

Synthesis and Structure of a New Open-Framework Tin(II) Phosphate, $[\text{NH}_3\text{CH}_2\text{CH}(\text{NH}_3)\text{CH}_3]_{0.5}[\text{Sn}_4\text{P}_3\text{O}_{12}] \cdot \text{H}_2\text{O}$, Possessing One-Dimensional Channels¹

Srinivasan Natarajan²

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, P.O. Box 6436, Bangalore 560 064, India

Received February 5, 1999; in revised form April 10, 1999; accepted April 21, 1999

A new tin(II) phosphate, $[\text{NH}_3\text{CH}_2\text{CH}(\text{NH}_3)\text{CH}_3]_{0.5}[\text{Sn}_4\text{P}_3\text{O}_{12}] \cdot \text{H}_2\text{O}$, was synthesized by hydrothermal technique. It crystallizes in monoclinic space group $P2_1/c$ (No. 14) with lattice parameters $a = 7.326(1) \text{ \AA}$, $b = 23.614(3) \text{ \AA}$, $c = 9.081(1) \text{ \AA}$, $\beta = 102.8(1)^\circ$, $V = 1532.1(1) \text{ \AA}^3$, $Z = 3$, $R = 4.3\%$. The structure consists of one-dimensional channels, constituting a network of strictly alternating SnO_3 and PO_4 moieties connected through vertices. The structure-directing amine molecule 1,2-diaminopropane occupies the channels along with water molecules.

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Key Words: hydrothermal methods; open-framework materials; tin(II) phosphates.

INTRODUCTION

Research in the area of solid-state chemistry has undergone a lot of changes in the last two decades, with subtle approaches taking over techniques that employ harsh conditions for the synthesis of solids (1). The design and synthesis of framework materials having micro- and mesoporosity are a challenge to the synthetic chemist, as such materials are being used in the areas of catalysis, sorption, and separation processes (2, 3). The synthesis and characterization of a large number of metal phosphates of different structures have been carried out in the last decade or so by employing hydro/solvo-thermal conditions in the presence of structure-directing organic amines (templates) (4, 5). It is established that open-framework tin(II) phosphate compounds can be synthesized with the aid of organic structure-directing amines (6–9). The chemistry of bivalent tin and its related compounds, especially the phosphates, continues to yield unexpected results with the isolation of materials having one $[\text{C}_6\text{N}_2\text{H}_{18}]^{2+} 2[\text{SnPO}_4]^-$ (ladderlike chains) (6),

two $[\text{C}_2\text{N}_2\text{H}_{10}]^{2+} [\text{Sn}_2(\text{PO}_4)_2]^{2-} \cdot \text{H}_2\text{O}$ (7) (layers, intercalated with amine), and three $0.5[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3]^{2+} [\text{Sn}_4\text{P}_3\text{O}_{12}]^-$ (8a), $0.5[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]^{2+} [\text{Sn}_4\text{P}_3\text{O}_{12}]^-$ (8b), $0.5[\text{H}_3\text{NCH}_2\text{CH}_2\text{CH}(\text{NH}_3)\text{CH}_2\text{CH}_3]^{2+} [\text{Sn}_4\text{P}_3\text{O}_{12}]^-$ (8c) dimensionally extended networks. The basic structural building block, present in all these materials, a four-membered ring made of $[\text{Sn}_2\text{P}_2\text{O}_4]$ units, has also been isolated and characterized (9). The tin(II) phosphates are, in general, made from networking between the three-coordinated trigonal-pyramidal SnO_3 , the four-coordinated distorted square-pyramidal SnO_4 , and the tetrahedral PO_4 moieties. In this paper, the structure of a new tin(II) phosphate material, possessing eight-membered one-dimensional channels, synthesized hydrothermally in the presence of 1,2-diaminopropane as the structure-directing agent is presented.

