

The Crystal Structure of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ and its Relation to the Structures of Hodrushite and Cuprobismutite

BY K. MARIOLACOS, V. KUPČÍK, MASA AKI OHMASA AND G. MIEHE

Mineralogisch-Kristallographisches Institut der Universität Göttingen, D-3400 Göttingen, Germany (BRD)

(Received 11 September 1974; accepted 14 October 1974)

The crystal structure of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ has been determined from three-dimensional intensity data. Two formula units are contained in a monoclinic cell, space group $C2/m$, with $a_0 = 17.539$ (3), $b_0 = 3.931$ (13), $c_0 = 12.847$ (3) Å and $\beta = 108.0$ (1)°. The structure was solved by Patterson, Fourier and difference syntheses, and was then refined by least-squares calculations. The final discrepancy index for all 796 independent reflexions is 12.2%. Bismuth atoms have both octahedral and tetragonal pyramidal coordinations, and Cu atoms are surrounded by four S atoms. Two of the cell constants of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ are similar to those of hodrushite, $\text{MBi}_5\text{Cu}_4\text{S}_{11}$ [M: Bi, Fe, Pb; Kupčík, V. & Makovický, E. (1968). *Neues Jb. Miner. Mh.* pp. 236–237], and of cuprobismutite [Nuffield, E. W. (1952). *Amer. Min.* 37, 447–452]. From the relation between the structures of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ and hodrushite, the structure of cuprobismutite was proposed. The coincidence between observed and calculated intensities of the powder data is satisfactory. These three substances are described as layer structures. Both $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ and cuprobismutite have single-layer structures, and hodrushite has a double-layer structure and contains one layer of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ and one layer of cuprobismutite.

Experimental

In a systematic investigation involving synthetic and crystallographic studies of the Pb–Cu–Bi–S system, a new compound has been obtained. The material was synthesized by a chemical transport reaction by the method of Rabenau & Rau (1969). A powder of 3 parts PbS, 5 parts Bi_2S_3 and 1 part Cu_2S was mechanically mixed to form the charge for this synthesis. This mixed sulphide was sealed in a silica glass tube together with a transport material (0.1N HCl solution). The tube, which was tilted at 20° from the horizontal, was

kept at $340 \pm 10^\circ\text{C}$ with a temperature gradient of 10°C for 11 days. In the product, larger crystals of Bi_2S_3 ($\sim 200 \times 200 \times 800 \mu\text{m}$) with small amounts of Pb and Cu, and fine needles of a new compound ($\sim 6 \times 6 \times 200 \mu\text{m}$) were found. The chemical composition of this new compound was determined by electron microprobe analyses as $\text{Cu}_4\text{Bi}_5\text{S}_{10}$.

A crystal of size $7 \times 7 \times 250 \mu\text{m}$ was selected. Weissenberg photographs were measured and these data were used to refine the cell constants by a least-squares method. These cell constants are similar to those predicted by Koderá, Kupčík & Makovický (1970). The only observed systematic absence is hkl with $h+k \neq 2n$, which indicates $C2$ (No. 5), Cm (No. 8) and $C2/m$ (No. 12) as possible space groups.

Crystal data

$\text{Cu}_4\text{Bi}_5\text{S}_{10}$, monoclinic, space group $C2/m$. $a_0 = 17.539 \pm 0.003$, $b_0 = 3.931 \pm 0.013$, $c_0 = 12.847 \pm 0.003$ Å; $\beta = 108.0 \pm 0.1^\circ$; $Z = 2$; $D_{\text{calc}} = 6.39 \text{ g cm}^{-3}$; $\mu = 1154 \text{ cm}^{-1}$ (Cu $K\alpha$ radiation). The elongation axis is [010].

The intensities were collected from layers $h0l$ to $h3l$ by an automatic Weissenberg diffractometer (STADI-2 system of Stoe) with Ni-filtered Cu radiation. Because the crystal was very small, diffracted intensities were rather weak. Therefore the intensities of the independent reflexions were measured twice to minimize the error of the measurements. The two sets of data were averaged, and then corrected for the Lorentz–polarization factor. No absorption correction was made, because μr was about 0.4. Of the 796 observed reflexions, 105 had an intensity lower than $2\sigma(I)$ and were considered as unobserved. For an unobserved reflexion, $\sigma(F)/3$ was assigned as F observed.

