

A three-dimensional tin(II) phosphonatobenzenesulfonate with Sn_4O_{12} clusters

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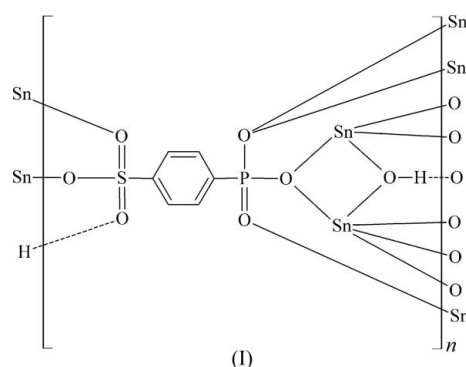
The hydrothermal reaction of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ with 4-phosphonobenzenesulfonic acid (H_3L) and sodium hydroxide has yielded the title compound, poly[μ -hydroxido- μ_7 -(4-phosphonatobenzenesulfonato)-ditin(II)], $[\text{Sn}_2(\text{C}_6\text{H}_4\text{O}_6\text{PS})(\text{OH})]_n$. The inorganic building unit is an Sn_4O_{12} cluster which is composed of edge-sharing SnO_4 and SnO_5 polyhedra. The clusters are interconnected *via* P and S atoms from the organic acid to form layers in the *ab* plane. These layers are linked to each other through pillaring benzene groups parallel to the *c* axis to form a three-dimensional structure.

Comment

The discovery of crystalline zirconium(IV) phosphates in 1964 sparked a surge of interest in the study of phosphate- and phosphonate-based inorganic–organic hybrid compounds (Clearfield *et al.*, 1964). This led to the class of crystalline zirconium(IV) phosphonates in 1978 (Alberti *et al.*, 1978). Originally, the scope of the research was focused on the synthesis of layered structures with metal(IV) ions and monophosphonic acids, but succeeding studies saw an expansion with the use of di- and trivalent metal ions and diphosphonic acids to generate new types of structures (Clearfield, 1998; Poojary *et al.*, 1996*a,b*). Subsequently, sulfonate groups were also incorporated in the metal phosphonates by post-synthetic sulfonation of the benzene rings (Yang *et al.*, 1987; Stein *et al.*, 1996). Some of these compounds were studied with respect to their proton-conducting abilities, which are relevant for polymer electrolyte membrane (PEM) fuel cells. Inorganic–organic hybrid compounds based on such polyfunctional acids have been reported to exhibit high proton conductivities (Adani *et al.*, 1998; Alberti *et al.*, 1992, 2003). The presence of strong acid sites also allows the application of such compounds for catalytic purposes (Alberti *et al.*, 1996).

Our research focuses on the use of organic linker molecules containing two or more different functional groups for the

synthesis of inorganic–organic hybrid compounds. In addition to the number of functional groups their geometry, coordination modes, charge and acidity have a strong influence on the formation of the final crystal structures (Maniam *et al.*, 2010). With the advent of phosphonoalkyl- and phosphonoarylsulfonic acids (Montoneri & Ricca, 1991*a,b*), many phosphonosulfonates with di- and trivalent metal ions were investigated (Sonnauer *et al.*, 2007, 2009; Sonnauer, Lieb & Stock, 2008; Sonnauer & Stock, 2008; Du *et al.*, 2006; Maniam *et al.*, 2010). By utilizing a new synthesis of phosphonoarylsulfonic acids, a rigid *para*-substituted 4-phosphonobenzenesulfonic acid (H_3L) was recently synthesized (Montoneri *et al.*, 2007). Employing this organic acid linker, we have synthesized five new compounds, namely $[\text{Pb}_2(\text{L})(\text{OH})]$, $[\text{Cu}_{1.5}(\text{L})(\text{H}_2\text{O})]$, $\text{NaCu}(\text{L})(\text{H}_2\text{O})_3$, $[\text{Cu}_2(\text{L})(\text{OH})(\text{H}_2\text{O})]$ and $[\text{Cu}_3(\text{L})_2(\text{H}_2\text{O})_2]$ (Maniam *et al.*, 2010).



