From the graphs, it is seen that the splitting is maximum when the crystallographic b axis is parallel to H_0, minimum when **c** is parallel to H_0, and intermediate when **a** is parallel to H_0.

This result is characteristic of a tetrahedrally coordinated lithium nucleus with z, y and x principal axes along the **b**, **a** and **c** directions respectively, confirming the results of Galigné *et al.* (1970) according to which two water oxygens in the ac plane at a distance of 2·045 Å from the lithium ion and two acetate oxygens in the bc plane at a distance of 1·895 Å from the lithium ion form a slightly distorted tetrahedron around the lithium ion [Figs. 3 and 4]. Consequently the component of the e.f.g. tensor along **c** should be very small and the components along **a** and **b** should be nearly equal. This is in agreement with our results.

The values of (e^2qQ/h), η, and the orientation and magnitudes of the principal components of the e.f.g. tensor obtained for the two rotations are given in Tables 1 and 2. The value of (e^2qQ/h) for ^{7}Li has been found to vary from 15 to 200 kHz. Our value of 154·6 kHz is on the high side, indicating considerable covalency.

Table 1. ^{7}Li *quadrupole coupling constant* (e^2qQ/h) *and asymmetry parameter* η *of* $Li(CH_3COO).2H_2O$

Axis of rotation	(e^2qQ/h)	η
b	154·6 kHz	0·86
c	154·6	0·90

Table 2. *Direction cosines of the principal axes of the* ^{7}Li *quadrupole coupling tensor in* $Li(CH_3COO).2H_2O$

Axis of rotation	Pıincipal components	a	b	c
b	f_{zz}	0	1	0
	f_{yy}	1	0	0
	f_{xx}	0	0	1
	f_{zz}	0	1	0
c	f_{yy}	1	0	0
	f_{xx}	0	0	1

References

Amirthalingam, V. & Padmanabhan, V. M. (1958). *Acta Cryst.* **11**, 896.

Clark, J. R. (1964). *Acta Cryst.* **17**, 459–461.

Cohen, M. H. & Reif, F. (1957). *Solid State Phys.* **5**, 321–438.

Galigné, J. L., Mouvet, M. & Falgueirettes, J. (1970). *Acta Cryst.* B**26**, 368–372.

Padmanabhan, A. C. & Srinivasan, R. (1972). *Acta Cryst.* B**28**, 3188–3190.

Acta Cryst. (1974). B**30**, 848

The Crystal Structure of $Bi_2Cu_3S_4Cl$

By J. Lewis Jr and V. Kupčík

Mineralogisch-Kristallographisches Institut der Universität Göttingen, Germany (BRD)

(*Received* 10 *September* 1973; *accepted* 23 *October* 1973)

Crystals of $Bi_2Cu_3S_4Cl$ were prepared and the structure was determined from three-dimensional diffractometer data. The substance is orthorhombic, with $a_o=20·719$, $b_o=10·308$, and $c_o=4·00$ Å. The space group is $P2_12_12_1$ with $Z=4$. The reliability index is 6·6 % for 937 reflexions. The bismuth coordination polyhedra are connected by common edges and form chains of the type $(Bi_2S_4)^{2-}_{\infty}$ and $(BiS_2Cl)^{2-}_{\infty}$ which lie parallel to the c axis. These chains are linked over a 2_1 axis by chlorine atoms so that channels are formed. Splitting of the Cu(1) atom site into two nearly equivalent sites statistically occupied by copper atoms of unusual coordination is considered.

