Crystal data

NbSb$_2$
$M_r = 336.4$
Monoclinic
$C2/m$
$a = 10.218$ (3) Å
$b = 3.630$ (1) Å
$c = 8.315$ (3) Å
$\beta = 120.03$ (2)°
$V = 267.0$ (2) Å^3
$Z = 4$
$D_x = 8.368$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 11 reflections
$\theta = 6.5$–14.5°
$\mu = 23.925$ mm^{-1}
$T = 130$ K
Needle
0.20 × 0.05 × 0.04 mm
Metallic

Data collection

Syntex $P2_1$ diffractometer
ω scans
Absorption correction: empirical based on F_o^2 and F_c^2 differences (*XABS*2; Parkin, Hope & Moezzi, 1993)
$T_{\min} = 0.02$, $T_{\max} = 0.105$
367 measured reflections
347 independent reflections
330 observed reflections $[F > 2.0\sigma(F)]$

$R_{\rm int} = 0.0131$
$\theta_{\max} = 27.5°$
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 4$
$l = 0 \rightarrow 10$
2 standard reflections monitored every 198 reflections
intensity variation: ±2.0%

Refinement

Refinement on F^2
$R(F) = 0.0224$
$wR(F^2) = 0.0615$
$S = 1.29$
345 reflections
19 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2]$ where $P = (F_o^2 + 2F_c^2)$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.46$ e Å^{-3}
$\Delta\rho_{\min} = -1.36$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Sb(1)	0.4052 (1)	0	0.1128 (1)	0.006 (1)
Sb(2)	0.3526 (1)	1/2	0.4654 (1)	0.006 (1)
Nb	0.1522 (1)	0	0.1904 (1)	0.006 (1)

Table 2. *Selected geometric parameters* (Å)

Sb(1)—Nb	2.907 (1)	2×	Sb(2)—Sb(2)	3.037 (1)	2×
Sb(1)—Nb	2.918 (1)	2×	Nb—Nb	3.138 (2)	
Sb(1)—Nb	2.961 (1)		Nb—Sb(1)	2.907 (1)	2×
Sb(1)—Sb(1)	3.304 (1)	3×	Nb—Sb(1)	2.918 (1)	2×
Sb(2)—Nb	2.834 (1)	2×	Nb—Sb(1)	2.961 (1)	
Sb(2)—Nb	2.887 (1)		Nb—Sb(2)	2.834 (1)	2×
Sb(2)—Sb(2)	2.770 (1)		Nb—Sb(2)	2.887 (1)	

The diffractometer was equipped with a locally modified LT-1 low-temperature apparatus. The cold-stream temperature was approximately 130 K. The system operated from a DEC VAXStation 3200 microcomputer. The structure was solved with *SHELXTL-Plus* (Sheldrick, 1991), using direct methods, and refined with *SHELXL* (Sheldrick, 1994).

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Lists of structure factors and anisotropic displacement parameters, and structure factors, atomic coordinates, anisotropic displacement parameters and bond distances for the title structure in space group $C2$ have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71723 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1041]

References

Brattas, I., Donaldson, J. D., Kjekshus, A., Nicholson, D. G. & Southern, J. T. (1975). *Acta Chem. Scand. Ser. A*, **29**, 217–219.
Calvert, L. D. (1992). *Acta Cryst.* **B48**, 113–114.
Furuseth, S. & Kjekshus, A. (1964*a*). *Acta Chem. Scand.* **18**, 1180–1195.
Furuseth, S. & Kjekshus, A. (1964*b*). *Nature* (*London*), **203**, 512.
Furuseth, S. & Kjekshus, A. (1965). *Acta Cryst.* **18**, 320–324.
Parkin, S., Hope, H. & Moezzi, B. (1993). *XABS*2. Department of Chemistry, Univ. of California, Davis, USA.
Pearson, W. B. (1967). *Handbook for Lattice Spacings and Structures of Metals*, Vol. 2, p. 7. London: Pergamon.
Pearson, W. B. (1972). *The Crystal Chemistry and Physics of Metals and Alloys*, p. 526. New York: Wiley.
Powder Diffraction File (1991). Metals and Alloys Subfile, 2nd ed. International Centre for Diffraction Data, Swarthmore, PA 19081, USA.
Schäfer, H. & Fuhr, W. (1965). *J. Less-Common Met.* **8**, 375–387.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1994). *J. Appl. Cryst.* In preparation.
Villars, P. & Calvert, L. D. (1985). *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, Vols. 1–3. Materials Park, OH: ASM International.
Weitz, G., Born, L. & Hellner, E. (1960). *Z. Metallkd.* **51**, 238–243.

