

# An Antimony Sulfide with Copper Pillars: [C<sub>4</sub>H<sub>12</sub>N<sub>2</sub>]<sub>0.5</sub>[CuSb<sub>6</sub>S<sub>10</sub>]

Anthony V. Powell,<sup>\*,†</sup> Raquel Paniagua,<sup>†</sup> Paz Vaqueiro,<sup>†</sup> and  
Ann M. Chippindale<sup>‡</sup>

Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom,  
and Department of Chemistry, The University of Reading, Whiteknights,  
Reading RG6 6AD, United Kingdom

Received August 14, 2001. Revised Manuscript Received October 11, 2001

A new copper–antimony sulfide, [C<sub>4</sub>H<sub>12</sub>N<sub>2</sub>]<sub>0.5</sub>[CuSb<sub>6</sub>S<sub>10</sub>], has been hydrothermally synthesized from binary metal sulfides in the presence of triethylenetetramine and characterized by single-crystal X-ray diffraction, thermogravimetry, elemental analysis, and SQUID magnetometry. The product ( $M_r = 1158.72$ ) crystallizes in the monoclinic space group  $P2_1/n$  with  $a = 11.2578(4)$  Å,  $b = 12.5259(5)$  Å,  $c = 13.9390(7)$  Å,  $\beta = 102.445(3)^\circ$ , and  $V = 1919.4$  Å<sup>3</sup>. The structure consists of cyclic Sb<sub>3</sub>S<sub>6</sub><sup>3-</sup> units in a boatlike conformation, linked by Sb–S bonds to form a complex Sb<sub>6</sub>S<sub>12</sub><sup>6-</sup> building block. Sb–S bonds serve to link Sb<sub>6</sub>S<sub>12</sub><sup>6-</sup> units to four others in a herringbone array, forming a sheet of stoichiometry Sb<sub>6</sub>S<sub>10</sub><sup>2-</sup>, containing 24-membered rings of alternating Sb and S atoms. Pairs of edge-sharing CuS<sub>4</sub> distorted tetrahedra form pillars which link Sb<sub>6</sub>S<sub>10</sub><sup>2-</sup> layers together. The interlayer space contains piperazine cations, formed by cyclization of the triethylenetetramine during synthesis. Bond-valence sums are consistent with the presence of antimony(III) and copper(I), requiring complete protonation of the amine.

## Introduction

Following the demonstration by Bedard and co-workers in 1989<sup>1</sup> that template-directed synthesis can be applied to effect the crystallization of tin and germanium sulfides, there has been considerable interest in the preparation of main-group chalcogenides in the presence of organic amines.<sup>2</sup> The majority of the materials produced to date are binary sulfide frameworks of the elements antimony,<sup>3–10</sup> tin,<sup>11,12</sup> indium,<sup>13</sup> and germanium.<sup>14–18</sup> A variety of complex building units

including the Sb<sub>3</sub>S<sub>6</sub><sup>3-</sup> semicube,<sup>3,5,7,8</sup> Ge<sub>4</sub>S<sub>10</sub><sup>4-</sup> adamantane cluster,<sup>15,17</sup> and the In<sub>10</sub>S<sub>20</sub><sup>10-</sup> supertetrahedron<sup>13</sup> have been observed. The metal–sulfide frameworks arising from linkage of these units commonly exhibit low-dimensional characteristics. This behavior is typified by the antimony sulfides for which a range of chainlike structural motifs, consisting of vertex-linked SbS<sub>3</sub><sup>3-</sup> pyramidal units, have been identified. Two- or three-dimensional structures may arise from interlocking of individual chains. Although this secondary linking generally occurs via Sb–S bonds, Sb–Sb linkages have been identified in [(NH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>]<sub>0.5</sub>[Sb<sub>7</sub>S<sub>11</sub>], a material that contains layers of stoichiometry Sb<sub>7</sub>S<sub>11</sub><sup>2–3</sup>.

To date, there have been relatively few reports of the incorporation of transition metals into solvothermally synthesized main-group sulfides. Ternary germanium sulfides in which Ge<sub>4</sub>S<sub>10</sub><sup>4-</sup> adamantane units are linked by tetrahedral Mn(II)<sup>17,19</sup> or Co(II),<sup>1</sup> linear two-coordinate Cu(I),<sup>16</sup> or dimeric (Ag<sub>2</sub>)<sup>2+</sup> or (Cu<sub>2</sub>)<sup>2+</sup> units<sup>18</sup> have been reported. In the material, [C<sub>7</sub>H<sub>13</sub>N][Mn<sub>0.25</sub>Ge<sub>1.75</sub>S<sub>4</sub>],<sup>20</sup> there is a statistical distribution of Mn(IV) and Ge(IV) among the MS<sub>4</sub> tetrahedra constituting the adamantane clusters. By contrast, the analogous clusters in [C<sub>4</sub>H<sub>12</sub>N]<sub>6</sub>[(Cu<sub>0.44</sub>Ge<sub>0.56</sub>S<sub>2.23</sub>)<sub>4</sub>(Ge<sub>4</sub>S<sub>8</sub>)]<sup>21</sup> contain only germanium: copper ions are confined to the linking tetrahedra which

\* To whom correspondence should be addressed. Fax: +44 (0)131 451 3180. E-mail: a.v.powell@hw.ac.uk.

