

LETTER TO THE EDITOR

A Novel Monomeric Tin(II) Phosphate, $[\text{N}(\text{C}_2\text{H}_5\text{NH}_3)_3]^{3+}[\text{Sn}(\text{PO}_4)(\text{HPO}_4)]^{3-} \cdot 4\text{H}_2\text{O}$, Connected through Hydrogen Bonding

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The tin(II) phosphate, $[\text{N}(\text{C}_2\text{H}_5\text{NH}_3)_3]^{3+}[\text{Sn}(\text{PO}_4)(\text{HPO}_4)]^{3-} \cdot 4\text{H}_2\text{O}$, contains monomeric $\text{Sn}_2(\text{PO}_4)_2(\text{HPO}_4)_2$ units which form a hydrogen-bonded network with the TREN amine ($\text{TREN} = \text{N}(\text{C}_2\text{H}_5\text{NH}_3)_3^{3+}$); triclinic, space group *P1* (no. 2), $a = 9.579(1)$, $b = 10.507(1)$, $c = 10.976(1)$ Å; $\alpha = 72.93(1)^\circ$, $\beta = 78.03(1)^\circ$, $\gamma = 69.82(1)^\circ$, $V = 984.2(1)$ Å³, $Z = 2$. The $\text{Sn}_2\text{P}_2\text{O}_4$ core of this unit is a common structural feature of open-framework tin phosphates and may play a role as a building block for this class of materials. © 1998 Academic Press

INTRODUCTION

Open-framework materials, such as the aluminosilicate zeolites, are widely used in the areas of catalysis, sorption, and ion-exchange processes (1). In this context, the study of open-framework metal phosphates is an area of particular interest due to both their wide structural diversity and their potential applications in catalysis and other areas. The aluminophosphates have received most of the attention. In addition to the well-known three-dimensional AlPO_4 frameworks (2), numerous examples of zero- (i.e., monomeric) (3), one- (4, 5), and two- (6, 7) dimensional aluminophosphates have also been reported in the literature. Recently, it was established that tin (II) forms open-framework phosphate materials under hydrothermal conditions in the presence of organic amines, and that these, too exhibit a wide range of architectures. For example, the tin(II) phosphates that have been isolated to date include a chain structure, $(\text{Sn}_2(\text{PO}_4)(\text{C}_2\text{O}_4)_{0.5})$ (8), a layered structure, $([\text{Sn}_2(\text{PO}_4)_2]^{2-}[\text{C}_2\text{N}_2\text{H}_{10}]^{2+} \cdot \text{H}_2\text{O})$ (9), and several three-dimensional extended networks $([\text{Sn}_4\text{P}_3\text{O}_{12}]^{-0.5}[\text{amine}]^{2+})$ (10–12). 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 the present work, we describe the synthesis and structure of a monomeric tin phosphate having a Sn/P ratio of 1:2. The individual tin phosphate moieties are connected to the claw-like organic amine (TREN, *tris*-(2-aminoethylamine)) and water molecules by hydrogen bonding.

EXPERIMENTAL

The title compound was synthesized by hydrothermal methods employing TREN as the structure-directing agent. In a typical experiment, 2.067 g of the tin oxalate was dispersed in 10 ml of water. To this mixture, 1.49 g of phosphoric acid was added and stirred vigorously, followed by 1.83 ml of TREN which was added under continuous stirring. The final mixture was sealed in a PTFE-lined stainless steel autoclave (Parr, USA), and heated at 150°C for 2 days under autogeneous pressure. The final composition of the mixture was 1.0 SnC_2O_4 :1.5 H_3PO_4 :1.0 TREN:55 H_2O . The resulting product, which contained large quantities of needle-shaped crystals and a very small amount of 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. Thermogravimetric analysis (TGA) under a nitrogen atmosphere in the temperature range from room temperature up to 800°C showed two weight losses. The results indicate that the solid loses water in the range 50–100°C, corresponding to about 12.5% (calc. 13%) weight loss, and then loses the amine molecule around 325–400°C, corresponding to about 28% (calc. 27.5%) weight loss. The powder X-ray diffraction pattern of the dehydrated sample reveals the original structure with a slight change in lattice parameters, while the sample heated to 400°C shows the presence of $\text{Sn}_2\text{P}_2\text{O}_7$ [JCPDS: 35–28].

