

LETTER TO THE EDITOR

First Example of a Tin(II) Oxy-Phosphate with an Open-Framework Structure: Synthesis and Structure of $[\text{NH}_4]^+[(\text{Sn}_3\text{O})_2(\text{PO}_4)_3]^-$

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The synthesis and structure of an open-framework material based on tin(II) oxyphosphate is described: $[\text{NH}_4]^+[(\text{Sn}_3\text{O})_2(\text{PO}_4)_3]^-$; colorless; space group = *Pbcn* (#60); $a = 6.7963(2)$; $b = 19.6000(4)$; $c = 12.5777(4)$ Å; $V = 1675.44(12)$ Å³; and $Z = 8$. The structure comprises a network of pyramidal SnO_3 and tetrahedral PO_4 moieties. There is a single oxygen atom bonding only the Sn atoms in this structure. The charge balancing $[\text{NH}_4]^+$ cations are located at one end of a star-shaped 10-ring channel and the Sn(II) lone-pairs protrude into this channel, preventing any access. © 1997 Academic Press

INTRODUCTION

The synthesis of open-framework materials, such as aluminosilicates and aluminophosphates, which are widely used in the areas of catalysis, ion-exchange, molecular recognition, optics, and electronics, is facilitated by the use of structure-directing agents (1). These are generally organic bases (in most cases some form of an organic amine) which are added to the starting inorganic gel. The porous architecture is built around them and the final structure of the inorganic framework depends, in most cases, on the shape and size of the amine molecule used in the initial mixture (2–5). The amine molecules are generally accommodated within the cavities and channels of these open structures and can be removed, in many cases, by postsynthesis treatments such as calcination or chemical extraction (leaching). We have recently established that open-framework tin phosphate compounds can be synthesized with the aid of organic

structure-directing molecules (6–8) by hydrothermal methods. We present here the synthesis and structure of a new tin oxyphosphate containing $[\text{NH}_4]^+$ cations in 10-ring channels. The compound is designated SnOPO-1.

EXPERIMENTAL

The title compound was synthesized by the hydrothermal method as described below. A starting mixture corresponding to the molar ratio $\text{SnC}_2\text{O}_4:1.0\text{P}_2\text{O}_5:2.0(\text{NH}_2)(\text{CH}_2)_4(\text{NH}_2):55\text{H}_2\text{O}$ was mixed and stirred until homogeneous, sealed in a PTFE-lined stainless steel autoclave (Parr, USA), and heated at 150°C for 2 days under autogeneous pressure. The resulting product, which contained a mixture of transparent crystals and white powder, was filtered off and washed thoroughly with deionized water. The powder X-ray diffraction pattern indicated that the product was a new material; the pattern is entirely consistent with the structure determined by single crystal X-ray diffraction.

A suitable single crystal (0.05 × 0.05 × 0.075 mm) was carefully selected under a polarizing microscope. Crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoK α radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected in 1321 frames with ω scans (width 0.30 and exposure time 10 s per frame). The unit-cell constants were determined by a least-squares fit of 3868 reflections in the range $10^\circ < 2\theta < 56^\circ$. Crystal data for SnOPO-1: orthorhombic, space group *Pbcn* (#60); $a = 6.7963(2)$; $b = 19.6000(4)$; $c = 12.5777(4)$ Å; $V = 1675.44(12)$ Å³; $Z = 8$; $M = 521.5(1)$; $D_{\text{calc.}} = 4.135(1)$ g cm⁻³. A total of 6801 reflections were collected and these were merged to give 2031 unique reflections ($R_{\text{merg.}} = 11.5$) of

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which 1279 were considered observed with $I > 3\sigma(I)$. The structure was solved by direct methods using SHELXS-86 (9) and difference Fourier syntheses. The absorption correction was based on symmetry equivalent reflections using the SADABS (10) 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 atoms. Full-matrix least-squares structure refinement against $|F|$ was carried out using the CRYSTALS (11) package of programs. The applied weighting scheme was based on Tukey and Prince with a three-term modified Chebyshev polynomial (12). The final Fourier map had minimum and maximum peaks of -1.37 and $1.97 e\text{\AA}^{-3}$, respectively. Final R values, $R = 3.54$, $R_w = 3.83$, and $S = 1.09$, were obtained for a total of 111 parameters. The atomic coordinates are given in Table 1.

