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Synthesis and structural characterization of a novel tin(II) phosphonate, $Sn_2(O_3PCH_3)(C_2O_4)$

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The title compound, $Sn_2(O_3PCH_3)(C_2O_4)$, was synthesized hydrothermally using methylphosphonic acid and tin oxalate in the presence of butylamine. It crystallizes in the monoclinic space group $P2_1/m$ (no. 14) with the lattice parameters $a=4.723(1)$, $b=15.196(1)$, $c=6.147(1)$ Å, $\beta=102.1(1)°$, $V=431.3(1)$ Å^3, $Z=4$. The final R values are $R=2.99$, $R_w=6.1$ and $S=1.04$. The structure comprises a network of vertex-linked truncated square-pyramidal SnO_4 units and tetrahedral O_3PC units which gives rise to three-membered rings, *via* a three-coordinate oxygen, which are linked together forming one-dimensional chains. These chains are connected together *via* the oxalate group forming the structure.

Introduction

The discovery of a series of microporous aluminophosphates by Wilson *et al.*[1] in 1982 opened up the possibility of designing new materials for sorption and catalysis. Variation of the starting gel compositions and synthesis conditions has led to the successful isolation and characterization of a large number of new aluminophosphate materials with profoundly different porous architectures; some of them adopt structures that are similar to the naturally occurring aluminosilicate zeolites, *e.g.*, $AlPO_4$-37 (faujasite) and $AlPO_4$-34 (chabazite), but others, *e.g.*, $AlPO_4$-5, appear to be unique. It is becoming apparent that open-framework materials based on phosphate based networks have an astonishingly diverse structural chemistry as shown by the synthesis and characterization of other metal phosphates, *viz.*, iron,[2] cobalt,[3,4] vanadium,[5] molybdenum[6] and zinc.[7] Most of these materials are synthesized in the presence of an organic amine as the structure directing agent. The organic moiety is normally accommodated within the cavities and channels of these open structures and, in many cases, can be removed by post-synthesis treatments such as calcination or chemical extraction (leaching).

In the course of a program aimed at producing new open-framework structures, we have recently shown that open-framework tin(II) phosphate compounds[8–11] can be synthesized with the aid of organic structure-directing molecules. It is observed that open structures based on phosphonate networks can also be made and show architectures that are similar to the phosphate networks; these materials have been the subject of intense scientific research recently.[12,13] The chemistry of metal phosphonates has undergone significant expansion due to their potential application in catalysis, sorption, ion exchange and intercalation chemistry.[12] Most of the earlier studies on the phosphonates have centered on d-block elements with the exception of the aluminium–organophosphonate system.[13] Recently, Haushalter *et al.* extended the phosphonate chemistry into the main group elements by using substituted phosphonic acids and made a variety of new open-framework architectures based on V and Sn.[14,15] From the diversity of the structures established for tin phosphates and phosphonates, it is clear that the system, like the aluminophosphates, can form chain, layered and three-dimensional networks. Further, the Sn^{II}–organophosphonate solids provide a basis for evaluating the directional influence of the Sn^{II} lone pair of electrons in controlling the structure of a solid. In this paper, the hydrothermal synthesis and single crystal X-ray structure of a new tin(II) phosphonate material are presented. The structure is made by the networking of vertex-linked truncated square-pyramidal $[SnO_4]$ units and tetrahedral $[O_3PC]$ units giving rise to three-membered rings, *via* a three-coordinate oxygen. These units are linked together forming one-dimensional chains which are connected together *via* the oxalate group forming the structure. To our knowledge, this is the first tin phosphonate material containing both four-coordinated tin and three-coordinated oxygen species in the same structure.

Experimental

The title compound, synthesized by the hydrothermal method employing methylphosphonic acid (Aldrich), is described below. In a typical experiment, 2.0671 g of the tin oxalate was dispersed in 10 ml of water. To this mixture 0.96 g of methylphosphonic acid was added and stirred vigorously. To this 1 ml of *n*-butylamine was added under continuous stirring. The final mixture was transferred and sealed in a PTFE-lined stainless steel autoclave (Parr, USA), and heated at 170 °C for 2 days under autogeneous pressure. The final composition of the mixture was $1.0\,SnC_2O_4 : 1.0\,CH_3PO(OH)_2 : 1.0$ butylamine : 55 H_2O. The resulting product, which contained large quantities of needle-shaped crystals and a very small amount of white powder, was filtered off and washed thoroughly with de-ionized water. The powder X-ray diffraction pattern indicated that the product was a new material; the pattern is entirely consistent with the structure determined by single crystal X-ray diffraction. We have carried out a retro-synthesis with no amine in the starting mixture and obtained a material identical to that presented in this paper.

