

The hybrid open-framework of tin(II) phosphonopropionate oxalate, $\text{Sn}_4(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2(\text{C}_2\text{O}_4)$

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The hydrothermal synthesis and single crystal XRD characterization of a three-dimensional open-framework tin(II) phosphonopropionate oxalate, $\text{Sn}_4(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2(\text{C}_2\text{O}_4)$, is described; the structure contains two different bifunctional linkers as well as SnO_3 and SnO_4 polyhedra each with a stereochemically active lone pair of electrons, and exhibits several types of channels.

Hybrid open-framework materials that contain both organic and inorganic moieties provide an attractive field of research due to their composite properties and the possibility of tuning the chemistry of such solids.¹ The potential of these hybrid materials lies in their use, for example, as sorbents, ion exchangers, catalysts or for charge storage. Striking examples are the silicon- and metal-oxide mesostructures, which are formed with the aid of organic surfactants.² The field of microporous hybrid materials is also of great interest and the use of bifunctional anionic units, for example diphosphonates ($[\text{O}_3\text{P}-\text{R}-\text{PO}_3]^{4-}$),³ aminophosphonates ($[\text{O}_3\text{P}-\text{R}-\text{NH}_2]^{2-}$),⁴ or phosphonocarboxylates ($[\text{O}_3\text{P}-\text{R}-\text{CO}_2]^{3-}$), has led to new materials. These contain a $\text{PO}_3/(\text{NH}_2/\text{CO}_2)/\text{metal}$ -inorganic core separated by tunable organic units ($\text{R} = \text{alkyl, aryl}$) bound to the phosphonate and/or the carboxylate or amino group. Whereas the chemistry of metal phosphonates has been investigated in detail⁵ and led to a large number of interesting materials, only a few metal phosphonocarboxylates have been reported. Thus, the phosphonocarboxylates of the following metals are known: Al,⁶ Ga,⁷ Pb,⁸ Bi,⁹ Zn,¹⁰ Cu,¹¹ Co,¹² V,¹³ Fe,¹⁴ Zr,¹⁵ Mn,¹⁶ Pr.¹⁷ On the other hand, open-framework metal phosphate oxalates and phosphonato oxalates have been recently reported which contain two kinds of anionic moieties (linkers) connecting the metal ions; for example, materials with Al, Sn or Fe as cations have been described.¹⁸ Here, we describe the synthesis and characterization of the open-framework tin phosphonopropionate oxalate, $\text{Sn}_4(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2(\text{C}_2\text{O}_4)$, which contains two different bifunctional linkers: the organic-inorganic hybrid ion, $(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)^{3-}$, and the oxalate ion, $\text{C}_2\text{O}_4^{2-}$.

The compound $\text{Sn}_4(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2(\text{C}_2\text{O}_4)$ was synthesized hydrothermally by reacting phosphonopropionic acid with tin oxalate in water.¹⁹ The single crystal structure²⁰ was solved by direct methods and refined using the SHELXTL software.²¹ The asymmetric unit contains 14 non-hydrogen atoms and is shown in Fig. 1(a). The structure of $\text{Sn}_4(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2(\text{C}_2\text{O}_4)$ consists of two crystallographically independent tin atoms having two different coordination geometries: Ψ -tetrahedral SnO_3 and Ψ -square pyramidal SnO_4 (the lone pair occupying the fourth and fifth coordination sites, respectively). These as well as the Sn–O bond lengths are shown in Fig. 1(b). All O-atoms of the phosphonate as well as the carboxylate group are coordinated to the Sn^{2+} ions. As can be seen from Fig. 2, each of the five oxygen atoms of the $(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)^{3-}$ ion is coordinating to one of the Sn^{2+} ions, thus being monodentate. The $\text{C}_2\text{O}_4^{2-}$ ion acts simultaneously as a chelating as well as a bridging unit, connecting exclusively the tin ions, Sn2.

