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Synthesis and structural characterization of a novel tin(II) oxyphosphate, $[NH_4^+]_2[Sn_3O(PO_4)_2]^{2-}\cdot H_2O$, containing one-dimensional chains constructed from tin phosphate cages

Srinivasan Natarajan*

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

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The hydrothermal synthesis and single crystal structure of a novel tin(II) oxyphosphate, $[NH_4^+]_2[Sn_3O(PO_4)_2]^{2-}\cdot H_2O$, made from the networking of distorted square-pyramidal SnO_4 and tetrahedral PO_4 moieties, is presented. Crystal data: $a=7.240(1)$, $b=19.552(3)$, $c=8.438(1)$ Å; $V=1194.5(3)$ Å^3; space group $Cmc2_1$ (no. 36) and $Z=2$. The structure, dominated by the presence of a large number of three-coordinated oxygen atoms and Sn–O–Sn linkages, creating an oxy-phosphate unit, consists of capped three-membered rings (cages) connected to each other *via* phosphate groups forming infinite one-dimensional chains. These chains are related to each other *via* multipoint hydrogen bonding involving the protonated ammonium and water molecules.

Introduction

The design and synthesis of new open-framework materials having micro- and meso-porosity is a challenge to the synthetic chemist, as such materials are being used in the areas of catalysis and separation processes.[1] The synthesis under hydro/solvo-thermal conditions provides a facile route for making materials with new open architectures as well as complex organic–inorganic composites. This methodology leads to the development of new classes of materials that can exploit the ability of polar organic molecules to direct the crystallization of inorganic frameworks through multipoint hydrogen bonding.[2] The hydrogen bonded interactions between the inorganic and organic moieties of a framework structure are all the more important when dealing with low dimensional materials as is becoming more apparent by the large number of available literature dealing with such materials.

The chemistry of bivalent tin and its related compounds, especially the phosphates and oxalates, synthesized in the presence of organic structure directing agents (amines) continues to yield unexpected results with the isolation of materials having one- $[Sn_2(PO_4)(C_2O_4)_{0.5}]$[3] (chain), two- $\{[Sn_2(PO_4)_2]^{2-}[C_2N_2H_{10}]^{2+}\cdot H_2O\}$[4] (layer) and three- $\{[Sn_4P_3O_{12}]^-0.5[NH_3(CH_2)_2NH_3]^{2+}$, $[Sn_4P_3O_{12}]^-0.5[NH_3(CH_2)_4NH_3]^{2+}\}$[5,6] dimensionally extended networks. The basic building unit, four-membered rings constructed by two Sn atoms and two P atoms ($Sn_2P_2O_4$ unit), present in all these materials, has also been isolated.[7] All these compounds contain either trigonal pyramidal SnO_3 or distorted square pyramidal SnO_4 units, vertex linked with tetrahedral PO_4 units to form the network. These solids, based on Sn(II), in addition to having novel architectures also provide a basis for evaluating the influence of the Sn(II) lone pair of electrons on the structural features as well as the importance of multipoint hydrogen bonding in the stability of such phases.

The synthesis and structure of a novel tin(II) oxyphosphate material having a 10-membered star shaped channel[8] has been reported recently. In the present work, the synthesis and structure of another novel tin(II) oxyphosphate, $[NH_4^+]_2[Sn_3O(PO_4)_2]^{2-}\cdot H_2O$, made by the networking of distorted square-pyramidal SnO_4 and tetrahedral PO_4 units is presented. This is the first report of a Sn(II) phosphate material formed entirely by four-coordinate Sn(II) atoms; all the previously reported Sn(II) phosphate[3–8] and phosphonate[9,10] materials contain both three- and four-coordinated Sn(II) atoms. The structure of this material consists of capped three-membered rings (cages) connected to each other *via* phosphate groups forming infinite chains. These chains are held together *via* multipoint hydrogen bonding involving the protonated ammonium and water molecules.

Experimental

Synthesis

The title compound, synthesized hydrothermally employing guanidium carbonate as the structure directing agent, is described below. In a typical experiment, 2.0671 g of tin oxalate (Aldrich) was dispersed in 10 ml of water. To this mixture 1.153 g of phosphoric acid (Aldrich) was added dropwise and the mixture stirred vigorously. Then 1.262 g of guanidium carbonate was added to the above very slowly under continuous stirring. The final mixture was transferred and sealed in a PTFE-lined stainless steel autoclave (Parr, USA), and heated at 175 °C for 3 days under autogeneous pressure. The final composition of the mixture was $1\,SnC_2O_4:1\,H_3PO_4:0.7$ guadinium carbonate$:55\,H_2O$. The resulting product, which contained a few single crystals along with some white powder, was filtered off and washed thoroughly with de-ionized distilled water (yield *ca.* 50%). The powder X-ray diffraction pattern of both the crushed single crystals as well as the white powder, taken independently, were found to be identical and indicated that the product was homogeneous and a new material; the pattern is entirely consistent with the structure determined by single crystal X-ray diffraction. Thermogravimetric analysis (TGA) was carried out in nitrogen atmosphere from room temperature up to 600 °C.

