

BRIEF COMMUNICATION

Synthesis and Structural Characterization of a Layered Tin(II) Phosphate, $[\text{Sn}_2(\text{PO}_4)_2]^{2-} [\text{C}_2\text{N}_2\text{H}_{10}]^{2+} \cdot \text{H}_2\text{O}$

Srinivasan Natarajan^{1,2} and Anthony K. Cheetham

Materials Research Laboratory, University of California, Santa Barbara, California 93116
E-mail: raj@jncasr.ac.in

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A new layered tin(II) phosphate $[\text{Sn}_2(\text{PO}_4)_2]^{2-} [\text{C}_2\text{N}_2\text{H}_{10}]^{2+} \cdot \text{H}_2\text{O}$ was synthesized by hydrothermal technique. It crystallizes in monoclinic space group $P2_1/c$ (No. 14) with lattice parameters $a = 9.4112(1) \text{ \AA}$; $b = 8.5998(1) \text{ \AA}$; $c = 15.9921(2) \text{ \AA}$; $\beta = 100.009(1)^\circ$; $V = 1274.61(2)$; $Z = 4$; $R = 2.06\%$; $R_w = 2.17\%$. The structure consists of inorganic layers, comprising a network of strictly alternating SnO_3 and PO_4 moieties and held together by strong hydrogen bonding between the layers. Protonated ethylenediamine and water molecules are trapped between the layers. © 1998 Academic Press

INTRODUCTION

The synthesis of inorganic materials with novel structures and properties provides opportunities for the development of new preparative techniques. An example of this is found in the synthesis of new families of open-framework structures by using hydrothermal methods in the presence of organic structure directing molecules (templates). For example, this strategy was used to explore the aluminophosphate family $\text{AlPO}_4\text{-}n$ (1, 2), some members of which have interesting applications in acid catalysis (3–5). Recent examples of such syntheses include the aluminophosphate STA-1 (6) and a number of zinc and indium phosphates (7–10). We have recently shown that open-framework tin(II) phosphate materials can be synthesized successfully with the aid of an organic structure directing molecule (11–15). Of particular interest is the tin(II) phosphate material that was synthesized in the presence of ethylenediamine (11). By suitable modification of the synthesis conditions, we have now been

able to make another completely new tin phosphate using the same structure directing molecule, viz., ethylenediamine. In this case, however, it stabilizes a lameller rather than a three-dimensional network. Here, we report the synthesis and structure of this unique lameller architecture of tin phosphate. The compound is designated as *en*-SnPO-2 (*en* = ethylenediamine). All previous lameller tin(II) phosphates contain simple metal cations or water molecules between the layers (16–19).

EXPERIMENTAL

The title compound was synthesized starting from a tin phosphate gel containing ethylenediamine as the structure directing molecule. Tin(II) oxalate (Aldrich), phosphoric acid (85 wt%, Aldrich), ethylenediamine (*en*, Aldrich), and water in the ratio $\text{SnC}_2\text{O}_4 : 1.0\text{P}_2\text{O}_5 : 2.0\text{en} : 55\text{H}_2\text{O}$ were mixed and stirred until homogeneous. The mixture had a pH of 4–5 at this stage. The mixture was sealed in a PTFE lined stainless steel autoclave (Parr, USA) and heated at 150°C for 2 days under autogeneous pressure. The resulting product, containing a mixture of white powder and a few single crystals, was filtered off and washed thoroughly with deionized water. The single crystals were easily separated by ultrasonification and used for further structural characterization.

Determination of Crystal Structure

A suitable needle-like single crystal 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 ($\text{MoK}\alpha$ radiation) operating at 50 kV and 40 mA. A full sphere of intensity data was

¹Corresponding author.

²Present address: Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur (P.O.), Bangalore 560 064, India

collected in 2082 frames with ω scans (width of 0.30° and exposure time of 30 s per frame). The unit cell constants were determined by a least-squares fit of 7923 reflections in the range $10 < 2\theta < 56^\circ$. Pertinent experimental data are given in Table 1.

