

- COPPENS, P. (1964). *Acta Cryst.* **17**, 573–578.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- COPPENS, P., PAUTLER, D. & GRIFFIN, J. F. (1971). *J. Amer. Chem. Soc.* **93**, 1051–1058.
- COPPENS, P., SABINE, T. M., DELAPLANE, R. G. & IBERS, J. A. (1969). *Acta Cryst.* **B25**, 2451–2458.
- COPPENS, P. & VOS, A. (1971). *Acta Cryst.* **B27**, 146–158.
- COTTON, F. A. & LA PRADE, M. D. (1968). *J. Amer. Chem. Soc.* **90**, 5418–5422.
- DAVIS, R. E. & PETTIT, R. (1970). *J. Amer. Chem. Soc.* **92**, 716–717.
- DEMUYNCK, J. & VEILLARD, A. (1973). *Theor. Chim. Acta*, **28**, 241–265.
- HAALAND, A. (1965). *Acta Chem. Scand.* **19**, 41–46.
- HANSON, J. C., SIEKER, L. C. & JENSEN, L. H. (1973). *Acta Cryst.* **B29**, 797.
- HAZELRIGG, M. K. JR & POLITZER, P. (1969). *J. Phys. Chem.* **73**, 1008–1011.
- HILLIER, I. H. & SAUNDERS, V. R. (1971). *Mol. Phys.* **22**, 1025–1034.
- HODGSON, K. O. & RAYMOND, K. N. (1973). *Inorg. Chem.* **12**, 458.
- International Tables for X-ray Crystallography* (1973). Vol. IV. In preparation.
- IWATA, M. & SAITO, Y. (1972). Abstracts IX International Congress on Crystallography, Kyoto, Japan, *Acta Cryst.* **A28**, S74.
- JOHNSON, C. K. (1970). *Crystallographic Computing*, pp. 220–226. Edited by F. R. AHMED. Copenhagen: Munksgaard.
- KEULEN, E. & JELLINEK, F. (1966). *J. Organometal. Chem.* **5**, 490–492.
- LEHMANN, M. S., LARSEN, F. K. & HAMILTON, W. C. (1972). Amer. Cryst. Assoc. Meeting Abstracts, Albuquerque, New Mexico, Abstract O9.
- MANOJLOVIC-MUIR, L., MUIR, K. W. & IBERS, J. A. (1969). *Discuss. Faraday Soc.* **47**, 84–92.
- NGAI, L. H., STAFFORD, F. E. & SCHÄFER, L. (1969). *J. Amer. Chem. Soc.* **91**, 48–49.
- RANSIL, B. J. (1960). *Rev. Mod. Phys.* **32**, 245–254.
- REES, B. & COPPENS, P. (1972). *J. Organometal. Chem.* **42**, C102–C104.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- SHULL, C. G. (1972). *Compilation of Coherent Neutron Scattering Amplitudes*, M.I.T.
- SIM, G. A. (1967). *Ann. Rev. Phys. Chem.* **18**, 57–80.
- STEWART, R. F. (1970). *J. Chem. Phys.* **53**, 205–213.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- WU, A., BIEHL, E. R. & REEVES, P. C. (1972). *J. Chem. Soc. Perkin II*, pp. 449–451.

Acta Cryst. (1973). **B29**, 2528

The Crystal Structure of Wittichenite, $\text{Cu}_3\text{BiS}_3^*$

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(Received 17 April 1973; accepted 5 June 1973)

Wittichenite, Cu_3BiS_3 , from the type locality in Wittichen, West Germany is orthorhombic, $a = 7.723$ (10), $b = 10.395$ (10), $c = 6.716$ (5) Å; $D_{\text{meas}} = 6.01$, $D_{\text{calc}} = 6.11$ g cm $^{-3}$; $Z = 4$; space group $P2_12_12_1$. The structure was solved by the heavy-atom method from 695 observed symmetry-independent reflexions $F_0^2 \geq 2\sigma F_0^2$ collected on a Picker four-circle FACS-1 diffractometer using Zr-filtered Mo $K\alpha$ ($\lambda = 0.71069$ Å) radiation. Spherical absorption corrections were applied to the data ($\mu R = 10.5$) and the structure was refined by full-matrix least-squares using anisotropic temperature factors to an R value of 4.9% ($R_w = 6.7\%$). The structure consists of infinite BiCu_3S_3 chains parallel to [001] which are linked by Cu–S bonds to form continuous sheets normal to [010]. Adjacent sheets are related by the 2_1 axes parallel to [100] and are linked by Cu–S and Bi–S bonds. Cu is in nearly trigonal planar coordination with S (Cu–S distances 2.255 to 2.348 Å; S–Cu–S angles 110.8 to 131.8°). The packing of CuS_3 polyhedra in the structure yields short Cu–Cu contacts ranging from 2.61 to 2.94 Å. Bi is trigonally coordinated by S (Bi–S distances 2.569 to 2.608 Å; S–Bi–S angles 94.2 to 98.7°). S is tetrahedrally coordinated by three copper atoms and one bismuth atom.

