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Synthesis and Structural Characterization of a Chiral Open-Framework Tin(II) Phosphate, $[CN_3H_6][Sn_4P_3O_{12}]$ (GUAN−SnPO)

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Nanoporous materials are of considerable interest due to both their wide structural diversity and their potential applications in catalysis and other areas.[1] The development of chiral sieve structures is particularly attractive, since it offers the possibility of providing new routes for the manufacture of optically pure organic compounds. A small number of chiral zeolites are known, including the interesting case of zeolite β, which is an intergrowth of two polymorphic forms, one of which is chiral.[2] There have also been several recent successes in the open-framework phosphate area. Harrison et al.[3] reported two closely related chiral sodium zincophosphates, $NaZnPO_4{\cdot}H_2O$-I and -II, both prepared in the absence of chiral structure directing agents (SDA), and Stalder and Wilkinson[4] used a chiral SDA to prepare a chiral gallophosphate. Zeolite-related cobalt(II) phosphates have also been reported.[5] Recently, it has been established that tin(II) forms open-framework phosphate materials under hydrothermal conditions in the presence of organic amines and that these exhibit a wide range of novel architectures. For example, the tin(II) phosphates that have been isolated to date include a chain structure, $(Sn_2(PO_4)(C_2O_4)_{0.5})$,[6] a layered structure, $([Sn_2(PO_4)_2]^{2-}[C_2N_2H_{10}]^{2+}H_2O)$,[7] and several three-dimensional extended networks $([Sn_4P_3O_{12}]^{-}0.5\text{-}[\text{amine}]^{2+})$.[8−10] These compounds contain either trigonal pyramidal SnO_3 or square pyramidal SnO_4 units, vertex linked with tetrahedral PO_4 units to form the framework. In this paper, we report a study of both the enantiomorphs of a chiral open-framework SnPO structure. It is noteworthy that the title compound, GUAN−SnPO, was obtained from a synthesis with an achiral SDA, guanidine.

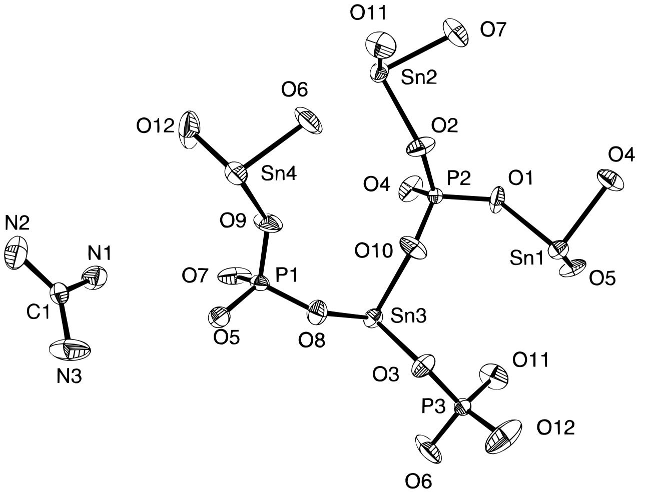

Figure 1. Asymmetric unit of GUAN−SnPO (thermal ellipsoids are given at 50% probability).

The title compound was synthesized by hydrothermal methods employing guanidine as the structure-directing agent. In a typical synthesis, 1.53 mL of phosphoric acid was first added to 1.8 g of guanidinium carbonate to remove CO_2, and then 2.0671 g of tin oxalate, 6 mL of water, and 4 mL of ethylene glycol (EG) were mixed to give a mixture in the ratio 1.0:2.0:2.0:33.0:6.0 SnC_2O_4:H_3PO_4:$[CN_3H_6]$:H_2O:EG. This was stirred until it became homogeneous, and the final mixture was sealed in a PTFE-lined stainless steel autoclave (Parr) and heated at 150 °C for 2 days under autogenous pressure. The resulting product, which contained a mixture of powder and colorless hexagonal needle crystals, was filtered and washed thoroughly with deionized water. The powder X-ray diffraction pattern indicated that the product was a new material. Thermogravimetric analysis (TGA) under a static air atmosphere in the range from room temperature up to 800 °C showed weight loss of 8.6% (calcd 8.3%) at around 400 °C, corresponding to the loss of the amine molecule. The chemical analysis gave the following results: Sn/P = 1.29% (calcd = 1.33%), C = 1.89% (calcd = 1.46%), H = 1.03% (calcd = 0.70%), N = 4.8% (calcd = 5.1%). The powder X-ray diffraction pattern of the decomposed sample at 400 °C shows the presence of $Sn_2P_2O_7$ (broad peaks).

