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The structure of $Cu_4Bi_4S_9$ and its relation to the structures of covellite, CuS and bismuthinite, Bi_2S_3

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Auszug

$Cu_4Bi_4S_9$ hat die Raumgruppe *Pbnm*; die Gitterkonstanten sind $a = 11{,}589(5)$, $b = 32{,}05(1)$, $c = 3{,}951(5)$ Å; $Z = 4$. Die nach dem Verfahren der symbolischen Addition bestimmte Struktur weist, wie nach der Valenzregel zu erwarten war, S_2-Gruppen mit einem (S-S)-Abstand von 2,10(2) Å auf. Die Struktur kann als Folge sich parallel (010) abwechselnder Cu-S- und Bi-S-Schichten beschrieben werden. Die Cu-S-Schichten sind stark gewellt; sie bestehen aus kurzen Ketten von Cu-Atomen, die von je vier- oder drei S-Atomen, ähnlich wie in der Covellinstruktur, umgeben sind. Diese Ketten sind tatsächlich durch (S—S)-Bindungen verknüpft. Die dreifach-koordinierten Cu-Atome liegen nicht in der Ebene der sie umgebenden drei S-Atome, sondern sind um 0,48(1) Å aus der Ebene herausgerückt. Der mittlere (Cu—S)-Abstand ist 2,25 Å. Die Bi-S-Schichten bestehen aus Bi-S-Polyedern, die denen in der Struktur des Wismutglanzes ähnlich sind. Die Struktur von $Cu_4Bi_4S_9$ ist ein neues Beispiel für Strukturen von Sulfosalzen, die sich aus Teilstücken zweier einfacherer Sulfidstrukturen zusammensetzen.

Abstract

The orthorhombic unit cell of $Cu_4Bi_4S_9$ crystals has dimensions: $a = 11.589(5)$, $b = 32.05(1)$, $c = 3.951(5)$ Å; space group *Pbnm*, and $Z = 4$. The structure, which has been determined with the symbolic addition procedure, contains, sulfur-sulfur bonds in a form of S_2 groups, as predicted from the valence rule with S—S distance of 2.095(17) Å. The structure can be described as an alternate stacking of Cu-S sheets and Bi-S slabs, parallel to (010). The Cu-S sheet is highly corrugated and built of links of four- and three-coordinated copper atoms which are closely related to those in the covellite structure. The links are, in fact, joined together by S—S bonds. The three-coordinated copper atom is not in the plane formed by three sulfur atoms but displaced from the plane by 0.48(1) Å; mean Cu—S distance is 2.25 Å. The Bi-S slabs consist of links of Bi-S polyhedra which are, in turn, closely related to those of the bismuthinite structure. The above feature of the structure thus offers a new example of sulfosalt structure which consists of fragments of two different kinds of simpler sulfide structures.

Introduction

The new crystalline phase $Cu_3Bi_3S_7$ (Sugaki and Shima, 1971), (which is actually $Cu_4Bi_4S_9$, as will be shown later) is characterized by two interesting features: First, the crystals have a relatively long periodicity of 32.05 Å along one direction (Sugaki and Shima, 1971), suggesting a complex structure. Secondly, the chemical composition (irrespective of whether it is $Cu_3Bi_3S_7$ or $Cu_4Bi_4S_9$) does not satisfy the relation $K = n_e/N = 8$ for normal valence compounds (Pearson, 1964; Takéuchi, 1970) since $K = 7.71$ for $Cu_3Bi_3S_7$, and $K = 7.78$ for $Cu_4Bi_4S_9$. Here, n_e is the total number of valence electrons, and N the number of sulfur atoms, each per formula unit.

Noting that two of the five valence electrons of M (= As, Sb, Bi) are in general unshared in the MS_3 units of sulfosalts, if we allot three valence electrons to M in evaluating the values of K, we find that the majority of sulfosalts satisfy the above relation for normal valence compounds. Thus we find, for example that in freieslebenite, $PbAgSbS_3$, (Hellner, 1957), $n_e = 2 + 1 + 3 + 6 \times 3 = 24$, $N = 3$; for jamesonite (Niizeki and Buerger, 1957*b*), $FePb_4Sb_6S_{14}$: $n_e = 2 + 2 \times 4 + 3 \times 6 + 6 \times 14 = 112$, $N = 14$, and for wallisite, $PbTlCuAs_2S_5$ (Takéuchi *et al.*, 1968): $n_e = 2 + 1 + 1 + 3 \times 2 + 6 \times 5 = 40$, $N = 5$. One of major exceptions is, however, provided by livingstonite, $HgSb_4S_8$, (Niizeki and Buerger, 1957*a*), for which $n_e = 1 + 3 \times 4 + 6 \times 8 = 61$, $N = 8$, giving $K = 7.625$. According to the valence rule given by Pearson (1964), such a value of K lower than eight suggests the existence of certain type of sulfur-sulfur bondings in the structure. In the complex structure of livingstonite, paired sulfur atoms like those in pyrite have indeed been found by Niizeki and Buerger (1957*a*). It was then suspected that the new material now being considered would contain a certain type of S—S bonds. We therefore worked out the structure of this material to elucidate the nature of the structure on one hand, and to verify, on the other, such a conjecture drawn from the valence rule. A brief account of the structure has appeared (Ozawa and Takéuchi, 1972).