Structure determination

A suitable colorless single crystal was carefully selected under a polarizing microscope and glued to the tip of a glass fiber using Superglue (cyanoacrylate). Crystal structure determination by X-ray diffraction was performed at room-temperature on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-Kα radiation, $\lambda=0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data were collected in 1321 frames with ω scans (width of 0.30° and exposure time of 40 s per frame). The final unit-cell constants were determined by a

Table 1 Summary of crystal data, intensity measurements and structure refinement parameters for $[NH_4^+]_2[Sn_3O(PO_4)_2]^{2-}\cdot H_2O$

Empirical formula	$Sn_3P_2O_{10}N_2H_{10}$
Crystal system	Orthorhombic
Space group	$Cmc2_1$ (no. 36)
Crystal size/mm	$0.04 \times 0.04 \times 0.125$
a/Å	7.240(1)
b/Å	19.552(3)
c/Å	8.438(1)
V/Å^3	1194.5(3)
Z	2
Formula mass	616.1(1)
D_c/g cm^{-3}	1.713
λ(Mo-Kα)/Å	0.71073
μ/mm^{-1}	3.27
Temperature of measurement/K	298
θ range/°	2.08–23.28°
Total data collected	4995
Index ranges	$-7 \leqslant h \leqslant 7$, $-21 \leqslant k \leqslant 20$, $-6 \leqslant l \leqslant 9$
Unique data	2299
Observed data $[\sigma > 2\sigma(I)]$	749
R_{int}	4.68
Refinement method	Full-matrix least-squares on $\lvert F^2 \rvert$
R indices $[\sigma > 2\sigma(I)]$	$R = 3.67$; $R_w = 7.83$
R (all data)	$R = 4.79$; $R_w = 8.47$
Goodness of fit/S	1.13
No. of variables	103
Largest difference map peak and hole/e Å^{-3}	0.699, −0.975

least-squares fit of 1379 reflections in the range $4 \leqslant 2\theta \leqslant 46.5°$ and are presented in Table 1. A total of 4995 reflections were collected in the range $-7 \leqslant h \leqslant 7$, $-21 \leqslant k \leqslant 20$, $-6 \leqslant l \leqslant 9$ and these were merged to give 2299 unique reflections ($R_{int.} = 0.0468$) of which 749 were considered to be observed $[I > 2\sigma(I)]$. The pertinent experimental conditions for the structure determination are listed in Table 1. The structure was solved by direct methods using SHELXS-86[11] and difference Fourier syntheses. Hydrogen atoms of the water and ammonia molecules were found in the difference Fourier map and held in the riding mode. Refinement of the Flack parameter to *ca.* 1.0 indicated that the incorrect absolute structure had been established in the initial model. The polarity of the model was reversed by changing the sign of the polar-axis z coordinate for all the atoms and re-refining the model, which resulted in a final value for the Flack parameter of −0.05(8) and residuals of $R = 0.0367$ and $R_w = 0.0783$. Re-refinement of this transformed coordinate set with the Flack parameter set to 1.00 led to residuals of $R = 0.0382$ and $R_w = 0.0902$. The last cycles of refinement included atomic positions and anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against $\lvert F^2 \rvert$ was carried out using the SHELXTL-PLUS[12] package of programs. The final Fourier map had a minimum and maximum peaks of −0.975 and 0.699 e Å^{-3}, respectively. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum, Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-408705. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/125.

