

Redetermination and Refinement of the Structure of Tetrabismuth Tetracopper Enneasulphide, $\text{Cu}_4\text{Bi}_4\text{S}_9$

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Abstract. $M_r = 1372.65$, orthorhombic, $Pnam$, $a = 31.68$ (1), $b = 11.659$ (4), $c = 3.972$ (6) Å, $V = 1478.65$ Å³, $Z = 4$, $D_x = 6.165$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 517.5$ cm⁻¹, $F(000) = 4540.19$, room temperature. Final $R = 0.033$ for 1129 independent observed reflections. A microprobe analysis gave $\text{Cu}_{4.02(1)}\text{Bi}_{3.97(1)}\text{S}_9$. Compared with the structure determinations of Takéuchi & Ozawa [*Proc. Jpn Acad.* (1974). **50**, 751–755; *Z. Kristallogr.* (1975). **141**, 217–232] ($R = 0.08$ for 816 independent reflections), the probably misprinted z parameter of Bi(1) is corrected, the occupancies of the Bi atoms are reduced from 1.0 to 0.98 (2) due to the Cu:Bi ratio and one of the two triangularly coordinated Cu atoms is split into two distorted CuS_4 tetrahedra with a decrease in the thermal parameters for these Cu atoms of more than 50%.

Introduction. The structure of hydrothermally grown $\text{Cu}_{4.2}\text{Bi}_{3.76}\text{S}_9$ (idealized formula $\text{Cu}_4\text{Bi}_4\text{S}_9$) was first determined by Takéuchi & Ozawa (1974) and an extended work was published by Takéuchi & Ozawa (1975). The lattice constants were reported as follows: $a = 11.589$ (5), $b = 32.05$ (1), $c = 3.951$ (5) Å, $Z = 4$, space group $Pbnm$. The asymmetric unit contained four Cu, four Bi and nine S atoms with occupancies of unity although the Cu:Bi ratio is 1:0.89. The thermal parameter of the Cu(4) atom in fivefold coordination (within triangular coordination of the three nearest S atoms) was extremely high ($B = 7.2$ Å²). These data, the probably misprinted z value of the Bi(1) atom of 0.25 (Takéuchi & Ozawa, 1974) and the significant differences in chemical composition and lattice constants of our single crystals from those of the material of Takéuchi & Ozawa (1974) demanded a structure refinement.

Experimental. In performing systematic single-crystal-growth investigations in the quaternary system $\text{CuS}-\text{Cu}_2\text{S}-\text{PbS}-\text{Bi}_2\text{S}_3$ by chemical vapour transport (CVT- I_2), single crystals of $\text{Cu}_4\text{Bi}_4\text{S}_9$ were grown. The synthesis was carried out in evacuated silica tubes (length = 150 mm, $\varnothing = 15$ mm) starting with the elements (99.998%) and I_2 (3 mg ml⁻¹ free volume) as

transport vapour. Needle-like crystals (length = 3–7 mm, $\varnothing = 0.02$ mm) grew in the cooler part of the tube, located in a temperature gradient between 978 and 723 K. DTA experiments on $\text{Cu}_4\text{Bi}_4\text{S}_9$ led to an upper thermal stability of 772 ± 3 K. The powder pattern was in good agreement with the $\text{Cu}_4\text{Bi}_4\text{S}_9$ data of Sugaki & Shima (1971).

The cell dimensions, $a = 31.68$ (1), $b = 11.659$ (4), $c = 3.972$ (6) Å, $Z = 4$, were similar to those of Takéuchi & Ozawa (1974). The space group $Pnam$ is in agreement with the study of Takéuchi & Ozawa (1974). The microprobe analysis with $\text{Cu}_{4.02(1)}\text{Bi}_{3.97(1)}\text{S}_9$ was slightly different from the analysis $\text{Cu}_{4.2}\text{Bi}_{3.76}\text{S}_9$ given by Takéuchi & Ozawa (1975).