<sup>†</sup> Heriot-Watt University.

<sup>‡</sup> The University of Reading.

(1) Bedard, R. L.; Wilson, S. T.; Vail, L. D.; Bennett, J. M.; Flanigen, E. M. In *Zeolites: Facts, Figures, Future*; Jacobs, P. A., van Santen, R. A., Eds.; Elsevier: Amsterdam, 1989.

(2) Sheldrick, W. S.; Wachhold, M. *Angew. Chem., Intl. Ed. Engl.* **1997**, *36*, 206.

(3) Powell, A. V.; Boissière, S.; Chippindale, A. M. *Chem. Mater.* **2000**, *12*, 1034.

(4) Wang, X.; Jacobson, A. J.; Liebau, F. *J. Solid State Chem.* **1998**, *140*, 387.

(5) Ko, Y.; Tan, K.; Parise, J. B.; Darovsky, A. *Chem. Mater.* **1996**, *8*, 493.

(6) Parise, J. B. *Science* **1991**, *251*, 293.

(7) Parise, J. B.; Ko, Y. *Chem. Mater.* **1992**, *4*, 1446.

(8) Tan, K.; Ko, Y.; Parise, J. B.; Park, J. B.; Darovsky, A. *Chem. Mater.* **1996**, *8*, 2510.

(9) Wang, X. *Eur. J. Solid State Inorg. Chem.* **1995**, *32*, 303.

(10) Tan, K.; Ko, Y.; Parise, J. B. *Acta Crystallogr. Sect C* **1994**, *50*, 1439.

(11) Jiang, T.; Lough, A.; Ozin, G. A.; Bedard, R. L.; Broach, R. J. *Mater. Chem.* **1998**, *8*, 721.

(12) Jiang, T.; Ozin, G. A. *J. Mater. Chem.* **1998**, *8*, 1099.

(13) Cahill, C. L.; Parise, J. B. *Dalton Trans.* **2000**, 1475.

(14) Krebs, B. *Angew. Chem., Intl. Ed. Engl.* **1983**, *22*, 113.

(15) MacLachlan, M.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *397*, 681.

(16) Tan, K.; Darovsky, A.; Parise, J. B. *J. Am. Chem. Soc.* **1995**, *117*, 7039.

(17) Cahill, C. L.; Parise, J. B. *Chem. Mater.* **1997**, *9*, 807.

(18) Bowes, C. L.; Huynh, W. U.; Kirkby, S. J.; Malek, A.; Ozin, G. A.; Petrov, S.; Twardowski, M.; Young, D.; Bedard, R. L.; Broach, R. *Chem. Mater.* **1996**, *8*, 2147.

(19) Yaghi, O. M.; Sun, Z.; Richardson, D. A.; Groy, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 807.

(20) Cahill, C. L.; Ko, Y.; Hanson, J. C.; Tan, K.; Parise, J. B. *Chem. Mater.* **1998**, *10*, 1453.

they occupy statistically with germanium. For the transition-metal-substituted antimony sulfides, complete cation segregation is found in  $[\text{Ni}(\text{C}_4\text{H}_{13}\text{N}_3)_2]_2\text{-}[\text{Sb}_4\text{S}_8]^{22}$  in which there are relatively weak secondary interactions between isolated cyclic  $\text{Sb}_4\text{S}_8^{4-}$  anions and charge-balancing  $\text{Ni}(\text{C}_4\text{H}_{13}\text{N}_3)_2^{2+}$  cations. Tris(ethylenediamine) complexes of iron, cobalt, and nickel also act as counterions to chainlike antimony sulfides<sup>23</sup> and it has been shown that thioantimonate anions can serve as linkages between transition-metal amine complexes.<sup>24</sup> Copper ions, however, appear to be more readily incorporated into the framework structure of antimony sulfides, forming part of the primary bonding network. For example, Schimek et al.<sup>25</sup> have reported the synthesis using supercritical ammonia of anionic copper–antimony sulfide frameworks in which  $\text{Cu}_8\text{S}_{13}$  cores are linked by antimony atoms to form channels which contain transition-metal hexamine cations. Similarly, in  $\text{Na}_2\text{CuSbS}_3$ ,  $\text{SbS}_3$  trigonal pyramids share vertexes with trigonal planar Cu(I) centers to form a layer of stoichiometry  $\text{CuSbS}_3$ .<sup>26</sup> More recently, the mixed-valent Cu(I)/Cu(II) sulfide  $[\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2]_{0.5}\text{-}[\text{Cu}_2\text{SbS}_3]^{27}$  and isostructural selenide<sup>28</sup> have been reported in which a Cu–Sb interaction completes a five-membered ring comprised of  $\text{SbQ}_3$  and  $\text{CuQ}_3$  units (Q = S, Se).

