Crystal Structure of $[Bi_{13\frac{1}{3}}\square_{\frac{2}{3}}Cu_2O_{16}](SO_4)_6$

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The aim of the present investigation has been to study how copper(II) is included in a bismuth oxide moeity. The title compound was synthesized and its crystal structure solved. The green crystals are orthorhombic with a = 20.550(3), b = 5.4364(11) and c = 7.4851(11) Å. The space group is *Pmmn* and Z = 1. R is 0.040 for the 875 reflections of the best data set registered. The main result is that copper(II) is included in a square endless Me_2O_2 layer which though pleated is similar to the $Pb_2F_2^{2+}$ layers in PbFCl and thus also to the $Bi_2O_2^{2+}$ layers in many bismuth oxide compounds. Similar pleated Me_2O_2 layers exist also in the previously known structure of $[Bi_2CoO_3]SO_4$. The Cu atoms of the present structure are coordinated to four *oxo* oxygen atoms at 1.95(1) Å and are situated 0.34(1) Å outside the square plane of the O atoms. The next nearest Cu–O distance is 2.87(3) Å to a sulphate oxygen atom. The SO_4 groups of the present compound are disordered in contrast to those of $[Bi_2CoO_3]SO_4$. Some positions of the sulphate oxygen atoms given here are only tentative.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

It has earlier been found that CuO reacts with BiOCl to form a mixed copper(I) bismuth oxide chloride in which Cu(I) does not participate in the Bi,O moeity.[1] It is also known[2] that $CoSO_4$ and Bi_2O_3 react to give $[Bi_2CoO_3]SO_4$. In the corresponding structure the $[Bi_2CoO_3]$ parts (or written in another way the Me_2O_2 parts) form slightly pleated walls which extend infinitely close to the *bc* plane. The SO_4 groups are ordered and situated between these walls (cf. Fig. 2 later). The present investigation was started to study possible reactions between CuO and $Bi_2O(SO_4)_2$.

Experimental

$[Bi_{13\frac{1}{3}}\square_{\frac{2}{3}}Cu_2O_{16}](SO_4)_6$ has formula weight 3746 and space group *Pmmn*. Cell dimensions are a = 20.550(3), b = 5.4364(11), c = 7.4851(11) Å and V = 836.2(3) Å^3 with Z = 1. D_x = 7.44 g cm^{-3}, D_m was not measured, μ(Mo $K\alpha$) = 683 and μ(Cu $K\alpha$) = 1391 cm^{-1}. CuO and $Bi_2O(SO_4)_2$ were mixed in the molar ratio 1:1 and heated for 80 min at 720 °C in an evacuated Pyrex glass tube.[3] The solidified green melt consisted of quadratic or nearly circular crystal needles and a main bulk that was also green. The latter was glassy and gave no lines in the powder photographs. Some single crystals were picked out, and Weissenberg and powder photographs could be interpreted in terms of the unit cells and space group given above. When the same synthesis was repeated at 480 °C and the heating time was increased to 23 h green crystalline needles also resulted; however, they were monoclinic with a = 29.475(5), b = 5.3382(13), c = 11.9106(25) Å and β = 91.80(2)°. No further measurements were made on these crystals. An orthorhombic crystal was mounted in a Nicolet *P3m* diffractometer using Mo $K\alpha$ radiation. The diffractometer was set up to register all reflections up to 2Θ = 80°, but it broke down because of a power failure after 1456 reflections had been measured, which corresponded to all reflections in the layers $0kl$–$11kl$ and a few in the $12kl$ layer. In this way 875 independent reflections with $I > 3\sigma(I)$ were measured. A new orthorhombic crystal (2) was then mounted in another diffractometer which was not quite in order. 1339 independent reflections with $I > 3\sigma(I)$ were measured up to 2Θ = 80° using Mo $K\alpha$ radiation. To see if there were any grave errors in the diffractometer measurements crystal (2) was remounted in a non-integrating Weissenberg camera and the layers $h0l$–$h4l$ were registered with Cu $K\alpha$ radiation. The intensities of 608 independent reflections were estimated visually using a calibrated scale.