Data collection: Stoe four-circle diffractometer, graphite monochromator, $\text{Mo } K\alpha$ radiation, 50 reflections used for measuring lattice parameters, $hkl = \pm 44, \pm 16, +5$, θ/ω scan, 2θ range 3–40°, step width $2\theta = 0.02^\circ$, $\Delta\omega = 0.02^\circ$; usual Lorentz, polarization and absorption corrections (*SHELX76*, Sheldrick, 1976); standard reflections 401 and 11,1,0, intensity variation $\pm 3.5\%$ and $\pm 0.4\%$ respectively; 9549 reflections, 1138 independent observed reflections with $I \geq 1.5\sigma(I)$; standard deviation of the intensities: $\sigma_I^2 = T + \{(\frac{2}{3}N - \frac{N}{6} + 1)/[\frac{N}{6} + (N - \frac{2}{3}N)]\} B + 2 \times 10^{-4}T^2$ ($N =$ number of stepscan steps, $T = \sum I$ under the peak from $\frac{N}{6}$ to $\frac{2}{3}N$, $B = \sum$ background intensities from point 1 to $\frac{N}{6}$ and $\frac{2}{3}N$ to N). Direct methods (*SHELX76*) for $hk0$ reflections led to atom parameters (x, y) corresponding to the parameters of the heavy atoms given by Takéuchi & Ozawa (1975). Applying the complete atom-parameter set of Takéuchi & Ozawa (1975) and the whole measured hkl -data set, the refinement failed. On checking the z parameters of the structure after Takéuchi & Ozawa (1975) the position of the Bi(1) atom had to be corrected from $z = 0.25$ to $z = 0.75$. Refinement calculations based on F . After this change an isotropic refinement starting with 17 atoms in the asymmetric unit with occupancies of unity gave an R value of 0.085. Because of the high temperature factor of Cu(4) ($B = 4.8$ Å²) [after Takéuchi & Ozawa (1975), $B = 7.2$ Å²] in the trigonal bipyramidal coordination this position was split into two half-occupied Cu positions [Cu(4) and Cu(5)] in neighbouring,

strongly distorted tetrahedral coordinations. With the inclusion of this splitting, further optimization of the Bi occupancies to 0.98 (2) according to the (measured) Cu:Bi ratio and elimination of nine aberrant reflections ($F_o \ll F_c$) the isotropic refinement gave an R value of 0.048 ($R_w = 0.053$). The anisotropic refinement gave an R value of 0.033 ($R_w = 0.04$) within $w = 1/\sigma^2$. Without the splitting of the Cu(4) position the isotropic refinement gave an R value of 0.059 ($R_w = 0.063$). $(\Delta/\sigma)_{\max} = 0.066$ [β_{33} for Cu(5)]; largest peaks in final difference Fourier map were $6.6 e \text{ \AA}^{-3}$ for Cu(1), $7.1 e \text{ \AA}^{-3}$ for Bi(3), for all other atoms $< 2.2 e \text{ \AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations were performed on the Univac U1100 computer of the GWD Göttingen with *SHELX76* (Sheldrick, 1976) for direct methods and *ORFLS* (Busing, Martin & Levy, 1962) for the refinement computing.

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1;* the atom distances are shown in the projection of the structure along the c axis in Fig. 1.

The chemical variation of $\text{Cu}_4\text{Bi}_4\text{S}_9$, represented by the Cu:Bi ratio leads to differences in the lattice and atom parameters and atom distances in comparison with the data given by Takéuchi & Ozawa (1974). Because of the chemical variation of $\text{Cu}_4\text{Bi}_4\text{S}_9$, a determination of the Bi occupancy was tried by refining the R_w value as a function of this occupancy from 0.9 to 1.0 in steps of 0.01. The comparison of the temperature factors of the four crystallographically independent Bi atoms does not allow significant occupancy differences. The Hamilton test (Hamilton, 1965) using 108 variables shows no significance for the occupancies from 0.96 to 1.0 ($\alpha = 0.25$), but reveals significance for the minimum R_w value relative to the R_w value of the occupancy of 0.95. This leads to occupancies of the Bi atoms of 0.98 (2), which agree with the Cu:Bi ratio of the chemical analysis. The Bi deficiency is probably compensated by heterotopic replacement of Bi by Cu. The probably misprinted Bi(1) parameter $z = 0.25$ by Takéuchi & Ozawa (1975) had to be changed to $z = 0.75$. This change was verified by the structure refinement. The splitting of the Cu(4) position into two half-occupied distorted tetrahedral positions [Cu(4)–Cu(5) = 0.59 (2) Å] was refined without correlation problems to give usual Cu–S coordinations and low isotropic temperature factors of 3.3 (2) Å² for Cu(4) and 0.9 (1) Å² for Cu(5). A

