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Communications

Synthesis and Structure of the Novel Nanoporous Tin(IV) Sulfide Material TPA–SnS–3

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The organic template mediated synthesis of a new family of tin(IV) sulfide-based open-framework materials, denoted as R–SnS–*n* (where *n* represents different structure types and R the occluded template), was first reported in 1989 by Bedard and co-workers at Union Carbide.[1,2] The source materials used in the preparations were amorphous and crystalline bulk forms of tin(IV) sulfide, SnS_2, and in most cases 1–2 μm size crystals were produced. Novel electronic, optical, and molecule discriminating device applications have been envisaged for this new class of nanoporous electronic materials.[3] The recent literature illustrates that interest in this class of nanomaterials is growing.[3-6] In this communication, we report a new method for the organic template mediated synthesis and growth of large crystals of this type of nanomaterial directly from elemental tin and sulfur constituents, as well as the first single-crystal XRD structure of the material denoted TPA–SnS–3, following the original denotation of Bedard's patent.[1,2]

Large single crystals of TPA–SnS–3 were prepared under hydrothermal conditions, from the reaction mixture composition

$$1Sn:2S:1{}^{n}Pr_4NOH:84H_2O$$

Tetrapropylammonium hydroxide (1.0 M, Aldrich) was diluted in water; sulfur (BDH) and tin (Alfa) were then added with stirring. Products were crystallized statically at 150 °C for 70 h, under autogenous pressure. The chemistry involved in the formation of this material has

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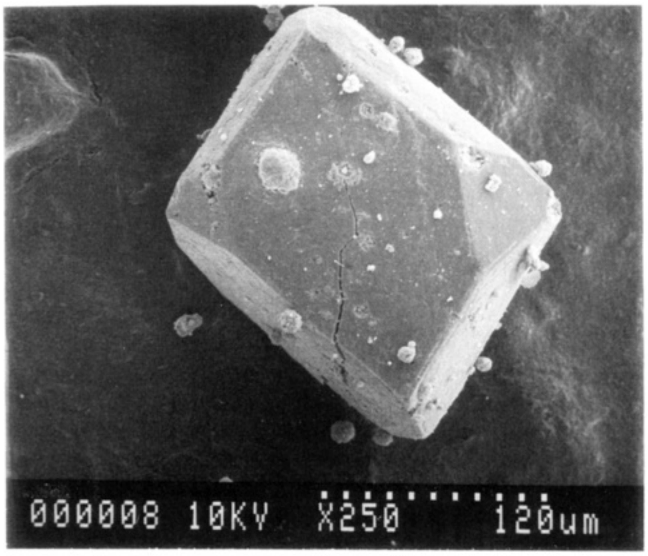

Figure 1. Scanning electron micrograph of a TPA−SnS−3 crystal.

Table 1. Summary of Structural Data for TPA−SnS−3 and TBA−SnS−3

	TPA−SnS−3	TBA−SnS−3
formula	$(^{n}\mathrm{Pr_4N})_2\mathrm{Sn_4S_9}$	$(^{n}\mathrm{Bu_4N})_2\mathrm{Sn_4S_9}$
a (Å)	15.515(3)	17.940(4)
b (Å)	15.855(3)	19.498(4)
c (Å)	18.627(4)	28.456(6)
β (deg)	110.43(3)	
space group	$P2_1/n$	*Pbcn*
ring size	32-atom	32-atom
pore dimensions (Å)[a]	20.65 × 9.32	19.8 × 11.3
interlamellar dimension (Å)[b]	14.05	14.2

[a] Dimensions defined from sulfur center to sulfur center (see Figure 2a). [b] Distance represents layer plane to layer plane (see Figure 2c).

been published elsewhere.[3h] Single crystals of up to 500 μm in size were synthesized by this method. A scanning electron micrograph of a representative TPA−SnS−3 crystal is shown in Figure 1.

