positions of the Bi atoms were taken from the Patterson map, while the S and 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, isotropic for O atoms and with anomalous-dispersion correction. The weighting function applied in the final cycle was $w = 5·07/[\sigma(F)^2 + 0·00048F^2]$. An empirical extinction parameter was also included in the final stage of the refinement, its value in the final cycle was 5·4 (7) $\times 10^{-3}$. Final $R$ values are: $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0·039$ and $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2} = 0·035$ for 58 parameters and 1356 reflexions. The final difference Fourier map was featureless.

The calculations were performed on the DEC-10 computer at the University Edvard Kardelj of Ljub-

**Table 1.** *Final positional parameters* ($\times 10^4$, *for* Bi $\times 10^5$) *and isotropic thermal parameters* (Å$^2 \times 10^3$, *for* Bi $\times 10^4$) *with e.s.d.'s in parentheses*

For Bi and S 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(1) | 53563 (6) | 15689 (3) | 40586 (8) | 87 (2) |
| Bi(2) | 18997 (7) | 13397 (3) | 71429 (9) | 128 (3) |
| S | 8745 (5) | 1331 (2) | 993 (6) | 10 (1) |
| O | 3898 (11) | 2317 (6) | 6500 (15) | 11 (1) |
| OH(1) | 3254 (12) | 522 (6) | 4997 (16) | 12 (2) |
| OH(2) | 3966 (13) | 752 (7) | 378 (17) | 15 (2) |
| O(1) | 7364 (13) | 2028 (7) | 1239 (18) | 20 (2) |
| O(2) | 9009 (13) | 575 (7) | 2907 (18) | 20 (2) |
| O(3) | 10524 (15) | 1824 (8) | 1320 (20) | 24 (2) |
| O(4) | 8073 (15) | 906 (9) | −1453 (21) | 26 (2) |

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

| | | | | |
|---|---|---|---|---|
| Bi(1)–OH(1) | 2·36 (1) | OH(1)–Bi(1)–OH(2) | 75·9 (3) |
| Bi(1)–OH(2) | 2·310 (9) | OH(1)–Bi(1)–O$^i$ | 110·3 (3) |
| Bi(1)–O | 2·297 (9) | OH(1)–Bi(1)–O | 68·6 (3) |
| Bi(1)–O$^i$ | 2·168 (8) | OH(2)–Bi(1)–O$^i$ | 75·7 (3) |
| Bi(1)–O(1) | 2·64 (1) | OH(2)–Bi(1)–O | 126·5 (3) |
| Bi(1)–O(1$^{ii}$) | 2·542 (9) | O–Bi(1)–O$^i$ | 80·6 (3) |
| Bi(2)–OH(1) | 2·17 (1) | OH(1)–Bi(2)–O | 74·6 (3) |
| Bi(2)–O | 2·168 (9) | OH(1)–Bi(2)–OH(2$^{iii}$) | 85·9 (4) |
| Bi(2)–OH(2$^{iii}$) | 2·159 (8) | O–Bi(2)–OH(2$^{iii}$) | 90·7 (3) |
| Bi(2)–O(2$^{iv}$) | 2·74 (1) | | |
| Bi(2)–O(3$^v$) | 2·74 (1) | Bi(1)–OH(1)–Bi(2) | 107·2 (3) |
| | | Bi(1)–OH(2)–Bi(2$^{vii}$) | 125·8 (5) |
| OH(1)–O(4$^{vi}$) | 2·77 (1) | Bi(1)–O–Bi(2) | 109·4 (3) |
| | | Bi(1)–O–Bi(1$^{ii}$) | 118·7 (4) |
| | | Bi(2)–O–Bi(1$^{ii}$) | 124·9 (4) |
| S–O(1) | 1·48 (1) | O(1)–S–O(2) | 109·0 (6) |
| S–O(2) | 1·48 (1) | O(1)–S–O(3) | 110·4 (6) |
| S–O(3) | 1·49 (1) | O(1)–S–O(4) | 108·4 (6) |
| S–O(4) | 1·44 (1) | O(2)–S–O(3) | 109·5 (6) |
| | | O(2)–S–O(4) | 109·9 (6) |
| | | O(3)–S–O(4) | 109·6 (7) |

