

# Pyrolysis Products of $\text{Bi}_2(\text{SO}_4)_3$ . II. Crystal Structure of $\text{Bi}_2\text{O}(\text{SO}_4)_2$

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The crystal structure of  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  has been determined from 1718 independent reflections to a final  $R$  of 0.069. The crystals are monoclinic, space group  $C2/c$ , with  $a = 32.160(9)$ ,  $b = 6.706(25)$ ,  $c = 22.612(16)$  Å,  $\beta = 119.55(5)^\circ$  and  $Z = 24$ . The crystal structure is built up of nearly planar  $\text{Bi}_4\text{O}_2^{8+}$  ions and  $\text{SO}_4^{2-}$  ions which are joined to form a three-dimensional network by means of strong bismuth-sulfate oxygen bonds. Infinite layers of composition  $[\text{Bi}_4\text{O}_2(\text{SO}_4)_4]_n$  extending parallel to the crystal plane  $2\ 0\ 1$  may, however, be visualized in the three-dimensional structure. Powder diffraction photographs indicate that  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  is not isotopic with  $\text{Nd}_2\text{O}(\text{SO}_4)_2$ . In contrast to  $\text{Sb}_2\text{O}(\text{SO}_4)_2$ , discrete monomeric molecules of the type  $\text{M}_2\text{O}(\text{SO}_4)_2$  do not occur in the present structure. The structure of  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  has much in common with the previously determined structure of  $\text{Sb}_2\text{O}_2(\text{OH})(\text{SO}_4)_4(\text{H}_2\text{O}_2) \cdot \text{H}_2\text{O}$ . Thus, separate, nearly planar  $\text{M}_4$  rhombuses occur in both structures and the oxo oxygen atoms are three-coordinated in a planar fashion by  $\text{M}$  in both cases. A short survey of cases of similar three-coordination in oxo ions of Bi, Sb and Sn is given. Chemical and crystallographic comparisons with oxide sulfates of antimony and rare earth metals are also given. The stereochemical activity of the lone electron pairs at the Bi atoms is discussed and related to the structural differences between the present compound and similar compounds containing Sb or rare earth elements.

The thermal decomposition of  $\text{Bi}_2\text{O}(\text{SO}_4)_3$  has been studied previously by thermochemical methods.<sup>1–3</sup> The first decomposition product found<sup>1,2</sup> was  $\text{Bi}_2\text{O}(\text{SO}_4)_2$ . Crystal structures of three subsequent pyrolysis products of  $\text{Bi}_2\text{O}(\text{SO}_4)_3$  viz.  $\text{Bi}_2\text{O}_2\text{SO}_4$ ,  $\text{Bi}_{26}\text{O}_{27}(\text{SO}_4)_2$  and  $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$ , have been investigated by X-ray methods.<sup>4</sup> All three compounds have Bi–O(oxo) parts which are structurally related to the fluorite structure; thus, the oxygen atoms of the complexes are tetrahedrally coordinated by 4 bismuth atoms. The present work describes an investigation of the crystal structure of  $\text{Bi}_2\text{O}(\text{SO}_4)_2$ , the aim having been to study how the bismuth and oxo oxygen atoms are accommodated in the structure. At the beginning of this work infinite chains of  $\text{OBi}_4$  tetrahedra sharing opposite edges, thus  $[\text{Bi}_2\text{O}]_n$ , did not seem unlikely. Infinite  $[\text{Pb}_2\text{O}]_n$  chains of this kind occur in  $\text{Pb}_2\text{OSO}_4$ ,<sup>5</sup> and  $\text{OBi}_4$  tetrahedra are common building elements in bismuth oxide compounds.

## Experimental

$\text{Bi}_2\text{O}(\text{SO}_4)_2$  has formula weight 626 and space group  $C2/c$ . Cell dimensions are  $a = 32.160(9)$ ,  $b = 6.7606(25)$ ,  $c = 22.612(16)$  Å,  $\beta = 119.55(5)^\circ$  and  $V = 4277(4)$  Å<sup>3</sup>, with  $Z = 24$ ,  $D_x = 5.84$  g cm<sup>-3</sup> and  $\mu(\text{MoK}\alpha) = 476$  cm<sup>-1</sup>. For  $D_m$ , *vide infra*.

Commercial  $\text{Bi}_2\text{O}(\text{SO}_4)_3$  from BDH was kept at 460 °C in an open Pt crucible for a prolonged period. Rough analyses indicated the composition  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$ , in good agreement with previous work. The samples so obtained were microcrystalline, and no crystals large enough for X-ray single-crystal work could be obtained. The samples were therefore transferred to gold capsules which were then enclosed in sealed and evacuated glass tubes. The glass tubes had become flattened out at the completion of the reaction, thus indicating very low pressures of  $\text{SO}_3$  and its decomposition products at the reaction

temperatures, viz. 560–720°C. The powder diffraction photographs of the present phase differ from those of the starting compound described above. The latter photographs contain a few lines due to  $\text{Bi}_2\text{O}_2\text{SO}_4$  but the main part of the sample is almost certainly identical to the  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  phase whose formation is indicated by thermochemical measurements.<sup>1,2</sup> The relationship between the initial sample and the present phase will be described further here. Although the partial pressure of gaseous products over the present phase is very low, enclosure (in glass tubes or other material) together with a reaction temperature of 550–560°C seem to be necessary for its formation. The present phase is stable in air. Further studies are needed to decide whether or not it is metastable. Single crystals were picked out from a sample heated to 720°C for 96 h. The sample was inhomogeneous and contained also fairly large single crystals of  $\text{Bi}_{26}\text{O}_{27}(\text{SO}_4)_{12}$ .<sup>4</sup> The present crystals were very small and occurred in sticky conglomerates. A single crystal having the form of an hexagonal cylinder with  $A = C = 0.013$  mm was mounted first in a Weissenberg camera and then in a Nicolet  $P3m$  diffractometer. The Weissenberg photographs indicated a  $C$ -centered monoclinic cell, space group  $Cc$  or  $C2/c$ , with the cell dimensions  $a = 32.2$ ,  $b = 6.7$ ,  $c =$

22.6 Å and  $\beta = 119.6^\circ$ . The powder photographs of eight of the above samples were indexed with this cell and were found to be nearly free of extra lines. There were no significant differences in their cell volumes. Analyses for  $\text{SO}_4^{2-}$  were performed by melting the samples with  $\text{KNaCO}_3$  and determining sulfur as  $\text{BaSO}_4$ . The results indicated compositions in the range  $\text{Bi}_2\text{O}_3 \cdot (1.71\text{--}2.03) \cdot \text{SO}_3$ . Densities were determined from the loss of weight in benzene and the usual precautions were taken. Two samples prepared as above at 580°C with reaction times of 2 h and 24 h, and with weights of about 0.9 g were investigated. The measured densities were  $5.19 \text{ g cm}^{-3}$  for the 2 h sample and  $5.27 \text{ g cm}^{-3}$  for the 24 h sample; the latter gave a powder diffraction pattern containing a few lines due to  $\text{Bi}_2\text{O}_2\text{SO}_4$ .

### Structure determination and refinement

Assuming a composition close to  $\text{Bi}_2\text{O}_3 \cdot 2\text{SO}_3$  and taking the observed densities of  $5.19\text{--}5.27 \text{ g cm}^{-3}$  into account, a cell content corresponding to  $\text{Bi}_{42/23}\text{O}_{20}(\text{SO}_4)_{44}$  was first assumed. This cell content leads to the composition  $\text{Bi}_2\text{O}_3 \cdot 2.06\text{SO}_3$  and a calculated density of  $5.23 \text{ g cm}^{-3}$ . It is compatible with either space group  $Cc$  or  $C2/c$  if one 4-fold position of Bi is only partially occupied

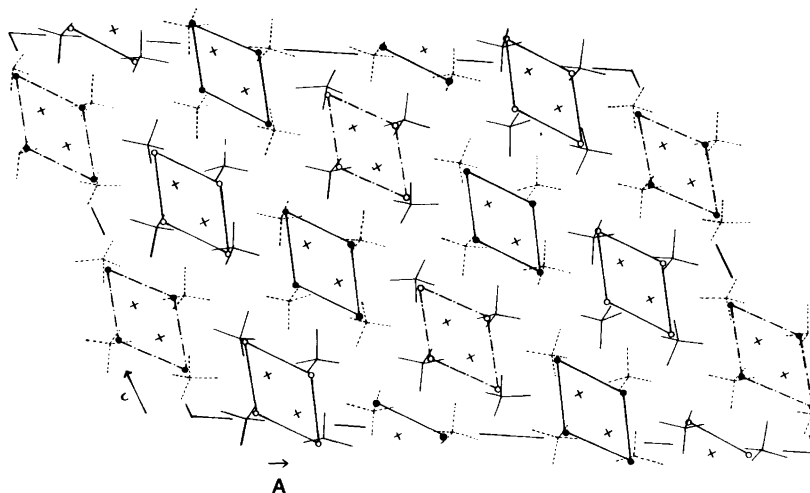


Fig. 1. Projection of the structure of  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  on the  $x,z$  plane. The sulfate ions but not their individual atoms are indicated. Dashed and solid lines indicate  $\text{SO}_4$  groups for which the S atoms have  $y$  close to 0 and  $\frac{1}{2}$ , respectively. Empty and filled circles denote Bi atoms with  $y$  close to 0 and  $\frac{1}{2}$ , respectively. Oxo oxygen atoms are denoted by crosses. Adjacent Bi(1)–Bi(4) atoms (see the text) are joined by full-drawn lines and adjacent Bi(5), Bi(6) atoms by dotted – and – dashed lines.