Structure determination and refinement

The only systematic extinctions found for the various data sets were $hk0$ absent for $h+k = 2n+1$ (cf. Table 4 later). The assumed extinction is characteristic of the space groups *Pmmn* (No. 59) and $Pmn2_1$ in its non-standard settings $P2_1mn$ and $Pm2_1n$. The various computer programs used originate from Ref. 4. The Nicolet data and the centric space group were first used. The heavy-atom positions were deduced from a three-dimensional Patterson function and those of the light atoms from electron density maps. The final result is given in Table 1. The data were corrected for absorption and extinction. Among the heavy atoms the position of Bi(3) was anomalous. Its four-fold site was not fully occupied and, moreover, difference electron maps showed the site to be split into two sites, denoted (*a*) and

Table 1. Final positional and thermal parameters for the present compound based on the Nicolet data and space group *Pmmn*. B_{eq} is calculated as $8\pi^2/3\ \Sigma(\text{r.m.s.})^2$.

Atom	*x*	*y*	*z*	No. of atoms	Site in *Pmmn*	B_{eq} and B^a
Bi(1)	0.14736(7)	1/4	0.00150(1)	4	4*f*	1.40(4)
Bi(2)	−0.02297(7)	1/4	0.14754(10)	4	4*f*	1.69(4)
Bi(3)	0.60098(28)	1/4	0.7033(4)	3.31(3)	4*f*	3.1(2)
Bi(4)	1/4	1/4	0.40319(14)	2	2*a*	1.51(5)
Cu	1/4	3/4	0.1777(5)	2	2*b*	0.9(1)
S(4)	0.0828(6)	1/4	0.5715(8)	4	4*f*	1.8(3)
S(5)	0.7743(9)	1/4	0.2308(13)	2	4*f*	2.7(15)

O(1)	0.0617(7)	−0.0027(19)	0.0704(12)	8	8*g*	1.1(2)
O(2)	0.1843(7)	0.0011(20)	0.2236(13)	8	8*g*	1.5(2)
O(41)	0.4603(14)	1/4	0.7271(26)	4	4*f*	2.7(4)
O(42)	0.4505(25)	1/4	0.408(5)	2	4*f*	2.1(7)
O(42A)	0.354(4)	1/4	0.596(6)	2	4*f*	3.2(9)
O(43)	0.1184(19)	0.021(6)	0.605(4)	4	8*g*	3.2(6)
O(43A)	0.0597(27)	0.055(11)	0.454(6)	4	8*g*	7.8(13)
O(51)	0.7654(29)	1/4	0.429(4)	2	4*f*	2.5(7)
O(52)	3/4	0.002(7)	0.161(4)	4	4*e*	6.7(8)
O(53)	0.658(4)	1/4	0.168(8)	2	4*f*	5.2(13)

[a]Values above the dashed line are $B_{eq}/\text{Å}^2$, while those below are $B/\text{Å}^2$.

(*b*), containing 2.98 atoms and 0.27 atoms, respectively. The distance (*a*)–(*b*) was 0.8 Å. To overcome this splitting not only β-tensors (anisotropic temperature factors) but also γ- and δ-tensors were, according to Gram-Charlier, introduced for the Bi(3) atoms. This was made possible through an option in the program Upals. Al non-zero γ- and δ-tensors had higher numerical values than their corresponding e.s.d.s. R_w dropped from 0.050 to 0.048, and the