Introduction

Wittichenite is a bismuth sulphosalt of copper, apparently first described in 1805 by Selb (Hintze, 1904)

from Wittichen in Baden, Germany, under the name Kupferwismutherz. The original chemical analysis, which established the composition as Cu_3BiS_3 , was performed by Klaproth in about 1807. Later the mineral was renamed wittichit and finally wittichenit (wittichenite) in 1853.

The early mineralogists recognized a second copper bismuth sulphosalt in the ores from Wittichen, namely

* A report of this work was presented at the American Crystallographic Association meeting, Florida, January 1973, Paper H2.

kupferwismuthglanz, later re-named emplektit (empletite), with composition CuBiS_2 . A third name, klapprothite (or klapprotholite), thought to represent a compound of composition $\text{Cu}_6\text{Bi}_4\text{S}_9$, arose from investigations of the ores from the Daniel Mine in Wittichen. Detailed study (Nuffield, 1947) has shown that specimens labelled klapprothite from Wittichen are mixtures of wittichenite and empletite and examination of specimens labelled klapprothite from elsewhere have not confirmed the existence of klapprothite.

A morphological and X-ray study of a well-developed crystal of wittichenite by Nuffield (1947) established the space group as $P2_12_12_1$ and provided the cell dimensions $a=7.68$, $b=10.33$, $c=6.70$ Å. Material synthesized by fusion of the elements in the course of the study gave a measured density of 6.19, compared with 6.01 measured by Fronzel (Dana, 1944) on natural wittichenite labelled klapprothite, and 6.19 calculated for the cell with $4[\text{Cu}_3\text{BiS}_3]$.

Wittichenite has a metallic lustre. It breaks with a good conchoidal fracture. No cleavage has been observed. Face development is rare. The morphological habit is prismatic parallel to $[001]$.

Experimental

The present study was undertaken on a specimen from the Daniel Mine in the type locality of Wittichen (Royal Ontario Museum specimen M 23304) on which a few rough, short-prismatic and heavily striated crystals of wittichenite were identified. An electron microprobe analysis of material selected from this specimen gave values which are in excellent agreement with the ideal composition, Cu_3BiS_3 (Table 1).

Table 1. *Electron microprobe analysis of wittichenite from the Daniel Mine, Wittichen*

	wt. %	Atomic proportions	
		Actual	Ideal
Cu	37.79	2.98	3
Bi	42.56	1.02	1
S	19.13	2.99	3

Total 99.48.

Analyst: Elvira Gasparri.

Because of the irregular shape of the crystals and the high value of the linear absorption coefficient (440.2 cm^{-1} for $\text{Mo } K\alpha$), it was decided to grind spheres and apply spherical absorption corrections. The crystal that was finally used for data collection had a mean diameter of 0.46 mm and was spherical to within 0.04 mm of this value. The main deviation from sphericity was between the poles which were slightly flattened due to remnant $\{001\}$ faces.

Lattice parameters were calculated from a number of high- θ reflexions measured on zero-layer Weissenberg and precession films, calibrated with copper powder lines and extrapolated to $\theta=90^\circ$ against the absorption function of Nelson & Riley (1945):

$$a=7.723 (10), \quad b=10.395 (10), \quad c=6.716 (5) \text{ \AA}.$$

The calculated density for the new cell dimensions and the ideal cell contents $4[\text{Cu}_3\text{BiS}_3]$, is 6.11 g cm^{-3} .

Intensity data were collected on a Picker four-circle FACS-1 diffractometer in the $\theta-2\theta$ scan mode up to 55° in 2θ , using Zr-filtered $\text{Mo } K\alpha$ ($\lambda=0.71069$ Å) radiation. A scan rate of $0.5^\circ \text{ min}^{-1}$ with a 40 s background count on each side of the peak was used to improve the counting statistics of the weaker reflexions. Copper foil attenuators were automatically inserted into the diffracted beam whenever the counting rate exceeded 10000 c.p.s. The intensities of two standard reflexions were monitored every 40 reflexions. The variation throughout the data collection was less than 1.5%.

In total, 722 symmetry-independent reflexions were collected. The data were scaled by reference to the standard reflexions and corrected for Lorentz and polarization factors. The spherical absorption factors calculated by Weber (1969) for a μR value of 10.5 were applied to the data. A total of 695 intensities had $|F^2| \geq 2\sigma|F^2|$.

Determination and refinement of the structure

The position of Bi was obtained from a three-dimensional Patterson map. The remainder of the structure was solved by conventional heavy-atom methods.