Table 1. Final positional and thermal parameters for the least-squares refinements of the structure of Bi<sub>2</sub>O(SO<sub>4</sub>)<sub>2</sub>.

Atom	x	y	z	B/Å <sup>2</sup>
Bi(1)	.6457(1)	.5530(4)	.2060(1)	0.94(5)
Bi(2)	.6041(1)	.5090(4)	.0174(1)	0.93(5)
Bi(3)	.7266(1)	.5678(4)	.1274(1)	0.91(5)
Bi(4)	.6862(1)	.4599(4)	-.0599(1)	0.93(4)
Bi(5)	.0240(1)	.5098(4)	.1204(1)	0.88(5)
Bi(6)	.9386(1)	.5389(5)	.1908(1)	1.06(5)
S(1)	.6398(9)	.033(3)	.2219(10)	0.8(3)
S(2)	.5848(8)	-.003(3)	-.0019(9)	1.1(3)
S(3)	.7492(6)	.055(2)	.1766( 8)	0.3(2)
S(4)	.6975(8)	-.029(3)	-.0428(10)	1.2(3)
S(5)	.0238(9)	.041(3)	.1010(10)	1.1(3)
S(6)	.9208(7)	.047(3)	.1781( 8)	0.8(3)
O(1)	.0072(14)	.540(5)	.202(2)	-0.6(6)
O(2)	.6554(16)	.539(7)	.120(2)	0.5(7)
O(3)	.6732(18)	.498(7)	.020(2)	0.9(8)
O(11)	.6297(18)	-.097(7)	.166(2)	1.0(8)
O(12)	.6642(21)	.219(8)	.212(3)	1.4(9)
O(13)	.6764(21)	-.058(9)	.292(3)	2.1(10)
O(14)	.6011(18)	.096(7)	.228(2)	1.0( 8)
O(21)	.6162(17)	-.162(6)	.001(2)	0.5(8)
O(22)	.5480(19)	-.068(8)	.016(2)	1.4(9)
O(23)	.5563(18)	.046(7)	-.077(2)	1.1(8)
O(24)	.6133(21)	.185(7)	.036(2)	1.2(9)
O(31)	.7870(21)	-.007(8)	.163(3)	2.1(10)
O(32)	.7731(16)	.088(6)	.254(2)	0.3( 7)
O(33)	.7234(24)	.232(9)	.137(3)	2.2(12)
O(34)	.7117(19)	-.107(8)	.154(2)	1.3( 9)
O(41)	.6619(16)	.133(6)	-.053(2)	0.3(7)
O(42)	.7360(18)	.073(7)	-.055(2)	1.2(8)
O(43)	.7208(17)	-.111(7)	.029(2)	0.8(8)
O(44)	.6725(20)	-.198(7)	-.093(2)	1.1(9)
O(51)	.0432(15)	.173(5)	.159(2)	-0.2(6)
O(52)	-.0061(18)	.143(7)	.045(2)	0.9(8)
O(53)	.0726(16)	-.022(7)	.106(2)	0.7(7)
O(54)	-.0008(22)	-.141(8)	.111(3)	1.8(10)
O(61)	.8939(16)	-.010(6)	.101(2)	0.3(7)
O(62)	.9576(22)	.203(8)	.192(3)	1.4(10)
O(63)	.9483(18)	-.121(7)	.214(2)	0.7(8)
O(64)	.8824(22)	.104(9)	.188(3)	2.2(11)

Table 2. Selected distances (Å) and angles (°) within the crystal structure of  $\text{Bi}_2\text{O}(\text{SO}_4)_2$ . The numbers under the heading "Version" refer to the point position 8 (f) in space group  $C2/c$ , 2nd SETTING. 1 or absent corresponds to  $x, y, z$  (Table 1), 2 to  $\bar{x}, \bar{y}, \bar{z}$  and so on. E stands for equatorial, A for axial (see Fig. 3 and the text). O(1)–O(3) are oxo oxygen atoms.

Bi–Bi distances	Version	Angles Bi–Bi–Bi	Version	Bi–O distances	Version
Bi(1)–Bi(2) 3.801(5)	1	Bi(2)–Bi(1)–Bi(3) 54.7(1)	1	Bi(2)–O( 2) 2.09(4)	1 E
Bi(1)–Bi(3) 3.808(4)	1	Bi(1)–Bi(2)–Bi(4) 125.3(1)	1	O( 3) 2.20(5)	1 E
Bi(1)–Bi(5) 4.597(4)	5	Bi(1)–Bi(3)–Bi(4) 124.9(1)	1	O(24) 2.22(5)	1 A
Bi(2)–Bi(3) 3.495(5)	1	Bi(2)–Bi(4)–Bi(3) 54.2(1)	1	–O(21) 2.32(4)	1 A
				–O(53) 2.65(2)	5
Bi(2)–Bi(4) 3.834(4)	1	Bi(6)–Bi(5)–Bi(6) 2·54.1(1)	3	–O(61) 2.71(4)	6
Bi(2)–Bi(5) 4.960(5)	6	Bi(5)–Bi(6)–Bi(5) 2·124.8(1)	3	–O(52) 2.93(5)	6
				–O(54) 3.28(6)	6
				Average 2.45	
Bi(3)–Bi(4) 3.839(5)	1	Bi–O distances	Version		
Bi(3)–Bi(4) 4.960(4)	6	Bi(1)–O( 2) 2.12(4)	1 E	Bi(3)–O( 2) 2.22(5)	1 E
Bi(4)–Bi(4) 4.611(6)	6	–O(32) 2.32(5)	7 E	–O( 3) 2.24(4)	1 E
Bi(5)–Bi(6) 3.798(4)	1	–O(12) 2.32(5)	1 A	–O(33) 2.29(6)	1 A
Bi(5)–Bi(6) 3.826(5)	3	–O(53) 2.38(4)	5 –	–O(34) 2.39(5)	1 A
		–O(11) 2.50(5)	1 A	–O(42) 2.64(5)	6
Bi(6)–Bi(6) 3.512(7)	3	–O(31) 2.70(5)	7	–O(32) 2.69(4)	7
		–O(64) 2.97(6)	7	–O(13) 2.86(6)	7
		–O(51) 3.03(4)	5	–O(43) 3.05(5)	1
		Average 2.47		Average 2.48	
Bi–O distances	Version	Bi–O distances	Version	Sulfate tetrahedra	Closest Bi
Bi(4)–O( 3) 2.04(4)	1 E	Bi(6)–O( 1) 2.09(4)	1 E	S(3)–O(31) 1.46(6)	2.70
–O(61) 2.29(4)	6 E	–O( 1) 2.18(4)	3 E	–O(32) 1.48(6)	2.32
–O(41) 2.37(4)	1 A	–O(63) 2.35(5)	1 A	–O(33) 1.52(6)	2.29
–O(44) 2.40(5)	1 A	–O(62) 2.35(5)	1 A	–O(34) 1.54(4)	2.39
–O(42) 2.58(5)	6	–O(23) 2.72(5)	6		
–O(64) 2.67(6)	6	–O(14) 2.73(5)	7	S(4)–O(43) 1.51(5)	2.90
–O(31) 2.88(5)	6	–O(44) 3.32(5)	6	–O(41) 1.52(5)	2.37
–O(43) 2.90(5)	6			–O(44) 1.53(5)	2.40
–O(42) 3.04(5)	6			–O(42) 1.56(5)	2.58
Average 2.52		Average 2.40		S(5)–O(52) 1.34(5)	2.93
Bi(5)–O( 1) 2.18(4)	1 E	Sulfate tetrahedra	Closest Bi	–O(51) 1.46(4)	2.41
–O(23) 2.30(5)	6 E	S(1)–O(14) 1.39(6)	2.54	–O(54) 1.53(6)	2.47
–O(51) 2.41(4)	1 A	–O(11) 1.44(5)	2.50	–O(53) 1.58(5)	2.38
–O(54) 2.47(6)	1 A	–O(13) 1.55(6)	2.86		
–O(14) 2.54(5)	5	–O(12) 1.56(6)	2.32	S(6)–O(64) 1.41(6)	2.29
–O(22) 2.83(5)	6			–O(63) 1.42(5)	2.35
–O(22) 2.87(5)	5	S(2)–O(21) 1.45(5)	2.32	–O(62) 1.50(6)	2.35
–O(52) 2.89(5)	1	–O(22) 1.50(6)	2.83	–O(61) 1.56(4)	2.29
–O(11) 3.11(5)	5	–O(23) 1.52(5)	2.30		
Average 2.56		–O(24) 1.55(5)	2.22		

contd

Table 2. (contd)