Results and discussion

The asymmetric unit consists of 13 non-hydrogen atoms [Fig. 1(a)] and final atomic coordinates for all the non-hydrogen atoms are given in Table 2. This materials forms a new anionic tin(II) oxyphosphate structure built up from the vertex linking between distorted square pyramidal SnO_4 and tetrahedral PO_4 building blocks. The framework has the formula $[Sn_3O(PO_4)_2]^{2-}$ and charge neutrality is achieved by the incorporation of protonated ammonium molecules; there are two $[NH_4]^+$ ions per framework formula unit. The entire architecture is constructed by four-coordinate Sn(II) atoms and tetrahedral PO_4 units. To our knowledge, this is the first

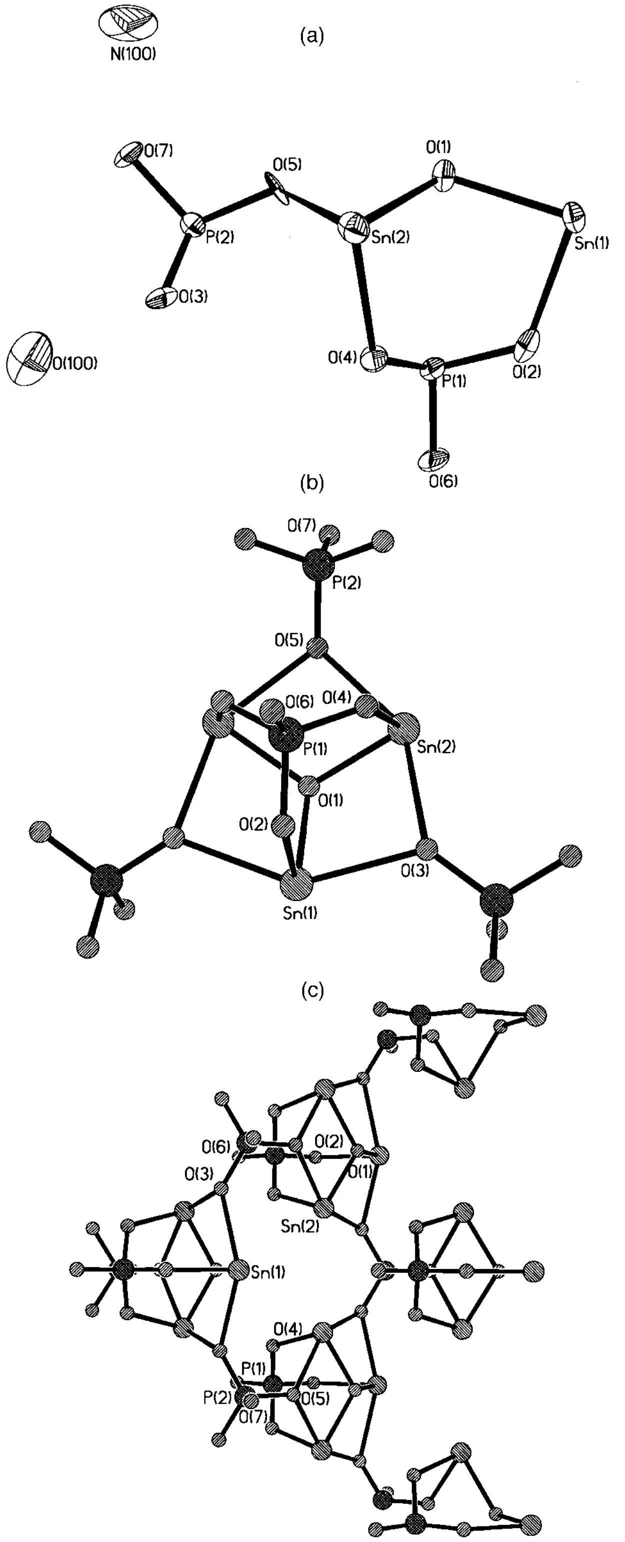

Fig. 1 (a) Asymmetric unit of $[NH_4^+]_2[Sn_3O(PO_4)_2]^{2-}\cdot H_2O$. Thermal ellipsoids are shown at 50% probability. (b) The basic building block showing the cage-like structure with the terminal phosphate groups. (c) View showing the connectivity between the cages, forming six-membered rings along the b axis, through the phosphate groups.

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[NH_4{}^+]_2[Sn_3O(PO_4)_2]^{2-}\cdot H_2O$

Atom	*x*	*y*	*z*	$U_{eq}{}^a$
Sn(1)	10000	8675(1)	9852(2)	26(1)
Sn(2)	7568(1)	7410(1)	7759(4)	22(1)
P(1)	10000	8627(3)	5938(8)	17(2)
P(2)	10000	6357(3)	5104(10)	18(2)
O(1)	10000	7696(6)	8954(16)	16(3)
O(2)	10000	9070(6)	7469(15)	22(4)
O(3)	8237(13)	6574(4)	4197(12)	22(3)
O(4)	8249(12)	8167(4)	5937(11)	18(2)
O(5)	10000	6724(7)	6741(14)	20(4)
O(6)	10000	9128(7)	4533(19)	27(5)
O(7)	10000	5581(6)	5379(18)	26(4)
N(100)	7697(28)	5155(11)	8001(43)	59(8)
O(100)	10000	5932(10)	625(32)	73(7)

