A novel layered indium sulfide material consisting of corner and edge shared InS_4 tetrahedra: synthesis and structural characterization of DPA-InS-SB3

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A novel layered indium sulfide inorganic/organic composite material has been synthesized under solvothermal conditions and characterized *via* single crystal X-ray diffraction.

Metal sulfide based microporous solids were first reported by Bedard *et al.* in 1989.[1] The ability of main group metals to coordinate tetrahedrally with sulfur, as Al and Si do with oxygen in the molecular sieve oxides[2] suggested that a new family of materials with structures resembling those of the zeolites (for example) could exist. These compounds however, did not contain the MS_4 tetrahedra that might be expected in materials structurally related to the oxides. Rather, complex building units such as the $Sb_3S_6{}^{3-}$ semi-cube,[3] the Sn_3S_4 semi-cube,[1,4] the $[Ge_4S_{10}]^{4-}$ adamantine unit,[5] and the $[In_{10}S_{20}]^{10-}$ and $[Sn_{10}S_{20}O_4]^{8-}$ supertetrahedra[6,7] condense to form structures analogous to zeolites,[5c] neso-,[5d] iono-[5e] and tecto-silicate materials.[5a,b] We report here the synthesis and structure of a novel layered sulfide material consisting of linked InS_4 tetrahedra: DPA-InS-SB3 [DPA = dipropylamine, $(C_3H_7)_2NH$].

The synthesis of DPA-InS-SB3 (**1**) was achieved by reacting elemental In and elemental S with the organic structure directing agent dipropylamine in the approximate molar ratio 1 : 2.3 : 3.5. Reactant slurries were sealed in Pyrex tubes and held static at 180 °C under autogenous pressures for 5 days. The resultant product, a white powder, was washed with ethanol and water and allowed to air dry. Large single crystals up to 0.2 mm on edge were obtained and isolated for X-ray diffraction. Qualitative electron probe microanalysis (EPMA) on the crystals revealed the presence of In, S, and N.

The structure of **1** was determined from single crystal X-ray diffraction† data and is shown in Fig. 1. The primary structural building units of this material are InS_4 tetrahedra which corner and edge link to form layers that stack along (100). Alternatively, the structure can be viewed in terms of In_6S_{11} subunits that form infinite chains running along (010) [Fig. 1(*b*)]. Within the chains, all tetrahedra are linked to one another *via* corner sharing of vertex sulfur atoms. Between chains however, InS_4 tetrahedra edge share [In6–S11–In6; Fig. 1(*b*)] to stitch the chains together approximately along (011) and $(0\bar{1}1)$. This connectivity gives rise to pores within the layers that measure 6.9 × 12.8 Å and an interlayer spacing of 8.8 Å as determined from the shortest S–S distances. The layers are similar to those found in Sn–S compounds,[4] but stack such that the pores are aligned throughout the entire structure in a direction perpendicular to the In–S sheets. Although the structure of **1** is not a three-dimensional framework, its unidimensional pore topology (Fig. 1) resembles zeolites such as theta-1[8] and ZSM-23[9] and certain aluminophosphates.[10]

The In–S bond lengths range from 2.420 to 2.534 Å, with an average of 2.432 Å. These values are consistent with those reported in other In–S materials containing tetrahedrally coordinated In.[11] Bond valence sums[12] gave no indication of any mixed valency in indium, which has been observed previously in In–S compounds.[13] Sulfur coordination with In ranges from one to three. The singly coordinated sulfur [S7, Fig. 1(*b*)], is also bound to a hydrogen atom to form a terminal –SH group. The edge sharing of two InS_4 tetrahedra gives one short In–In (In6–In6) contact of 3.299 Å, as opposed to an average of about 3.9 Å for other In–In distances within **1**, and 3.24 Å in indium metal.[14]

The strain associated with this geometry is reflected in the S–In6–S [S11, 10, 6; Fig. 1(*b*)] bond angles which range from