Sulfate tetrahedra, angles				O-O distances outside the sulfate tetrahedra < 2.60 Å	Version	
O(11)-S(1)-O(12)	106(3)	O(41)-S(4)-O(42)	105(3)	O(1)-O(1)	2.42(7)	3
O(11)-S(1)-O(13)	113(3)	O(41)-S(4)-O(43)	112(3)	O(2)-O(53)	2.55(6)	5
O(11)-S(1)-O(14)	117(3)	O(41)-S(4)-O(44)	110(3)	O(3)-O(61)	2.51(6)	6
O(12)-S(1)-O(13)	107(3)	O(42)-S(4)-O(43)	109(3)			
O(12)-S(1)-O(14)	108(3)	O(42)-S(4)-O(44)	112(3)			
O(13)-S(1)-O(14)	107(3)	O(43)-S(4)-O(44)	108(3)			
O(21)-S(2)-O(22)	113(3)	O(51)-S(5)-O(52)	109(3)			
O(21)-S(2)-O(23)	103(3)	O(51)-S(5)-O(53)	98(3)			
O(21)-S(2)-O(24)	112(3)	O(51)-S(5)-O(54)	112(3)			
O(22)-S(2)-O(23)	104(3)	O(52)-S(5)-O(53)	115(3)			
O(22)-S(2)-O(24)	115(3)	O(52)-S(5)-O(54)	112(3)			
O(23)-S(2)-O(24)	108(3)	O(53)-S(5)-O(54)	110(3)			
O(31)-S(3)-O(32)	106(3)	O(61)-S(6)-O(62)	110(3)			
O(31)-S(3)-O(33)	113(3)	O(61)-S(6)-O(63)	107(3)			
O(31)-S(3)-O(34)	109(3)	O(61)-S(6)-O(64)	101(3)			
O(32)-S(3)-O(33)	113(3)	O(62)-S(6)-O(63)	104(3)			
O(32)-S(3)-O(34)	111(3)	O(62)-S(6)-O(64)	116(3)			
O(33)-S(3)-O(34)	106(3)	O(63)-S(6)-O(64)	118(3)			

or if the Bi defects are spread over several Bi positions. The linear absorption coefficient used, viz.  $\mu(\text{MoK}\alpha) = 420 \text{ cm}^{-1}$ , was calculated from

these data. Using a Nicolet *P3m* diffractometer, 1718 independent reflections with  $I > 3\sigma(I)$  were registered using  $\text{MoK}\alpha$  radiation. Lorentz-polar-

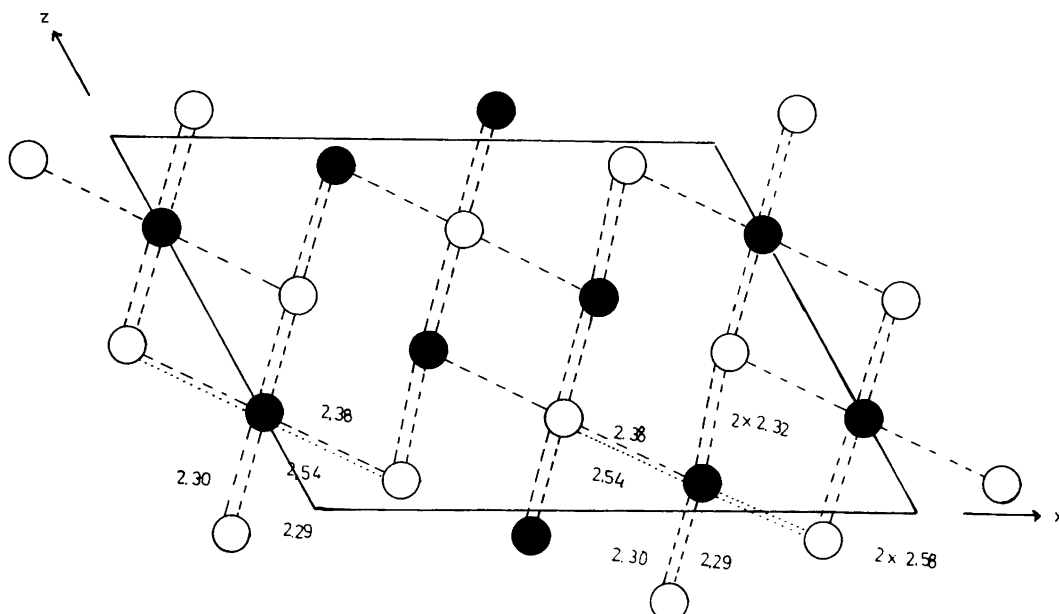


Fig. 2. Schematic drawing of the packing of  $[\text{Bi}_4\text{O}_2(\text{SO}_4)_4]_n$  columns extending infinitely along the  $b$  axis. The columns are represented by empty and filled circles for the corresponding  $\text{Bi}_4$  rhombuses situated at  $y \sim 0$  and  $\sim \frac{1}{2}$ , respectively. Bi-O( $\text{SO}_4$ ) distances between different columns are indicated by dashed lines if they are less than 2.50 Å and by dotted lines if they are in the range 2.50–2.63 Å.

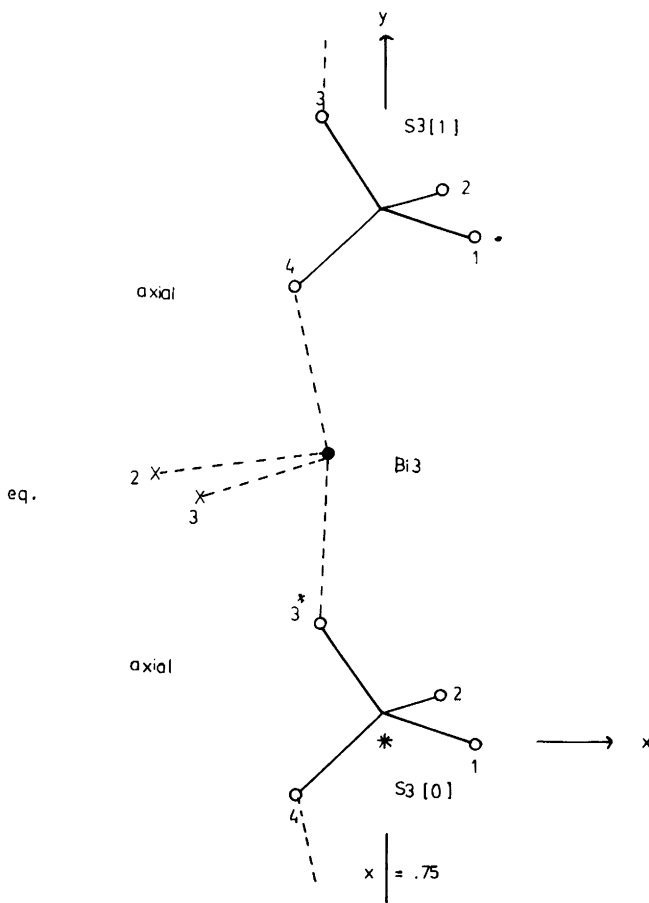


Fig. 3. Projection of an infinite  $-\text{SO}_4-\text{Bi}-\text{SO}_4-$  string along the  $z$  axis onto the  $x,y$  plane. Empty and filled circles denote  $\text{O}(\text{SO}_4)$  and Bi atoms, respectively. The crosses denote oxo oxygen atoms. Dashed lines indicate short Bi-O distances. The numbers refer to Table 2. A  $\psi$ -trigonal bipyramid,  $\text{BiO}_4\text{E}$ , with axial and equatorial ligands is also shown. The electron pair, E, is not visualized.

ization and numerical absorption corrections were made using standard computer programmes.<sup>6</sup>

A three-dimensional Patterson function was calculated. Efforts were made to interpret this function on the basis of space group  $C2/c$ . The best, though not satisfactory result was obtained assuming six 8-fold (general) Bi positions in the unit cell. Partial occupancy in accordance with the above-mentioned cell content was then tried but the results did not improve very much. The positions of the Bi atoms obtained in these calculations were ordered in nets with rows parallel to the  $1\ 0\ 1$  and  $\bar{1}\ 0\ 1$  diagonals (Fig. 1). Keeping both the patterns of the Bi atoms and their  $y$  parameters constant, positions of pseudo 2-fold axes were sought for. One of these positions proved to be correct, which thus led to a change

of origin and subsequent rapid convergence of the least-squares refinements. Difference electron density maps interleaved by least-squares refinements showed the cell content to be  $24\ \text{Bi}_2\text{O}(\text{SO}_4)_2$  units. With isotropic temperature factors for all atoms the final  $R$  factors are  $R = 0.069$  and  $R_w = 0.072$ , with  $S = 1.32$  for 1718 reflections (a slight improvement was obtained on introducing anisotropic temperature factors for the Bi atoms; all these factors were positive. This led to  $R = 0.067$ ,  $R_w = 0.070$  and  $S = 1.28$  for 1717 reflections. These results are not described further here). Final thermal and positional parameters are given in Table 1 and selected distances in Table 2. An  $x,z$  projection of the structure is shown in Fig. 1. Important features of the structure are shown in Figs. 2, 3, 4a and 5. Lists of  $|F_o|$  and  $|F_c|$  are available from the author on request.