The structure was solved by direct methods using SHELXS-86 (20) and difference Fourier syntheses. The absorption correction was based on symmetry equivalent reflections using SADABS (21). Other effects such as absorption by the glass fiber were simultaneously corrected. All the hydrogen positions were located from difference Fourier maps. The last cycles of refinement included atomic positions for all atoms, anisotropic thermal parameters for all nonhydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares structure refinement against $|F|$ was carried out using the CRYSTALS (22) package of programs. The applied weighting scheme was based on Tukey and Prince with a three-term modified Chebyshev polynomial (23). The final Fourier map had a maximum and minimum of 0.56 and $-0.68 \text{ e } \text{\AA}^{-3}$, respectively. The final atomic coordinates, anisotropic thermal parameters, and selected bond distances and bond angles are given in Tables 2–5.

Description of the Structure

The asymmetric unit of the tin phosphate (*en*-SnPO-2) is given in Fig. 1. The structure is based on a network of

TABLE 1
Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for $[\text{Sn}_2(\text{PO}_4)_2]^{2-} \cdot [\text{C}_2\text{N}_2\text{H}_{10}]^{2+} \cdot \text{H}_2\text{O}$

Formula	$[\text{Sn}_2(\text{PO}_4)_2]^{2-} \cdot [\text{C}_2\text{N}_2\text{H}_{10}]^{2+} \cdot \text{H}_2\text{O}$
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
Crystal size (mm)	$0.05 \times 0.075 \times 0.125$
a (Å)	9.4112(1)
b (Å)	8.5998(1)
c (Å)	15.9921(2)
β (deg)	100.009(1)
Volume (Å ³)	1274.61(2)
Z	4
Formula mass	507.44(1)
ρ (g cm ⁻³)	2.64(1)
λ (MoK α) (Å)	0.71073
μ (mm ⁻¹)	42.18
Total no. of data collected	13,023
No. of unique data	3091
No. of observed data ($\sigma > 3\sigma(I)$)	2288
R_{merg}	3.38
R	2.06
R_w	2.17
Goodness of fit (S)	1.12
No. of variables	203

TABLE 2
Atomic Coordinates and Isotropic Displacement Parameters for the Nonhydrogen Atoms in $[\text{Sn}_2(\text{PO}_4)_2]^{2-} \cdot [\text{C}_2\text{N}_2\text{H}_{10}]^{2+} \cdot \text{H}_2\text{O}$

Atom	x/a	y/b	z/c	$U_{\text{eq}}/U_{\text{iso}}$
Sn(1)	0.80766(3)	0.18062(3)	0.22007(2)	0.0232
Sn(2)	0.69685(2)	0.70730(3)	0.24932(1)	0.0199
P(1)	1.03848(9)	0.4066(1)	0.15168(6)	0.0185
P(2)	0.58766(9)	0.3927(1)	0.32153(6)	0.0200
O(1)	0.9828(3)	0.3372(4)	0.2288(2)	0.0315
O(2)	0.9296(3)	0.0802(3)	0.3309(2)	0.0309
O(3)	0.7320(3)	0.3294(4)	0.3030(2)	0.0382
O(4)	0.6098(3)	0.5690(3)	0.3372(2)	0.0273
O(5)	1.1833(3)	0.3252(3)	0.1453(2)	0.0262
O(6)	0.4691(3)	0.3694(3)	0.2425(2)	0.0306
O(7)	0.5493(3)	0.3134(3)	0.3986(2)	0.0313
O(8)	0.9342(3)	0.3835(3)	0.0700(2)	0.0287
O(100)	0.6650(4)	0.8349(6)	0.0068(3)	0.0467
N(1)	0.9608(4)	0.8060(4)	0.0458(2)	0.0302
N(10)	1.3216(4)	0.5473(5)	0.0319(2)	0.0293
C(1)	1.0301(5)	0.9608(5)	0.0413(3)	0.0332
C(10)	1.4273(4)	0.5220(5)	$-0.0255(3)$	0.0274

strictly alternating SnO_3 and PO_4 moieties, creating layers in which the vertices are shared. The pyramidal SnO_3 and tetrahedral PO_4 groups form a framework with the formula $[\text{Sn}_2(\text{PO}_4)_2]^{2-}$. Charge neutrality is achieved by the incorporation of the organic in its diprotonated form: there are two different ethylenediamine molecules, lying on independent symmetry centers, each contributing $0.5[\text{H}_3\text{en}]^{2+}$ ions per framework formula unit (*en* = ethylenediamine). The compound also has one water molecule present between the layers.