Structure factor calculations with the Bi position gave $R=0.39$, where R is defined as: $\sum||F_o| - |F_c|| / \sum|F_o|$. A subsequent F_o Fourier map revealed one Cu and the three S positions. The other two Cu positions were

Table 2. *Fractional coordinates and temperature factors*

Fractional coordinates and anisotropic thermal parameters $\times 10^5$; values in parentheses are estimated standard deviations as obtained from the last cycle of least-squares refinement;

$$T = \exp [- (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$B (\text{\AA}^2)$
Bi	19716 (10)	-24401 (7)	12860 (12)	230 (15)	314 (8)	856 (20)	-20 (8)	33 (12)	-2 (10)	1.24
Cu(1)	35179 (52)	40167 (37)	13762 (56)	852 (64)	689 (34)	1069 (74)	346 (36)	22 (60)	41 (47)	2.10
Cu(2)	19037 (84)	10470 (43)	7838 (60)	2433 (113)	720 (40)	914 (72)	590 (61)	312 (88)	234 (47)	2.75
Cu(3)	5727 (44)	46445 (35)	-2628 (59)	403 (53)	487 (31)	1552 (82)	66 (32)	257 (60)	-36 (43)	1.87
S(1)	-44584 (78)	24619 (57)	10918 (83)	433 (90)	364 (47)	705 (109)	8 (56)	-164 (82)	25 (73)	1.32
S(2)	-31767 (82)	43669 (56)	-40779 (92)	325 (85)	338 (44)	752 (126)	52 (55)	8 (105)	-36 (60)	1.47
S(3)	-32136 (83)	6949 (53)	-41380 (86)	370 (87)	276 (42)	626 (120)	23 (52)	2 (100)	-78 (56)	1.49

located from a second Fourier map calculated with refined phases. Four cycles of XFLS (Ellison, 1962) isotropic least-squares refinement with all atoms in the structure-factor calculation reduced the R value to

0.08. At this stage corrections for anomalous dispersion were introduced using the values computed by Cromer (1965). Two cycles of anisotropic least-squares refinement brought the R value to 0.05. The scattering

Table 3. Comparison of observed and calculated structure factors listed as 10F_o and 10F_c

Unobserved values indicated by an asterisk. Phase angles are in millicycles.

Table with multiple columns (L, FD, FC, ALPHA) and rows of numerical data representing structure factors. Includes sub-headers for L, FD, FC, ALPHA and values for observed (10F_o) and calculated (10F_c) factors.

factors used in these calculations were taken from Cromer & Mann (1968).

The initial weights of the structure factors were derived from the counting statistics as described by Stout & Jensen (1968). However, the standard deviation of an observation of unit weight calculated from the expression

$$S_1 = [\sum w \Delta F^2 / (m - n)]^{1/2}$$

in which w is the weight, m the number of observations and n the number of parameters varied in the least-squares refinement, had a value of 2.52 indicating slight errors in the assignment of the weights to the structure factors. A plot of $\overline{\Delta F_o}/\overline{F_o}$ vs. $1/\overline{F_o}$ for groups of 50 reflexions was fitted by a least-squares routine to a second order polynomial from which the expression $(0.039F_o + 1.30 + 24.37/F_o)$ was derived for σ_{F_o} and used in the final weighting scheme, $w = 1/\sigma_{F_o}^2$. Extra cycles of anisotropic refinement with new weights converged to $R = 0.049$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.067$. The final value of S_1 equalled 1.06.

A difference Fourier map revealed an excess electron density of about $2.8 \text{ e } \text{Å}^{-3}$ in the vicinity of the Bi atom, the actual centre of the atom being located at $+1.5 \text{ e } \text{Å}^{-3}$. The remainder of the map did not reveal any anomalies.

The atomic positional parameters and their corresponding temperature factors are listed in Table 2. The comparison of observed and calculated structure factors is given in Table 3.

An attempt to establish the absolute configuration of the structure (Ibers & Hamilton, 1964), resulted in $R = 0.048$ for the enantiomorph. The ratio R_1/R_2 is 1.02 and according to Hamilton's (1965) significance test, the value, $\mathcal{R}_{1.632, 0.01} = 1.005$, indicates that the enantiomorph can be accepted as a correct model at a 0.01 significance level. However, the result of the test should be treated with some reservation in the present case. Because Bi is a strong anomalous scatterer (Mo $K\alpha$, $\Delta f' = -4.54$, $i\Delta f'' = 10.65$), one would expect a more pronounced difference between the two R values. The explanation for the small difference must lie in the

material itself. Wittichenite, like most sulphosalt minerals, has a non-uniform mosaic spread over the volume of the crystal. This is likely to produce systematic errors in the intensities of some reflexions. The configuration shown here (Table 2) is the one which corresponds to the higher R value.

Discussion of the structure

Tables 4 and 5 give, respectively, the interatomic distances and angles in the wittichenite structure and their estimated standard deviations as calculated from the ORFFE (Busing, Martin & Levy, 1964) program. The

