

Rapid communication

A novel inorganic–organic compound: Synthesis and structural characterization of tin(II) phenylbis(phosphonate), $\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)$

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Abstract

A novel tin(II) phenylbis(phosphonate) compound has been synthesized hydrothermally and its structure has been determined by single crystal X-ray diffraction. The structure is monoclinic, space group $P2_1/c$ (no. 14), $a = 4.8094(4)$, $b = 16.2871(13)$, $c = 6.9107(6)$ Å; $\beta = 106.292(6)^\circ$, $V = 519.59(7)$ Å³, $Z = 2$. The three-dimensional structure consists of 3-coordinated tin and 4-coordinated phosphorus double layers separated (pillared) by phenyl rings. These phenyl rings are placed 4.8 Å apart along the a -axis in the structure resulting in lower surface area (~ 14 m²/g). The porosity has been increased by replacing phenyl groups by methyl groups (~ 31 m²/g).

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1. Introduction

Organic–inorganic hybrid materials appear as a creative alternative for obtaining new materials with unusual properties [1]. The challenge for such porous materials is to increase and modulate the pore sizes for selective adsorption and other applications. Pure inorganic systems often have their limitations owing to the relatively small sizes of the polyhedral centers and their limited means of connection. The strategy is to incorporate organic functionality within a robust inorganic framework and to avail both metal and organic species for the guest molecules within the pores and even functionalize the organic part [2]. These hybrid materials have potential applications in catalysis, photonics, separation, gas storage and molecular sensing in addition to the structural diversity [3].

The history of hybrid phosphonate materials may be traced back to the preparation of zirconium phosphonate by Alberti et al. [4] and Jacobson et al. [5] who used intercalation as the main tool to increase the interlayer spacing of the layered materials. For example, zirconium phenylphosphonate is a layered compound [6], but Dines et al. [7] demonstrated that by utilizing a terminal bisphosphonic acid the layers can be cross-linked. By using spacer molecules they claimed to have created porosity. Investigations of di-, tri-, and tetra-valent metal phosphonates in recent years have yielded exciting structural diversity with interesting chemistries and applications [8–19]. However, it has recently been shown that the zirconium bis-phosphonates prepared in aqueous systems do not produce pores of uniform size [14]. By use of organic solvents Wang et al. were able to produce zirconium biphenylene bis(phosphonate) with high surface areas (350–400 m²/g) and narrow pore size distribution in the 10–20 Å range [8]. No spacer molecules were necessary. Metals such as tin(II), lead(II), and antimony(III) are of special interest since

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the lone pair at the metal center leads to interesting topologies and could give rise to open-framework materials with redox/acidic catalytic properties [20–22]. Recently, there was an interesting report in the literature that a layered tin(II) phosphonate has been prepared using phenylphosphonic acid as the ligand [23]. In the present work, we demonstrate that by choosing terminal bifunctional groups such as monophenylbis(phosphonic acid), one can connect these layers to form three-dimensional materials. The synthesis and structure of tin(II) phenylbis(phosphonate), a three-dimensional material is reported here for the first time. Also, substitution/incorporation of methyl phosphonic acid for part of the phenyl phosphonic acid yields fine particles with higher surface area than the tin(II) phenylphosphonate.

2. Experimental

The tin (II) compound was synthesized by hydrothermal methods. In a typical synthesis, 1.03 g of tin(II) oxalate, 0.6 g of monophenylbis(phosphonic acid) and 20 g water in the molar ratio 2:1:1000 were mixed. This mixture was stirred until it became homogeneous and the final mixture was sealed in a PTFE-lined stainless steel autoclave and heated at 140 °C for 3 days under autogenous pressure. The resulting product, which contained a mixture of powder and colorless tiny crystals, was filtered and washed thoroughly with de-ionized water. The powder X-ray diffraction pattern indicated that the product was a new material. Thermo Gravimetric Analysis (TGA) was performed under airflow from room temperature to 800 °C. Experimental weight loss (calculated weight loss = 12.8%, observed weight loss = 14.44%) corresponds to the burning of organic moiety to the final product of $\text{Sn}_2\text{P}_2\text{O}_7$, which was confirmed by a powder X-ray diffraction pattern of the final product [JCPDS: 35-28]. The surface area measurements were performed on an Autosorb-6 (Quantachrome) unit using nitrogen adsorption at liquid nitrogen temperature. Both pure N_2 as an adsorbate and N_2 in helium as a carrier gas were utilized. Pre-calcined samples were outgassed at 200–390 °C. The resulting experimental data were analyzed using the software supplied by Quantachrome Corporation and surface areas were calculated on the basis of the BET model.

