

# Pyrolysis Products of $\text{Bi}_2(\text{SO}_4)_3$ . Crystal Structures of $\text{Bi}_{26}\text{O}_{27}(\text{SO}_4)_{12}$ and $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$

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The crystal structure of  $\text{Bi}_{34(2/3)}\text{O}_{36}(\text{SO}_4)_{16}$  has been determined from 1251 independent counter reflections to a final  $R$  of 0.081. The crystals are monoclinic, space group  $C2/c$ , with  $a = 24.67(2)$ ,  $b = 5.650(3)$ ,  $c = 15.139(7)$  Å,  $\beta = 97.67^\circ$  and  $Z = 1$ . The cell content may also be formulated as  $\text{Bi}_{26}\text{O}_{27}(\text{SO}_4)_{12}$ , with  $Z = 4/3$ . The structure is built up of  $\text{Bi}_2\text{O}_2$ -like "steps" and free  $\text{SO}_4^{2-}$  ions. Relationships to the structures of  $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ ,  $\text{La}_2\text{O}_2\text{SO}_4$  and  $\text{La}_2\text{MoO}_6$  are discussed.

The crystal structure of  $\text{Bi}_{28}\text{O}_{32}(\text{SO}_4)_{10}$  has been determined from 1217 independent counter reflections to a final  $R$  of 0.065. The crystals are monoclinic, space group  $C2/m$ , with  $a = 21.638(7)$ ,  $b = 5.657(2)$ ,  $c = 15.087(8)$  Å,  $\beta = 119.1(4)^\circ$  and  $Z = 1$ . The cell content may also be formulated as  $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$ , with  $Z = 2$ . The structure is disordered in the  $y$  direction. It is built up of isolated "CaF<sub>2</sub>"-like blocks of  $\text{Bi}_{14}\text{O}_{16}^{10+}$ , which extend infinitely in the  $b$  direction, and free  $\text{SO}_4^{2-}$  ions. Both the present structures show rows of (Bi+S) atoms which are parallel to a crystal  $h0l$  plane with simple indices, different for the two structures.

Some measurements have also been made on the previously known  $\text{Bi}_2\text{O}_2\text{SO}_4$  phase.

The bismuth ion is apt to give oxo salts, both in solution and in solid state reactions. With some salts, such as the nitrate or basic nitrate,  $\text{Bi}_2\text{O}_3$  is formed quite easily on heating. With other anions, e.g.  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , the anions persist intact even at temperatures where  $\text{Bi}_2\text{O}_3$  has a marked volatility. One of the pyrolysis products of  $\text{BiCl}_3$ ,  $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ , has previously been studied by X-ray diffraction.<sup>1</sup> The present investigation was started to investigate crystal structures of pyrolysis products of  $\text{Bi}_2(\text{SO}_4)_3$  in order to study

the successive changes from free  $\text{Bi}^{3+}$  ions via  $\text{Bi}_2\text{O}_2$  layers to more complicated Bi<sub>n</sub>O complexes.

## Experimental

Some crystal data for the present compounds are given in Table 1. Commercial  $\text{Bi}_2(\text{SO}_4)_3$  from BDH was subjected to prolonged heating in a Pt crucible at 460°C. Rough analyses of these samples indicated the composition  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ , in

Table 1. Survey of some crystallographic properties of the present compounds.

Formula	Formula weight	Space group	$a/\text{Å}$	$b/\text{Å}$	$c/\text{Å}$	$\beta^\circ$	$V/\text{Å}^3$	$D_r/\text{gcm}^{-3}$	$Z$	$D_x/\text{gcm}^{-3}$	$\mu(\text{MoK}\alpha)/\text{cm}^{-1}$
$\text{Bi}_{34(2/3)}\text{O}_{36}(\text{SO}_4)_{16}$	9358	$C2/c$	24.67(2)	5.650(3)	15.139(7)	97.67(5)	2091(2)	7.18	1	7.43	695
$\text{Bi}_{28}\text{O}_{32}(\text{SO}_4)_{10}$	7324	$C2/m$	21.638(7)	5.657(2)	15.087(8)	119.1(4)	1614(1)	7.52	1	7.54	730
$\text{Bi}_2\text{O}_2\text{SO}_4$	546	$I2_1$ $Im$ or $I2/m$	4.1026(4)	4.2343(6)	13.5432(13)	90.16(1)	235.3(1)	7.63	2	7.71	714

good agreement with previous work.<sup>2,3</sup>  $\text{Bi}_2\text{O}_2\text{SO}_4$  was obtained on heating  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$  in air at  $480^\circ\text{C}$  for 48 h (cf. Ref. 2). Single crystals could not be obtained. The powder photographs indicated a nearly pure phase with a monoclinically deformed  $\text{NaBi}_3\text{O}_4\text{Cl}_2$  structure. The structure is thus related to those described for  $\text{La}_2\text{O}_2\text{SO}_4$  and  $\text{La}_2\text{MoO}_6$ ,<sup>5,6</sup> although the sulfate tetrahedra may be disordered. Moreover, the cell dimensions as obtained here may not be the true ones. The present samples of  $\text{Bi}_2\text{O}_2\text{SO}_4$  were fused with  $\text{KNaCO}_3$  for a short time and their sulfur contents were determined by precipitation of  $\text{BaSO}_4$ . The results indicated the composition  $\text{Bi}_2\text{O}_3 \cdot (0.9-1.0)\text{SO}_3$ . No further work was done on  $\text{Bi}_2\text{O}_2\text{SO}_4$ .