*Discussion.* The conclusion drawn from calculations based on the X-ray diffraction results is thus that the composition of the present phase is  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  and not  $\text{Bi}_2\text{O}_3 \cdot 2.06\text{SO}_3$  as was assumed above. The cell content  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  is reasonably consistent with the analytical composition, i.e.  $\text{Bi}_2\text{O}_3 \cdot (1.73\text{--}2.03)\text{SO}_3$ , but not with the observed density of  $5.23 \text{ g cm}^{-3}$ , the calculated density being  $5.84 \text{ g cm}^{-3}$ . A structure with partial occupation of all atom sites seems highly improbable. As mentioned above, there are no significant differences in the cell volumes for the eight samples prepared at temperatures from  $560^\circ\text{C}$  (2 h) to  $740^\circ$  (24 h). The fairly normal temperature factors for all the atoms (Table 1) and the reasonable (within  $3\sigma$ ) S–O distances also disfavour a disordered structure. The low experimental density is therefore not easy to explain, especially since there is no evidence of the presence of low-density amorphous bismuth compounds in the samples. One possible, but not altogether satisfactory explanation is that  $\text{SO}_3$  is formed in the decomposition of the samples at  $460^\circ\text{C}$  in sealed glass tubes and that on cooling, this  $\text{SO}_3$  reacts with minute amounts of water from the inner walls of the tubes to form  $\text{H}_2\text{SO}_4$ . The  $\text{H}_2\text{SO}_4$  so formed may afterwards absorb atmospheric moisture. This model may account for the low density and also explain why the conglomerates are sticky. However, such a mechanism would probably imply the build-up of measurable  $\text{SO}_3$  pressures at  $580^\circ\text{C}$ , which was not observed. The question of the low density must therefore be left open. With the composition  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  and a calculated density of  $5.84 \text{ g cm}^{-3}$  the linear absorption coefficient,  $\mu(\text{MoK}\alpha)$ , used is too low; however, no new absorption corrections were made.

### Description and discussion of the structure

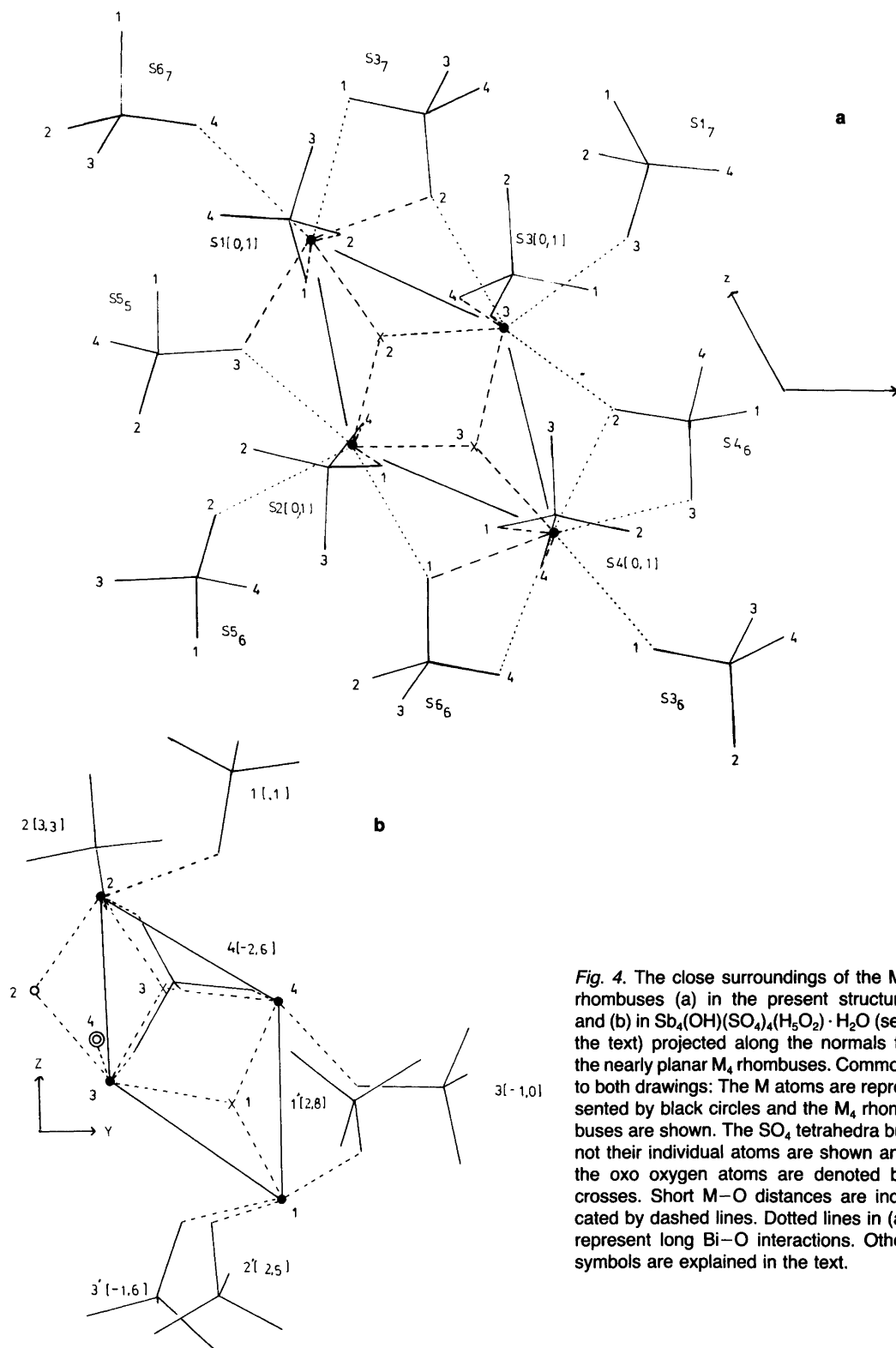
Fig. 1 shows a projection of the crystal structure on the  $x, z$  plane. The Bi and S atoms occur in rows parallel to the crystal planes  $\bar{2}01$ ,  $101$  and  $101$ . Fig. 1 and Table 2 also show that the Bi atoms occur in groups of four, so that the short distances within each group are smaller than distances to other groups. The groups are nearly planar with angular sums of  $358\text{--}359^\circ$  and they are perpendicular to the  $y$  axis. They form approximate rhombuses with angles  $55$  and  $125^\circ$  (Table 2). All non-sulfate oxygen atoms [O(1)

–O(3) in Table 1] are located within these groups in the same plane as that formed by the Bi atoms.

Two crystallographically different  $\text{Bi}_4$  groups are present in the unit cell, one comprising Bi(1)–Bi(4), O(2) and O(3), and the other Bi(5), Bi(6) and O(1) (Table 2). The atoms of the latter group are related by a 2-fold axis. Each planar  $\text{Bi}_4\text{O}_2^{8+}$  group is joined to other groups of the same kind via  $\text{SO}_4$  groups. A detailed picture of the Bi(1)–Bi(4) group is shown in Fig. 4a, where the atoms are numbered as in Table 2. An  $x, z$  projection is shown which has its origin at the center of gravity of the  $\text{Bi}_4$  (Version 1) rhombus. The various versions (Table 2) are given as indices for the S atoms. The Bi atoms, situated at  $y \approx 0.5$ , have the same numbers as the adjacent S atoms which are situated at  $y \approx 0$  and  $y \approx 1$  above and below the Bi atoms. Thus, each of the Bi atoms of the  $\text{Bi}_4$  group is connected to two  $\text{SO}_4$  groups in the vertical direction. The corresponding Bi–O distances are less than  $2.50 \text{ \AA}$ . In this way infinite  $-\text{SO}_4-\text{Bi}-\text{SO}_4-\text{Bi}-$  strings are formed along the  $y$  axis. Fig. 3 shows such a string for Bi(3). The situation is the same for the Bi(5), Bi(6) rhombuses at the 2-fold axes of the unit cell (Fig. 1). A consequence for the whole structure is that infinite columns of composition  $\text{Bi}_4\text{O}_2(\text{SO}_4)_4$  extend along the  $y$  direction. Fig. 2 gives a schematic picture of the short Bi– $\text{SO}_4$ –Bi contacts between different columns and it also shows the packing of the  $\text{Bi}_4\text{O}_2^{8+}$  rhombuses. Bond lengths less than  $2.64 \text{ \AA}$  are given for each of the Version 1 (Table 1)  $\text{Bi}_4$  rhombuses. It is seen from the figure that the packing  $\text{Bi}_4\text{O}_2^{8+}$  groups is approximately body-centered cubic. Fig. 2 as a whole gives some indication that the different columns are joined by strong bonds to layers parallel to the crystal plane  $\bar{2}01$  and that the layers are then connected by weaker bonds. Thus, one description of the present structure is that it is built up of layers of composition  $[\text{Bi}_4\text{O}_2(\text{SO}_4)_4]_n$  which are infinite in two dimensions and which have strong bonds within the layers.

