

# New open-framework layered tin(II) phosphates intercalated with amines

R. Vaidhyanathan and Srinivasan Natarajan\*

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., P.O. Box 6436, Bangalore 560 064, India. E-mail: raj@jncasr.ac.in

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Two new Sn(II) phosphate materials, **I** and **II**, have been synthesized hydrothermally using 1,3-diaminopropane and 1,3-diamino-2-hydroxypropane as structure-directing organic amines. The solids **I** and **II** have layered architectures

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protonated amine molecules which interact with the framework through hydrogen bonding. Crystal data for compound **I**:  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]^{2+} 2[\text{SnPO}_4]^-$ ,  $M = 501.9$ , monoclinic, space group  $C2/c$ ,  $a = 18.097(1)$ ,  $b = 7.889(1)$ ,  $c = 9.151(1)$  Å,  $\beta = 111.84(1)^\circ$ ,  $V = 1212.6(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $R = 0.033$  and  $R_w = 0.061$  [791 observed reflections with  $I = 2\sigma(I)$ ]; compound **II**  $[\text{NH}_3(\text{CH}_2\text{CHOHCH}_2)\text{NH}_3]^{2+} 2[\text{SnPO}_4]^-$ ,  $M = 517.9$ , monoclinic, space group  $C2/c$ ,  $a = 18.133(1)$ ,  $b = 7.858(1)$ ,  $c = 9.344(1)$  Å,  $\beta = 111.3(1)^\circ$ ,  $V = 1240.5(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $R = 0.040$  and  $R_w = 0.11$  [867 observed reflections with  $I = 2\sigma(I)$ ].

## Introduction

Open-framework materials are of considerable interest due to their wide structural diversity and potential applications in catalysis and other areas.<sup>1</sup> Continued research in this area has shown that new materials with novel architectures can be made in the presence of structure-directing organic amines.<sup>2</sup> Recently, it has been established that open-framework tin(II) phosphates can be made under hydrothermal conditions.<sup>3-9</sup> The chemistry of bivalent tin and its related compounds, especially the phosphates<sup>3-9</sup> and phosphonates,<sup>10,11</sup> continues to yield unexpected results. In the tin phosphate family, the isolation of materials having one-  $[\text{C}_6\text{N}_2\text{H}_{18}]^{2+} 2[\text{SnPO}_4]^-$  (ladder-like chains),<sup>7</sup> two-  $[\text{C}_2\text{N}_2\text{H}_{10}]^{2+} [\text{Sn}_2(\text{PO}_4)_2]^{2-} \cdot \text{H}_2\text{O}$  (layers, intercalated with amine)<sup>8</sup> and three-dimensionally  $\{0.5[\text{H}_3\text{N}(\text{CH}_2)_2\text{NH}_3]^{2+} [\text{Sn}_4\text{P}_3\text{O}_{12}]^-\}$ ,<sup>3</sup>  $\{0.5[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]^{2+} [\text{Sn}_4\text{P}_3\text{O}_{12}]^-\}$ ,<sup>4</sup>  $\{0.5[\text{H}_3\text{NCH}_2\text{CH}_2\text{CH}(\text{NH}_3)\text{CH}_2\text{CH}_3]^{2+} [\text{Sn}_4\text{P}_3\text{O}_{12}]^-\} \cdot \text{H}_2\text{O}$ <sup>6</sup> extended networks clearly indicates that the system is very versatile like the aluminophosphate family of open-framework materials. One of the basic structural building blocks, present in most of these materials, a 4-membered ring composed of a  $[\text{Sn}_2\text{P}_2\text{O}_4]$  moiety has also been isolated and characterized.<sup>9</sup> The main structural feature present in all the tin phosphate and phosphonate materials is the presence of either three- and/or four-coordinated Sn(II) atoms that are vertex linked to  $\text{PO}_4$  tetrahedra, forming channels and cavities. In general, it is observed that the Sn:P ratio in these tin phosphates is greater than 1. In this paper, we report the synthesis and structure of two simple open-framework tin(II) phosphates, having a Sn:P ratio of 1.0, prepared under hydrothermal conditions in the presence of 1,3-diaminopropane (DAP, compound **I**) or 1,3-diamino-2-hydroxypropane (DAHP, compound **II**) as the structure-directing agent.