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A suitable single crystal ($0.12 \times 0.07 \times 0.07 \text{ mm}^3$) was carefully selected under a polarizing microscope and mounted at the end of a thin glass fiber using superglue (cyanoacrylate). Crystal structure determination was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 KW sealed tube X-ray source (MoK α radiation) operating at 50 kV and 40 mA. A full sphere of intensity data was collected in 2082 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 4422 reflections in the range $4^\circ < 2\theta < 50^\circ$. Crystal data for $[\text{Sn}(\text{PO}_4)(\text{HPO}_4)]^{3-}[\text{N}(\text{C}_2\text{H}_5\text{NH}_3)_3]^{3+} \cdot 4\text{H}_2\text{O}$ is as follows: triclinic, space group $P1$ (no. 2), $a = 9.579(1)$, $b = 10.507(1)$, $c = 10.976(1) \text{ \AA}$; $\alpha = 72.93(1)^\circ$, $\beta = 78.03(1)^\circ$, $\gamma = 69.82(1)^\circ$, $V = 984.2(1) \text{ \AA}^3$, $Z = 2$, $M = 533.89$, and $\rho_{\text{calc.}} = 2.926 \text{ g cm}^{-3}$. A total of 8518 reflections were collected in the range $-12 \leq h \leq 12$, $-13 \leq k \leq 13$, $-14 \leq l \leq 14$. These were merged to give 3431 unique data ($R_{\text{merg.}} = 11.2$). The structure was solved by direct methods using SHELXS-86 (13) and difference Fourier syntheses. The absorption correction was based on symmetry equivalent reflections using SADABS (14) 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 nonhydrogen atoms. Final $R = 5.3$, $R_w = 10.5$, and $S = 1.1$ were obtained for 226 parameters. The final Fourier map minimum and maximum were -0.778 and 0.844 e\AA^{-3} , respectively. Full-matrix-least-squares structure refinement against $|F^2|$ was carried out using the SHELXSTL-PLUS (15) package of programs.

RESULTS AND DISCUSSION

The structure is based upon strong hydrogen bonding between $\text{Sn}_2(\text{PO}_4)_2(\text{HPO}_4)_2$ units and the amine/water molecules. The asymmetric unit contains 25 nonhydrogen atoms (Fig. 1); atomic coordinates are given in Table 1. Trigonal pyramidal SnO_3 units are vertex linked via oxygens to phosphorus atoms, forming the $\text{Sn}_2(\text{PO}_4)_2(\text{HPO}_4)_2^{6-}$ units. Of the 12 oxygens in the asymmetric unit, 8 are bonded to Sn and/or P and the remaining 4 are found to be water molecules. Three oxygen atoms, O(1), O(2), and O(3), are coordinated to both a Sn and a P atom. Of the remaining 5 oxygens in the inorganic unit, 4 are found to be terminal P–O oxygens (O(4–7)), and the last oxygen, O(8), is protonated. The Sn–O distances are in the range 2.092–2.145 Å (avg. 2.116 Å) and the O–Sn–O bond angles are in the range 80.6 – 90.6° (avg. 86.5°), typical of three-coordinated Sn in the 2+ oxidation state and in agreement with other previously reported tin phosphate materials (8–12). The P–O distances are in the range 1.507–1.583 Å (avg. 1.535 Å) and the O–P–O angles in the range 102.5 – 114.1° (avg. 109.4°). The $\text{Sn}_2(\text{PO}_4)_2(\text{HPO}_4)_2^{6-}$ unit

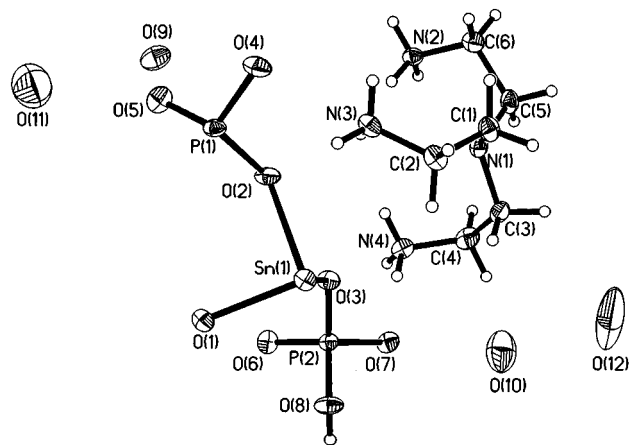


FIG. 1. Asymmetric unit of $[\text{Sn}(\text{PO}_4)(\text{HPO}_4)]^{3-}[\text{N}(\text{C}_2\text{H}_5\text{NH}_3)_3]^{3+} \cdot 4\text{H}_2\text{O}$ (thermal ellipsoids are given at 30% probability).