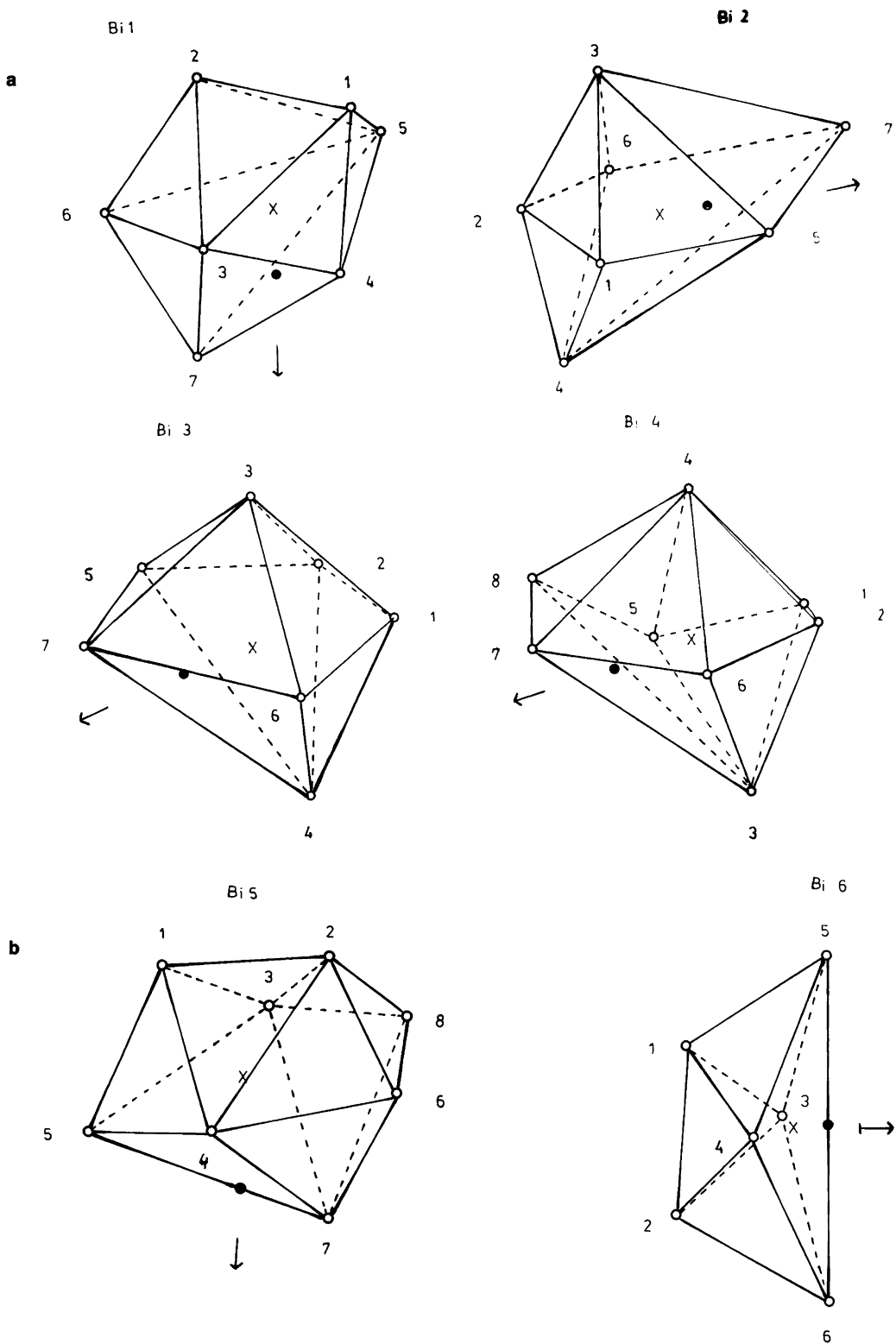
*Coordination of Bi.* Interatomic distances and angles are summarized in Table 2, in which an arbitrary limit of  $3.0 \text{ \AA}$  has been set for the Bi–O interactions. The average Bi–O distances range from  $2.40$  (6-coordination) to  $2.56 \text{ \AA}$  (8-coordination). The occurrence of short Bi–O distances ( $2.04 \text{ \AA}$ ) and also the irregular total coordination geometries for Bi (Figs. 4a and 5)

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*Fig. 4.* The close surroundings of the  $M_4$  rhombuses (a) in the present structure and (b) in  $Sb_4(OH)(SO_4)_4(H_5O_2) \cdot H_2O$  (see the text) projected along the normals to the nearly planar  $M_4$  rhombuses. Common to both drawings: The M atoms are represented by black circles and the  $M_4$  rhombuses are shown. The  $SO_4$  tetrahedra but not their individual atoms are shown and the oxo oxygen atoms are denoted by crosses. Short M–O distances are indicated by dashed lines. Dotted lines in (a) represent long Bi–O interactions. Other symbols are explained in the text.





**Fig. 5.** Clinographic ( $120^\circ$ ) representation of the coordination polyhedra of Bi in the present compound. Crosses and empty circles represent Bi and oxygen atoms, respectively. For each polyhedron the O atoms are numbered in the order in which they appear in Table 2. For the black circles and the arrows, see the text.

indicate that the inert electron pairs at Bi are stereochemically active. The stereochemical influence of such pairs can be predicted with the help of the VSEPR model discussed in some textbooks and originating from a paper by Gillespie and Nyholm in 1957. The stereochemical influence of inert pairs has also been treated by Orgel<sup>7</sup> and by other authors. Extensions of the VSEPR model have been made by Andersson, Galy and coworkers.<sup>8,9</sup> They use a hard-sphere model in which the inert electron pair is assumed to act as if it were an oxygen atom; it has a measurable distance to the central atom and occupies a volume in the crystal structures equal to that of an oxygen atom. Due to a large extent to the stimulating views put forward in Refs. 8 and 9 there has been renewed interest in the crystal chemistry of lone-pair elements, especially antimony. A common oxygen coordination of lone-pair elements is the  $\psi$ -trigonal bipyramid,  $\text{MO}_4\text{E}$ , E and  $\psi$  representing the lone pair. Fig. 3 shows an example of such a polyhedron and also explains the concept "equatorial" and "axial". The axial distances in a number of  $\psi$ -trigonal bipyramids found in crystal structures containing lone-pair elements are 1.1–1.2 times greater than the equatorial distances.<sup>10</sup> It is seen from Table 2 that the

present Bi atoms have 4–5 close oxygen neighbours at distances of less than 2.50 Å. It is also seen from Table 2 and from Fig. 4a (in part) that the Bi atoms fall into two groups, those in contact with only one oxo oxygen atom, viz. Bi(1), Bi(4) and Bi(5), and those which are bonded to two such atoms, viz. Bi(2), Bi(3) and Bi(6).

Efforts were first made to rationalize the coordination of Bi on the basis of  $\psi$ -trigonal bipyramids. For Bi(2), Bi(3) and Bi(6) it is natural to regard the oxo oxygen atoms as being equatorial and the next nearest oxygen atoms as axial. Even considering the e.s.d.'s there are gaps for these atoms between the 4th and 5th oxygen atoms. The same may be true also for Bi(4), where the oxo oxygen atom and the next nearest oxygen have been chosen as equatorial and the remaining two atoms in the close coordination sphere as axial. For the atoms Bi(1) and Bi(5) there are perceptible gaps first between the 5th and 6th oxygen atoms. Starting from the five closest neighbours, all O–Bi–O angles were calculated and the oxygen atoms forming the largest angles were regarded as being axial. The two closest atoms were then chosen as equatorial (Table 2). The angles  $\text{O}_{\text{eq}}\text{--Bi--O}_{\text{eq}}$  are given in Table 3 and are compared with corresponding angles in other

Table 3. Survey of  $\text{O}_{\text{eq}}\text{--Bi--O}_{\text{eq}}$  and  $\text{O}_{\text{ax}}\text{--Bi--O}_{\text{ax}}$  angles ( $^\circ$ ) in assumed  $\psi$ -trigonal bipyramids in the present compound, and in related bismuth and antimony compounds.

