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A new mixed-valent copper–antimony sulfide: $[H_2NCH_2CH_2NH_2]_{0.5}[Cu_2SbS_3]$

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A mixed-valent copper–antimony sulfide, $[H_2NCH_2CH_2NH_2]_{0.5}[Cu_2SbS_3]$, has been solvothermally synthesized from binary metal sulfides in the presence of ethylenediamine and characterised by single-crystal X-ray diffraction, thermogravimetry, elemental analysis and SQUID magnetometry. The structure of this material consists of chains of fused 5-membered rings of stoichiometry Cu_2SbS_3, linked into two-dimensional slabs of approximate thickness 5 Å. Neutral ethylenediamine molecules reside between the slabs, to which they are hydrogen bonded. Magnetic susceptibility data yield an effective magnetic moment per formula unit of 0.94(6) μ_B, consistent with the presence of copper-(I) and -(II) species in the metal sulfide framework.

Introduction

Template-directed synthesis is increasingly used for the preparation of novel inorganic materials under solvothermal conditions. The template molecule, typically an organic amine, is added to a gel or slurry of inorganic reactants prior to heating under autogenous pressure. The template exerts a structure-directing influence on the crystallisation process, resulting in the formation of metastable materials with open-framework structures, in which the organic moiety is retained within tunnels or pores. This synthetic methodology has been widely applied to the synthesis of oxide-based materials and it provides a convenient method for the laboratory preparation of naturally occurring aluminosilicates (zeolites) as well as main-group and transition-metal phosphates[1,2] and metal oxides[3] with novel framework topologies.

In the late 1980s, Bedard *et al.*[4] reported that a similar strategy could be applied to effect the crystallisation of tin and germanium sulfides. This observation led to considerable interest in the solvothermal synthesis of open-framework chalcogenides.[5] The majority of materials produced to date, contain the main-group elements antimony,[6–13] tin,[14,15] indium[16] and germanium.[17–21] A variety of complex secondary building units including the $Sb_3S_6^{3-}$ semicube,[6,8,10,11] $Ge_4S_{10}^{4-}$ adamantane unit[18,20] and the $In_{10}S_{20}^{10-}$ supertetrahedron,[16] which are not observed in oxides, may be identified in the structures of these materials. The metal sulfide frameworks arising from linkage of secondary building units show pronounced low-dimensional characteristics. This is exemplified by the antimony sulfides, which exhibit a range of chain-like structural motifs. The $Sb_4S_7^{2-}$ chain is particularly prevalent and may occur in isolation, with individual chains separated by template molecules,[10,22,23] or may be bridged to form $Sb_8S_{14}^{2-}$,[11] $Sb_8S_{13}^{2-}$,[13] or $Sb_{10}S_{16}^{2-}$ [12] double chains. Individual chains may also interlock *via* Sb–S or Sb–Sb[6] bonds to form two- or three-dimensional structures.

In contrast with oxide-based materials, there have been relatively few reports of solvothermal synthesis of main-group sulfides in which transition-metal cations are incorporated within the framework. The preparation has been described of ternary germanium sulfides in which $Ge_4S_{10}^{4-}$ adamantane units are linked by tetrahedral manganese(II)[20,24] or cobalt(II),[4] linear two-co-ordinate copper(I),[19] or dimeric $(Ag_2)^{2+}$ or $(Cu_2)^{2+}$ units.[21] In the material $[C_7H_{13}N][Mn_{0.25}Ge_{1.75}S_4]$[25] the MS_4 tetrahedra of which the adamantane cluster is composed are statistically occupied by both Mn^{IV} and Ge^{IV}. However in $[C_4H_{12}N]_6[(Cu_{0.44}Ge_{0.56}S_{2.23})_4(Ge_4S_8)]$[26] the clusters contain only germanium and there is statistical occupancy by copper and germanium of the linking tetrahedra. This disorder causes a deviation from the stoichiometry appropriate to a network of $Ge_4S_{10}^{4-}$ linked by 3-connected MS_4 tetrahedra and results in mixed-valent copper. Schimek *et al.*[27] have reported the synthesis using supercritical ammonia, of anionic copper–antimony sulfide frameworks, in which Cu_8S_{13} cores are linked by antimony atoms to form channels containing transition-metal hexamine cations. Using similar conditions, a silver–antimony sulfide containing chains of edge-linked tetrahedra in which silver and antimony alternate is produced. Recently, Chen *et al.*[28] described the solvothermal synthesis of copper–antimony selenides in the presence of ethylenediamine and an alkali-metal selenide. Although no alkali-metal ions are incorporated in the final product, use of sodium and potassium selenides led to the formation of two different layered materials with closely related structures, both of which contain copper in two valence states (Cu^I/Cu^{II}).