^{a}Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

time an open-framework tin phosphate material is constructed by four-coordinated Sn(II) atoms alone. The exclusive presence of four-coordinate Sn(II), in the current material, leads to the presence of a large number of Sn–O–Sn type linkages. These linkages create a situation where more than one type of oxygen atom has three-coordination. Oxygen atom O(1) bonds to three tin atoms and two other oxygens, O(3) and O(5), are also three coordinate but bonded to two tin atoms and one phosphorus atom. However, it should be noted that the three-coordinate oxygen atoms do not create a situation where P–O–P bondings occur, in accord with the principle that lies at the heart of Löwenstein's rule.[13]

The entire framework is constructed from a cage-like unit as shown in Fig. 1(b). This unit, *viz.*, the capped three-ring, seen for the first time, is built up from three two-membered rings formed by the Sn–O–Sn linkages creating a bowl with the oxygen [O(1)], bonding to three tin atoms, forming the base of the bowl. The bowl is closed with a capping phosphate group forming a cage [Fig. 1(b)]. The individual cages, in turn, are connected to each other through another phosphate group [Fig. 1(c)]. The linkage between the capped three-membered rings and the phosphate groups occurs *via* a three-coordinate oxygen atom [Fig. 1(b) and (c)]. This type of bonding creates a heavily distorted six-membered ring along the *b* axis [Fig. 1(c)].

The linkages between the cage and the phosphate groups create zigzag infinite one dimensional chains along the *a* axis (Fig. 2). Along the *c* axis the structure presents continuous ribbons made of the caged three-rings and phosphate groups (Fig. 3). The ammonium and water molecules occupy spaces in between these ribbons/chains held together by strong multipoint hydrogen bonded interactions (Fig. 2 and 3). The ammonium molecules arise from the decomposition of the starting amine used for the synthesis, *viz.*, guanidium carbonate.

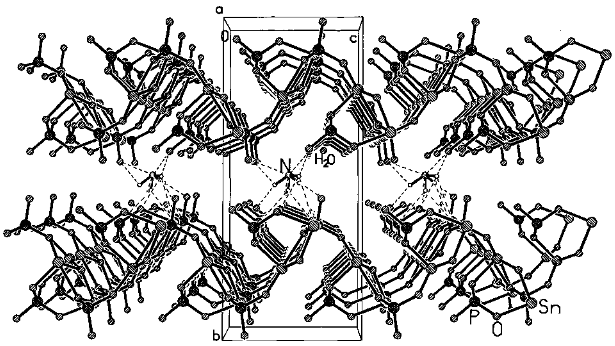

Fig. 2 Structure of $[NH_4{}^+]_2[Sn_3O(PO_4)_2]^{2-}\cdot H_2O$ showing the one-dimensional chains along the *a* axis.

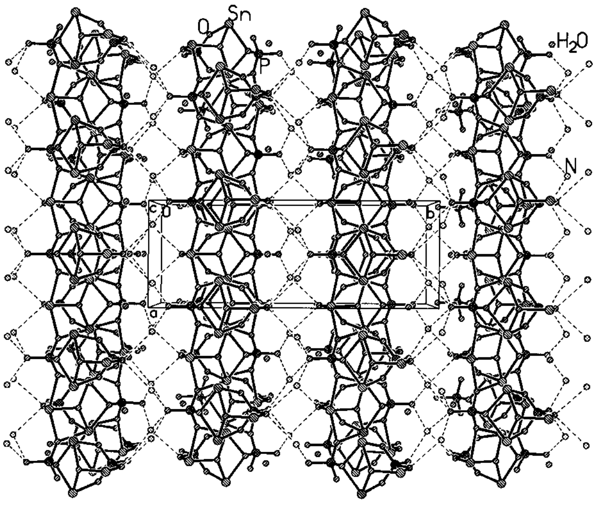

Fig. 3 Structure of $[NH_4{}^+]_2[Sn_3O(PO_4)_2]^{2-}\cdot H_2O$ showing the chains and the interactions between the ammonium and water molecules along the *c* axis (hydrogens on the ammonium and water molecules are omitted).