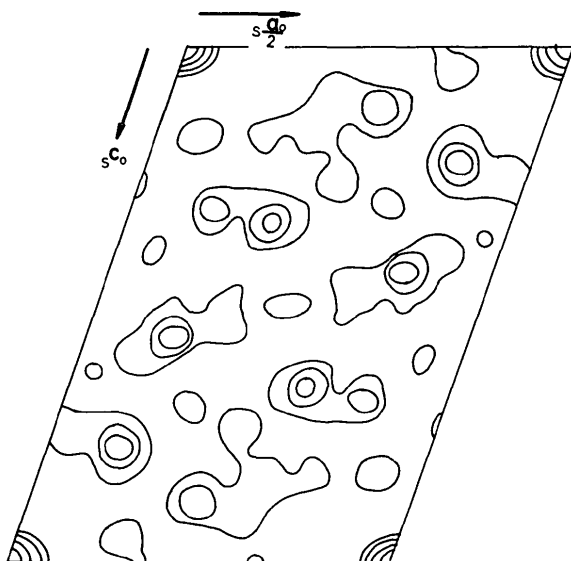


Fig. 1. Patterson projection $P(uw)$ of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$.

Structure determination

The reflexions from the layers with $k = 2n$ ($n = 0, 1$) show approximately the same intensity distributions. The intensity distributions of the odd layers are similar to each other, but different from those of even layers. This feature suggests that most atoms should be on the planes $y=0$ and $\frac{1}{2}$, and that $C2$ could be omitted as a possible space group. Cm was also excluded by the interpretation of the Patterson projection, $P(uw)$ (Fig. 1). The x and z parameters of the heavy atoms (bismuth) were determined from $P(uw)$, and those of the copper and the sulphur atoms were found from the succeeding Fourier and difference syntheses. The y parameters of the atoms, which are either 0 or $\frac{1}{2}$, were determined from generalized projections $P_1(uw)$ and $g_1(xz)$. The discrepancy index R at this stage was 20%. The positional parameters and isotropic temperature factors of the atoms were refined by the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962). Scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1968) were used. Individual weights, $1/\sigma^2(F_o)$, based on counting statistics were used during the refinements. The final discrepancy index $R = \sum\{|F_o| - |F_c|\}/\sum|F_o|$ was 12.2%, and the weighted discrepancy index $R' = \{\sum w(|F_o| - |F_c|)^2\}^{1/2}/\{\sum w|F_o|^2\}^{1/2}$ was 8.3% for all 796 reflexions, and 10.6% and 8.1% respectively when unobserved reflexions were excluded. A three-dimensional difference synthesis showed no significant anomaly at this stage. Refinements of anisotropic temperature factors were not made, because the very low diffracted intensities from the crystal were expected to contain rather high experimental errors.

The atomic positions and the isotropic temperature factors are listed in Table 1. The observed and the calculated structure factors are presented in Table 2.

Table 1. *Fractional coordinates and temperature factors*
Estimated standard deviations in parentheses.

	x	y	z	B
Bi(1)	0	0	0	1.43 (7)
Bi(2)	0.1963 (2)	0	0.3427 (2)	2.28 (6)
Bi(3)	0.4127 (2)	0	0.2240 (2)	2.26 (6)
Cu(1)	0.2076 (7)	$\frac{1}{2}$	0.0608 (9)	4.16 (25)
Cu(2)	0.4018 (6)	$\frac{1}{2}$	0.4736 (8)	3.23 (22)
S(1)	0.0443 (8)	$\frac{1}{2}$	0.1684 (11)	0.15 (25)
S(2)	0.2586 (8)	$\frac{1}{2}$	0.2452 (11)	0.46 (26)
S(3)	0.3364 (8)	0	0.4962 (11)	0.29 (25)
S(4)	0.3463 (9)	$\frac{1}{2}$	0.0268 (12)	0.83 (28)
S(5)	0.4818 (8)	$\frac{1}{2}$	0.3613 (13)	0.42 (26)

Description of the structure

The structure of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ is illustrated in Fig. 2. The interatomic distances are given in Table 3 and the bond angles are given in Table 4.