EXPERIMENTAL

The title compound was synthesized starting from a mixture containing 1,2-diaminopropane (DAP, Aldrich) as the structure-directing agent. Tin(II) oxalate (Aldrich), phosphoric acid (85 wt%, Aldrich), DAP, and water in the ratio $1.0\text{SnC}_2\text{O}_4 : 1.0\text{H}_3\text{PO}_4 : 1.0\text{DAP} : 55\text{H}_2\text{O}$ were stirred to attain homogeneity and then sealed in 23-ml PTFE-lined stainless-steel autoclaves (Parr, USA). The fill factor was about 50% and the pH of the mixture was 5.5. The sealed pressure bombs were heated at 175°C for 48 h under autogeneous pressure. At the end of the reaction, the pH was found to be ~ 4 . The evolution of the acidity in the reaction mixture indicates that some of the amine molecules were consumed during the reaction. The resulting products contained some colorless crystals admixed with white powder. The products were filtered and washed thoroughly with deionized water. The single crystals were easily separated by sonification under water in an ultrasonic bath. The total yield of the product (single crystals) is $\sim 40\%$. A portion of the single crystals were powdered and characterized using

¹ Dedicated to Professor C. N. R. Rao on his 65th Birthday.² To whom correspondence should be addressed. E-mail: raj@jncasr.ac.in. Fax: +91-80-846-2766.

powder X-ray diffraction (XRD). The XRD pattern recorded was found to be complex and indicated a mixture of phases. Careful analysis under a polarized microscope revealed that the product is a mixture of needles and rodlike crystals, with the rodlike crystals dominating the mixture. The yield of the needles is about 10% of the total mixture of the single crystals obtained after the sonification process, indicating that it is a minority product of the reaction. A variation of the synthesis conditions facilitated synthesis of the rodlike crystals in pure form; the structural details are discussed elsewhere (10). Efforts to synthesize the title compound in pure form, however, were not successful.

A suitable colorless needlelike single crystal of the title compound was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (superglue) adhesive. 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 were collected at room temperature in 1321 frames with ω scans (width of 0.03° and exposure time of 20 s per frame). Pertinent experimental details for the structure determination are presented in Table 1.

TABLE 1
Crystal Data and Structure Refinement Parameters for
[NH₃CH₂CH(NH₃)CH₃]_{0.5}[Sn₄P₃O₁₂] \cdot H₂O

Empirical formula	C ₃ N ₂ H ₁₆ O ₂₆ Sn ₈ P ₆
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
Crystal size	0.06 \times 0.08 \times 0.16 mm
<i>a</i>	7.326(1) Å
<i>b</i>	23.614(3) Å
<i>c</i>	9.081(1) Å
α	90.0°
β	102.8(1)°
γ	90.0°
Volume	1532.1(1) Å ³
<i>Z</i>	2
Formula mass	1631.8
ρ_{calc}	2.76 g cm ⁻³
λ (MoK α)	0.71073 Å
μ	5.13 mm ⁻¹
θ range	1.72°–23.23°
Total data collected	6228
Index ranges	– 8 $\leq h \leq$ 8, – 22 $\leq k \leq$ 26, – 8 $\leq l \leq$ 10
Unique data	2184
Observed data [$\sigma > 2\sigma(I)$]	1764
Refinement method	Full-matrix least-squares on $ F^2 $
R_{merg}	0.09
<i>R</i> indexes [$I > 2\sigma(I)$]	$R_1 = 0.04$, $wR_2 = 0.10$
<i>R</i> indexes (all data)	$R_1 = 0.05$, $wR_2 = 0.10$
Goodness of fit (<i>S</i>)	0.977
No. of variables	214
Largest difference map peak and hole	1.57 and – 1.28 e Å ³

TABLE 2
Atomic Coordination ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for [NH₃CH₂CH(NH₃)CH₃]_{0.5}[Sn₄P₃O₁₂] \cdot H₂O

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Sn(1)	1266(1)	3312(1)	7232(1)	18(1)
Sn(2)	– 2658(1)	792(1)	5490(1)	18(1)
Sn(3)	2769(1)	1460(1)	7463(1)	17(1)
Sn(4)	7079(1)	2629(1)	8825(1)	18(1)
P(1)	– 2646(4)	– 636(1)	5363(3)	15(1)
P(2)	3988(4)	2533(1)	5657(3)	14(1)
P(3)	– 971(4)	1367(1)	8826(3)	15(1)
O(1)	– 2889(10)	– 988(3)	6761(9)	26(2)
O(2)	3476(10)	3126(3)	6151(9)	21(2)
O(3)	363(9)	1129(3)	10242(8)	20(2)
O(4)	– 1845(9)	– 57(3)	5959(8)	20(2)
O(5)	– 2032(10)	870(3)	7918(9)	23(2)
O(6)	– 5439(9)	560(3)	5732(8)	21(2)
O(7)	78(10)	1696(3)	7805(9)	22(2)
O(8)	2471(10)	2108(3)	5833(9)	22(2)
O(9)	1340(10)	938(3)	5489(9)	21(2)
O(10)	– 2347(10)	1770(3)	9347(9)	23(2)
O(11)	5938(10)	2352(3)	6566(8)	21(2)
O(12)	4190(10)	2549(3)	4016(8)	20(2)
O(100)	– 3627(31)	1136(9)	11470(28)	187(9)
N(1) ^b	– 1849(18)	125(7)	11990(27)	104(8)
C(1) ^b	– 3401(47)	– 69(14)	10647(16)	286(38)
C(2) ^b	– 3214(47)	– 136(9)	9028(27)	133(16)
C(3) ^b	– 4465(35)	– 267(18)	9071(25)	161(17)