Material

The crystals, which were kindly placed at our disposal by Prof. Sugaki, are prismatic, having length of up to about 1 mm. The table shown below gives the average of seven microprobe analyses carried out on the material (Sugaki, 1972).

	weight %	atom %
Cu	19.8	24.8
Bi	58.3	22.2
S	21.4	53.0
Total	99.5	100.0

For seven sulfur atoms, the result yields the formula, $Cu_{3.27}Bi_{2.93}S_7$, and for nine sulfur atoms $Cu_{4.20}Bi_{3.76}S_9$. The latter one, which may well be expressed by $Cu_4Bi_4S_9$, was later confirmed through structure analysis.

Lattice constants and space group

The crystal was orthorhombic, and the unit-cell dimensions obtained with the precession method were as follows:

$$a = 11.589(5)\ \text{Å}, \qquad b = 32.05(2)\ \text{Å}, \qquad c = 3.951(5)\ \text{Å}.$$

These are essentially same as those given by SUGAKI and SHIMA (1971). This unit cell contains $4\,Cu_4Bi_4S_9$, giving calculated density of 6.238 g cm^{-3}. The diffraction symmetry is *mmm Pbn-*, which permits *Pbnm* (D_{2h}^{16}) or *Pbn*2_1 (D_{2v}^{9}) as possible space groups. The former centric space group has been confirmed through structure analysis.

Structure determination

Crystals we so far examined by x-ray were unexceptionally found to be bundles of several crystals having their *c* axes in common. Even crystals which were defined by sharp crystal faces and showed no slight evidence of bundles did exhibit composite x-ray patterns. Therefore we finally decided to use such a composite crystal to collect intensity data. The shape of the crystal we used was well approximated to that of a cylinder having dimensions of 0.04 mm in diameter and 0.18 mm in length. Reflections were recorded, using copper radiation, in multiple-film Weissenberg photographs, and those given by one main component crystal were carefully separated in the films. Integrated intensities of a total of 894 non-equivalent reflections were then eye-estimated using a calibrated spot scale. The intensities were corrected for Lorentz and polarization effects and absorption with the UNICS program system (SAKURAI, 1967).

Analysis of the structure was performed with the symbolic addition procedure (KARLE and KARLE, 1966) using *hk*0 reflections. The program written by ASHIDA (1967) was used to calculate the normalized structure factors, E. Of 474 reflections of the $hk0$ zone, 65 have E's with magnitude greater than 1.5, and 145 have E's with magnitude greater than 1.0. Initial signs were assigned to a set of three E's to fix the origin, and one symbolic sign to each E having a large magnitude. After several iterations of the symbolic addition procedure, signs of 143 of above-mentioned 145 E's were assigned with high probability. The set of signs was then used to calculate a two-dimensional E map. This clearly revealed four outstandingly heavy peaks in the asymmetric unit of the projection, showing that four nonequivalent Bi atoms are contained in the unit cell. This situation immediately led to the view that the chemical formula, $Cu_4Bi_4S_9$, was more adequate than $Cu_3Bi_3S_7$ which had been proposed by SUGAKI and SHIMA (1971). The E map also revealed some of the positions of Cu atoms as well as some of the S atoms. A Fourier map synthesized with structure-factor signs based upon the four Bi-atom positions revealed peaks for four Cu atoms and locations for nine sulfur atoms in the c-axis projection. Since the length of the c axis is very short, each of these atoms should be on a mirror plane if we assume the centric space group *Pbnm*, either at the level of $c/4$ or $3c/4$. The z level of each atom was then readily determined by taking account of bond lengths.

