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$[Co(en)_3][Sb_{12}S_{19}]$: A New Antimony Sulfide with a Zeolite-like Structure Containing One-Dimensional Channels

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Solvothermal synthesis affords access to the first truly three-dimensional antimony–sulfide framework which contains one-dimensional circular channels.

Porous arrays on a nanometer scale are found in many crystalline materials that exhibit tetrahedral-based oxide frameworks, such as zeolites and AlPOs.[1] In these materials, the presence of a regular array of channels and cavities gives rise to a high degree of selectivity for sorptive and reactive processes, leading to their applications as catalysts, ion exchangers, and molecular sieves. Sulfide-based open-framework materials have attracted increased attention in recent years, owing to their potential as next-generation zeotype materials, in which the ion-exchange and catalytic properties of zeolites may be combined with the semiconducting properties of metal sulfides. This is exemplified by the recently reported microporous frameworks, $[A_{4-x}B_xS_8]^{x-}$ (where $A = Ge^{4+}$ or Sn^{4+} and $B = Ga^{3+}$ or In^{3+}), which are strongly photoluminescent while exhibiting ion-exchange capacities comparable to those of zeolites.[2]

Since 1989,[3] solvothermal synthesis has been increasingly used for the preparation of a variety of chalcogenides containing the main-group elements tin, germanium, arsenic, antimony, and indium.[4] The structures of these materials are characterized by secondary building units, such as $Sb_3S_6^{3-}$ semicubes,[5] $In_{10}S_{20}^{10-}$ supertetrahedra,[6] and adamantane-like $Ge_4S_{10}^{4-}$ units,[7] which differ markedly from those found in oxide materials. Such sulfide phases are generally prepared in the presence of an organic base, which acts as a structure-directing agent and is commonly retained within pores or cavities of the resultant metal−sulfide matrix. Much of our recent work[8] has focused on the preparation of novel antimony sulfides through reactions in which polyamines serve as the structure-directing agents.

Antimony sulfides prepared by solvothermal methods commonly exhibit low-dimensional structures, in contrast to the wide range of three-dimensional structures adopted by the aluminosilicates and phosphates.[9] In particular, a range of chainlike structural motifs, consisting of vertex-linked SbS_3^{3-} pyramidal units, have been identified.[10] Structures of higher dimensionality only arise from interlocking of $Sb_xS_y^{z-}$ units by weaker (>2.8 Å) secondary Sb−S interactions.[11−13] In this work, we have prepared what we believe to be the first truly three-dimensional antimony sulfide, $[Co(en)_3][Sb_{12}S_{19}]$. Remarkably, in this structure primary antimony−sulfur bonds form a three-dimensional network and generate a regular array of isolated channels of approximately circular cross-section. The diameter of these channels, ca. 5 Å, is very similar to those in the commercially important zeolite, ZSM-5.[9]

$[Co(en)_3][Sb_{12}S_{19}]$ was prepared from a mixture of CoS (0.134 g, 1.5 mmol) and Sb_2S_3 (0.500 g, 1.5 mmol) which was loaded into a 23 mL Teflon-lined stainless steel autoclave. A solution of S in ethylenediamine (0.3 mg/mL, 3 mL) was added to form a mixture with an approximate molar composition Sb_2S_3/CoS/S/en of 1:1:0.02:30. After stirring the mixture, the container was closed, heated at 170 °C for 6 days, and then cooled to room temperature at a cooling rate of 20 °C h^{-1}. The product consists of red polycrystalline powder and red platelike crystals of the title

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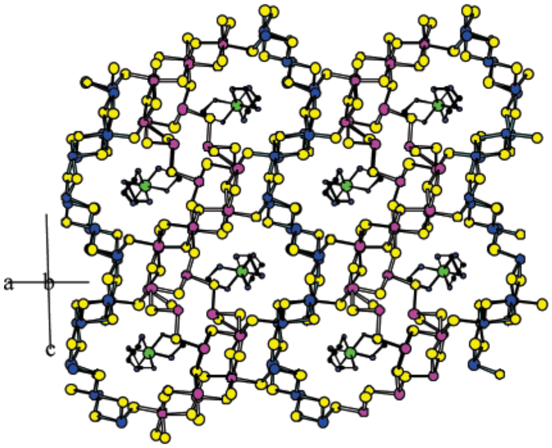