TABLE 3
Anisotropic Thermal Parameters for $[\text{Sn}_2(\text{PO}_4)_2]^{2-} \cdot [\text{C}_2\text{N}_2\text{H}_{10}]^{2+} \cdot \text{H}_2\text{O}$

Atom	$U(11)$	$U(22)$	$U(33)$	$U(23)$	$U(13)$	$U(12)$
Sn(1)	0.0233(1)	0.0251(1)	0.0221(1)	$-0.00155(9)$	0.00524(9)	$-0.00196(9)$
Sn(2)	0.0199(1)	0.0220(1)	0.0180(1)	$-0.00256(9)$	0.00223(8)	$-0.00071(9)$
P(1)	0.0174(4)	0.0164(4)	0.0220(4)	0.0008(3)	0.0027(3)	0.0001(3)
P(2)	0.0195(4)	0.0167(4)	0.0255(4)	$-0.0018(3)$	0.0055(3)	$-0.0014(3)$
O(1)	0.031(1)	0.044(2)	0.031(2)	0.005(1)	0.013(1)	$-0.009(1)$
O(2)	0.053(2)	0.018(1)	0.031(2)	0.000(1)	$-0.002(1)$	0.003(1)
O(3)	0.030(1)	0.044(2)	0.064(2)	$-0.019(2)$	0.016(1)	0.006(1)
O(4)	0.038(1)	0.019(1)	0.031(1)	$-0.003(1)$	0.009(1)	$-0.004(1)$
O(5)	0.023(1)	0.038(1)	0.025(1)	0.007(1)	0.004(1)	0.013(1)
O(6)	0.039(2)	0.033(1)	0.025(1)	$-0.000(1)$	$-0.001(1)$	$-0.014(1)$
O(7)	0.034(1)	0.033(1)	0.031(1)	0.011(1)	0.005(1)	0.000(1)
O(8)	0.024(1)	0.033(1)	0.030(1)	$-0.004(1)$	$-0.005(1)$	0.002(1)
O(100)	0.037(2)	0.097(3)	0.045(2)	0.035(2)	0.015(2)	0.014(2)
N(1)	0.036(2)	0.028(2)	0.027(2)	0.005(1)	0.001(1)	0.004(1)
N(10)	0.021(2)	0.034(2)	0.035(2)	$-0.004(2)$	0.000(1)	0.001(1)
C(1)	0.045(3)	0.028(2)	0.030(2)	0.002(2)	$-0.005(2)$	$-0.006(2)$
C(10)	0.023(2)	0.033(2)	0.029(2)	$-0.006(2)$	$-0.002(2)$	0.006(2)

TABLE 4
Selected Interatomic Distances for
[Sn₂(PO₄)₂]²⁻ [C₂N₂H₁₀]²⁺ · H₂O

Moiety	Distance (Å)
Sn(1)–O(1)	2.115(3)
Sn(1)–O(2)	2.120(3)
Sn(1)–O(3)	2.057(3)
Sn(2)–O(4)	2.112(3)
Sn(2)–O(5)	2.117(2)
Sn(2)–O(6)	2.114(3)
P(1)–O(1)	1.541(3)
P(1)–O(2)	1.539(3)
P(1)–O(5)	1.551(3)
P(1)–O(8)	1.505(3)
P(2)–O(3)	1.539(3)
P(2)–O(4)	1.545(3)
P(2)–O(6)	1.546(3)
P(2)–O(7)	1.506(3)
N(1)–C(1)	1.490(5)
C(1)–C(1)	1.504(8)
N(10)–C(10)	1.482(5)
C(10)–C(10)	1.513(7)

The framework consists of macroanionic sheets formed by the networking of SnO₃ and PO₄ groups creating rings bound by six *T* atoms (*T* = Sn and P) (Fig. 2). There are two crystallographically independent Sn atoms in the asymmetric unit and two independent P atoms. All the Sn atoms are coordinated by three oxygen atoms, with Sn–O contacts

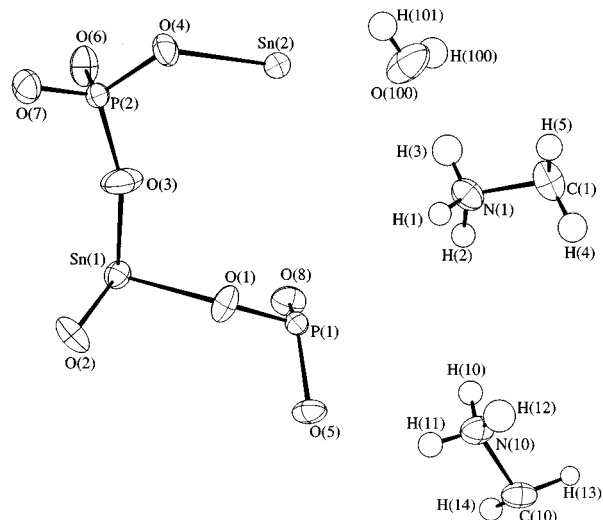


FIG. 1. Asymmetric unit of *en*-SnPO-2. Thermal ellipsoids are shown at 30% probability.