We have an ongoing program of research designed to synthesize materials in which transition-metal cations are incorporated within frameworks with marked low-dimensional characteristics. Here, we describe the synthesis and characterization of a new amine-templated copper–antimony sulfide,  $[\text{C}_4\text{H}_{12}\text{N}_2]_{0.5}[\text{CuSb}_6\text{S}_{10}]$ . This material is interesting as segregation of antimony and copper ions produces a novel open-framework structure containing antimony–sulfide layers linked by pillars of edge-sharing  $\text{CuS}_4$  tetrahedra, giving the first example of a pillared-layer antimony sulfide.

## Experimental Section

The structure-directing agent, triethylenetetramine (TETN), was pretreated by bubbling  $\text{H}_2\text{S}$  through it for 90 min prior to use. The amine (0.9 mL) and water (1.6 mL) were then added to  $\text{Sb}_2\text{S}_3$  (0.83 g) and  $\text{Cu}_2\text{S}$  (0.47 g) with stirring, to produce a slurry of approximate molar composition  $\text{Sb}_2\text{S}_3\text{:Cu}_2\text{S}\text{:amine}\text{:H}_2\text{O}$  of 1:1:2:30. The slurry was sealed into a Teflon-lined stainless steel autoclave, heated at 473 K for a period of 10 days and then cooled slowly to room temperature at  $1\text{ K min}^{-1}$ . The solid product, which was collected by filtration and washed with deionized water and ethanol prior to drying in air, consisted of a mixture of large black crystals and black polycrystalline material. Powder X-ray diffraction data for a ground sample of the bulk product were collected with a Philips PA2000 powder diffractometer using Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418\text{ \AA}$ ). An orthorhombic phase with refined unit-cell parameters,  $a = 5.991(7)\text{ \AA}$ ,  $b = 3.798(4)\text{ \AA}$ , and  $c =$

**Table 1. Crystallographic Data for  $[\text{C}_4\text{H}_{12}\text{N}_2]_{0.5}[\text{CuSb}_6\text{S}_{10}]$**

formula	$\text{C}_2\text{H}_6\text{CuNS}_{10}\text{Sb}_6$
$M_r$	1158.72
crystal system	monoclinic
space group	$P2_1/n$
$T/K$	293
$a/\text{\AA}$	11.2578(4)
$b/\text{\AA}$	12.5259(5)
$c/\text{\AA}$	13.9390(7)
$\beta/\text{deg}$	102.445(3)
$V/\text{\AA}^3$	1919.4
$Z$	4
$\mu_{\text{Mo K}\alpha}/\text{cm}^{-1}$	10.51
$\rho_{\text{calc}} (\text{g cm}^{-3})$	4.01
measured data	6529
unique data	3515
observed data ( $I \geq 3\sigma(I)$ )	3048
$R_{\text{merge}}$	0.025
residual electron density (min, max) ( $\text{e \AA}^{-3}$ )	−1.98, 1.16
number of parameters refined	199
$R$	0.024 <sup>a</sup>
$R_w$	0.031 <sup>a</sup>

<sup>a</sup> Refinement against  $F$ .

14.49(1)  $\text{\AA}$ , was identified in the diffraction pattern and is consistent with the identification of the black polycrystalline material as Wolfsbergite,  $\text{CuSbS}_2$ .<sup>29</sup> The black crystals were separated from the bulk sample by hand picking. Powder X-ray diffraction data for ground single crystals can be indexed on the basis of the monoclinic unit cell determined from the single-crystal diffraction study below, with refined unit-cell parameters,  $a = 11.245(5)\text{ \AA}$ ,  $b = 12.512(5)\text{ \AA}$ ,  $c = 13.957(10)\text{ \AA}$ , and  $\beta = 102.44(3)^\circ$ .