^a *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

^b Disordered atoms with a site occupancy factor (SOF) of 0.5.

The structure was solved by direct methods using SHELXS-86 (11) and difference Fourier syntheses. An absorption correction based on symmetry equivalent reflections was applied using the SADABS (12) program. Other effects, such as absorption by the glass fiber, were simultaneously corrected. The structure-directing amine molecule is heavily disordered, making the unequivocal identification difficult from the Fourier map. The last cycles of refinement included atomic positions and anisotropic thermal parameters for all the framework atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS (13) package of programs. Final *R* values for all the data— $R = 0.04$, $R_w = 0.10$, and $S = 0.98$ —were obtained for a total 214 parameters. The final atomic coordinates and bond distances and angles for the framework are given in Tables 2 and 3.

RESULTS AND DISCUSSION

The structure is based on a network of strictly alternating trigonal-pyramidal SnO₃ and tetrahedral PO₄ units in which all the vertices are shared. The SnO₃ and PO₄ units

TABLE 3
Selected Bond Distances and Angles for $[\text{NH}_3\text{CH}_2\text{CH}(\text{NH}_3)\text{CH}_3]_{0.5}[\text{Sn}_4\text{P}_3\text{O}_{12}] \cdot \text{H}_2\text{O}$

Moiety	Distance (Å)	Moiety	Distance (Å)
Sn(1)–O(1) ^a	2.122(7)	P(1)–O(1)	1.559(8)
Sn(1)–O(2)	2.115(7)	P(1)–O(4)	1.540(8)
Sn(1)–O(3) ^b	2.216(8)	P(1)–O(6) ^f	1.541(7)
Sn(2)–O(4)	2.107(7)	P(1)–O(9) ^e	1.532(8)
Sn(2)–O(5)	2.158(8)	P(2)–O(2)	1.542(7)
Sn(2)–O(6)	2.167(7)	P(2)–O(8)	1.531(8)
Sn(3)–O(7)	2.137(7)	P(2)–O(11)	1.544(7)
Sn(3)–O(8)	2.107(8)	P(2)–O(12)	1.530(8)
Sn(3)–O(9)	2.237(8)	P(3)–O(3)	1.539(7)
Sn(4)–O(10) ^c	2.105(8)	P(3)–O(5)	1.543(8)
Sn(4)–O(11)	2.139(8)	P(3)–O(7)	1.538(8)
Sn(4)–O(12) ^d	2.202(8)	P(3)–O(10)	1.534(8)
Moiety	Angle (°)	Moiety	Angle (°)
O(1) ^a –Sn(1)–O(2)	87.1(3)	O(9) ^e –P(1)–O(1)	111.1(4)
O(1) ^a –Sn(1)–O(3) ^b	85.8(3)	O(4)–P(1)–O(1)	106.9(5)
O(2)–Sn(1)–O(3) ^b	82.4(3)	O(6) ^f –P(1)–O(1)	109.6(4)
O(4)–Sn(2)–O(5)	83.5(3)	O(8)–P(2)–O(12)	110.2(4)
O(4)–Sn(2)–O(6)	88.2(3)	O(8)–P(2)–O(11)	111.7(4)
O(5)–Sn(2)–O(6)	84.9(3)	O(12)–P(2)–O(11)	104.5(4)
O(7)–Sn(3)–O(8)	87.6(3)	O(8)–P(2)–O(2)	109.6(5)
O(7)–Sn(3)–O(9)	88.7(3)	O(12)–P(2)–O(2)	110.1(4)
O(8)–Sn(3)–O(9)	83.1(3)	O(11)–P(2)–O(2)	110.6(5)
O(10) ^c –Sn(4)–O(11)	86.5(3)	O(3)–P(3)–O(10)	107.9(4)
O(10) ^c –Sn(4)–O(12) ^d	86.9(3)	O(3)–P(3)–O(7)	112.2(4)
O(11)–Sn(4)–O(12) ^d	80.7(3)	O(10)–P(3)–O(7)	108.9(4)
O(9) ^e –P(1)–O(4)	111.0(4)	O(3)–P(3)–O(5)	108.7(5)
O(9) ^e –P(1)–O(6) ^f	108.0(4)	O(10)–P(3)–O(5)	110.4(4)
O(4)–P(1)–O(6) ^f	110.2(4)	O(7)–P(3)–O(5)	108.8(4)