varying between 2.057 and 2.120 Å (ave. 2.097 Å for Sn(1) and 2.114 Å for Sn(2)) and the O–Sn–O bond angles lying between 84.4 and 87.4° (ave. 84.8° for Sn(1) and 87° for Sn(2)). These values are in excellent agreement with other tin(II) phosphates previously reported (11–19). The three oxygen atoms form a trigonal pyramid around the Sn with the lone pair of electrons on the Sn(II) atoms presumably occupying the base vertex of a tetrahedron. As with the other previously known layered tin(II) phosphates (16–19),

TABLE 5
Selected Bond Angles for [Sn₂(PO₄)₂]²⁻ [C₂N₂H₁₀]²⁺ · H₂O

Moiety	Angle (deg)
O(1)–Sn(1)–O(2)	84.4(1)
O(1)–Sn(1)–O(3)	85.1(1)
O(2)–Sn(1)–O(3)	85.0(1)
O(4)–Sn(2)–O(5)	87.4(1)
O(5)–Sn(2)–O(6)	87.4(1)
O(5)–Sn(2)–O(6)	86.1(1)
O(1)–P(1)–O(2)	108.2(2)
O(1)–P(1)–O(5)	107.7(2)
O(2)–P(1)–O(5)	107.7(2)
O(1)–P(1)–O(8)	112.5(2)
O(2)–P(1)–O(8)	111.3(2)
O(5)–P(1)–O(8)	109.3(2)
O(3)–P(2)–O(4)	106.3(2)
O(3)–P(2)–O(6)	109.4(2)
O(4)–P(2)–O(6)	108.5(2)
O(3)–P(2)–O(7)	110.0(2)
O(4)–P(2)–O(7)	110.9(2)
O(6)–P(2)–O(7)	111.6(2)
N(1)–C(1)–C(1)	110.0(4)
N(10)–C(10)–C(10)	110.2(4)

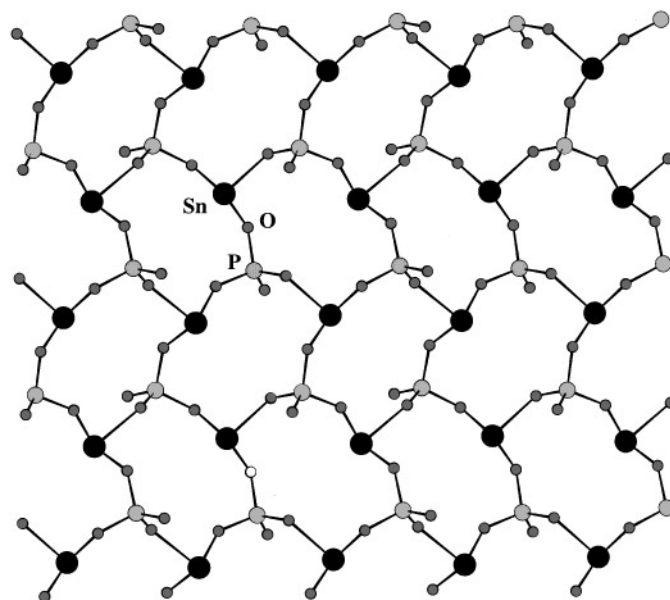


FIG. 2. Figure showing the plane view (along *c* axis) of a single layer with the 6-membered rings and connectivity between SnO₃ and PO₄ groups.

the lone pair of electrons associated with the Sn(II) in this material points perpendicular to the plane of the layers.