Bi(1) is at the origin of the unit cell, and is surrounded by six sulphur atoms in octahedral coordination. An octahedral coordination of bismuth in sulphosalts has also been found in the structures of hodrushite

and CuBi_5S_8 (Ohmura & Nowacki, 1973). The other two bismuth atoms, Bi(2) and Bi(3), occupy distorted tetragonal pyramids with five sulphur atoms. Of the five distances, three distances (~ 2.7 Å) are shorter than the other two (~ 3.0 Å). This coordination around bismuth is the one typically found in sulphosalts structures (Kupčik, 1972).

Cu(1) is surrounded by three sulphur atoms in a

Table 2. *Observed and calculated structure factors*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	1	23	19	12	0	0	85	89	7	1	1	316	366
0	0	2	42	77	12	0	0	77	79	7	1	2	192	197
0	0	3	294	211	12	0	0	332	345	7	1	3	118	115
0	0	4	304	305	12	0	0	41	41	7	1	4	432	431
0	0	5	295	201	12	0	0	74	74	7	1	5	24	24
0	0	6	280	279	12	0	0	70	70	7	1	6	261	251
0	0	7	261	261	12	0	0	177	177	7	1	7	679	683
0	0	8	196	183	12	0	0	179	175	7	1	8	58	58
0	0	9	196	183	12	0	0	179	175	7	1	9	127	126
0	0	10	230	201	12	0	0	221	221	7	1	10	117	116
0	0	11	111	103	12	0	0	109	109	7	1	11	87	82
0	0	12	111	103	12	0	0	109	109	7	1	12	112	112
0	0	13	137	131	12	0	0	208	204	7	1	13	112	109
0	0	14	137	131	12	0	0	208	204	7	1	14	29	29
0	0	15	135	129	12	0	0	191	187	7	1	15	113	113
0	0	16	135	129	12	0	0	191	187	7	1	16	113	113
0	0	17	149	141	12	0	0	215	215	7	1	17	141	141
0	0	18	149	141	12	0	0	215	215	7	1	18	141	141
0	0	19	167	160	12	0	0	237	237	7	1	19	167	167
0	0	20	167	160	12	0	0	237	237	7	1	20	167	167
0	0	21	221	207	12	0	0	243	243	7	1	21	221	221
0	0	22	221	207	12	0	0	243	243	7	1	22	221	221
0	0	23	221	207	12	0	0	243	243	7	1	23	221	221
0	0	24	221	207	12	0	0	243	243	7	1	24	221	221
0	0	25	221	207	12	0	0	243	243	7	1	25	221	221
0	0	26	221	207	12	0	0	243	243	7	1	26	221	221
0	0	27	221	207	12	0	0	243	243	7	1	27	221	221
0	0	28	221	207	12	0	0	243	243	7	1	28	221	221
0	0	29	221	207	12	0	0	243	243	7	1	29	221	221
0	0	30	221	207	12	0	0	243	243	7	1	30	221	221
0	0	31	221	207	12	0	0	243	243	7	1	31	221	221
0	0	32	221	207	12	0	0	243	243	7	1	32	221	221
0	0	33	221	207	12	0	0	243	243	7	1	33	221	221
0	0	34	221	207	12	0	0	243	243	7	1	34	221	221
0	0	35	221	207	12	0	0	243	243	7	1	35	221	221
0	0	36	221	207	12	0	0	243	243	7	1	36	221	221
0	0	37	221	207	12	0	0	243	243	7	1	37	221	221
0	0	38	221	207	12	0	0	243	243	7	1	38	221	221
0	0	39	221	207	12	0	0	243	243	7	1	39	221	221
0	0	40	221	207	12	0	0	243	243	7	1	40	221	221
0	0	41	221	207	12	0	0	243	243	7	1	41	221	221
0	0	42	221	207	12	0	0	243	243	7	1	42	221	221
0	0	43	221	207	12	0	0	243	243	7	1	43	221	221
0	0	44	221	207	12	0	0	243	243	7	1	44	221	221
0	0	45	221	207	12	0	0	243	243	7	1	45	221	221
0	0	46	221	207	12	0	0	243	243	7	1	46	221	221
0	0	47	221	207	12	0	0	243	243	7	1	47	221	221
0	0	48	221	207	12	0	0	243	243	7	1	48	221	221
0	0	49	221	207	12	0	0	243	243	7	1	49	221	221
0	0	50	221	207	12	0	0	243	243	7	1	50	221	221
0	0	51	221	207	12	0	0	243	243	7	1	51	221	221
0	0	52	221	207	12	0	0	243	243	7	1	52	221	221
0	0	53	221	207	12	0	0	243	243	7	1	53	221	221
0	0	54	221	207	12	0	0	243	243	7	1	54	221	221
0	0	55	221	207	12	0	0	243	243	7	1	55	221	221
0	0	56	221	207	12	0	0	243	243	7	1	56	221	221
0	0	57	221	207	12	0	0	243	243	7	1	57	221	221
0	0	58	221	207	12	0	0	243	243	7	1	58	221	221
0	0	59	221	207	12	0	0	243	243	7	1	59	221	221
0	0	60	221	207	12	0	0	243	243	7	1	60	221	221
0	0	61	221	207	12	0	0	243	243	7	1	61	221	221
0	0	62	221	207	12	0	0	243	243	7	1	62	221	221
0	0	63	221	207	12	0	0	243	243	7	1	63	221	221
0	0	64	221	207	12	0	0	243	243	7	1	64	221	221
0	0	65	221	207	12	0	0	243	243	7	1	65	221	221
0	0	66	221	207	12	0	0	243	243	7	1	66	221	221
0	0	67	221	207	12	0	0	243	243	7	1	67	221	221
0	0	68	221	207	12	0	0	243	243	7	1	68	221	221
0	0	69	221	207	12	0	0	243	243	7	1	69	221	221
0	0	70	221	207	12	0	0	243	243	7	1	70	221	221
0	0	71	221	207	12	0	0	243	243	7	1	71	221	221
0	0	72	221	207	12	0	0	243	243	7	1	72	221	221
0	0	73	221	207	12	0	0	243	243	7	1	73	221	221
0	0	74	221	207	12	0	0	243	243	7	1	74	221	221
0	0	75	221	207	12	0	0	243	243	7	1	75	221	221
0	0	76	221	207	12	0	0	243	243	7	1	76	221	221
0	0	77	221	207	12	0	0	243	243	7	1	77	221	221
0	0	78	221	207	12	0	0	243	243	7	1	78	221	221
0	0	79	221	207	12	0	0	243	243	7	1	79	221	221
0	0	80	221	207	12	0	0	243	243	7	1	80	221	221
0	0	81	221	207	12	0	0	243	243	7	1	81	221	221
0	0	82	221	207	12	0	0	243	243	7	1	82	221	221
0	0	83	221	207	12	0	0	243	243	7	1	83	221	221
0	0	84	221	207	12	0	0	243	243	7	1	84	221	221
0	0	85	221	207	12	0	0	243	243	7	1	85	221	221
0	0	86	221	207	12	0	0	243	243	7	1	86	221	221
0	0	87	221	207	12	0	0	243	243	7	1	87	221	221
0	0	88	221	207	12	0	0	243	243	7	1	88	221	221
0	0	89	221	207	12	0	0	243	243	7	1	89	221	221
0	0	90	221	207	12	0	0	243	243	7	1	90	221	221
0	0	91	221	207	12	0	0	243	243	7	1	91	221	221
0	0	92	221	207	12	0	0	243	243	7	1	92	22	