Table 5. *Interatomic angles*

Estimated standard deviation of all angles is $0.5^\circ(2\sigma)$

Metal-atom polyhedra	Bi	S(1 ^{iv})—Bi—S(2 ^{iv})	98.7°
		S(1 ^{iv})—Bi—S(3 ^{iv})	94.2
		S(2 ^{iv})—Bi—S(3 ^{iv})	95.2
	Cu(1)	S(1 ^{iv})—Cu(1)—S(3 ^{iv})	124.2
		S(1 ^{iv})—Cu(1)—S(3 ^{iv})	123.7
		S(3 ^{iv})—Cu(1)—S(3 ^{iv})	111.4
	Cu(2)	S(1 ⁱⁱⁱ)—Cu(2)—S(2 ⁱⁱⁱ)	131.8
		S(1 ⁱⁱⁱ)—Cu(2)—S(2 ^{iv})	116.2
		S(2 ⁱⁱⁱ)—Cu(2)—S(2 ^{iv})	110.8
	Cu(3)	S(1 ⁱⁱⁱ)—Cu(3)—S(2 ⁱⁱ)	121.2
		S(1 ⁱⁱⁱ)—Cu(3)—S(3 ^{iv})	114.7
		S(2 ⁱⁱ)—Cu(3)—S(3 ^{iv})	124.0
Sulphur-atom polyhedra	S(1)	Bi ^{iv} —S(1)—Cu(1 ⁱ)	115.2
		Bi ^{iv} —S(1)—Cu(2 ⁱⁱⁱ)	90.4
		Bi ^{iv} —S(1)—Cu(3 ⁱⁱⁱ)	101.3
		Cu(1 ⁱ)—S(1)—Cu(2 ⁱⁱⁱ)	83.0
		Cu(1 ⁱ)—S(1)—Cu(3 ⁱⁱⁱ)	136.3
		Cu(2 ⁱⁱⁱ)—S(1)—Cu(3 ⁱⁱⁱ)	121.5
	S(2)	Bi ^{iv} —S(2)—Cu(2 ⁱⁱⁱ)	114.7
		Bi ^{iv} —S(2)—Cu(2 ^{iv})	96.5
		Bi ^{iv} —S(2)—Cu(3 ⁱⁱⁱ)	115.2
		Cu(2 ⁱⁱⁱ)—S(2)—Cu(2 ^{iv})	128.3
		Cu(2 ⁱⁱⁱ)—S(2)—Cu(3 ⁱⁱⁱ)	117.0
		Cu(2 ^{iv})—S(2)—Cu(3 ⁱⁱⁱ)	80.2
	S(3)	Bi ^{iv} —S(3)—Cu(1 ⁱⁱⁱ)	97.8
		Bi ^{iv} —S(3)—Cu(1 ^{iv})	103.8
		Bi ^{iv} —S(3)—Cu(3 ^{iv})	86.1
		Cu(1 ⁱⁱⁱ)—S(3)—Cu(1 ^{iv})	132.8
		Cu(1 ⁱⁱⁱ)—S(3)—Cu(3 ^{iv})	72.2
		Cu(1 ^{iv})—S(3)—Cu(3 ^{iv})	68.1

Table 4. *Interatomic distances*

Symmetry positions: i x, y, z ; ii $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$; iii $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$; iv $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$.
Estimated standard deviations in parentheses.

	Bi	Cu(1)	Cu(2)	Cu(3)
Metal-atom polyhedra	S(1 ^{iv}) 2.608 (6) Å	S(1 ⁱ) 2.256 (7) Å	S(1 ⁱⁱⁱ) 2.257 (7) Å	S(1 ⁱⁱⁱ) 2.259 (7) Å
	S(2 ^{iv}) 2.569 (6)	S(3 ⁱⁱⁱ) 2.306 (7)	S(2 ⁱⁱⁱ) 2.255 (8)	S(2 ⁱⁱ) 2.261 (7)
	S(3 ^{iv}) 2.600 (6)	S(3 ^{iv}) 2.314 (7)	S(2 ^{iv}) 2.309 (7)	S(3 ^{iv}) 2.348 (8)
Sulphur-atom polyhedra	S(1)	S(2)	S(3)	
	Bi ^{iv} 2.608 (6) Å	Bi ^{iv} 2.569 (6) Å	Bi ^{iv} 2.600 (6) Å	
	Cu(1 ⁱ) 2.256 (7)	Cu(2 ⁱⁱⁱ) 2.255 (8)	Cu(1 ⁱⁱⁱ) 2.306 (7)	
	Cu(2 ⁱⁱⁱ) 2.257 (7)	Cu(2 ^{iv}) 2.309 (7)	Cu(1 ^{iv}) 2.314 (7)	
	Cu(3 ⁱⁱⁱ) 2.259 (7)	Cu(3 ⁱⁱⁱ) 2.261 (7)	Cu(3 ^{iv}) 2.348 (8)	
Shortest metal-metal distances	Bi—Bi ⁱⁱⁱ 4.232 (1) Å			
	Cu(1)—Cu(3 ⁱ) 2.610 (5)			
	Cu(2)—Cu(3 ⁱⁱⁱ) 2.944 (8)			
	Cu(3)—Cu(1 ⁱ) 2.743 (6)			

Table 6. Average Cu-S distances and average S-Cu-S angles in Cu-S_3 polyhedra, and deviations of the polyhedra from planarity

Average Cu-S distances	Average S-Cu-S angles	Atoms in the plane*	Atoms out of the plane	A	B	C	D
2.292 Å	119.8°	S(1) [†] , S(3 ^{III}), S(3 ^{IV})	Cu(1) 0.101 Å	-0.692	-0.552	-0.465	4.717
2.274	119.6	S(1 ^{III}), S(2 ^{III}), S(2 ^{IV})	Cu(2) -0.150	-0.849	-0.526	-0.058	1.699
2.289	120.0	S(1 ^{III}), S(2 ^{IV}), S(3 ^{IV})	Cu(3) 0.029	-0.290	0.226	-0.929	-1.157

* The equation of the plane is $Ax + By + Cz + D = 0$.