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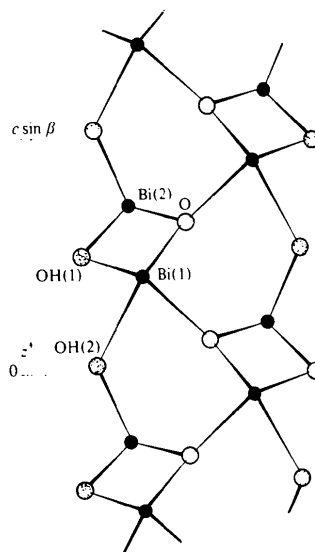


Fig. 1. The [Bi$_2$O(OH)$_2$] polycation, projected along a.

ljana 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. The structure of the polycation in the projection along **a** is shown in Fig. 1. The interatomic distances and angles are given in Table 2.

**Discussion.** The structure consists of sulfate anions and $[Bi_2O(OH)_2]^{2+}$ polycations in the form of infinite double chains parallel to [001], which can be described as composed of two $[Bi(OH)^{2+}]_n$ chains, interconnected by bridging O atoms. It is obvious that this polycation is a product of further hydrolysis of the planar rhomboidal $[Bi_2(OH)_2]^{4+}$ group, which is present in $[Bi_2(H_2O)_2(SO_4)_2(OH)_2]$ (see the preceding paper) and probably in solutions. The geometries of the $Bi_2O_2$ fragments in both structures are very similar. The infinite double chain is formed after the deprotonation of one OH group of the $[Bi_2(OH)_2]^{4+}$ cation by copolymerization of this species with an additional $OH^-$ anion [OH(2) in Fig. 1]. The Bi(1)—OH(1)—Bi(2) and Bi(1)—O—Bi(2) angles of the four-membered ring, 107·2 (3) and 109·4 (3)° respectively, are nearly of the same value as the corresponding angles in $[Bi_2(H_2O)_2$-$(SO_4)_2(OH)_2]$ in contrast to the Bi(1)—OH(2)—Bi(2ᵛⁱⁱ) angle, which is greater, 125·8 (5)°. The four-membered ring is essentially planar [the distances of the atoms to

the least-squares plane are: Bi(1) 0·024, Bi(2) 0·026, OH(1) −0·025 and O −0·026 Å]. The $|Bi_2O(OH)_2|$ type of polycation has not been observed among the structures of bismuth basic nitrates (Lazarini, 1981). The coordination spheres of both Bi atoms are completed by additional O atoms of the $SO_4^{2-}$ anions; the coordination polyhedra are irregular. A weak hydrogen bond between OH(1) and O(4ᵛⁱ), 2·77 (1) Å, can be assumed.

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# Structure du Diphosphate Acide de Manganèse(III): MnHP₂O₇

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**Abstract.** MnHP₂O₇, monoclinic, $P2_1/n$, $a = 7·951$ (4), $b = 12·645$ (8), $c = 4·922$ (2) Å, $\beta = 100·92$ (5)°, $Z = 4$, $D_x = 3·142$ Mg m⁻³. The crystal structure has been refined, using 765 independent reflexions, to a final $R$ value of 0·028. The hydrogen-bond scheme is given.

**Introduction.** On ne connaît qu'un nombre assez restreint de phosphates de manganèse trivalent. On ne peut guère citer que le monophosphate MnPO₄ (Shafer, Shafer & Roy, 1956) et le polyphosphate Mn(PO₃)₃ (Bagieu-Beucher, 1978). La présente étude décrit la préparation chimique et la structure cristalline du premier diphosphate de manganèse trivalent: MnHP₂O₇.

**Partie expérimentale.** De très nombreux essais ont été effectués par chauffage à diverses températures de mélanges de carbonate de manganèse(II) et d'acide phosphorique dans des proportions variées. Des cristaux prismatiques violet très foncé de MnHP₂O₇ sont obtenus en chauffant à 473 K durant 18 h un mélange de 0,57 g de MnCO₃ dans 7 cm³ d'acide phosphorique à 85%. Si le chauffage est prolongé à cette température cette espèce disparaît au profit d'un composé non encore identifié cristallisant sous la forme de fines aiguilles rose pâle.

A l'aide d'un cristal prismatique de dimensions 0,10 × 0,10 × 0,15 mm, 765 réflexions indépendantes ont été mesurées à l'aide d'un diffractomètre automatique

   