Combustion analysis gave C 1.98, H 0.48, and N 0.94% which compares favorably with values calculated from the crystallographically determined formula  $[\text{C}_4\text{H}_{12}\text{N}_2]_{0.5}[\text{CuSb}_6\text{S}_{10}]$  (C 1.98, H 0.5, N 1.2%). Analytical electron microscopy was performed with a Philips CM20 transmission electron microscope fitted with an EDAX PV9900 analysis system. Using  $\text{Sb}_2\text{S}_3$  and  $\text{CuS}$  as intensity standards, Sb:S and Cu:S ratios of 0.56(3):1 and 0.09(1):1 were obtained for the finely ground single crystals. These values compare well with those of 0.6:1 and 0.1:1 for the crystallographically determined composition. Thermogravimetric analysis was performed using a DuPont Instruments 951 thermal analyzer. Approximately 12 mg of hand-picked crystals, finely ground, were heated under a flow of dry nitrogen over the temperature range 303–643 K at a heating rate of  $2\text{ K min}^{-1}$ . A gradual weight loss of 4.2% observed over the temperature range 573–600 K is consistent with the removal of the organic amine (calculated 3.8%). Powder X-ray diffraction data indicated that thermal decomposition produces a poorly crystalline material in which both  $\text{Sb}_2\text{S}_3$  and  $\text{CuSbS}_2$  can be identified from a number of broad diffuse reflections.

A black crystal of  $[\text{C}_4\text{H}_{12}\text{N}_2]_{0.5}[\text{CuSb}_6\text{S}_{10}]$  was mounted on a thin glass fiber on a Marresearch Image Plate System with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.7107\text{ \AA}$ ). The crystal was positioned 70 mm from the image plate and 95 frames were measured at  $2^\circ$  intervals with a counting time of 2 min. Data were processed and corrected for absorption using the program XDS.<sup>30</sup> The crystal was determined to be monoclinic with lattice parameters  $a = 11.2578(4)\text{ \AA}$ ,  $b = 12.5259(5)\text{ \AA}$ ,  $c = 13.9390(7)\text{ \AA}$ ,  $\beta = 102.445(3)^\circ$ , and unit-cell volume  $1919.4\text{ \AA}^3$ . Crystallographic data are summarized in Table 1. The structure was solved in space group  $P2_1/n$  using the direct methods program SHELXS,<sup>31</sup> which located all of the metal atoms and most of the S atoms. The remaining S atoms and the C and N atoms of the template were located by difference Fourier methods. All Fourier calculations and subsequent full-

(21) Tan, K.; Ho, Y.; Parise, J. B.; Darovsky, A. *Chem. Mater.* **1996**, *8*, 448.

(22) Bensch, W.; Näther, C.; Stähler, R. *Chem. Commun.* **2001**, 477.

(23) Stephan, H.-O.; Kanatzidis, M. G. *Inorg. Chem.* **1997**, *36*, 6050.

(24) Stähler, R.; Bensch, W. *Dalton Trans.* **2001**, 2518.

(25) Schimek, G. L.; Kolis, J. W.; Long, G. J. *Chem. Mater.* **1997**, *9*, 2776.

(26) Jerome, J. E.; Schimek, G. L.; Drake, G. W.; Kolis, J. W. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 765.

(27) Powell, A. V.; Boissière, S.; Chippindale, A. M. *Dalton Trans.* **2000**, 4192.

(28) Chen, Z.; Dilks, R. E.; Wang, R.; Lu, J. Y.; Li, J. *Chem. Mater.* **1998**, *10*, 3184.

(29) Razmara, M. F.; Henderson, C. M. B.; Patrick, R. A. D. *Miner. Mag.* **1997**, *61*, 79.

(30) Kabsch, W. *J. Appl. Crystallogr.* **1988**, *21*, 916

(31) Sheldrick, G. M. SHELXS-86 Program for Crystal Structure Determination, University of Göttingen, Germany, 1986.

**Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters ( $\text{\AA}^2$ ) for Non-hydrogen Atoms in  $[\text{C}_4\text{H}_{12}\text{N}_2]_{0.5}[\text{CuSb}_6\text{S}_{10}]$** 

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
Sb(1)	0.15547(3)	0.87438(2)	0.67978(2)	0.0148
Sb(2)	0.13522(3)	0.98330(2)	0.11671(2)	0.0157
Sb(3)	-0.12680(3)	0.75829(2)	0.72229(2)	0.0155
Sb(4)	0.14539(3)	0.71891(2)	0.42617(2)	0.0142
Sb(5)	0.36081(3)	0.89501(2)	0.96690(2)	0.0138
Sb(6)	0.13535(2)	0.13314(2)	0.83098(2)	0.0134
Cu(1)	-0.05064(6)	0.90539(5)	0.46231(4)	0.0262
S(1)	-0.1551(1)	0.95311(8)	0.71444(7)	0.0162
S(2)	-0.1572(1)	0.78598(8)	0.53990(7)	0.0167
S(3)	0.1559(1)	0.90784(8)	0.49737(7)	0.0144
S(4)	0.1497(1)	0.90606(8)	0.89251(7)	0.0155
S(5)	0.35661(9)	0.98156(7)	0.12828(7)	0.0128
S(6)	0.3630(1)	0.69640(8)	0.44638(8)	0.0154
S(7)	0.1963(1)	0.07082(8)	0.67933(7)	0.0142
S(8)	-0.3390(1)	0.71105(8)	0.71043(8)	0.0172
S(9)	0.3696(1)	0.82717(8)	0.72935(8)	0.0168
S(10)	0.14651(9)	0.64210(8)	0.59575(7)	0.0129
N(1)	0.0352(5)	0.5899(4)	0.0624(4)	0.0320
C(1)	0.0272(6)	0.4813(5)	0.1032(4)	0.0368
C(2)	0.0649(5)	0.5846(4)	0.9644(4)	0.0297