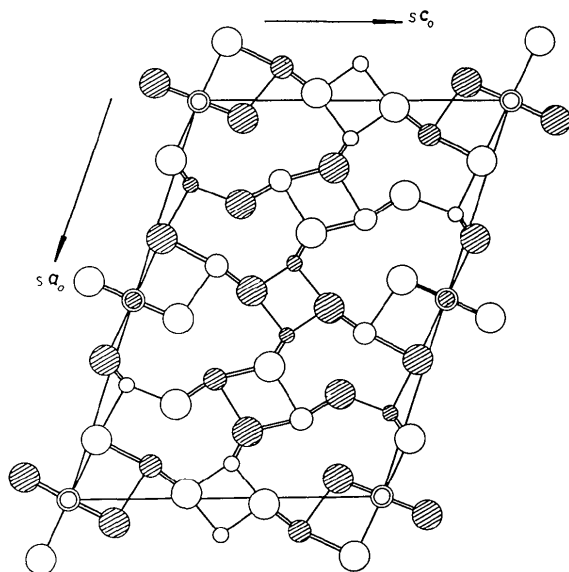


Fig. 2. The structure of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ projected on (010). The open circles indicate the atoms at $y=0$, and the shaded circles indicate the atoms at $y=\frac{1}{2}$. The smallest circles represent copper atoms, the medium circles and the double circles bismuth atoms, and the largest circles sulphur atoms.