The approximate atomic coordinates thus derived were next refined by least-squares with the full-matrix program, ORFLS, written by BUSING, MARTIN and LEVY (1962) and modified by IITAKA for HITAC 5020E at the Computer Center of the University of Tokyo. At a very early stage of refinement, we noticed that one of the copper atoms, Cu(4), showed a very large temperature factor, $B \simeq 6$ Å^2. We initially located this specific atom at the tetrahedral position formed by S(8), S(1)′ and the two S(1)″ (the two S(1)″ atoms are related to each other by a translation of c), (Fig. 1). Least-squares calculation, however, shifted the Cu atom by about 0.3 Å towards the plane formed by three sulfur atoms, S(8) and two S(1)″. Because of such an unexpected large shift, we then placed the atom in the plane of the three sulfur atoms. The atom was then shifted by next cycle of least-squares calculation towards the initial tetrahedral position by about 0.2 Å, and the magnitude of the isotropic temperature coefficient was not reduced. The final location of Cu(4) which we obtained by the isotropic refinement was between the tetrahedral position and the triangular position but slightly closer to the latter.

For subsequent anisotropic refinement, we omitted 49 very weak reflections and applied the weighting scheme reported by CRUICKSHANK

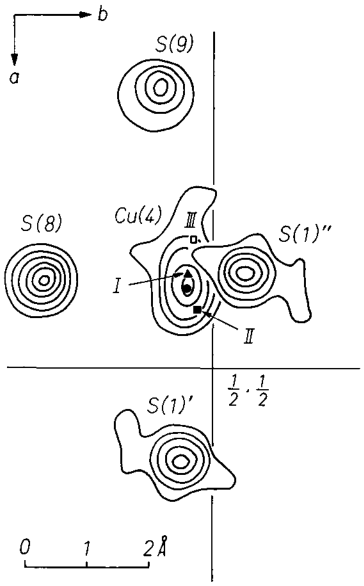


Fig. 1. Final electron density showing Cu(4) and its neighbours; contours are drawn, starting from 1 e Å^{-3}, at an interval of 4 e Å^{-3}. Final position of Cu(4) obtained by refinement is indicated by a dot. I: the center of triangle formed by S(8) and two S(1)'', II: the center of tetrahedron formed by S(8), S(1)', and two S(1)'', III: the center of tetrahedron formed by S(8), S(9), and two S(1)''

Table 1. *Fractional atomic coordinates with their standard deviations*

	x	y	z
Cu(1)	0.3832(7)	0.1359(3)	0.75
Cu(2)	0.3363(8)	0.1911(3)	0.25
Cu(3)	0.4247(7)	0.3042(2)	0.25
Cu(4)	0.3936(15)	0.4827(4)	0.25
Bi(1)	0.36697(18)	0.02775(7)	0.25
Bi(2)	0.09953(18)	0.09028(7)	0.25
Bi(3)	0.13895(17)	0.27871(6)	0.25
Bi(4)	0.23286(17)	0.39072(6)	0.75
S(1)	0.1327(11)	0.0205(4)	0.75
S(2)	0.3254(9)	0.0987(3)	0.25
S(3)	0.0926(10)	0.1543(4)	0.75
S(4)	0.2424(9)	0.1909(4)	0.75
S(5)	0.4851(10)	0.2351(4)	0.25
S(6)	0.3158(10)	0.3143(4)	0.75
S(7)	0.0747(10)	0.3564(4)	0.25
S(8)	0.3882(9)	0.4125(4)	0.25
S(9)	0.1195(9)	0.4708(5)	0.25

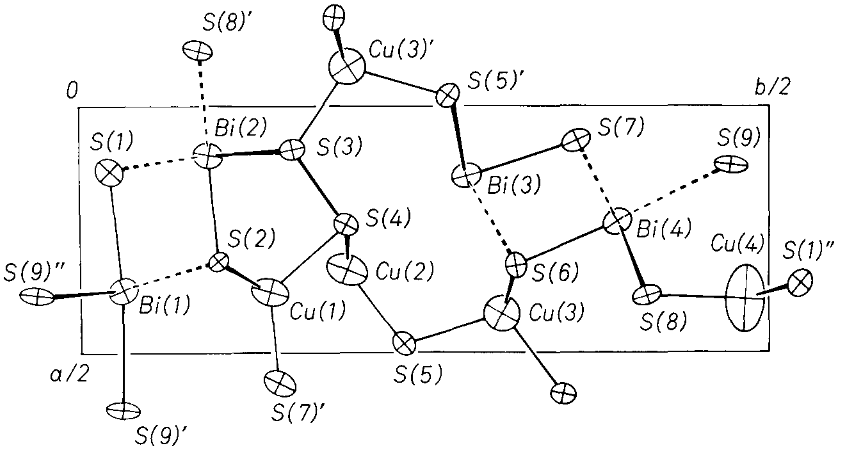


Fig. 2. The *c*-axis projection of the structure of $Cu_4Bi_4S_9$, showing thermal ellipsoids of the atoms

Table 2. *Thermal parameters of atoms with standard deviations in parentheses* (anisotropic parameters have been multiplied by 10^5)