† The symmetry code is the same as in Table 4.

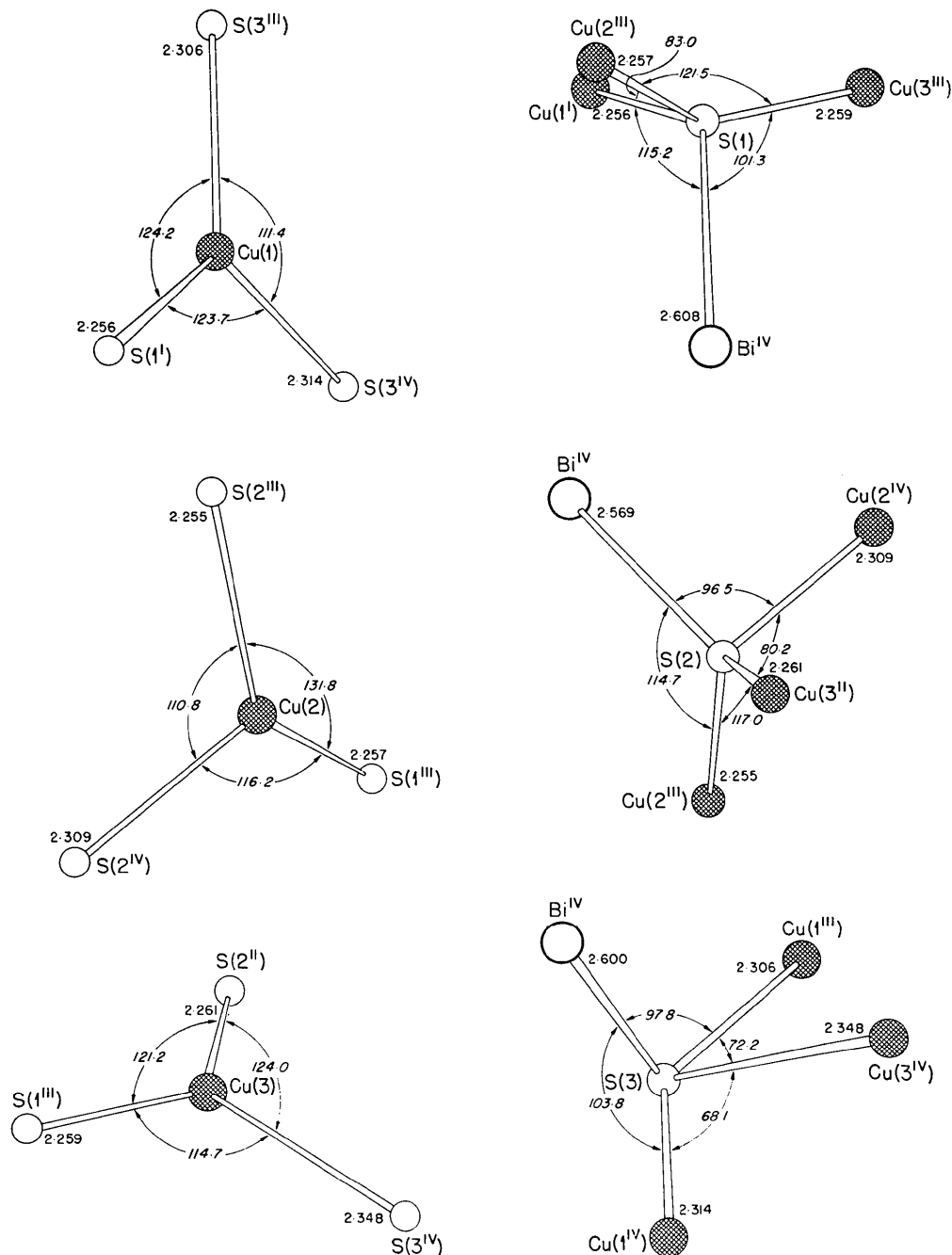


Fig. 1. Cu in trigonal planar coordination with S. Coordination of 3Cu and 1Bi about S.

standard deviations include the errors in cell parameters.

All Cu atoms are in nearly trigonal planar coordination with S. The Cu-S distances range from 2.255 to 2.348 Å and the S-Cu-S angles from 110.8 to 131.8° (Fig. 1). Table 6 gives the averages of these values and the offset of the Cu atom from the S plane for each of the three CuS₃ polyhedra. Although Cu is usually tetrahedrally coordinated by S in the ore minerals, trigonal coordination has been observed in a few structures including low-chalcite Cu₂S (Evans, 1971), the unnamed PbCu₄Bi₅S₁₁ (Kupčík & Makovický, 1968),

and the isostructural compounds binnite Cu₁₂As₄S₁₃ (Wuensch, Takéuchi & Nowacki, 1966) and tetrahedrite Cu₁₂Sb₄S₁₃ (Wuensch, 1964). The Cu-S distances in the CuS₃ polyhedra in these minerals vary between 2.20 and 2.89 Å with an average of about 2.28 Å. The wittichenite values are, therefore, normal.