* Lists of structure factors, anisotropic temperature factors and atom distances, listed together with the data set of Takéuchi & Ozawa (1974) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39587 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

sulphur–sulphur distance of 2.103 (8) Å [S(3)–S(4)] indicates sulphur–sulphur bonding. The structure description of $\text{Cu}_4\text{Bi}_4\text{S}_9$ by Takéuchi & Ozawa (1975) as a mosaic of covellite and bismuthinite structure fragments is verified.

Table 1. Atomic coordinates, *s.o.f.*'s (special occupancy factors) and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = \frac{1}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33}).$$

	s.o.f	x	y	z	B_{eq} (Å ²)
Cu(1)	1.0	0.1353 (1)	0.3833 (2)	0.75	1.33 (6)
Cu(2)	1.0	0.1912 (1)	0.3360 (3)	0.25	2.13 (8)
Cu(3)	1.0	0.3048 (1)	0.4245 (2)	0.25	1.48 (6)
Cu(4)	0.5	0.4808 (3)	0.3634 (3)	0.25	3.2 (2)
Cu(5)	0.5	0.4834 (4)	0.4136 (7)	0.25	0.8 (1)
Bi(1)	0.98	0.0278 (2)	0.3670 (7)	0.75	1.22 (1)
Bi(2)	0.98	0.0903 (2)	0.0987 (1)	0.25	1.41 (1)
Bi(3)	0.98	0.2786 (1)	0.1385 (1)	0.25	1.20 (1)
Bi(4)	0.98	0.3908 (2)	0.2324 (1)	0.75	1.09 (1)
S(1)	1.0	0.0206 (1)	0.1313 (4)	0.75	0.9 (1)
S(2)	1.0	0.0987 (1)	0.3244 (4)	0.25	0.9 (1)
S(3)	1.0	0.1542 (1)	0.0931 (4)	0.75	0.7 (1)
S(4)	1.0	0.1922 (1)	0.2410 (4)	0.75	0.8 (1)
S(5)	1.0	0.2357 (1)	0.4852 (4)	0.25	0.8 (1)
S(6)	1.0	0.3150 (1)	0.3169 (4)	0.75	0.8 (1)
S(7)	1.0	0.3570 (1)	0.0773 (4)	0.25	0.6 (1)
S(8)	1.0	0.4113 (1)	0.3895 (4)	0.25	0.8 (1)
S(9)	1.0	0.4700 (1)	0.1202 (4)	0.25	0.9 (1)

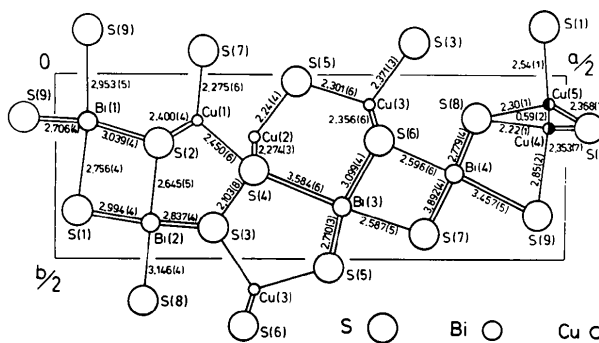


Fig. 1. Projection of the structure of $\text{Cu}_4\text{Bi}_4\text{S}_9$ along the c axis with bond distances (Å).

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