**Table 3. Selected Bond Lengths ( $\text{\AA}$ ) and Bond Valences (v.u.) for  $[\text{C}_4\text{H}_{12}\text{N}_2]_{0.5}[\text{CuSb}_6\text{S}_{10}]$** 

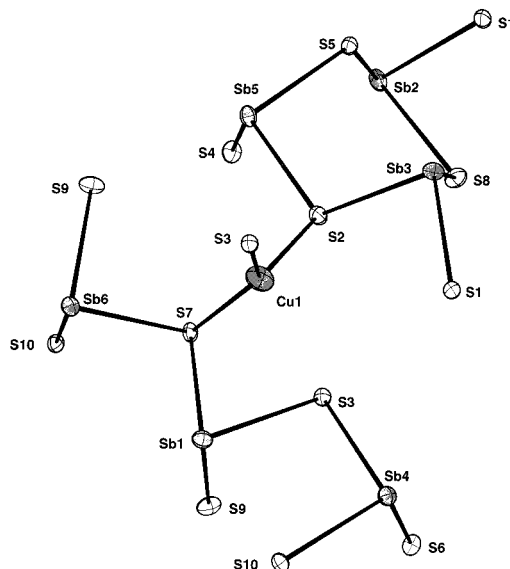
		$\nu^a$			$\nu^a$
Sb(1)–S(3)	2.578(1)	0.71	Sb(5)–S(2) <sup>d</sup>	2.511(1)	0.85
Sb(1)–S(7)	2.503(1)	0.87	Sb(5)–S(4)	2.383(1)	1.20
Sb(1)–S(9)	2.433(1)	1.05	Sb(5)–S(5)	2.507(1)	0.86
Sb(1)–S(1)	3.761(1)	0.03	Sb(5)–S(9)	3.440(1)	0.07
Sb(1)–S(4)	3.006(1)	0.22	Sb(5)–S(10) <sup>c</sup>	3.212(1)	0.13
Sb(1)–S(10)	3.130(1)	0.16	Sb(5)–S(10) <sup>e</sup>	3.361(1)	0.09
	<b>3.04</b>			<b>3.20</b>	
Sb(2)–S(1) <sup>b</sup>	2.449(1)	1.00	Sb(6)–S(7)	2.484(1)	0.91
Sb(2)–S(5)	2.463(1)	0.97	Sb(6)–S(9) <sup>c</sup>	2.568(1)	0.73
Sb(2)–S(6) <sup>c</sup>	2.812(1)	0.38	Sb(6)–S(10) <sup>c</sup>	2.451(1)	1.00
Sb(2)–S(8) <sup>d</sup>	2.748(1)	0.45	Sb(6)–S(4)	2.965(1)	0.25
Sb(2)–S(4)	3.309(1)	0.10	Sb(6)–S(6) <sup>c</sup>	3.199(1)	0.13
Sb(2)–S(4) <sup>b</sup>	3.471(1)	0.06	Sb(6)–S(8) <sup>i</sup>	3.404(1)	0.08
	<b>2.96</b>			<b>3.10</b>	
Sb(3)–S(1)	2.460(1)	0.97	Cu(1)–S(2)	2.325(1)	0.28
Sb(3)–S(2)	2.515(1)	0.84	Cu(1)–S(3)	2.271(1)	0.33
Sb(3)–S(8)	2.432(1)	1.05	Cu(1)–S(3) <sup>j</sup>	2.735(1)	0.09
Sb(3)–S(5) <sup>e</sup>	3.267(1)	0.11	Cu(1)–S(7) <sup>j</sup>	2.298(1)	0.31
Sb(3)–S(6) <sup>f</sup>	3.201(1)	0.13			<b>1.01</b>
	<b>3.10</b>				
Sb(4)–S(3)	2.559(1)	0.74	Cu(1)–Cu(1) <sup>b</sup>	2.740(1)	
Sb(4)–S(6)	2.422(1)	1.08	N(1)–C(1)	1.485(8)	
Sb(4)–S(10)	2.550(1)	0.76	N(1)–C(2)	1.476(8)	
Sb(4)–S(5) <sup>g</sup>	3.067(1)	0.19	C(1)–C(2) <sup>k</sup>	1.491(8)	
Sb(4)–S(8) <sup>h</sup>	3.174(1)	0.14			
Sb(4)–S(9) <sup>e</sup>	3.719(1)	0.03			
	<b>2.94</b>				

