

A layered tin(II) phosphonate, [Sn(C₆H₅O₃P)]_n

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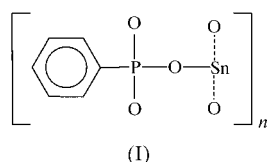
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Poly[tin(II)- μ -phenylphosphonato], [Sn(C₆H₅O₃P)]_n, was synthesized solvothermally at 423 K and crystallized in the monoclinic system, space group *Cc*. The inorganic layers consist of alternating pyramidal Sn and tetrahedral P centers, joined by doubly bridging O atoms. The corner-sharing SnO₃ and PO₃C₆H₅ polyhedra define a corrugated layer of six-membered rings. The layers are connected along the unique *b* axis by interdigitated phenyl rings of the phenylphosphonate groups.

Comment

We are currently interested in the synthesis and characterization of extended germanates and stannates, the primary target being new materials for ion-exchange and catalytic applications. Using both traditional organic amine and non-traditional templating agents, we have discovered a series of framework and lower dimensionality materials based on lower group 14 metals (Salami *et al.*, 2001). We name these new materials BING-*n*, where BING is an acronym for the State University of New York (SUNY) at Binghamton, and *n* stands for a particular material.

Cheetham and co-workers have recently described a series of tin oxalates (Ayyappan *et al.*, 1998; Natarajan *et al.*, 1999) and tin phosphates (Natarajan & Cheetham, 1997; Natarajan *et al.*, 1998; Ayyappan *et al.*, 2000; Liu *et al.*, 2000). The latter contain interlayer or extra-framework organic ammonium groups. Cheetham and co-workers have also recently reported a tin oxalate methylphosphonate (Adair *et al.*, 1998). Here, we describe the crystal structure of BING-3, a layered tin phenylphosphonate, (I).



Compound (I) was synthesized in non-aqueous pyridine solvent containing tin oxalate, hydrogen fluoride and phenyl-

phosphonic acid. The structure consists of a tin phosphonate layer, where the Sn and P centers are three-coordinate in the plane of the layer *via* O atoms (Figs. 1 and 2). The fourth coordination site for the P atoms is an out-of-plane phenyl group; these groups alternate above and below the plane of the layer (Fig. 1). The Sn centers have pyramidal coordination, with three O atoms bridging to neighboring P centers. A lone pair of electrons is also present on the Sn atom. Oxalate is not present in the structure and was obviously eliminated from the Sn reagent under the synthetic conditions used.

The P and Sn atoms alternate in the layer and, with respect to the metal atoms, define a graphite-like arrangement of edge-sharing six-membered rings in the *ac* plane (Fig. 2). The interdigitated phenyl rings create a hydrophobic interlayer region that caps and separates the layers. The asymmetric unit

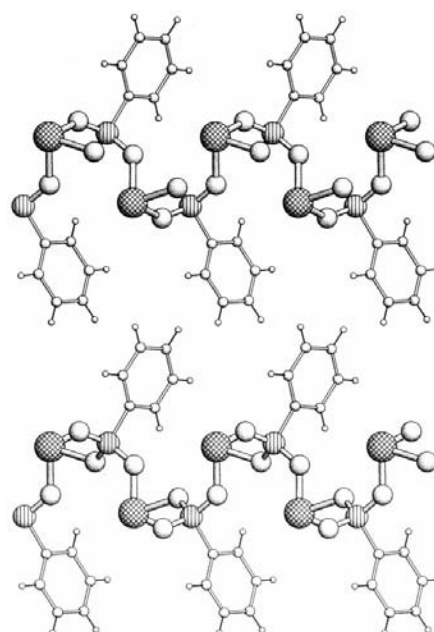


Figure 1

The crystallographic projection of (I) along *a*, highlighting the separation of the tin phosphonate layers by interdigitated phenyl rings (Sn are shown as hatched circles, P as striped circles, O as large grey circles, C as medium grey circles and H as small grey circles).

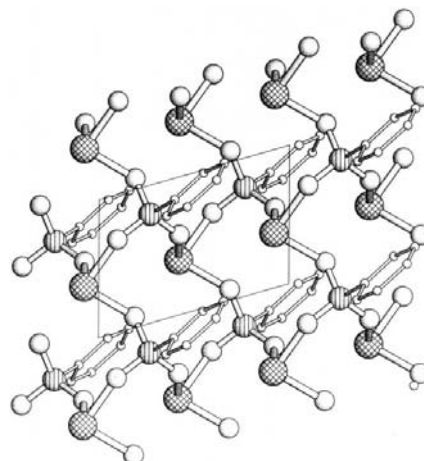


Figure 2

The *b* projection of one tin phosphonate layer of (I), with H atoms omitted for clarity. The shading scheme is as for Fig. 1.

is relatively simple, containing only one Sn and one P atom (Fig. 3).