## Experimental

Compounds **I** and **II** were synthesized by hydrothermal methods starting from a tin phosphate gel containing DAP or DAHP as the structure-directing agent. In a typical synthesis, 2.088 g of tin(II) oxalate (Aldrich) was dispersed in 10 ml of water and 1.38 ml of 85 wt% aqueous  $\text{H}_3\text{PO}_4$  (Aldrich) was

added to the mixture under continuous stirring. 1.314 ml of DAP (**I**) or 1.821 g of DAHP (**II**) was added to the mixture which was stirred until homogeneous. The final composition of the mixture was  $\text{SnC}_2\text{O}_4 \cdot 2.0\text{H}_3\text{PO}_4 \cdot 1.5\text{DAP}/2.0\text{DAHP} \cdot 55\text{H}_2\text{O}$ . The mixture was sealed in a Teflon lined stainless steel autoclave (Parr, USA) and heated initially at 150 °C for 48 h and then finally at 180 °C for 36 h for compound **I** and at 150 °C for 120 h for compound **II**. The resulting product containing predominantly large plate-like single crystals and a small quantity of powder was filtered and washed thoroughly with deionised water. The powder X-ray diffraction patterns for both the compounds were identical and indicated that the product was a new material; the pattern is entirely consistent with the structure determined by single-crystal X-ray diffraction (Table 1). Thermogravimetric analysis (TGA) was carried

**Table 1** Powder X-ray diffraction data for compound **I**,  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]^{2+} 2[\text{SnPO}_4]^-$

$d_{\text{obs}}/\text{Å}$	$d_{\text{calc}}/\text{Å}$	$I_{\text{rel}}$	$h$	$k$	$l$
8.4064	8.3990	100	2	0	0
4.5625	4.5660	11.4	3	1	0
4.2023	4.1995	11.7	4	0	0
3.9312	3.9337	12.3	1	1	-2
3.7652	3.7681	18.5	4	0	-2
3.5748	3.5702	31.2	2	2	0
3.3242	3.3246	12.9	2	0	2
2.9723	2.9743	21.4	2	2	-2
2.8902	2.8901	26.9	0	2	2
2.7982	2.7997	4.8	6	0	0
2.5427	2.5420	15.1	2	2	2
2.4084	2.4101	6.4	7	1	-2
2.2662	2.2691	1.6	2	0	-4
2.2393	2.2323	1.8	3	3	-2
2.1965	2.1971	4.6	3	1	-4
2.1281	2.1295	4.0	1	1	-4
	2.1271	1.2	5	3	-1
2.1008	2.0998	3.7	8	0	0
2.0165	2.0179	4.3	6	0	2
1.9698	1.9721	2.1	0	4	0
1.9413	1.9436	7.1	9	1	-2
	1.9408	8.7	7	1	-4
1.8607	1.8618	1.1	6	2	-4

out under an oxygen atmosphere from room temperature to 600 °C at a rate of 5 °C min<sup>-1</sup>.

## Structure determination

A suitable colorless plate-like single crystal of **I** or **II** was selected and mounted at the tip of a glass fiber using 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 (Mo-K $\alpha$  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  $\omega$  scans (width of 0.30° and exposure time of 10 s per frame). The final unit cell constants were determined by a least-squares fit of 1703 reflections for **I**, and 2229 reflections for **II** in the range  $4 \leq 2\theta \leq 46.5$  and are presented in Table 2. A total of 2412 reflections for **I** were collected in the ranges  $-16 \leq h \leq 20$ ,  $-8 \leq k \leq 8$ ,  $-10 \leq l \leq 5$  and were merged to give 873 unique reflections ( $R_{\text{int}} = 0.0414$ ), of which 791 were considered to be observed [ $I > 2\sigma(I)$ ]. In the case of **II**, 2549 reflections were collected in the ranges  $-19 \leq h \leq 20$ ,  $-8 \leq k \leq 8$ ,  $-10 \leq l \leq 7$  and were merged to give 898 unique reflections ( $R_{\text{int}} = 0.0481$ ), of which 867 were considered to be observed [ $I > 2\sigma(I)$ ]. Pertinent details for the structure determination are listed in Table 2.