A suitable colorless needle-shaped single crystal ($0.04 \times 0.04 \times 0.125$ mm) 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 full sphere of intensity data was collected in 2082 frames with ω 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 2577 reflections in the range $5 \leqslant 2\theta \leqslant 55°$. The lattice parameters are: $a=4.723(1)$; $b=15.196(1)$; $c=6.147(1)$ Å; $\beta=102.1(1)°$; $V=431.3(1)$ Å^3; space group $=P2_1/m$ (no. 14) and $Z=4$. A total of 4357 reflections were collected and these were merged to

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Table 1 Summary of crystal data, intensity measurements and structure refinement parameters for $Sn_2(O_3PCH_3)(C_2O_4)$

empirical formula	$SnPO_4C_2H_2$
crystal system	monoclinic
space group	$P2_1/m$ (no. 14)
crystal size/mm	$0.04 \times 0.04 \times 0.125$
a/Å	4.723(1)
b/Å	15.196(3)
c/Å	6.147(1)
β/°	102.1(1)
volume/Å^3	431.3(2)
Z	4
formula mass	239.7(1)
ρ/g cm^{-3}	2.77
λ(Mo-Kα/Å	0.71073
μ/mm^{-1}	4.64
2θ range/°	5.0–55.0
total data collected	4357
index ranges	$-6 \leqslant h \leqslant 6$, $-19 \leqslant k \leqslant 20$, $-8 \leqslant l \leqslant 8$
unique data	1094
observed data [$I > 2\sigma(I)$]	900
R_{merg}	4.23
R indices [$I > 2\sigma(I)$]	$R = 2.99$; $R_w = 6.1$
R (all data)	$R = 4.33$; $R_w = 6.4$
goodness of fit, S	1.04
no. of variables	71
largest difference map peak and hole/e Å^{-3}	0.810 and -0.860

give 1094 unique reflections ($R_{\mathrm{merg.}} = 4.23$) of which 900 were considered observed with $I > 2\sigma(I)$. The pertinent experimental conditions for the structure determination are listed in Table 1.

The structure was solved by direct methods using SHELXS-86[16] and difference Fourier syntheses. The absorption correction was based on symmetry equivalent reflections using the SADABS[17] program. Other effects, such as absorption by the glass fiber, were simultaneously corrected. All the hydrogen positions were located in the difference Fourier map. The last cycles of refinement included atomic positions for all the atoms 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 $|F^2|$ was carried out using the SHELXSTL-PLUS[18] package of programs. The final Fourier map had minimum and maximum peaks of -0.86 and 0.81 e Å^{-3}, respectively. Final R values, $R = 2.99$ and $R_w = 6.1$ and $S = 1.04$, were obtained for a total of 71 parameters. The final atomic coordinates are given in Table 2. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/92.

Results and Discussion

The asymmetric unit of $Sn_2(O_3PCH_3)(C_2O_4)$ is given in Fig. 1. The entire structure can be considered to be built from the networking of the truncated square-pyramidal $[SnO_4]$ units which are vertex-linked through oxygen with the tetrahedral $[PO_3C]$ units. The connectivity between these units is such that they form three-membered rings (*i.e.*, 2 tin and 1 phosphorus) which are linked to form one-dimensional chains along the a axis as shown in Fig. 2 and 3. The individual chain units are related to each other by the mirror plane and are connected by the oxalate group forming the structure (Fig. 3). Thus, while the chains form the one-dimensional unit, the linkages between the chains form a zig-zag layer type of arrangement along the ab plane, the layers being made of three- and six-membered rings (Fig. 2). The layers, in turn, are held together by the lone pairs of electrons of the Sn^{II} atoms as well as by the interaction between the methyl group of the phosphonate and the lone pair of electrons. Similar types of inter-layer interactions have been observed earlier for other tin(II) phosphonates.[15]

