

NOTE

Room Temperature Synthesis and Structural Characterization of $\text{Sn}(\text{O}_3\text{PCH}_2\text{CH}_3)$: A Layered Phase of the Sn(II)-Organophosphonate System

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The title compound, $\text{Sn}(\text{O}_3\text{PCH}_2\text{CH}_3)$, (**1**), was synthesized from a mixture of SnF_2 , $\text{CH}_3\text{CH}_2\text{PO}_3\text{H}_2$, and H_2O in the mole ratio 1:0.85:1741 at 25°C for 1 h. Phosphonate (**1**) crystallizes in the orthorhombic space group *Pbca* with $a = 7.785(2)$, $b = 7.450(1)$, $c = 20.026(4)$ Å, $V = 1161.5(6)$ Å³, $Z = 8$, and $R = 0.0797$. The two-dimensional structure of (**1**) is composed of corner sharing $\{\text{SnO}_3\}$ pyramids and $\{\text{O}_3\text{PC}\}$ tetrahedra that alternate to form four- and eight-member polyhedral rings within the layers. The ethyl groups of the phosphonate tetrahedra are directed outward from both faces of the layer, effectively forming inorganic layers alternating with organic bilayers. © 1997 Academic Press

INTRODUCTION

The chemistry of metal phosphonates has undergone significant recent expansion due to their potential applications in catalysis, sorption, ion exchange, and intercalation chemistry (1). In general, current work has centered on *d*-block metal complexes of organophosphonate ligands which demonstrate a wide variety of structural types, including mononuclear species (2), complex molecular clusters (3), one-dimensional chains (4), layered structures (5–9), and three-dimensional frameworks (10–12). With the exception of the aluminum–organophosphonate system (13), however, interest in metal phosphonates has not extended appreciably to the main group metals, and the organophosphonate complexes of these metals remain relatively unexplored. While molecular clusters of tin–organophosphonates have been described (14), only two examples of structurally characterized

solid phases from this system have been reported (15), the one-dimensional material $[\text{Sn}(\text{HO}_3\text{PCH}_2\text{PO}_3\text{H})] \cdot \text{H}_2\text{O}$ and the three-dimensional solid $[\text{Sn}_2\{\text{O}_3\text{PC}(\text{OH})(\text{CH}_3)\text{PO}_3\}]$. These Sn(II)–organodiphosphonate solids provide the sole basis for evaluating the influence of the Sn(II) lone pair electrons on the structural features of such phases. In this paper, we report the synthesis of the layered material, $\text{Sn}(\text{O}_3\text{PCH}_2\text{CH}_3)$, (**1**), whose structure consists of corner-sharing $\{\text{SnO}_3\}$ pyramids and $\{\text{O}_3\text{PC}\}$ tetrahedra which alternate to form four- and eight-polyhedral rings. The ethyl groups of the phosphonate tetrahedra project from both faces of the layer such that, viewing the layers edge-on, there are alternating inorganic layers and organic bilayers.

EXPERIMENTAL

Synthesis

The title compound was synthesized conventionally from a mixture of SnF_2 (0.025 g, 0.16 mmole), $\text{CH}_3\text{CH}_2\text{PO}_3\text{H}_2$ (0.015 g, 0.14 mmole), and H_2O (5 mL, 278 mmole). The solids were placed in a Pyrex test tube (15 mm diameter, 125 mm length), and the water was added. The mixture was allowed to sit at room temperature, open to the atmosphere, for 1 h, at which time the product was collected by vacuum filtration. Colorless plates of (**1**) were obtained in 32% yield (based on Sn; 36% based on ligand). IR (KBr pellet, cm^{-1}): 2971(m), 1458(w), 1411(w), 1277(w), 1232(w), 1097(s), 1021(s), 735(m), 546(m), 485(m).