The structure was solved by direct methods using SHELXS-86<sup>12</sup> and difference Fourier syntheses. The absorption correction was based on symmetry equivalent reflections using the SADABS<sup>13</sup> program. Other effects, such as absorption by the glass fiber, were simultaneously corrected. All the hydrogen positions were found in the difference Fourier maps and for the final refinement the hydrogen atoms on the amine molecule were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares structure refinement against  $|F^2|$  was carried out using the SHELXTL-PLUS<sup>14</sup> package of pro-

**Table 3** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{Å}^2 \times 10^3$ ) for non-hydrogen atoms in **I**,  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]^{2+}2[\text{SnPO}_4]^-$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
Sn(1)	2612(1)	-5136(1)	-381(1)	18(1)
P(1)	3448(1)	-2684(2)	2613(2)	15(1)
O(1)	3544(2)	-3652(5)	1203(4)	22(1)
O(2)	3510(2)	-3974(5)	3902(5)	22(1)
O(3)	2598(2)	-1918(5)	1996(4)	24(1)
O(4)	4076(2)	-1332(5)	3184(5)	24(1)
N(1)	5564(3)	-1981(6)	5420(6)	26(1)
C(1)	5363(4)	-3017(8)	6585(7)	30(2)
C(2)	5000	-1924(12)	7500	29(2)

<sup>a</sup>*U*(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

grams. The final Fourier map had minimum and maximum peaks of  $-0.575$  and  $0.656 \text{ e Å}^{-3}$  for compound **I** and  $-1.093$  and  $1.442 \text{ e Å}^{-3}$  for compound **II**. Final *R* values,  $R = 0.033$  and  $R_w = 0.061$  and  $S = 1.11$  were obtained for a total of 83 parameters for **I** and  $R = 0.040$  and  $R_w = 0.11$  and  $S = 1.28$  were obtained for a total of 89 parameters for **II**. The final atomic coordinates, bond distances and bond angles are presented in Tables 3 and 4 for **I** and 5 and 6 for **II**.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See 'Information for Authors', *J. Mater. Chem.*, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/157.

See <http://www.rsc.org/suppdata/jm/1999/1807/> for crystallographic files in .cif format.

## Results and discussion

Two new tin(II) phosphates,  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]^{2+}2[\text{SnPO}_4]^-$  (**I**) and  $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{NH}_3]^{2+}2[\text{SnPO}_4]^-$  (**II**), have been synthesized by hydrothermal methods and the structures

**Table 2** Crystal data and structure refinement parameters for **I**,  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]^{2+}2[\text{SnPO}_4]^-$ , and **II**,  $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{NH}_3]^{2+}2[\text{SnPO}_4]^-$

	Compound <b>I</b>	Compound <b>II</b>
Empirical formula	$\text{Sn}_2\text{P}_2\text{O}_8\text{C}_3\text{N}_2\text{H}_{12}$	$\text{Sn}_2\text{P}_2\text{O}_9\text{C}_3\text{N}_2\text{H}_{12}$
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
Crystal size/mm	$0.06 \times 0.1 \times 0.14$	$0.06 \times 0.12 \times 0.16$
<i>a</i> /Å	18.097(1)	18.133(1)
<i>b</i> /Å	7.889(1)	7.858(1)
<i>c</i> /Å	9.151(1)	9.344(1)
$\alpha$ /°	90.0	90.0
$\beta$ /°	111.84(1)	111.3(1)
$\gamma$ /°	90.0	90.0
Volume/Å <sup>3</sup>	1212.6(2)	1240.5(1)
<i>Z</i>	4	4
Formula mass	501.9	517.9
$\rho_{\text{calc}}/\text{g cm}^{-3}$	2.118	2.58
$\lambda(\text{Mo-K}\alpha)/\text{Å}$	0.71073	0.71073
$\mu/\text{mm}^{-1}$	3.31	5.31
$\theta$ range/°	2.42–23.26	2.41–23.28
Total data collected	2412	2549
Index ranges	$-16 \leq h \leq 20$ , $-8 \leq k \leq 8$ , $-10 \leq l \leq 5$	$-19 \leq h \leq 20$ , $-8 \leq k \leq 8$ , $-10 \leq l \leq 7$
Unique data	873	898
Observed data [ $\sigma > 2\sigma(I)$ ]	791	867
Refinement method	Full-matrix least-squares on $ F^2 $	Full-matrix least-squares on $ F^2 $
<i>R</i> indices [ $I > 2\sigma(I)$ ]	$R = 0.026$ , $R_w = 0.059$	$R = 0.039$ , $R_w = 0.11$
<i>R</i> indices (all data)	$R = 0.033$ , $R_w = 0.061^a$	$R = 0.040$ , $R_w = 0.11^b$
Goodness of fit ( <i>S</i> )	1.11	1.28
No. of variables	83	89
Largest difference map peak and hole/ $\text{e Å}^{-3}$	0.656 and $-0.575$	1.442 and $-1.093$