Experimental

The crystals were synthesized in a closed Pyrex glass ampoule with a volume of 20 ml; 2·2 ml of HCl (conc.) and 0·01 mol each of PbS, Cu_2S and Bi_2S_3 were used for synthesis. The temperature maintained over a period of 60h was 240 °C and the calculated pressure was 270 bar. Other by-products were CuCl, $PbCl_2$ and H_2S. The composition was determined from electron-microprobe analysis as well as from crystal-structure analysis. The size of the crystal used for the investigation was 400 × 25 × 13·5 μm. The Weissenberg equi-inclination technique with Cu $K\alpha$ radiation was used for the determination of lattice parameters and space group. The only observed systematic absences were $h00$ with $h=2n+1$; $0k0$ with $k=2n+1$ and $00l$ with $l=2n+1$, thus uniquely establishing the space group as $P2_12_12_1$. For the structure determination, the intensities of 937 reflexions with $\sin\theta$ up to 0·42 were collected on a Weissenberg diffractometer (STADI-2 system from

Stoe) using Mo $K\alpha$ radiation. The data were corrected for absorption with the program *CORIN* by Paulus. Crystal data are given in Table 1.

Table 1. *Crystal data*

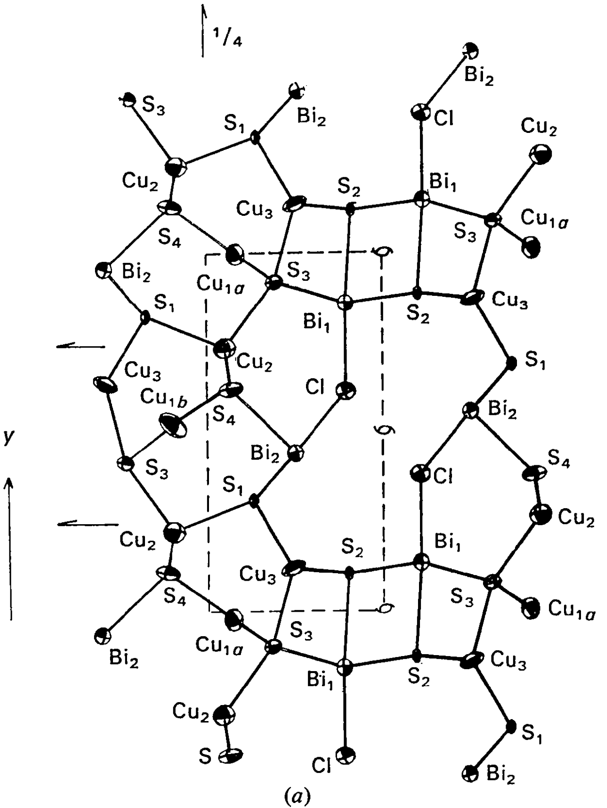
a_o	20·719 ± 0·007 Å
b_o	10·308 ± 0·003
c_o	4·00 ± 0·01
D_{calc}	6·00 g cm^{-3}

Structure determination and refinement

The coordinates of the bismuth atoms were obtained from the Patterson function. Approximate atomic coordinates for the copper, sulphur and chlorine atoms were then found from the Fourier projections *hk*0 and *h*0*l*. With these coordinates and estimated isotropic temperature factors the resulting *R* value was 14%. The isotropic temperature factor for one

Table 2. *Atomic coordinates* (× 10^4) *and occupancy*

	x	*y*	*z*	*N*
Bi(1)	1972	8562	3460	1
Bi(2)	1307	4420	2638	1
Cu(1*a*)	487	−130	2880	0·5
Cu(1*b*)	363	130	4173	0·5
Cu(2)	337	7269	7757	1
Cu(3)	1286	1285	8293	1
S(1)	732	3128	7621	1
S(2)	2041	1132	2755	1
S(3)	998	9130	7587	1
S(4)	425	6150	2808	1
Cl	1993	6117	7636	1



(*a*)

Fig. 1. (*a*) An asymmetric unit (dotted lines) in the direction [001] extended to show canals.

Table 3. *Anisotropic temperature parameters and their isotropic equivalents* ($\beta \times 10^4$)

$B = \sum \beta_{ij} h_i h_j$ (from refinement 5 in Table 7).