Decomposition of amine molecules during hydrothermal reactions has been observed before.[8]

The Sn–O bond lengths are in the range 2.058–2.457 Å (av. 2.276 Å), and the O–Sn–O bond angles lie between 72.7 and 146.2° (av. 91.7°). These values are in excellent agreement with those for other tin phosphate materials where Sn atoms are four coordinate[3,4] with respect to oxygen. However, the longest bond distance [Sn(1)–O(3) 2.460 Å] and the largest bond angles [O(3)–Sn(1)–O(3) 145.1° and O(5)–Sn(2)–O(3) 146.2°] are observed for linkages involving the three-coordinate oxygen atoms. The P–O distances are in the range 1.536–1.555 Å (av. 1.546 Å) and the O–P–O bond angles are in the range 106.7–111.6° (av. 109.5°). These values are comparable to those observed in other phosphate materials. Important bond distances and angles are presented in Table 3.

Thermogravimetric analysis (TGA) of the title compound was carried out in the presence of nitrogen from room temperature to 600 °C. Only one weight loss was observed in the region of 300–400 °C, which corresponds to about 11.5% of the total mass of the sample and can be directly correlated to the decomposition of very strongly hydrogen bonded water and ammonium molecules (calc. *ca.* 10%). The powder X-ray

Table 3 Selected bond distances (Å) and angles (°) for $[NH_4{}^+]_2[Sn_3O(PO_4)_2]^{2-}\cdot H_2O^a$

Sn(1)–O(1)	2.058(11)	Sn(1)–O(2)	2.153(13)
Sn(1)–O(3)^a	2.457(10)	Sn(1)–O(3)^b	2.457(10)
Sn(2)–O(1)	2.104(8)	Sn(2)–O(4)	2.190(10)
Sn(2)–O(5)	2.375(9)	Sn(2)–O(3)^b	2.400(9)
P(1)–O(6)	1.54(2)	P(1)–O(2)	1.555(14)
P(1)–O(4)	1.554(9)	P(1)–O(4)^c	1.554(9)
P(2)–O(7)	1.536(13)	P(2)–O(3)	1.547(10)
P(2)–O(3)^c	1.547(10)	P(2)–O(5)	1.56(2)
O(1)–Sn(1)–O(2)	89.4(5)	O(1)–Sn(1)–O(3)^a	74.5(2)
O(2)–Sn(1)–O(3)^a	82.0(2)	O(1)–Sn(1)–O(3)^b	74.5(2)
O(2)–Sn(1)–O(3)^b	82.0(2)	O(3)^a–Sn(1)–O(3)^b	145.1(4)
O(1)–Sn(2)–O(4)	88.2(4)	O(1)–Sn(2)–O(5)	72.7(3)
O(4)–Sn(2)–O(5)	87.8(4)	O(1)–Sn(2)–O(3)^b	75.0(4)
O(4)–Sn(2)–O(3)^b	81.4(3)	O(5)–Sn(2)–O(3)^b	146.2(3)
O(6)–P(1)–O(2)	106.7(8)	O(6)–P(1)–O(4)	111.6(5)
O(2)–P(1)–O(4)	108.8(5)	O(6)–P(1)–O(4)^c	111.6(5)
O(2)–P(1)–O(4)^c	108.8(5)	O(4)–P(1)–O(4)^c	109.3(7)
O(7)–P(2)–O(3)	110.2(6)	O(7)–P(2)–O(3)^c	110.2(6)
O(3)–P(2)–O(3)^c	111.2(9)	O(7)–P(2)–O(5)	108.8(10)
O(3)–P(2)–O(5)	108.3(5)	O(3)^c–P(2)–O(5)	108.3(5)

^{a}Symmetry transformations used to generate equivalent atoms: $^a x-1/2,\ -y+1/2,\ z+1/2$; $^b -x+1/2,\ -y+1/2,\ z+1/2$; $^c -x,\ y,\ z$.

diffraction pattern of the decomposed sample indicates a poorly crystalline phase, for which all the lines correspond to those of the crystalline phase $Sn_2P_2O_7$ (JCPDS: 35-28); it seems likely that an amorphous phase with a Sn : P ratio greater than 3 : 2 is also present.

The synthesis of a novel tin oxyphosphate material containing one-dimensional chains constructed from capped tin phosphate cages is accomplished. The exclusive presence of four-coordinate Sn^{II} atoms along with a large number of three-coordinate oxygens makes this material unique amoung framework tin phosphates. This new phase, together with previously reported Sn(II) phosphate solids, illustrates profound structural influences of relatively minor modifications in reaction conditions and/or changes in the starting source for the tin. While the isolation of a one-dimensional solid with a $[SnO_4]$ distorted-square pyramidal core along with three-coordinate oxygen 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.

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