The Bi atom and its three closest S neighbours occupy the corners of a trigonal pyramid with Bi at the vertex (Fig. 2). The Bi-S bond lengths are 2.569, 2.600 and 2.608 Å; the S-Bi-S angles are nearly orthogonal, ranging from 94.2 to 98.7°. More distant S neighbours occur at 3.434 Å and beyond this value (Table 7).

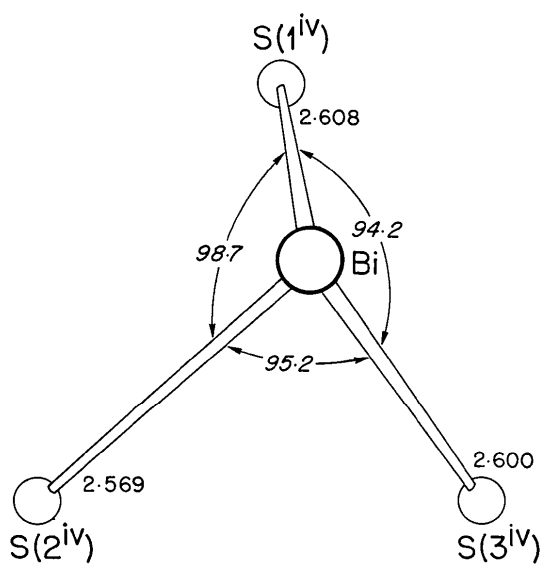


Fig. 2. Bi in trigonal pyramidal coordination with S.

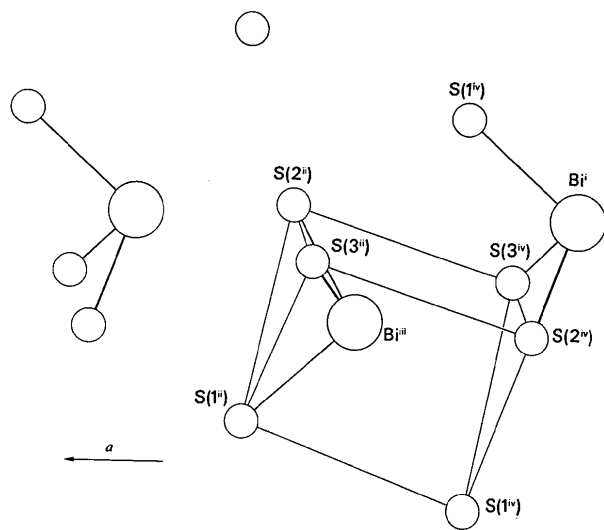


Fig. 3. Arrangement of Bi along [100]. Bi-Bi = 4.232 Å. Biⁱⁱⁱ-S distances: S(2ⁱⁱ) 2.569, S(3ⁱⁱ) 2.600, S(1ⁱⁱ) 2.608, S(3^{iv}) 3.434, S(2^{iv}) 3.558, S(1^{iv}) 3.766, 3.992 Å.

Table 7. Closest S neighbours to Bi

Bi at $x=0.20, y=0.76, z=0.13$.			
No.	S	z^*	Bi-S
1	2 ^{iv}	-0.09	2.569 Å†
2	3 ^{iv}	-0.09	2.600
3	1 ^{iv}	0.39	2.608
4	3 ⁱⁱ	0.09	3.434
5	2 ⁱⁱ	0.09	3.558
6	2 ⁱⁱⁱ	0.41	3.706
7	1 ⁱⁱ	0.61	3.766
8	3 ⁱⁱⁱ	0.41	3.891
9	1 ⁱⁱ	-0.39	3.992

* Fractional coordinates of S atoms.

† E.s.d. 0.006-0.007 Å.

Kohatsu & Wuensch (1971) have compared the coordination of Bi in the known bismuth ore mineral structures. Three short (2.7 ± 0.15 Å), nearly orthogonal Bi-S bonds may be identified in all the structures. Three or four more distant S neighbours are also present of which the fourth and fifth S atoms at distances of 3.0 ± 0.15 Å usually complete a square pyramid about the Bi atom. When the fourth and fifth S atoms are taken into account, a square pyramid of S atoms about Bi can also be observed in wittichenite. However, the coordination of S about Bi in wittichenite has certain unique features. Firstly, the three nearest S atoms are closer to the Bi atom than in the other structures and secondly, the first of the more distant neighbours is at 3.43 Å, rather than at about 3.0 Å. The Bi coordination in wittichenite is, therefore, more rigorously trigonal and resembles the coordination which is characteristic for S about As and to a lesser extent about Sb, in the sulphosalts in which these semi-metals prevail.