A tiny crystal was chosen, coated with a cryogenic protectant (mineral oil), and was then mounted on a nylon loop which in turn was fixed to a magnetic base. The mounted crystal was then placed in a cold nitrogen stream (Oxford) maintained at 110 K. A BRUKER GADDS D8 DISCOVER X-ray three-circle diffractometer equipped with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and with a graphite monochromator with a 0.5 mm collimator and a Hi-star multi-wire two-dimensional

area detector (crystal to detector distance = 50 mm) was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the FRAMBO software suite, version 4.1.13 [25]. The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions.

Initially, 180 data frames were taken at widths of 0.5° with an exposure time of 30 s. The reflections obtained from these frames were indexed using cell_now program [26] and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the hkl overlays on several frames of data. No super-cell or erroneous reflections were observed.

Crystal data for $\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)$ are as follows: monoclinic, space group $P2_1/c$ (no. 14), $a = 4.8094(4)$, $b = 16.2871(13)$, $c = 6.9107(6) \text{ \AA}$; $\beta = 106.292(6)^\circ$, $V = 519.59(7) \text{ \AA}^3$, $Z = 2$, $M = 471.41$, and $\rho_{\text{calc}} = 3.013 \text{ kg/m}^3$. A total of 4226 reflections were collected in the range $-5 < h < 5$, $-18 < k < 17$, $-7 < l < 7$. These were merged to give 714 unique data ($R_{\text{merge}} = 6.27\%$). The structure was solved by direct methods using SHELXS [27] and difference Fourier syntheses. The absorption correction was based on symmetry equivalent reflections using the SADABS [28] program. The last cycles of refinement included atomic positions and anisotropic thermal parameters for all the nonhydrogen atoms. Final $R = 2.67\%$, $R_w = 5.63\%$ [$I > 2\sigma(I)$] and $S = 0.955$ were obtained for 73 parameters. The final Fourier map minimum and maximum were -0.557 and 0.714 e/\AA^3 , respectively. Full matrix-least-squares structure refinement against F^2 was carried out using the SHELXSTL-PLUS [29] programs.

3. Results and discussion

The hydrothermal reaction of tin(II) oxalate, monophenylbis(phosphonic acid) and water in the molar ratio 2:1:1000 at 140 °C for 3 days yielded a mixture of single crystals and powder. The powder X-ray diffraction pattern of the obtained material was very new. The thermogravimetric analysis on this compound showed a total weight loss of 14.44% (calculated weight loss = 12.8%) corresponding to the burning of the organic moiety of the $[\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)]$ compound to the final product of $\text{Sn}_2\text{P}_2\text{O}_7$, which was confirmed by powder X-ray diffraction pattern of the final product [JCPDS: 35-28]. Interestingly, the organic is removed in two steps. The first weight loss after removal of about 1% solvent begins at 350 °C and is complete at 400 °C with a weight loss of 6.25%. The remaining weight loss (~8%) begins at 522 °C and is complete at 600 °C. Additional studies are underway to identify the reasons for this odd behavior.

The asymmetric unit of tin(II) phenylbis(phosphonate), is relatively simple containing only one Sn and one P atom (totally 8 non-hydrogen atoms) displayed in Fig. 1. The atomic coordinates are given in Table 1 and

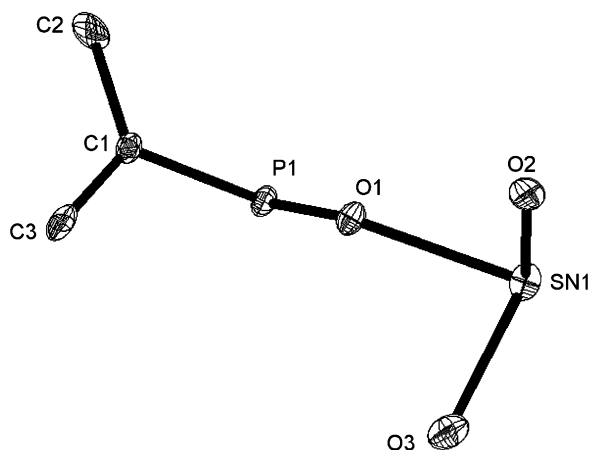


Fig. 1. Asymmetric unit of $\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)$ (thermal ellipsoids are given at 50% probability).