RESULTS AND DISCUSSION

The structure, $[\text{NH}_4]^+[(\text{Sn}_3\text{O})_2(\text{PO}_4)_3]^-$, is based on a network of pyramidal SnO_3 and tetrahedral PO_4 moieties. The asymmetric unit contains 13 independent non-hydrogen atoms (Fig. 1); one vertex of all the SnO_3 units is a common oxygen, (O(3)), and the remaining vertices are connected to phosphorus atoms forming a three-dimensional network creating star-shaped 10-membered ring channels (Fig. 2). The $[\text{NH}_4]^+$ cation formed by the decomposition of the amine during the synthesis is present at one end of these 10-membered ring channels (Fig. 2a). The lone pair of electrons associated with Sn(II) atoms is also located within this channel, preventing access (Fig. 2b).

TABLE 1
Atomic Coordinates and Isotropic Displacement Parameters for the Non-hydrogen Atoms in $[\text{NH}_4]^+[(\text{Sn}_3\text{O})_2(\text{PO}_4)_3]^-$

| Atom | x/a | y/b | z/c | $U_{\text{eq.}}/U_{\text{iso}}$ |
|--------|------------|------------|-------------|---------------------------------|
| Sn(1) | 0.1701(1) | 0.04895(4) | 0.11040(5) | 0.0173 |
| Sn(2) | 0.2934(1) | 0.09301(4) | -0.15573(5) | 0.0182 |
| Sn(3) | -0.0196(1) | 0.20613(3) | 0.00947(5) | 0.0173 |
| P(1) | 0.5000 | 0.2429(2) | -0.2500 | 0.0155 |
| P(2) | 0.3530(4) | -0.0811(1) | -0.0320(2) | 0.0165 |
| O(1) | 0.216(1) | -0.0185(4) | -0.0236(6) | 0.0237 |
| O(2) | 0.483(1) | 0.0660(4) | 0.1123(6) | 0.0184 |
| O(3) | 0.154(1) | 0.1212(4) | -0.0138(5) | 0.0181 |
| O(4) | 0.569(1) | 0.0986(4) | -0.0785(6) | 0.0230 |
| O(5) | 0.340(1) | 0.2009(4) | -0.1963(6) | 0.0238 |
| O(6) | 0.099(1) | 0.2113(4) | 0.1656(5) | 0.0190 |
| O(7) | -0.234(1) | 0.1408(4) | 0.0781(6) | 0.0199 |
| N(100) | 0.5000 | 0.1902(7) | 0.2500 | 0.0245 |