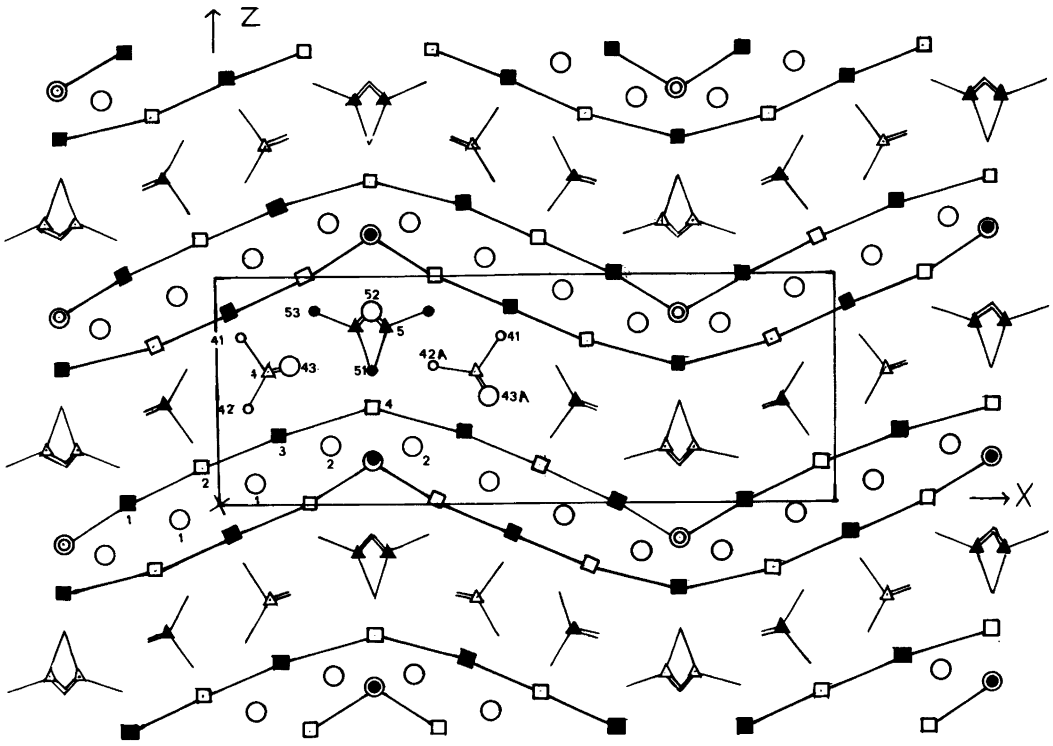

Fig. 1. Projection of the present structure on the *xz*-plane. One unit cell is outlined. Empty and filled squares, double circles, triangles and small circles indicate Bi, Cu, S and O(SO_4) atoms at $y = \frac{1}{4}$ and $y = \frac{3}{4}$, respectively. The *oxo* oxygen atoms O(1) and O(2), $y \approx 0, \frac{1}{2}$, are denoted by large empty circles, as are the O(SO_4) atoms 43,43A and 52. For the numbers, the lines joining the *Me* atoms and for the SO_4 groups in general, see the text. The splitting of O(51) is not shown.

difference map did not show any splitting of the Bi(3) site. The final R factors for the 875 Nicolet reflections were $R = 0.040$ and $R_w = 0.048$. S was 1.5113. Fig. 1 shows a projection of the structure on the *ac*-plane. It is seen from Table 1 that one bismuth site, one sulfur site and six oxygen sites are partially occupied. The isotropic temperature factors of the atoms O(43A) and O(52) are high. Therefore data with $h > 12$ were also investigated using crystal (2), since the first crystal was lost. The 608 Weissenberg data were corrected for absorption assuming the crystal to be a cylinder with the *b*-axis parallel to the cylinder axis. The result of the calculations was about the same as for the Nicolet data. Because of the limited number of relections the Bi(3) atom was considered as two atoms. Probably owing to the fact that k(max) was only 4, the B values for the half-occupied sites with $y \neq \frac{1}{4}$ were high and their positions uncertain. The *y*-parameter of O(43A) had to be fixed, and the distance S(5)–2O(52) was exceptionally low [1.30(11) Å,

Table 2. Selected distances (in Å) *Me–Me* and *Me*–O as obtained from the Nicolet data, present satructure. Selected distances and angles (°) within the SO_4 groups as obtained from Nicolet data (N), crystal (2) diffractometer data (D) and Weissenberg data W. Short distances obtained from N and D data are also given.