	β_{11}	β_{22}	β_{33}	β_{12}	Equivalent B
Cu(1)	537(59)	98(9)	5672	—22(18)	3.2 Å^2
Cu(2)	579(60)	126(11)	6569	—62(20)	3.7
Cu(3)	610(60)	82(8)	5304	— 7(17)	3.2
Cu(4)	2290(211)	109(13)	12522	37(40)	7.2
Bi(1)	418(15)	60(2)	3737	7(4)	2.2
Bi(2)	407(14)	62(2)	3774	— 5(4)	2.3
Bi(3)	387(13)	56(2)	3496	3(4)	2.1
Bi(4)	404(14)	55(2)	3538	10(4)	2.1
S(1)	347(85)	45(10)	3039	—18(24)	1.8
S(2)	233(69)	32(9)	2069	22(22)	1.2
S(3)	310(75)	46(11)	2669	4(24)	1.7
S(4)	221(71)	37(10)	2268	—18(22)	1.3
S(5)	279(79)	33(9)	2390	—21(22)	1.3
S(6)	306(77)	32(9)	2389	— 3(23)	1.4
S(7)	282(79)	58(12)	3278	37(24)	1.8
S(8)	162(66)	55(11)	2477	23(21)	1.3
S(9)	134(69)	78(14)	2953	—21(23)	1.5

(1964). When the refinement converged the *R* value was reduced to 9.6%. If we omit 29 very strong lower-order reflections, the value is reduced to 8.0% for 816 reflections.

The result of the chemical analyses given previously might suggest, instead of $Cu_4Bi_4S_9$, a formula, $Cu_{4+x}Bi_{4-x}S_9$, with $x \simeq 0.2$. If this were true, vacancies would be distributed at the Bi positions, and excess copper atoms would be located around the vacant Bi positions as in the case of $Cu_{2+x}Bi_{6-x}S_9$ ($x = 1.21$) (OHMASA, 1973). Such a situation is, however, not likely for the present material because no anomalous residual peaks are observed in the final difference Fourier map, and no thermal parameters of Bi atoms are unusual. The final atomic coordinates and thermal parameters are respectively given in Table 1 and Table 2. The *c*-axis projection of the structure is given in Fig. 2, showing the thermal ellipsoids of the atoms.

Discussion of the structure

Existence of paired sulfur atoms

The structure contains, as predicted from the valence rule, sulfur-sulfur bonds. The bond occurs in the structure between S(3) and S(4), forming an S_2 group (Fig. 2) like those in pyrite, FeS_2. The S—S bond length of the S_2 groups is found to be 2.095(17) Å. This value is compared below with those of the S_2 groups found in other structures.

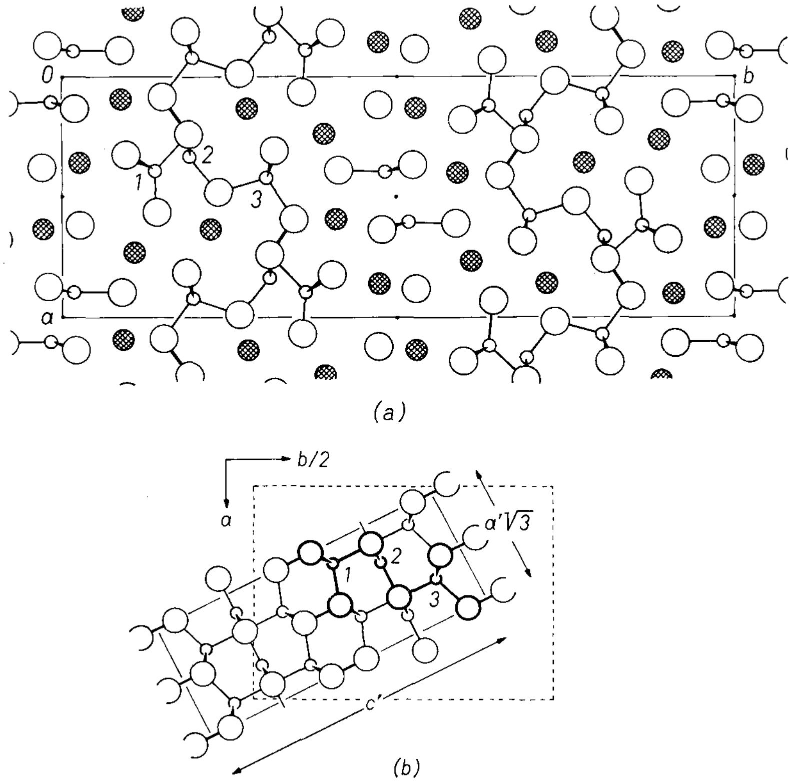
	$Cu_4Bi_4S_9$	livingstonite[1] $HgSb_4S_8$	covellite[2] CuS	pyrite[3] FeS_2	marcasite[4] FeS_2
S—S distance	2.10	2.07	2.09	2.10	2.21

[1] NIIZEKI and BUERGER (1957a); [2] BERRY (1954); [3] EWALD and HERMANN: Strukturbericht, 1913—1928, p. 153; [4] BUERGER (1931, 1937).