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Cu$_3$Bi$_4$V$_2$O$_{14}$, a New Compound

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Abstract

The title compound has an infinite three-dimensional structure that contains eight-coordinate bismuth(III), five- and six-coordinate copper(II) and four-coordinate vanadium(V). The mean bond distances are: Bi—O

2.57 (31) Å, Cu—O 1.956 (27) (in the square planes), 2.64 (10) Å (out-of-plane distances), and V—O 1.713 (29) Å. The shortest Cu—Cu distance is 3.063 (3) Å.

Comment

Crystals of namibite ($CuBi_2VO_6$) (Knorring & Sahama, 1981) in a mineral sample (Birch & Pring, 1991) from the Iron Monarch mine in South Australia were unsuitable for single-crystal data collection. This prompted attempts to synthesize namibite. $CuBi_2O_4$ (0.40 g) (Weller & Lines, 1989) was finely ground with $VO(OH)_2.H_2O$ (0.14 g) (Morgan & Moss, 1913) and heated in an alumina crucible at 873 K for 16 h, cooled, then ground and heated again for 4 d at 1023 K, after which it was cooled at 0.5 K min^{-1} to room temperature. A crystal selected from this preparation proved to be that of the title compound, the structure of which is reported here.

The structure of $Cu_3Bi_4V_2O_{14}$ (Fig. 1) comprises an infinite three-dimensional cation and oxygen framework of eight-coordinate bismuth(III), five- and six-coordinate copper(II) and four-coordinate vanadium(V) ions. The coordination of each ion is shown in Fig. 1. The two crystallographically independent Bi-ion coordination polyhedra were shown to be 4,4-bicapped trigonal pyramids (King, 1969) using *POLYHEDRON* (Johnson, Taylor & Cox, 1980). The mean Bi—O bond distance is 2.57 (31) Å† within the range 2.239 (12)–3.050 (11) Å. The mean Bi—O distance compares favourably with that found recently (Pring, Gatehouse & Birch, 1990) in francisite [$Cu_3Bi(SeO_3)_2O_2Cl$, 2.48 (22) Å] for eight-coordinate bismuth(III).

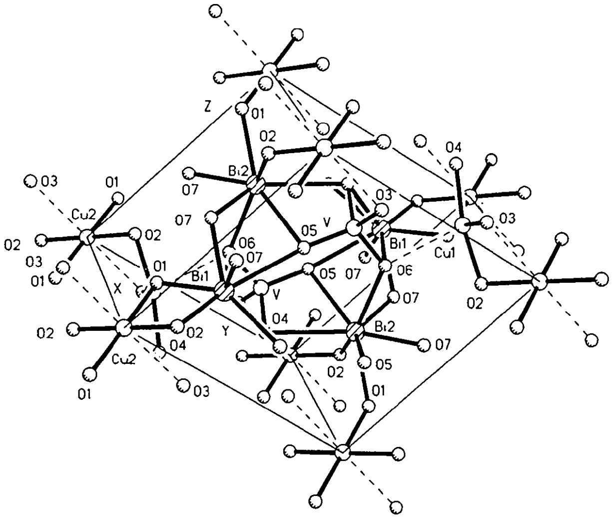

Fig. 1. The structure of $Cu_3Bi_4V_2O_{14}$. Labelled atoms are not necessarily those whose coordinates are given.

Both Cu atoms have square-planar coordination [for Cu1, the mean Cu—O distance in the square plane is 1.93 (1) Å, with a fifth O atom at 2.75 (1) Å; for Cu(2), the mean Cu—O distance in the square plane is 1.98 (1) Å, with two further O atoms at 2.58 (2) Å]. In francisite the mean (in the square plane) Cu—O distances were Cu1—O 1.94 (3) and Cu2—O 1.97 (1) Å and the longer contacts were to Cl ions. The tetrahedral V ion has a mean V—O distance of 1.71 (3) Å, within the range 1.69 (2)–1.75 (1) Å.