<sup>a</sup> Bond valences and their sums calculated using parameters from ref 35. <sup>b</sup> Note: Symmetry transformations used to generate equivalent atoms:  $-x, 2 - y, 2 - z, c^{1/2} - x, 1/2 + y, 3/2 - z, d^{1/2} + x, 3/2 - y, 1/2 + z, e, x - 1/2, 3/2 - y, z - 1/2, f, x - 1/2, 3/2 - y, 1/2 + z, g, 1/2 - x, y - 1/2, 3/2 - z, h, 1/2 + x, 3/2 - y, z - 1/2, i, 1/2 + x, 1/2 + y, 3/2 - z, j, -x, 2 - y, 1 - z, k, -x, 1 - y, 2 - z$ .

matrix least-squares refinements were carried out using the CRYSTALS suite of programs.<sup>32</sup> The hydrogen atoms of the template were placed geometrically and a 3-term Chebyshev polynomial applied as a weighting scheme. Final refined atomic parameters and isotropic thermal parameters are provided in Table 2, while selected bond distances are presented in Table 3.

## Results and Discussion

The local coordination of the framework atoms is shown in Figure 1. With the exception of Sb(2), each of



**Figure 1.** Local coordination of the framework atoms showing the atom-labeling scheme and thermal ellipsoids at 50% probability. The two crystallographically distinct  $\text{Sb}_3\text{S}_6^{3-}$  six-membered rings, one comprising Sb(1), Sb(4), and Sb(6) and the other Sb(2), Sb(3), and Sb(5), have boatlike conformations.

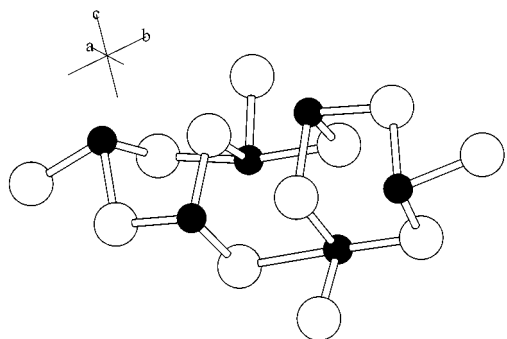
the crystallographically distinct antimony atoms is coordinated to three sulfur atoms at distances in the range 2.383(1)–2.578(1)  $\text{\AA}$ . These  $\text{SbS}_3$  primary structural units have an approximately trigonal pyramidal geometry with S–Sb–S angles in the range 78.37(3)–98.94(4)°. Sb(2) has, in addition to its two sulfur neighbors at 2.449(1) and 2.463(1)  $\text{\AA}$ , two further sulfur neighbors at slightly longer distances of 2.748(1) and 2.812(1)  $\text{\AA}$ , giving this atom 2 + 2 coordination. All antimony atoms have additional sulfur neighbors at distances in the range 2.965(1)–3.719(1)  $\text{\AA}$ , less than the sum of the van der Waals' radii of Sb and S (3.80  $\text{\AA}$ ).<sup>33</sup> The presence of both short and long Sb–S bonds has been observed in a number of templated antimony–sulfide structures.<sup>3,7,9,10</sup> By initially considering only those Sb–S distances < 2.748(1)  $\text{\AA}$ , we may identify two crystallographically distinct  $\text{Sb}_3\text{S}_6^{3-}$  rings formed by vertex-linking of groups of three  $\text{SbS}_3$  units. One of these rings contains Sb(1), Sb(4), and Sb(6) and the other Sb(2), Sb(3), and Sb(5). Both adopt a boatlike conformation (Figure 1). Although  $\text{Sb}_3\text{S}_6^{3-}$  secondary building units have been identified in a number of solvothermally synthesized antimony sulfides,<sup>3,5,7,8</sup> they generally adopt a chairlike conformation which has been termed a “semicube”. However, a boatlike conformation of  $\text{Sb}_3\text{S}_6^{3-}$  has been identified in  $\text{RbSb}_3\text{Se}_5$ ,<sup>34</sup> while  $[(\text{CH}_3\text{NH}_2)_{1.03}\text{K}_{2.97}][\text{Sb}_{12}\text{S}_{20}] \cdot 1.34\text{H}_2\text{O}$  provides a rare example of a structure in which both chair- and boatlike forms of  $\text{Sb}_3\text{S}_6^{3-}$  are found.<sup>4</sup> Linkage of  $\text{Sb}_3\text{S}_6^{3-}$  rings to form a complex  $\text{Sb}_6\text{S}_{12}^{6-}$  unit (Figure 2) occurs via longer Sb–S interactions (Sb(6)–S(4), 2.977(5)  $\text{\AA}$ ; Sb(2)–S(6), 2.812(1)  $\text{\AA}$ ) which are weaker than those in the primary  $\text{SbS}_3$  units. Additional interactions between Sb(5)–S(10) and Sb(4)–S(5) at distances of 3.212(1) and 3.067(1)  $\text{\AA}$  respectively may further stabilize this unit. Individual  $\text{Sb}_6\text{S}_{12}^{6-}$  units are linked in turn by sharing exo-cyclic

(32) Watkin, D. J.; Prout, C. K.; Carruthers, R. J.; Betteridge, P. CRYSTALS, issue 10; Chemical Crystallography Laboratory: Oxford, 1996 (computer program).