These values, except that of marcasite, agree well with the value of 2.08 Å for twice the sulfur covalent radius.

Cu-S sheets

One of marked features of the structure is that the S_2 groups, in conjunction with copper atoms in 3- or 4-coordination, form highly corrugated sheets (Fig. 3*a*). The building unit of the sheets consists of links of two Cu-S tetrahedra and one Cu-S triangle. These units are joined together by S_2 groups to form sheets parallel to (010). It is notable that we find in the structure of covellite, CuS, (OFTEDAL, 1932; BERRY, 1954) the same type of links of two CuS_4 tetrahedra and one CuS_3 triangle (Fig. 3*b*). The bond lengths and angles are listed in Table 3 and Table 4 respectively.



(a)

(b)

Fig. 3. *(a)* The *c*-axis projection of the structure of $Cu_4Bi_4S_9$, showing the Cu—S sheets. Numbers indicate Cu(1) tetrahedron, Cu(2) triangle, and Cu(3) tetrahedron, groups which together form the unit of a sheet. *(b)* The structure of covellite, as viewed along the *a* axis. Heavy lines show the links of two tetrahedra and one triangle which correspond to the unit of the sheet in $Cu_4Bi_4S_9$. The projection is so placed, with respect to the cell edges of $Cu_4Bi_4S_9$ (dotted lines), that the links are located at the position corresponding to that of the above unit in $Cu_4Bi_4S_9$

As will be observed in Fig. 2 and Fig. 3, the Cu(2) atom is not exactly in the plane formed by three sulfur atoms, S(5) and two S(4). A calculation showed that it is out of plane by 0.48(1) Å. Because of this, the mean value of the S—Cu(2)—S bond angles is smaller than 120° and shows a value of 115.5° (Table 4). A three-coordinated Cu atom similar to this has been reported in the structure of anilite (KOTO and MORIMOTO, 1970); Cu(5) of the anilite structure is slightly out of plane formed by three sulfur atoms, and our calculation yield a mean S—Cu(5)—S angle of 117°. For the case of our structure, this

Table 3. *Bond lengths between metal and sulfur atoms*

	Cu(1)	Cu(2)	Cu(3)	Cu(4)	Bi(1)	Bi(2)	Bi(3)	Bi(4)
S(1)				2.77 2.34^{d}	2.73	3.01^{d}		
S(2)	2.40^{d}				3.05^{d}	2.63		
S(3)			2.36			2.85^{d}		
S(4)	2.40	2.26^{d}					3.64^{d}	
S(5)		2.23	2.32				2.70^{d}	
S(6)			2.37^{d}				3.07^{d}	2.63
S(7)	2.23						2.60	2.91^{d}
S(8)				2.25		3.15^{d}		2.76^{d}
S(9)				3.20	2.93 2.69^{d}			3.50^{d}
Average	2.36	2.25	2.36	2.31^{a}	2.70^{a}	2.78^{a}	2.67^{a}	2.72^{a}
						2.87^{b}	2.83^{b}	2.79^{b}
					2.86^{c}	2.95^{c}	3.06^{c}	3.00^{c}

Each bond length indicated by *d* has a multiplicity of two. Estimated error in bond lengths other than Cu(4)—S is ± 0.01 Å; for Cu(4)—S bonds the error is ± 0.02 Å. [a] Average of three shortest bonds. [b] Average of five shortest bonds. [c] Average of all bonds.

situation would seem to be related to the fact that Cu(2) has a close neighbour of Bi(3) at a distance of 3.62 Å (Fig. 2). If Cu(2) were in the plane formed by the three sulfur atoms, calculation shows that the distance would be reduced to about 3.1 Å. This value is considered to be too small for the Cu—Bi separation. The displacement of Cu(2) from the plane, in turn, has resulted in reducing (compared to the corresponding Cu—Cu distance in covellite) the distance between Cu(2) and Cu(1) (Fig. 1); the distance is found to be 2.71 Å.