Three O atoms, O1, O2 and O3, bridge the two Cu atoms, with O3 common to Cu1, Cu2 and V; O1 and O2 also bond to the two Bi atoms. The Bi and V ions have O4, O5 and O6 in common.

The bond valence sums (Brown & Altermatt, 1985) are Cu1 2.07, Cu2 1.96, V 5.12, Bi1 2.98, Bi2 2.96, and the O atoms have a mean value of 1.92 (18).

The shortest cation–cation distance is from Cu1 to Cu2 [3.063 (3) Å].

There are a number of compounds known in the Bi–Cu, Bi–V and Cu–V systems; however, there appears to have been only one report of a compound in which all three elements occur together. That is in $Bi_4V_2O_{11}$ in which some of the vanadium has been replaced by copper resulting in a 'high performance oxide ion conductor' (Abraham, Boivin, Mairesse & Nowogrocki, 1990).

Further work on the system Bi–Cu–V–O is being carried out.

Experimental

Crystal data

$Cu_3Bi_4V_2O_{14}$
M_r = 1352.4
Triclinic
$P\bar{1}$
a = 5.317 (2) Å
b = 7.916 (4) Å
c = 8.095 (5) Å
α = 74.58 (5)°
β = 89.38 (4)°
γ = 70.39 (3)°
V = 308.2 (3) $Å^3$
Z = 1
D_x = 7.286 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 20 reflections
θ = 6–16°
μ = 63.28 mm^{-1}
T = 293.0 (10) K
Tabular
0.25 × 0.025 × 0.025 mm
Red/black pleochroic

Data collection

Nicolet $R3m/V$ diffractometer
ω scans
Absorption correction: from crystal shape (*SHELXTL-Plus*; Sheldrick, 1991)
T_{min} = 0.168, T_{max} = 0.304
3622 measured reflections
1811 independent reflections

1382 observed reflections [$I > 3\sigma(I)$]
R_{int} = 0.048
θ_{max} = 30.00°
$h = -7 \rightarrow 7$
$k = -11 \rightarrow 11$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 197 reflections intensity variation: 1%

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† For mean bond distances the numbers in parentheses are standard deviations, for bond lengths these numbers are standard uncertainties.

Refinement

Refinement on F
$R = 0.0398$
$wR = 0.0576$
$S = 0.54$
1382 reflections
73 parameters
Calculated weights
$w = 1/[\sigma^2(F) + 0.0096F^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 6.41$ e Å^{-3}
$\Delta\rho_{\min} = -5.37$ e Å^{-3}
Extinction correction: modified Larson (1970) method (*SHELXTL-Plus*; Sheldrick, 1991)
Extinction coefficient: 0.0045 (3)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.3.1 and 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Bi1	0.10793 (9)	−0.20460 (6)	0.69944 (6)	0.0096 (2)
Bi2	0.42486 (10)	0.15405 (7)	0.63975 (6)	0.0106 (2)
Cu1	−0.3625 (3)	−0.2236 (2)	−0.0257 (2)	0.0086 (5)
Cu2	0	0	0	0.0078 (7)
V	0.2506 (5)	−0.4285 (3)	0.2456 (3)	0.0087 (7)
O1	0.2904 (19)	−0.0696 (13)	−0.1488 (12)	0.008 (2)
O2	0.2261 (18)	0.0437 (13)	0.1669 (12)	0.010 (2)
O3	−0.0010 (30)	−0.3373 (22)	0.0868 (19)	0.040 (3)
O4	−0.4742 (23)	−0.3906 (17)	0.1548 (15)	0.022 (2)
O5	0.1811 (24)	−0.3213 (18)	0.4045 (16)	0.024 (2)
O6	0.3302 (20)	0.3292 (14)	0.3250 (13)	0.013 (2)
O7	0.2474 (17)	−0.0025 (13)	0.5043 (11)	0.006 (2)

Table 2. *Selected geometric parameters* (Å)