In the present work, we describe the structure of a new Sn^{2+} -based phosphonatobenzenesulfonate, *viz.* poly[μ -hydroxido- μ_7 -(4-phosphonatobenzenesulfonato)-ditin(II)], (I), which crystallizes in the triclinic space group $P\bar{1}$. To the best of our knowledge, this compound is the first tin(II) phosphonosulfonate. As seen in Fig. 1, the asymmetric unit of (I) contains two Sn^{2+} ions, a fully deprotonated organic linker (L) and one hydroxide ion. The X-ray scattering factors of the P and S atoms are very similar, but they were successfully distinguished by comparing the S–O [1.460 (3)–1.469 (4) Å] and P–O [1.532 (3)–1.548 (3) Å] bond lengths. The fact that S–O bonds are generally shorter than P–O bonds has also been observed in other metal phosphonosulfonates (Du *et al.*, 2006; Sonnauer *et al.*, 2007, 2009; Sonnauer, Lieb & Stock, 2008;

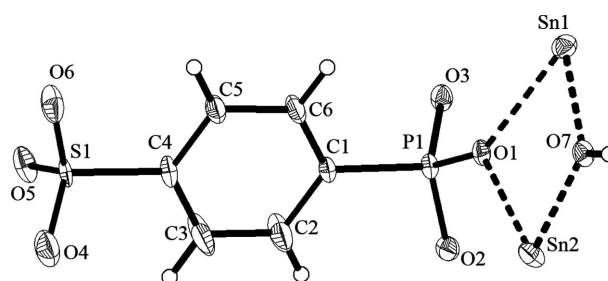
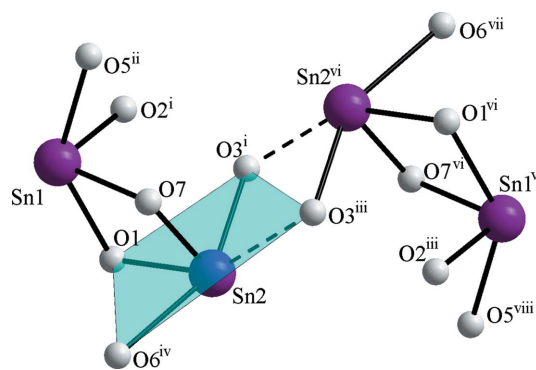


Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Coordinative Sn–O bonds are marked as broken lines.

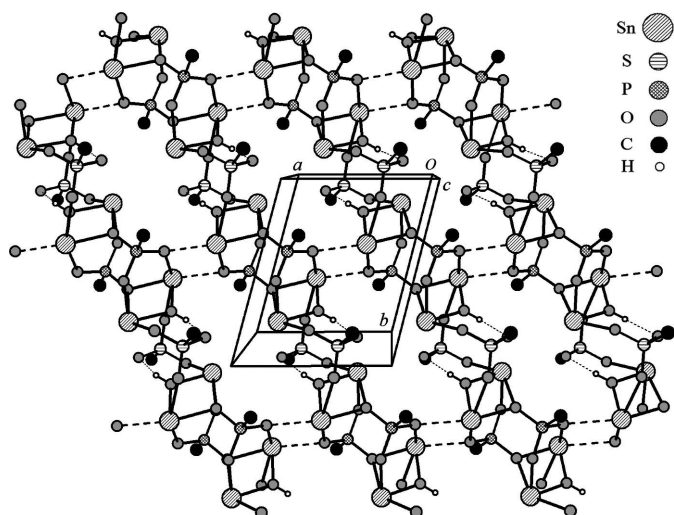

Figure 2

The coordination environment of the Sn1 and Sn2 atoms. Including only bond lengths $< 2.7 \text{ \AA}$, two distorted seesaw-type polyhedra are observed. Edge sharing leads to the formation of dimeric Sn_2O_6 clusters (solid lines). By considering the $\text{Sn2}-\text{O3}^{\text{iii}}$ bond of $2.726(3) \text{ \AA}$ (dashed line), one distorted seesaw SnO_4 and one distorted square-pyramidal SnO_5 polyhedron are observed (the shaded area marks the basal form formed by O1, O3ⁱ, O3ⁱⁱⁱ and O6^{iv}). Edge sharing leads to tetrameric Sn_4O_{12} clusters. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $x - 1, y, z + 1$; (iii) $x - 1, y, z$; (iv) $-x, -y + 2, -z$; (vi) $-x - 1, -y + 1, -z + 1$; (vii) $x - 1, y - 1, z + 1$; (viii) $-x, -y + 1, -z$.]