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)$. $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U^{ij} tensor

Atoms	x	y	z	$U(\text{eq})$
Sn(1)	9760(1)	6682(1)	9059(1)	16(1)
P(1)	5856(4)	8394(1)	7565(3)	11(1)
O(1)	7969(9)	7851(3)	9114(6)	13(1)
O(2)	12935(9)	7054(3)	11769(7)	15(1)
O(3)	7052(10)	6309(3)	10872(7)	20(1)
C(1)	5322(14)	9302(4)	8892(10)	11(2)
C(2)	6458(14)	10059(4)	8552(10)	20(2)
C(3)	3850(18)	9250(5)	10380(11)	21(2)

Table 2

Bond lengths (\AA) and angles (deg) for $\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)$

Sn(1)–O(1)	2.095(4)	O(3)–Sn(1)–O(2)	88.28(18)
Sn(1)–O(3)	2.133(5)	O(3)#1–P(1)–O(1)	113.7(3)
Sn(1)–O(2)	2.145(4)	O(3)#1–P(1)–O(2)#2	112.3(2)
P(1)–O(3)#1	1.520(5)	O(1)–P(1)–O(2)#2	109.6(3)
P(1)–O(1)	1.533(4)	O(3)#1–P(1)–C(1)	105.7(3)
P(1)–O(2)#2	1.541(5)	O(1)–P(1)–C(1)	106.3(3)
P(1)–C(1)	1.796(7)	O(2)#2–P(1)–C(1)	109.0(3)
O(2)–P(1)#3	1.541(5)	P(1)–O(1)–Sn(1)	135.0(3)
O(3)–P(1)#4	1.520(5)	P(1)#3–O(2)–Sn(1)	122.1(3)
C(1)–C(2)	1.396(10)	P(1)#4–O(3)–Sn(1)	141.9(3)
C(1)–C(3)	1.405(10)	C(2)–C(1)–C(3)	118.5(6)
C(2)–C(3)#5	1.377(10)	C(2)–C(1)–P(1)	121.5(5)
C(3)–C(2)#5	1.377(10)	C(3)–C(1)–P(1)	119.9(5)
O(1)–Sn(1)–O(3)	85.76(18)	C(3)#5–C(2)–C(1)	121.8(6)
O(1)–Sn(1)–O(2)	85.58(17)	C(2)#5–C(3)–C(1)	119.7(7)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y+3/2, z-1/2$; #2 $x-1, -y+3/2, z-1/2$; #3 $x+1, -y+3/2, z+1/2$; #4 $x, -y+3/2, z+1/2$; #5 $-x+1, -y+2, -z+2$.

selected bond distances and angles in Table 2. The Sn and P centers are three- and four-coordinated, respectively. The trigonal pyramidal SnO_3 (lone pair occupying the pyramidal position) units are vertex linked via oxygens to phosphorus atoms in the present structure. The structure is made of double tin phosphate (DTP), $\text{Sn-O}_3\text{-P}$ layers separated by phenyl rings, viewed along the c -axis (Fig. 2). The Sn atoms are arranged in rows parallel to the a -axis. Each phosphonate group bonds to three Sn atoms across two of the metal rows. Adjacent rows are alternately displaced along the b -axis as shown in Fig. 2. The Sn–O distances are in the range 2.095–2.145 \AA (avg. 2.124 \AA) and O–Sn–O bond angles are in the range 85.58–88.28° (avg. 86.54°), typical of

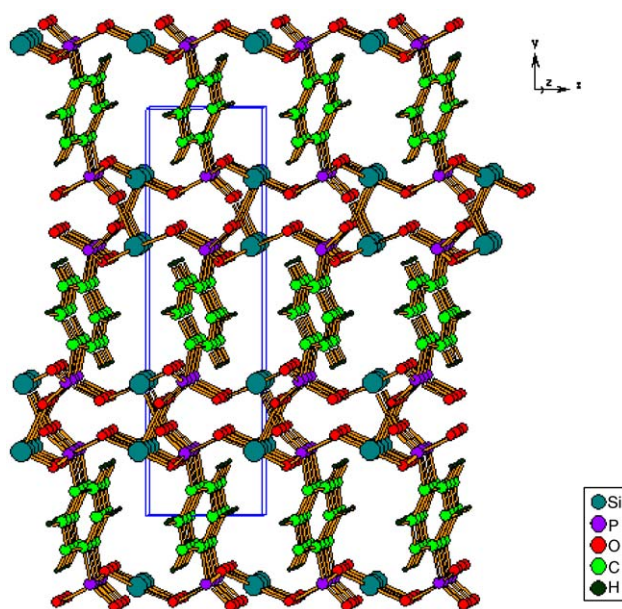


Fig. 2. Three-dimensional structure of $\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)$ viewed along c -axis.

