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Structure of the Bismuth Chloride Sulphide $\text{Bi}_4\text{Cl}_2\text{S}_5$

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Abstract. $\text{Bi}_4\text{Cl}_2\text{S}_5$, rhombohedral, $R\bar{3}$, $a = 19.804$ (5), $c = 12.359$ (3) Å, $Z = 15$, $V = 4197.4$ Å³, $D_c = 6.33$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 60.89$ mm⁻¹, $F(000) = 6690$. Systematic absences hkl , $-h + k + l = 3n$. Final $R = 0.056$. The structure has: (a) statistical occupancy of the anions sites by S and Cl ($S + \text{Cl} = X$); (b) unusual Bi– X coordination polyhedra. One Bi has nine X neighbours at 2.88, 2.90, and 3.44 Å; the remaining three are irregularly surrounded by eight X between 2.62 and 3.66 Å.

Introduction. Besides BiHalS (Hal: Cl, Br, I) and the halogen-poor $\text{Bi}_9\text{Hal}_3\text{S}_{27}$, only $\text{Bi}_4\text{Cl}_2\text{S}_5$ could be prepared (Krämer, 1976a). The analogous bromide, iodide, or compounds with other S/Hal ratios seem not to exist at the S-rich parts of the corresponding Bi_2S_3 – BiHal_3 systems. To elucidate the structural relationships between $\text{Bi}_4\text{Cl}_2\text{S}_5$ and the above compounds its crystal structure was determined.

The vapour-grown crystals were black, elongated-hexagonal prisms. Intensities from a single crystal ($56 \times 65 \times 300$ µm) were collected on an automatic four-circle diffractometer (Enraf–Nonius CAD-4) with graphite-monochromatized Mo $K\alpha$ radiation and an ω – 2θ scan mode.

The correct space group $R\bar{3}$, replacing the previously reported $R\bar{3}m$, $R3m$, or $R32$ (Krämer, 1976a), was determined by comparison of the intensity distributions in point groups $\bar{3}$ and $\bar{3}m$. The former yields an internal R of 8.7%, the latter 52%.

Calculations were performed with the XRAY (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and MULTAN systems (Main, Lessinger, Woolfson, Germain & Declercq, 1977). 3052 independent reflexions were measured, 1153 of which had $I > 3\sigma(I)$. Intensities were corrected for absorption by the program ORABS, which computes transmission factors and mean path lengths by Gaussian integration.

The four Bi positions were located with MULTAN. Subsequent Fourier maps yielded six anion positions. Refinement on all positional, isotropic extinction, and anisotropic thermal parameters resulted in a final $R = 0.056^*$ and an average shift/error of 1.4×10^{-2} .

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33943 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
Bi(1)	2186 (1)	307 (1)	770 (2)
Bi(2)	2124 (1)	259 (1)	3932 (2)
Bi(3)	1730 (1)	2387 (1)	2512 (2)
Bi(4)	0	0	2666 (5)
<i>X</i> (1)	817 (6)	1520 (6)	859 (10)
<i>X</i> (2)	3041 (7)	2213 (7)	752 (11)
<i>X</i> (3)	4502 (6)	4109 (6)	783 (9)
<i>X</i> (4)	4994 (8)	2519 (8)	990 (10)
<i>X</i> (5)	2529 (7)	3714 (8)	986 (10)
<i>X</i> (6)	758 (6)	1366 (7)	4009 (10)

Table 2. Interatomic distances (Å)