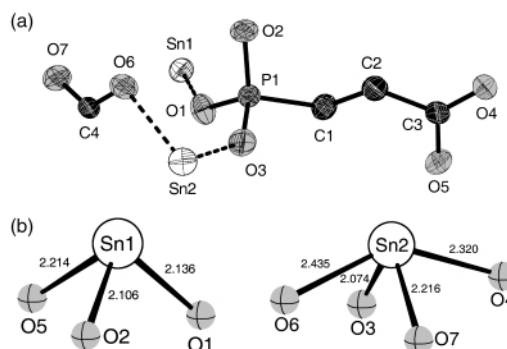


Fig. 1 (a) Asymmetric unit of $\text{Sn}_4(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2(\text{C}_2\text{O}_4)$. (b) Tin atoms having three- and four-coordination geometries.

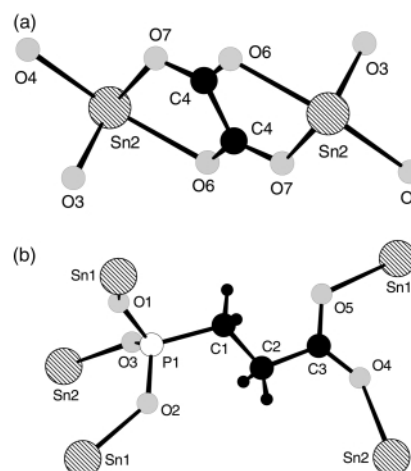


Fig. 2 Coordination behavior of the oxalate ion (a) and the phosphonopropionate ion (b) in $\text{Sn}_4(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2(\text{C}_2\text{O}_4)$.

The complex connectivities give rise to an interesting open-framework structure which can be described as follows. Layers of Sn/O/P and C involving only the phosphonopropionate and Sn^{2+} ions are formed by connecting the three- and four-coordinated tin atoms through the phosphonate and the carboxylate groups of the $(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)^{3-}$ ion (Fig. 3). The connection of these layers through the alkyl group, CH_2CH_2 , leads to a double layered arrangement reminiscent of pillared materials. The three-dimensional network is achieved via the coordination of the $\text{C}_2\text{O}_4^{2-}$ ions, which connect the double layers. This arrangement leads to the formation of several narrow channels into some of which the $\text{Sn}(\text{II})$ lone pairs are pointing (Figs. 3 and 4). Two kinds of distinct channels are found along $[001]$, as well as along $[100]$, due to the alternating sequence of oxalate and phosphonopropionate ions, and they should differ extensively in their hydrophilic properties. Interestingly, in contrast to many open framework structures, there is no structure-directing agent present in the compound.

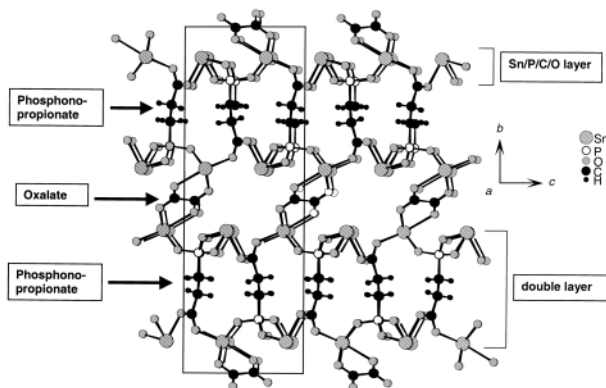


Fig. 3 Three-dimensional structure of $\text{Sn}_4(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2(\text{C}_2\text{O}_4)$ showing channels along $[100]$.

One way to explain this could be the constrained geometry of the SnO polyhedra due to the lone pairs of electrons. But, since the lone pairs occupy the space in the channels we do not expect the compound to be microporous.