trigonal planar coordination (Cu-S: 2.30 Å), and the fourth sulphur atom occupies the apex of a trigonal pyramid at a distance of 2.60 Å. The four sulphur atoms around Cu(2) form a distorted tetrahedron.

Structural relation between $\text{Cu}_4\text{Bi}_5\text{S}_{10}$, hodrushite and cuprobismutite

The structure of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ is closely related to that of hodrushite, $\text{MCu}_4\text{Bi}_5\text{S}_{11}$ (M: Bi, Fe, Pb; Koderá *et al.*, 1970). The Patterson projection, $P(uw)$, of hodrushite shows a very strong maximum at $u=0.189$ and $w=0.548$ (Fig. 3). If the origin of a second identical $P(uw)$ projection is shifted to coincide with this maximum in the first $P(uw)$ projection, then the positions and the relative heights of most peaks in both projections coincide. This indicates that the vector between the origin and the maximum ($u=0.189$, $w=0.548$) is a pseudotranslation vector. This vector divides the unit cell of hodrushite into two parts* where a_0 and b_0 of the two

* A different choice of axes for hodrushite is used in this paper from that in the papers of Kupčik & Makovický (1968) and Koderá *et al.* (1970) to conform to *International Tables for X-ray Crystallography* and to use the same axes for all three substances.

Table 3. *Interatomic distances in $\text{Cu}_4\text{Bi}_5\text{S}_{10}$*

Estimated standard deviations are in parentheses.

	S(1)	S(2)	S(3)	S(4)	S(5)
Bi(1)	2.846 (9) (4 ×)			2.821 (20) (2 ×)	
Bi(2)		2.735 (12) (2 ×)	2.630 (17) (1 ×) 3.035 (12) (2 ×)		
Bi(3)	2.619 (19) (1 ×)			3.131 (12) (2 ×)	2.666 (10) (2 ×)
Cu(1)		2.258 (18) (1 ×)		2.316 (11) (2 ×) 2.602 (25) (1 ×)	
Cu(2)			2.339 (12) (2 ×)		2.304 (21) (1 ×) 2.446 (19) (1 ×)

Table 4. *Bond angles in $\text{Cu}_4\text{Bi}_5\text{S}_{10}$*

Estimated standard deviations are in parentheses.

	Superscript			
	none	x	y	z
i	x	-1+y	z	
ii	$\frac{1}{2}-x$	$\frac{1}{2}+y$	1-z	
iii	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	1-z	
iv	$\frac{1}{2}-x$	$\frac{1}{2}+y$	-z	
v	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	-z	
vi	$\frac{1}{2}+x$	$-\frac{1}{2}+y$	z	
vii	$-\frac{1}{2}+x$	$-\frac{1}{2}+y$	z	
S(1)—Bi(1)—S(1 ⁱ)	87.4 (3) ^o		S(4)—Bi(3)—S(5)	92.9 (3) ^o
S(1 ^{vi})—Bi(1 ^{vi})—S(1 ^v)	92.7 (3)		S(4)—Bi(3)—S(5 ⁱ)	167.4 (1.4)
S(1)—Bi(1)—S(4 ^v)	87.3 (4)		S(5)—Bi(3)—S(5 ⁱ)	95.0 (3)
S(1 ^{vi})—Bi(1 ^{vi})—S(4)	92.7 (4)		S(2)—Cu(1)—S(4)	95.1 (7)
S(2)—Bi(2)—S(2 ⁱ)	91.9 (4)		S(2)—Cu(1)—S(4 ^{iv})	118.6 (5)
S(2)—Bi(2)—S(3)	86.0 (5)		S(4)—Cu(1)—S(4 ^{iv})	100.4 (6)
S(2)—Bi(2)—S(3 ⁱⁱ)	92.0 (3)		S(4 ^{iv})—Cu(1)—S(4 ^v)	116.2 (5)
S(2)—Bi(2)—S(3 ⁱⁱⁱ)	164.8 (1.3)		S(3)—Cu(2)—S(3 ⁱ)	114.4 (6)
S(3)—Bi(2)—S(3 ⁱⁱⁱ)	79.6 (4)		S(3)—Cu(2)—S(5)	119.7 (6)
S(3 ⁱⁱ)—Bi(2)—S(3 ⁱⁱⁱ)	80.7 (3)		S(3 ^{vi})—Cu(2 ⁱⁱⁱ)—S(5 ⁱⁱⁱ)	101.6 (5)
S(1 ^{vi})—Bi(3)—S(4)	85.2 (4)		S(5 ^{vi})—Cu(2 ⁱⁱⁱ)—S(5 ⁱⁱⁱ)	92.1 (7)
S(1 ^{vi})—Bi(3)—S(5)	85.6 (5)			
S(4)—Bi(3)—S(4 ⁱ)	77.8 (3)			

