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Synthesis and Structural Characterization of Solid Phases of the Sn(II)–Organophosphonate System: The 1-Dimensional $[Sn(HO_3PCH_2PO_3H)] \cdot H_2O$ and the 3-Dimensional $[Sn_2\{O_3PC(OH)(CH_3)PO_3\}]$

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The first Sn(II)–organophosphonate solid phases have been prepared and structurally characterized by single crystal X-ray diffraction. The one-dimensional species $[Sn(HO_3PCH_2PO_3H)] \cdot H_2O$ (1) was prepared conventionally from a mixture of $SnCl_2$, $CH_2(PO_3H_2)_2$, and H_2O in the mole ratio 1:2.9:8.17 kept at 4°C for 12 h. The three-dimensional phase $[Sn_2\{O_3PC(OH)(CH_3)PO_3\}]$ (2) was prepared hydrothermally from a mixture of $SnCl_2$, $CH_3C(OH)(PO_3H)_2$, 1,4 diaminopropane · HCl, and H_2O in the mole ratio 1:3.87:1.9:2215 with pH adjusted to 3.5 by addition of $(CH_3)_4NOH$, heated at 150°C for 135.5 h. Compound 1 consists of linear chains of $\{SnO_3\}$ pyramids bridged by $(HO_3PCH_2PO_3H)^{2-}$ groups. The structure of 2 is a three-dimensional open framework. Crystal data: 1, triclinic $P\bar{1}$ $a = 4.8777(1)$ Å, $b = 8.786(2)$ Å, $c = 9.446(2)$ Å, $\alpha = 84.52(3)°$, $\beta = 78.78(3)°$, $\gamma = 74.39(3)°$, $V = 382.0(2)$ Å^3, $Z = 2$, $D_{calc} = 2.701$ g cm^{-3}, structure solution and refinement based on 1059 reflections converged at $R = 0.060$; 2, monoclinic $P2_1/c$, $a = 10.889(2)$ Å, $b = 8.556(2)$ Å, $c = 9.460(2)$ Å, $\beta = 96.92(2)°$, $V = 874.9(4)$ Å^3, $D_{calc} = 3.336$ g cm^{-3}, structure solution and refinement based on 1121 reflections, converged at $R = 0.055$. © 1996 Academic Press, Inc.

The recent expansion of the chemistry of metal–organophosphonate compounds reflects their applications in catalysis, ion exchange, sorption, and intercalation chemistry (1). The organophosphonate compounds of the *d*-block metals exhibit a remarkable range of structural types, including mononuclear species (2), complex molecular clusters (3), one-dimensional structures (4), layered materials (5–8), and open three-dimensional frameworks (9, 10). However, with the exception of the aluminum–organophosphonate system (11), the organophosphonate phases of the main group metals remain largely unexplored. Consequently, while molecular clusters of the tin–organophosphonate system have been described (12) as well as Sn(IV)/phenylphosphonates of poor crystallinity assumed to possess the α-layered structure (13), no structurally characterized solid phases have been reported to date, nor has the influence of lone pair electrons on structural characteristics been evaluated in the specific case of Sn(II)–organophosphonates (14). In this article, we report the preparations and structures of two Sn(II)–organophosphonate solids, the one-dimensional phase $[Sn(HO_3PCH_2PO_3H)] \cdot H_2O$ (**1**) and the three-dimensional tetrahedral-pyramidal framework material, $[Sn_2\{O_3PC(OH)(CH_3)PO_3\}]$ (**2**).[1]

A mixture of $SnCl_2$, $CH_2(PO_3H_2)_2$, and H_2O in the mole ratio 1:2.9:817 was kept at 4°C for 12 h. Colorless needles of **1** were obtained in 5% yield. The infrared spectrum of **1** exhibited a medium intensity band at 3492 cm^{-1}, associated with υ(O–H) of the water of crystallization, and a series of strong bands at 921, 1084, and 1375 cm^{-1}, attributed to υ(P–O) of the diphosphonate group.