Crystallographic data[7] obtained from a single-crystal XRD structure analysis for TPA−SnS−3[8] are summarized in Table 1. The crystallographically defined chemical composition of this material is $(^{n}\mathrm{Pr_4N})_2\mathrm{Sn_4S_9}$, which is confirmed by bulk elemental analysis (calculated for $(^{n}\mathrm{Pr_4N})_2\mathrm{Sn_4S_9}\cdot\mathrm{H_2O}$: Sn, 41.18; S, 24.98; C, 24.98; N, 2.43; H, 4.86; $\mathrm{H_2O}$, 1.56. Found: Sn, 40.92; S, 25.78; C, 24.59; N, 2.29; H, 4.89; $\mathrm{H_2O}$, 1.53). The occluded water was not located in the SCXRD analysis. Graphical representations of the TPA−SnS−3 structure are illustrated in Figure 2. TPA−SnS−3 can be described as having a corrugated nanoporous layer structure with the constituent layer pores registered to create channels through and between the layers, when viewed in certain directions. The organic template molecules reside in the void spaces within and between the layers (Figure 2B,C). One structurally interesting feature of the constituent layers of TPA−SnS−3 is the presence of periodic arrays of $\mathrm{Sn_3S_4}$ broken-cube clusters. These $\mathrm{Sn_3S_4}$ clusters are interconnected through tetrahedral edge-bridging (μ-$\mathrm{S_2SnS_2}$) spacer units as well as double sulfide $(\mu\text{-S})_2$ bridge bonds, to form distorted elliptical-shaped 32-atom rings when viewed orthogonally to the layers, see Figure 2A. Note that the TPA−SnS−3 structure contains both four-coordinate pseudotetrahedral $\mathrm{SnS_4}$ and 5-coordinate pseudotrigonal bipyramidal $\mathrm{SnS_5}$ units, which is to be contrasted with the R−SnS−1 structure type[3,6] in which the tin centers are exclusively of the latter variety. In R−SnS−1 the $\mathrm{Sn_3S_4}$ clusters are connected together solely by double sulfide $(\mu\text{-S})_2$ bridge linkages to form hexagonal-shaped rings, circumscribed by 24 alternating Sn and S atoms. Both R−SnS−1 and R−SnS−3 contain 2- and 3-coordinate sulfur. In TPA−SnS−3, the constituent sheets have developed a unique periodic curvature, which results in a parallel stacked, corrugated nanoporous layer structure (Figure 2). The TPA−SnS−3 structure can also be viewed in terms of a staircase, having holes that completely fill the horizontal and vertical parts of each step. When viewed perpendicularly to the steps of these corrugations, the pores have a quasi-rectangular shape (Figure 2D). The angle between the vertical and horizontal components constituting the steps in the corrugated layer is about 88°.

In the course of these studies, large crystals of a novel material denoted TBA−SnS−3 have also been synthesized directly from elemental tin and sulfur source materials, as described above, by replacing TPAOH by tetrabutylammonium hydroxide (TBAOH). The quality of the crystals, however, was not sufficiently high to permit a full single-crystal XRD structure refinement of both the framework constituents and the occluded template species in this material. Nevertheless, the refinement was sufficiently accurate to allow definition of the topology and chemical composition of the framework in this material. The framework composition of TBA−SnS−3 was established to be $[\mathrm{Sn_4S_9}]^{2-}$, which has

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[7] TPA−SnS−3: $\mathrm{Sn_4S_9}\cdot\mathrm{C_{24}H_{56}N_2}$, $M = 1360.0$, monoclinic, space group $P2_1/n$, $a = 15.515(3)$, $b = 15.855(3)$, $c = 18.627(4)$ Å, $\beta = 110.43(3)°$, $V = 4294(2)$ Å^3, $Z = 4$, $D_c = 1.76$ g cm^{-3}, μ(Mo K) = 27.6 cm^{-1}, $F(000) = 2232$, $2 < 2\theta < 45$, 5584 unique data, $R_{\mathrm{int}} = 0.0547$, $R = 0.051$ [for $I > 2\sigma(I)$], maximum peak in final difference fourier 1.01 e Å^{-3}. Data for TPA−SnS−3 crystals were collected on an Enraf-Nonius CAD4 diffractometer. Initial attempts to calculate orientation matrices and unit-cell dimensions, with the diffractometer control software, were unsuccessful. The orientation matrices used for data collection were determined using the program DIRAX.[10] All data sets were corrected for Lorentz and polarization effects and also for absorption.[11] The structure was solved by direct methods. The Sn and S atoms were refined with anisotropic thermal parameters by full-matrix least-squares refinement on F.[11] The atoms of both template molecules were refined with anisotropic thermal parameters and hydrogen atoms were added in calculated positions (C−H 0.96 Å). All crystallographic calculations were carried out using the SHELXTL PC[12] version and SHELXL-93[13] on a 486−66 personal computer.

[8] Although the simulated powder XRD pattern of this purported TPA−SnS−3 material does not completely match that reported in the original patent for so-called TPA−SnS−3, we have discovered that under some conditions the experimental powder XRD pattern of our material does match that reported in Bedard's patent.[1] What has been established in our study is that, dependent upon the sample preparation for powder X-ray data collection, the experimental powder XRD pattern can resemble either that of the simulation from the single crystal structure data or that of TPA−SnS−3 reported in the original patent of Bedard. The TPA−SnS−3 reported in this work can easily transform to the TPA−SnS−3 described in the original patent, simply by grinding the material. The layer spacing (i.e., the distance between Miller index plane [−111]) decreases from 10.42 Å before grinding to 9.85 Å after grinding. It has also been discovered that single crystals of TPA−SnS−3 can be synthesized through different methods. The same single crystal structure as that reported in this work is always obtained, although the powder patterns vary from a dominant TPA−SnS−3 as reported in Bedard's patent to a dominant one as reported in this work or to a mixture of these two phases, depending on the powder XRD sample preparation. We believe that as-synthesized TPA−SnS−3 has the structure reported in this paper and transforms only to what we consider to be the polytype reported in the original patent by postsynthesis treatment, such as grinding. This is another example of the framework flexibility that has been discovered for this novel class of nanoporous R−SnS−n materials.[3f]