Substance	Atom	$\text{O}_{\text{eq}}\text{--M--O}_{\text{eq}}$	$\text{O}_{\text{ax}}\text{--M--O}_{\text{ax}}$	Reference
$\text{Bi}_2\text{O}(\text{SO}_4)_2$	Bi(1)	74(2)	161(2)	This work
	Bi(2)	75(2)	163(2)	
	Bi(3)	72(2)	150(2)	
	Bi(4)	70(2)	154(2)	
	Bi(5)	71(1)	162(2)	
	Bi(6)	69(1)	160(1)	
	Average	72	158	
$\alpha\text{--Bi}_2\text{O}_3$	Average	90	160	11
$\beta\text{--Bi}_2\text{O}_3$		115	172	Through 12
$\text{Bi}_{12}\text{GeO}_{20}$	Average	86	161	11, 13
$[\text{Bi}_5\text{O}_4(\text{OH})_4](\text{ClO}_4)_6 \cdot 7\text{H}_2\text{O}$		90	126	14
$[\text{Bi}_6\text{O}_5(\text{OH})_3](\text{NO}_3)_5 \cdot 3\text{H}_2\text{O}$	Average	90	124	15
$[\text{Bi}_6(\text{H}_2\text{O})(\text{NO}_3)_4(\text{OH})_4](\text{NO}_3)_5$	Average	89	127	16
$\text{Sb}_4\text{O}_2(\text{OH})(\text{SO}_4)_4(\text{H}_5\text{O}_2) \cdot \text{H}_2\text{O}$	Sb(1)	84	160	17
	Sb(4)	93	140	
28 Sb–(O,F) compounds up to the year 1976	Average	83–95	134–165	18

bismuth oxide compounds, with average values for a quite large number of antimony oxide compounds and also with angles in  $\text{Sb}_4\text{O}_2(\text{OH})(\text{SO}_4)_4(\text{H}_5\text{O}_2) \cdot \text{H}_2\text{O}$ ,<sup>17</sup> the structure of which is related to the present one (*vide infra*). The present  $\text{O}_{\text{ax}}-\text{Bi}-\text{O}_{\text{ax}}$  angles are in fair agreement with the corresponding angles in both the bismuth and antimony compounds cited in Table 3. The  $\text{O}_{\text{eq}}-\text{Bi}-\text{O}_{\text{eq}}$  angles of  $72^\circ$  are, however, small in comparison with those found in other bismuth compounds, which with one exception show values of about  $90^\circ$ . It should be noted that the  $\text{O}_{\text{eq}}$  atoms for the present Bi(2), Bi(3) and Bi(6) atoms are all oxo oxygen atoms for which a choice as equatorial atoms is natural (see above). The atoms Sb(1) and Sb(4)<sup>17</sup> correspond to Bi(1), Bi(4) and Bi(5) in the present study. No direct explanation of the small  $\text{O}_{\text{eq}}-\text{Bi}-\text{O}_{\text{eq}}$  angles can be given but some general remarks may be made. It is pointed out<sup>14</sup> that the square  $\text{Bi}_2\text{O}_2^{2+}$  groups present in many bismuth oxide compounds can be regarded as  $\psi$ -trigonal bipyramids with all angles equal to  $116^\circ$ . It also follows from the expression for the polarization energy<sup>7</sup> that because of the larger average M–O distances the influence of the lone pair in Bi may be less than it is for Sb in Sb oxide compounds. Thus, one may expect less rigid  $\psi$ -trigonal bipyramids in Bi compounds than in Sb compounds.

*Total coordination of Bi.* An effort has been made here to visualize the irregular Bi–O coordination in  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  (Figs. 4a and 5). The supposed direction of action of the stereochemically active lone electron pair has been indicated in the following way in Fig. 5: A line is drawn from the center of the edge  $\text{O}_{\text{eq}}-\text{O}_{\text{eq}}$  in each polyhedron through the respective Bi atom. A black point shows where this line intersects a polyhedral face, and an arrow shows the direction of the line. Bi(1), Bi(2) and Bi(3) are 7-coordinate and their coordination polyhedra may be described as highly distorted pentagonal bipyramids with the axial oxygen atoms (Table 2) as vertices. One way to look at these polyhedra is the following: Suppose that the Bi atoms had no lone electron pairs and that they under such circumstances were coordinated by regular pentagonal bipyramids with all equatorial angles  $72^\circ$  and all axial angles  $180^\circ$ . Introducing now an active electron pair, the atoms (3,4),5,6,7 (Fig. 5) are pushed away owing to the resulting repulsive forces but one of the

equatorial angles ( $72^\circ$ ) is retained. This line of reasoning is much the same as that put forward by Orgel<sup>7</sup> and by Brown,<sup>19</sup> but their ideal coordination figure was an octahedron instead of a regular pentagonal bipyramid. As indicated above, the observed equatorial angles of about  $70^\circ$  may be explained also in other ways. Bi(6) is 6-coordinate, but using the concepts put forward in Refs. 8 and 9 it may be described as a fairly regular  $\text{BiO}_6\text{E}$  pentagonal bipyramid with the axial oxygen atoms (Table 2) at the vertices and the lone pair situated at the tail of the arrow (Fig. 5) about  $1 \text{ \AA}$  from the Bi atom.

Bi(4) and Bi(5) are 8-coordinate and their coordination polyhedra may in turn be described as an hexagonal bipyramid with the axial (Table 2) oxygen atoms as vertices, and a dodecahedron or square antiprism with 1,2,6,4 and 3,8,7,5 (Fig. 5) as "square faces". The directions of the arrows shown in Fig. 5 are in fair agreement with the expected repulsive forces in front of (and behind) the inert pair. The Bi–O distances obtained here are in good agreement with previous measurements.<sup>11–16</sup>

*Coordination of the oxo oxygen atoms.* Table 4 shows that the oxygen atoms O(1), O(2) and O(3) in the present structure are coordinated in an almost planar fashion by three bismuth atoms. A survey of the incidence of planar or slightly pyramidal 3-coordination of oxygen atoms is given in Ref. 20 (see p. 496). One example given is that of the ion  $[\text{OFe}_2(\text{SO}_4)_6(\text{H}_2\text{O})_3]^{5-}$ . Douglade and Mercier<sup>17</sup> mention (planar) O(3)–3 Sb 3-coordination in the structure of  $\text{Sb}_4\text{O}_2(\text{OH})(\text{SO}_4)_4(\text{H}_5\text{O}_2) \cdot \text{H}_2\text{O}$  and they also point out the occurrence of similar coordination in some other antimony oxide compounds.<sup>21,22</sup> Lazarini<sup>15,16</sup> reports values for O–3Bi angles in the cuboctahedral ions  $[\text{Bi}_6\text{O}_5(\text{OH})_3]^{5+}$  and  $[\text{Bi}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})(\text{NO}_3)]^{5+}$  which indicate nearly planar coordination of the oxygen atoms. Though not explicitly stated,<sup>14</sup> the same type of coordination occurs in the related ion  $[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}$ . The ions  $[\text{Ce}_6\text{O}_4(\text{OH})_4]^{12+}$  and  $[\text{U}_6\text{O}_4(\text{OH})_4]^{12+}$ , as well as some other compounds (see Ref. 20, p. 646), have the same structure. Table 4 summarizes data for a number of Bi and Sb compounds and one Sn compound in which the oxo oxygen atoms are 3-coordinated in a nearly planar fashion. There may, of course, be many more exam-

Table 4. Planar or slightly pyramidal 3-coordination of oxo oxygen atoms in some oxide compounds of lone-pair elements. The angles are given in degrees. A limit has been set at angular sums less than 350°. The letters a–d refer to different oxygen atoms in the same unit cell.