contains a four-ring, $\text{Sn}_2\text{P}_2\text{O}_4$ (Fig. 2a), that is a common structural feature of most of our tin (II) phosphate structures. We are currently exploring the possibility that this unit might be an intermediate in the formation of this family

TABLE 1
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for $[\text{Sn}(\text{PO}_4)(\text{HPO}_4)]^{3-}[\text{N}(\text{C}_2\text{H}_5\text{NH}_3)_3]^{3+} \cdot 4\text{H}_2\text{O}$

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> (eq) |
|-------|-----------|-----------|-----------|---------------|
| Sn(1) | 9082(1) | −1391(1) | −3326(1) | 26(1) |
| P(1) | 12444(2) | −1264(2) | −4595(2) | 24(1) |
| P(2) | 7611(2) | −3425(2) | −4013(2) | 23(1) |
| O(1) | 8582(5) | −285(4) | −5204(4) | 28(1) |
| O(2) | 11364(5) | −2190(4) | −4107(4) | 31(1) |
| O(3) | 8990(5) | −3222(4) | −3660(4) | 29(1) |
| O(4) | 13424(5) | −1538(5) | −3563(4) | 35(1) |
| O(5) | 13311(5) | −1526(5) | −5865(4) | 37(1) |
| O(6) | 7802(5) | −3325(5) | −5445(4) | 33(1) |
| O(7) | 7348(5) | −4773(5) | −3205(4) | 31(1) |
| O(8) | 6290(5) | −2132(5) | −3668(5) | 34(1) |
| O(9) | 14590(6) | −3719(6) | −7023(5) | 49(1) |
| O(10) | 6840(9) | −4569(8) | −621(6) | 83(2) |
| O(11) | 14540(13) | −2577(11) | −9680(10) | 137(4) |
| O(12) | 7107(16) | −7151(11) | 1063(9) | 178(6) |
| N(1) | 11528(6) | −7861(6) | −1512(5) | 30(1) |
| N(2) | 14069(6) | −9197(6) | −3196(5) | 30(1) |
| N(3) | 12241(6) | −5152(5) | −2933(5) | 32(1) |
| N(4) | 9459(6) | −7281(6) | −3483(5) | 34(1) |
| C(1) | 11778(8) | −6887(7) | −920(6) | 37(2) |
| C(2) | 11278(8) | −5370(7) | −1677(6) | 36(2) |
| C(4) | 9456(8) | −8292(8) | −2233(7) | 40(2) |
| C(3) | 9934(8) | −7848(7) | −1244(6) | 35(2) |
| C(5) | 12526(8) | −9291(7) | −1096(6) | 35(2) |
| C(6) | 14088(8) | −9473(7) | −1795(6) | 35(2) |