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[1] Crystal data for $CH_6O_7P_2Sn$ (**1**): triclinic, $P\bar{1}$, $a = 4.8777(1)$ Å, $b = 8.786(2)$ Å, $c = 9.446(2)$ Å, $\alpha = 84.52(3)°$, $\beta = 78.78(3)°$, $\gamma = 74.39(3)°$, $V = 382.0(2)$ Å^3, $Z = 2$, $D_{calc} = 2.701$ g cm^{-3}. Structure solution and refinement based on 1059 reflections with $I_o \geq 3\sigma(I_o)$(MoK_α, $\lambda = 0.71073$ Å) converged at $R = 0.060$ ($R_w = 0.063$; goodness of fit = 1.46). Crystal data for $C_2H_4O_7P_2Sn_2$ (**2**); monoclinic, $P2_1/c$, $a = 10.889(2)$ Å, $b = 8.556(2)$ Å, $c = 9.460(2)$ Å, $\beta = 96.92(2)°$, $V = 874.9(4)$ Å^3, $D_{calc} = 3.336$ g cm^{-3}. Structure solution and refinement based on 1121 reflections with $I_o \geq 3\sigma(I_o)$(MoK_α, $\lambda = 0.71073$ Å) converged at $R = 0.055$ ($R_w = 0.069$; goodness of fit = 1.88). Atomic coordinates, bond lengths and angles, and thermal parameters for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre.

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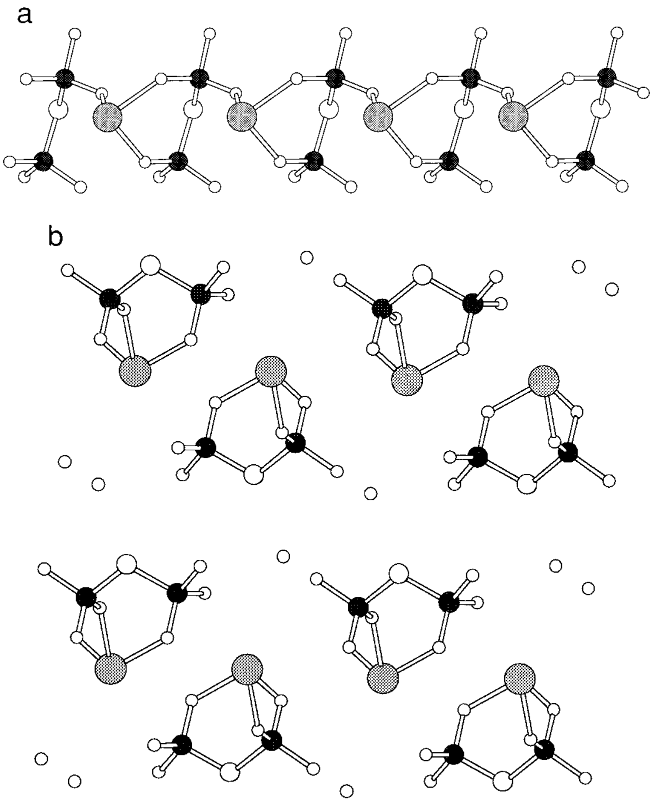

FIG. 1. (a) A view of a one-dimensional strand of **1**. (b) A view of the packing of the one-dimensional chains of **1**, parallel to the chain axis, and showing the locations of the water molecules. Selected bond lengths (Å) and angles (°): Sn–O, 2.123(9)–2.17(1); P–O(Sn), 1.51–1.53(1); P=O, 1.51(1); P–O(H), 1.58; O–Sn–O, 83.4(4)–85.7(4).