Figure 1. $[Co(en)_3][Sb_{12}S_{19}]$ viewed along [010]. The $Co(en)_3^{2+}$ cations are located in the one-dimensional channels of the $[Sb_{12}S_{19}]^{2-}$ framework. Key: antimony atoms within the ribbons discussed in the text, large blue circles; remaining antimony atoms, magenta; sulfur, yellow; cobalt, green; carbon, black; nitrogen, small blue circles. (Hydrogen atoms are omitted for clarity.)

compound, together with a small number of yellow crystals, identified by single-crystal X-ray diffraction as the previously reported $[Co(en)_3][Sb_4S_7]$.[14] The CHN analysis of handpicked crystals gave. Found: C, 3.56; H, 1.12; N, 3.66. Calcd: C, 3.12; H, 1.05; N, 3.64%.

The crystal structure[15] of $[Co(en)_3][Sb_{12}S_{19}]$ (Figure 1) contains 12 crystallographically distinct antimony atoms. With the exception of Sb(11) and Sb(12), each of the antimony atoms is coordinated to three sulfur atoms at distances in the range 2.404(4)−2.581(4) Å. These SbS_3 primary structural units have the characteristic trigonal pyramidal geometry found in other templated antimony sulfides with S−Sb−S angles lying in the range 84.8(1)−102.7(1)°. The coordination number of atoms Sb(11) and Sb(12) is, however, four, with two short (2.446(4)−2.475(3) Å) and two longer (2.617(4)−2.814(3) Å) Sb−S bonds. Four-coordinate Sb(III) atoms with similar bonding distances have been previously observed in Sb_2S_2 rings.[16] Bond-valence sums[17] are consistent with an oxidation state of +3 for all antimony atoms. In common with the majority of one- and two-dimensional antimony sulfides synthesized to date,[10] all antimony atoms have additional sulfur neighbors at longer distances (2.91−3.79 Å), less than the sum of van der Waals' radii (3.80 Å) of antimony and sulfur.[18] When these additional antimony−sulfur interactions are taken into account, each antimony atom exhibits a distorted octahedral coordination, with the exceptions of Sb(3) and Sb(8), which are five-coordinate. However, Sb−S distances above 3 Å make only a small contribution (ca. 0.2 valence units) to the valence sum. Therefore, in the following discussion of the structure, only Sb−S distances in the range 2.4−2.8 Å will be considered, although Sb−S bonds at distances ≤2.581(4) Å are sufficient to define the three-dimensional structure.

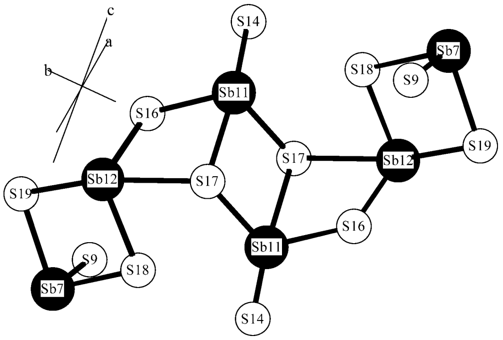

Figure 2. $Sb_6S_{12}^{6-}$ secondary building unit formed by three edge-sharing Sb_2S_2 rings and two corner-sharing Sb_2S_2 rings.

The structure of $[Co(en)_3][Sb_{12}S_{19}]$ contains Sb_2S_2 rings. Three of these secondary building units (containing Sb(11) and Sb(12)) share edges to form a unit to which two further Sb_2S_2 rings are linked by common vertices to form a cluster of stoichiometry $Sb_6S_{12}^{6-}$ (Figure 2). $Sb_6S_{12}^{6-}$ clusters are connected by $Sb_3S_7^{5-}$ units, composed of three vertex-linked SbS_3^{3-} trigonal pyramids, to form ribbons which are directed along [001] (highlighted in Figure 1). Cross-linking of ribbons is effected through $Sb_6S_{12}^{6-}$ rings, consisting of six vertex-linked SbS_3^{3-} trigonal pyramids, which share common sulfur atoms (S(14)) with the ribbons. Further cross-linking in the (010) plane and in the [010] direction is provided by a complex chain containing three corner-sharing and one edge-sharing SbS_3^{3-} trigonal pyramids.

