SHORT-FORMAT PAPERS

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Structure of the New Mineral Mückeite, $BiCuNiS_3$

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Abstract. $Bi_{1-x}CuNiSb_xS_3$ ($x = 0{\cdot}1$ by refinement), $M_r = 418{\cdot}7$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}514$ (3), $b = 12{\cdot}557$ (6), $c = 4{\cdot}8880$ (2) Å, $V = 460{\cdot}39$ Å^3, $Z = 4$, $D_m = 5{\cdot}88$, $D_x = 6{\cdot}04$ g cm^{-3}, λ(Mo $K\alpha$) = 0·710713 Å, $\mu = 445{\cdot}94$ cm^{-1}, $F(000) = 739{\cdot}2$, $T = 295$ K, final anisotropic $R = 0{\cdot}050$ for 827 unique reflections with $F \geq 1{\cdot}5\sigma(F)$ using a model of two intergrown domains. The structure is a new type of $ABCX_3$ compound. The Bi atom forms a trigonal pyramid with the three nearest S atoms. Additionally, with regards to a fourth S atom at a greater distance, the resulting polyhedron is very similar to the TeO_4 polyhedron in $Zn_2Te_3O_8$ [Hanke (1966). *Naturwissenschaften*, **53**, H. 11, 273]. Cu and Ni can either occupy the $M(1)$ position, which is tetrahedrally coordinated by sulfur, or the $M(2)$ position, which is coordinated by four S atoms in the quadratic base and two Bi at the vertices of a tetragonal dipyramid. From crystal chemical considerations it is suggested that the positions $M(1)$ and $M(2)$ are occupied by Cu and Ni respectively. The verification of these occupancies by Δ synthesis using synchrotron radiation is in progress.

Experimental. The single crystals of mückeite were found in the former mine 'Grüne Au', Schutzbach, Siegerland (FRG). The mineral shows a solid-solution series with the Sb end-member lapieite, $CuNiSbS_3$. Mückeite was first described by Schnorrer-Köhler, Neumann & Doering (1989). The size of the measured crystal was 0·11 × 0·04 × 0·13 mm. Density was measured by Berman balance. The measuring device and parameters were: Stoe four-circle diffractometer, graphite monochromator, Mo $K\alpha$, cell constants by least-squares fit of 20 reflections with $2\theta > 22°$, 2θ–ω scan technique, range $10 < 2\theta < 90°$, h −9/9, k −15/15, l 0/6, 65 steps/reflection, 0·03°/step, intensity check by the reflections 201 and $2\bar{3}2$ measured every 90 min, intensity variation < 6·7%; 4068 reflections measured, Lorentz–polarization (Langhoff, 1981) and absorption correction (Sheldrick, 1976), transmission factors 0·006–0·049; after averaging 1098 reflections (merging $R = 0{\cdot}085$), 827 reflections with $F \geq 1{\cdot}5\sigma(F)$ used for refinement; structure solution by Patterson method and difference Fourier analysis. Scattering factors and anomalous scattering parameters were taken from *International Tables for X-ray Crystallography* (1974), for neutral atoms. Refinements were carried out by *ORFLS* (Busing, Martin & Levy, 1962). Final isotropic and anisotropic refinements for 827 unique reflections considering a one domain single crystal lead to R values of 0·065 and 0·06 respectively. The resulting residual electron density maxima of 3·5 e Å^{-3} in the vicinity of $M(1)$ and Bi shows distances too short to be attributed to a statistically occupied site. Therefore a model of the combination of two domains was postulated. The domain ratio was determined by electron density calculations and verified by iterative refinement (significance test after Hamilton, 1965) to be 96·2 (7)% and 3·8 (7)%. The domain combination can be described by the transformation of the atom positions: $x' = x$, $y' = \frac{1}{2} - y$ and $z' = -z$. This model leads to an R value of 0·050 showing a maximum $\Delta\rho$ of 1·0 e Å^{-3} only in the vicinity of Bi. The coherent intergrowth of the domains coincides with the predominant cleavage. $wR = 0{\cdot}05$ with $w = 1/\sigma^2$, $S = 1{\cdot}2328$.

Atomic parameters are given in Table 1, distances and angles in Tables 2 and 3.†

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† Lists of structure fractors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52106 (21 pp.). Copies may be obtained through the Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atom coordinates with anisotropic temperature parameters of the last refinement*