Bi(1)– <i>X</i> (1)	2.73 (2)	Bi(2)– <i>X</i> (2)	3.08 (1)
	2.66 (2)	<i>X</i> (3)	2.70 (1)
<i>X</i> (2)	2.95 (3)	<i>X</i> (4)	3.66 (2)
	3.28 (1)	<i>X</i> (5)	2.62 (2)
	3.34 (1)	<i>X</i> (6)	3.28 (3)
<i>X</i> (4)	2.62 (2)		2.65 (2)
<i>X</i> (5)	3.41 (1)		3.20 (2)
Bi(3)– <i>X</i> (1)	2.70 (1)	Bi(4)– <i>X</i> (1)	3.44 (1) $\times 3$
<i>X</i> (2)	3.53 (2)	<i>X</i> (4)	2.90 (1) $\times 3$
<i>X</i> (3)	2.62 (2)	<i>X</i> (6)	2.88 (1) $\times 3$
	3.05 (2)		
<i>X</i> (4)	3.07 (2)		
<i>X</i> (5)	2.97 (1)		
	3.50 (2)		
<i>X</i> (6)	2.71 (1)		

Scattering factors for Bi^{3+} , S^{2-} (Cromer & Waber, 1965), and Cl^- (*International Tables for X-ray Crystallography*, 1974) were used and corrected for anomalous dispersion. The atomic coordinates are listed in Table 1, interatomic distances in Table 2.

Discussion. 75 S plus 30 Cl atoms occupy statistically six general positions. A space-filling of about 58.8% was evaluated indicating a light-packed framework of anions. Their mutual interatomic distances are: $X(1)$ has ten neighbours at 3.36 to 3.97 Å, $X(4,5)$ have nine neighbours between 3.27 and 3.97 Å, and $X(2,3,6)$ have eight neighbours between 3.27 and 3.90 Å.

$\text{Bi}(1-3)$ are in general positions whereas $\text{Bi}(4)$ is in a special position on the $\bar{3}$ axis. The eightfold coordination of $\text{Bi}(1-3)$ is very similar and can be derived from the $[\text{BiS}_5]$ pyramid found in many Bi sulphosalts (Kupčik, 1972). The five anions at the vertices of this pyramid are strongly bonded (2.62–3.05 Å); above the basal plane three additional anions are rather weakly bonded (3.07–3.66 Å), Fig. 1(a). This coordination is closely related to that found in $\text{InBi}_2\text{ClS}_4$ (Krämer, 1976b).

The unusual ninefold coordination of $\text{Bi}(4)$ is shown in Fig. 1(b). The coordination polyhedron is a distorted tri-capped trigonal prism, the bond lengths being 2.88, 2.90, and 3.44 Å ($3\times$). Fig. 2 shows an idealized projection of the complete structure. Differential

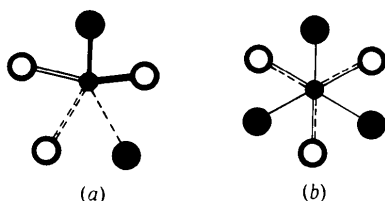


Fig. 1. Coordinations of Bi atoms. (a) $\text{Bi}(1-3)$, eightfold; $\text{Bi}-X$ distances: heavy lines 2.62–2.73 Å, thin lines 2.95–3.05 Å, broken lines 3.07–3.66 Å; (b) $\text{Bi}(4)$, ninefold; $\text{Bi}-X$ distances: thin lines 2.88 and 2.90 Å, broken lines 3.44 Å.

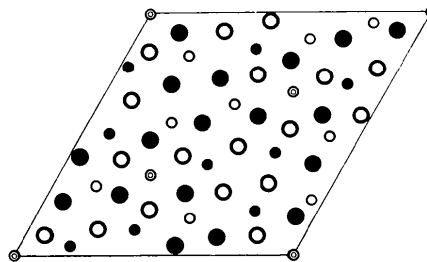


Fig. 2. Idealized projection of the $\text{Bi}_4\text{Cl}_2\text{S}_5$ structure. Small dots (heights $z \approx 0.25/0.60/0.90$), rings (0.10/0.40/0.75), and double rings (0.27/0.73) are Bi; large dots (0.23/0.60/0.90) and rings (0.70/0.43/0.75) are anions.

thermal analyses down to 123 K yield no hints of a phase transition to suggest ordering of the anions.

Numerical calculations were performed on the Univac 1100/81 computer of the Rechenzentrum der Universität Freiburg. Financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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