Me–Me distances < 3.90		*Me*–O distances < 3.20		*Me*–O distances < 3.20	
Bi(1)–2Bi(3)	3.631(3)	Bi(1)–2O(2)	2.27(1)	Bi(3)–2O(43A)	2.20(6)
Bi(1)–Bi(2)	3.667(2)	Bi(1)–2O(1)	2.29(1)	Bi(3)–2O(2)	2.26(1)
Bi(1)–Bi(4)	3.673(1)	Bi(1)–2O(52)	2.79(2)	Bi(3)–2O(1)	2.31(1)
Bi(1)–2Cu	3.685(2)	Bi(1)–2O(53)	3.01(3)	Bi(3)–2O(43)	2.76(3)
Bi(1)–2Bi(2)	3.895(1)	Bi(1)–O(41)	3.02(3)	Bi(3)–O(41)	2.90(3)
Bi(2)–2Bi(2)′	3.628(1)	Bi(1)–O(42A)	3.04(4)	Bi(3)–2O(42)	3.03(2)
Bi(2)–Bi(3)	3.692(4)	Bi(2)–2O(1)	2.26(1)	Bi(4)–4O(2)	2.34(1)
Bi(2)–2Bi(3)	3.889(4)	Bi(2)–2O(1)′	2.29(1)	Bi(4)–2O(42A)	2.57(8)
Bi(3)–Cu	3.189(6)	Bi(2)–O(42)	2.45(4)	Bi(4)–2O(51)	3.01(1)
Bi(4)–2Cu	3.200(2)	Bi(2)–O(53)	2.77(8)	Cu–4O(2)	1.95(1)
		Bi(2)–2O(41)	2.90(1)	Cu–2O(52)	2.87(3)
		Bi(2)–2O(43A)	3.04(5)	Cu–2O(51)	2.91(3)
		Bi(2)–2O(43)	3.07(3)		

Distances and angles within the SO_4 groups

Distances	N	D	W
S(4)–O(41)	1.46(3)	1.45(6)	1.45(6)
S(4)–O(42)	1.40(4)	1.44(14)	1.43(9)
S(4)–2O(43)	1.47(3)	1.44(6)	1.43(12)
S(4)–O(41)	1.46(3)	1.45(6)	1.45(6)
S(4)–O(42A)	1.31(9)	1.49(9)	1.36(11)
S(4)–2O(43A)	1.46(6)	1.64(12)	[1.55(10)]
S(5)–O(51)	1.49(3)	1.39(8)	1.39(8)
S(5)–O(53)	1.48(8)	1.48(6)	1.55(9)
S(5)–2O(52)	1.53(3)	1.47(8)	1.30(11)
Angles			
O(41)–S(4)–O(42)	114(2)	120(6)	122(4)
O(41)–S(4)–2O(43)	99(1)	99(3)	99(5)
O(42)–S(4)–2O(43)	113(1)	118(4)	111(5)
O(43)–S(4)–O(43)′	116(3)	99(5)	116(9)
O(41)–S(4)–O(42A)	119(2)	121(4)	118(5)
O(41)–S(4)–2O(43A)	107(2)	111(4)	[113(5)]
O(42A)–S(4)–2O(43A)	114(3)	97(4)	[108(6)]
O(43A)–S(4)–O(43A)′	93(4)	118(8)	[95(8)]
O(51)–S(5)–O(53)	116(4)	114(4)	114(5)
O(51)–S(5)–2O(52)	107(2)	105(4)	108(5)
O(53)–S(5)–2O(52)	102(1)	104(2)	104(3)
O(52)–S(5)–O(52)	123(2)	125(6)	119(8)

Short distances	N	D
Bi(3)–2O(43A)	2.20(6)	1.88(11)
O(53)–2O(43)	2.39(6)	2.39(7)

Table 2]. The final R-values for the 608 Weissenberg reflections were $R = 0.083$ and $R_w = 0.100$; S was 1.5212. The results for the crystal (2) diffractometer data were about the same as for the Weissenberg and Nicolet data. It was difficult to localize the O(43A) atoms, and in some treatments of the data it was impossible.