As shown in Fig. 1a, the structure of **1** consists of linear chains, constructed of $\{Sn(II)O_3\}$ pyramids bridged unsymmetrically by $(HO_3PCH_2PO_3H)^{2-}$ groups. One $\{HO_3P\}$ terminus of each diphosphonate group serves to bridge two adjacent Sn(II) sites through each of two oxygen donors, leaving the third oxygen pendant and protonated. The other $\{HO_3P\}$ terminus bonds to a single Sn(II) site, resulting in pendant {P=O} and {P—OH} sites. The P–O bond distances clearly distinguish the various sites: P=O, 1.51(1) Å; P—O(H), 1.58 Å; P—O(Sn), 1.51(1)–1.53(1) Å. As illustrated in Fig. 1b, the water molecules of **1** occupy the interstrand regions and exhibit extensive hydrogen bonding to the pendant {P=O} and {P—OH} groups. When the $\{Sn(HO_3PCH_2PO_3H)\}_\infty$ chains are viewed on end, the $\{SnO_3\}$ pyramids and the diphosphonate groups are observed each to adopt eclipsed orientations, such that the Sn(II) lone pairs project to the same side of the chain. The chains pack so as to align the strands to produce alternating inorganic $\{SnO_3\}$ and organic "layers," suggesting that under appropriate conditions further condensation will provide a true two-dimensional phase.

In addition to the intimate coordination to three oxygens in the pyramidal $\{SnO_3\}$ core, each Sn(II) site exhibits three additional Sn $\cdots$ O contacts at 3.10–3.24 Å with phosphate oxygens of neighboring chains. Such three long–three short coordination is not uncommon for Sn(II) solids (15), and a similar pattern may be observed in the one-dimensional materials $SnHPO_4$ and $SnHPO_3$ (16).

The pH of a mixture of $SnCl_2$, $CH_3C(OH)(PO_3H_2)_2$, 1,4 diaminopiperazinehydrochloride, and H_2O in the mole ratio 1:3.87:1.9:2215 was adjusted to 3.5 by addition of $(CH_3)_4NOH$. Upon heating in a glass tube at 40% fill volume for 135.5 h at 150°C, colorless rhombs of **2** were isolated in 40% yield. The infrared spectrum of **2** exhibited prominent features at 977, 1059, and 1134 cm^{-1}, consistent with the presence of the diphosphonate group.

The complex three-dimensional structure adopted by **2** is illustrated in Fig. 2a. As viewed parallel to the crystallographic **a** axis, the linkage of $\{SnO_3\}$ pyramids and diphosphonate tetrahedra produces an open framework structure with cavities aligned parallel to the **a** axis. The methyl groups of the hydroxyethyl backbone of the diphosphonate and the nonbonding electron pairs of the Sn(II) sites project into these channels. A second set of channels runs parallel to the **c** axis, as shown in Fig. 2b. The hydroxyl groups of the organic backbone project into these tunnels, which interpenetrate the channels parallel to the **a** axis. As shown in Fig. 2c, each diphosphonate group serves to bridge six Sn(II) sites through each of the six oxygen donors. The connectivity of the two fundamental structural motifs, $\{SnO_3\}$ pyramids and $\{O_3PC\}$ tetrahedra, produces four- and eight-polyhedral rings, shown in Fig. 2d, which fuse in turn to produce the unusually complex framework of the solid.

While a number of one-dimensional Sn(II)-oxyacid phases, noted previously, and several two-dimensional materials, such as $Sn_2(OH)(PO_4)$ (17) and $Sn_3(PO_4)F_3$ (18), have been described, **2** appears to provide a unique example of a three-dimensional phase for the Sn/PO_4^{3-} and Sn/RPO_3^{2-} classes of materials.

The isolation of both low-dimensionality and three-dimensional solids for the Sn(II)–organodiphosphonate system illustrates the profound structural influences of relatively minor modifications in reaction conditions and/or organophosphonate substituents. While it is evident that the Sn(II) lone pair produces stereochemical consequences, the exploitation of this unit in a structure-directing role in the synthesis of micorporous materials requires further evaluation.

