

Novel Two-Dimensional Tin Sulfide Networks: Preparation and Structural Characterization of $\text{Sn}_4\text{S}_9[(\text{C}_3\text{H}_7)_4\text{N}]_2$ and $\text{Sn}_4\text{S}_9[(\text{C}_3\text{H}_7)_4\text{N}] \cdot [(\text{CH}_3)_3\text{NH}]$

Younghee Ko,* Kemin Tan,* David M. Nellis,† Stephen Koch,† and John B. Parise*,†,1

*CHiPR² and Department of Earth and Space Sciences, and †Department of Chemistry, State University of New York, Stony Brook, New York 11794

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A new framework with the composition $[\text{Sn}_4\text{S}_9]^{2-}$ has been synthesized hydrothermally in the presence of tetrapropylammonium (TPA) hydroxide. The structures of two compounds possessing this framework, $\text{Sn}_4\text{S}_9[(\text{C}_3\text{H}_7)_4\text{N}]_2$ (1) and $\text{Sn}_4\text{S}_9[(\text{C}_3\text{H}_7)_4\text{N}] \cdot [(\text{CH}_3)_3\text{NH}]$ (2), have been solved using single-crystal X-ray diffraction data. Both crystallize in the space $P2_1/n$ ($Z = 4$) with unit cell parameters $a = 15.497(5)$ Å, $b = 15.826(4)$ Å, $c = 18.594(5)$ Å, $\beta = 110.40(1)^\circ$ for (1), and $a = 14.832(4)$ Å, $b = 18.612(6)$ Å, $c = 15.039(6)$ Å, $\beta = 96.90(3)^\circ$ for (2). These compounds are layered with organic cations accommodated between Sn–S sheets containing apertures composed of 16 SnS_5 and SnS_4 polyhedra. Both materials contain TPA⁺ cations, and (2) also incorporates trimethylammonium cation, a breakdown product of TPA. © 1995 Academic Press, Inc.

INTRODUCTION

Hydrothermal recrystallization of simple main group sulfides in the presence of organic amines has been used as a route to produce novel open framework materials (1–6). The diversity of coordination environment displayed by the sulfides leads to a rich structural chemistry based upon edge and corner sharing of metal-centered polyhedra. For example, among the solid state thio compounds containing tin are monomeric (7, 8) dimeric, and polymeric species. The dimeric forms, $\text{Sn}_2\text{S}_7^{6-}$ and $\text{Sn}_2\text{S}_6^{4-}$, are composed of two corner-sharing (9) and two edge-sharing tetrahedra (10), respectively. The polymeric species form either as corner-sharing tetrahedral chains (11) or as three-dimensional framework structures (12, 13).

We have recently described layered materials containing the polythiostannate anions $[\text{Sn}_5\text{S}_{12}]^{4-}$ (Dab–SnS–SBI)³ and $[\text{Sn}_3\text{S}_7]^{2-}$ (TMA–SnS–I) (6). The nomenclature adopted here follows that established by Bedard and co-

workers (2). These structures consist of flat sheets composed of semicube clusters bonded via sulfur bridges. This connectivity outlines apertures consisting of 10 and 12 polyhedra in the case of Dab–SnS–SBI and TMA–SnS–I, respectively. The organic amines added as templates, or products resulting from their breakdown, reside between the sheets and within the apertures. Some of these organic cations are ion exchangeable with a variety of alkali, alkali earth, and transition metal cations (6). Similar sheet structures have also been reported in the selenium analogues (14).

The role of organic amines as structure-directing agents in the synthesis of microporous materials has been a subject of research for some time (15–17). The geometry of the template within the crystalline structure formed from hydrothermal treatment provides valuable information about possible templating mechanisms. In this paper, we report the structural characterization of two new tin sulfides designated TPA–SnS–4² and TPA–SnS–4a with a common Sn–S framework topology and composition.