Other ways of describing the disorder of the $S(4)O_4$ tetrahedron failed. For a data set that had not been corrected for absorption the least-squares calculations did, however, converge, with B[O(43A)] = 5.6 Å^2. The Bi(3) and Bi(4) atoms were treated as Bi(3) in the Nicolet data refinement. Most of the γ- and δ-coerfficients were numerically less than their e.s.d.s, showing that nothing was gained by giving Bi(4) anharmonic thermal motions. The final R_1 was 0.086 for 1329 reflections, $R_w = 0.113$ and $S = 1.6245$. R_2 for all 1339 reflections was 0.089. Selected distances and angles for the crystal (2) calculations are given in Table 2 together with those of crystal (1). To sum up, the crystal (2) data led to the same structure as the crystal (1) data, but the e.s.d.s were much higher (Table 2). It has been mentioned that the structure finally arrived at with space group *Pmmn* is disordered. The non-centric space groups are $P2_1mn$ and $Pm2_1n$. $Pm2_1n$ was ruled out, but the refinements could proceed with space group $P2_1mn$. Two versions were found possible: they differ with respect to the two SO_4 tetrahedra, which correspond to the two orientations of the $S(4)O_4$ tetrahedron given in Table 1. Their R factors differ very little. The highest were $R_1 = 0.083$ $R_w = 0.106$ and $S = 1.5232$ for 1330 reflections. $R_2 = 0.085$ for all 1339 reflections. The O(43A) atoms were still difficult to localize, their B-values were 4.0–4.6 Å^2. The O(52) atoms also had $B > 4$ Å^2. Some of the S–O distances were even worse than in the centric case given in Table 2. Although the values of R and R_w are lower for the acentric case than for the centric one, the present author prefers the centric solution. There seems to be no reason for the structure to be acentric, (Fig. 1) and the distances and angles within the SO_4 groups did not improve in the acentric treatment. Lists of $|F_o|$ and $|F_c|$ for the two diffractometer data sets areavailable on request.

Description and discussion of the structure

Sulphate tetrahedra. Table 2 shows the distances and angles within the sulphate tetrahedra as obtained from the centric treatments of the three data sets. h(max) for the Nicolet data was 12 and k(max) for the Weissenberg data was 4. The y-parameter of O(43A) (Table 2) had to be fixed in the refinements of the Weissenberg data. The e.s.d.s of the distances and angles are high. A difference between crystal (1) and crystal (2) with respect to the orientation of their SO_4 groups can not be altogether excluded. The single crystals originated from a melt for which the main bulk showed no lines in the powder photographs.

A disorder of the structure and especially of its sulphate groups is therefore conceivable. Table 2 shows two orientations of the $S(4)O_4$ tetrahedron. Considering the high e.s.d.s, the ones comprising the O(41–43) atoms give fairly reasonable distances and angles for all three data sets, whereas the opposite is true for the tetrahedron comprising the "A" atoms. The calculations were performed assuming the site of O(41) to be fully occupied and the rest of the O(4*i*) sites being only half-occupied. Calculations omitting the "A" sites and assuming a full occupation of the (42) and (43) sites failed. The distances and angles for the S(5) tetrahedra are fairly normal for the diffractometer data only. The atoms O(53) could be pushed out from $y = \frac{1}{4}$ in the Nicolet data refinements with somewhat better figures of merit. In Fig. 1 small numbers are attached to the atoms in the vicinity of one Cu atom. They correspond for each atomic species to the numbers given in Table 1. One pair of disordered S(5) tetrahedra is fully outlined, and one S(4)[O (41–43)] tetrahedron and one S(4)[O(41–42A–43A)] tetrahedron are also shown with numbered atoms. The rest of the S(5) tetrahedra are only indicated, as are the S(4)[O (41–43)] tetrahedra.

To sum up, the SO_4 tetrahedra of the present structure are disordered and the second orientation of the $S(4)O_4$ tetrahedron given here is only tentative. For the remaining tetrahedra the e.s.d.s are high, but the distances and angles are fairly normal for the diffractometer data.