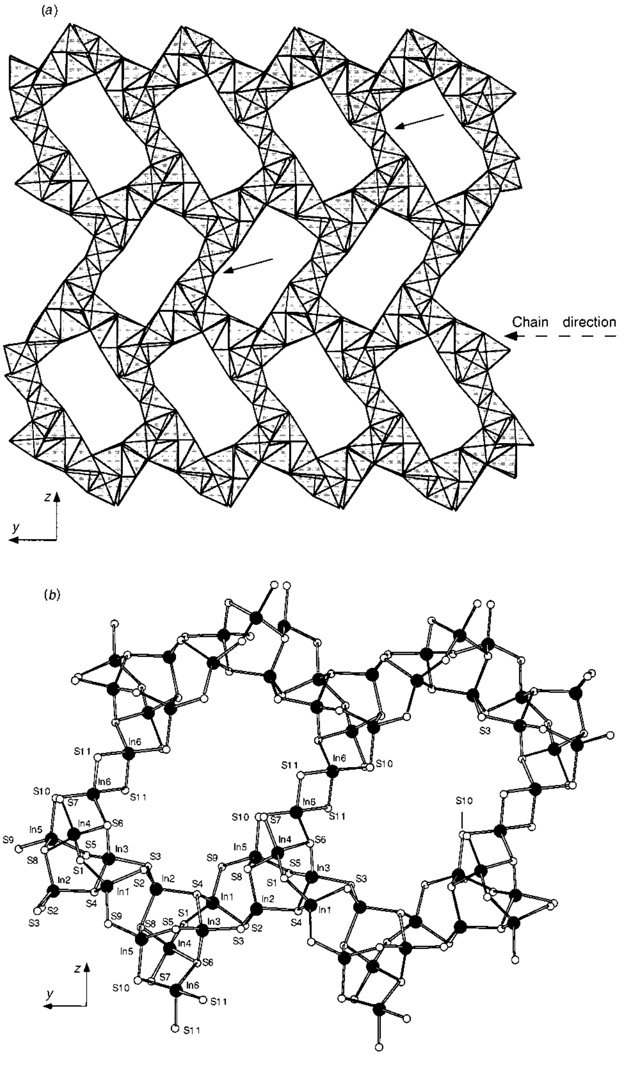

Fig. 1 (*a*) A view down (100) of a single layer of DPA-InS-SB3: $[(C_3H_7)_2NH_2]_3In_6S_{11}H$. This polyhedral representation shows the corner linking of tetrahedra within the In–S chains along (010) (dashed arrow) and the edge sharing of tetrahedra (bold arrows) to link chains together. For clarity, the ordered DPA cations have been omitted and only two edge sharing locations are labeled. (*b*) A labeled portion of two pores from a single layer of **1** in the same orientation as in (*a*). The pore size (6.9 × 12.8 Å) was determined from S3–S3 and S10–S10 distances.

96.23(6) to 120.01(8)° as opposed to an ideal tetrahedral value of 109.5°.

The organic component of **1** is located within the extra-framework voids of the structure. A hydrogen bonded host/guest relationship is proposed as protons on the nitrogen atoms are within 2.3–2.6 Å of sulfur atoms on the In–S framework. IR spectroscopy suggests that the DPA molecules are protonated although a second hydrogen on one of the three N atoms was not located in the X-ray analysis. A medium absorption band at 1579 cm^{-1} corresponding to a N–H bend of a secondary amine salt and strong N–H stretching bands (3000–2700 cm^{-1}) were observed.[15] A weak band at 2515 cm^{-1} was assigned to the S–H stretching vibration[15] of S7–H (see above). With respect to these designations, all nitrogen atoms were assumed to be protonated to balance the 3− charge on the $In_6S_{11}H$ framework, thus giving an overall stoichiometry of $[(C_3H_7)_2NH_2]_3In_6S_{11}H$.

Other experiments involving treatment of elemental In and S in the presence of amines have resulted in formation of the $[In_{10}S_{20}]^{10-}$ supertetrahedral building unit.[6] It is possible that the amount of water or the size of the amine in a preparation dictates which building unit will form. An investigation of the mother liquors from which these In–S materials crystallize is in progress.

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Notes and References

† *Crystal structure data* for DPA-InS-SB3 $[(C_3H_7)_2NH_2]_3In_6S_{11}H$: M = 1346.15, monoclinic, space group $P2_1/c$, a = 12.2366(3), b = 12.2834(3), c = 28.5484(6) Å, β = 101.960(1), Z = 4, μ(Mo-Kα) = 3.804 mm^{-1}; Data collection at 298(2) K; Siemens SMART Platform CCD: 20 419 reflections collected, 7334 unique; R indices [$I > 2\sigma(I)$ = 5965]: R_1 = 0.0370, wR_2 = 0.0721; R indices (all data): R_1 = 0.0531, wR_2 = 0.0722. CCDC 182/935.

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