<sup>a</sup> $w = 1/[\sigma^2(F_o)^2 + (0.0197P)^2 + 10.2010P]$  where  $P = [F_o^2 + 2F_c^2]/3$ . <sup>b</sup> $w = 1/[\sigma^2(F_o)^2 + (0.0619P)^2]$  where  $P = [F_o^2 + 2F_c^2]/3$ .

**Table 4** Selected bond distances and bond angles for **I**,  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]^{2+}2[\text{SnPO}_4]^-$ 

Distance/Å		Angle/°	
Sn(1)–O(1)	2.122(4)	O(1)–Sn(1)–O(2) <sup>a</sup>	83.4(2)
Sn(1)–O(2) <sup>a</sup>	2.088(4)	O(1)–Sn(1)–O(3) <sup>c</sup>	86.9(2)
Sn(1)–O(3) <sup>b</sup>	2.130(4)	O(2) <sup>a</sup> –Sn(1)–O(3) <sup>b</sup>	89.8(2)
P(1)–O(1)	1.563(4)	O(1)–P(1)–O(2)	108.2(2)
P(1)–O(2)	1.530(4)	O(1)–P(1)–O(3)	106.8(2)
P(1)–O(3)	1.551(4)	O(2)–P(1)–O(3)	108.5(2)
P(1)–O(4)	1.503(4)	O(1)–P(1)–O(4)	109.4(2)
		O(2)–P(1)–O(4)	112.0(2)
		O(3)–P(1)–O(4)	111.7(2)
N(1)–C(1)	1.492(8)	N(1)–C(1)–C(2)	110.8(5)
C(1)–C(2)	1.512(8)	C(1)–C(2)–C(1) <sup>d</sup>	110.5(8)
C(2)–C(1) <sup>d</sup>	1.512(8)		

Symmetry transformations used to generate equivalent atoms: <sup>a</sup> $x, -y-1, z-1/2$ ; <sup>b</sup> $-x+1/2, -y-1/2, -z$ ; <sup>c</sup> $x, -y-1, z+1/2$ ; <sup>d</sup> $x+1, y, -z+3/2$ .

**Table 5** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{Å}^2 \times 10^3$ ) for non-hydrogen atoms in **II**,  $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{NH}_3]^{2+}2[\text{SnPO}_4]^-$ 

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) <sup>a</sup>
Sn(1)	2630(1)	-5165(1)	-430(1)	20(1)
P(1)	3457(1)	-2745(2)	2517(2)	16(1)
O(1)	3552(2)	-3698(5)	1126(4)	24(1)
O(2)	3503(2)	-4079(5)	3749(5)	27(1)
O(3)	2617(2)	-1960(5)	1949(4)	23(1)
O(4)	4094(2)	-1419(6)	3098(5)	29(1)
O(10) <sup>b</sup>	5601(5)	-1005(11)	8467(9)	41(3)
N(1)	5535(3)	-2017(7)	5422(6)	30(1)
C(1)	5323(4)	-3080(10)	6559(8)	31(2)
C(2)	5000	-1937(12)	7500	23(2)

<sup>a</sup>*U*(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. <sup>b</sup>Site occupancy factor (SOF)=0.5.