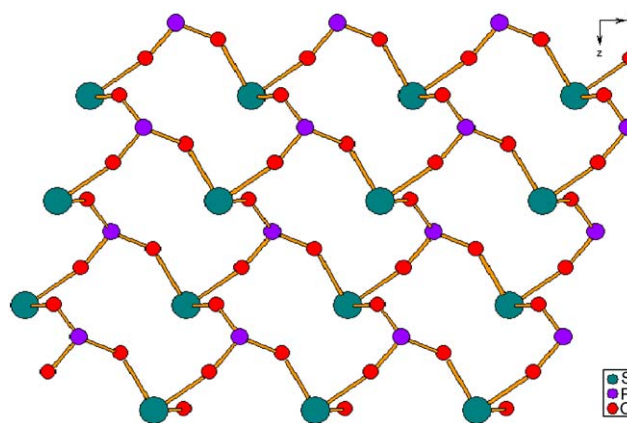


Fig. 3. The view of the Sn–P layers of $\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)$ in the ac plane.

three-coordinated Sn in the 2+ oxidation state and in agreement with the previously reported tin(II) phosphate/phosphonate materials [22,23]. The P atom is connected to three oxygens in the *ac* plane of the layer (Fig. 3). The Sn and P atoms alternate in the layer, and with respect to the metal atoms, define a graphite-like arrangement of edge-sharing 12-membered rings in the *ac* plane (Fig. 3). The fourth coordination site for the P atoms is the carbon atom from the out-of-plane phenyl group. The P–O distances are in the range 1.520–1.541 Å (avg. 1.531 Å) and the O–P–O angles in the range 109.6–113.7° (avg. 111.9°). The phenyl groups arrange in *cis*- and *trans*-fashion alternatively between the DTP

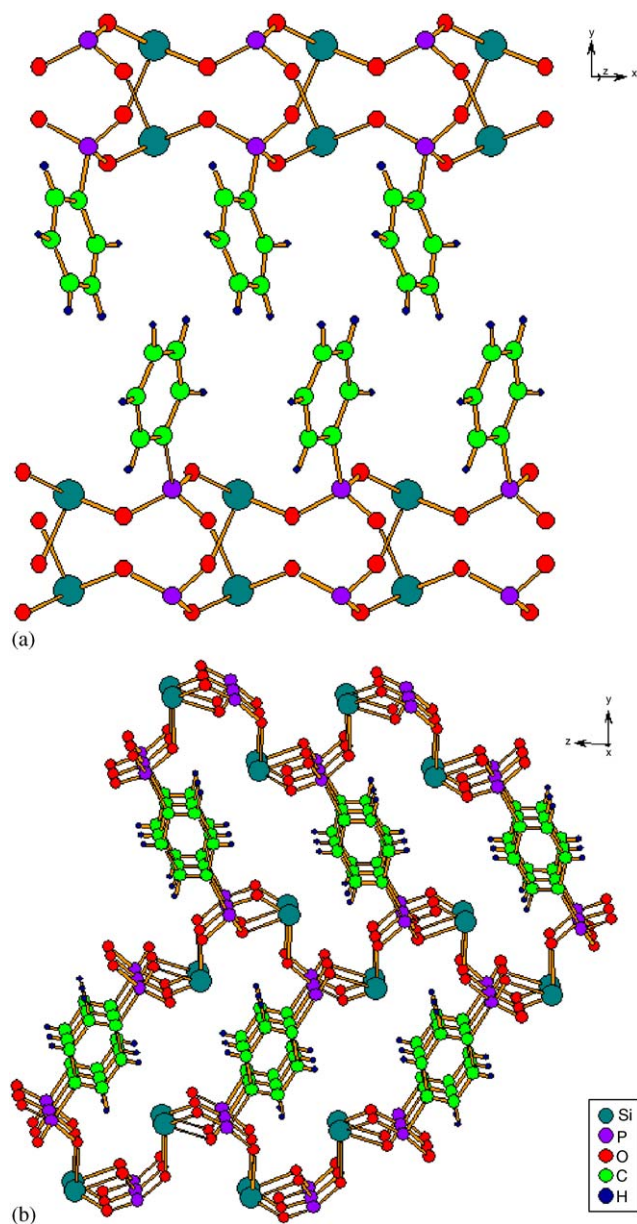


Fig. 4. (a) The layer-structure of the reported tin(II) phenylphosphonate (from Ref. [24]). (b) The structure of $\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)$ along the *bc* plane.

layers, doubling the interlayer spacing along the *b*-axis (Fig. 2). The narrow tunnel along the *c*-axis is made of 16-membered rings (4.8×9.8 Å) containing phenyl groups (Fig. 2).