Links of Bi-S polyhedra

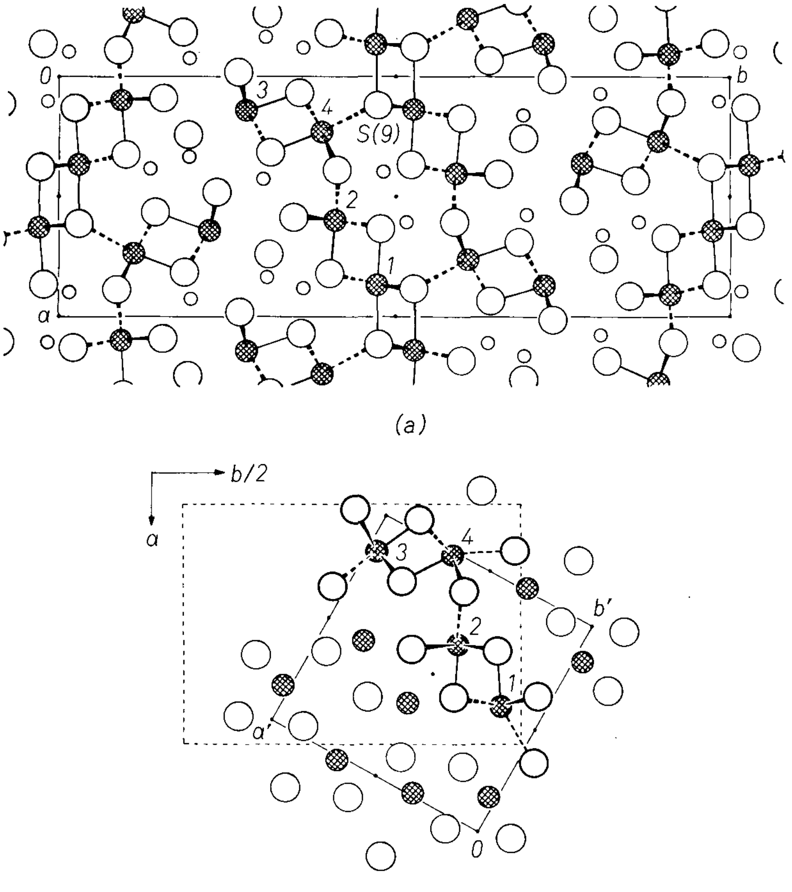
Each region of the structure bounded by two Cu-S sheets in the unit cell is composed of links of polyhedra formed by sulfur atoms about Bi atoms (Fig. 4). Of four nonequivalent Bi atoms, Bi(1) is

Table 4. S(p)—S(q) *distances, and* S(p)—M(j)—S(q) *angles*

M	j	p	q	Angle	Distance	M	j	p	q	Angle	Distance
Cu	1	2	2*	110.6°	3.95 Å	Cu	3	6	6*	113.5°	3.95 Å
		2	4	100.0	3.68[d]			6	5	106.9	3.77[d]
		2	7′	109.1	3.78[d]			5	3′	106.8	3.76
		4	7′	126.1	4.13			6	3′	111.3	3.90[d]
		Mean		109.2	3.83			Mean		109.5	3.84
Cu	2	4	4*	122.3	3.95	Cu	4	1″	1″*	115.4	3.95
		4	5	111.9	3.71[d]			1″	8	120.9	3.99[d]
		Mean		115.6	3.79			Mean		119.1	3.98
Bi	1	9″	9″*	94.3	3.95	Bi	3	5′	5′*	93.8	3.95
		9″	1	90.0	3.83[d]			5′	7	88.1	3.69[d]
		Mean		91.4	3.87			Mean		90.0	3.78
		9′	9″	87.3	3.88[d]			7	6	89.4	3.68[d]
		9′	2	98.4	4.53[b]			6	6*	80.2	3.95
		2	2*	80.7	3.95			6	4	73.6	4.05
		2	1	84.6	3.89[d]			4	4*	65.7	3.95
		2	9″	92.3	4.15			4	5′	72.2	3.81
								5′	6	91.8	4.15
Bi	2	3	3*	87.7	3.95	Bi	4	8	8*	91.3	3.95
		3	2	87.4	3.79[d]			8	6	89.8	3.81[d]
		Mean		87.5	3.84			Mean		90.3	3.86
		2	1	87.1	3.90[d]			6	7	83.0	3.68[d]
		1	1*	82.1	3.95			7	7*	85.5	3.95
		1	8′	70.5	3.56			7	9	69.9	3.70
		8′	8′*	77.7	3.95			9	9*	68.9	3.95
		8′	3	64.1	3.19			9	8	69.8	3.63
		1	3	94.8	4.31			7	8	91.2	4.05

Notation of atoms is given in Fig. 1; stars denote sulfur atoms which are related to those of the same notation by the translation of c. Each pair of an angle and a distance, both having multiplicity of two, is indicated by *d* in the last columun of the corresponding row. Estimated errors are ± 1.0° in angles, and ± 0.02 Å in distances.

