Reports

An Antimony Sulfide with a Two-Dimensional, Intersecting System of Channels

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A novel open antimony sulfide framework of composition $[Sb_3S_5]^-$ has been synthesized hydrothermally, in the presence of tetramethyl ammonium ions. Determination of the crystal structure demonstrates that the $(Me_4N)^+$ molecules (Me, methyl) occlude a system of intersecting channels at 90° to one another. The three-dimensional framework is assembled from a new building unit, flat s-shaped buckled sheets of edge-linked 4-rings containing Sb_2S_2 moieties. These are cross-linked in two directions to form the system of channels.

CRYSTALLINE SUBSTANCES WITH structures composed of regular arrays of pores and channels, such as the aluminosilicate-zeolites and other molecular sieves, are important in materials science and mineralogy as selective sorbets, catalysts, and ion exchangers (*1*). A regular array of nanometer-sized pores imparts upon these materials their reactant- and product-selective properties (*2*), making them particularly useful in catalyzing a variety of reactions. More recently their selectivity and large internal voids have been used to stabilize small clusters (*3, 4*) of semiconducting materials. One of the limitations to the preparation of these materials is their sensitivity to the atmosphere and tendency to react with the oxide framework of the zeotype used. Reports of the successful synthesis of a variety of sulfide frameworks (*5*) suggests the possibility of obtaining novel channel structures, perhaps displaying building principles diverse from those of the silicates and phosphates. Furthermore, open sulfide frameworks could provide more inert platforms for host-guest chemistry involving small-particle sulfides and selenides (*3, 4*).

Techniques developed for the growth of single crystals of the metallophosphates (*1, 6*) have been used to synthesize single crystals of new frameworks based on Sb-S. The crystal structure of at least one of these is reminiscent of the molecular sieves. However, the structural principles upon which it is built are quite distinct from those reported earlier (*5*) and involve mixed edge and corner linkages rather than strict corner sharing of tetrahedral moieties. This result suggests that new classes of sulfide frameworks can be synthesized. The syntheses have been effected by heating slurries of Sb_2S_3 in thick-walled Pyrex tubes. Freshly prepared Sb_2S_3 and $Me_4N{\cdot}SH$, in the molar ratio 3:2, were stirred to form a black slurry and heated at 180°C for 1 week. The $Me_4N{-}SH$ molecule was used in the hope that it would act as a template (*1*), organizing a growing sulfide network about itself and becoming included in the final crystalline solid. This technique is similar to that used in previous studies (*5*), with the exception that the template is introduced to the reaction as $Me_4N{\cdot}SH$, rather than in the form of a hydroxide or bicarbonate solution. The material produced was light orange in color and contained chunky single crystals up to 1 mm on edge. Microprobe analysis confirmed the presence of nitrogen, as was to be expected for a growth mechanism that included the template. The measurable elements, Sb, S, N, and O, were in the ratio 3:5:1:0; there was no evidence for partial substitution of S by O. A comparison of the x-ray powder diffraction pattern with that of known phases suggested the material was a new phase, which was confirmed by subsequent studies of the single crystals.

Data collected from photographs taken with a precession camera indicated monoclinic symmetry (*7*). The diffraction pattern was further characterized by the presence of diffuse maxima, which occur in pairs about reciprocal lattice points suggestive of a sixfold increase in the unique (*b*) axis. In order to simplify the task of determining the structure, these weak diffuse reflections, incommensurate with the stronger data, were ignored. The structure determined (*7*) represents a substructure, the finer detail of which includes a perturbation giving rise to the incommensurate superstructure.