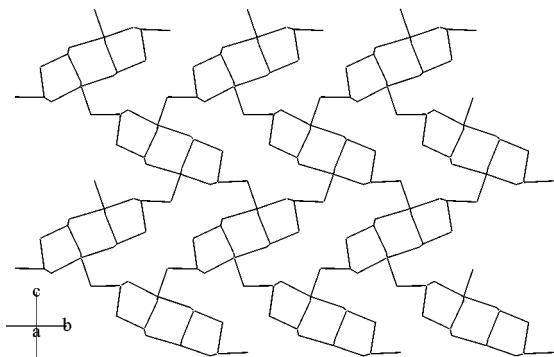
(33) Bondi, A. J. Phys. Chem. **1964**, *68*, 441.

(34) Sheldrick, W. S.; Hausler, H.-J. Z. Anorg. Allg. Chem. **1988**, *557*, 98.



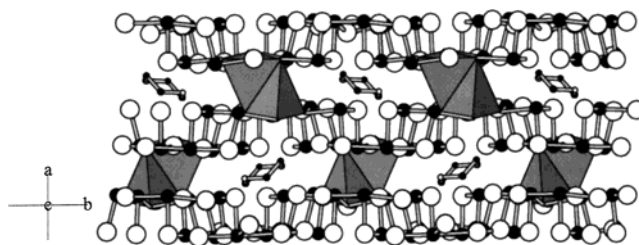


**Figure 2.** Linkage of the two crystallographically distinct  $\text{Sb}_3\text{S}_6^{3-}$  rings via  $\text{Sb}(6)\text{-S}(4)$  and  $\text{Sb}(2)\text{-S}(6)$  bonds to form a complex  $\text{Sb}_6\text{S}_{12}^{6-}$  building unit. Key: antimony, solid circles; sulfur, open circles.



**Figure 3.** View along  $[100]$  of a skeletal representation of the herringbone arrangement generated by the linkage of the  $\text{Sb}_6\text{S}_{12}^{6-}$  units via four  $\text{Sb-S}$  bonds to form layers of stoichiometry  $\text{Sb}_6\text{S}_{10}^{2-}$  which lie parallel to the  $(100)$  crystallographic plane. Amine cations have been omitted for clarity.

sulfur atoms ( $2 \times \text{S}(1)$ ,  $2 \times \text{S}(2)$ ) to form sheets of stoichiometry  $\text{Sb}_6\text{S}_{10}^{2-}$ ,  $\approx 2.6 \text{ \AA}$  thick, which lie parallel to the  $(100)$  crystallographic plane. Within the sheets, the  $\text{Sb}_6\text{S}_{12}^{6-}$  units adopt a herringbone array, generating irregularly shaped 24-membered rings of alternating antimony and sulfur atoms within the  $(100)$  plane (Figure 3) with cross-ring  $\text{S}\cdots\text{S}$  distances in the range  $\approx 3.5\text{--}15.4 \text{ \AA}$ . The  $\text{Sb}_6\text{S}_{10}^{2-}$  layers are linked into a three-dimensional array by copper atoms which form pillars between successive antimony-sulfide sheets. Each copper atom is coordinated to three sulfur atoms at distances in the range  $2.271(1)\text{--}2.325(1) \text{ \AA}$ . A fourth sulfur neighbor at a longer distance of  $2.735(1) \text{ \AA}$ , which is less than the sum of van der Waals' radii of  $3.20 \text{ \AA}$ , gives each copper atom a distorted tetrahedral geometry reflected in  $\text{S-Cu-S}$  angles which lie in the range  $78.76(4)\text{--}121.03(4)^\circ$ . A similar combination of three short and one longer  $\text{Cu-S}$  distance has been observed in  $[\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2]_{0.5}[\text{Cu}_2\text{SbS}_3]$ .<sup>27</sup> Two distorted  $\text{CuS}_4$  tetrahedra share a common edge ( $2 \times \text{S}(3)$ ) to form pillars which link neighboring antimony-sulfide sheets (Figure 4). The copper pillars cause successive antimony-sulfide layers to adopt an  $ABAB$  stacking sequence, such that the 24-membered rings in neighboring sheets are not aligned, thus preventing the establishment of a tunnel network perpendicular to the sheet. However, within the interlayer space, the copper pillars may be considered to define two mutually perpendicular intersecting channel systems aligned parallel to the antimony-sulfide layers. In the as-prepared material, these channels contain the organic species.