^a $-x, y + \frac{1}{2}, -z + \frac{3}{2}$.

^b $x, -y + \frac{1}{2}, z - \frac{1}{2}$.

^c $x + 1, y, z$.

^d $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

^e $-x, -y, -z + 1$.

^f $-x - 1, -y, -z + 1$.

form a framework with the formula $[\text{Sn}_4\text{P}_3\text{O}_{12}]^-$. Charge neutrality is achieved by the incorporation of the template in its diprotonated form: there is $0.5[\text{H}_3\text{NCH}_2\text{CH}(\text{NH}_3)\text{CH}_3]^{2+}$ ion per framework formula unit. The solid also contains one molecule of water. The asymmetric unit contains 19 framework nonhydrogen atoms (Fig. 1). The three phosphate groups are linked via oxygens to four tin atoms to form the building block of the framework. All the P–O distances are in the range 1.532–1.559 Å (ave. 1.539 Å) and the bond angles are in the range 104.5°–112.2° (ave. 109.5°) (Table 3), which is in good agreement with those previously observed (6–9). All the Sn atoms are three-coordinated with respect to oxygen with Sn–O distances in the range 2.107–2.237 Å (ave. 2.151 Å) and the O–Sn–O bond angles are in the range 80.7°–88.7° (ave. 85.5°) (Table 3). These values are typical of three-coordinated Sn in the 2+ oxidation state

and are in excellent agreement with values for other previously known tin phosphates in the literature (6–9, 14–16). The three oxygen atoms form a trigonal pyramid around the Sn, with the lone pair of electrons on the Sn atoms presumably occupying the base vertex of a tetrahedron. The bond valence sum calculations carried out on the framework indicate that the individual bond valences of Sn, P, and O are 2+, 5+, and 2–, respectively (17).

The entire framework structure can be considered to be built from the networking of four-, six-, and eight-membered rings. The four- and six (slightly distorted)-membered rings are so connected as to form one-dimensional eight-membered channels along the *a* axis (Fig. 2). The width of this channel is 9.52×5.38 Å (longest and shortest atom–atom distances not including the van der Waals radii). The size of the channels observed in the present material is comparable to those seen in aluminosilicate zeolites and certain detemplated microporous AIPOs (aluminophosphates) (2). Along the *c* axis, the six-membered rings are connected to each other in a zig-zag fashion via four-membered windows forming a chainlike arrangement. Two such zig-zag chains are connected via four-membered rings forming an eight-membered ring (Fig. 3). The 1,2-diaminopropane used as the template in the synthesis is disordered and occupies spaces in the middle of the channels along with the water molecule. The type of disorder observed in the present solid is complicated as all the atoms of the amine molecule are disordered. Though it is known that structure-directing amines may be disordered in framework solids (18) this is probably one of the rare occurrences where all the atoms are disordered, making the unequivocal identification of the molecule difficult. A representation of a possible fit of the disorder in the amine molecule is presented in Fig. 4.

Thermogravimetric analysis (TGA) was carried out in the range 30–600°C on hand-picked single crystals (needlelike) in static air. The results indicate two distinct steps. The first mass loss of about 2.6% in the region 150–180°C corresponds to the loss of water present in the channels (calc. 2.2%) and the second mass loss of 4.5% in the region 350–400°C corresponds to the loss of the amine molecules (calc. 4.7%). The decomposed sample was poorly crystalline as found by powder X-ray diffraction, with the XRD 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 > 4 : 3 is also present.