Metal atoms. With the exception of the Bi(3) atom and the sulphate oxygen atoms O(42*i*) and O(43*i*) the least-squares refinements of all other atoms proceeded in a quite normal way and led to nearly identical sites for all data sets. The cell content of the present compound has been given as $[Bi_{13\frac{1}{3}}\square_{\frac{2}{3}}Cu_2O_{16}](SO_4)_6$, $Z = 1$. Table 1 shows the atomic parameters as obtained from the Nicolet data. It is seen that all metal sites except that of Bi(3) are fully occupied. The same is true for the other data sets and also for the acentric refinements. Table 3 summarizes the number of atoms at the Bi(3) site (corresponding) for the various data sets, while Table 4 shows weak $hk0$ reflections with $h+k = 2n+1$. All numbers are smaller than the expected one, $3\frac{1}{3}$, but deviate by 3σ at most from the assumed value. The *Me–Me* and *Me*–O distances (Nicolet data) are summarized in Table 2. The Bi–Bi distances are normal for a Me_2O_2 layer with Bi as the main *Me* component, but some of the Bi–Cu distances are quite short and may be due to the fact that the normal Cu(II)–O distances are shorter than the normal Bi–4O distances. The Bi–O_{oxo} [O(1),O(2)] dis-

Table 3. Number of atoms at the Bi(3) site of the present structure as found from different refinements.

Space group	Data	Number of atoms[a]
Pmmn	N	3.31(3)
Pmmn	D	3.19(6)
Pmmn	W	3.21(12)
$P2_1mn$ (i)	D	3.08(10)
$P2_1mn$ (ii)	D	3.09(10)

[a]Theoretical value $3\frac{1}{3}$.

Table 4. Weak *hk*0 reflections with $h+k=2n+1$ in the data sets N, D and W. The total number of *hk*0 reflections for N, D and W are in turn 43,108 and 49.

hkl	N	D	W
010	+	+	[a]
210	–	+	–
430	–	+	–
900	–	+	–
940	–	–	+
1030	–	+	–
1320		+	–
2030		+	–
2940		+	
3500		+	

[a]Not measured.

tances are normal for a Me_2O_2 layer, as are the Cu–O_{oxo} distances for a nearly coplanar four-coordination. The position of O(43A) (see above) is uncertain, and the distance Bi(3)–2O(43A) is short (Table 2). The situation is worse for the other data sets (see the columns headed Short distances in Table 2). For a number of $(BiO)_nX_m$ compounds each Bi atom is at the apex of a flat square pyramid, the O atoms forming the basis plane. This close four-coordination is often completed by a varying number of next-nearest neighbours. In the present compound these conditions are rigidly fulfilled for the Bi(1), Bi(2) and Bi(4) atoms and their coordination will not be further discussed. If the uncertain sites of the atoms O(43A) are included in the close coordination sphere of Bi(3), a fairly regular trigonal prism will result (Fig. 1). The Cu atoms have a close coordination of four oxygen atoms at the normal distance 1.95(1) Å. They are situated 0.34(1) Å outside the square plane of the O atoms. The next-nearest oxygen neighbours to Cu are 2C(52) atoms at 2.87(3) Å. Including these atoms the coordination polyhedron of Cu will be a trigonal prism (Fig. 1). Table 2 also includes some short obtained from the diffractometer data (centric treatments). Corresponding short distances, not given here, exist also for the other treatments. The sites of O(43), O(43A) and O(53) are only half-occupied.

Architecture and comparison with other structures

Taking the unit cells' content and the crystal structure into account, the composition of the present compound may be written $[MeO]_{(8/3)}SO_4$. In the same way the compounds