The presence of redox active species within frameworks with marked low-dimensional characteristics offers the potential to produce unusual magnetic and transport properties. For this reason we are currently investigating the incorporation of transition-metal cations into antimony sulfide frameworks and here present the first results of this study: the synthesis of a new mixed-valent copper–antimony sulfide.

Experimental

Synthesis and characterisation

Ethylenediamine was pre-treated by bubbling H_2S through it for 3 h prior to use. Sb_2S_3 (0.89 g) and Cu_2S (0.81 g) were added with stirring to 4.5 mL of ethylenediamine to produce a slurry with an approximate molar composition $Sb_2S_3 : Cu_2S :$ ethylenediamine of 1 : 2 : 30. The slurry was sealed into a Teflon-lined stainless steel autoclave and heated at 473 K for 8 days prior to cooling to room temperature at 1 K min^{-1}. The solid product was collected by filtration, washed with portions of deionised water and ethanol and dried in air at room temperature. It con-

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sisted of a mixture of orange plate-like crystals, rectangular metallic grey crystals and black polycrystalline material. Subsequent efforts to produce a single-phase material by extending the reaction time or adjusting the composition of the reaction mixture always led to the same mixture of single crystals and polycrystalline material. The metallic grey crystals were identified as Sb_2S_3 by single-crystal X-ray diffraction. Powder X-ray diffraction data on a ground portion of the bulk sample were collected with nickel-filtered Cu-Kα radiation ($\lambda = 1.5418$ Å) using a Philips PA2000 powder diffractometer. The strongest peaks in the pattern could be indexed on the basis of a tetragonal unit cell with refined parameters $a = 5.377(2)$, $c = 10.740(3)$ Å, which are in good agreement with those of the ternary phase Cu_3SbS_4.[29] With the exception of two features at $2\theta = 9$ and 12°, the remaining peaks could be indexed on the basis of the monoclinic unit cell determined from the single-crystal X-ray diffraction study with refined unit-cell parameters $a = 6.154(6)$, $b = 18.623(9)$, $c = 6.497(6)$ Å, $\beta = 113.02(5)°$.

The orange crystals were separated from the bulk sample by hand-picking. Combustion analysis gave C, 2.84; H, 1.16; N, 3.72%, which compare favourably with values calculated from the crystallographically determined formula $[C_2H_8N_2]_{0.5}$-$[Cu_2SbS_3]$ (C, 3.20; H, 1.07; N, 3.73%). Thermogravimetric analysis was performed using a DuPont Instruments 951 thermal analyser. Approximately 6.4 mg of orange crystals were heated under a flow of dry nitrogen over the temperature range 273–563 K at a heating rate of 5 K min^{-1}. A gradual weight loss of 8.76%, observed over the temperature range 353–513 K, is consistent with removal of the organic template (calculated 8.01%). Powder X-ray diffraction indicated that thermal decomposition produces a poorly crystalline material, in which Cu_3SbS_4 can tentatively be identified from a number of broad diffuse reflections. Analytical electron microscopy was performed on ground orange crystals, coated with carbon to minimise charging effects, using a Hitachi S-2700 scanning electron microscope fitted with a PGT IMIX-XE detection system. Using Sb_2S_3 and Cu_2S as intensity standards, Sb : S and Cu : S ratios of 0.33(2) and 0.65(5) : 1 were obtained, which compare with values of 0.33 and 0.67 : 1 for the crystallographically determined composition. Magnetic susceptibility data were collected using a Quantum Design MPMS5 SQUID susceptometer. 4.2 mg of orange crystals were loaded into gelatin capsules at room temperature and data were collected over the temperature range $80 \le T/K \le 300$ after cooling in the measuring field of 10 kG.