A suitable single crystal was carefully selected under a polarizing microscope, and X-ray data were collected on a Siemens SMART CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo Kα radiation) operating at 50 kV and 40 mA. About 1.3 hemispheres of intensity data were collected in 1321 frames with ω scans (width of 0.30° and exposure time of 10 s per frame). The unit-cell constants were determined by a least-squares fit of 8192 reflections in the range $4° < 2\theta < 50°$. Crystal data for $[Sn_4P_3O_{12}]^{-}$-$[CN_3H_6]^{+}$: tetragonal, space group $P4_3$ (No. 78), $a = 8.8881(1)$ Å, $c = 20.6029(4)$ Å, $V = 1627.59$ (4) Å^3, $Z = 4$, $M = 819.76$, and $\rho_{\text{calc}} = 3.345$ g cm^{-3}. A total of 8517 reflections were collected in the range $-11 \le h \le 10$, $-11 \le k \le 11$, $-27 \le l \le 25$. These were merged to give 2807 unique data ($R_{\text{merg.}} = 4.4\%$). The structure

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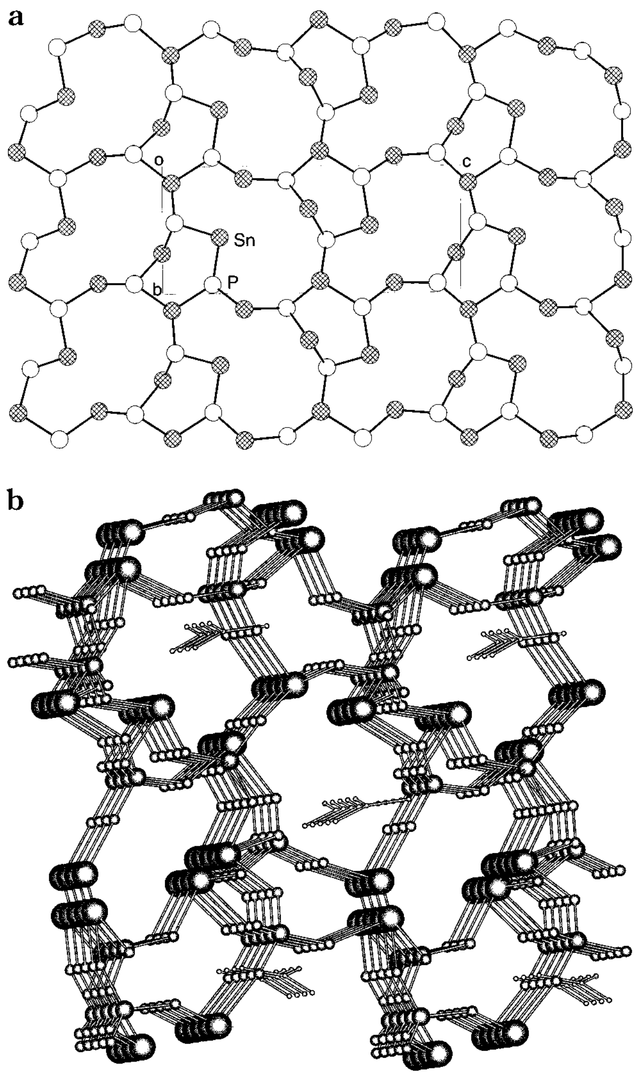

Figure 2. (a) One of the puckered sheets of six-membered ($Sn_3P_3O_6$) and 12-membered ($Sn_6P_6O_{12}$) rings in GUAN−SnPO, which lie perpendicular to [100] and [010]; tin, hatched circles; phosphorus, open circles; oxygen, not shown. (b) View of the structure down [010]; tin, large shaded circles; phosphorus, medium shaded circles; oxygen, small shaded circles. Guanidinium ions are shown as smaller balls and sticks.

was solved by direct methods using SHELXS-86[11] and difference Fourier syntheses. The absorption correction was based on symmetry equivalent reflections using the SADABS[12] program. Other effects such as absorption by the glass fiber were simultaneously corrected. The last cycles of refinement included atomic positions and anisotropic thermal parameters for all the non-hydrogen atoms. Final $R(F) = 2.5\%$, $R_w(F^2) = 5.5\%$ and $S = 1.188$ were obtained for 226 parameters and 2763 reflections with $I > 2\sigma(I)$. The final Fourier map minimum and maximum were −1.31 and 0.75 e $Å^{-3}$. Full-matrix-least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL[13] package of programs.