Maniam *et al.*, 2010). Looking along the $\text{P1} \cdots \text{S1}$ axis, the O atoms of the phosphonate and sulfonate groups are located in a staggered conformation but, in contrast to the ideal torsion angle of 60° , the $\text{O}-\text{P} \cdots \text{S}-\text{O}$ torsion angles vary from $40.79(19)$ to $76.92(18)^\circ$.

The crystal structure of (I) is built of Sn–O polyhedra containing sterically active lone pairs of electrons. These are also observed in many tin(II) phosphonates, such as $[\text{Sn}_2(\text{O}_3\text{PCH}_3)(\text{C}_2\text{O}_4)]$, $[\text{Sn}_4(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2(\text{C}_2\text{O}_4)]$, $[\text{Sn}(\text{C}_6\text{H}_5\text{O}_3\text{P})]$ and $[\text{Sn}(\text{O}_3\text{PCH}_2\text{NHC}_4\text{H}_8\text{NHCH}_2\text{PO}_3)]$, which contain SnO_3 , SnO_4 and Sn_2O_7 polyhedra (Adair *et al.*, 1998; Stock *et al.*, 2000; Lansky *et al.*, 2001; Zhang *et al.*, 2008). Depending on how the Sn–O bond distances are taken into account, the crystal structure of (I) can be described in different ways.

Including only Sn–O distances less than 2.7 \AA , two distorted seesaw-type SnO_4 polyhedra are observed. Sn1 is connected to atoms O1, O2ⁱ, O5ⁱⁱ and O7 (all symmetry codes are as in Fig. 2), with bond lengths in the range $2.124(3)$ – $2.425(3) \text{ \AA}$ (Table 1) and $\text{O}-\text{Sn1}-\text{O}$ angles in the range $69.82(10)$ – $140.63(10)^\circ$. The two longest Sn1–O bonds (to O1 and O5ⁱⁱ) lie in the pseudo-axial positions, while the two shorter Sn1–O bonds (to O2ⁱ and O7) and the lone pair are in the equatorial plane. Sn2 is connected to atoms O1^{vi}, O3ⁱ, O6^{iv} and O7, with bond lengths in the range $2.108(3)$ – $2.587(3) \text{ \AA}$. The $\text{O}-\text{Sn2}-\text{O}$ angles in the distorted seesaw geometry vary from $73.59(10)$ to $152.13(10)^\circ$. The observed Sn–O distances and $\text{O}-\text{Sn}-\text{O}$ angles are in very good agreement with those reported in the seesaw-type SnO_4 units of the layered tin(II) phosphonate $[\text{Sn}_2(\text{O}_3\text{PCH}_3)(\text{C}_2\text{O}_4)]$ and the three-dimensional structure of $[\text{Sn}_4(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2(\text{C}_2\text{O}_4)]$ (Adair *et al.*, 1998; Stock *et al.*, 2000). This form of polyhedron is also similar to those observed in α -SnO, with Sn–O distances of 2.223 \AA and an $\text{O}-\text{Sn}-\text{O}$ -angle range of 74.36 – 117.44° (Levi, 1924). Edge sharing of the two distorted seesaw-type SnO_4


Figure 3

Packing diagram showing the interconnection of dimeric clusters *via* phosphonate and sulfonate groups to form chains. Taking the $\text{Sn2}-\text{O3}^{\text{iii}}$ bond of $2.726(3) \text{ \AA}$ (thick dashed lines) into account, tetrameric Sn_4O_{12} clusters are formed and the formerly described chains are connected to form layers in the ab plane. The positions of lone pairs are indicated by the narrow voids between the opposing Sn1^{2+} ions. Hydrogen bonds are shown as thin dashed lines. The layers are then linked to each other by the benzene groups along the c axis. Atoms C2, C3, C5 and C6 and their respective H atoms have been omitted for clarity. [Symmetry code: (iii) $x - 1, y, z$.]

polyhedra in (I) leads to dimeric units which are in close proximity to each other [$\text{Sn2}-\text{O3}^{\text{iii}} = 2.726(3) \text{ \AA}$] and are connected through the phosphonate and sulfonate groups to form chains (Fig. 3). These chains are connected by the benzene rings of the phosphonobenzenesulfonate ions to form a layered structure.