Crystal structure determination

Intensity data were collected using an Enraf-Nonius DIP2020 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). Images were processed using the DENZO and SCALEPACK suite of programs.[30] Experimental information is given in Table 1. The structure was solved by direct methods using the SIR 92 program.[31] Subsequent full-matrix least-squares refinements and Fourier syntheses were carried out using the CRYSTALS suite of programs.[32] Structure solution using intensity data collected at 293 and 270 K produces the same copper–antimony sulfide framework but with orientational disorder of the ethylenediamine molecules corresponding to *ca.* 50% occupancy of two sites by the carbon atoms of the amine.

CCDC reference number 186/2187.

See http://www.rsc.org/suppdata/dt/b0/b005111j/ for crystallographic files in .cif format.

Results and discussion

Selected bond lengths and angles are presented in Table 2. The local co-ordination of the framework atoms is depicted in Fig. 1. Each antimony atom is co-ordinated to three sulfur atoms at distances in the range 2.423(2)–2.445(2) Å in an approximately trigonal pyramidal geometry with S–Sb–S angles of between 98.49(6) and 101.03(6)°. In addition, each antimony atom has a fourth sulfur neighbour at a much longer distance of 3.691(2) Å, which is less than the sum of the van der Waals radii of Sb and S (3.80 Å).[33] Each of the two crystallographically distinct copper atoms also has three sulfur near neighbours at distances in the range 2.261(2)–2.368(2) Å and Cu(2) has an additional sulfur neighbour at 3.100(2) Å, slightly less than the sum of the respective van der Waals radii (3.2 Å). The co-ordination about Cu(2) is almost trigonal planar with S–Cu(2)–S angles in the range 113.78(7)–123.59(7)° whilst Cu(1) shows a slight distortion towards trigonal pyramidal geometry. This distortion involves displacement of Cu(1) towards the antimony atom. The Cu(1)–Sb distance of 2.660(1) Å, which is considerably shorter than Cu–Sb distances in the high-temperature ternary phases $CuSbS_2$ (3.42 Å)[34] and Cu_3SbS_3 (3.31 Å),[35] but comparable with that in the alloy Cu_2Sb (2.62 Å),[36] indicates significant intermetallic bonding. The Cu–Sb bond completes a nearly planar five-membered ring (Fig. 1) formed from linking of primary SbS_3 and CuS_3 units. Rings are fused along the edges formed by Cu(2)–S(3) and Cu(1)–Sb bonds to form puckered chains directed along [10−1] (Fig. 2). Individual chains are in turn linked *via* Cu(1)–S(2) and Sb–S(1) bonds to form layers, approximately 5 Å thick, which are parallel to the (001) crystallographic plane (Fig. 3). Within Cu_2SbS_3 layers there is an additional weaker interchain Cu–Sb interaction (Cu(2)–Sb = 3.100(1) Å). Furthermore, the separation between Cu(1) and Cu(2) in neighbouring chains is only 2.674(1) Å, which compares with a Cu–Cu distance of 2.56 Å in the bulk metal.[37] With the exception of Cu_3SbS_3 (Cu–Cu 2.60 Å),[35] Cu–Cu distances in the high-temperature ternary phases are generally longer (3.20–3.80 Å). The short distance determined in this study suggests that there is a significant interchain Cu–Cu interaction. Template molecules, which are formulated as neutral species, reside between Cu_2SbS_3 slabs (Fig. 4) with

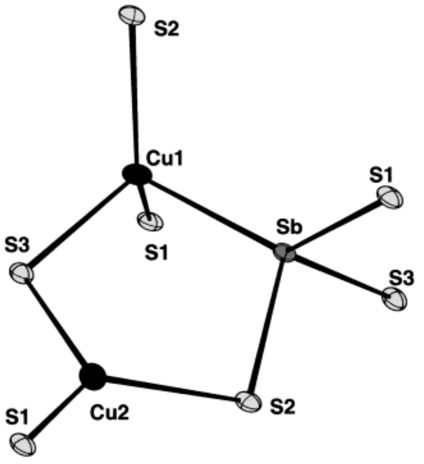

Fig. 1 Local co-ordination of the framework atoms in $[C_2N_2H_8]_{0.5}$-$[Cu_2SbS_3]$ showing the atom labelling scheme and ellipsoids at 50% probability.