**Table 6** Selected bond distances and bond angles for **I**,  $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{NH}_3]^{2+}2[\text{SnPO}_4]^-$ 

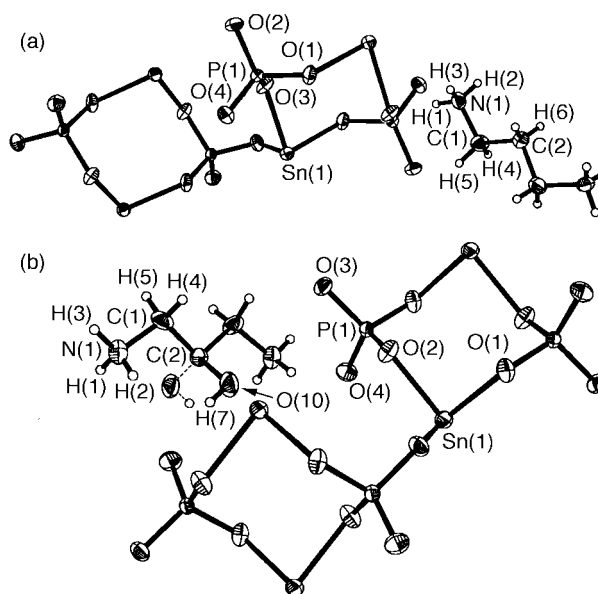
Distance/Å		Angle/°	
Sn(1)–O(1)	2.114(4)	O(1)–Sn(1)–O(2) <sup>a</sup>	87.3(2)
Sn(1)–O(2) <sup>a</sup>	2.131(4)	O(1)–Sn(1)–O(3) <sup>b</sup>	83.8(2)
Sn(1)–O(3) <sup>b</sup>	2.081(4)	O(2) <sup>a</sup> –Sn(1)–O(3) <sup>b</sup>	89.0(2)
P(1)–O(1)	1.564(4)	O(1)–P(1)–O(2)	107.4(2)
P(1)–O(2)	1.548(4)	O(1)–P(1)–O(3)	107.7(2)
P(1)–O(3)	1.536(4)	O(2)–P(1)–O(3)	107.9(2)
P(1)–O(4)	1.503(4)	O(1)–P(1)–O(4)	109.3(2)
O(3)–Sn(1) <sup>c</sup>	2.081(4)	O(2)–P(1)–O(4)	112.3(2)
O(3)–Sn(1) <sup>b</sup>	2.131(4)	O(3)–P(1)–O(4)	112.1(2)
N(1)–C(1)	1.507(9)	N(1)–C(1)–C(2)	109.4(7)
C(1)–C(2)	1.516(10)	C(1) <sup>d</sup> –C(2)–C(1)	107.3(9)
C(2)–C(1) <sup>d</sup>	1.516(10)	C(1) <sup>d</sup> –C(2)–O(10) <sup>d</sup>	108.8(5)
C(2)–O(10) <sup>d</sup>	1.351(10)	C(1)–C(2)–O(10) <sup>d</sup>	108.7(4)

<sup>a</sup> $x, -y-1, z-1/2$ ; <sup>b</sup> $-x+1/2, -y-1/2, -z$ ; <sup>c</sup> $x, -y-1, z+1/2$ ; <sup>d</sup> $-x-1, y, -z+3/2$ .