The three-coordinated tin (Sn1) has two oxygens (O1 and O2) from two $-\text{PO}_3$ groups and one oxygen (O5) from a $-\text{CH}_2\text{CO}_2$ group, thus connecting three phosphonopropionate ions. The four-coordinated tin (Sn2) is surrounded by the third oxygen of the $-\text{PO}_3$ group (O3), the other oxygen of the $-\text{CH}_2\text{CO}_2$ group (O4) and the two oxygens of the oxalate ion (O6 and O7), thereby connecting two phosphonopropionate ions and one oxalate ion. Thus, all oxygen atoms of the phosphonopropionate and the oxalate ions are involved in the coordination of the Sn^{2+} ions. The $\text{Sn}-\text{O}$ bond lengths vary from 210.6(3) to 243.5(3) pm, with the shortest bonds [210.6(3), 210.6(3), 207.4(3) pm] from oxygens of the $-\text{PO}_3$ group and the longer bonds [221.4(3)–243.5(3) pm] from the $-\text{CO}_2$ groups. These values are consistent with those reported in other $\text{Sn}(\text{II})$ compounds.¹⁸ The phosphorus atom is tetrahedrally surrounded by three oxygen [152.9(3)–153.7(3) pm] and one carbon atom [178.7(4) pm]. These values agree well with those found in other metal phosphonates.

The IR spectrum of $\text{Sn}_4(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2(\text{C}_2\text{O}_4)$ clearly shows the presence of the carboxylic group (1514, 1403 cm^{-1}), the CH_2 group (2924, 2856 cm^{-1}), and the phosphonate group (900–1100 cm^{-1}); the vibrations of the oxalate ion at 1644,

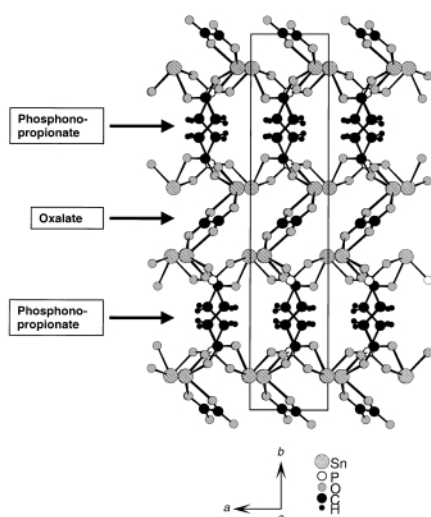


Fig. 4 Three-dimensional structure of $\text{Sn}_4(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2(\text{C}_2\text{O}_4)$ showing channels along $[001]$.

1632, 1430 and 1310 cm^{-1} are in good agreement with previously reported values.