EXPERIMENTAL

Synthesis and Characterization

Typically, single crystals of $\text{Sn}_4\text{S}_9[(\text{C}_3\text{H}_7)_4\text{N}]_2$ (TPA–SnS–4) and $\text{Sn}_4\text{S}_9[(\text{C}_3\text{H}_7)_4\text{N}] \cdot [(\text{CH}_3)_3\text{NH}]$ (TPA–SnS–4a) were produced from freshly prepared SnS_2 (1.4 mmole) $(\text{C}_3\text{H}_7)_4\text{NOH}$ (1 mmole), elemental sulfur (1 mmole), and H_2O (14 mmole). Slurries of these starting materials were heated at 150°C under autogenous hydrothermal conditions in Pyrex-lined bombs for 18 hr in the case of TPA–SnS–4 and for 72 hr for TPA–SnS–4a. The crystals produced were 0.1–0.5 mm in size. Both crystallized as yellowish-orange rhombic plates. They were washed with water and ethanol and dried in air to produce yields of about 95% based on tin sulfide. Electron microprobe analysis for Sn, S, and N gave an approximate ratio of 4 : 9 : 2 for these elements in both compounds. The X-

¹ To whom correspondence should be addressed.

² Center for High Pressure Research: NSF-funded Science and Technology Center.

TABLE 1
Summary of X-Ray Diffraction Data for TPA-SnS-4 and TPA-SnS-4a

Compound	Crystal data	
	(C ₁₂ H ₂₈ N) ₂ · Sn ₄ S ₉ TPA-SnS-4	(C ₁₂ H ₂₈ N)(C ₃ H ₉ NH) · Sn ₄ S ₉ TPA-SnS-4a
Formula weight	1136.02	1009.82
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
Cell dimensions		
<i>a</i> (Å)	15.497(5)	14.832(4)
<i>b</i> (Å)	15.826(4)	18.612(2)
<i>c</i> (Å)	18.594(5)	15.039(6)
β (°)	110.40(1)	96.90(3)
Volume (Å ³)	4274(4)	4121(6)
<i>Z</i>	4	4
ρ_{calc} (g cm ⁻³)	1.765	1.627
	Intensity measurements	
λ (MoK α) (Å)	0.71073	0.71073
Scan mode	$\theta/2\theta$	$\theta/2\theta$
max θ (°)	27	25
Standard reflections	3 measured every hour	3 measured every hour
Reflections collected	7173	5565
Unique reflections with $ F_0 > 3\sigma F_0 ^2$	3717	2148
μ (mm ⁻¹)	2.762	2.854
	Structure solution and refinement	
Parameters refined	352	251
Agreement factors	$R = 0.042$, ^a $R_w = 0.041$ ^b	$R = 0.072$, ^a $R_w = 0.063$ ^b
Weighting scheme	$w = [\sigma^2(I) + 0.0016I^2]^{-1/2}$	$w = [\sigma^2(I) + 0.0009I^2]^{-1/2}$
Std. error in observation of unit wt	1.16	1.73
$\Delta/\sigma_{\text{max}}$	0.04	0.03

$$^a R = \Sigma(|F_0| - |F_c|)/\Sigma|F_0|.$$

$$^b R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}.$$

ray powder diffraction pattern of the phase formed after 18 hr of hydrothermal treatment, matched that reported for TPA-SnS-4 (2), while that for the material designated TPA-SnS-4a was unique. The ion-exchange experiments for these compounds were done in aqueous solutions, using either metal chloride or acetate salts at 50°C.

Structure Determination

TPA-Sn-4. A single crystal with dimensions 0.15 × 0.15 × 0.07 mm was selected for structure determination. It was glued to the end of a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Cell parameters (Table 1) were obtained from the least-squares analyses of 25 machine-centered reflections with 11° < θ < 12°. The data set for structure solution and refinement was collected to $\theta = 27^\circ$. The crystal showed no significant intensity decay upon monitoring three check reflections every hour throughout the data collection. Systematic absences uniquely identified the space group as *P*2₁/*n*.

The structure was solved by direct methods using SHELXS-86 (18) and refined with the TEXSAN (19) package of crystallographic programs. An absorption correc-

tion was applied by using DIFABS (19). The positions and the isotropic temperature factors of the 56 H atoms on the two ordered tetrapropylammonium cations (TPA⁺) were calculated and included in the structure factor calculations but not refined.³ All other atoms were refined anisotropically. A summary of the experimental details is given in Table 1. The final discrepancy factors were $R = 0.042$ and $R_w = 0.041$. The atomic parameters and selected interatomic distances and angles are given in Tables 2a and 3a.

TPA-Sn-4a. A single crystal with dimensions 0.20 × 0.20 × 0.10 mm was used to collect data in the manner similar to that described above. This compound also crystallized in the space group *P*2₁/*n*. During data collection to $\theta = 25^\circ$, three standard reflections monitored every hour showed no significant intensity decay.