**Figure 4.** View along  $[001]$  showing the pillared layer structure of  $[\text{C}_4\text{H}_{12}\text{N}_2]_{0.5}[\text{CuSb}_6\text{S}_{10}]$ . Each pillar is constructed from a pair of edge-sharing  $\text{CuS}_4$  tetrahedra which are shown in a polyhedral representation. Key: antimony, large solid circles; sulfur, large open circles; nitrogen, small open circles; carbon, small solid circles.

Formal valence considerations imply that all antimony atoms are trivalent, a view which is supported by the calculated bond-valence sums (Table 3).<sup>35</sup> Copper generally exists in the monovalent state in a sulfide matrix. However, mixed  $\text{Cu(I)/Cu(II)}$  copper valency has been identified in the mixed-metal sulfides  $[\text{C}_4\text{H}_{12}\text{N}_2]_{6-}[(\text{Cu}_{0.44}\text{Ge}_{0.56}\text{S}_{2.23})_4(\text{Ge}_4\text{S}_8)]$ <sup>21</sup> and  $[\text{C}_2\text{H}_8\text{N}_2]_{0.5}[\text{Cu}_2\text{SbS}_3]$ .<sup>27</sup> Both contain two crystallographically distinct copper sites in contrast to the single copper site in  $[\text{C}_4\text{H}_{12}\text{N}_2]_{0.5-}[\text{CuSb}_6\text{S}_{10}]$ . Bond-valence sums indicate that copper is present as the closed-shell species  $\text{Cu(I)}$ . This is consistent with a measured molar magnetic susceptibility for ground crystals of ca.  $-3.0 \times 10^{-4} \text{ emu}$ , obtained using a Quantum Design MPMS2 Superconducting Quantum Interference Device (SQUID) susceptometer. Formal oxidation states of  $\text{Sb(III)}$  and  $\text{Cu(I)}$  produce an anionic metal-sulfide framework with a single negative charge. Therefore, to provide the necessary charge balancing, the template molecules are doubly protonated.

Although TETN was used as the templating agent in the reaction described here, structural analysis identifies the organic species present in the product as piperazine. This suggests that the reaction conditions have resulted in cyclization of the TETN, leading to in situ formation of the effective templating agent piperazine. Decomposition of TETN to ethylenediamine and cyclized species has been reported<sup>36</sup> to occur under conditions similar to those employed in synthesis here. Parise and Ko have observed similar cyclization of TETN at long reaction times during the synthesis of  $[\text{C}_4\text{H}_8\text{N}_2][\text{Sb}_4\text{S}_7]$ .<sup>7</sup> In the material prepared here, piperazine cations reside within the interlayer space between copper pillars, located in positions above and below the 24-membered rings of the  $\text{Sb}_6\text{S}_{10}^{2-}$  sheet. The template species are arranged such that the two nitrogen atoms are directed at different neighboring antimony-sulfide layers. Each nitrogen atom has one sulfur neighbor at a distance of  $3.349(4) \text{ \AA}$  in the sheet at which it is directed and two further neighbors in the adjacent sheet at distances in the range  $3.441(5)\text{--}3.491(5) \text{ \AA}$ , implying the possible presence of a hydrogen-bonding interaction between the template and the framework.

In conclusion, we have succeeded in synthesizing a new copper-antimony sulfide in which two-dimensional antimony sulfide layers are linked into a three-dimen-

(35) Brese, N. E.; O'Keefe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

(36) Hutchinson, W. M.; Collett, A. R.; Lazzell, C. L. *J. Am. Chem. Soc.* **1945**, *67*, 1966.

sional structure by pillars of copper atoms which form pairs of edge-linked  $\text{CuS}_4$  tetrahedra. To the best of our knowledge, this is the first example of a pillared layer antimony sulfide. The copper pillars define two mutually perpendicular channel systems aligned parallel to the antimony sulfide layers and containing the organic component. Attempts to remove the organic species by thermal methods led to the collapse of the structure. Mild oxidizing agents may provide a means of removing the organic component, thereby affording access to the microporosity.

**Acknowledgment.** A.M.C. thanks the University of Reading RETF fund for a Research Fellowship.

**Supporting Information Available:** Tables listing all bond distances and angles, anisotropic thermal parameters for non-hydrogen atoms and structure factors, a figure showing the  $[\text{C}_4\text{H}_{12}\text{N}_2]_{0.5}[\text{CuSb}_6\text{S}_{10}]$  structure, and an X-ray crystallographic file (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM010751F