Substance	Angles M–O–M				Range	Reference
Bi <sub>2</sub> O(SO <sub>4</sub> ) <sub>2</sub>	Bi(6)–O(1)–Bi(6')	111(2)			104–129	This work
	Bi(5)–O(1)–Bi(6')	123(2)				
	Bi(5)–O(1)–Bi(6)	126(2)				
	Bi(2)–O(2)–Bi(3)	108(2)				
	Bi(1)–O(2)–Bi(3)	123(2)				
	Bi(1)–O(2)–Bi(2)	129(2)				
	Bi(2)–O(3)–Bi(3)	104(2)				
	Bi(3)–O(3)–Bi(4)	127(2)				
	Bi(2)–O(3)–Bi(4)	129(2)				
[Bi <sub>6</sub> O <sub>5</sub> (OH) <sub>3</sub> ] <sup>5+</sup>	a	b	c	d	108–125	15
	108	109				
	120	118				
[Bi <sub>6</sub> (OH) <sub>4</sub> O <sub>4</sub> (H <sub>2</sub> O)(NO <sub>3</sub> ) <sub>3</sub> ] <sup>5+</sup>	114	112	116	114	112–121	16
	119	117	117	119		
	119	121	119	120		
Sb <sub>4</sub> O <sub>2</sub> (OH)(SO <sub>4</sub> ) <sub>4</sub> (H <sub>5</sub> O <sub>2</sub> ) · H <sub>2</sub> O	106	110			106–130	17
	126	111				
	129	130				
Sb <sub>4</sub> O <sub>4</sub> (OH) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	108	108			108–127	21
	117	120				
	127	124				
Sb <sub>4</sub> O <sub>5</sub> (OH)(ClO <sub>4</sub> ) · ½ H <sub>2</sub> O	103	100	108		100–143	22
	112	116	112			
	143	143	140			
Sb <sub>4</sub> O <sub>5</sub> Cl <sub>2</sub>	98	108			98–136	23
	125	114				
	136	134				
Sn <sub>3</sub> O(OH) <sub>2</sub> (SO <sub>4</sub> )	117				117–124	24, 25
	119					
	124					

ples. Although perhaps arguing in a circle, it can be stated that the M atoms in the present compound and in Sb<sub>4</sub>O<sub>2</sub>(OH)(SO<sub>4</sub>(H<sub>5</sub>O<sub>2</sub>) · H<sub>2</sub>O occur in isolated M<sub>4</sub> rhombuses with angles close to 60 and 120°, and that the M–M distances are such that trigonal holes occur where oxygen ions can fit. The same is true for the cuboctahedral ions or compounds,<sup>14–16,20</sup> where the octahedral faces provide the trigonal holes.

*Sulfate tetrahedra.* Table 2 shows that some of the S–O distances deviate quite considerably from

the expected value of 1.49 Å. From a statistical point of view,  $\Delta/\sigma(\Delta)$  has a value of 3 for the S(5)–O(52) distance and values of less than 2 for the rest of the distances. It is also seen from the Table that there is no obvious correlation between the S–O(i) distances and the corresponding closest Bi–O(i) distances. The probability that the present distances are all correct due to some unknown effect seems remote. It also seems unlikely that a number of the e.s.d.'s in the S–O bond lengths in Table 2 act favourably in only one direction. Thus, there is probably a

systematic error in the above distances. One possible source of error is that the space group could be  $Cc$  and not  $C2/c$ . Calculations using the programme MULTAN 80 were made at an early stage of this investigation in order to solve the structure but they failed both for space group  $Cc$  and  $C2/c$ . The intensity distribution obtained indicated centric or hypercentric symmetry. As regards the Bi atoms, these kinds of symmetry are also clear from Figs. 1 and 2. It is very probable that the heavy Bi atoms have centric symmetry, but the possibility that the light atoms have a lower symmetry has not been investigated. Another cause of the discrepancies found may be errors in the absorption corrections. It is, however, at least the author's personal opinion that such errors do not greatly affect the positional parameters but that they increase the e.s.d.'s. The high symmetry of the heavy Bi atoms has the effect that the present structure may be regarded as a superstructure with a restricted number of strong reflections among a very large number of weak or absent reflections. Of 5822 measured reflections only 1718 had  $I > 3 \sigma(I)$ . Thus, longer exposure times should have been used. One cause of the partly abnormal S—O distances may thus be diffraction errors. Errors in S—O distances and angles are more easily recognized than errors in Bi—O distances, although the latter are, of course, affected by these same errors.

*Comparisons with antimony compounds.* On the average, Sb—O distances are smaller than Bi—O distances and as mentioned above, this difference can explain the fact that the influence of the inert pair is stronger in Sb compounds than in Bi compounds. As also stated earlier here, there has been renewed interest in crystal structures of antimony oxide compounds. Geometrical properties of the  $\psi$ - $\text{SbO}_4$  trigonal bipyramid have been summarized for a large number of compounds,<sup>18</sup> and the results are shown in Table 3 and discussed above. There are a large number of published works on crystal structures of antimony compounds and the present discussion will be limited to recently published structures of antimony oxide sulfates. The structures chosen are  $\text{Sb}_6\text{O}_7(\text{SO}_4)_2$ ,<sup>18</sup>  $\text{Sb}_2\text{O}(\text{SO}_4)_2$ ,<sup>26</sup> and  $\text{Sb}_4\text{O}_2(\text{OH})(\text{SO}_4)_4(\text{H}_5\text{O}_2) \cdot \text{H}_2\text{O}$ .<sup>17</sup> All these compounds were prepared from more or less concentrated  $\text{H}_2\text{SO}_4$  and  $\text{Sb}_2\text{O}_3$ , partly at elevated temperatures.  $\text{Sb}_6\text{O}_7(\text{SO}_4)_2$  is stable in air, but the other two com-

pounds were enclosed in capillaries while the reflections were registered. In  $\text{Sb}_6\text{O}_7(\text{SO}_4)_2$ ,<sup>18</sup> space group  $Ccc2$ , the Sb atoms are (3+1)-coordinated by oxo oxygen atoms, and the author of Ref. 18 chooses to describe the antimony coordination figure as a  $\psi$ - $\text{SbO}_3$  tetrahedron. The tetrahedra share oxygen corners and edges to form infinite  $[\text{Sb}_{12}\text{O}_{14}]_n$  columns along the  $z$  axis (5.9 Å) with their centres at  $x=0$ ,  $y=0$  in the unit cells. The columns are joined by Sb— $\text{SO}_4$ —Sb bonds. The stoichiometry of  $\text{Sb}_6\text{O}_7(\text{SO}_4)_2$  is not very far from that of the Bi compound  $\text{Bi}_{14}\text{O}_{16}(\text{SO}_4)_5$ ,<sup>4</sup> but the structures differ widely since the  $[\text{Bi}_{14}\text{O}_{16}]_n$  blocks have a fluorite-related structure. The structure of the compound  $\text{Sb}_2\text{O}(\text{SO}_4)_2$ ,<sup>26</sup> space group  $P4_12_12$  or  $P4_32_12$ , is built up of discrete  $\text{Sb}_2\text{O}(\text{SO}_4)_2$  molecules held together only by van der Waals forces. The atoms of each molecule are related by a 2-fold axis passing through the oxo oxygen atom. The coordination figure for Sb is a  $\psi$ - $\text{SbO}_3$  tetrahedron. The structure of  $\text{Sb}_2\text{O}(\text{SO}_4)_2$  thus has very little in common with the present structure of  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  in which planar  $\text{Bi}_4\text{O}_8^{8+}$  groups are a characteristic feature. The hydrated compound  $\text{Sb}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 2\text{H}_2\text{O}$ , formulated  $\text{Sb}_4\text{O}_2(\text{OH})(\text{SO}_4)_4(\text{H}_5\text{O}_2) \cdot \text{H}_2\text{O}$  by the authors<sup>17</sup> has, however, a great deal in common with  $\text{Bi}_2\text{O}(\text{SO}_4)_2$ . Douglade and Mercier<sup>17</sup> discuss the planar group  $\text{Sb}_4\text{O}_2(\text{OH})$  and also the (planar) 3-coordination of the oxo oxygen atom O(3). In this connection they also point out similar cases of 3-coordination in some other Sb compounds (see above). Though there basically is nothing to add to the structure description given in,<sup>17</sup> some further use of their data is made here to facilitate comparison with the present structure. As stated,<sup>17</sup> the  $\text{Sb}_4$  rhombus is planar to within  $\pm 0.04$  Å. The angles within the rhombuses are 55, 57, 121 and 126°. The perimetric distances are 3.35, 3.56, 3.78 and 3.80 Å, and the shortest distance between different rhombuses is 4.58 Å. The structure of  $\text{Sb}_4\text{O}_2(\text{OH})(\text{SO}_4)_4(\text{H}_5\text{O}_2) \cdot \text{H}_2\text{O}$  is compared to the present one in Figs. 4a and 4b. Fig. 4a has already been discussed. Fig. 4b was constructed in the following way: The coordinates from<sup>17</sup> were recalculated to Å with unchanged axial directions and the matrix

$$\begin{pmatrix} 0.8606 & 0.2210 & -0.4589 \\ 0 & 0.9010 & 0.4339 \\ 0.5094 & -0.3734 & 0.7753 \end{pmatrix}$$