surrounded by six sulfur atoms in the form of an distorted octahedron, while each of other three Bi atoms has seven near sulfur atoms: six neighbours at corners of a distorted trigonal prism and the seventh beyond a rectangular face. The difference in coordination is reflected in the difference of mean Bi—S distances. The mean of the Bi(1)—S distances is 2.86 Å, while those of Bi(2)—S, Bi(3)—S, and Bi(4)—S are respectively 2.95 Å, 3.06 Å, and 3.00 Å. The mean Bi—S distance in



(a)

(b)

Fig. 4. *(a)* The *c*-axis projection of the structure of $Cu_4Bi_4S_9$, showing the Bi—S bonds. Numbers indicate four Bi-S polyhedra which form links having a strong resemblance to the bismuthinite structure. The numbers correspond to the notation for the Bi atoms. *(b)* The structure of bismuthinite as viewed along the *c* axis. The Bi—S bonds are shown which correspond to those in the $Cu_4Bi_4S_9$ structure. The cell edges of $Cu_4Bi_4S_9$ are indicated so as to facilitate comparing the Bi—S bonds with corresponding ones in $Cu_4Bi_4S_9$; corresponding polyhedra in the both structures are indicated by the same numbers

the Bi(1)—S octahedron is about 5% smaller than those in the Bi—S heptahedra. In each polyhedron about Bi, we recognize three shortest Bi—S bonds characteristic of trivalent metal atoms in sulfosalts. The average of three shortest Bi—S bonds in the structure is found to be 2.72(1) Å, and the average of the S—Bi—S bond angles 89.8(1.0)°.

This average bond length agrees with the corresponding value for aikinite (OHMASA and NOWACKI, 1970; KOHATSU and WUENSCH, 1971) and with the average of bridge and nonbridge Bi—S bond lengths which were given by TAKÉUCHI and SADANAGA (1969) in their previous survey of bond lengths in sulfosalt structures. The corresponding value for bismuthinite is, however, 2.68 Å (KUPČIK and VESELÁ-NOVÁKOVÁ, 1970) which is slightly smaller than the above value. On the other hand, the above average bond angle for $Cu_4Bi_4S_9$ is smaller than the value of 92.0° which was obtained by the same survey (TAKÉUCHI and SADANAGA, 1969). Accurately determined structures reported after the survey give mean values of 87.0° (OHMASA and NOWACKI, 1970) and 87.8° (KOHATSU and WUENSCH, 1971) both for aikinite, and 88.3° for bismuthinite (KUPČIK and VESELÁ-NOVÁKOVÁ, 1970). These values and the value for $Cu_4Bi_4S_9$ altogether give a new mean value of 88.2° for S—Bi—S bond angle in sulfosalts.

The array of four nonequivalent Bi-S polyhedra indicated in Fig. 4*a* is surprisingly similar to that of four Bi-S polyhedra in the bismuthinite structure given in Fig. 4*b*. Only major difference between the two is in the position of S(9) with respect to the Bi(4) atom. This sulfur atom in the structure of $Cu_4Bi_4S_9$ is at the level of $c/4$, while the corresponding sulfur atom in the bismuthinite structure is at $3c/4$. With this exception, all the corresponding atoms are in the same level. Because of such a salient feature, the Bi-S regions of the structure may be regarded as being made up of the fragments of the bismuthinite structure. Therefore, the structure of $Cu_4Bi_4S_9$, as a whole, can be described as an alternate stacking of Cu-S sheets related to the covellite structure and Bi-S slabs related to the bismuthinite structure. This situation seems to offer an important rule that complex sulfosalt structures, in general, tend to be related to simple sulfide structures formed by the metal atoms involved in the sulfosalts. Though there are a number of sulfosalt structures related to the PbS structure (HOFMANN, 1935; HELLNER, 1958; TAKÉUCHI and SADANAGA, 1969), the structure of $Cu_4Bi_4S_9$ is of new type and more general in that it is related to two sulfide structures.