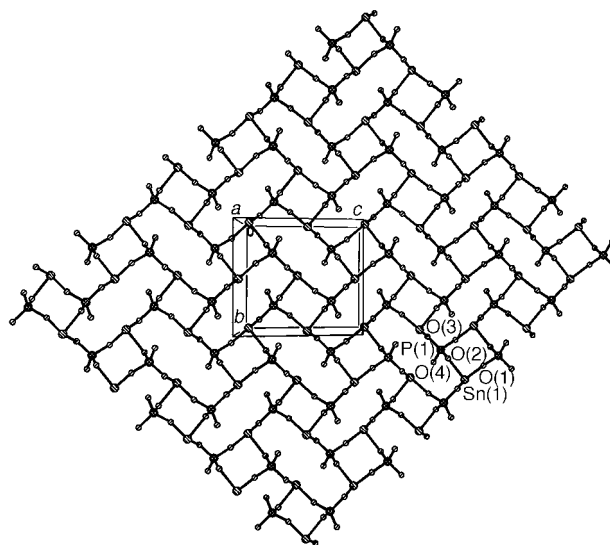
determined by single crystal X-ray diffraction methods. Since the synthesis involves kinetically controlled solvent-mediated reactions, there is no apparent correlation between the starting composition and the stoichiometry of the solid product. Both **I** and **II** have identical structures, forming layers that are intercalated by the structure-directing organic amine molecules. The structure of **I** and **II** is based on a network of strictly alternating  $\text{SnO}_3$  and  $\text{PO}_4$  units. The  $\text{SnO}_3$  and  $\text{PO}_4$  units form infinite layers with the framework formula  $[\text{SnPO}_4]^-$ . Charge neutrality is achieved by the incorporation of the organic amine in its diprotonated form; there are 0.5 [amine]<sup>2+</sup> ions per framework formula unit. The asymmetric unit contains 9 and 10 independent non-hydrogen atoms for

**I** and **II** respectively [Fig. 1(a) and (b)]. The Sn atom is coordinated to three oxygens and occupies the vertex of a trigonal pyramid; the lone pair presumably occupies the fourth vertex of the tetrahedron.

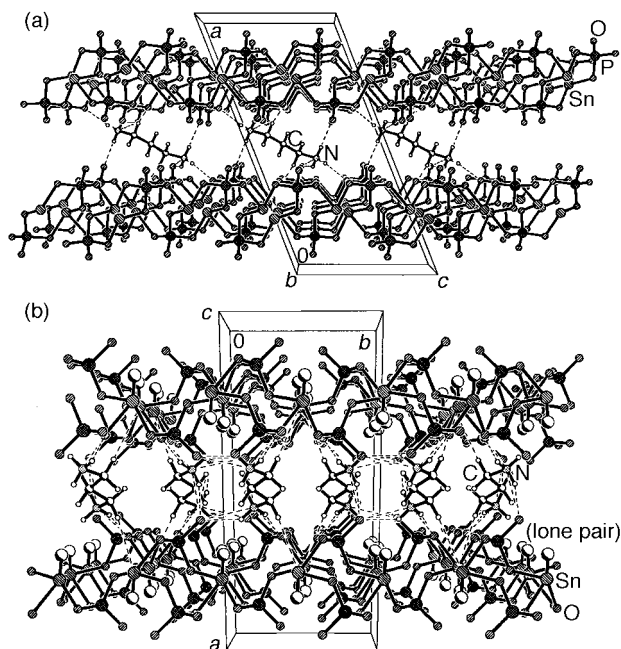
The structure of **I** and **II** is constructed by the networking of  $\text{SnO}_3$  and  $\text{PO}_4$  units forming infinite anionic layers. The connectivity between these moieties creates 4- and 8-membered rings along the *a* axis formed by the T atoms (T=Sn, P) (Fig. 2). Each 4-membered ring is attached to four 8-membered rings and each 8-membered ring is connected to four 4-membered rings. One of the basic building units present in many of the tin phosphates and other related materials, *viz.* the  $\text{M}_2\text{P}_2\text{O}_4$  unit (M=Sn in the present case),<sup>9</sup> is also seen in both **I** and **II**. The structure-directing amine molecules (DAH in **I** and DAHP in **II**) are located between the layers [Fig. 3(a), (b) and 4]. The individual layers are held together by the doubly protonated DAP molecules in **I** [Fig. 3(a) and (b)] and DAHP molecules in **II** (Fig. 4) through hydrogen bonding. **I**



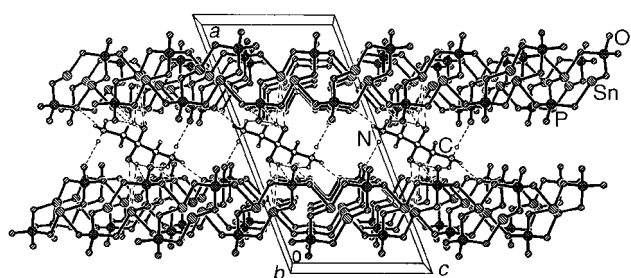
**Fig. 1** (a) ORTEP plot of **I**,  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]^{2+}2[\text{SnPO}_4]^-$ . (b) ORTEP plot of **II**,  $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{NH}_3]^{2+}2[\text{SnPO}_4]^-$ ; the dotted line represents the other position of the OH group of the amine. In both the materials, the asymmetric unit is labelled.