The “openness” of a structure is defined in terms of the tetrahedral atom density (2), (framework density, FD) defined as the number of tetrahedral atoms per 1000 Å³. In the present material the number of T atoms per 1000 Å³ (here Sn and P) is 13.7 [tin(II), though, is three coordinated, along with the lone pair of electrons may be considered as a tetrahedral atom]. These values are in the middle-range FD values observed in aluminosilicate zeolites (2) where the presence of channels is common. Furthermore, the position

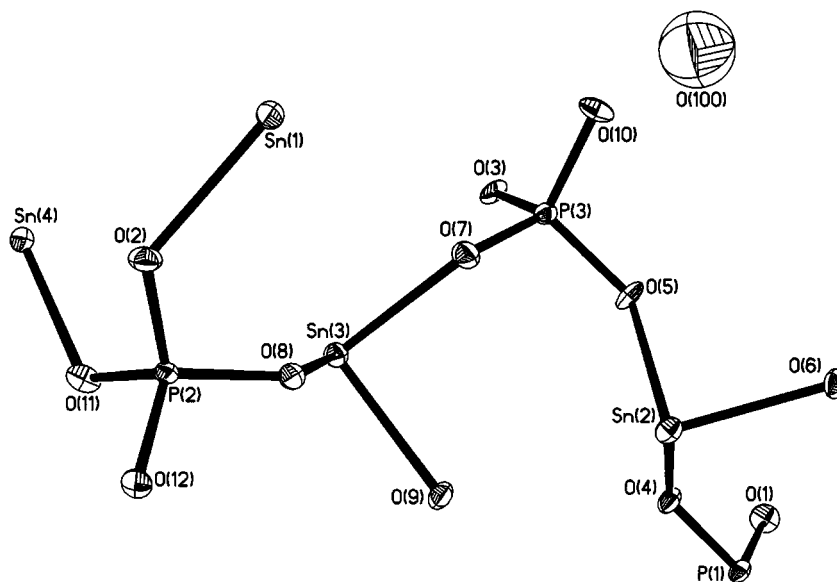


FIG. 1. Local coordination of the framework atoms of $[\text{NH}_3\text{CH}_2\text{CH}(\text{NH}_3)\text{CH}_3]_{0.5}[\text{Sn}_4\text{P}_3\text{O}_{12}] \cdot \text{H}_2\text{O}$ showing the atom labeling scheme. Thermal ellipsoids are given at 30% probability.