The present structure has a very close resemblance to the layered tin(II) phosphonate reported by Lansky et al. [24]. They have used the mono-functional phenylphosphonic acid as the ligand to connect tin(II) metal and obtained a layered material as shown in Fig. 4a [24]. In contrast, the bi-functional ligand such as phenylbis (phosphonic) acid, as in the present case, yielded a three-dimensional tin(II) phosphonate. The layers are creneled as seen in a view down the *a*-axis (Fig. 4b) and connected to adjacent layers through the phenyl rings. In another interesting view, pillared tin(II) phosphonate could be obtained by inserting a Sn–O–P layer (after rotating by 180°) between the hydrophobic phenyl rings of the reported [24] layered tin(II) phosphonate along the *b*-axis (Fig. 4a and b). The present structure also contains 12-membered rings, viewed along the *a*-axis, incorporating phenyl groups (Fig. 4b).

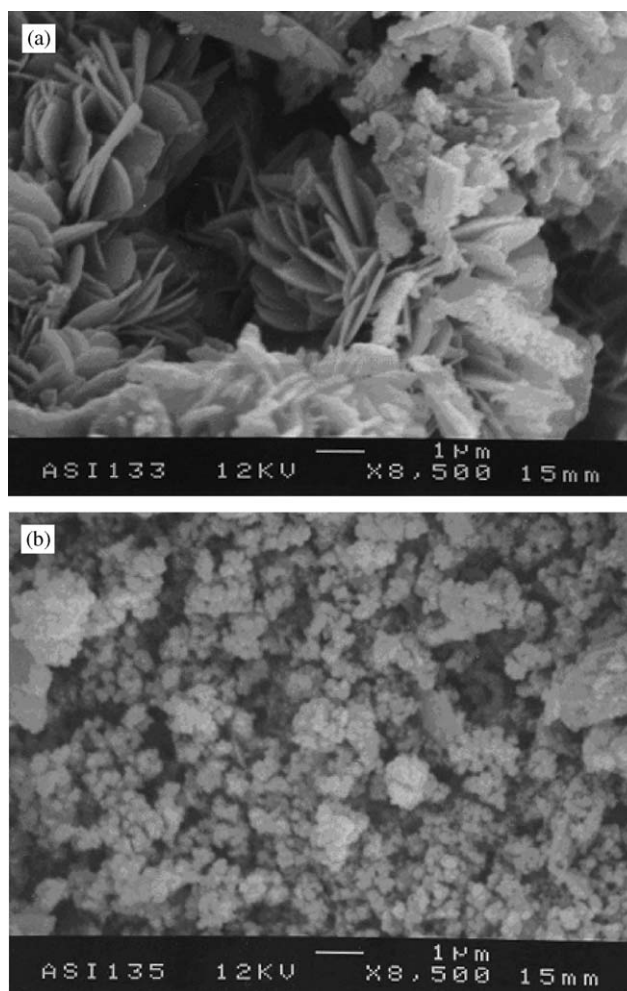


Fig. 5. SEM pictures of (a) $\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)$ and (b) $\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)_{0.5}(\text{CH}_3\text{PO}_3)$.

In order to create porosity in the tin(II) phenylbis(phosphonate) structure, methyl phosphonic acid was used to replace half the phenyl phosphonic acid having the starting composition $\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_5\text{PO}_3)_{0.5}(\text{CH}_3\text{PO}_3)$. The product did not contain any single crystals but only the powder and at present we are not successful in indexing the powder pattern. The surface area results were encouraging; $14\text{ m}^2/\text{g}$ for the pure phenylbis(phosphonate), $[\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)]$ compound and $31\text{ m}^2/\text{g}$ for the mixed $\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)_{0.5}(\text{CH}_3\text{PO}_3)$ derivative. The nitrogen adsorption isotherm resembles Type II for $[\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)]$ compound and Type IV for the mixed $\text{Sn}_2(\text{PO}_3\text{C}_6\text{H}_4\text{PO}_3)_{0.5}(\text{CH}_3\text{PO}_3)$ derivative. The higher surface area of $31\text{ m}^2/\text{g}$ arises mainly from the external surfaces but with 25% of the pores being internal. Examination of Figs. 4a and b suggests that replacement of the phenyl by biphenyl groups and spacing them with methyl group should yield highly porous products. Such syntheses are in process (Fig. 5).

Acknowledgments

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