On heating  $\text{Bi}_2\text{O}_2\text{SO}_4$  in a sealed and evacuated glass tube for 20 h at  $620^\circ\text{C}$  a new phase with the cell dimensions  $a = 24.67$ ,  $b = 5.66$ ,  $c = 15.14 \text{ \AA}$  and  $\beta = 97.6^\circ$  was formed. The space group is  $Cc$  or  $C2/c$  and the observed density is  $7.18 \text{ g cm}^{-3}$ . The density may be too low since small amounts of  $\text{SO}_3$  possibly released in the syntheses may afterwards react with atmospheric moisture and thus lower the density. No effort was, however, made to free the samples from occluded  $\text{H}_2\text{SO}_4$ . Single crystals were obtained on heating  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$  at  $760^\circ\text{C}$  for 20 h in a gold tube inside an evacuated Pyrex tube. A number of samples were analysed for  $\text{SO}_4^{2-}$  as described above. The analytical result was  $\text{Bi}_2\text{O}_3 \cdot (0.9-1.1)\text{SO}_3$ . This phase is called  $\text{Bi}_2\text{O}_3 \cdot 0.9 \text{ SO}_3$  in the following. A single crystal was mounted in a Nicolet P3m diffractometer and 4311 independent reflections were recorded using  $\text{MoK}\alpha$  radiation. Corrections for absorption and for Lorentz and polarization effects were made using standard computer programmes.

On heating  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$  in an open vessel at temperatures between  $580^\circ\text{C}$  and  $740^\circ\text{C}$ , a monoclinic phase with  $a = 21.65$ ,  $b = 5.66$ ,  $c = 15.01 \text{ \AA}$  and  $\beta = 119^\circ$  was formed. Possible space groups are  $C2$ ,  $Cm$  or  $C2/m$ . The observed density is  $7.52 \text{ g cm}^{-3}$ . Single crystals were obtained on heating  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$  in an evacuated glass tube for 2 min at  $860^\circ\text{C}$ , crushing the tube at room temperature, inserting the sample in a new glass tube and heating for 2 h at  $860^\circ\text{C}$ . Based on the weight losses of the initial  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$  samples, the composition was expected to lie within the limits  $\text{Bi}_2\text{O}_3 \cdot (0.68-0.75)\text{SO}_3$ . The same phase is mentioned in Refs. 2-4. The composition and

cell dimensions according to Ref. 2 are for  $\text{Bi}_2\text{O}_3 \cdot 0.67\text{SO}_3$ ,  $a(\text{tetragonal}) = 14.75$  and  $c = 12.47 \text{ \AA}$ . This phase is called  $\text{Bi}_2\text{O}_3 \cdot 0.67\text{SO}_3$  in the following. A single crystal was mounted in a Nicolet P3m diffractometer and 3854 independent reflections were recorded using  $\text{MoK}\alpha$  radiation. Corrections for absorption and for Lorentz and polarization effects were made as described above. The single crystal used was a flat needle with the  $b$  direction along the needle axis. The  $ab$  plane was parallel to the largest surface of the needle.

### Structure determination and refinement

*$\text{Bi}_2\text{O}_3 \cdot 0.9\text{SO}_3$  phase.* A three-dimensional Patterson function was calculated assuming space group  $C2/c$ ; it could be interpreted with the positions of 52 (Bi+S) atoms ordered in rows of squares in the  $xz$  projection (cf. Fig. 1). The structure could not, however, be solved on that basis. Space group  $Cc$  was therefore assumed and direct methods in the form of the program MULTAN 80 were applied. In evaluating the various sets, use was made of the rows of squares mentioned above. The first solution gave positions of 36 Bi atoms and 12 S atoms, and thus indicated  $\text{Bi}_2\text{O}_3 \cdot 0.67\text{SO}_3$ , which is far from the expected composition  $\text{Bi}_2\text{O}_3 \cdot \sim 1\text{SO}_3$ . It was then found that the positions of the Bi atoms were nearly centrosymmetrically related, and space group  $C2/c$  was therefore tried again. In this way 36 Bi, 16 S and 100 O atom positions were found in the unit cell. No short S-S distances occurred. Assuming 100 oxygen atoms per unit cell, 4/3 Bi atoms must be missing. In the isotropic least-squares refinements, Bi(5) (see Table 2) had the largest temperature factor of the Bi atoms. The unit cell was therefore assumed to contain only 8/3 Bi. No refinements of the occupancy factors for the Bi atoms were made. Anisotropic temperature factors were then introduced for all Bi atoms. Bi(2) (see Table 2) showed an imaginary r.m.s. component which could be made real on replacing  $U_{22}$  by  $3\sigma(U_{22})$ . It was, however, given an isotropic temperature factor in the following refinements. The final  $R$  factors based on reflections with  $I > 3\sigma(I)$  are  $R_2 = 0.081(1251)$ ,  $R_1 = 0.080(1249)$ ,  $R_w = 0.087$  and  $S = 1.72$ . With the assumed number of 100 oxygen atoms per unit cell the composition will be  $\text{Bi}_{34(2/3)}\text{O}_{36}(\text{SO}_4)_{16}$  or  $\text{Bi}_2\text{O}_3 \cdot 0.92\text{SO}_3$ , in good agreement with the expected composition  $\text{Bi}_2\text{O}_3 \cdot (0.9-1.1)\text{SO}_3$ .