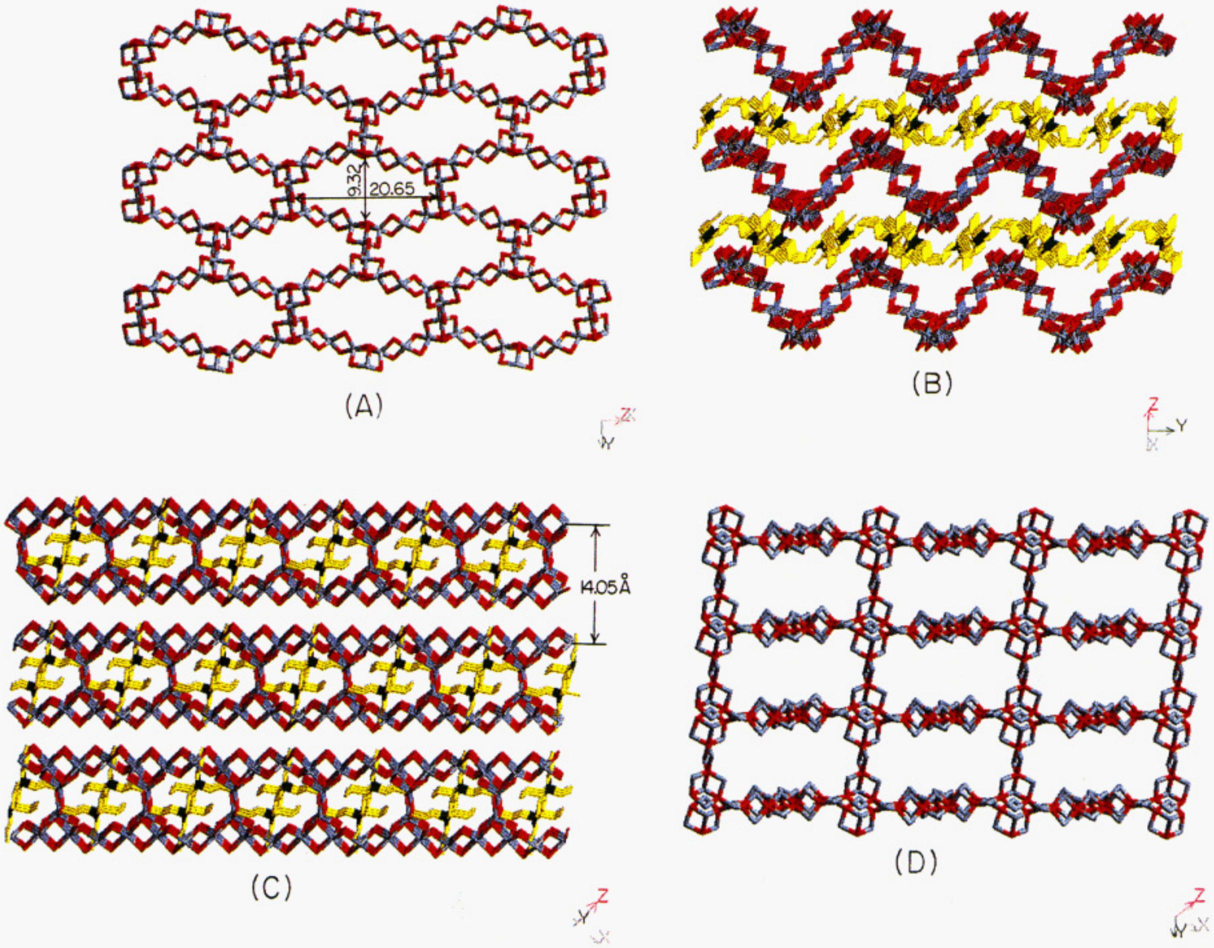

Figure 2. Illustrations of the structure of TPA−SnS−3 (color notation: gray, Sn; red, S; yellow, C; green, N), (A) projection of the [−101] plane with the template cations omitted for clarity (note the elliptical-shaped 32-atom rings built up of Sn_3S_4 broken-cube clusters which are linked together by tetrahedral edge-bridging (μ-S_2SnS_2) spacer units as well as double sulfide (μ-S)$_2$ bridge bonds), (B) projection of the [101] plane including the template cations TPA^+ that are located between the layers (note the corrugated architecture of both the tin sulfide framework and the imbibed TPA^+ template), (C) projection of the [010] plane including the template cations that are located within the layers (note that the corrugated nature of the TPA−SnS−3 layers creates the illusion of 20-atom rings when the structure is viewed in this direction), (D) projection of the [−111] plane with the template cations omitted for clarity (note that as described in the text, the corrugated layers can be viewed as a staircase and when viewed normally to the steps, the elliptical-shaped 32-atom rings become pseudorectangular).