In the case of phosphorus, the P atom is tetrahedrally coordinated to four oxygen atoms. Of the four oxygen atoms, three of the coordinating oxygen atoms are bonded to Sn atoms and have P–O bond lengths ranging from 1.539–1.551 Å. The remaining P–O contacts (i.e., P(1)–O(8) and P(2)–O(7) of lengths of 1.505 and 1.506 Å) are formally P=O double bonds. Terminal P=O groups in, for example, $\text{H}_3\text{PO}_4 \cdot 0.5\text{H}_2\text{O}$ are 1.485 and 1.495 Å long (24). The double bond nature of the P=O bond is also reflected in the bond angles: all the O–P–O bond angles (106.3–109.4°) are less than the O–P=O angles (110–112.5°). These values are in excellent agreement to other P–O distances and angles found in many of the alumino- and gallophosphates reported in the literature (1, 25–27).

Multipoint hydrogen bonding plays an important role in linking the template and water molecules with the anionic sheets made by SnO_3 and PO_4 moieties. Important hydrogen bond distances and angles are given in Table 6. There are two crystallographically distinct protonated ethylenediamine molecules, and each one independently participates in hydrogen bonding with the inorganic layers along the *a* and *b* axes (Fig. 3a and b). The strongest hydrogen bond-

Moiety	Distance (Å)	Moiety	Angle (deg)
O(2)–H(1)	1.99(5)	O(2)–H(1)–N(1)	158(4)
O(3)–H(4)	2.80(6)	O(3)–H(4)–C(1)	157(3)
O(3)–H(12)	2.95(7)	O(3)–H(12)–N(10)	144(5)
O(4)–H(100)	2.01(7)	O(4)–H(100)–O(100)	170(6)
O(5)–H(11)	2.27(6)	O(5)–H(11)–N(10)	149(4)
O(7)–H(101)	1.92(7)	O(7)–H(101)–O(100)	165(6)
O(7)–H(12)	1.95(8)	O(7)–H(12)–N(10)	152(6)
O(8)–H(2)	1.82(6)	O(8)–H(2)–N(1)	171(4)
O(8)–H(10)	1.84(6)	O(8)–H(10)–N(10)	173(5)
O(100)–H(3) ^a	1.86(7)	O(100)–H(3)–N(1)	173(5)
O(100)–H(14) ^a	2.62(5)	O(100)–H(14)–C(10)	122(3)
O(100)–H(11) ^a	2.82(6)	O(100)–H(11)–N(10)	120(4)

^aIntralayer.

ing is between the oxygens O(2), O(7), and O(8) and the hydrogens of the amine molecules: O(2)–H(1) = 1.99 Å, O(2)–H(1)–N(1) = 158°; O(7)–H(12) = 1.95 Å, O(7)–H(12)–N(10) = 152°; O(8)–H(2) = 1.82 Å, O(8)–H(2)–N(1) = 171°; O(8)–H(10) = 1.84 Å, O(8)–H(10)–N(10) = 173°. The water