parts are common to the original unit cell (Fig. 4). The resultant two sets of c_0 and β coincide with the c_0 and the β of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ and of cuprobismutite (Table 5). Therefore the unit cells of the $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ and of cuprobismutite are joined with their b_0 in antiparallel relationship to form the hodrushite cell. Besides the pseudotranslation, the structure of hodrushite has partial symmetry elements, twofold axes and 2_1 axes in good approximation, as illustrated in Fig. 4. These partial symmetry elements are valid as the symmetry elements in the $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ structure, where the arrangement of atoms is practically the same as that in the corresponding part of hodrushite (Fig. 5).

Table 5. The cell constants of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$, hodrushite and cuprobismutite

	$\text{Cu}_4\text{Bi}_5\text{S}_{10}$		Cuprobismutite	
	This study	Kodera <i>et al.</i>	This study	Nuffield
a_0	17.539 Å	17.575 Å	17.52 ± 0.02 Å	17.65 Å
b_0	3.931	3.927	3.912 ± 0.001	3.93
c_0	12.847	27.205	15.24 ± 0.01	15.24
β	108.0°	$92^\circ 9'$	$101.26 \pm 0.07^\circ$	100.5°

Proposed structure of cuprobismutite

The considerations in the preceding section enable the structure of cuprobismutite to be predicted. The systematic absence observed by Nuffield permits $C2/m$, $C2$ and Cm as the possible space groups. Because $C2/m$ is common to bismuth sulphosalts and its symmetry coincides with the partial symmetry of hodrushite, the space group of cuprobismutite is assumed to be $C2/m$. In order to choose the symmetry centre as the origin of the cuprobismutite cell, its origin must be shifted $c_0/2$ of the $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ cell in the structure of hodrushite (Fig. 4). The proposed structure of cuprobismutite is illustrated in Fig. 5. The chemical formula which corresponds to this structure is $\text{Cu}_4\text{Bi}_7\text{S}_{12}$ instead of the formula CuBiS_2 proposed by Nuffield. The deviation of the composition from CuBiS_2 has recently been suggested by synthetic studies in the system $\text{Bi}_2\text{S}_3\text{-Cu}_2\text{S}$ by Buhlmann (1971), and in the system Cu-Bi-S by Sugaki & Shima (1971). The deviation of the composition from CuBiS_2 was also noted by Taylor, Radtke & Christ (1973) from electron microprobe analyses of natural specimens.

Unfortunately, attempts to synthesize single crystals of this compound have failed. However, a synthetic fine powder was kindly supplied by Professor Moh (Heidelberg), and the validity of the proposed structure could be tested. Table 6 shows the comparison of the observed and the calculated intensities. The d spacings were measured with a Guinier camera (Cu radiation/quartz monochromator). The intensities are the average of the photometric measurements from Guinier photographs and the measurements from a powder diffractometer. Preferred orientation was observed, but was almost eliminated by careful preparation of the specimens. All observed peaks correspond to the re-

flexions with large calculated values of I and the agreement of I_{calc} with I_{obs} is satisfactory. The discrepancy index $R'' = \sum |I_{\text{obs}} - I_{\text{calc}}| / \sum I_{\text{obs}}$ is 16% for the reflexions listed in Table 6, which confirms the crystal structure. The positional coordinates of atoms and the isotropic temperature factors used for the calculations of intensities are listed in Table 7. Further attempts to postulate a structure with more copper atoms led to a poorer fit between I_{obs} and I_{calc} .

