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A Novel 3-Dimensional Open Framework Sulfide Based upon the $[In_{10}S_{20}]^{10-}$ Supertetrahedron: DMA-InS-SB1

Christopher L. Cahill,[†] Younghee Ko,[‡] and John B. Parise*,[†,‡]

Department of Chemistry and Department of Geosciences, State University of New York, Stony Brook, New York 11794

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Inorganic frameworks capable of occluding ions and organic molecules are of interest as selective agents for molecular sieving, catalysis, ion exchange, ion conduction, and host−guest chemistry.[1] The most well-known of these materials are the zeolites, which can be defined structurally as framework aluminosilicates that contain corner-linked $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra.[2] Such connectivity gives rise to channels, cavities, and cages of dimensions determined by the edge lengths of their tetrahedral building units. For example, the edge length of an $[SiO_4]^{4-}$ tetrahedron in a zeolite is approximately 2.6 Å. Therefore, the size of an aperture bound by a four-ring of these building units will be restricted to 3.7 Å on a diagonal.[1,2]

More recently, the range of materials capable of forming open frameworks has been extended to include the sulfides. First proposed in 1989 by Bedard et al.,[3,4] compounds in this family are composed of $[M_xS_y]^{z-}$ clusters rather than $[SiO_4]^{4-}$ or $[AlO_4]^{5-}$ tetrahedra. While such clustering is uncommon in the oxides, several novel 3-dimensional frameworks based on this sulfide chemistry have been synthesized, many of which contain the $[Ge_4S_{10}]^{4-}$ adamantine building unit.[5−10] The longer edge lengths of these polyhedral building units and their subsequent corner sharing or linking through transition metal centers naturally lead to larger apertures within their structures. Apart from the presence of larger pores, the introduction of S, and indeed Se,[11] allows for the possibility of semiconducting properties in these materials. This contrasts the aluminosilicates which are invariably insulators. We report here the synthesis of a new framework material, DMA-InS-SB1,[12] formed from corner linking the $[In_{10}S_{20}]^{10-}$ supertetrahedral cluster (see Figure 1). The solid solution series DMA-InS(Se)-SB1 has also been prepared.

The $[In_4S_{10}]^{8-}$ cluster has been known for some time and is analogous to the familiar $[Ge_4S_{10}]^{4-}$ adamantine unit.[13,14] This material, however, has not been reported to form 3-dimensional frameworks. Hydrothermal treatment of In_2S_3 in the presence of alkali metals results in 2-dimensional structures containing the adamantine building unit. In this study, hydrothermal treatment of elemental sulfur and elemental indium in the presence of the organic structure-directing agent dimethylamine (DMA) leads to formation of the $[In_{10}S_{20}]^{10-}$ supertetrahedron and its subsequent polymerization to form a 3-dimensional framework.

The DMA-InS-SB1 material was synthesized hydrothermally from a slurry containing 0.5 g of In, 0.348 g of S, 1.0 g of dimethylamine (DMA), and 1.0 g of H_2O. The reactant mixture was sealed in a Pyrex tube and held static at 180 °C under autogenous pressure for 1 week. The resultant product, a white solid, was collected, washed with ethanol and water, and dried in air. Single crystals suitable for X-ray structural analysis were isolated from this batch. Qualitative electron probe microanalysis revealed the presence of In, S, and N.

The structure[15] of DMA-InS-SB1 (see Figure 2) consists of corner-linked $[In_{10}S_{20}]^{10-}$ clusters which form an open framework with an overall stoichiometry of $[In_{10}S_{18}]$.$^{6-}$ The DMA molecules, although not explicitly located, are assumed to be protonated and to reside in void spaces defined by the framework.[16] Each indium atom is tetrahedrally coordinated to four sulfur atoms. In turn, three bonding environments exist for the sulfurs: terminal, bridging, and trigonal. Average bond lengths for each of these coordinations are 2.425, 2.437, and 2.494 Å, respectively. The shorter terminal M−sulfur distance has been noted previously; it is typical of tetrahedral $[M_xS_y]^{z-}$ clusters[4,7−10] and reflects the underbonding[17] of sulfur coordinated to one indium versus those coordinated to two and three indium atoms.

The topology of the DMA-InS-SB1 framework (see Figure 3) can best be visualized if each $[In_{10}S_{20}]^{10-}$ cluster is represented by a node placed at its center and

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[†] Department of Chemistry.

[‡] Department of Geosciences.