Some comments on the proposed structure may be made: Firstly, the  $R$  values are comparatively high; the present author's opinion is that this may be due to inadvertences in the description of the external form of the single crystal. Secondly, even taking into consideration the fact that density measurements based on weight losses in benzene usually give low values for high densities, the observed density of  $7.18 \text{ g cm}^{-3}$  is 1–2% too low. One possible reason for this has been discussed earlier above. Another cause may be a slight defect also in the oxygen atom positions, possibly that of atom O(5) (see Table 2), so

that the number of oxygen atoms is less than 100 and the number of Bi atoms less than 34.67, with the "new" defects possibly spread over all Bi positions. However, in view of the small discrepancy between observed and calculated densities no attempts were made to investigate this hypothesis.

Final thermal and positional parameters are given in Table 2, and selected distances in Table 3.

*$\text{Bi}_2\text{O}_3 \cdot 0.67\text{SO}_3$  phase.* A three-dimensional Patterson function was calculated. It could be interpreted roughly assuming either space group

Table 2. Final positional and thermal parameters obtained in the least-squares refinement of the structures of  $\text{Bi}_{34(2/3)}\text{O}_{36}(\text{SO}_4)_{16}$  and  $\text{Bi}_{28}\text{O}_{32}(\text{SO}_4)_{10}$ . The anisotropic temperature factors for Bi are based on the expression  $\exp[-2\pi^2(U_1a^2h^2 + \dots + 2U_{23}b^*c^*kl)]$ .

$\text{Bi}_{34(2/3)}\text{O}_{36}(\text{SO}_4)_{16}$									
Atom	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Bi(1)	.9531(1)	.0350(8)	.6097(2)	.015(2)	.054(2)	.023(1)	-.009(2)	.007(1)	-.014(2)
Bi(3)	.8746(1)	-.0271(6)	.2824(2)	.029(2)	.013(1)	.014(1)	.006(1)	.001(1)	-.001(1)
Bi(4)	.8419(1)	.4691(6)	.1284(2)	.023(2)	.005(1)	.006(1)	.002(1)	-.003(1)	-.002(1)
Bi(5) <sup>a</sup>	0	.3767(10)	.25	.028(4)	.011(2)	.020(3)	0	.012(3)	0
Atom	$x$	$y$	$z$	$B$	Atom	$x$	$y$	$z$	$B$
Bi(2)	.2682(1)	.0027(4)	.8261(2)	0.43(3)	O(6)	.624(2)	.016(8)	.142(3)	1.1(7)
S(1)	.5704(9)	.003(4)	.0869(13)	1.7(3)	O(7)	.575(2)	-.036(10)	-.017(4)	2.0(9)
S(2)	.1800(8)	.027(4)	.0225(12)	1.2(3)	O(8)	.538(2)	.210(7)	.099(3)	0.6(7)
O(1)	.907(3)	.228(8)	.178(4)	1.0(9)	O(9)	.536(2)	-.210(8)	.115(4)	0.9(8)
O(2)	.402(3)	.240(9)	.186(5)	1.4(10)	O(10)	.219(2)	-.055(7)	.111(3)	0.9(7)
O(3)	.302(3)	.234(7)	.226(5)	0.8(8)	O(11)	.125(2)	-.023(9)	.018(3)	1.2(7)
O(4)	.801(3)	.236(7)	.230(5)	1.0(8)	O(12)	.205(2)	-.100(6)	-.055(3)	0.3(6)
O(5)	0	-.012(19)	.25	3.4(17)	O(13)	.195(2)	.271(5)	.013(2)	-0.3(5)
$\text{Bi}_{28}\text{O}_{32}(\text{SO}_4)_{10}$									
For atoms with $y > 0.200$ in the Table, $G$ is equal to 1.00 in the present space group $C2/m$ . For S(1) $G = 0.25$ and for the rest of the atoms $G = 0.50$ .									
Atom	$x$	$y$	$z$	$B$	Atom	$x$	$y$	$z$	$B$
Bi(1)	.5367(1)	0	.3944(2)	0.84(4)	O(3)	.313(3)	0	.166(4)	2.2(9)
Bi(2)	.0067(1)	0	.2102(2)	0.94(4)	O(4)	.338(3)	.209(11)	.045(4)	4.5(11)
Bi(3)	.1253(1)	0	.0776(2)	0.75(3)	O(5)	.434(4)	0	.193(6)	3.5(13)
Bi(4)	.6470(2)	.0592(5)	.2623(3)	0.87(5)	O(6)	.828(3)	0	.303(4)	1.5(8)
Bi(5)	.1791(2)	.0868(6)	.4647(2)	0.74(5)	O(7)	.939(4)	0	.311(6)	4.2(15)
Bi(6)	.7536(1)	.0203(10)	.1302(2)	0.78(5)	O(8)	.921(2)	.205(10)	.438(4)	4.0(10)
Bi(7)	.2875(1)	.0223(9)	.3466(2)	0.73(5)	O(9)	.652(3)	0	.493(5)	2.5(10)
S(1)	.5000	0	0	0.6(3)	O(10)	.570(1)	.250(6)	.324(2)	0.9(4)
S(2)	.3562(9)	0	.1163(14)	1.2(3)	O(11)	.198(1)	.253(6)	.172(2)	0.7(4)
S(3)	.9041(9)	0	.3707(14)	0.9(2)	O(12)	.099(3)	.077(11)	.191(5)	1.8(12)
O(1)	.445(4)	.114(16)	.002(7)	3.1(16)	O(13)	.229(1)	.251(4)	.390(2)	-0.0(3)
O(2)	.532(3)	.188(13)	.091(6)	1.7(11)					