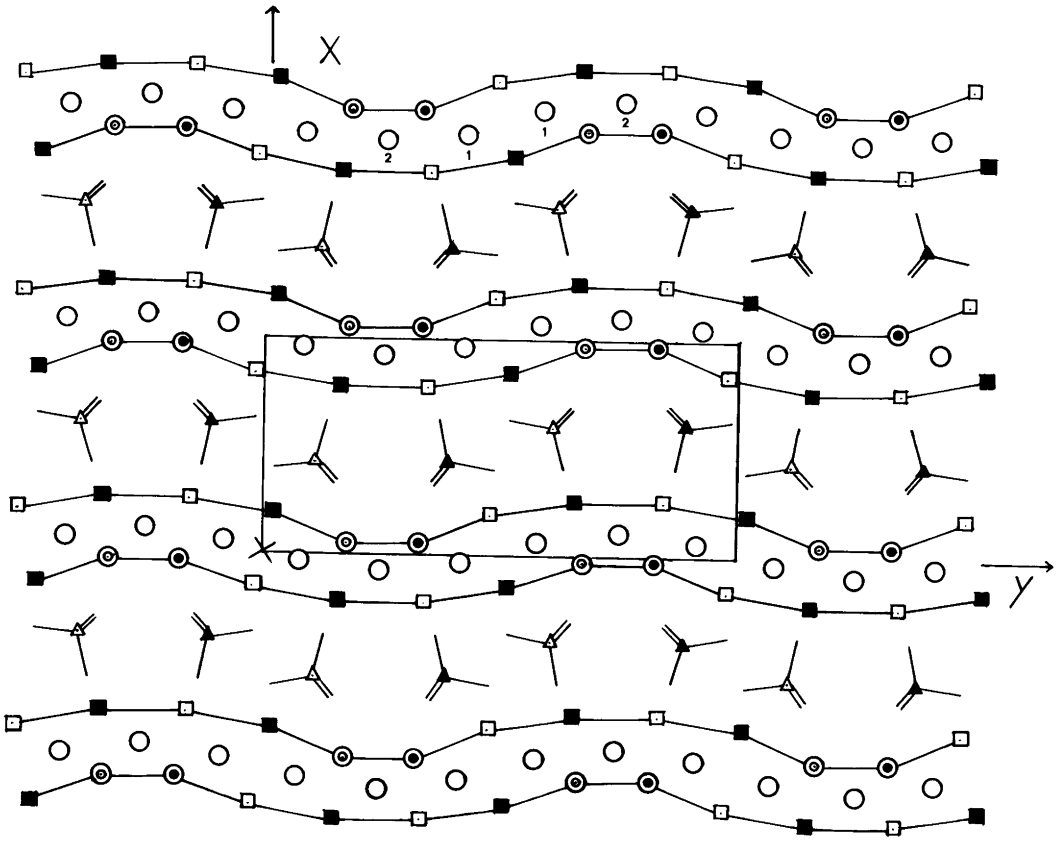

Fig. 2. Projection of the structure of $Bi_2CoO_3SO_4$, according to data in Ref. 2, on its *xy*-plane. One unit cell is outlined. Empty and filled squares, double circles and triangles indicate Bi, Co and S atoms at $z = \frac{1}{4}$ and $z = \frac{3}{4}$, respectively. Large empty circles denote *oxo* oxygen atoms, O(2) and O(1), at or close to $z = 0, \frac{1}{2}$. The sulfate groups but not their oxygen atoms are marked out. For the lines joining the *Me* atoms, see the text.

$Bi_2CoO_3SO_4$,[2] $LiBi_3O_4Cl_2$[5] and $SrBi_3O_4Cl_3$[5] may be written $[MeO]_3SO_4$, $[MeO]_2Cl$ and $[MeO]_{(4/3)}Cl$, respectively. They are all built up from square *Me*O layers interleaved with anionic layers such as PbFCl with its $Pb_2F_2^{2+}$ layers interleaved with (double) Cl^- layers. When Bi is replaced by Co(II) (Fig. 2) or Cu(II) (Fig. 1), some deformations take place and the layers become pleated. To indicate the *Me*O layers the *Me* atoms on each side of the *oxo* oxygen atoms ¦O(2)–O(1)–O(1)–O(2)¦ square pleated layers are joined by solid lines in Fig. 1. The *Me* atoms in Fig. 2 on each side of the similarly pleated layers O(2)–O(1)–O(1)–(2) (cf. Ref. 2) are also joined by solid lines. For the ideal case with no pleating see Fig. 20.8(a) in Ref. 5, p. 898. In the special case of the present compound the tendency of Cu(II) to form four coplanar bonds to oxygen moves the Cu atoms towards the square O(2) layer and thereby shortens the Cu–2Bi(1) and Cu–Bi(4) distances (Fig. 1 and Table 1).

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