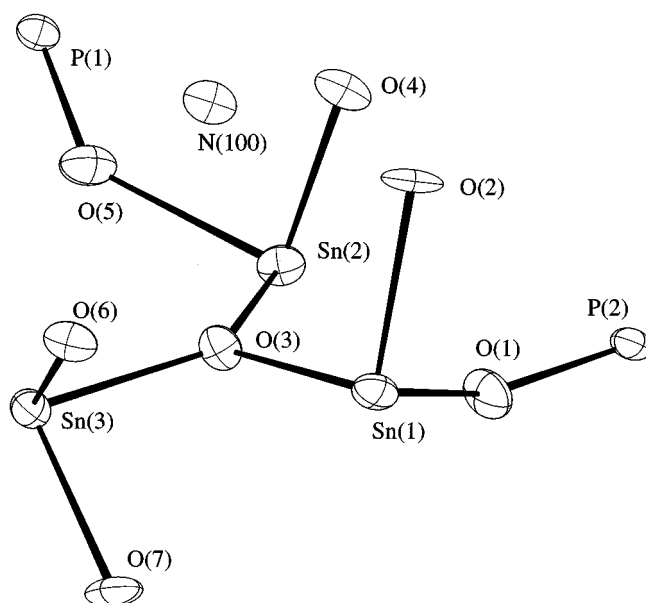
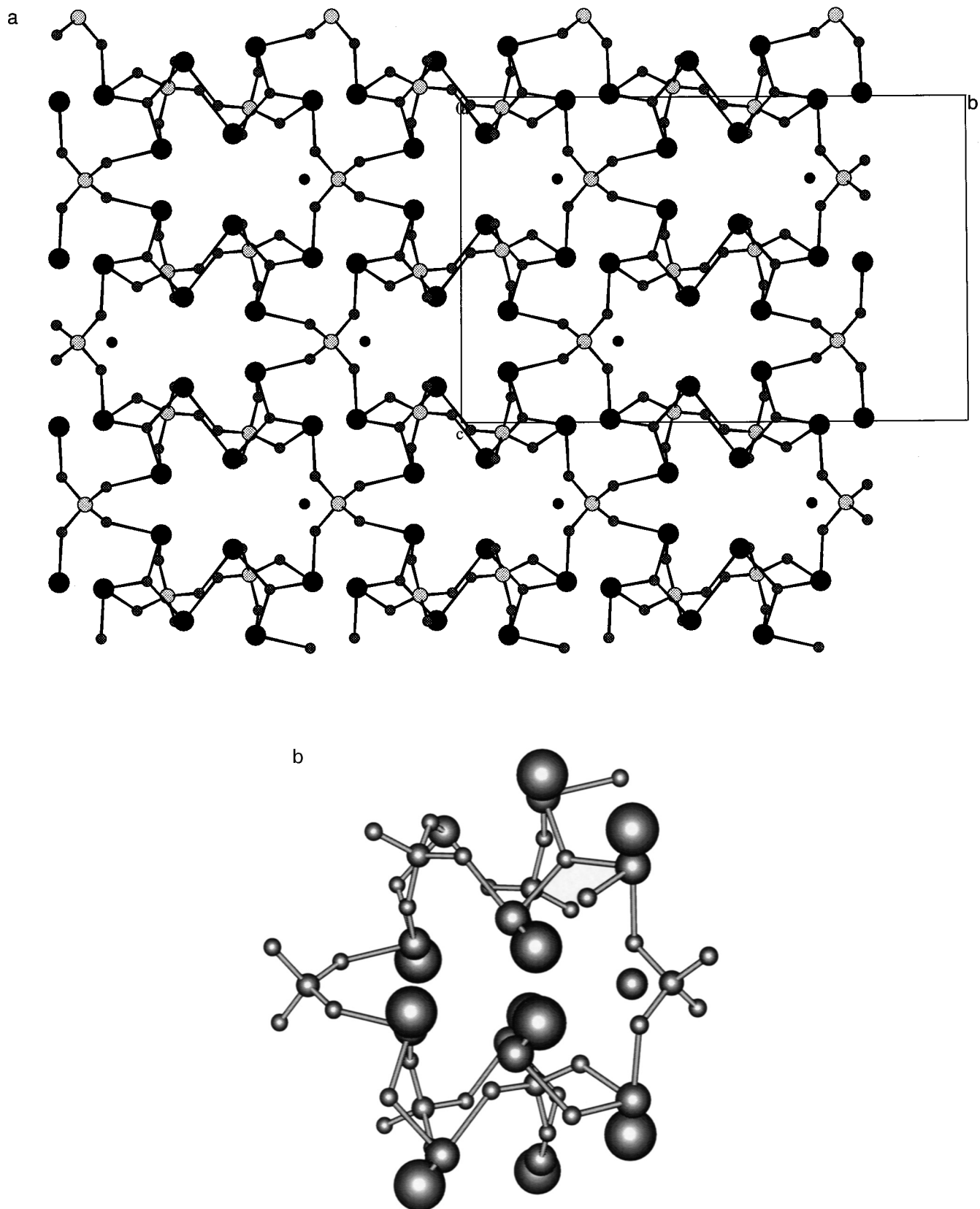


FIG. 1. Asymmetric unit of SnOPO-1. Note that O(3) is coordinating only to three Sn atoms.

All the Sn–O bond distances lie in the range from 2.063 to 2.165 Å (average 2.127 Å) and the O–Sn–O bond angles are in the range 80.8° to 90.5° (average 86.92°); this is typical of three-coordinated Sn in the +2 oxidation state. The values are in excellent agreement with other tin(II) phosphates previously reported (6–8, 13, 14). The P–O distances are within the range 1.522 to 1.545 Å (average 1.543 Å) and the O–P–O bond angles are in the range 108.0 to 114.5° (average 109.44°). These values, too, are comparable to other aluminophosphates and galliophosphates reported in the literature (15–17).

Thermogravimetric analysis (TGA) on the tin oxyphosphate was carried out in the presence of flowing air from room temperature up to 700°C. The results show a single weight loss in the region 300–350°C. The weight loss corresponds to about 3% of the total mass of the sample and can be directly correlated to the decomposition and loss of ammonia. The powder X-ray diffraction pattern of the decomposed sample indicates a poorly crystalline phase with all of the lines corresponding to the crystalline phase $\text{Sn}_2\text{P}_2\text{O}_7$ [JCPDS: 35-28]; it seems likely that an amorphous phase with a Sn:P ratio $> 3:2$ is also present.

The synthesis of a tin oxyphosphate with an open-framework structure has been successfully accomplished. Our ongoing research indicates the existence of other related structures and we are currently pursuing chemical methods for removing the occluded template materials in order to exploit this class of materials for base catalysis.



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