Crystallography

A single crystal, having the dimensions $0.30 \times 0.35 \times 0.10$ was selected for indexing. Structural measurements for compound (**1**) were performed on a Rigaku AFC5S diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation

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TABLE 1
Summary of Crystallographic Data for Sn(O₃PCH₂CH₂), (1)

Empirical formula	C ₂ H ₅ O ₃ PSn
Formula weight	226.7
Unit cell dimensions	$a = 7.785(2) \text{ \AA}$ $b = 7.4500(10) \text{ \AA}$ $c = 20.026(4) \text{ \AA}$
Volume	1161.5(6) Å ³
Space group	<i>Pbca</i>
Z	8
Density (calc.)	2.593 g/cm ³
Absorption coefficient	4.576 mm ⁻¹
Temperature (K)	253
Radiation	MoK α ($\lambda = 0.71073 \text{ \AA}$)
Final R indices (obs. data)	$R = 7.97\%$, $wR = 8.92\%$

TABLE 3
Selected Bond Lengths (Å) and Angles (°) for Sn(O₃PCH₂CH₂), (1)

Sn(1)–O(1)	2.095(21)	Sn(1)–O(2A)	2.100(22)
Sn(1)–O(3A)	2.089(22)	P(1)–O(1)	1.533(23)
P(1)–O(2)	1.583(24)	P(1)–O(3)	1.567(24)
P(1)–C(1)	1.687(39)	O(2)–Sn(1A)	2.100(22)
O(3)–Sn(1B)	2.089(22)	C(1)–C(2)	1.535(53)
O(1)–Sn(1)–O(2A)	82.5(8)	O(1)–Sn(1)–O(3A)	88.3(9)
O(2A)–Sn(1)–O(3A)	90.8(9)	O(1)–Sn(1)–O(2)	109.5(13)
O(1)–P(1)–O(3)	113.5(13)	O(21)–P(1)–O(3)	110.3(13)
O(1)–P(1)–C(1)	109.7(18)	O(2)–P(1)–C(1)	108.7(17)
O(3)–P(1)–C(1)	105.0(17)	Sn(1)–O(1)–P(1)	141.0(14)
P(1)–O(2)–Sn(1A)	123.2(13)	P(1)–O(3)–Sn(1B)	137.6(14)
P(1)–C(1)–C(2)	116.6(30)		

($\lambda(\text{MoK}\alpha) = 0.71073 \text{ \AA}$). The data were collected at a temperature of $-20 \pm 1^\circ\text{C}$ using the ω scan technique to 45° in 2θ at a scan speed of $8^\circ/\text{min}$. Crystallographic data for (1) are listed in Table 1. The intensities of three standard reflections measured after every 150 reflections remained constant throughout the data collection. An empirical absorption correction using the program DIFABS was applied to all data (16) and the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods (17). Tin, phosphorous, and oxygen atoms were refined anisotropically. Neutral atom scattering factors were taken from Cromer and Waber (18) and anomalous dispersion corrections were taken from those of Creagh and McAuley (19). All calculations were performed using the SHELXTL (20) crystallographic software package. Atomic positional parameters and isotropic temperature factors for (1) are given in Table 2. Selected bond lengths and angles for (1) are listed in Table 3.

TABLE 2
Atomic Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors ($\text{\AA}^2 \times 10^3$) for Sn(O₃PCH₂CH₂), (1)

	x	y	z	$U(\text{eq})^a$
Sn(1)	5785(3)	3024(3)	5563(1)	22(1)
P(1)	10052(13)	3626(13)	5912(5)	20(3)
O(1)	8398(26)	2594(29)	5755(11)	24(8)
O(2)	11347(27)	3439(31)	5306(11)	26(9)
O(3)	9743(28)	5654(30)	6081(11)	24(8)
C(1)	10981(55)	2761(55)	6602(18)	49(13)
C(2)	9838(50)	2579(48)	7222(17)	41(11)

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

RESULTS AND DISCUSSION

The title compound was synthesized at room temperature from a mixture of SnF₂, CH₃CH₂PO₃H₂, and H₂O in the mole ratios 1:0.85:1740. The colorless plates observed for (1) were not evident in attempts to reproduce the results using SnCl₂. The synthesis of (1) is similar to that of the one-dimensional material [Sn(HO₃PCH₂PO₃H)] · H₂O, as both were done in test tubes, with (1) at room temperature and Sn(HO₃PCH₂PO₃H) · H₂O at 4°C (the latter synthesis produced crystals at room temperature although a single crystal suitable for X-ray characterization could not be isolated). The infrared spectra of (1) exhibits bands at 1097 and 1021 cm⁻¹ associated with $\nu(\text{P}-\text{O})$ of the organophosphonate.