<sup>a</sup>Occupancy factor,  $G$ , in the present space group  $C2/c$  is 1/3.

Table 3. Selected distances (Å) and angles (°) for (a)  $\text{Bi}_{34(2/3)}\text{O}_{36}(\text{SO}_4)_{16}$  and (b)  $\text{Bi}_{28}\text{O}_{32}(\text{SO}_4)_{10}$ . The oxygen atoms are in some cases doubly indexed in case (b). The first number refers to the atom in Table 2 and the second is defined by  $x, y, z$  (Table 2), 1 or absent,  $x, \bar{y}, z, 2$ , and so on, as for space group  $C2/m$ , 2nd SETTING, in the International Tables. For (a), the atoms O(1)–O(5) are non-sulfate, and for (b), the atoms O(9)–O(13).

<b>(a) <math>\text{Bi}_{34(2/3)}\text{O}_{36}(\text{SO}_4)_{16}</math></b>				
S(1)–O(8) 1.43(5)	O(6)–S(1)–O(7) 113(3)	Bi(1)–O(1) 2.21(6)	Bi(3)–O(2) 2.15(6)	
S(1)–O(6) 1.47(5)	O(6)–S(1)–O(8) 111(3)	Bi(1)–O(2) 2.22(6)	Bi(3)–O(3) 2.31(6)	
S(1)–O(9) 1.56(5)	O(6)–S(1)–O(9) 111(3)	Bi(1)–O(5) 2.28(1)	Bi(3)–O(1) 2.36(6)	
S(1)–O(7) 1.60(6)	O(7)–S(1)–O(9) 106(3)	Bi(1)–O(11) 2.56(5)	Bi(3)–O(4) 2.39(7)	
	O(8)–S(1)–O(9) 105(3)	Bi(1)–O(8) 2.58(5)	Bi(3)–O(6) 2.82(6)	
	O(7)–S(1)–O(8) 110(3)	Bi(1)–O(9) 2.74(5)	Bi(3)–O(10) 2.99(5)	
		Bi(1)–O(7) 2.84(6)		
S(2)–O(11) 1.38(5)	O(10)–S(2)–O(11) 117(3)		Bi(4)–O(1) 2.16(6)	
S(2)–O(13) 1.44(4)	O(10)–S(2)–O(12) 104(3)	Bi(2)–O(4) 2.25(7)	Bi(4)–O(2) 2.22(6)	
S(2)–O(12) 1.57(5)	O(10)–S(2)–O(13) 103(2)	Bi(2)–O(3) 2.26(6)	Bi(4)–O(4) 2.35(7)	
S(2)–O(10) 1.61(5)	O(11)–S(2)–O(12) 111(3)	Bi(2)–O(4)' 2.30(7)	Bi(4)–O(3) 2.40(6)	
	O(11)–S(2)–O(13) 117(3)	Bi(2)–O(3)' 2.34(6)	Bi(4)–O(12) 2.57(4)	
	O(12)–S(2)–O(13) 103(2)	Bi(2)–O(12) 2.60(4)	Bi(4)–O(13) 2.66(4)	
		Bi(2)–O(6) 2.64(5)	Bi(4)–O(7) 2.86(5)	
		Bi(2)–O(10) 2.71(4)		
		Bi(2)–O(13) 2.79(4)	Bi(5)–O(5) 2.20(11)	
Shortest O–O distance			Bi(5)–O(9) 2.38(6)	
outside the tetrahedra			Bi(5)–O(1) 2.55(6)	
O(2)–O(3) 2.62(10)				
<b>(b) <math>\text{Bi}_{28}\text{O}_{32}(\text{SO}_4)_{10}</math></b>				
S(1)–O(1) 1.37(9)	O(1)–S(1)–O(1)' 124(8)	Bi(1)–O(10.1) 2.09(3)	Bi(5)–O(13.1) 2.12(2)	
S(1)–O(2) 1.60(7)	O(1)–S(1)–O(2) 2.108(4)	Bi(1)–O(9.1) 2.20(6)	Bi(5)–O(13.2) 2.70(2)	
	O(1)–S(1)–O(2)' 2.109(4)	Bi(1)–O(5.1) 2.76(7)	Bi(5)–O(9.5) 2.49(2)	
	O(2)–S(1)–O(2)' 97(5)	Bi(1)–O(8.7) 2.78(5)	Bi(5)–O(13.8) 2.31(2)	
		6-coordinated	Bi(5)–O(13.7) 2.85(2)	
S(2)–O(3) 1.45(6)	O(3)–S(2)–O(4) 2.111(2)	Bi(2)–O(10.5) 2.13(3)	Bi(5)–O(10.6) 2.46(3)	
S(2)–O(5) 1.50(7)	O(3)–S(2)–O(5) 111(4)	Bi(2)–O(12.1,12.2) 2.20(1)	Bi(5)–O(10.5) 2.97(3)	
S(2)–O(4) 1.52(6)	O(4)–S(2)–O(4)' 102(4)	Bi(2)–O(7.1) 2.58(5)	7-coordinated	
	O(5)–S(2)–O(4) 2.111(3)	Bi(2)–O(2.5, 2.6) 2.76(7)	Bi(6)–O(11.6) 2.05(3)	
		5-coordinated	Bi(6)–O(11.5) 2.20(3)	
S(3)–O(7) 1.43(8)	O(6)–S(3)–O(7) 109(4)	Bi(3)–O(12.1,12.2) 2.09(6)	Bi(6)–O(6.1) 2.31(5)	
S(3)–O(6) 1.46(5)	O(6)–S(3)–O(8) 2.108(2)	Bi(3)–O(11.1) 2.10(3)	Bi(6)–O(4.3) 2.63(6)	
S(3)–O(8) 1.47(5)	O(7)–S(3)–O(8) 2.114(3)	Bi(3)–O(1.7, 1.8) 2.60(9)	Bi(6)–O(4.4) 2.73(6)	
	O(8)–S(3)–O(8)' 104(4)	Bi(3)–O(2.5, 2.6) 2.77(7)	Bi(6)–O(3.5) 2.94(2)	
		Bi(3)–O(4.7) 2.87(6)	6-coordinated	
Shortest O–O distances		7-coordinated	Bi(7)–O(9.3) 2.13(6)	
outside the tetrahedra		Bi(4)–O(13.6) 2.17(2)	Bi(7)–O(13.1) 2.11(2)	
O(2)–O(12.6) 2.01(10)	O(2)–O(12.5) 2.66(10)	Bi(4)–O(13.5) 2.57(2)	Bi(7)–O(13.2) 2.28(2)	
O(11)–O(12.1) 2.50(7)	O(11)–O(12.2) 2.96(7)	Bi(4)–O(11.6) 2.38(3)	Bi(7)–O(11.1) 2.73(3)	
O(10)–O(12.6) 2.59(7)	O(10)–O(12.5) 3.02(7)	Bi(4)–O(11.5) 2.75(3)	Bi(7)–O(11.2) 2.85(3)	
		Bi(4)–O(12.6) 2.32(6)	Bi(7)–O(8.6) 2.96(5)	
		Bi(4)–O(12.5) 2.93(6)	.....	
O(9)–O(10) 2.69(6)		Bi(4)–O(10.1) 2.52(3)	Bi(7)–O(8.5) 3.10(5)	
		Bi(4)–O(10.2) 2.87(3)	6-coordinated	
		Bi(4)–O(2.1) 2.68(7)		
		Bi(4)–O(2.2) 2.94(7)		
		8-coordinated		