The relationships between the structures of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$, hodrushite and cuprobismutite are thus clarified. The common features of these three compounds are as follows: (a) they belong to the monoclinic system and their space group is $C2/m$ (or Cm), (b) two of the three cell dimensions are 17 and 4 Å, (c) the octahedrally coordinated heavy atom occupies the symmetry centre or the origin.

These structures may be described as layer structures; the structures of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$ and cuprobismutite

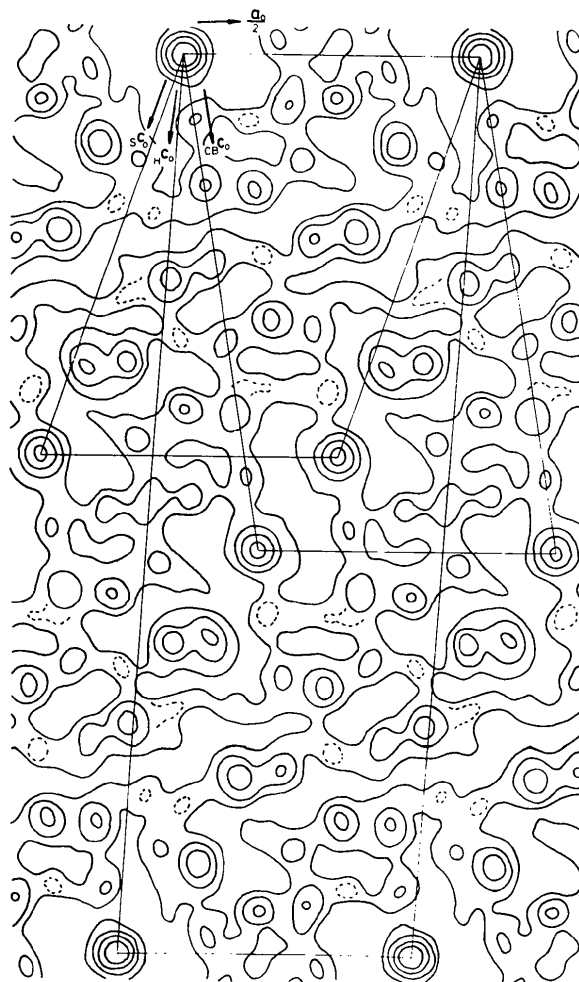


Fig. 3. Patterson projection $P(uv)$ of hodrushite. The s_{c_0} , ${}_{H}c_0$ and c_{b_0} correspond to the c axes of $\text{Cu}_4\text{Bi}_5\text{S}_{10}$, hodrushite and cuprobismutite respectively.

Table 7. Atom parameters of cuprobismutite used to calculate the intensities listed in Table 6

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Bi(1)	0	0	$\frac{1}{2}$	2.5
Bi(2)	0.256	$\frac{1}{2}$	0.129	2.5
Bi(3)	0.009	0	0.220	2.5
Bi(4)	0.174	$\frac{1}{2}$	0.406	2.5
Cu(1)	0.412	0	0.021	3.5
Cu(2)	0.357	0	0.358	3.5
S(1)	0.337	$\frac{1}{2}$	0.006	1.5
S(2)	0.033	$\frac{1}{2}$	0.110	1.5
S(3)	0.350	0	0.209	1.5
S(4)	0.163	0	0.275	1.5
S(5)	0.017	$\frac{1}{2}$	0.380	1.5
S(6)	0.338	$\frac{1}{2}$	0.440	1.5

octahedral coordination may be less favourable to bismuth than the other types such as trigonal or tetragonal pyramids, it is likely that other elements (*e.g.* Pb, Fe and so forth), even in small amounts, catalyse the formation of these compounds (Moh, 1973). Therefore $\text{Cu}_4\text{Bi}_5\text{S}_{10}$, hodrushite and cuprobismutite may belong to a quaternary system, M–Cu–Bi–S (M: Pb, Fe), with a small amount of M, or they may be formed in the Cu–Bi–S system as a metastable phase only under the condition that a small amount of M is present. A similar behaviour of minor elements has been reported by Bernhardt (1972) in his study on the sulphide system, $\text{Cu}_2\text{FeSnS}_4\text{–CuFeS}_2$.