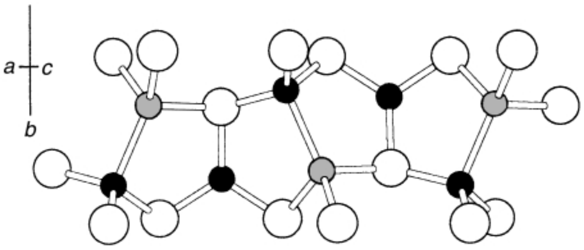

Fig. 2 Cu_2SbS_3 chains running parallel to [10−1] formed from fused 5-membered copper–antomony sulfide rings. Key: copper, large black circles; antimony, large shaded circles; sulfur, large open circles.

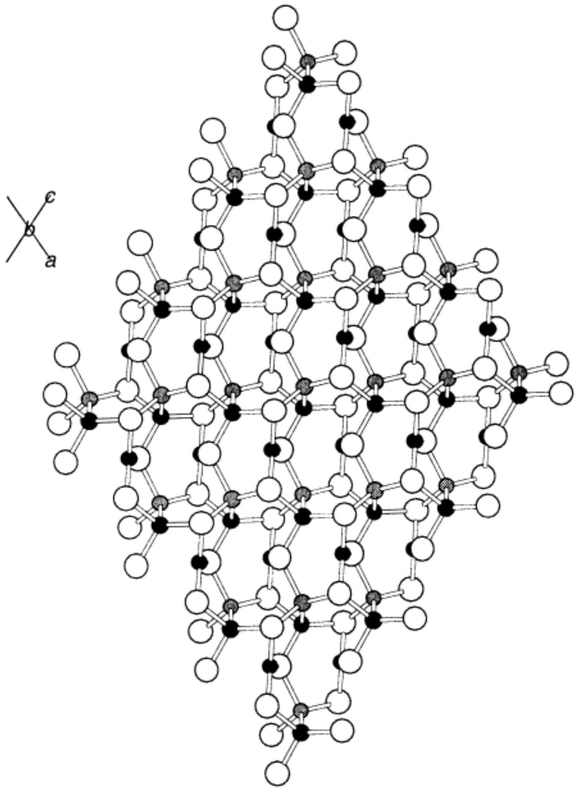

Fig. 3 View along the [010] direction showing the Cu_2SbS_3 slabs, generated by linking chains of 5-membered rings *via* Cu(1)–S(2) and Sb–S(1) bonds. Slabs are *ca.* 5 Å thick and lie parallel to the (001) plane. Key as for Fig. 2. Interchain Cu···Cu contacts (2.674(1) Å) are omitted for clarity.