The title compound forms a layered structure, shown in Fig. 1a, composed of alternating corner sharing {SnO₃} pyramids and {O₃PC} tetrahedra. These building blocks come together to form the four- and eight-polyhedra rings evident in Fig. 1b. The larger eight-member ring is composed of one {SnO₃} pyramid and one phosphonate tetrahedron from each of four four-member rings. Thus, four four-rings are connected through each eight-polyhedral ring. Each phosphonate tetrahedron serves to bridge three Sn(II) sites through each of the three oxygen donors as shown in Fig. 1c.

The structure of (1) shows proximate coordination of the Sn(II) similar to that found in the previously reported Sn(II)-ethylenediphosphonate solid [Sn(HO₃PCH₂PO₃H)] · H₂O, (A), and the three-dimensional solid [Sn₂{O₃PC(OH)(CH₃)PO₃}], (B), with three oxygens intimately coordinated in the pyramidal {SnO₃} core. However, the Sn(II) centers in each of the three compounds exhibit variations in the three long-three short coordination commonly observed in Sn(II) solids (21). In (A), the three short bonds range from 2.123 to 2.172 Å, while the three longer Sn...O contacts with

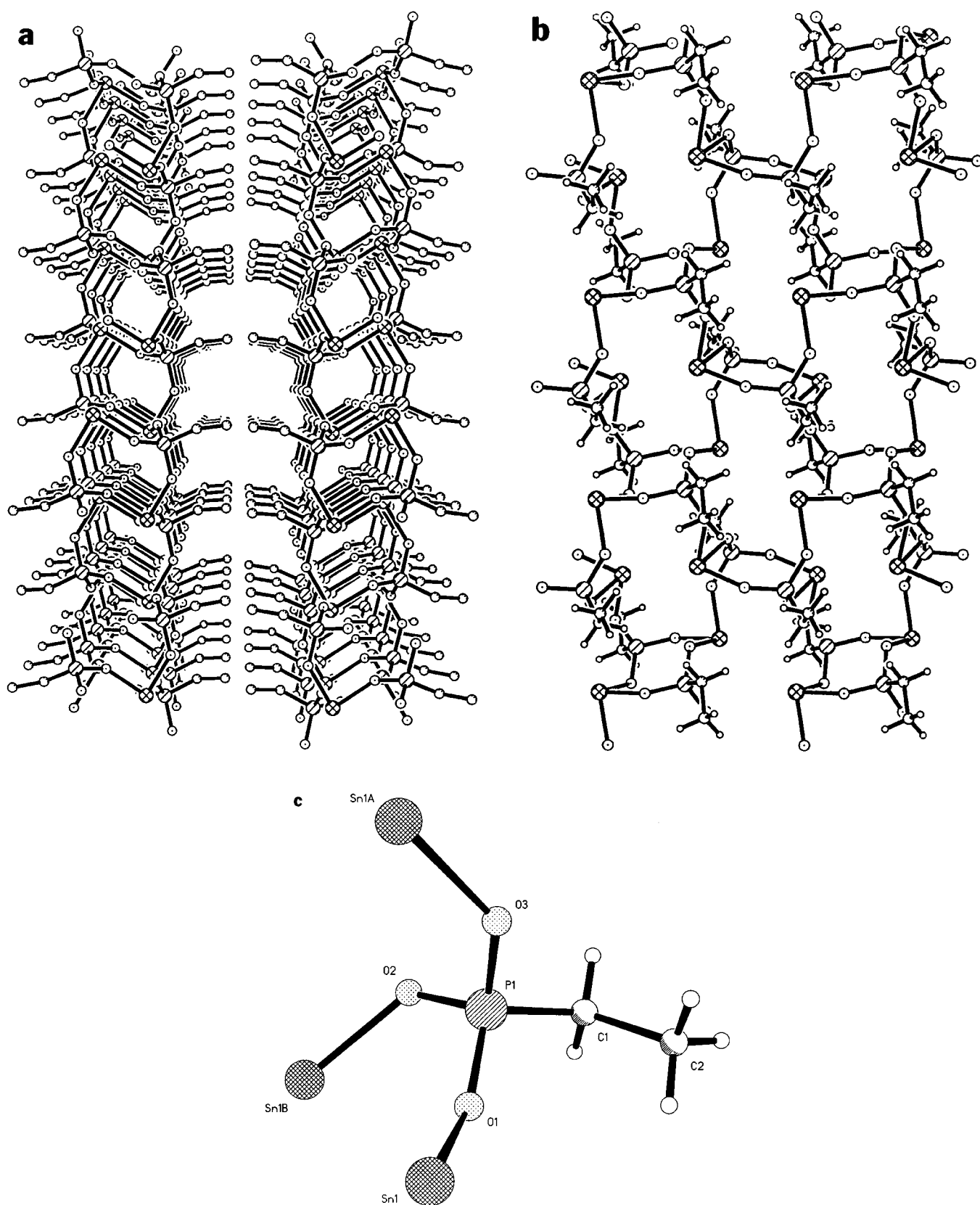


FIG. 1. (a) A view of the layers of (I). (b) A view of single layer of (I) parallel to c. (c) The environment of a phosphonate group.

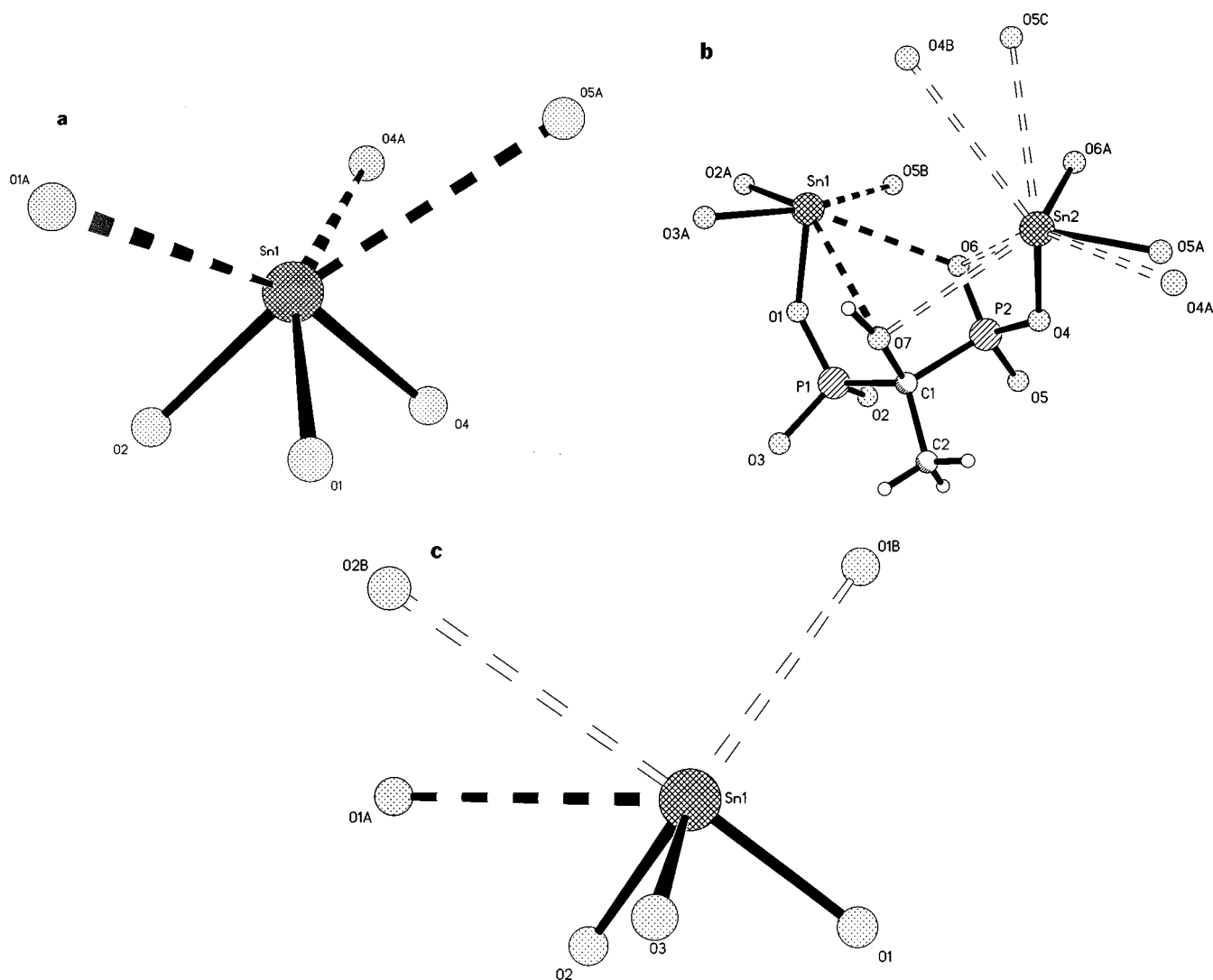


FIG. 2. (a) The environment of Sn(1) in (A). (b) A view of (B) showing the environment of Sn(1) and Sn(2). (c) The environment of the Sn(II) center in (I).