been confirmed by elemental analysis. Indexing of the PXRD pattern of this material confirms the space group and unit cell dimensions obtained by SCXRD analysis (Table 1), and moreover establishes the phase identity. The structure of the porous layers in TBA−SnS−3 is found to resemble that of TPA−SnS−3, except that the 32 atom-ring elliptical-shaped pores are regular in the former and distorted in the latter material (Figure 3). A comparison of the pore size and shape and interlamellar spacings between these two R−SnS−3 materials is summarized in Table 1. The TPA and TBA cations appear to have a templating function in the assembly of these nanoporous R−SnS−3 materials. The size and shape of the void spaces within and between the layers bear some correspondence with the steric requirements of the charge-balancing cations; see Figures 2 and 3 and Table 1. Note that the hexagonal-shaped 24-atom ring nanoporous layers found in the R−SnS−1 structure type has been templated by the smaller tetramethylammonium and tetraethylammonium (TMA and TEA) cations.[3,6]

From the results of this structural study of R−SnS−3 materials, as well as that of other R−SnS−n materials,[3f] one of the most thought-provoking structural features to emerge is the ability of their nanoporous layer frameworks to undergo elastic deformations in response to changes in the identity and loading of the imbibed guest molecules. The loading of template or adsorbate molecules can cause different degrees and types of framework distortion. A similar kind of framework flexibility has also been reported for oxide-based zeolite materials such as RHO and ZSM-5.[9] What makes the flexible open-framework R−SnS−n materials unique is their semiconductor character as compared to the insulating property of zeolites.[3j] The basic 32-atom ring nanoporous layered structure that exists in both TPA−SnS−3 and TBA−SnS−3 can have different pore sizes, shapes, and interlamellar spacings (Table 1). Through a type of "shearing" motion, the regular elliptical-shaped 32-atom rings in TBA−SnS−3 become distorted elliptical shapes in TPA−SnS−3 (Figures 2 and 3). This is

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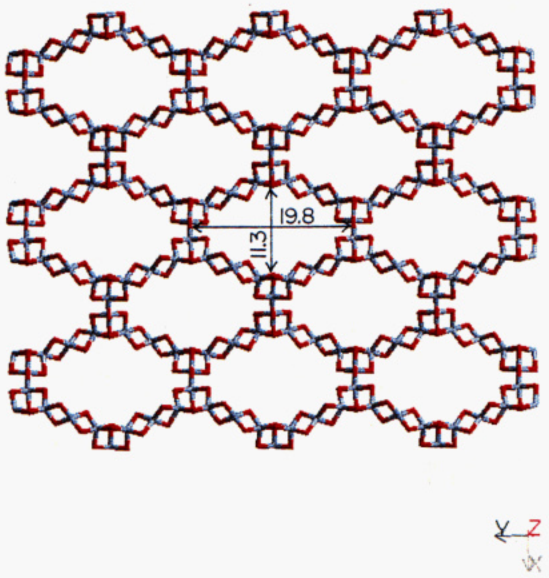

Figure 3. Illustration of the structure of TBA−SnS−3 (color notation: gray, Sn; red, S; yellow, C; green, N). Projection of the [001] plane with the template cations omitted for clarity. Note that the overall structure of the open-framework of TBA−SnS−3 is the same as that of TPA−SnS−3, however, the size (in Å) and shape of the elliptical-shaped 32-atom rings are different.

accompanied by a concomitant change in the angle of corrugation from about 90° to 88°. In this context, it cannot be overemphasized that the guest-induced elastic deformability of this class of materials is almost certainly responsible for the difficulties that we have encountered in the preparation of high-quality crystals of TBA−SnS−3 for a full single-crystal XRD structural analysis. Ironically, it is the notable flexibility of this class of nanoporous tin(IV) sulfides that makes them of considerable interest as the chemoselective element for incorporation into a new generation of molecular recognition devices.[3i]

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Supplementary Material Available: Tables that summarize data for the crystal structure analysis data of TPA−SnS−3 (7 pages); observed and calculated structure factor values (13 pages). Ordering information is given on any current masthead page.

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