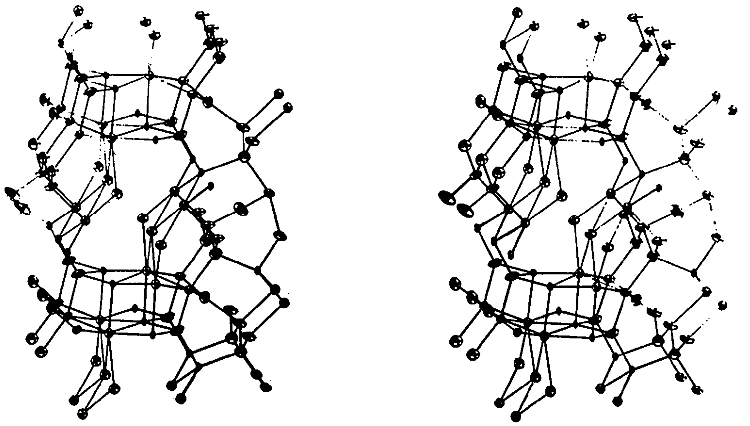
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	*B*
Bi(1)	7 (1)	39 (2)	388 (12)	−0 (1)	−0 (2)	0 (5)	1·89
Bi(2)	9 (1)	40 (2)	366 (11)	−0 (1)	4 (2)	6 (6)	1·93
Cu(2)	18 (2)	51 (7)	442 (52)	1 (3)	−5 (10)	−16 (20)	2·72
Cu(3)	18 (2)	39 (7)	645 (59)	10 (3)	−12 (11)	−25 (20)	2·83
S(1)	− 1 (2)	37 (12)	282 (75)	−1 (4)	1 (13)	3 (33)	0·70
S(2)	− 0 (2)	27 (11)	237 (67)	−0 (4)	−10 (13)	−44 (28)	0·36
S(3)	10 (3)	30 (13)	255 (73)	1 (5)	22 (15)	4 (37)	1·46
S(4)	21 (4)	26 (12)	255 (91)	5 (6)	34 (17)	4 (33)	1·74
Cl	14 (3)	40 (13)	130 (68)	−1 (5)	1 (16)	53 (28)	1·15

	B	r.m.s. (Å)
Cu(1*a*)	2·79	0·188
Cu(1*b*)	2·97	0·194

Table 4. *Interatomic distances* (Å)

In Tables 4 and 5 the standard deviations in parentheses refer to the last digit.

	S(1)	S(2)	S(3)	S(4)	Cl
Bi(1)–		2·67 (1), 2·69 (1) 3·08 (1)	2·67 (1), 3·15 (1)		3·02 (1), 3·43 (1) Å
Bi(2)–	2·68 (1), 2·69 (1)		2·55 (1)		3·01 (1) (2×)
Cu(1*a*)–			2·29 (2), 2·49 (2)	2·33 (2)	
Cu(1*b*)–			2·16 (2)	2·1 (2)	
Cu(2)–	2·39 (2)		2·36 (1)	2·3 (2), 2·33 (2)	
Cu(3)–	2·24 (2)	2·72 (2), 2·38 (2)	2·32 (2)		

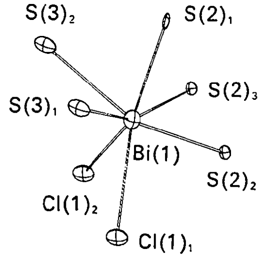


(*b*)

Fig. 1. (*cont.*) (*b*) Stereodiagram of the unit in Fig. 1 (*a*).

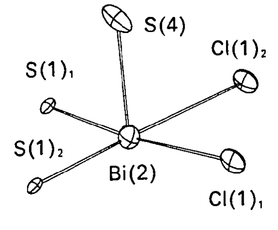
Table 5. *Bond angles and coordination polyhedra*

Bi(1)



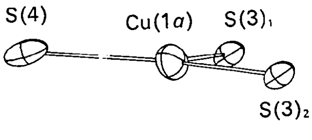
S(2)$_1$-Bi(1)-S(2)$_2$	84·9 (4)°
S(2)$_1$-Bi(1)-S(2)$_3$	77·6 (4)
S(2)$_1$-Bi(1)-S(3)$_1$	83·6 (4)
S(2)$_1$-Bi(1)-S(3)$_2$	76·8 (4)
S(2)$_1$-Bi(1)-Cl(1)$_1$	152·3 (7)
S(2)$_1$-Bi(1)-Cl(1)$_2$	131·0 (4)