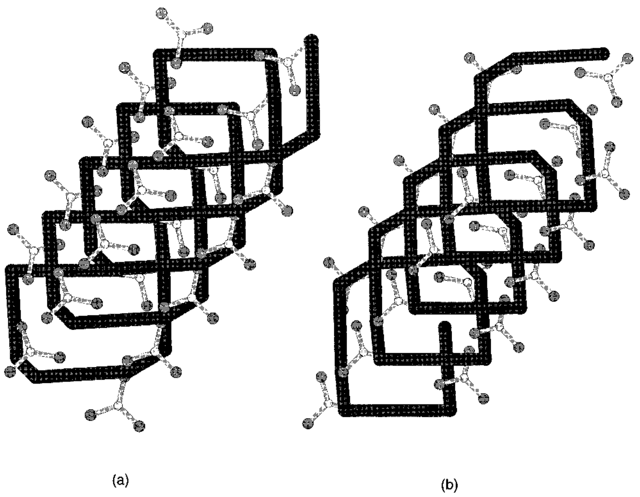

Figure 3. The tin atoms are connected along *c* to show the chirality of the channels in (a) the $P4_3$ structure and (b) the $P4_1$ structure; guanidinium ions are shown as balls and sticks.

The structure of GUAN−SnPO is based upon a network of alternating trigonal pyramidal SnO_3 and tetrahedral PO_4 units, as in other 3d Sn(II) phosphates.[8,9] The asymmetric unit is shown in Figure 1. The Sn−O distances are in the range 2.063−2.164 Å-(ave 2.104 Å) and the O−Sn−O bond angles are in the range 83.3−91.6° (ave 85.7°), typical of three-coordinated Sn in the 2+ oxidation state and in agreement with related materials.[6−10] The P−O distances are in the range 1.507−1.541 Å (ave 1.528 Å) and the O−P−O angles in the range 105.6−111.8° (ave 109.5°). The framework is constructed of puckered sheets of six-membered ($Sn_3P_3O_6$) and 12-membered ($Sn_6P_6O_{12}$) rings, which are perpendicular to [100] and [010] (Figure 2a). The sheets are stacked in an AB sequence along [100] and [010]. Charge neutrality is achieved by incorporating the planar guanidinium cations into the tortuous channel structure defined by the 12-rings (Figure 2b). The width of this channel is 8.3 × 6.7 Å, atom to atom; the planes of the organic cations lie perpedicular to [001]. The shortest distances between the nitrogens of the guanidinium and the oxygens of the framework are 2.997, 2.929, and 3.012 Å, respectively, for N1−O3, N2−O10, and N3−O1, confirming that there is hydrogen bonding between the amine and the host structure.

The structure of GUAN−SnPO is chiral (space group $P4_3$), even though the synthesis conditions involved an achiral SDA. It has previously been found that structures containing pyramidal selenite (SeO_3^{2-}) units have a strong tendancy to be acentric or chiral.[14] The same trend may hold for materials containing the pseudo-isoelectronic SnO_3^{4-} unit. Refinement of the Flack polarity parameter (0.019(26)) confirmed that the right-handed enantiomorph had been obtained in our initial structure determination (refinement in $P4_1$ yielded a Flack polarity parameter of 1.005(38)). By visual inspection of the sample morphology, we were able to select a crystal of the left-handed enantiomorph for a second structure determination. The structure was refined in space group $P4_1$, yielding an *R* factor of 3.2% and a Flack polarity parameter of 0.069(62) (refinement in $P4_3$ yielded a value of 0.919(67)). In all other respects, the structures of the two enatiomorphs are identical, as expected. The chirality of the channels in

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the two enantiomorphs can clearly be seen when the tin atoms are connected along *c* (Figure 3).

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Supporting Information Available: X-ray crystallography data for GUAN–SnPO (5 pages). Ordering information is given on any current masthead page.

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