The shortest Bi-Bi contacts (4.232 Å) are in the (010) plane in which Bi is arranged in a zigzag fashion parallel to [100]. The BiS₃ polyhedra along such a row point in the same direction and may be pictured as loosely connected into a chain in which each Bi atom shares two of its three closest S atoms with one other Bi atom (Fig. 3). The coordinating S polyhedra have the form of trigonal prisms which are joined by sharing an edge in the basal plane. In such a prism, the Bi atom has three close and three considerably more distant S neighbours (atoms 4, 5 and 7 of Table 7) at 3.434, 3.558 and 3.766 Å.

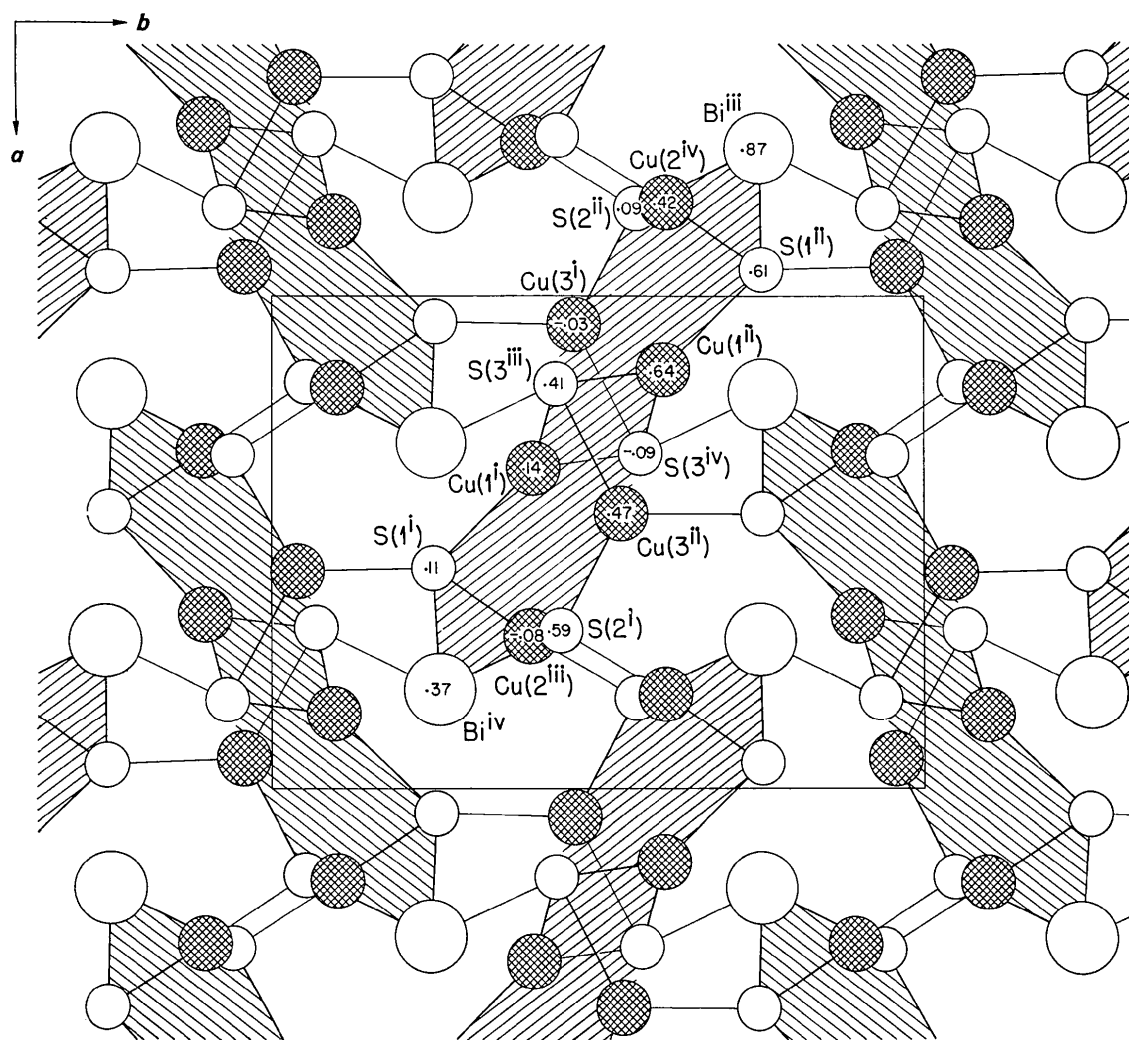


Fig. 4. Projection of the wittichenite structure on (001). Fractional coordinates are given for one chain.