Table 2 Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [Å$^2 \times 10^3$] for $Sn_2(O_3PCH_3)(C_2O_4)$

atom	x	y	z	U(eq)^a
Sn(1)	2068(1)	6056(1)	1048(1)	19(1)
P(1)	−2347(4)	7500	2734(3)	16(1)
O(1)	2457(8)	5858(2)	4702(6)	26(1)
O(2)	5147(8)	4806(2)	2236(5)	28(1)
O(3)	714(10)	7500	2233(8)	21(1)
O(4)	6145(7)	6656(2)	1754(6)	27(1)
C(1)	−2116(22)	7500	5660(15)	36(2)
C(10)^b	5748(10)	4699(3)	4284(8)	19(1)

^{a}Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor ^{b}Carbon atom belonging to the oxalate group.

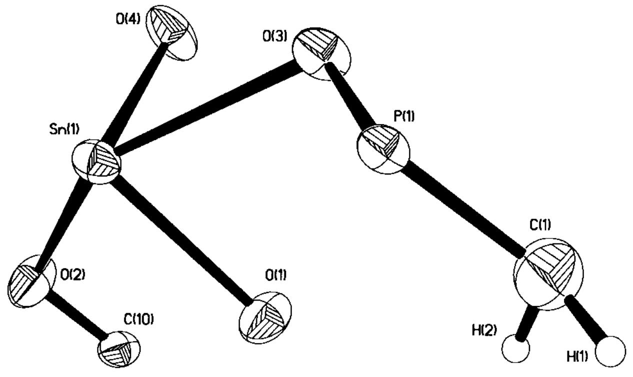
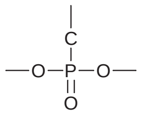


Fig. 1 Asymmetric unit of $Sn_2(O_3PCH_3)(C_2O_4)$. The thermal ellipsoids are given at 50% probability.

It is well established that the branched phosphate unit shown facilitates the formation of chain or cyclic phosphates.[19]



$$\text{—O—}\underset{\underset{\displaystyle \text{O}}{\|}}{\overset{\overset{\displaystyle |}{\text{C}}}{\overset{|}{\text{P}}}}\text{—O—}$$

Methylphosphonic acid, which was used in the synthesis, can generate similar branched phosphate units in solution and one might expect the formation of cyclic or chain architectures to result from such interactions. The present solid, indeed, possesses three-membered cyclic rings, made of two Sn atoms and one P atom *via* a three-coordinated oxygen, connected together forming linear chains (Fig. 2). Unlike the known tin(II) compounds, where Sn atoms are normally three-coordinated (trigonal pyramidal), the present material exhibits a rather unusual four-coordinated Sn^{II} (truncated square-pyramidal). Recently, it has been observed that the presence of four-coordinated Sn^{II} atoms in an open-framework structure probably promotes the formation of three-coordinated oxygen atoms[20] and the title compound possesses such three-coordinated oxygen units too.

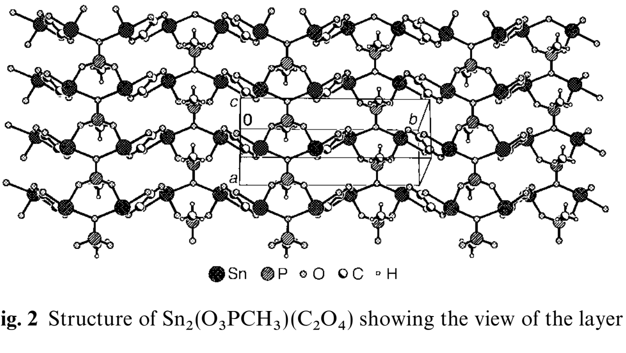


Fig. 2 Structure of $Sn_2(O_3PCH_3)(C_2O_4)$ showing the view of the layer

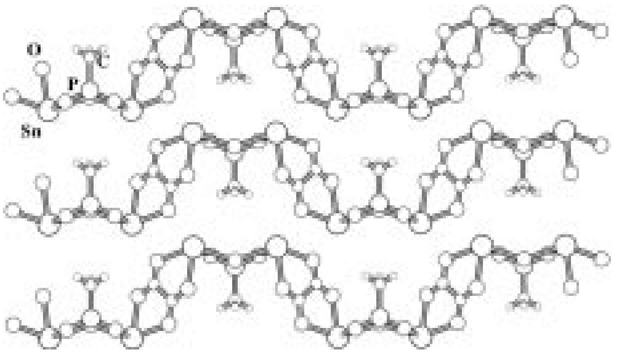


Fig. 3 Structure of $Sn_2(O_3PCH_3)(C_2O_4)$ viewed along the *a* axis showing the three-membered rings and the connectivity between them