The topology of the framework was determined using an automated Patterson map interpretation technique (20). Subsequent Fourier difference maps revealed an ordered TPA⁺ cation as well as four peaks, interpreted as repre-

³ Lists of these calculated positions are available from the authors.

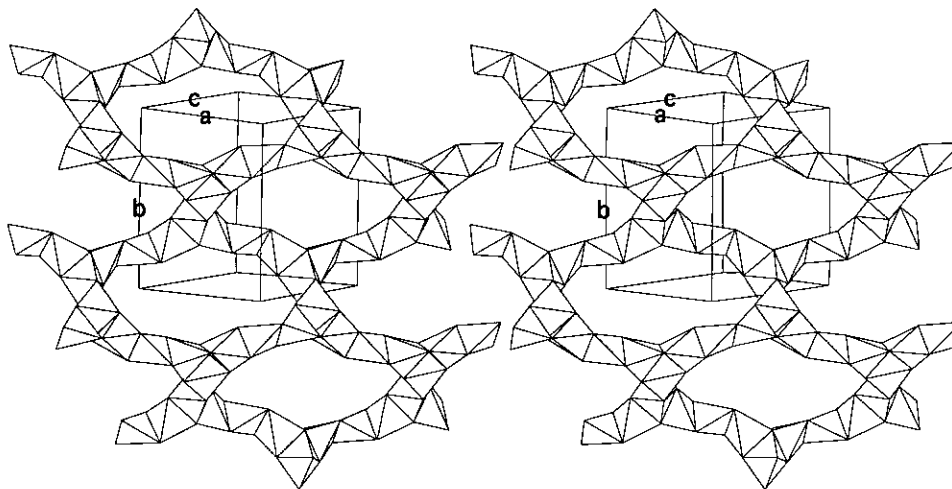


FIG. 1. Stereo drawing of an undulating sheet consisting of edge-sharing Sn-S polyhedra in the structure of TPA-SnS-4 (Fig. 2a). The sheet is parallel to $(1, 0, \bar{1})$. TPA-SnS-4a has a similar framework topology, shown in Fig. 2b. The coordination geometry about the Sn-centered polyhedra is shown in Fig. 3.

senting a trimethylammonium cation. Refinement of the site occupancies for the latter species, with isotropic thermal parameters (B_{iso}) constrained to 7.0 \AA^2 , suggested that these sites are partially occupied. The multiplicities for the four sites were averaged and then fixed at 0.7. In the final least-squares cycles, all atoms except those associated with the trimethylammonium cation were refined anisotropically. The discrepancy indexes R and R_w converged to 0.072 and 0.063, respectively. Experimental details were summarized in Table 1, while the atomic parameters and interatomic distances and angles are given in Tables 2b and 3b.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Both structures consist of similarly undulating $[\text{Sn}_4\text{S}_9]^{2-}$ sheets (Fig. 1), stacked parallel to $[1, 0, \bar{1}]$. Successive sheets are related by a shear perpendicular to this direction (Fig. 2). The primary building units for the sheets are distorted edge-sharing Sn-S polyhedra, one SnS_4 tetrahedron and three SnS_5 trigonal bipyramids (Fig. 3). The coexistence of four- and five-coordinated Sn also occurs in thio compounds such as $\text{Na}_4\text{Sn}_3\text{S}_8$ (13) in which chains of edge-sharing trigonal bipyramids are connected by SnS_4 tetrahedra, forming a three-dimensional structure. In the cases of TPA-SnS-4 and TPA-SnS-4a, three SnS_5 polyhedra form a Sn_3S_4 semicube, as displayed inside the box at the top right of Fig. 3. The semicube is a secondary building unit that has been characterized in other hydrothermally synthesized tin and antimony sulfides (3-6). The two edge-sharing, oppositely oriented semicubes, as outlined by dashed lines in Fig. 3, can be treated as a new parallelepiped-like building block with the four shortest

edges shared by tetrahedra. As two opposite edges of a tetrahedron are related by a 90° rotation, each block is then rotated about 90° or -90° with respect to its neighbors. The bridging of the blocks through these tetrahedra leads to the undulating sheet, which is characterized by elliptical apertures surrounded by 16 Sn-S polyhedra (Fig. 1).

The environment about each Sn in these two closely related compounds is very similar (Table 3). The Sn-S bond distances in the tetrahedra in the two phases range from 2.347(8) to 2.432(8) \AA . In the trigonal bipyramids, equatorial Sn-S bonds vary from 2.335(8) to 2.490(8) \AA , while axial Sn-S bonds are significantly longer, ranging from 2.514 to 2.724(4) \AA (Table 3). A formal oxidation state of +4 was assigned to tin on the basis of calculations of the bond strength sums from the surrounding sulfur atoms (21), and this implies a net charge of -2 on the sheet.