was used in order to render the  $Sb_4$  rhombus approximately parallel to the new  $YZ$  plane. The atoms are numbered as in Ref. 17 and the  $X$  values ( $\text{\AA}$ ) for the Sb and S atoms are given in parentheses. The  $Sb_4O_4(OH)$  and  $O(H_2O)$  atoms have  $X$  close to zero.  $O(OH)$  and  $O(H_2O)$  are denoted by empty single and double circles, respectively. Only part of the unit cell is shown. A corresponding part of the present structure is shown as an  $x, y$  projection in Fig. 4a. Figs. 4a and 4b are drawn to the same scale and reveal a striking similarity between the  $Bi_4O(2)O(3)$  groups and the  $Sb_4O(1)O(3)$  groups. The similarity can also be extended to the corresponding  $Sb_4O(1)O(2)O(3)$  and  $Bi_4O(2)O(3)O(53)$  groups if it is remembered that the  $y$  value for  $O(53)$ , Version 5, in the present structure is about 0.5. The short  $O(2)-O(3)$  distance of 2.41  $\text{\AA}$  discussed in Ref. 17 has its counterpart in the  $O(2)-O(53)$  distance, Version 5 (Table 2). Differences between the two structures are that the present  $Bi_4$  rhombuses are linked vertically by means of the adjacent  $SO_4$  tetrahedra (Figs. 1, 3 and 4a) and that such linking is absent in  $Sb_4O_2(OH)(SO_4)_4(H_2O)_2 \cdot H_2O$ . An  $x, z$  projection<sup>17</sup> shows the linking between different  $Sb_4$  rhombuses. The coordination polyhedra of the Sb atoms and the locations of the different lone pairs have been discussed at some length in Ref. 17; the close coordination of the corresponding Bi and Sb atoms is compared in Table 3.  $Sb(2)$  and  $Sb(3)$  in  $Sb_4O_2(OH)(SO_4)_4(H_2O)_2 \cdot H_2O$  form a double octahedron, and this fairly regular polyhedron contrasts with the irregular coordination of  $Bi(1)-Bi(5)$ , shown here in Fig. 5.

*Comparison with rare earth compounds.* Old textbooks state that  $2Bi(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$  is isotypic with the corresponding Ce, La, Nd, Pr, Sm, Eu, Gd and Tb compounds, and that this property has been used by Urbain to separate the above rare earth elements. Other examples of the similarity of Bi and Ln (Ln = lanthanide) compounds are provided by the oxide halides  $LnOX$  ( $X = Cl, Br, I$ ), which are isotypic with  $BiOX$ , and by one modification of  $BiPO_4$  which has the monazite-type structure. The similarity of  $\gamma$ - and  $\beta$ - $BiTaO_4$  with  $LaTaO_4$  has been pointed out by Sleight and Jones<sup>27</sup> in connection with their interest in ferroelastic transitions. From comparisons of some cell volumes these authors concluded that  $Bi^{3+}$  and  $La^{3+}$  have very similar sizes.

A somewhat more comprehensive list is given in Ref. 28 (see p. 50). Sleight and Jones<sup>27</sup> also ascribe the gamma to beta transition in  $BiTaO_4$  (not present in  $LaTaO_4$ ) to the presence of lone electron pairs at the Bi atoms.

Some further examples of lone-pair influences may be mentioned here: Rare earth atoms can replace Bi atoms in the perovskite  $Bi(1)$  positions in  $Bi_4Ti_3O_{12}$ . A substitution involving only 1–2 % of Ln atoms destroys the polarization along  $c$  in this ferroelectric compound.<sup>29</sup> The authors propose that this is due to changes in the interactions between lone pairs belonging to different  $Bi(1)$  atoms. The related structures of  $NdBi_5O_8Br_2$  and  $Bi_3O_4Br$ <sup>30</sup> provide an additional example of how the presence of small amounts of rare earth elements eliminates the influence of the Bi lone electron pairs.

Turning now to the oxide sulfates of Bi and rare earth elements, there has been extensive thermochemical work on hydrated  $Ln_2(SO_4)_3$ .<sup>31,32</sup> Hitherto, only two types of oxide sulfates have been found in this thermochemical work, viz.  $Ln_2O(SO_4)_2$  and  $Ln_2O_2SO_4$ . Compounds with  $Ln_2O_3/SO_3$  ratios  $>1$  do not seem to occur. Thermochemical work on the decomposition of  $Bi_2(SO_4)_3$ <sup>1,2</sup> has identified the compounds  $Bi_2O(SO_4)_2$  and  $Bi_2O_2SO_4$ , and also some phases with  $Bi_2O_3/SO_3$  ratios  $>1$ .<sup>1,2,3</sup> A crystallographic study of one of the latter phases has been made.<sup>4</sup> The structural relationships between  $Bi_2O_2SO_4$  and  $La_2O_2SO_4$  have been discussed in Ref. 4. Up to 1981<sup>32</sup> only one lanthanide compound of composition  $Ln_2O(SO_4)_2$  was known with certainty, namely  $Nd_2O(SO_4)_2$ .<sup>33</sup>  $Nd_2O(SO_4)_2$  has been characterized in various ways; X-ray powder diffraction data are also given. Spacings ( $\text{\AA}$ ) and relative intensities have been published for 8 lines from 3.01  $\text{\AA}$  down to 1.287  $\text{\AA}$ . Comparisons with the powder photographs for the  $Bi_2O(SO_4)_2$  phase<sup>1,2</sup> discussed above and for the present  $Bi_2O(SO_4)_2$  phase are thereby possible. The photographs of the present phases are crowded with lines from 6.1 and 6.6  $\text{\AA}$ , respectively, and downwards; it therefore does not seem probable that  $Nd_2O(SO_4)_2$  is isotypic with any of the present compounds.

It is seen from Table 2 that the average Bi–O distances vary from 2.40 to 2.56  $\text{\AA}$  for 6- to 8-coordination. For comparison with rare earth sulfates the present author has preferred anhydrous compounds, and numerous structures have been

solved for double sulfates of rare earth elements and  $\text{NH}_4^+$  or alkali metals which do not contain water.  $\text{NH}_4\text{La}(\text{SO}_4)_2$ <sup>34</sup> is taken as an example here. The  $\text{La}^{3+}$  ion is surrounded by 7 oxygen atoms at close distances which form a fairly regular monocapped trigonal prism. There are two more distant oxygen atoms at 2.901 Å. The range of distances in the close 7-coordination of La is 2.420–2.557 Å and thus falls in the same range as the  $\text{Bi}^{3+}$ –O distances in the present compound. Though very irregular  $\text{La}^{3+}$ –O polyhedra may occur in lanthanum oxide compounds, the coordination is on average more regular than in bismuth compounds.

### Summary

The crystal structure of  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  contains discrete, nearly planar  $\text{Bi}_4$  rhombuses with angles close to 60 and 120°. The oxo oxygen atoms are situated at the trigonal holes of these rhombuses, and formal  $\text{Bi}_4\text{O}_2^{8+}$  ions may be visualized. Strictly speaking, the structure consists of a three-dimensional network in which infinite layers of composition  $[\text{Bi}_4\text{O}_2(\text{SO}_4)_4]_n$  with strong internal bonds extend parallel to the crystal plane  $\bar{2}01$  and are joined by somewhat weaker  $\text{Bi}$ – $\text{SO}_4$ – $\text{Bi}$  bonds. The present structure has no relationship to that of the compound  $\text{Sb}_2\text{O}(\text{SO}_4)_2$ , which is built up of discrete monomeric molecules. Powder photographs indicate that  $\text{Bi}_2\text{O}(\text{SO}_4)_2$  is not isotypic with  $\text{Nd}_2\text{O}(\text{SO}_4)_2$ . The present structure is, however, very closely related to the structure of  $\text{Sb}_4\text{O}_2(\text{OH})(\text{SO}_4)_4(\text{H}_5\text{O}_2) \cdot \text{H}_2\text{O}$ , which has discrete planar  $\text{Sb}_4$  rhombuses with oxo oxygen atoms at their trigonal holes as in the present compound. Similar three-coordination of oxo oxygen atoms is also present in cuboctahedral ions or compounds such as  $[\text{Bi}_6\text{O}_4(\text{OH})_4]^{6+}$ ,  $[\text{Ce}_6\text{O}_4(\text{OH})_4]^{12+}$  and  $[\text{U}_6\text{O}_4(\text{OH})_4]^{12+}$ , where the  $\text{O}^{2-}$  ions fit into the trigonal holes provided by the faces of the metal-ion octahedra. Nearly planar three-coordination of  $\text{O}^{2-}$  also occurs in many oxo complexes of lone-pair elements. The close coordination of the present Bi atoms may be described by  $\psi$ – $\text{BiO}_4$  trigonal bipyramids, but the  $\text{O}_{\text{eq}}$ – $\text{Bi}$ – $\text{O}_{\text{eq}}$  angles of 72° found here differ from the angles of about 90° found for most other  $\psi$ -trigonal bipyramids in Bi and Sb compounds. The total coordination of the Bi atoms is irregular. Three of the six Bi atoms present in the asymmetric part of the unit cell have coordina-

tion polyhedra which may be described as pentagonal bipyramids. The average Bi–O distances, 2.40–2.56 Å, are normal and in the same range as for  $\text{Nd}^{3+}$  and  $\text{La}^{3+}$ .

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