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Notes and references

- 1 A. K. Cheetham, G. Férey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268.
- 2 A. Monnier, F. Schüth, Q. Huo, D. Kumar, R. S. Maxwell, D. Margolese, G. D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke and B. F. Chmelka, *Science*, 1993, **261**, 1299; A. Firouzi, G. D. Stucky and B. F. Chmelka, *Synthesis of Porous Materials*, ed. M. L. Occelli and H. Kessler, Marcel Dekker, New York, 1997, p. 379.
- 3 A. Distler, L. Lohse and S. C. Sevov, *J. Chem. Soc., Dalton Trans.*, 1999, 1805; V. Soghomonian, Q. Chen, R. C. Haushalter and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 223.
- 4 S. Drumel, P. Janvier, D. Deniaud and B. Bujoli, *J. Chem. Soc., Chem. Commun.*, 1995, 1051.
- 5 J. Zubieta, *Comments Inorg. Chem.*, 1994, **16**, 153; C. Bhardway, H. Hu and A. Clearfield, *Inorg. Chem.*, 1993, **32**, 4294.
- 6 G. B. Hix, D. S. Wragg, P. A. Wright and R. E. Morris, *J. Chem. Soc., Dalton Trans.*, 1998, 3359.
- 7 F. Fredoueil, D. Massiot, D. M. Poojary, M. Bujoli-Doeuff, A. Clearfield and B. Bujoli, *Chem. Commun.*, 1998, 175.
- 8 S. Ayyappan, G. Diaz de Delgado, A. K. Cheetham, G. Férey and C. N. R. Rao, *J. Chem. Soc., Dalton Trans.*, 1999, 2905.
- 9 P. Janvier, S. Drumel, P. Piffard and B. Bujoli, *C. R. Acad. Sci. Paris, Ser. II*, 1995, **320**, 29.
- 10 S. Drumel, P. J. Janvier, M. Bujoli-Doeuff and B. Bujoli, *Inorg. Chem.*, 1995, **34**, 148.
- 11 S. Drumel, P. J. Janvier, M. Bujoli-Doeuff and B. Bujoli, *New J. Chem.*, 1995, **19**, 239.
- 12 A. Distler and S. C. Sevov, *Chem. Commun.*, 1998, 959.
- 13 E. M. Sabbar, M. E. de Roy and J. P. Besse, *Mater. Res. Bull.*, 1999, **34**, 1023; E. M. Sahbar, M. E. de Roy, A. Ennaqadi, C. Gueho and J. P. Besse, *Chem. Mater.*, 1998, **10**, 3856.
- 14 B. Bujoli, A. Courilleau, P. Palvadeau and J. Rouxel, *Eur. J. Solid State Inorg. Chem.*, 1992, **29**, 171.
- 15 D. A. Burwell and M. E. Thompson, *Chem. Mater.*, 1991, **3**, 14; D. A. Burwell, K. G. Valentine, J. H. Timmermans and M. E. Thompson, *J. Am. Chem. Soc.*, 1992, **114**, 4144.
- 16 N. Stock, G. D. Stucky and A. K. Cheetham, in preparation.
- 17 F. Serpaggi and G. Férey, *Inorg. Chem.*, 1999, **38**, 4741.
- 18 A. Choudhury, S. Natarajan and C. N. R. Rao, *J. Solid State Chem.*, 1999, **146**, 538; A. Choudhury, S. Natarajan and C. N. R. Rao, *Chem. Mater.*, 1999, **11**, 2316; S. Natarajan, *J. Solid State Chem.*, 1998, **139**, 200; B. Adair, S. Natarajan and A. K. Cheetham, *J. Mater. Chem.*, 1998, **8**, 1477; H.-M. Lin, K.-H. Lii, Y.-C. Jiang and S.-L. Wang, *Chem. Mater.*, 1999, **11**, 519; Z. A. D. Lethbridge and P. Lightfoot, *J. Solid State Chem.*, 1999, **143**, 58.
- 19 In a typical experiment, 206 mg (1 mmol) of tin oxalate and 154 mg (1 mmol) of phosphonocarbonylic acid were mixed in 10 g water, stirred to obtain homogeneity, transferred to a 23 ml Teflon bottle and sealed in a stainless steel autoclave (Parr, USA). The reaction was carried out at 150 °C for 48 h under autogeneous pressure. The resulting product, which mainly contained needle-like crystals, was filtered off and washed thoroughly with deionized water. The powder X-ray diffraction pattern of the powdered crystals indicated that the product was a new material.
- 20 Single crystal structure determination by X-ray diffraction (crystal size: 0.03 × 0.03 × 0.2 mm) was performed on a Siemens Smart-CCD diffractometer. *Crystal data* for $\text{Sn}_4(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2)_2(\text{C}_2\text{O}_4)$: $M = 864.84$, monoclinic, space group $P2_1/c$, $a = 4.7895(14)$, $b = 23.242(7)$, $c = 8.1438(3)$ Å, $\beta = 94.240(6)^\circ$, $V = 903.4(5)$ Å³, $Z = 2$, $\mu = 5.714$ mm⁻¹. Total data 9081 reflections; observed data 2105 reflections; $R_{\text{int}} = 0.0617$. Final $R1 = 0.0373$, $wR2 = 0.0542$, $\text{GOF} = 0.967$ (all data), for 127 parameters. CCDC 182/1808. See <http://www.rsc.org/suppdata/cc/b0/b006511k/> for crystallographic files in .cif format.
- 21 SHELXTL X-ray Single Crystal Analysis System, Version 5.1, Bruker AXS, Madison, WI, 1998.