The framework of $Sb_2S_5{\cdot}Me_4N$ is composed of two related structural elements, one of which is shown in Fig. 1. All Sb atoms in the structure are four-coordinated to S, and the coordination geometry shows the effect of the sterochemically active $5s^2$ lone pair for Sb^{3+}, shown in the form of a cartoon in Fig. 1B. Each Sb is coordinated to S by three short bonds, between 2.4 and 2.5 Å long, and by a longer bond at 3 Å, with the lone pair presumably occupying the fifth site to complete a trigonal bipyramid. This results in a sawhorse arrangement, shown for Sb(1) in Fig. 1B. The four-coordinated Sb atoms share two S atoms to

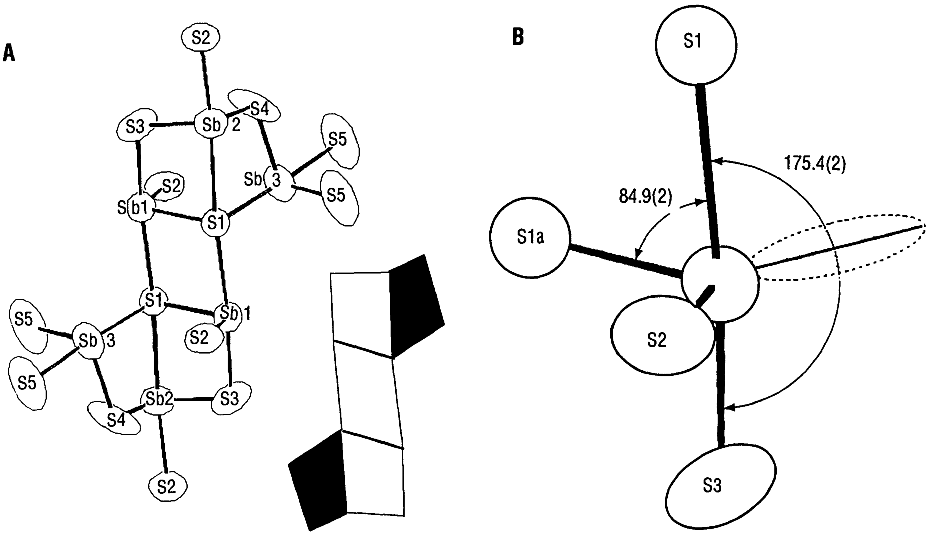

Fig. 1. Representations of (**A**) the s-shaped $[Sb_6S_8]^{2+}$ moiety, consisting of fused 4-rings of $[Sb_2S_2]^{2+}$, and (**B**) the sawhorse coordination for the Sb atoms with a sterochemically active lone pair of electrons, here represented as a lobe perpendicular to the S1–Sb1–S3 bonds. In Figs. 2 and 3 the s-shaped moiety in (A) is represented by the cartoon shown to the right. The thermal ellipsoids shown in (A) are drawn at the 50% level of probability.

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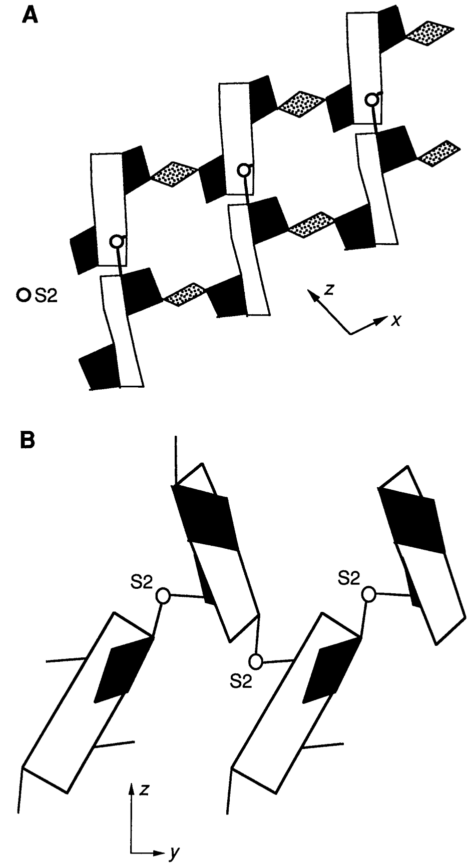

Fig. 2. (**A**) Schematic representation of the interconnection of s-shaped moieties vertically, along [101], and along [100]. In the *x*-direction connection is achieved through two Sb3–S5–Sb3 bridges, which form the stippled 4-ring. A linkage out of the plane of the drawing is made through the S2 atom, here represented as a circle. Representation (**B**) is a view at almost 90° to (A) and shows the connections Sb1–S2–Sb2 responsible for the channels in this direction.