The similarity of the SnS frameworks for the two materials, and the relationship between the interlayer charge-compensating cations, suggest that TPA-SnS-4a evolved from TPA-SnS-4. In the latter case, two crystallographically distinct TPA^+ cations were located in the structure. One cation resides close to the center of the space between the sheets. The second type of TPA^+ cation sits above the sheet with one arm, C(10)-C(11)-C(12), extending into an aperture in the framework from above. Another, crystallographically related to the first by a center of symmetry, extends an arm into the opening from below. These features are illustrated in Fig. 2a where, for clarity, only crystallographically unique amines are depicted.

In the structure of TPA-SnS-4a, only the TPA^+ residing above the sheet is intact with a propyl group

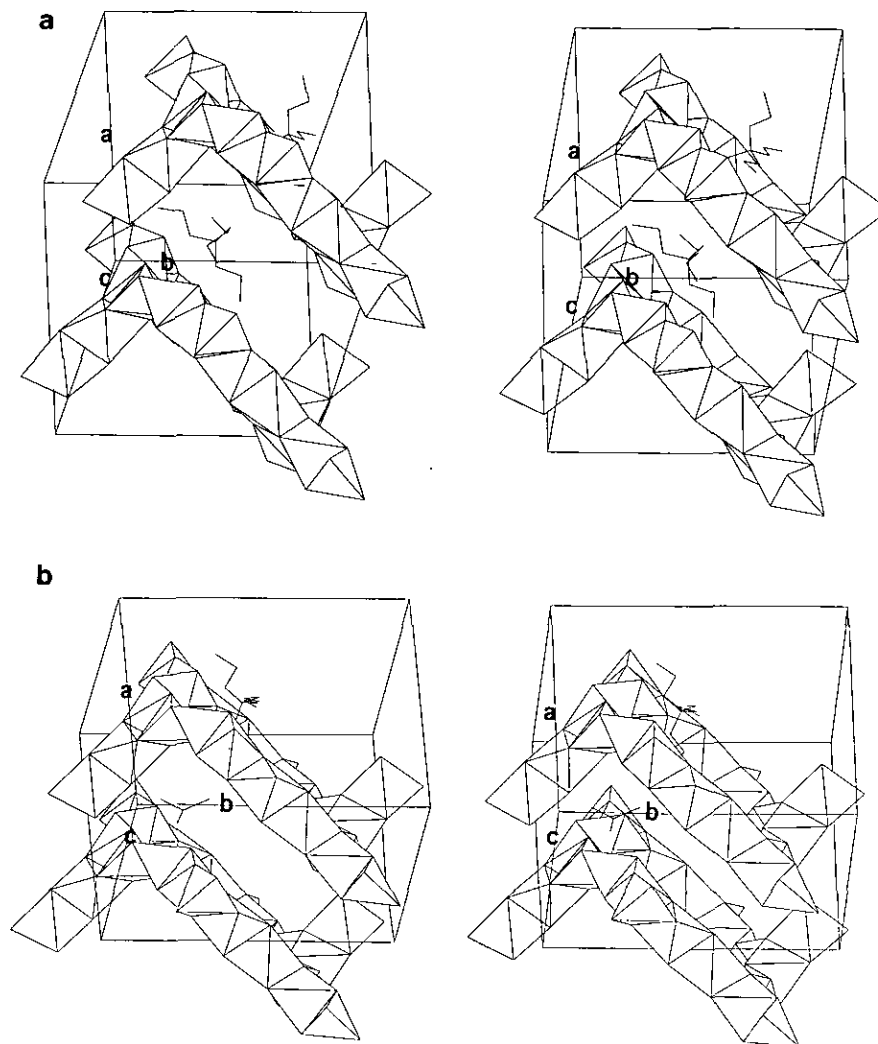


FIG. 2. Stereo drawings of cross sections through the undulating sheets in (a) TPA-SnS-4 and (b) TPA-SnS-4a. For clarity, only two crystallographically independent amines are shown in each structure. The TPA⁺ sitting above the sheet, with one arm extending into the aperture in TPA-SnS-4, is almost unchanged during the transformation to the 4a structure. The other TPA⁺, residing close to the center of the space between the sheets, is decomposed to trimethylammonium in the transformation from 4 to 4a.