Due to our interest in open-framework paramagnetic materials for magnetic-based applications, we have also performed the analogous synthesis with an equimolar amount of manganese sulfate in place of tin oxalate. We obtained a crystalline material, $[\text{Mn}(\text{C}_6\text{H}_5\text{O}_3\text{P})]$, whose crystal structure

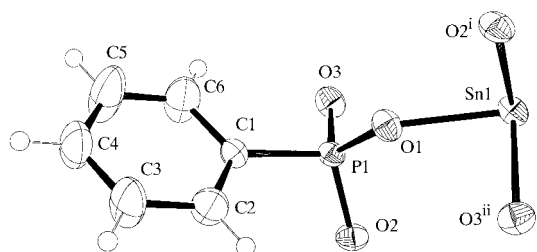


Figure 3
The molecular structure of (I), with the atom-labelling scheme and 50% probability displacement ellipsoids [symmetry codes: (i) $1+x, 1-y, \frac{1}{2}+z$; (ii) $x, 1-y, \frac{1}{2}+z$]. H atoms are shown as small spheres of arbitrary radii.

turned out to have been previously reported by Mallouk and co-workers (Cao *et al.*, 1988). Due to the success of both systems in making layered materials solvothermally, we are currently investigating Sn–Mn mixed-metal systems as a way of controlling paramagnetic site separation and therefore the magnetic properties of the resultant materials.

Experimental

The reaction mixture consisted of pyridine, hydrogen fluoride, phenylphosphonic acid and $[\text{Sn}(\text{C}_2\text{O}_4)]$ in a molar ratio of 16:2:4:1, respectively. Solvothermal synthesis was conducted in a 23 ml capacity Teflon-lined Parr autoclave at 423 K for 3 d. The crystals of (I) were colorless plates and the product was determined to be phase-pure using powder X-ray diffraction.

Crystal data

$[\text{Sn}(\text{C}_6\text{H}_5\text{O}_3\text{P})]$	$D_x = 2.319 \text{ Mg m}^{-3}$
$M_r = 274.76$	Mo $K\alpha$ radiation
Monoclinic, C_c	Cell parameters from 4836 reflections
$a = 4.8149 (3) \text{ \AA}$	$\theta = 6.6\text{--}62.7^\circ$
$b = 24.6603 (15) \text{ \AA}$	$\mu = 3.40 \text{ mm}^{-1}$
$c = 6.9111 (4) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 106.4180 (10)^\circ$	Needle, colorless
$V = 787.14 (8) \text{ \AA}^3$	$0.28 \times 0.07 \times 0.02 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	2165 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.038$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 31.6^\circ$
$T_{\text{min}} = 0.729, T_{\text{max}} = 0.934$	$h = -6 \rightarrow 7$
6264 measured reflections	$k = -34 \rightarrow 34$
1326 independent reflections (plus 969 Friedel-related reflections)	$l = -10 \rightarrow 9$
	Intensity decay: 0.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$wR(F^2) = 0.066$	$\Delta\rho_{\text{max}} = 1.23 \text{ e \AA}^{-3}$
$S = 1.07$	$\Delta\rho_{\text{min}} = -0.81 \text{ e \AA}^{-3}$
2295 reflections	Absolute structure: Flack (1983)
120 parameters	Flack parameter = 0.50 (3)
All H-atom parameters refined	

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Sn1–O1	2.097 (3)	P1–O3	1.521 (3)
Sn1–O3 ⁱ	2.125 (3)	P1–O2	1.539 (3)
Sn1–O2 ⁱⁱ	2.133 (3)	P1–C1	1.791 (4)
P1–O1	1.521 (3)		
O1–Sn1–O3 ⁱ	86.03 (13)	O1–P1–C1	106.39 (19)
O1–Sn1–O2 ⁱⁱ	86.37 (12)	O3–P1–C1	106.10 (19)
O3 ⁱ –Sn1–O2 ⁱⁱ	89.49 (12)	O2–P1–C1	109.07 (19)
O1–P1–O3	113.76 (18)	P1–O1–Sn1	134.83 (19)
O1–P1–O2	109.53 (19)	P1–O2–Sn1 ⁱⁱⁱ	122.18 (19)
O3–P1–O2	111.71 (18)	P1–O3–Sn1 ^{iv}	141.8 (2)

Symmetry codes: (i) $x, 1-y, \frac{1}{2}+z$; (ii) $1+x, 1-y, \frac{1}{2}+z$; (iii) $x-1, 1-y, z-\frac{1}{2}$; (iv) $x, 1-y, z-\frac{1}{2}$.

Table 2

Selected contact distances (\AA).

Sn1...O2 ⁱ	3.226 (3)	Sn1...Sn1 ^{iv}	4.3373 (3)
Sn1...O1 ⁱⁱ	3.373 (3)	Sn1...Sn1 ⁱⁱⁱ	4.3373 (3)
Sn1...O3 ⁱⁱⁱ	3.416 (3)		

Symmetry codes: (i) $1+x, y, z$; (ii) $x, 1-y, z-\frac{1}{2}$; (iii) $1+x, 1-y, \frac{1}{2}+z$; (iv) $x, 1-y, \frac{1}{2}+z$.

The refined C–H distances are 0.93 (2) and 0.94 (2) (\AA). The Flack (1983) parameter of 0.5 indicated inverse twinning, which was refined and resulted in a 1:1 ratio of the direct and inverted structures. However, refinement from a different crystal yielded a ratio of 1:4.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997) and ATOMS (Dowty, 1999); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1323). Services for accessing these data are described at the back of the journal.

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