$C2$  or  $C2/m$ , but since two strong maxima occurred at  $\nu = 0.08$  ( $b = 5.7 \text{ \AA}$ ), space group  $C2$  was preferred. Least-squares refinements gave an  $xz$  projection of (Bi+S) atoms similar to that for  $\text{Bi}_2\text{O}_3 \cdot 0.9\text{SO}_3$  (cf. Fig. 3). 28 Bi and 10 S atoms were located in the unit cell, and since no short S-S distances occurred, the composition could be fixed at  $\text{Bi}_{28}\text{O}_{32}(\text{SO}_4)_{10}$  or  $\text{Bi}_2\text{O}_3 \cdot 5/7 \text{ SO}_3$ , in good agreement with the expected composition  $\text{Bi}_2\text{O}_3 \cdot (0.69-0.75)\text{SO}_3$  and also with the data given in Refs. 2-4. The calculated density is  $7.54$  and the observed value is  $7.52 \text{ g cm}^{-3}$ . The oxygen atoms were then located. With isotropic temperature factors and using reflections with  $I > 2\sigma(I)$ , the final  $R_w$  was  $0.100(1645)$  and  $S = 1.59$  (the anomalous dispersion of the Bi and S atoms was taken into consideration in the calculations using space group  $C2$  but not when space group  $C2/m$  was assumed). Bi-O distances, and distances and angles within two of the three sulfate tetrahedra [corresponding to S(1) and S(2) in Table 2] were in fair agreement with accepted data. The third tetrahedron, S(3), showed, however, abnormal distances and angles. Besides this, many of the non-sulfate oxygen atoms had negative temperature factors. Neither the use of reflections with  $I > 1.5\sigma(I)$  nor the introduction of anisotropic temperature factors for the Bi atoms improved the results. Some of these temperature factors acquired negative values [Bi(1), Bi(5)], and a high  $U_{22}$  was obtained for Bi(4), corresponding to one r.m.s. component being  $0.4 \text{ \AA}$ . Bi(4) was split into two atoms, 41 and 42, with different  $y$  parameters, and a new refinement was made. The resulting  $x, z$  for 41 and 42 were nearly the same, but  $y$  differed. A disordered structure in  $C2/m$  based on the results in  $C2$  was therefore tried. There are seven 4-fold Bi positions in  $C2$ . Trial and error calculations in  $C2/m$  were made assuming some of the Bi atoms to be ordered and located at the position 4( $i$ ) and some to be disordered and situated at the position 8( $j$ ) with the occupancy factor  $G = 0.5$ . The result was that Bi(1)-Bi(3) are situated at 4( $i$ ), and Bi(4)-Bi(7) at 8( $j$ ) (see Table 2). S(1) was finally assumed to occupy the special position 2( $b$ ),  $1/2, 0, 0$ . The site 4( $g$ ) was also tried for S(1), but  $y$  differed only  $3.2\sigma(y)$  from zero and  $R_w$  increased somewhat. The site symmetries of positions 2( $b$ ) and 4( $g$ ) are  $2/m$  and 2, respectively. In both cases, 8 oxygen atoms must be introduced to obtain a tetrahedron around each S(1). The "S(1) oxygen atoms" must