phosphonate oxygens from neighboring chains are at 3.096 to 3.243 Å as shown in Fig. 2a. Compound (B) possesses two distinct tin centers, Sn(1) and Sn(2), which exhibit vastly different Sn(II) environments as shown in Fig. 2b. Sn(1) has three short Sn...O contacts at 2.096 to 2.162 Å and three long contacts, two with phosphonate oxygens at 3.110 and 3.137 Å and one with the hydroxyl group of the phosphonate ligand at 3.180 Å. While Sn(2) also exhibits three short contacts at 2.100 to 2.129 Å, instead of the three longer contacts in the 3.10 to 3.24 Å range observed for the other Sn(II) centers mentioned, this Sn(II) center exhibits five very long contacts ranging from 3.422 to 3.711 Å.

The {SnO₃} core of (I) exhibits Sn–O bonds with lengths ranging from 2.089 to 2.100 Å, shown in Fig. 2c, which are short relative to those of the Sn(II) centers in (A) and (B).

There are also three long Sn...O contacts, ranging from 3.260 to 3.506 Å. The shortest of these contacts, at 3.260 Å, is similar to those seen in (A). The others, at 3.484 and 3.506 Å, are in length similar to those of the Sn(2) site in (B), which are too remote to be considered a true second coordination sphere. The next nearest contact for Sn(1) in (I) is an oxygen at 3.797 Å, which is considerably longer than those considered as the three long interactions. There are additional Sn...Sn contacts in (I) at 3.904 Å while the three Sn(II) centers in (A) and (B) exhibit no additional Sn...Sn distances closer than 4.182 to 4.322 Å (see Table 4). It appears that in the two- and three-dimensional materials the steric constraints imposed by the {SnO₃} pyramidal unit preclude formation of the conventional three long–three short interaction seen in compounds of lower-dimensionality.

TABLE 4
Selected Sn...O Distances for (1), (A), and (B) in Figs. 2a–c (Å)

(1)		(B)	
Sn1–O1	2.095	Sn1–O1	2.096
Sn1–O2	2.100	Sn1–O2A	2.118
Sn1–O3	2.089	Sn1–O3A	2.162
Sn1–O1A	3.260	Sn1–O5B	3.137
Sn1–O1B	3.484	Sn1–O6	3.110
Sn1–O2B	3.506	Sn1–O07	3.180
(A)		Sn2–O4	2.100
Sn1–O1	2.172	Sn2–O5A	2.129
Sn1–O2	2.170	Sn2–O6A	2.127
Sn1–O4	2.123	Sn2–4A	3.549
Sn1–O1A	3.243	Sn2–O4B	3.711
Sn1–O4A	3.131	Sn2–O5C	3.692
Sn1–O5A	3.096	Sn2–O6	3.515
		Sn2–O7	3.422

The structure of (1) shares a common motif of the family of layered metal–organophosphonate phases: the ethyl groups project from both faces of the inorganic Sn/O/P layer to produce a repeating pattern of alternating inorganic layers and organic bilayers with a repeat distance of 7.76 Å. However, in contrast to the hydrothermal techniques generally employed to prepare metal–organophosphonate phases, (1) is prepared in good yield at room temperature. This observation suggests that functional subunits may be introduced so as to tune the structure/function properties of the material. Furthermore, a variety of intercalates may be incorporated by either pre- or postsynthesis introduction in order to impart the control offered by supramolecular architecture to the intracrystalline environments of these extended arrays.

CONCLUSION

The title compound is an example of a layered Sn(II)–organophosphonate solid phase, whose structure exhibits the motif of alternating organic–inorganic layers. This new phase, together with the two previously reported Sn(II)–organophosphonate solids, shows the profound effects which slight changes in organophosphonate substituent and reaction conditions may have on the solid product. While the isolation of a two-dimensional solid with the {SnO₃}

pyramidal core provides more 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 synthesis of potentially open-framework materials.

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