**Fig. 2** Structure showing the connectivity within a single layer along the [100] direction. Note that four 4-membered rings surround one 8-membered ring and *vice versa*.



**Fig. 3** (a) Structure of **I**,  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]^{2+}2[\text{SnPO}_4]^-$ , along the *b* axis showing the layers and the position of the amines. The dotted lines show the hydrogen bonding interactions. (b) Structure of **I**,  $[\text{NH}_3(\text{CH}_2)_3\text{NH}_3]^{2+}2[\text{SnPO}_4]^-$ , along the *c* axis showing the layers and the position of the amines. The dotted lines show the hydrogen bonding interactions. Note that the lone pair of electrons of Sn(II) points perpendicular to the layers.



**Fig. 4** Structure of **II**,  $[\text{NH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{NH}_3]^{2+}2[\text{SnPO}_4]^-$ , along the *b* axis showing the interaction between the layers and the amine. The dotted lines show the hydrogen bonding between the amine and the framework.

and **II** thus represent another example of framework solids possessing alternating anionic and cationic layers. It is interesting to note that both **I** and **II** have a unique architecture constructed by the minimum basic structural motif, *i.e.* one  $\text{SnO}_3$  and one  $\text{PO}_4$  unit (see Fig. 1), which is needed for the formation of an open-framework tin phosphate material.

The Sn–O bond lengths are in the range 2.081–2.131 Å (av. 2.113 Å for **I** and 2.109 Å for **II**) and the O–Sn–O bond angles are between 83.4 and 89.8° (av. 86.7° for **I** and **II**), which is typical of three coordinate Sn(II)<sup>3–9</sup> (Tables 4 and 6). The Sn atoms are linked to P *via* the oxygen bridges. The P–O distances are in the range 1.503–1.564 Å (av. 1.537 Å for **I** and 1.538 Å for **II**). The P–O(4) distance of 1.503 Å that is observed in both **I** and **II** arises from the formal P=O double bond. Terminal P=O groups in, for example  $\text{H}_3\text{PO}_4 \cdot 0.5\text{H}_2\text{O}$ , are generally between 1.485 and 1.495 Å in length.<sup>15</sup> The O–P–O bond angles are in the range 106.8–112.3° (av. 109.4° for **I** and 109.5° for **II**). The largest bond angles are observed for bonds involving the P=O linkage (109.4–112.3°), indicating the multiple-bond nature of the P=O bonds. These values are in agreement with other phosphate-based open-framework structures.<sup>2–9</sup>

The lone pair of electrons which is associated with Sn(II)

**Table 7** Important hydrogen bond distances and angles for **I** and **II**

	Distance/Å		Angle/°
<b>Compound I</b>			
O(1)–H(1)	2.017(1)	O(1)–H(1)–N(1)	165.3(1)
O(4)–H(2)	2.140(1)	O(4)–H(2)–N(1)	139.5(1)
O(4)–H(3)	1.909(1)	O(4)–H(3)–N(1)	158.8(1)
<b>Compound II</b>			
O(4)–H(1)	1.944(1)	O(4)–H(1)–N(1)	152.6(1)
O(4)–H(2)	2.290(2)	O(4)–H(2)–N(1)	136.3(1)
O(1)–H(3)	2.024(1)	O(1)–H(3)–N(1)	161.8(2)
O(1)–H(4)	2.591(1)	O(1)–H(4)–C(1)	150.9(1)
O(3)–H(4)	2.541(1)	O(3)–H(4)–C(1)	122.4(1)
O(4)–H(7) <sup>a</sup>	1.793(1)	O(4)–H(7)–O(10) <sup>a</sup>	160.8(1)

<sup>a</sup>Intra-layer.