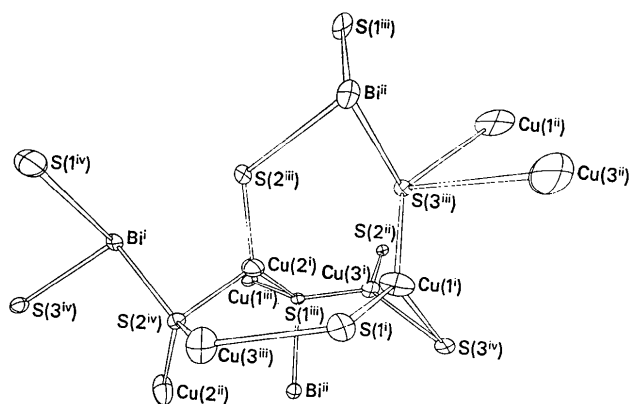


Fig. 5. ORTEP plot of part of wittichenite structure showing anisotropic thermal vibrations of the atoms drawn with 50% probability.

Each S atom coordinates one Bi and three Cu atoms (Fig. 1). The metal–S–metal angles given in Table 5 indicate a wide departure from the ideal tetrahedral bond angle of $109^{\circ}28'$. A comparison of the mean S–Bi and S–Cu bond lengths in wittichenite with the sums of the corresponding covalent, tetrahedral radii (Evans, 1964) shows that S–Bi distances are slightly longer and S–Cu distances slightly shorter than the sums.

	Mean S–metal distances in wittichenite	Sum of tetrahedral covalent radii (Evans, 1964)
S–Bi	2.59 Å	2.50 Å
S–Cu	2.29	2.39

Fig. 4 is a projection of the structure of wittichenite on (001). The most prominent and distinct structural feature is a series of infinite BiCu_3S_3 chains extending

parallel to [001]. Each chain is symmetrical about a central 2_1 axis. The chains are situated with the intermediate dimension, which is about 10.4 Å in length, parallel to (120) or $(1\bar{2}0)$. Parallel chains are linked by Cu-S bonds at intervals of 3.36 Å along [001] and overlap slightly to form continuous sheets normal to [010]. Adjacent sheets are related by 2_1 axes parallel to [100] and linked by Cu-S and Bi-S bonds. The two types of bond alternate along [100] at intervals of $\frac{1}{2}a$ and occur at intervals of $1c$ along [001]. The unit cell contains two sheets.

The three kinds of Cu_3S_3 polyhedron have distinctly different functions in the structure. The Cu(1) polyhedra form the cores of the chains and lie entirely within individual chains. Only two S atoms of each Cu(2) polyhedron lie in the same chain; the third S is in an overlapping chain and therefore the Cu(2) polyhedra link the chains into sheets. Similarly, only two S atoms of each Cu(3) polyhedron are in the same chain; the third S is in the chain of an adjacent sheet. Thus the Cu(3) polyhedra assist in binding the sheets into a three-dimensional structure.

The structure of wittichenite bears a resemblance to other sulphosalt structures that consist of frameworks of complex, essentially discrete chains (e.g. aikinite, PbCuBiS_3), but the similarity is superficial. The wittichenite chains are basically Cu_3S_3 in composition and characterized by trigonal planar coordination of S about Cu (Fig. 5). The more common coordination in sulphosalts is tetrahedral.

We wish to express our thanks to Miss Elvira Gasparini for the electron microprobe analysis, to Dr J. Mandarino of the Royal Ontario Museum for the loan of a specimen, to Dr Klaus Dichmann for providing us with the weighting program and to the National Research Council for a grant (to E.W.N.) to support the work.

Note added in proof:— A short account of an independent solution of the structure of wittichenite has recently

been given by Matzat (1972). The refinement was carried to an R value of 13.5% with isotropic temperature factors. The interatomic distances and angles are in substantial agreement with our values.

References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
- DANA, J. D. & DANA, E. S. (1944). In *Syste uof Mineralogy*. Vol. 1, 7th ed., p. 418. Edited by C. PALACHE, H. BERMAN & C. FRONDEL. New York: John Wiley.
- ELLISON, R. D. (1962). An extensively modified version of *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- EVANS, H. T. JR (1971). *Nature Phys. Sci.* **232**, 69–70.
- EVANS, R. C. (1964). *Crystal Chemistry*. 2nd ed. Cambridge Univ. Press.
- HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.
- HINTZE, C. (1904). *Handbuch der Mineralogie*. Vol. 1, part 1, p. 1120.
- IBERS, J. & HAMILTON, W. C. (1964). *Acta Cryst.* **17**, 781–782.
- KOHATSU, I. & WUENSCH, B. J. (1971). *Acta Cryst.* **B27**, 1245–1252.
- KUPČÍK, V. & MAKOVICKÝ, E. (1968). *Neues Jb. Miner. Mh.* **7**, 236–237.
- MATZAT, E. (1972). *Tschermaks Min. Petrogr. Mitt.* **18**, 312–316.
- NELSON, J. B. & RILEY, D. P. (1945). *Proc. Phys. Soc.* **57**, 160–177.
- NUFFIELD, E. W. (1947). *Econ. Geol.* **42**, 147–160.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 457. New York: Macmillan.
- WEBER, K. (1969). *Acta Cryst.* **B25**, 1174–1178.
- WUENSCH, B. J. (1964). *Z. Kristallogr.* **119**, 437–453.
- WUENSCH, B. J., TAKÉUCHI, Y. & NOWACKI, W. (1966). *Z. Kristallogr.* **123**, 1–20.