The authors thank Professor G. Moh (Heidelberg) who supplied the synthetic specimen of cuprobismutite, and Dr E. Makovický (København) for valuable discussions. The computation was performed on the

UNIVAC 1108 of the Gesellschaft für Wissenschaftliche Datenverarbeitung, Göttingen.

References

- BERNHARDT, H.-J. (1972). *Neues Jb. Miner. Mh.* pp. 553–556.
- BERRY, L. G. & THOMPSON, R. M. (1962). *X-ray Powder Data for Ore Minerals: The Peacock Atlas, Geol. Soc. Amer. Mem.* **85**, 281.
- BUHLMANN, E. (1971). *Neues Jb. Miner. Mh.* pp. 137–141.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- International Tables for X-ray Crystallography* (1968). Vol. III, 2nd ed., Tables 3.3.1, 3.3.3. Birmingham: Kynoch Press.
- KODERA, M., KUPČÍK, V. & MAKOVICKÝ, E. (1970). *Miner. Mag.* **37**, 641–648.
- KUPČÍK, V. (1972). In Wedepohl: *Handbook of Geochemistry*, Vol. II/3, 83-A.
- KUPČÍK, V. & MAKOVICKÝ, E. (1968). *Neues Jb. Miner. Mh.* pp. 236–237.
- LE BIHAN, M.-TH. (1962). *Bull. Soc. Fr. Minér. Crist.* **85**, 15–47.
- MOH, G. (1973). Private communication.
- NUFFIELD, E. W. (1952). *Amer. Min.* **37**, 447–452.
- OHMASA, M. & NOWACKI, W. (1973). *Z. Kristallogr.* **137**, 422–432.
- RABENAU, A. & RAU, H. (1969). Private communication.
- SUGAKI, A. & SHIMA, H. (1971). *Proceedings of the IMA- IAGOD Meetings*, 1970. IMA Volume, Special Paper No. 1, pp. 270–271.
- TAYLOR, C. M., RADTKE, A. S. & CHRIST, C. L. (1973). *J. Res. U.S. Geol. Surv.* **1**, 99–103.

Acta Cryst. (1975). **B31**, 708

The Structure of 2,3-Dichloro-1,1-dicyano-3,3-diphenylpropene

BY R. SCHLODDER AND JAMES A. IBERS

Department of Chemistry, Northwestern University, Evanston, Illinois 60201, U.S.A.

(Received 25 July 1974; accepted 11 October 1974)

The crystal and molecular structure of 2,3-dichloro-1,1-dicyano-3,3-diphenylpropene, $\text{C}_{17}\text{Cl}_2\text{H}_{10}\text{N}_2$, has been determined from 2067 X-ray data above background collected by counter methods. The material crystallizes with eight molecules in space group *Pbca* (D_{2h}^{15}) of the orthorhombic system in a cell of dimensions $a = 15.403$ (3), $b = 19.219$ (4), $c = 10.138$ (2) Å. The observed and calculated densities are 1.39 (1) and 1.386 g cm⁻³. The structure has been solved by direct methods and refined by full-matrix least-squares methods to a final *R* index on *F* of 0.036. The $\text{C}=\text{C}(\text{CN})_2$ portion of the molecule closely resembles that in tetracyanoethylene. Whereas the olefinic C–Cl bond length is 1.715 (2) Å, the paraffinic C–Cl bond length is 1.836 (2) Å. The material was prepared by the reaction of diphenylcarbene with 1,1-dichloro-2,2-dicyanoethylene. The structure found here indicates that the reaction involves the insertion of diphenylcarbene into a C–Cl bond.

Introduction

In an earlier investigation of the bonding of the unsymmetrical olefin 1,1-dichloro-2,2-dicyanoethylene to

a transition metal the complex $\text{Pt}[\text{Cl}_2\text{C}=\text{C}(\text{CN})_2][\text{P}(\text{C}_6\text{H}_5)_3]_2$ was prepared and its structure determined (McAdam, Francis & Ibers, 1970). Because of the difference in Pt–C (of Cl) versus Pt–C (of CN) bond