Bi1—O1^{i}	2.239 (12)	Cu1—O2^{v}	1.916 (11)
Bi1—O7	2.243 (10)	Cu1—O4	1.928 (12)
Bi1—O2^{ii}	2.263 (10)	Cu1—O3	1.943 (15)
Bi1—O7^{ii}	2.351 (8)	Cu1—O1^{vi}	1.942 (8)
Bi1—O5	2.760 (14)	Cu1—O6^{v}	2.752 (12)
Bi1—O6^{iii}	2.837 (10)	Cu1—Cu2	3.063 (3)
Bi1—O6^{ii}	2.845 (13)	Cu2—O1	1.970 (9)
Bi1—O4^{iv}	3.050 (11)	Cu2—O1^{v}	1.970 (9)
Bi2—O7^{iii}	2.266 (9)	Cu2—O2	1.988 (11)
Bi2—O2^{iii}	2.271 (8)	Cu2—O2^{v}	1.988 (11)
Bi2—O7	2.271 (12)	Cu2—O3	2.576 (18)
Bi2—O1^{i}	2.405 (10)	Cu2—O3^{v}	2.576 (18)
Bi2—O6	2.519 (10)	V—O3	1.691 (15)
Bi2—O5^{iii}	2.804 (15)	V—O4^{vii}	1.711 (13)
Bi2—O4^{ii}	2.887 (15)	V—O6^{viii}	1.754 (11)
Bi2—O5^{ii}	3.028 (12)	V—O5	1.694 (15)

Symmetry codes: (i) $x, y, 1+z$; (ii) $-x, -y, 1-z$; (iii) $1-x, -y, 1-z$; (iv) $-x, -1-y, 1-z$; (v) $-x, -y, -z$; (vi) $x-1, y, z$; (vii) $1+x, y, z$; (viii) $x, y-1, z$.

Data collection, cell refinement and data reduction were performed with Nicolet *R3m/V* software. Structure solution, structure refinement, preparation of molecular graphics and generation of material for publication were performed using *SHELXTL-Plus* (Sheldrick, 1991).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1063). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Abraham, F., Boivin, J. C., Mairesse, G. & Nowogrocki, G. (1990). *Solid State Ionics*, **40/41**, 934–937.
Birch, W. & Pring, A. (1991). Private communication.
Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.
Johnson, M., Taylor, J. C. & Cox, G. W. (1980). *J. Appl. Cryst.* **13**, 188–189.
King, R. B. (1969). *J. Am. Chem. Soc.* **91**, 7211–7216.
Knorring, O. V. & Sahama, Th. G. (1981). *Schweiz. Mineral. Petrogr. Mitt.* **61**, 7–12.
Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.
Morgan, G. T. & Moss, H. W. (1913). *J. Chem. Soc.* **103**, 78–90
Pring, A., Gatehouse, B. M. & Birch, W. D. (1990). *Am. Miner.* **75**, 1421–1425.
Sheldrick, G.M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Weller, M. T. & Lines, D. R. (1989). *J. Solid State Chem.* **82**, 21–29.

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Li_3BS_3

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Abstract

The structure of lithium orthothioborate, Li_3BS_3, obtained by crystallizing the corresponding glass, consists of quasi-planar Li_3BS_3 entities in which B atoms are tricoordinated by S atoms. Tetrahedra of S atoms around Li are linked to one another *via* corners and/or edges. This structure, which exhibits a higher symmetry than other $M_3B(O,S)_3$ structures, such as Li_3BO_3 or Tl_3BS_3, appears to be a new member of the M_3AX_3 group of compounds.

Comment

Lithium thioborate compounds, designated as $(1-x)B_2S_3 - xLi_2S$, have been found to give homogeneous glasses for $0.5 \leq x \leq 0.75$ and $x = 0.375$. These glasses exhibit a very high Li^+ ion conductivity ($\simeq$ 0.1 Ω^{-1} m^{-1} at room temperature). Some of the authors have undertaken an extensive study of their structure to discover its relation to their ionic conductivity (Ménétrier, Estournès & Levasseur, 1992). Among the crystalline phases of this system, $Li_{6+2n}(B_{10}S_{18})S_n$, $n = 2$ (corresponding to $x = 0.5$), is the only one for which the crystal structure has been determined (Zum Hebel, Krebs, Grüne

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