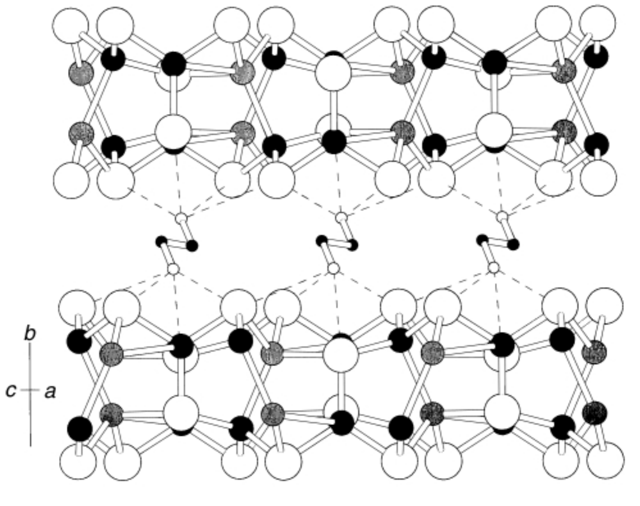

Fig. 4 View along the [101] direction showing the location of neutral ethylenediamine template molecules between Cu_2SbS_3 slabs. Dashed lines show the short sulfur–nitrogen distances (3.203(6)–3.485(7) Å) and indicate a possible network of hydrogen bonds. Key: copper, large black circles; antimony, large shaded circles; sulfur, large open circles; carbon, small black circles; nitrogen, small open circles. Hydrogen atoms of the template are omitted for clarity.

Table 1 Crystallographic data for $[C_2N_2H_8]_{0.5}[Cu_2SbS_3]$

Formula	$CH_4Cu_2NS_3Sb$
M_r	375.07
Crystal system	Monoclinic
Space group	$P2_1/n$
T/K	150
a/Å	6.101(1)
b/Å	18.445(3)
c/Å	6.518(1)
β/°	112.92(1)
V/Å^3	675.56
Z	4
μ/cm^{-1}	11.05
Measured data	2759
Unique data	1327
Observed data ($I > 3\sigma(I)$)	1128
R_{merg}	0.049
R	0.0553[a]
R_w	0.0645[a]

[a] Refinement against F.

the terminal nitrogen atoms directed at the two neighbouring layers which are separated by a distance of *ca.* 4 Å. Each nitrogen atom of the template has four sulfur neighbours in the framework at distances in the range 3.203(6)–3.485(7) Å, implying the possible presence of hydrogen bonding between the template and the framework.

The four copper–antimony sulfides which have been structurally characterised to date, all possess structures related to those of zinc blende or wurtzite. In the case of Cu_3SbS_4 ordering of cations over the tetrahedral sites gives rise to three-dimensional superstructures,[29] whereas Cu_3SbS_3 [35] contains 25% of vacancies on the anion sublattice. The layered structure of $CuSbS_2$ [34] is derived from that of wurtzite by the introduction of cleavage planes, resulting in SbS_3 trigonal pyramidal units. In all cases copper is present as tetrahedral Cu^I. However, Pfitzner *et al.* recently reported[38] $Cu_{12}Sb_4S_{13}$ in which both tetrahedral and trigonal planar co-ordination of copper is observed, together with trigonal pyramidal SbS_3. This material provides a rare example of mixed valency, with an average copper oxidation state of +1.17. The Cu_2SbS_3 framework of the material prepared here by solvothermal methods is markedly different from that of these high-temperature materials. The Cu_2SbS_3 framework is isostructural with the analogous selenide synthesized from the metal chlorides and selenium in the presence of ethylenediamine and sodium selenide, reported by Chen *et al.*[28] Under the conditions employed here, it was not possible to prepare the sulfide analogue of the second phase prepared by Chen *et al.* in the presence of potassium selenide, suggesting that, although not incorporated in the product, alkali-metal ions play a role in the crystallisation process.

If the ethylenediamine template is present in its non-protonated form, the Cu_2SbS_3 framework must be neutral. Assuming normal valence states for antimony and sulfur, this requires copper to be present in two valence states, Cu^I and Cu^{II}. Similar mixed valency has been proposed for the analogous selenide.[28] However, the structural study alone is unable to establish the degree of protonation of the template unambiguously, as the refinement is insufficiently sensitive to protons. Considerable support for the mixed-valent nature of the compound is provided by susceptibility data which reveal that the material is paramagnetic. A fully protonated ethylenediamine would require all of the copper atoms to be in the univalent state, resulting in a diamagnetic material. The theoretical spin-only moment for equimolar amounts of Cu^+ and Cu^{2+} is 1.22 μ_B per copper atom. Magnetic susceptibility data for $[H_2NCH_2CH_2NH_2]_{0.5}[Cu_2SbS_3]$ follow Curie–Weiss behaviour (Fig. 5) with a Curie constant of 0.22(3) cm^3 K mol^{-1}. This corresponds to an effective magnetic moment per copper atom of 0.94(6) μ_B thus ruling out the possibility of exclusively univalent copper and supporting the suggestion of mixed copper valency. Li[39] has observed similar paramagnetic behaviour in the corresponding selenide. The reduction in moment from the spin-only value indicates some degree of magnetic interaction, consistent with the relatively small negative Weiss constant (−32(7) K). In the mixed-valent compound $[C_4H_{12}N]_6[(Cu_{0.44}Ge_{0.56}S_{2.23})_4(Ge_4S_8)]$,[26] Cu^I and Cu^{II} have been associated respectively with crystallographic sites with three- and four-fold sulfur co-ordination. In the present case, the