Of the four oxygens bonded to the Sn atoms, two belong to the oxalate group with Sn—O distances of 2.235 and 2.411 Å, the third oxygen is at a distance of 2.092 Å and the fourth oxygen has the longest distance of 2.439 Å; this is the three-coordinated oxygen (bonds two Sn and one P atoms) (Table 3). The Sn—O—Sn angles are in the range 70.8–142.9° (av. 93.4°). The largest angles, again, are observed for the three-coordinated oxygen. Similar structural features have also been observed recently in other tin phosphates exhibiting four-coordinated Sn^{II} and three-coordinated oxygen atoms.[20] In the case of the $[O_3PC]$ tetrahedra, the distances vary from 1.528 to 1.779 Å and the angles from 107.5–114.1°. The longest distance is for the P—C bond. From the P—O/C distances and O—P—O/C angles, it is clear that the $[O_3PC]$ tetrahedron is uniform in nature, in agreement with those observed previously.[12–15]

The structure of the title compound is unique in that the oxalate group provides the link between the two tin phosphonate chains, the oxalate group having formed by the decomposition of the tin oxalate used in the starting mixture. The structure has some similarities to the previously reported structure of stannous hydroxide phosphate, $Sn_2(OH)PO_4$.[21,22] In the structure of stannous hydroxide phosphate, the SnO_3 and PO_4 units are connected *via* the —OH groups. Four-membered zig-zag chains are present in the structure along the *b* axis, while the layers formed along the *ab* plane are held together *via* the lone pair of electrons of the Sn^{II} atoms. In the present structure we observe that the layers formed along the *ab* plane are again held together by the lone pair of electrons. However, the presence of the four-coordinate Sn^{II} and three-coordinate oxygens is unique and leads to three-membered ring chains rather than the four-membered ones observed for $Sn_2(OH)PO_4$. Also, it is to be noted that most of the tin phosphate and phosphonate materials reported in the literature[9–15] contain only phosphate or phosphonate groups directly attached to the tin atoms and the present study is one of the few examples illustrating the use of other structural moieties, *viz.*, oxalate ions, forming part of the framework along with the phosphate groups. At present, efforts are underway to introduce other anions as part of the framework to create new structures based on tin and phosphorus.

Table 3 Selected bond distances and bond angles for $Sn_2(O_3PCH_3)(C_2O_4)$

bond distances/Å			
Sn(1)—O(1)	2.235(3)	Sn(1)—O(2)	2.411(3)
Sn(1)—O(3)	2.439(2)	Sn(1)—O(4)	2.092(3)
P(1)—O(3)	1.540(5)	P(1)—O(4)×2	1.528(3)
P(1)—C(1)	1.779(9)	C(10)—O(1)×2	1.265(6)
C(10)—O(2)	1.241(6)	C(10)—C(10)	1.540(9)
bond angles/°			
O(1)—Sn(1)—O(2)	70.84(1)	O(1)—Sn(1)—O(3)	78.04(1)
O(1)—Sn(1)—O(4)	88.4(2)	O(2)—Sn(1)—O(3)	142.9(2)
O(2)—Sn(1)—O(4)	79.04(1)	O(3)—Sn(1)—O(4)	80.42(1)
O(4)—P(1)—O(4)	114.1(3)	O(4)—P(1)—O(3)×2	107.5(2)
O(4)—P(1)—C(1)×2	108.8(2)	O(3)—P(1)—C(1)	109.9(4)
C(10)—O(2)—Sn(1)	113.9(3)	C(10)—O(1)—Sn(1)	119.4(3)
O(2)—C(10)—O(1)	125.1(4)	O(2)—C(10)—C(10)	117.8(5)
O(1)—C(10)—C(10)	117.5(5)		

In conclusion, the title compound forms another example of the isolation of a low-dimensional tin phosphonate material. This new phase, together with the previously reported Sn^{II} organophosphonate 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 $[SnO_4]$ truncated 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 phosphonate materials.

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