plays an important role in the structures of these materials. The stereoactive lone pair manifests itself in the lattice by creating open space between the two layers in these tin phosphates. As can be seen from Fig. 3(a), the electron lone pair of Sn(II) points perpendicular to the plane of the layers. Similar lone pair positionings have been observed in many layered tin(II) phosphates and related materials.<sup>16,17</sup>

Multipoint hydrogen bonding interactions have helped in the structural stability, and possibly in the formation, of many of the open-framework materials that have low dimensional character, and a large number of examples exist in the literature.<sup>5,7–9,18–26</sup> In **I** and **II**, the hydrogens of the amine molecule interact strongly with the framework oxygens, especially with the double bonded oxygen. The important hydrogen bonding interactions are: H(3)–O(4)=1.909 Å; O(4)–H(3)–N(1)=158.8° for compound **I** and H(1)–O(4)=1.944 Å; O(4)–H(1)–N(1)=152.5° for compound **II**. In the case of compound **II**, the OH group attached to the amine molecule also participates in *intra-* as well as *inter-*layer hydrogen bonding. The inter-molecular hydrogen bonds with the framework oxygens are nearly planar: H(7)–O(4)=1.793 Å; O(4)–H(7)–O(10)=160.9°. Complete hydrogen bonding interactions are presented in Table 7. **I** and **II** thus illustrate the importance of multipoint hydrogen bonding in the stability of two dimensional solids.

The thermogravimetric analyses (TGA) carried out on **I** and **II** indicate that there is only one mass loss in the region 350–400 °C in both cases. The mass loss of 15% observed for **I** and 17% for **II** corresponds to the loss of amine in both the cases (calc. 15.2% for **I** and 17.8% for **II**). The loss of the amine molecule causes the material to lose its layered architecture. The powder XRD patterns of samples calcined at 450 °C in air for 24 h indicate that the resultant solid is amorphous with very weak reflections.

The structures of **I** and **II** have similar features to other previously known layered phosphates of aluminium, antimony and zirconium. Of particular interest is the similarity to the layered aluminium phosphates reported by Chippindale *et al.*<sup>22</sup> and the phosphatoantimonates reported by Piffard *et al.*<sup>23–25</sup> In the case of the former, the macroanionic sheets (made of  $\text{AlO}_4$  and  $\text{PO}_4$  moieties) are held together by strong hydrogen bonded interactions involving the double bonded oxygens of the phosphate groups and the organic template molecules. In the case of the phosphatoantimonates, the layers are made up of corner shared  $\text{PO}_4$  tetrahedra and  $\text{SbO}_6$  octahedra. The interlamellar space is occupied by  $\text{Na}^+$  or  $\text{K}^+$  ions which are readily replaced by protons ( $\text{H}^+$ ) *via* washing with dilute acids. The interlamellar space is also filled with  $\text{H}_2\text{O}$  molecules during the proton exchange. Similar structural features are also seen in the so called  $\alpha$ -ZrP ( $\alpha$ -Zr( $\text{HPO}_4$ )<sub>2</sub>· $\text{H}_2\text{O}$ ) structure.<sup>26</sup> The present compounds have many of the interesting structural features common to the aforementioned layered phosphates. The presence of trigonal-pyramidal  $\text{SnO}_3$  and

tetrahedral PO<sub>4</sub> units linking to form the layers and the interactions with the organic amine molecule leads to the unique architecture seen in these materials.

## Conclusions

The synthesis of two new layered tin(II) phosphate materials consisting of alternating inorganic–organic layers has been accomplished. These materials, together with previously reported Sn(II) phosphate and phosphonate solids, illustrate the profound structural influence of relatively minor modifications in reaction conditions and/or changes in the starting source for the tin. The present compounds represent another example illustrating the importance of multipoint hydrogen bonding in the synthesis and stability of open-framework materials. The stereoactive lone pair of Sn(II) manifests itself in the structure and points perpendicular to the plane of the layers. Our continuing research on tin phosphates indicates that other related structures are formed under hydrothermal conditions using alternative structure-directing agents. While the isolation of a two-dimensional solid with strictly alternating SnO<sub>3</sub> and PO<sub>4</sub> moieties 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 for the synthesis of potentially open-framework phosphate materials.

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