therefore be disordered. The S(2) and S(3) atoms and half of the number of their O atoms had  $y$  close to zero in the  $C2$  refinements, and they were all assumed to occupy the position 4( $i$ ). The atom O(12) (see Table 2) had  $y$  close to zero in the  $C2$  refinements but acquired a high  $B$  in the  $C2/m$  refinements; it was therefore assumed to be disordered and to occupy the position 8( $j$ ). The rest of the O atoms had  $y = 0.20-0.25$  in the  $C2$  calculations; these positions could be "paired" to give positions 8( $j$ ). It is worth mentioning that the single crystal used showed normal extinctions when positioned in a polarisation microscope so that the light passed approximately parallel to the  $c$ -axis. Using reflections with  $I > 2\sigma(I)$ , refinements gave  $R_w = 0.089(1636)$  and  $S = 1.40$ , as compared to  $R_w = 0.100(1645)$  and  $S = 1.59$  for the  $C2$  refinement above. Using reflections with  $I > 3\sigma(I)$ , the refinements in  $C2/m$  gave  $R = 0.065(1217)$ ,  $R_w = 0.064(1215)$  and  $S = 1.16$ . There has of course been some arbitrariness in the present structure solutions, especially in the choice of the positions 4( $i$ ) and 8( $j$ ) with  $G = 0.5$ . Distances and angles for the disordered S(1) tetrahedron deviate more from the accepted values and have larger e.s.d.'s than is the case for the other  $\text{SO}_4^{2-}$  tetrahedra. Final thermal and positional parameters are given in Table 2, and selected distances in Table 3. Lists of  $|F_o|$  and  $|F_c|$  for the present structures are available from the author on request.

## Discussion

$\text{Bi}_{34(2/3)}\text{O}_{36}(\text{SO}_4)_{16}$ . A projection of the structure is shown in Fig. 1. The Bi atoms, the S atoms and the O atoms all occur in rows which are approximately parallel to the crystal plane 103. The Bi atoms and the "fluorite" oxygen atoms may be thought of as forming chains of edge-sharing tetrahedra,  $\text{OBi}_4$ , which are infinite in the  $b$  direction. Four such chains form a group by renewed edge-sharing. The groups of four chains are joined to each other by corner-sharing at the 2-fold axes passing through the Bi(5) atoms. The  $\text{SO}_4^{2-}$  tetrahedra are free from each other but they also occur in groups of four. These groups are related by the inversion centres at the positions 4( $a$ ) of space group  $C2/c$ . If the atoms at the 2-fold axes, Bi(5) and O(5), are removed from the unit cell, a composition  $\text{Bi}_{32}\text{O}_{32}(\text{SO}_4)_{16}$  or  $\text{Bi}_2\text{O}_2\text{SO}_4$  will result. A certain resemblance can