Bi(2)



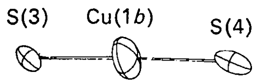
S(1)$_1$—Bi(2)-S(1)$_2$	96·4 (4)°
S(1)$_1$—Bi(2)-Cl(1)$_2$	90·3 (4)
Cl(1)$_1$-Bi(2)-S(1)$_2$	90·1 (4)
Cl(1)$_1$-Bi(2)-Cl(1)$_2$	83·2 (3)
S(4) —Bi(2)-S(1)$_1$	90·5 (4)
S(4) —Bi(2)-S(1)$_2$	92·8 (4)
S(4) —Bi(2)-Cl(1)$_1$	85·1 (4)
S(4) —Bi(2)-Cl(1)$_2$	87·2 (4)

Cu(1*a*)



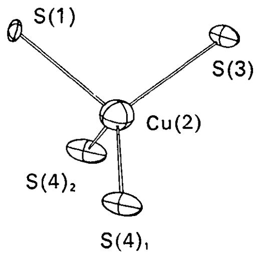
S(4) -Cu(1*a*)-S(3)$_1$	131·5 (7)°
S(4) -Cu(1*a*)-S(3)$_2$	114·8 (7)
S(3)$_1$-Cu(1*a*)-S(3)$_2$	113·7 (7)

Cu(1*b*)



S(4) -Cu(1*b*)-S(3)	162·4 (20)°

Cu(2)

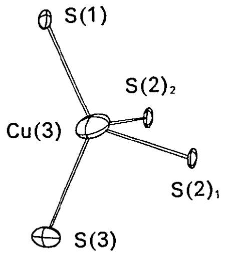


S(1) -Cu(2)-S(3)	103·6 (5)°
S(1) -Cu(2)-S(4)$_1$	108·1 (5)
S(1) -Cu(2)-S(4)$_2$	101·8 (5)
S(3) -Cu(2)-S(4)$_1$	112·5 (5)
S(3) -Cu(2)-S(4)$_2$	109·8 (5)
S(4)$_1$-Cu(2)-S(4)$_2$	119·4 (6)

copper atom, Cu(1), was very large (7·2). A difference synthesis (isotropic) showed an unusual anisotropic gradient in the region of Cu(1). An anisotropic refinement was attempted and the weighted *R* index omitting zeros dropped to 8·0%. The largest calculated root-mean-square amplitude for the copper atom being

Table 5 (*cont.*)

Cu(3)



$S(2)_1$–Cu(3)–$S(2)_2$	103·2 (5)°
$S(2)_1$–Cu(3)–S(1)	104·3 (5)
$S(2)_1$–Cu(3)–S(3)	89·6 (5)
S(1) –Cu(3)–S(3)	131·9 (6)
S(1) –Cu(3)–$S(2)_2$	119·0 (6)
$S(2)_2$–Cu(3)–S(3)	101·4 (5)

discussed was 0·47 Å. By splitting this one site into two, each with an occupancy of 0·5, the weighted reliability index dropped to 7·3 % and the temperature factor assumed normal proportions: 2·79 and 2·97 (for the isotropic equivalents). By a final mixed refinement with all atoms anisotropic except Cu(1) and with Cu(1) split, the weighted *R* index without zeros dropped to 6·5 % and the two nearly equivalent sites were 0·637 Å apart. The difference synthesis confirmed these results and a statistical occupancy can be considered the best probable description of this anomaly.

Results and description of the structure

Atomic coordinates, temperature parameters, interatomic distances and bond angles are given in Tables 2–5. The structure is illustrated in Fig. 1.