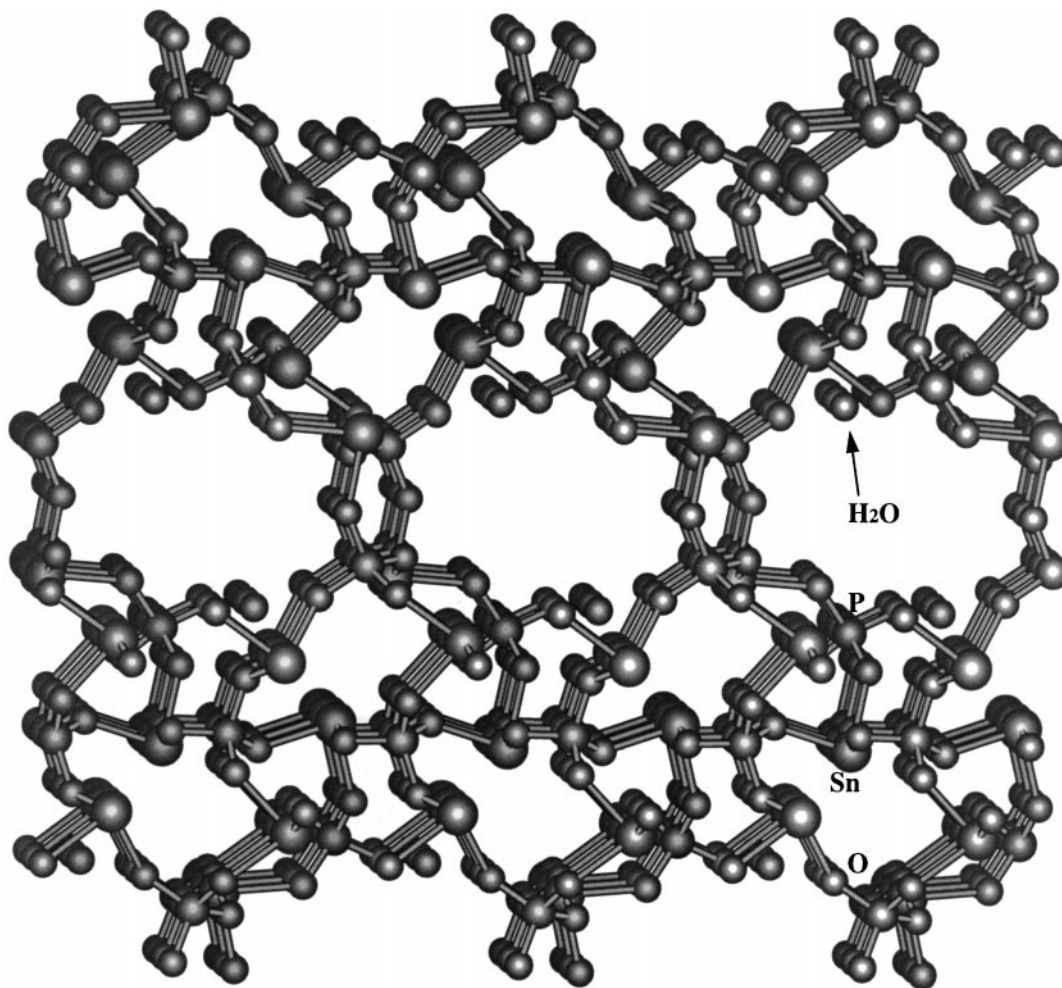


FIG. 2. Structure of $[\text{NH}_3\text{CH}_2\text{CH}(\text{NH}_3)\text{CH}_3]_{0.5}[\text{Sn}_4\text{P}_3\text{O}_{12}] \cdot \text{H}_2\text{O}$ along the a axis showing the one-dimensional star-shaped channel.