(C(4)–C(5)–C(6)) inside a hole while the other TPA⁺ had decomposed to (CH₃)₃NH⁺ during prolonged heating (Fig. 2b). Trimethylamine is known to be one of the products of the breakdown of tetrapropylammonium hydroxide under the conditions used for the synthesis of TPA-SnS-4a (22). Because H was not located in this study, the assignment of the product molecule as (CH₃)₃NH⁺ instead of neutral (CH₃)₃N is based on previous work (3–6) and the assumption that the extra protons required for charge compensation are bound to trimethylamine. However, this assignment does not exclude the possibility of a neutral (CH₃)₃N and charge-compensating H being bound to the framework or other disordered species, which were not found in the structure determination. Indeed, the partial site occupancy of the (CH₃)₃NH⁺ suggests there might well be other protonated species within the channels.

The breakdown of the TPA molecules in transforming from the 4 to the 4a structure induces a shrinkage of the spacing between the undulating layers (Fig. 1). The intersheet distance decreases from 13.69 to 11.18 Å, while the framework topology remains relatively unchanged. The distance between undulations, for example, is 9.94 Å in the case of TPA-SnS-4 and 9.91 Å for TPA-SnS-4a. A similar collapse was also observed in a series of tin sulfides templated by the tetramethylammonium cation (23).

The charged framework and the large elliptical openings within the structure suggest that these compounds may be capable of ion exchange. We recently reported (6) alkaline earth, alkali, and some transition metal ions exchange for (N(CH₃)₄)⁺ in the related TMA-SnS-1 structure. However, TPA-SnS-4 and TPA-SnS-4a are not

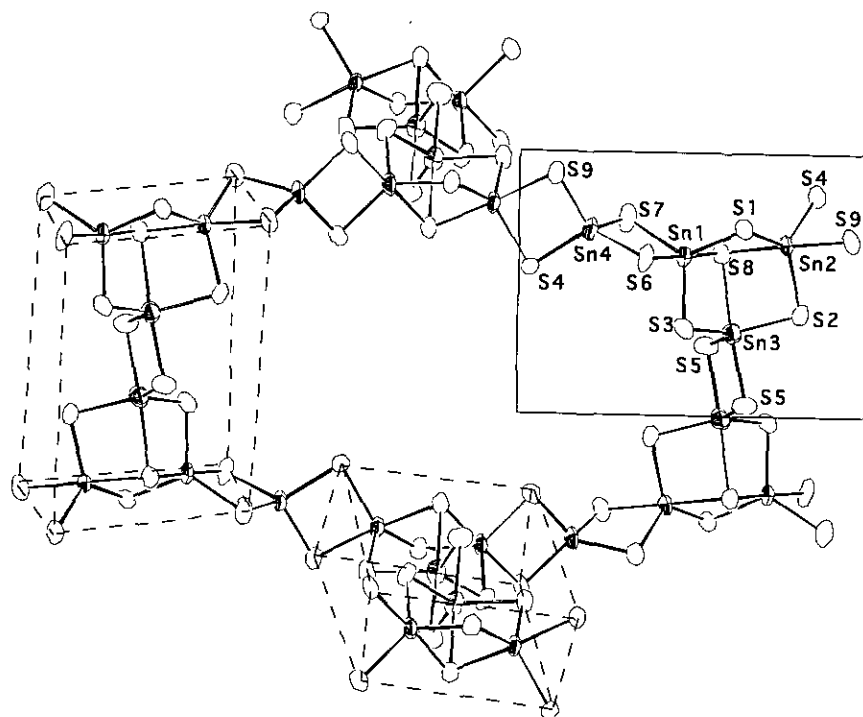


FIG. 3. ORTEP (24) drawing (60% probability ellipsoids) of an aperture within a sheet of TPA-SnS-4 oriented as shown in Fig. 1. The aperture is surrounded by 4 SnS₄ tetrahedra and 12 SnS₅ trigonal bipyramids. The primary building units and crystallographically independent Sn and S atoms (Tables 2 and 3) are outlined at the top right corner. Building blocks consisting of two linked semicubes (see text) are outlined by dashed lines; they are related by 90° rotation about [1, 0, 1]. TPA-SnS-4a has a similar ring structure.

capable of ion exchange under the same conditions. The possible explanations for this include the size of the TPA⁺ cation and the undulating nature of the Sn-S framework structure, which does not allow for facile transport within and between the layers.

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