Bonds to S(2), S(2′) and S(3), S(3′) atoms build the base plane, and one bond to a S(2) atom builds the peak of a slightly distorted quadratic pyramid surrounding Bi(1). The coordination is completed by two bonds to Cl atoms stretching out from the base plane. The bismuth atom is outside the pyramid, 0·4 Å from the base plane and 0·33 Å from the centre of the base plane in the **c** direction. Bi(2) pyramids are linked over parallel S–S edges in the base plane and thus build chains of the description $(\mathrm{Bi_2S_4})_\infty^{2-}$ that lie parallel to the *c* axis. The connecting edges of these chains are not parallel to the *hk*0 plane. The Bi(2) polyhedron can also be described as a distorted quadratic pyramid, but in this case the base plane is formed by bonds to S(1) and to chlorine atoms. The distortion is less with regard to the bismuth atom, the distances from the base plane and that from the centre of the base plane in the **c** direction being 0·2 Å and 0·06 Å, respectively.

The coordination of the copper atoms found in $\mathrm{Bi_2Cu_3S_4Cl}$ varies considerably. Cu(2) is surrounded by four sulphur atoms at nearly equal distances (2·3–2·39 Å). The form of the polyhedron is nearly perfectly tetrahedral. The Cu(3) polyhedron is trigonal pyramidal with three short, nearly planar arranged

Table 6. *Comparison of bond lengths*

(*a*) Bond lengths (Å) found in $(\mathrm{MeS_2X})_\infty^{2-}$ chains of some well studied bismuth sulphohalogenides.

	Bi–S	Bi–S	Bi–X
$\mathrm{Bi_2Cu_3S_4Cl}$	2·55	2·68, 2·69	3·01 (2 ×)
BiSI (Haase-Wessel, 1972)	2·57	2·73 (2 ×)	3·18 (2 ×)
$\mathrm{Bi(Bi_2S_3)_9I_3}$ (Miehe & Kupčík, 1971)	2·60	2·77, 2·76	3·57, 3·60

(*b*) Bond lengths (Å) found in $(\mathrm{Bi_2S_4})_\infty^{2-}$ chains in bismuthinite, aikinite and $\mathrm{Bi_2Cu_3S_4Cl}$.

	Bi–S	Bi–S	Bi–S	Bi–S or –Cl	Bi–S or –Cl
$\mathrm{Bi_2S_3}$ (2 ×) (Kupčík & Veselá-Nováková, 1970)	2·69	2·67 (2 ×)	3·07 (2 ×)	3·05	3·33
$\mathrm{CuPbBiS_3}$ (Ohmasa & Nowacki, 1970)	2·66	2·76 (2 ×)	2·95 (2 ×)	3·16	3·53
$\mathrm{Bi_2Cu_3S_4Cl}$	2·67	2·67, 2·69	3·08, 3·15	3·02	3·43

Table 7. *Refinement data*

To avoid correlations, scale factors, atom coordinates and temperature factors were refined separately. The number of cycles used was the same in each case.

	Isotropic refinements		Anisotropic refinements		Mixed refinement with only Cu(1) isotropic
	1 [without splitting]	2 [with splitting]	3 [without splitting]	4 [with splitting]	5 [Cu(1) split]
R value including zeros	0·106	0·101	0·100	0·098	0·091
R value omitting zeros	0·098	0·093	0·091	0·089	0·082
Weighted *R* value including zeros	0·086	0·081	0·075	0·073	0·066
Weighted *R* value omitting zeros	0·085	0·080	0·074	0·072	0·065
B or isotropic equivalents and largest principle axis of the thermal ellipsoid of Cu(1*a*, *b*)	7·2 (0·6)	2·73 (0·3) 3·95 (0·4)	4·7/0·138 (0·01)	2·79/0·044 (0·01) 2·97/0·070 (0·01)	2·70 (0·28) 3·48 (0·33)

bonds (average length 2·3 Å) and one bond that is 2·72 Å long. Neither of the statistically distributed Cu(1*a*) and Cu(1*b*) atoms is tetrahedrally or even distorted-tetrahedrally coordinated with regard to sulphur.