E.s.d.'s are in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{eq} (Å^2)
Bi0.9 Sb0.1	0·37685 (14)	0·13292 (8)	0·93528 (14)	0·00882 (10)	0·00266 (5)	0·01825 (23)	0·00017 (7)	0·00008 (16)	−0·00016 (9)	1·80 (9)
M(1)	0·38250 (54)	0·43787 (20)	0·97540 (58)	0·01014 (39)	0·00329 (16)	0·02693 (100)	0·00035 (25)	−0·00031 (63)	0·00032 (29)	2·3 (1)
M(2)	0·12824 (77)	0·25020 (21)	0·50418 (48)	0·00767 (35)	0·00232 (12)	0·01695 (70)	−0·00028 (16)	0·00092 (36)	0·00007 (20)	1·60 (7)
S1	0·1289 (13)	0·40728 (40)	0·7166 (10)	0·00917 (70)	0·00241 (25)	0·0217 (16)	−0·00035 (60)	−0·0043 (216)	−0·00011 (51)	1·9 (1)
S2	0·37848 (77)	0·29743 (38)	0·2816 (9)	0·00731 (62)	0·00298 (25)	0·0202 (15)	−0·00027 (40)	0·0003 (9)	0·00036 (44)	1·8 (1)
S3	0·1262 (13)	0·09262 (39)	0·2901 (9)	0·00903 (67)	0·00229 (24)	0·0220 (16)	−0·00026 (60)	0·0050 (17)	−0·00049 (48)	1·9 (1)

Table 2. *Atom distances* (Å) *with e.s.d.'s in parentheses*

	S(1)	S(1′)	S(2)	S(2′)	S(3)	S(3′)	S(3″)
Bi,Sb	2·596 (8)	3·735 (4)	2·670 (4)	3·805 (3)	2·609 (5)	2·919 (5)	3·703 (4)
M(1)	2·276 (3)	2·319 (6)	2·313 (3)	—	2·277 (5)	—	—
M(2)	2·229 (3)	—	2·230 (4)	2·252 (4)	2·238 (3)	—	—

M(2)—Bi = 3·18 (3)   *M*(2′)—Bi = 3·21 (3)

Table 3. *Bond angles* (°) *with e.s.d.'s in parentheses*

S(1)—*M*(1)—S(1′)	113·1 (5)	S(1)—Bi—S(2)	74·48 (3)
S(1)—*M*(1)—S(2)	102·4 (3)	S(1)—Bi—S(1′)	99·30 (5)
S(1)—*M*(1)—S(3)	108·9 (4)	S(1)—Bi—S(3)	93·12 (4)
S(2)—*M*(1)—S(1)	108·6 (4)	S(1)—Bi—S(3″)	88·60 (4)
S(2)—*M*(1)—S(3)	104·5 (3)	S(1′)—Bi—S(2′)	49·99 (3)
S(3)—*M*(1)—S(1)	117·9 (7)	S(1′)—Bi—S(3′)	61·02 (5)
S(1)—*M*(2)—S(2)	91·20 (4)	S(1′)—Bi—S(3″)	70·49 (3)
S(1′)—*M*(2)—S(2)	89·40 (3)	S(2)—Bi—S(3)	74·53 (3)
S(2)—*M*(2)—S(3)	90·83 (3)	S(2)—Bi—S(2′)	96·37 (8)
S(3)—*M*(2)—S(2)	88·56 (4)	S(2′)—Bi—S(3′)	50·39 (6)
Bi—*M*(2)—Bi	179·51 (4)	S(3)—Bi—S(3′)	99·80 (2)
		S(3)—Bi—S(3″)	88·12 (4)
		S(3′)—Bi—S(3″)	69·95 (3)

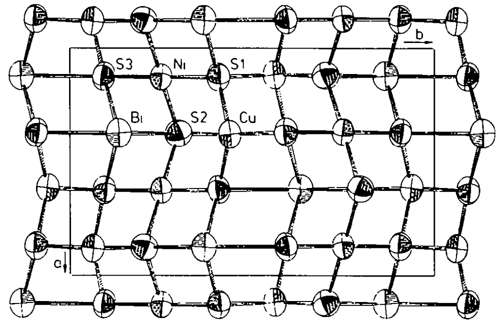

Fig. 1. Projection of the mückeite structure parallel to $\mathbf{c}_0$.

Related literature. The projection of the mückeite structure on the *ab* plane (Fig. 1) shows parallel ribbons of different *M*—S series parallel and perpendicular to $\mathbf{b}_0$. The mutual connection of these ribbons is similar to the *M*—S chain connection parallel to $\mathbf{a}_0$ in sphalerite.

In addition to the $M(1)S_4$ tetrahedron and the $Bi—M(2)_2S_4$ polyhedron, the structure of mückeite contains a tetragonal dipyramid, $M(2)—Bi_2S_4$. The latter polyhedron is similar to the $Ni—Bi_2S_4$ octahedron in hauchecornite, $Ni_9(Bi,Sb)_2S_8$ (Kocman & Nuffield, 1974), but shows longer Ni—Bi distances of 3·18 and 3·21 Å. The Ni—Bi distance in hauchecornite is 2·70 Å, lying within the range of Ni—Bi distances (2·65 to 2·83 Å) in Bi_3Ni (Glagoleva & Ždanov, 1954).