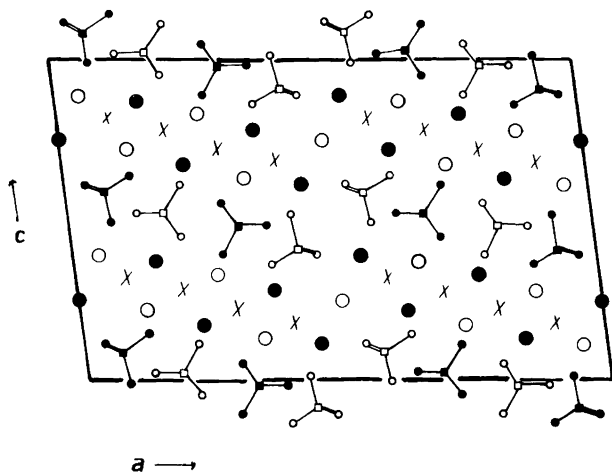


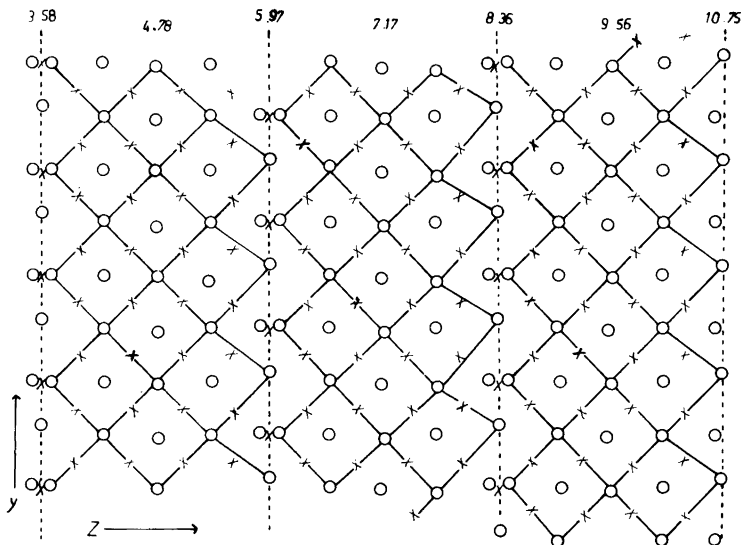
Fig. 1. Projection of  $\text{Bi}_{34(2/3)}\text{O}_{36}(\text{SO}_4)_{16}$  on the  $x,z$  plane. Non-sulfate oxygen atoms are denoted by crosses, sulfate oxygen atoms by small circles, sulfur atoms by squares and bismuth atoms by large circles. Empty and filled circles and squares denote atoms at  $y = 0$  and  $y = \frac{1}{2}$ , respectively. The O atoms joined by double lines to the S atoms are situated at  $y = \pm 0.20$ . The O(5) and O(13) atoms (Table 2) are not shown.

therefore be expected between the present compound and  $\text{Bi}_2\text{O}_2\text{SO}_4$ . It was mentioned earlier above that the structure of  $\text{Bi}_2\text{O}_2\text{SO}_4$ , though not known in detail, is of the  $\text{NaBi}_3\text{O}_4\text{Cl}_2$  structure type.  $\text{Bi}_2\text{O}_2^{2+}$  layers replace  $(\text{NaBi}_3\text{O}_4)^+$  layers and  $\text{SO}_4^{2-}$  replaces  $\text{Cl}^-$ .  $\text{Bi}_2\text{O}_2$ -like parts also occur in the structure of  $\text{Bi}_{34(2/3)}\text{O}_{36}(\text{SO}_4)_{16}$ . Fig. 2 shows three groups of 4 ( $\text{OBi}_4$ ) tetrahedral chains projected along the normal to the 103 crystal plane. Square  $\text{Bi}_2\text{O}_2$  groups can be visualized in

each of the "steps". The "extra" oxygen atoms, O(5), at the 2-fold axes are also shown in the figure. The  $\text{Bi}_2\text{O}_2$ -like parts of the present structure occur in "steps" with sequential "heights" along the normal to the 103 crystal plane (Fig. 2). Similar steps have been observed previously for a bismuth oxide chloride,  $\text{Bi}_{24}\text{O}_{31}\text{Cl}_{10}$ .<sup>1</sup>

Table 3 gives selected distances and angles within the structure of  $\text{Bi}_{34(2/3)}\text{O}_{36}(\text{SO}_4)_{16}$ . The Bi, O distances are normal, but especially the dis-

Fig. 2. Orthogonal projection of a slab of composition  $\text{Bi}_{17(1/3)}\text{O}_{18}$  on the 103 plane in  $\text{Bi}_{34(2/3)}\text{O}_{36}(\text{SO}_4)_{16}$ . Three "steps" separated by 2-fold axes (dashed lines) are shown. The 2-fold axes are situated at different distances from 103, indicated by numbers directly above the dashed lines. The oxygen atoms (crosses) form in each step a plane parallel to 103; the distance to 103 is indicated between the dashed lines. The Bi atoms (circles) form in each step two planes parallel to 103, one above and one below (at equal distances) the plane of the crosses. One of the Bi planes in each step is indicated by solid lines. Z is a direction within the 103 plane perpendicular to the y axis.



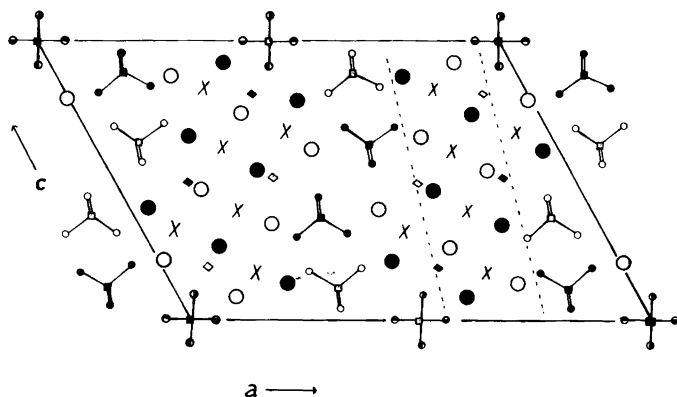


Fig. 3. Projection of  $\text{Bi}_{28}\text{O}_{32}(\text{SO}_4)_{10}$  on the  $x,z$  plane. Oxygen atoms at  $y = \pm 0.25$  are denoted by crosses, atoms O(9), O(12) (Table 2) are denoted by rhombs, sulfate oxygen atoms by small circles, sulfur atoms by squares and bismuth atoms by large circles. Empty and filled circles etc. indicate atoms at  $y = 0$  and  $y = \frac{1}{2}$ , respectively. Dashed lines include a  $\text{Bi}_2\text{O}_2$ -like part of the structure.

tances and angles for the S(2) tetrahedron deviate somewhat from the accepted values.