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(15) Crystal data for DMA-InS-SB1: $[(CH_3)_2NH_2]_6In_{10}S_{18}$, orthorhombic, *Pbca*, $a = 19.0794(10)$, $b = 19.0878(10)$, $c = 31.673(2)$ Å, $V = 11534.6(10)$ Å,^{3} Dc = 1.987 mg/m^3, μ(Mo (Kα) = 4.569 mm^{-1}, $Z = 8$, $\lambda = 0.71073$ Å, colorless hexagonal plate, 0.03 × 0.03 × 0.006 mm. Data (54,613 reflections) was collected at 23 °C on a Siemens SMART Platform CCD yielding 10 162 independent reflections ($R_{int} = 0.0812$). Solution (direct methods); refinement (full matrix least-squares refinement on F^2; (SHELXTL-V5.0) [SHELXTL-Plus V5.0, Siemens Industrial Automation Inc., Madison, WI] used 4748 reflections ($I > 2\sigma(I)$); $R_1 = 0.0750$, $wR_2 = 0.1869$, where $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $wR_2 = \sqrt{}(\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^4])$.

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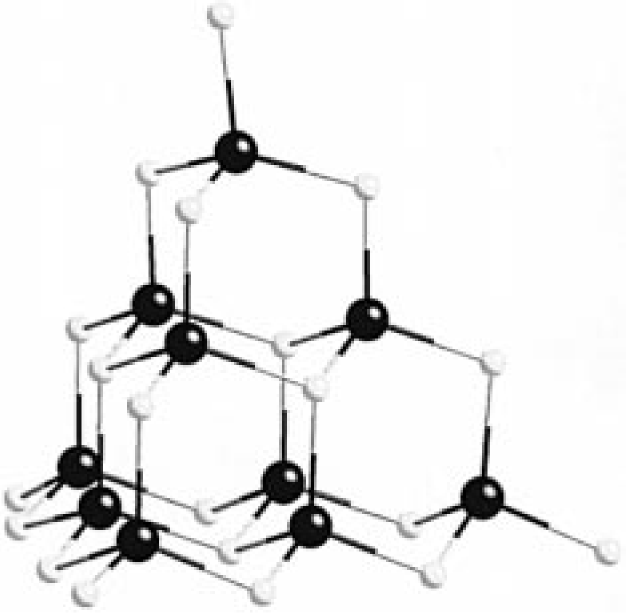

Figure 1. $[In_{10}S_{20}]^{10-}$ supertetrahedron. Dark and light circles represent indium and sulfur atoms, respectively.

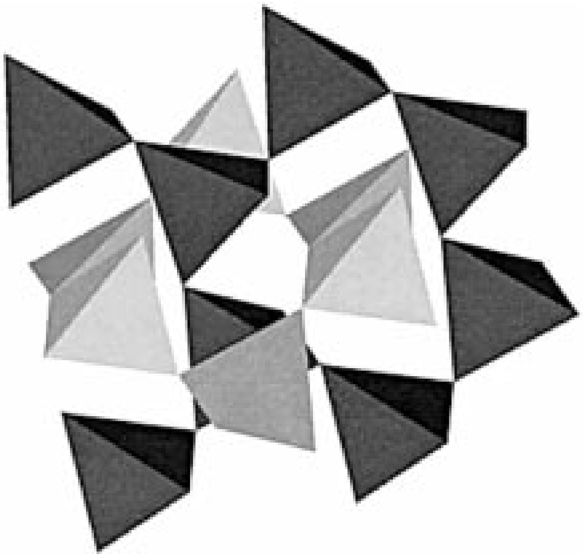

Figure 2. Polyhedral representation of a portion of the DMA-InS-SB1 framework shown approximately down [010]. Each tetrahedron represents one $[In_{10}S_{20}]^{10-}$ cluster which is corner-linked through sulfur atoms to form 6-rings. The lighter and darker tetrahedra respectively form two interpenetrating, nonintersecting diamond lattices.

bridging sulfur atoms are replaced by straight lines.[18] Using this representation, the structure is seen to consist of two interpenetrating, nonintersecting diamond lattices. This is the first example of two interwoven 4-connected nets in the sulfides, although a similar structure has been reported in the Sn−O−S system.[19,20]

The DMA-InS(Se)-SB1 solid solution series has been synthesized in a manner similar to the preparation of the title compound. Stoichiometric amounts of Se replaced S in the reactant mixtures of the hydrothermal syntheses. Compounds at 0, 25, 50, 75, and 100% Se were confirmed to be of the SB1 structure type by X-ray powder diffraction while their compositions were verified by quantitative electron probe microanalysis (EPMA).