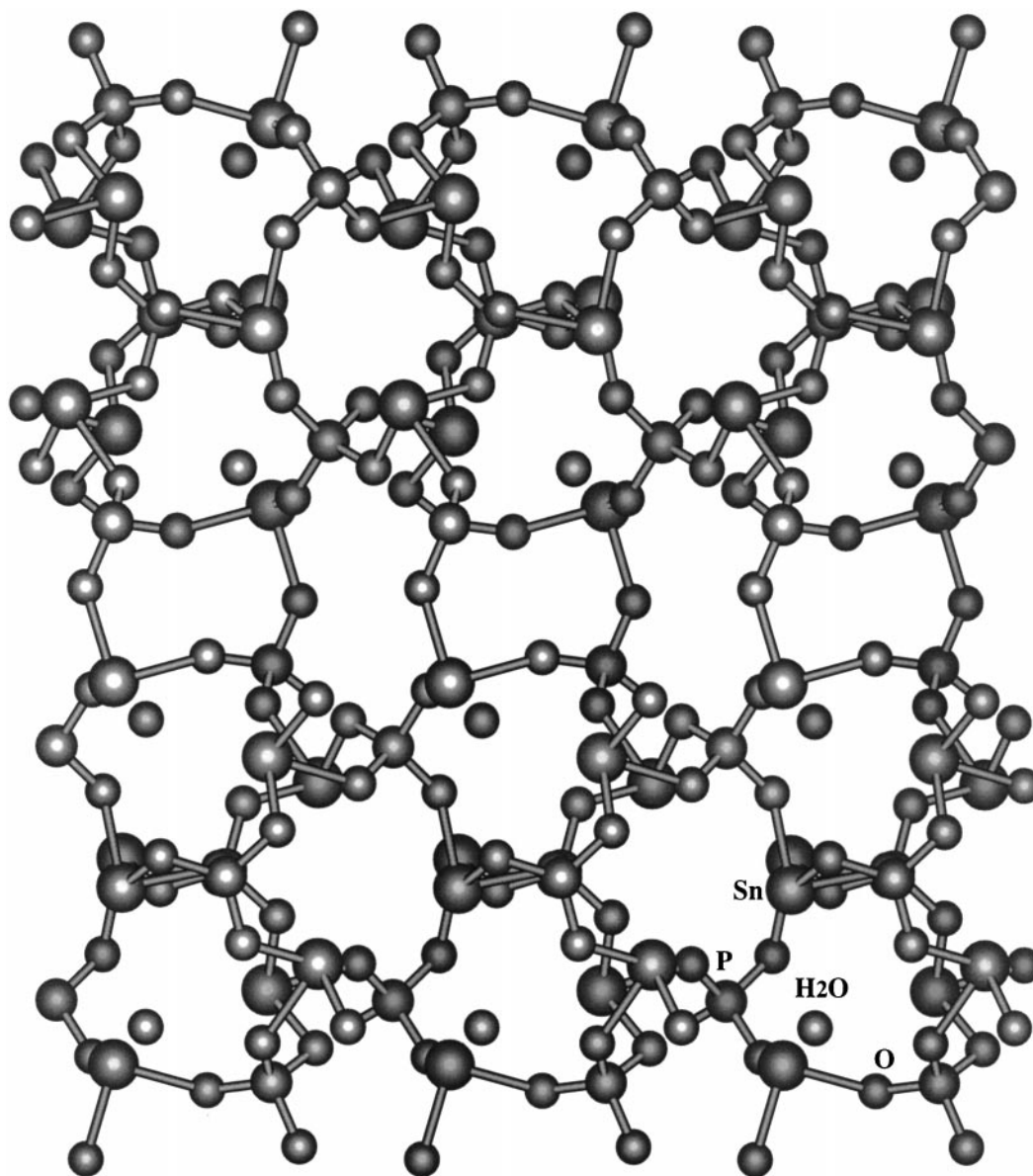


FIG. 3. Structure of $[\text{NH}_3\text{CH}_2\text{CH}(\text{NH}_3)\text{CH}_3]_{0.5}[\text{Sn}_4\text{P}_3\text{O}_{12}] \cdot \text{H}_2\text{O}$ along the c axis showing the connectivity between the four-, six-, and eight-membered rings.

of the amine is such that the branched-chain 1,2-diamino propane forms a well-defined eight-membered channel system. It is interesting to note that the framework formula of $[\text{Sn}_4\text{P}_3\text{O}_{12}]^-$ has been observed in four different phases (8a-c, 19), and in all but one (19) channel structures are formed. It is to be noted that edge or face sharing between tin(II) pyramids (SnO_3) and phosphate tetrahedra (PO_4) has not been observed in any of the earlier known tin(II) phosphates. This may be because, with normal P-O distances and O-P-O angles and with a Sn-O distance of $\sim 2.2 \text{ \AA}$, the O-Sn-O bond angle would have to be $\sim 70^\circ$. This is

much smaller than the ligand bond angles usually observed for Sn(II) species (Table 3) (6-9, 14-16).

In conclusion, the synthesis and structural characterization of a new tin(II) phosphate material possessing one-dimensional channels were realized. Successful synthesis of a channel structure by employing a branched-chain diamine indicates that it may be beneficial to probe the effect of other similar amines in the synthesis of such framework materials. This new phase, together with the previously reported Sn(II) phosphate solids, illustrates profound structural influences of relatively minor modifications in reaction conditions

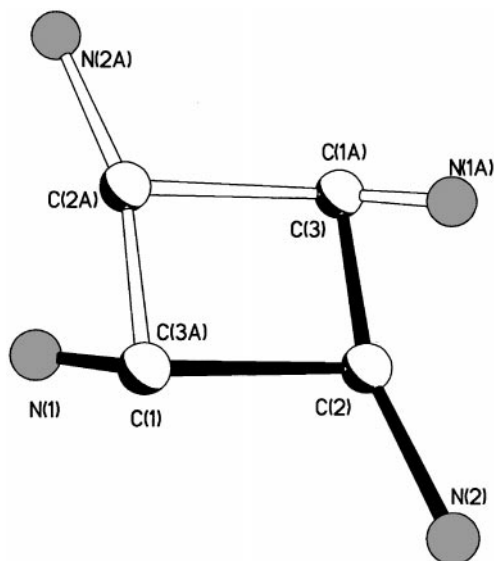


FIG. 4. Diagram showing the probable disorder of the amine molecule in $[\text{NH}_3\text{CH}_2\text{CH}(\text{NH}_3)\text{CH}_3]_{0.5}[\text{Sn}_4\text{P}_3\text{O}_{12}] \cdot \text{H}_2\text{O}$.

and/or changes in the starting source for the tin. While the isolation of a one-dimensional channel structure provides information about the stereochemical consequences of the Sn(II) lone pair electrons, further evaluation is required to exploit the structure-directing influences of this unit in the presence of other organic amines in the synthesis of potentially open-framework phosphate materials.

ACKNOWLEDGMENT

The author thanks Professor C. N. R. Rao, FRS, for his keen interest, help, and encouragement.

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