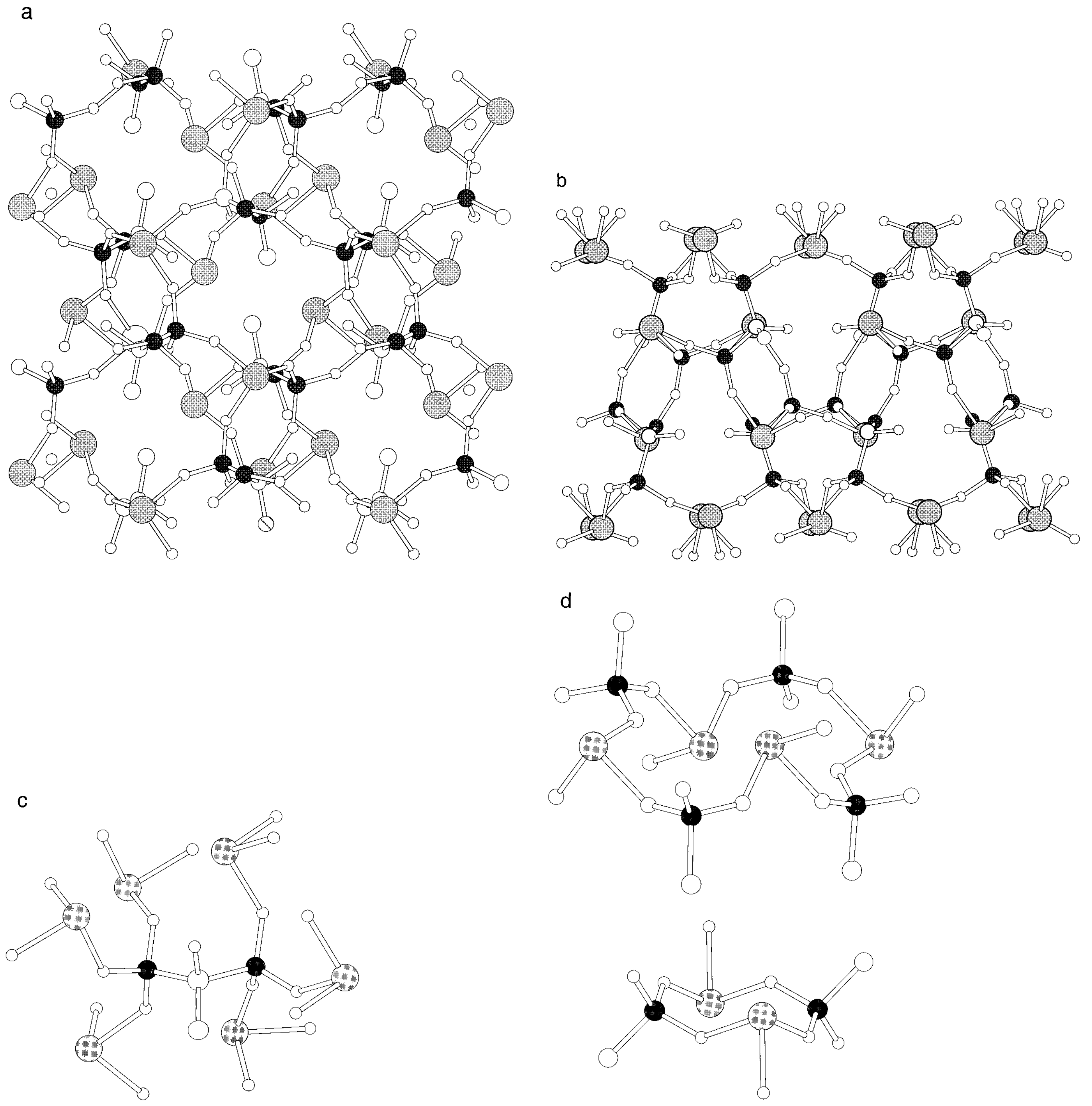

FIG. 2. (a) A view of the three-dimensional framework of **2** viewed parallel to the **a** axis. (b) A view parallel to **c**. (c) The environment of a diphosphonate group. (d) The four- and eight-polyhedra rings from which the structure of **2** is constructed. Selected bond lengths (Å) and angles (°): Sn–O, 2.10(1)–2.16(1); P–O, 1.51(1)–1.55(1); O–Sn–O, 83.3(5)–92.0(5).

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