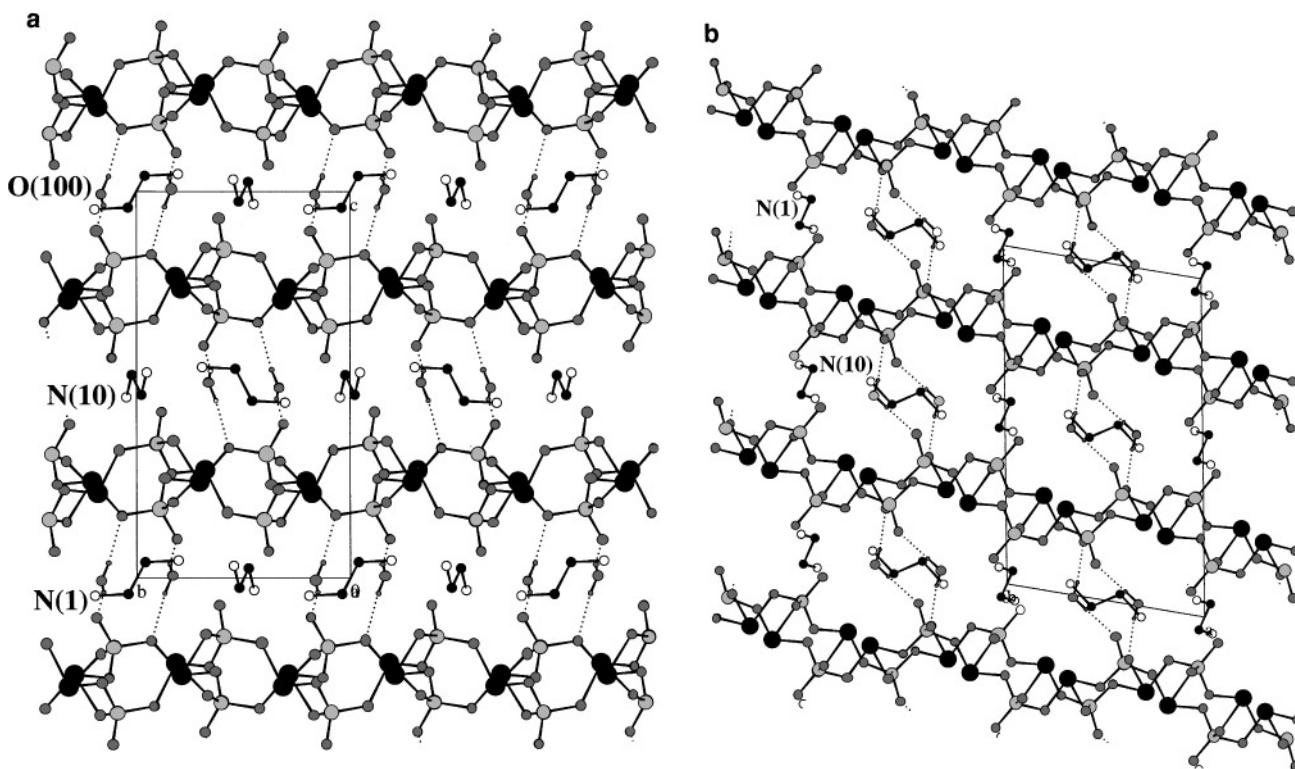


FIG. 3. (a) Structure of *en*-SnPO-2 viewed down the *a* axis showing the hydrogen bonding between the water molecule and the layers [small black circles = C; small open circles = N; small partially filled circles = O(water)]. The hydrogens on the amine molecules are not shown for clarity. N(1) and N(10) are the nitrogens from two crystallographically different amine molecules. (b) Structure of *en*-SnPO-2 viewed down the *b* axis [small black circles = C; small open circles = N; small partially filled circles = O(water)]. The hydrogens on the amine molecules are not shown for clarity.

molecules present in the organic layer also participate in hydrogen bonding as seen in Fig. 3a and b. The strongest interactions are between O(4) and O(7) with the hydrogen of the water molecules: O(4)–H(100) = 2.01 Å, O(4)–H(100)–O(100) = 170°; O(7)–H(101) = 1.92 Å, O(7)–H(101)–O(100) = 165°. There also exists strong intralayer hydrogen bonding between the ethylenediamine and the water molecule (Table 6).

The structure of *en*-SnPO-2 has features similar to other previously known layered phosphates; aluminum phosphates, antimony phosphates, and zirconium phosphates. Of particular interest is the similarity to the layered aluminum phosphates reported by Chippindale *et al.* (25) and the phosphoantimonates reported by Piffard *et al.* (28–30). In the case of the former, the macroanionic sheets (made of AlO₄ and PO₄ moieties) are held together by strong hydrogen bond interactions involving the double bonded oxygens of the phosphate groups and the organic template molecules. In the case of the later, the layers are made up of corner sharing PO₄ tetrahedra and SbO₆ octahedra. The interlamellar space is occupied by Na⁺ or K⁺ ions which are easily replaced by protons (H⁺) by washing with dilute acids. The interlamellar space is also filled with H₂O molecules during the proton exchange. Similar structural features are also seen in the so called α -ZrP (α -Zr(HPO₄)₂ · H₂O) structure (31). The present structure has many of the interesting structural features common to the aforementioned layered phosphate structures, but the presence of interlayer water molecule along with the organic amine and the strong intra- and interlayer hydrogen bonding (see Fig. 3a and b; Table 6) yields a unique architecture for this novel material.

CONCLUSIONS

The synthesis and structural characterization of a novel layered tin phosphate consisting of alternating inorganic–organic layers has been accomplished. The present solid, together with the previously reported Sn(II) phosphate (11), illustrates the profound effects which slight changes in compositions and ambient conditions may have on the solid product. The present solid represents another example illustrating the importance of multipoint hydrogen bonding in the synthesis and stability of open-framework materials. Our continuing research on tin phosphates indicates that a large number of related structures are formed under hydrothermal conditions using other structure directing agents, and it is becoming apparent that the system, like the aluminophosphates, can form chain, layered, and three-dimensional open-framework architectures.

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