This complex linkage of antimony and sulfur generates a primary-bonded three-dimensional framework in which there is a regular array of one-dimensional channels parallel to [010]. These channels have a circular cross-section of ca. 8 Å diameter (measured from atom to atom). When the van der Waals' radii of Sb and S are taken into account, the effective aperture dimension of the channel is ca. 5 Å. This is comparable to the channel diameters observed in zeolites containing apertures of 10-membered rings, such as ZSM-5. Within the channels lie $[Co(en)_3]^{2+}$ cations, in which Co−N distances are in the range 2.159(8)−2.183(8) Å. Cations with both $\Delta(\delta\delta\lambda)$ and $\Lambda(\lambda\lambda\delta)$ conformations are present as a result of the centrosymmetric nature of the structure; the material is therefore achiral. Distances between nitrogen atoms in $[Co(en)_3]^{2+}$ and sulfur atoms in the framework lie in the range 3.30−3.65 Å, suggesting a hydrogen bonding interaction between the cations and the framework similar to that in low-dimensional antimony sulfides templated by metal complexes.[19] $[Co(en)_3]^{2+}$ cations in neighboring channels along [101] are displaced by $c/2$ with respect to each other.

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(15) Crystal data: $[Co(en)_3][Sb_{12}S_{19}]$, $M = 2309.69$, monoclinic, space group $P2_1/c$, $a = 17.3727(3)$ Å, $b = 8.8672(2)$ Å, $c = 28.7129(6)$ Å, $\beta = 91.4844(7)°$, $V = 4421.7$ Å^3, $Z = 4$, $T = 293$ K, μ(Mo Kα) = 8.482 mm^{-1}, 17957 reflections measured, 9916 unique reflections ($R_{int} = 0.090$), 4120 observed with ($I > 3\sigma(I)$) which were used in all calculations. Final values of $R(F)$ and $wR(F)$ were 0.0348 and 0.0407, respectively.

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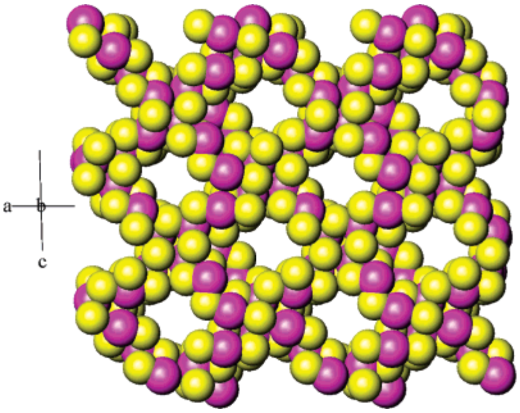

Figure 3. Space-filling representation of the $[Sb_{12}S_{19}]^{2-}$ framework illustrating the pores parallel to [010] (key: antimony, magenta; sulfur, yellow).

Thermogravimetric analysis[20] indicates that $[Co(en)_3][Sb_{12}S_{19}]$ is stable up to 280 °C. Decomposition occurs in a single step with a weight change of 8.2% (7.8% calculated for complete loss of three ethylenediamine molecules). Powder X-ray diffraction of the decomposition product indicates that thermal decomposition produces a poorly crystalline material, in which only antimony sulfide, Sb_2S_3, can be identified. In conclusion, we present the first example of an open-framework antimony sulfide containing a one-dimensional channel system. In the as-prepared material, the channels contain the $[Co(en)_3]^{2+}$ charge-balancing cations. The aperture dimensions of the channels are comparable with those of small molecules, suggesting that provided the charge-balancing cations can be removed the material should have applications in catalysis. The thermal stability of $[Co(en)_3][Sb_{12}S_{19}]$ suggests that access to the miroporosity may indeed be possible. Our current investigations are directed toward the use of ion-exchange to achieve this aim.

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Supporting Information Available: Crystallographic data (atomic positions, thermal parameters and bond lengths) in the form of a CIF file together with observed and simulated powder X-ray diffractograms, an infrared spectrum, and thermogravimetric data. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for the structure reported in this paper also available at the Cambridge Crystallographic Data Centre, with the CCDC reference number 238924.

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(20) Thermogravimetric analysis was performed using a DuPont Instruments 951 thermal analyzer. Approximately 10 mg of finely ground crystals was heated under a flow of dry nitrogen over the temperature range 25−290 °C at a heating rate of 2 °C min^{-1}.