Cu(1*a*) has a distorted-trigonal planar coordination of the sort (2+1). The nearest Cu–Cu bond is 2·87 Å long. The Cu(1*b*) atom is linearly coordinated with regard to sulphur. Cu(1*b*) is 2·79 and 2·91 Å distant from the nearest copper atoms.

Discussion

Two distinct types of bismuth polyhedra are found in this structure. One is common to most known thiohalogenides and is characteristic of chains of the type $(\mathrm{MeS_2X})_\infty^{2-}$ [see Table 6(*a*)]. The other is characteristic of sulphosalts such as those given in Table 6(*b*).

The coordinates of Cu(2) and Cu(3) are not unusual. The isotropic and anisotropic temperature factors were extremely large for Cu(1) (the root-mean-square amplitude being 0·47 Å) when one atom site was assumed. If this one position was separated into two nearly equivalent statistically occupied sites, the least-squares refinement proceeded despite the strong interaction between the atomic positions and the temperature factors. The distance between the two sites is compatible with the root-mean-square amplitude. As is seen in Table 7 the *R* index is lowest after a mixed refinement with splitting. The calculated difference syntheses confirm that the suspected splitting, *i.e.* statistical occupancy, is indeed the proper solution. The work of Kalbskopf (1972) on freibergite and the fact that such an effect has been observed in several sulphosalts lends circumstantial support to this interpretation.

The bond lengths found in the trigonal planar coordinated copper atoms in Cu_2S (Evans, 1971), wittichenite (Matzat, 1972), anilite (Koto & Morimoto, 1970), hodrushite (Kupčík & Makovický, 1968) and $Bi_2Cu_3S_4Cl$ are compared in Table 8. For discussion of anomalous Cu behaviour see Kupčík (1972).

Table 8. Cu–S *bond lengths for nearly trigonal planar-coordinated* Cu *atoms*

	Cu–S	Cu–S
Cu_2S	2·21, 2·17	2·89
	2·35, 2·27	2·43
	2·25, 2·32	2·50
Cu_3BiS_3	2·25, 2·30	2·34
	2·28, 2·25	2·34
Cu_7S_4	2·24 (2×)	2·35
(Pb, Ag, Bi)$Cu_4Bi_5S_{11}$	2·27, 2·33	2·58
$Bi_2Cu_3S_4Cl$	2·29, 2·33	2·49

Nearly linear coordination with very short Cu–S bonds has not yet been observed in sulphosalts. One is, however, reminded of the copper coordination in Cu_2O.

The calculations were performed on the UNIVAC 1108 computer at the Gesellschaft für wissenschaftliche Datenverarbeitung, Göttingen, using programs from the Mineralogisch-Kristallographische Institute Göttingen as well as the programs *ORFLS* by Busing, Martin & Levy, and *CORIN* by Paulus. We would like to express our gratitude to the Deutsche Forschungsgemeinschaft for the loan of several instruments. We are further indebted to Dr A. Schneider and Dipl. Min. J. Lange for their help with the microprobe analysis.

References

EVANS, H. T. JR (1971). *Nature, Lond.* **232**, 69–70.

HAASE-WESSEL, W. (1974). In preparation.

KALBSKOPF, R. (1972). *Miner. petrogr. Mitt.* **18**, 147–155.

KOTO, K. & MORIMOTO, N. (1970). *Acta Cryst.* **B26**, 915–924.

KUPČÍK, V. (1972). *Fortschr. Miner.* **50**, 55–56.

KUPČÍK, V. & MAKOVICKÝ, E. (1968). *Neues Jahrb. Miner. Mh.* pp. 236–237.

KUPČÍK, V. & VESELÁ-NOVÁKOVÁ, L. (1970). *Tschermaks Miner. petrogr. Mitt.* **14**, 55–59.

MATZAT, E. (1972). *Tschermaks Miner. petrogr. Mitt.* **18**, 312–316.

MIEHE, G. & KUPČÍK, V. (1971). *Naturwissenschaften*, **4**, 19.

OHMASA, M. & NOWACKI, W. (1970). *Z. Kristallogr.* **132**, 71–86.