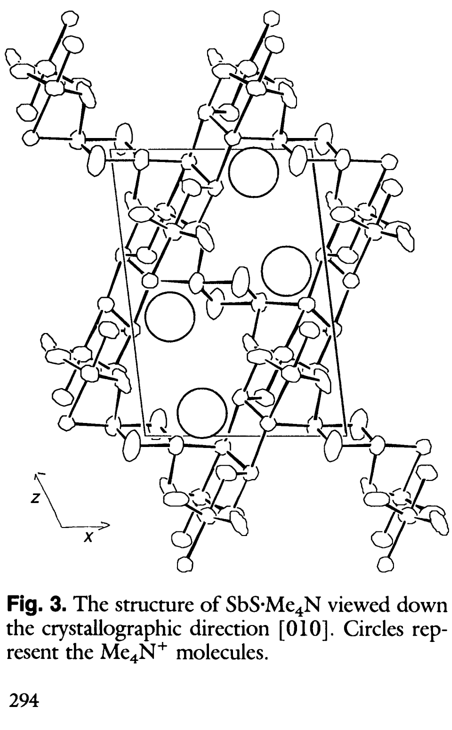

Fig. 3. The structure of SbS·Me_4N viewed down the crystallographic direction [010]. Circles represent the Me_4N^+ molecules.

form the flat s-shaped structure shown in Fig. 1A, a collection of four fused 4-rings with composition $[Sb_2S_2]^{2+}$. The s-shaped units are located close to the origin and body center of the unit cell (7) and are interconnected in two directions (Fig. 2). The buckled sheets of s-shaped units, close to the (010) plane, are connected together both by Sb3–S5–Sb3 bridges along the crystallographic direction [100] and by Sb1–S2–Sb2 bridges along [001]; compare Fig. 1 and Fig. 2A. These connections outline a channel along [010]. The second system of channels is formed along [100] by the interconnection of s-shaped units through Sb1–S2–Sb2 bridges, as shown in Fig. 2B.

The Me_4N molecules are contained within the channels as shown schematically in Fig. 3. Two orientations of the molecule randomly occupy the same site in the substructure. This feature, along with the disorder in one Sb and two S sites close to the Me_4N site, suggest that ordering of the template molecule within the channels may be responsible for the observed incommensurate superstructure.

It may be possible to connect the motif shown in Fig. 1 in a variety of ways; the obvious extensions of this work are the use of different templates and other lone-pair cations in attempts to produce new open frameworks. Along these lines, a number of materials based on Sb_2S_3 have been synthesized and await characterization. The building principles for these and the other sulfide frameworks reported previously (*5*) also require elucidation, with a view toward enumerating possible sulfide networks and synthesizing materials with larger cavities and channels.

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Local Structure and Chemical Shifts for Six-Coordinated Silicon in High-Pressure Mantle Phases

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Most of the earth's mantle is made up of high-pressure silicate minerals that contain octahedrally coordinated silicon (Si^{VI}), but many thermodynamically important details of cation site ordering remain unknown. Silicon-29 nuclear magnetic resonance (NMR) spectroscopy is potentially very useful for determining short-range structure. A systematic study of silicon-29 chemical shifts for Si^{VI} has revealed empirical correlations between shift and structure that are useful in understanding several new calcium silicates. The observed ordering state of a number of high-pressure magnesium silicates is consistent with the results of previous x-ray diffraction studies.

UNLIKE THE SILICATE MINERALS OF the crust and uppermost mantle of the earth, the silicates that form the bulk of the planet contain silicon coordinated by six (Si^{VI}) instead of by four O atoms (Si^{IV}). The basic structures of the compositional end-members of the most abundant of these high-pressure phases (for example, $MgSiO_3$ perovskite and garnet) are now known, but many details remain uncertain. In particular, solid solution and disorder of cations among multiple sites can have major effects on thermodynamic stability and thus on the range of pressures and temperatures over which the minerals form in the earth.

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