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Structure of a Trinuclear Rhodium(I) Fluorophosphine Complex, $[Rh_3(\mu\text{-}Cl)_3\{\mu\text{-}H_3CN(PF_2)_2\}_3]$

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Abstract. Tris[μ-bis(difluorophosphino)methylamine]-tri-μ-chloro-trirhodium, $M_r = 916{\cdot}06$, monoclinic, $C2/c$, $a = 17{\cdot}323\,(2)$, $b = 10{\cdot}998\,(2)$, $c = 23{\cdot}226\,(3)$ Å, $\beta = 93{\cdot}03\,(1)°$, $V = 4419$ Å^3, $Z = 8$, $D_x = 2{\cdot}76$ g cm^{-3}, Mo $K\alpha_1$, $\lambda = 0{\cdot}70930$ Å, $\mu = 30{\cdot}8$ cm^{-1}, $F(000) = 3456$, $T = 298$ K. Final $R = 0{\cdot}030$ for 3811 observed data. The final product of the reaction of $[Rh_2Cl_2(CO)_4]$ with two equivalents of $H_3CN(PF_2)_2$ is shown to contain a triangular Rh_3 moiety with three edge-bridging chloride and three edge-bridging fluorophosphine ligands. The structure, in the shape of a truncated triangular pyramid, is a new type for closed trinuclear clusters. The coordination about each Rh atom is essentially square planar and the whole molecule possesses approximate C_{3v} symmetry. Although differing significantly, the Rh—Rh distances span a rather narrow range [3·0755 (4)–3·1180 (4) Å] and are considered non-bonding. The mean planes of the ligating atoms about each metal atom are inclined with respect to the plane of the three metal atoms by an average angle of 120·81 (4)°.

Experimental. Dark red-orange crystals of the title compound were obtained directly from the reaction mixture as previously described (Mague, Johnson & Lloyd, 1989). Enraf–Nonius CAD-4 diffractometer, crystal size 0·25 × 0·30 × 0·45 mm, cell dimensions from setting angles of 25 widely distributed reflections ($11{\cdot}53 \leq \theta \leq 25{\cdot}81°$), graphite-monochromated Mo $K\alpha$ radiation, 9046 reflections scanned, $\omega/2\theta$ mode, $3 \leq \theta \leq 26°$, index range h 0 to 21, k −13 to 13, l −28 to 28, scan speed 1·5–16·5° min^{-1}, scan range $(0{\cdot}80 + 0{\cdot}20\tan\theta)°$, 13% linear decay (average) from three intensity standards monitored every 7200 s, linear decay correction applied, orientation stable from three monitor reflections checked every 200 reflections, empirical absorption correction (North, Phillips & Mathews, 1968), transmission-factor range 0·741–1·000, hkl and $h\bar{k}l$ reflections averaged to give 4322 unique data, agreement on F for averaged reflections is 0·017, 3811 data with $I \geq 3\sigma(I)$ used in analysis, 15 reflections (marked by negative σ_F) excluded from final refinement because of highly asymmetric backgrounds, structure solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971) and refined by full-matrix least squares, non-H atoms refined anisotropically, 271 variables, H atoms located in difference map and included as fixed contributions riding on attached C atoms with isotropic thermal parameters 1·3 times those of the respective C atoms. $\sum w(\Delta F)^2$ minimized, final shifts all $\leq 0{\cdot}11\sigma$, $w = 1/\sigma_F^2$, $\sigma_F = \sigma_{F^2}/2F$, $\sigma_{F^2} = [\sigma_I^2 + (0{\cdot}04F^2)^2]^{1/2}$, residual electron density within 0·43 to −0·38 e Å^{-3}, $R = 0{\cdot}030$, $wR = 0{\cdot}038$, GOF = 2·72. Computations made on a PDP 11/73 with Enraf–Nonius *SDP* (Frenz, 1985) using complex neutral-atom scattering factors (Cromer & Waber, 1974; Cromer, 1974). Final atomic coordinates for non-H atoms are given in Table 1,* selected bond distances and interbond angles in Table 2. Figs. 1 and 2 show the full molecule viewed perpendicular to the Rh_3 plane and a perspective view of the inner coordination sphere, respectively.

Related literature. The ligand bis(difluorophosphino)methylamine has been previously found to form a number of complexes with unusual structures (King, Shimura & Brown, 1984; Newton, King, Chang, Pantaleo & Gimeno, 1977; Newton, King, Lee, Nørskov-Lauritsen & Kumar, 1982; Dulebohn, Ward & Nocera, 1988). In our studies of binuclear, 'A-frame'-type complexes we attempted to prepare such a complex of rhodium with this ligand (Mague *et al.*, 1989). Unexpectedly the product obtained proved to be the trinuclear complex $[Rh_3(\mu\text{-}Cl)_3\{\mu\text{-}H_3CN(PF_2)_2\}_3]$. Other examples of non-bonding Rh–Rh separations comparable to those found here are ones of 3·1520 (8) and 3·155 (4) Å found in the 'A-frame' complexes $[Rh_2(CO)_2(\mu\text{-}Cl)(DPM)_2]BF_4$ (Cowie & Dwight, 1979) and $[Rh_2(CO)_2(\mu\text{-}S)(DPM)_2]$ (Kubiak & Eisenberg, 1977) [DPM =

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* Tables of structure factors, anisotropic thermal parameters, r.m.s. amplitudes of displacement, H-atom positions, torsion angles, non-essential bond distances and angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52128 (56 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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