Note. $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

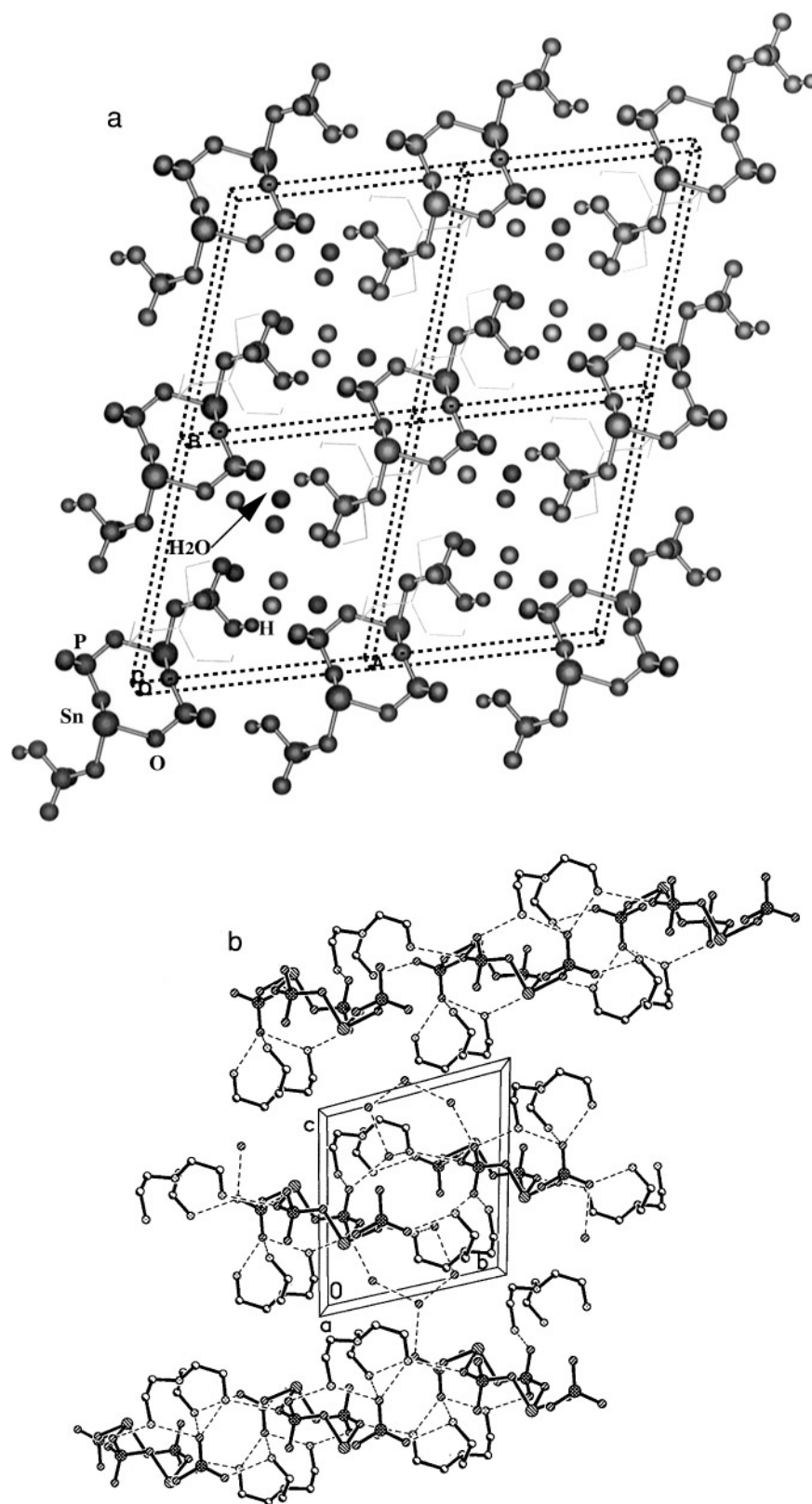


FIG. 2. (a) Structure of $[\text{Sn}(\text{PO}_4)(\text{HPO}_4)]^{3-} [\text{N}(\text{C}_2\text{H}_5\text{NH}_3)_3]^{3+} 4\text{H}_2\text{O}$ viewed along the c axis showing the tin phosphate monomer. (b) View of $[\text{Sn}(\text{PO}_4)(\text{HPO}_4)]^{3-} [\text{N}(\text{C}_2\text{H}_5\text{NH}_3)_3]^{3+} 4\text{H}_2\text{O}$ along the a axis showing some of the hydrogen bonding. The hydrogens on the amine molecule and the framework are not included.

of materials; a similar building block has been proposed in the AlPO_4 systems (3).

The amine employed in the present study, TREN, *tris*-amino(ethylamine), has three terminal nitrogens, all of which are protonated. The amine molecules are so arranged that they form three talons of a claw. The TREN cations interact through hydrogen bonding with the double-bonded oxygens as well as with the hydroxyl oxygen (Fig. 2b). Each amine molecule interacts with two inorganic units. Such an arrangement is quite unusual in inorganic systems, although a broadly similar type of behavior is seen in the 1,6-diaminohexane salt of a heteropolyoxometallate Keggin ion (16). Because of the position of the amine molecule and its interaction with the inorganic moiety, the entire structure has an inorganic–organic layer type of arrangement. The water molecules are found in the interlamellar space between these layers (Fig. 2b).

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