If the additional Sn–O distance of $2.726(3) \text{ \AA}$ is taken into account as a genuine bond, two kinds of polyhedra are observed, *viz.* distorted seesaw-type Sn1O_4 and irregular square-pyramidal Sn2O_5 polyhedra. The irregular SnO_5 square pyramid consists of the apical $\text{Sn2}-\text{O7}$ bond and the four basal $\text{Sn2}-\text{O}$ bonds to atoms O1, O3ⁱ, O3ⁱⁱⁱ and O6^{iv} (symmetry codes as in Fig. 2). Associated with the influence of the lone pair, the Sn^{2+} ion is located $0.514(1) \text{ \AA}$ below the basal plane, whereas apical atom O7 is positioned $1.591(3) \text{ \AA}$ above the plane (Fig. 2). Although this distance is much larger than the sum of the ionic radii (2.35 \AA ; McDonald *et al.*, 1980), it is much smaller than the sum of the van der Waals radii (3.70 \AA ; Kawamura *et al.*, 1999). A search of the Cambridge Structural Database (Allen, 2002) for Sn–O bond lengths in tin phosphonates yields values between 1.9 and 2.8 \AA , with a mean value around 2.2 \AA and, in the literature, bond lengths of up to 3 \AA are discussed (Ramaswamy *et al.*, 2008; Holt *et al.*, 1987). Accordingly, the next largest Sn–O distances in (I), which are $3.094(3)$ and $3.292(3) \text{ \AA}$ for $\text{Sn1} \cdots \text{O4}^{\text{iv}}$ and $\text{Sn2} \cdots \text{O2}$, respectively, were not considered in the structural description. Using Sn–O distances up to 2.73 \AA , edge sharing of the SnO_5 polyhedra is observed and thus Sn_4O_{12} clusters are formed (Fig. 2). These tetrameric clusters are connected by the phosphonate and sulfonate groups to form layers in the ab plane (Fig. 3), which are further connected by the benzene

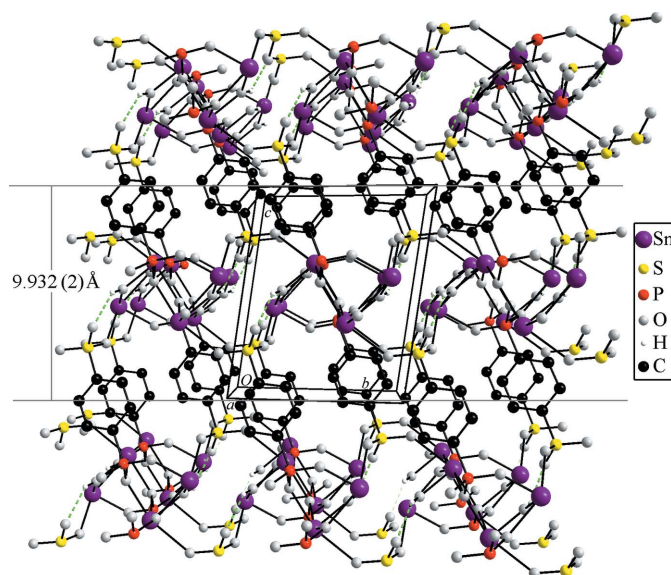


Figure 4
Schematic representation of the three-dimensional pillared layered structure of (I), viewed along the *a* axis, with an interlayer distance of 9.932 (2) Å. Aromatic H atoms have been omitted for clarity.

rings of the phosphonobenzene sulfonate ions to form a pillared layered structure (Fig. 4). An interlayer distance of 9.932 (2) Å separates the layers from each other along the *c* axis. In this arrangement, the presence of narrow voids indicates the position of the sterically active lone pairs. These are observed between opposing Sn1²⁺ ions [Sn1···Sn1(−*x*, −*y* + 2, −*z* + 1) = 4.335 (1) Å] (Fig. 3), whereas for Sn2²⁺ the lone pairs point towards the interlayer space occupied by the benzene rings.