Table 2 Selected bond lengths (Å) and bond angles (°) for $[C_2N_2H_8]_{0.5}[Cu_2SbS_3]$

Sb–S(1)	2.423(2)	Cu(1)–S(1)^{b}	2.340(2)	Cu(2)–S(1)	2.310(2)
Sb–S(2)	2.433(2)	Cu(1)–S(2)^{c}	2.313(2)	Cu(2)–S(2)^{e}	2.280(2)
Sb–S(3)	2.445(2)	Cu(1)–S(3)^{d}	2.368(2)	Cu(2)–S(3)^{c}	2.261(2)
Sb···S(3)^{a}	3.691(2)	Cu(1)···Cu(2)^{d}	2.674(1)	Cu(2)···S(3)^{c}	3.100(2)
Sb–Cu(1)	2.660(1)	Sb···Cu(2)	3.100(1)		
S(1)–Sb–S(2)	98.49(6)	S(1)^{b}–Cu(1)–S(2)^{c}	112.41(7)	S(1)–Cu(2)–S(2)^{e}	113.78(7)
S(1)–Sb–S(3)	101.03(6)	S(1)^{b}–Cu(1)–S(3)^{d}	103.24(7)	S(1)–Cu(2)–S(3)^{c}	123.59(7)
S(2)–Sb–S(3)	100.42(6)	S(2)^{c}–Cu(1)–S(3)^{d}	123.17(7)	S(2)–Cu(2)–S(3)^{c}	121.66(8)

Symmetry transformations used to generate equivalent atoms: ^{a} $1 + x, y, z$; ^{b} $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; ^{c} $x + \frac{1}{2}, \frac{1}{2} - y, z + \frac{1}{2}$; ^{d} $x + \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; ^{e} $x, y, 1 + z$.

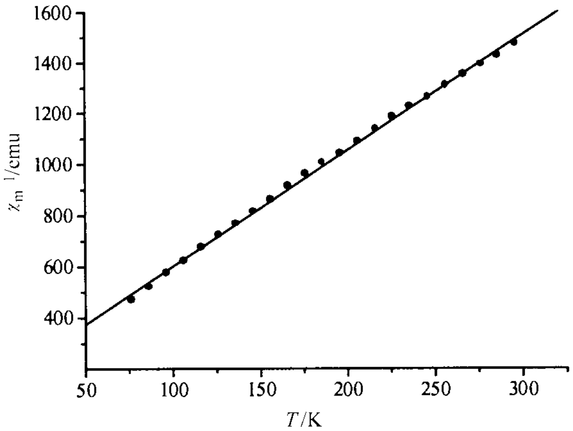

Fig. 5 Reciprocal magnetic susceptibility data for $[C_2N_2H_8]_{0.5}$-$[Cu_2SbS_3]$. Points are data collected on warming, after cooling in the measuring field of 10 kG. The straight line is obtained from fitting the Curie–Weiss expression to the data.

two crystallographically distinct sites have very similar environments, each with three sulfur near neighbours in an approximately trigonal planar array and intermetallic contacts to antimony and copper. The similarity of the two sites, together with the relatively short Cu–Cu separation, suggests that assignment of formal oxidation states to copper ions at each site is not meaningful and that they should be considered as forming a $(Cu_2)^{3+}$ dimeric species.

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