Environment of Cu(4)

The Bi-S slabs contain the fourth copper atom in the $Cu_4Bi_4S_9$ structure. This atom is located in the Cu(4) position (Fig. 2), and has, as mentioned earlier, a very large temperature factor. It is strongly anisotropic (Fig. 1). The Cu(4) position obtained by least-squares refinement is slightly displaced from the plane formed by three sulfur atoms, S(8) and two S(1)″; the magnitude of the displacement is found to be 0.15(2) Å. The final electron density showing Cu(4) and its neighbours (Fig. 1) seems to suggest that this copper atom is in fact statistically located at the triangular position I and at the tetrahedral position II (Fig. 1). On both sides of the triangular plane, Cu(4) has further near sulfur atoms at the distances of 3.20 Å and 2.77 Å (Fig. 5). At a distance of 3.35 Å, Cu(4) has the closest cation neighbour, Cu(4)′, which is related to Cu(4) by the center of symmetry at $[\frac{1}{2}\frac{1}{2}\frac{1}{2}]$. The three shortest Cu(4)—S bonds give a mean bond length of 2.31(2) Å, which is slightly larger than the corresponding value of 2.25(1) Å for Cu(2)—S bonds. This larger value for Cu(4)—S is probably related to the positional disorder of Cu(4).

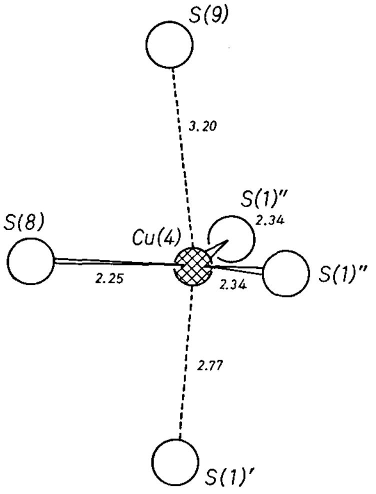


Fig. 5. Environment of Cu(4)

To compare these Cu—S bond lengths with those of other structures, we made a survey on the Cu—S bond lengths in sulfides and sulfosalts with the results as given in Table 5. As will be observed in this table, if we exclude structures related to zinc-blende or wurzite, mean Cu—S bond lengths are 2.34 Å and 2.27 Å respectively for four- and three-coordinated copper atoms. It is to be noted that the mean of the Cu(4)—S bond lengths in the $Cu_4Bi_4S_9$ structure is almost the same as the average of these two values.

Table 5. *Mean* Cu—S *distances in various structures*

four-coordinated copper				Mean Cu—S distance
$Cu_4Bi_4S_9$	2.36Å	seligmannite[6]	2.330Å	
binnite[1]	2.337	bournonite[6]	2.343	2.339 Å
tetrahedrite[2]	2.342	nuffieldite[7]	2.27	2.345 Å (omitting nuffieldite)
wallisite[3]	2.33	(Pb, Ag, Bi) $Cu_4Bi_5S_{11}$[8]	2.36	
aikinite[4]	2.367	anilite[9]	2.37	
aikinite[5]	2.354	covellite[16]	2.31	
structures related to zinc-blende or wurzite				
chalcopyrite[10]	2.32	cubanite[13]	2.31	
stannite[11]	2.31	luzonite[14]	2.321	2.314
enargite[12]	2.31			
three-coordinated copper				
$Cu_4Bi_4S_9$	2.28*	covellite[16]	2.19	
binnite[1]	2.240	anilite[9]	2.30*	2.265
tetrahedrite[2]	2.259	(Pb, Ag, Bi) $Cu_4Bi_5S_{11}$[8]	2.31*	2.278 (omitting covellite)
stromeyerite[15]	2.28			

* Copper atoms are shifted from the plane formed by three sulfur atoms.
[1] WUENSCH *et al.* (1966), [2] WUENSCH (1964), [3] TAKÉUCHI *et al.* (1968), [4] OHMASA and NOWACKI (1970), [5] KOHATSU and WUENSCH (1971), [6] EDENHARTER *et al.* (1970), [7] KOHATSU and WUENSCH (1973), [8] KUPČIK and MAKOVICKÝ (1968), [9] KOTO and MORIMOTO (1970), [10] PAULING and BROCKWAY (1932), [11] BROCKWAY (1934), [12] PAULING and WEINBAUM (1934), [13] AZAROFF and BUERGER (1955), [14] MARUMO and NOWACKI (1967), [15] FRUEH (1955), [16] BERRY (1954).

In Table 5, we notice that the value for nuffieldite (KOHATSU and WUENSCH, 1973) is significantly small compared to those for other sulfosalts. A closer examination into this structure has revealed that the copper atom is, in fact, close to three sulfur atoms, S(4) and two S(5)′, of the structure, giving a mean Cu—S distance of 2.26 Å. The mean of the three S—Cu—S angles is found to be 116.2° which is close to the corresponding value of the Cu(2)—S group in our structure. The copper atom in nuffieldite may therefore be considered to have a character of a threefold coordination though it has a fourth sulfur atom at a distance of 2.32 Å. Finally, we also find in Table 5 that the Cu—S bond lengths in the three-coordinated copper in the covellite structure give, compared to others, a very small mean value. To establish this value, further refinement of the structure may be desirable.

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