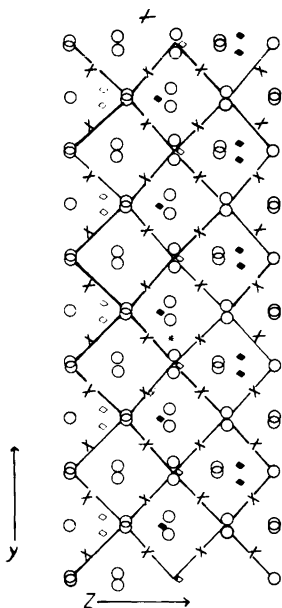


Fig. 4. Orthogonal projection of part of the  $\text{Bi}_{14}\text{O}_{16}$  block on the  $\bar{6}01$  plane in  $\text{Bi}_{28}\text{O}_{32}(\text{SO}_4)_{10}$ . The O atoms at  $y = \pm 0.25$  (crosses) form a plane parallel to  $\bar{6}01$ . Atoms O(9), O(12) (Table 2) are denoted by empty and filled rhombs, depending on their distance to  $\bar{6}01$ . The Bi atoms (circles) form two planes parallel to  $\bar{6}01$ , one above and one below (at equal distances) the plane of the crosses. The Bi atoms in one of these planes are joined by solid lines. Z is a direction within the  $\bar{6}01$  plane perpendicular to the y axis.

$\text{Bi}_{28}\text{O}_{32}(\text{SO}_4)_{10}$ . As in  $\text{Bi}_{34(2/3)}\text{O}_{36}(\text{SO}_4)_{16}$ , the Bi atoms, the S atoms and the O atoms all occur in rows in the  $x,z$  projection and extend infinitely in the  $b$  direction. The rows for the Bi and "fluorite" oxygen atoms are, for each atom, perpendicular to each other and are parallel to the crystal planes  $\bar{6}01$  and  $\bar{1}02$ . One formal description of the structure (cf. Fig. 3) is that it is built up of blocks of Bi and O atoms extending infinitely in the  $b$  direction but separated from each other in the  $a$  and  $c$  directions, and of pleated layers of  $\text{SO}_4^{2-}$  tetrahedra roughly parallel to the crystal plane 100. The Bi, O blocks of composition  $\text{Bi}_{14}\text{O}_{16}$  have a "fluorite"-like structure and contain 6 rows of  $(\text{OBi}_4)$  tetrahedral chains. Four of these rows extend parallel to the  $\bar{6}01$  plane in the same manner as one "step" in  $\text{Bi}_{34(2/3)}\text{O}_{36}(\text{SO}_4)_{16}$ . They are enclosed by dashed lines in Fig. 3 and are projected on the  $\bar{6}01$  plane in Fig. 4. Fig. 4 also shows the disorder in the  $b$  direction in the unit cell. The atoms within each  $\text{Bi}_{14}\text{O}_{16}$  block are related by an inversion center. Each block contains 4 "extra" oxygen atoms, O(9) and O(12), which do not occupy "CaF<sub>2</sub>" positions. One of them, O(12), is disordered.

$\text{Bi}_{28}\text{O}_{32}(\text{SO}_4)_{10}$  is a disordered structure and some restrictions for atoms within the same unit cell must be made. The disordered atoms O(1) and O(2) cannot both have  $y > 0$ , otherwise S(1) would be at the apex of a pyramid of oxygen atoms and very short O—O distances would result. It is seen from Tables 2 and 3 that the  $y$ 's of O(2) and O(12) must have the same sign, otherwise an O(2)—O(12) distance of only 2.0 Å would result.

The S(1) tetrahedron is disordered and especially the angles deviate quite considerably from

expected values. The angles would improve with the inclusion of a disordered S(1) atom with  $y \approx 0.02$  but the presence of such disorder receives very little or no support from the data (see above). The distances and angles within the S(2) and S(3) tetrahedra are normal. It is, however, seen from Table 2 that some of the S(2) and S(3) oxygen atoms have quite high temperature factors, and there may be some disorder even within these tetrahedra. The Bi-O distances (Table 3) are normal.

The present phases,  $\text{Bi}_{26}\text{O}_{27}(\text{SO}_4)_{12}$  with  $Z = 4/3$  and  $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$  with  $Z = 2$ , represent the first pyrolysis products of  $\text{Bi}_2(\text{SO}_4)_3$  after  $\text{Bi}_2\text{O}_2\text{SO}_4$ .  $\text{Bi}_{26}\text{O}_{27}(\text{SO}_4)_{12}$  probably cannot be prepared by pyrolysis of  $\text{Bi}_2(\text{SO}_4)_3$  and is not mentioned in Refs. 2–4.  $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$  is easily prepared. A trivial consequence of the loss of  $\text{SO}_3$  from  $\text{Bi}_2\text{O}_2\text{SO}_4$  to give  $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$  is that the Bi, O parts of the structure successively change from  $\text{Bi}_2\text{O}_2$  layers to “ $\text{CaF}_2$ ”-like blocks. Common to  $\text{Bi}_{26}\text{O}_{27}(\text{SO}_4)_{12}$  and  $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$  are the short  $b$  axis of 5.7 Å and the arrangement of

Bi atoms in rows of squares in the  $x, z$  projections. With some approximation, these rows also include the S atoms (See Figs. 1 and 3).

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