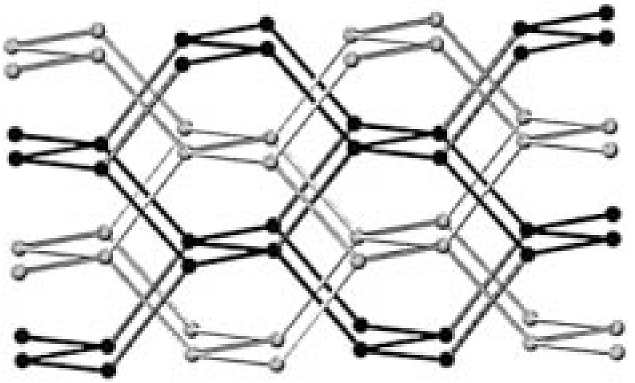

Figure 3. Framework topology of DMA-InS-SB1. The light and dark frames are two interpenetrating, nonintersecting diamond lattices. Each node on the nets represents the center of one tetrahedral $[In_{10}S_{20}]^{10-}$ cluster (Figure 1). Corner-linking through sulfur atoms is shown as straight lines.[18]

Colors range from white to black for the sulfide and selenide end members respectively. A spectroscopic study to quantify these optical properties and determine the bandgaps of these materials is in progress.

Thermogravimetric analysis on DMA-InS-SB1 (2 °C/min, in flowing nitrogen) indicates three weight loss events. The first, approximately 4% of the total mass of the sample, occurs during the ramp to 100 °C and is attributed to the loss of surface water. The second and third events, which begin at approximately 100 and 200 °C, respectively, sum to about 15% of the mass of the sample. These have been assigned to a two-stage loss of the DMA^+ cations. A weight loss of this amount is roughly equivalent to the loss of 6 DMA^+ cations per asymmetric unit.[16] Thermally driven "nonredox" template loss has been reported previously.[5,6] These studies suggest evolved volatiles contain organo-sulfur species produced by the hypothetical reaction

$$[(CH_3)_2NH_2]In_{10}S_{18} \rightarrow 5In_2S_3 + X\mathrm{RS} + Y\mathrm{R}'$$

The values of X and Y and the identities of R and R′ can be determined using TGA/mass spectroscopy.

A real time X-ray powder diffraction study was carried out to complement the TGA results.[21] This analysis demonstrates that, although the DMA-InS-SB1

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(16) The dimethylamine (DMA) added as a structure directing agent was not explicitly located in the structure. This implies that the molecules are either disordered or have broken down.[19,20] The SQUEEZE utility in PLATON [Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34] was used to examine the extraframework region and no difference Fourier peaks greater than 6.3 $e^-/Å^3$ were found; most were considered ghost peaks of the framework. The volume of this extraframework region could potentially host up to 12 DMA^+ cations per asymmetric unit. Six protonated DMA^+ cations are necessary for charge balance; thus the overall stoichiometry $[(CH_3)_2NH_2]_6In_{10}S_{18}$ has been assigned. Protonated guest molecules are not unprecedented (ref 5 and references therein). Additionally, thermogravimetric analysis suggests a weight loss equivalent to about 6 DMA molecules per asymmetric unit are evolved from the material prior to the formation of In_2S_3. Elemental analysis of DMA-InS-SB1 for C, H, and N supports this model yielding 6.36, 2.52, and 3.80 wt % of each element.

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framework begins to collapse during template loss (about 185 °C), there is a temperature regime between approximately 100 and 185 °C where the structure remains intact. By 200 °C the structure of the title compound has fully collapsed and by 220 °C the formation of the dense phase In_2S_3[22] is observed.

The synthesis of $[In_{10}S_{20}]^{10-}$ and its subsequent polymerization to yield a three-dimensional network suggests that many structural variants in the In−S system are possible via tailoring of the synthetic parameters. The incorporation of tetrahedrally coordinated transition metals to link individual clusters in a manner similar to the Ge−S system [6,7] could also be envisioned. Experimental modifications are currently underway to explore new frameworks in the In−S system. Further analysis of the DMA-InS(Se)-SB1 solid solution series will provide insight into transport, electronic and optical properties.

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Supporting Information Available: Crystal structure report consisting of a description of data collection and structure solution, crystal data, and structure factors (38 pages). Ordering information is given on any current masthead page.

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