Only one hydrogen bond is observed in (I) which involves the bond between the μ(O—H) hydroxide ion and an O atom of the sulfonate group (Fig. 3 and Table 2). This bond can be considered as a weak hydrogen bond (Libowitzky, 1999).

Experimental

All reagents and solvents were obtained commercially and used without further purification. 4-Phosphonobenzene sulfonic acid dihydrate (H₃L) was synthesized according to Montoneri *et al.* (2007). The reaction mixture consisted of tin(II) chloride dihydrate (6.8 mg, 0.03 mmol), H₃L (5.48 mg, 0.02 mmol), NaOH (0.06 mmol) and deionized water (200 μl). The mixture was heated in a 300 μl Teflon-lined high-throughput reactor at 423 K for 36 h (Stock, 2010). The mixture was cooled to room temperature over a period of 8 h, and colourless plate-like crystals were formed.

Crystal data

[Sn ₂ (C ₆ H ₄ O ₆ PS)(OH)]	$\gamma = 75.25 (3)^\circ$
$M_r = 489.56$	$V = 571.0 (2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.0045 (14) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 8.487 (2) \text{ \AA}$	$\mu = 4.72 \text{ mm}^{-1}$
$c = 10.0570 (17) \text{ \AA}$	$T = 293 \text{ K}$
$\alpha = 81.10 (2)^\circ$	$0.14 \times 0.10 \times 0.07 \text{ mm}$
$\beta = 86.17 (2)^\circ$	

Data collection

Stoe IPDS-1 diffractometer	6691 measured reflections
Absorption correction: numerical (<i>X-RED</i> and <i>X-SHAPE</i> ; Stoe & Cie, 2008)	2550 independent reflections
$T_{\min} = 0.380$, $T_{\max} = 0.581$	2146 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	155 parameters
$wR(F^2) = 0.071$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\max} = 0.82 \text{ e \AA}^{-3}$
2550 reflections	$\Delta\rho_{\min} = -1.10 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Sn1—O1	2.425 (3)	P1—O1	1.548 (3)
Sn1—O2 ⁱ	2.124 (3)	P1—O2	1.532 (3)
Sn1—O5 ⁱⁱ	2.412 (3)	P1—O3	1.532 (3)
Sn1—O7	2.156 (3)	P1—C1	1.798 (3)
Sn2—O1	2.243 (3)	S1—O4	1.460 (3)
Sn2—O3 ⁱ	2.345 (3)	S1—O5	1.469 (4)
Sn2—O3 ⁱⁱⁱ	2.726 (3)	S1—O6	1.460 (3)
Sn2—O6 ^{iv}	2.587 (3)	S1—C4	1.780 (4)
Sn2—O7	2.108 (3)		
O2 ⁱ —Sn1—O7	91.86 (11)	O3 ⁱ —Sn2—O3 ⁱⁱⁱ	74.32 (10)
O2 ⁱ —Sn1—O5 ⁱⁱ	78.78 (11)	O3 ⁱⁱⁱ —Sn2—O6 ^{iv}	119.16 (10)
O7—Sn1—O5 ⁱⁱ	80.57 (11)	O6 ^{iv} —Sn2—O1	73.59 (10)
O2 ⁱ —Sn1—O1	76.92 (10)	O7—Sn2—O1	74.32 (10)
O7—Sn1—O1	69.82 (10)	O6 ^{iv} —Sn2—O3 ⁱ	152.13 (10)
O5 ⁱⁱ —Sn1—O1	140.63 (10)	O1—Sn2—O3 ⁱⁱⁱ	147.69 (10)
O1—Sn2—O3 ⁱ	83.12 (9)		

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

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O7—H7···O4 ⁱⁱ	0.84	2.19	2.874 (4)	139

Symmetry code: (ii) $x - 1, y, z + 1$.

All H atoms were located in difference Fourier maps. Idealized values for the bond lengths (C—H = 0.93 Å and O—H = 0.84 Å) and angles were used and the H-atom parameters were refined using a riding model. The highest peak of 0.82 e Å^{−3} in the residual electron-density map is located 1.34 Å from H3 and the deepest hole of 1.10 e Å^{−3} is located 0.72 Å from Sn2.

Data collection: *X-AREA* (Stoe & Cie, 2008); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *XCIF* in *SHELXTL* (Sheldrick, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ3200). Services for accessing these data are described at the back of the journal.

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