BRIEF COMMUNICATION

Synthesis and Structure of a Tin(II) Phosphatooxalate, $Sn_2(PO_4)[C_2O_4]_{0.5}$, Containing One-Dimensional Tin Phosphate Chains

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   The synthesis and structure of a new tin(II) phosphato-oxalate, $Sn_2(PO_4)[C_2O_4]_{0.5}$, containing one-dimensional tin phosphate chains are presented. The structure comprises a network of pyramidal SnO_3, truncated square, pyramidal SnO_4, and tetrahedral PO_4 moieties which gives rise to one-dimensional tin phosphate chains separated by the oxalate groups. These linkages create Sn–O–Sn bonding in this structure. © 1998 Academic Press

INTRODUCTION

   Hydrothermal methods have been extensively used to prepare zeolitic materials and, especially, metal phosphates with open-framework architectures. Since the discovery of three-dimensional aluminum phosphates in 1982 by Flanigen and co-workers (1, 2), there has been intense activity in this area of research (3, 4). Recently, open-framework structures based on tin(II) phosphate materials have been synthesized with the aid of organic structure-directing molecules (5–7). From the diversity of the structures found in the tin phosphate materials, it was apparent that the system, like the aluminophosphates, can form chain, layered, and three-dimensional open-framework structures. In this communication, the synthesis and structure of a new material containing one-dimensional chains made of tin phosphate units separated by oxalate units are presented.

EXPERIMENTAL

   The title compound was synthesized by the hydrothermal method as described below. The starting mixture corresponding to the molar ratio $SnC_2O_4 : 1.0 P_2O_5 : 1.0$ butylamine : $55 H_2O$ was mixed and stirred until homogeneous, sealed in a PTFE-lined stainless-steel autoclave (Parr), and

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heated at 170°C for 2 days under autogeneous pressure. The resulting product, which contained a large quantity of needle-shaped crystals and a very small amount of white powder, was filtered off and washed thoroughly with deionized water. The powder X-ray diffraction pattern indicated that the product was a new material; the pattern is entirely consistent with the structure determined by single-crystal X-ray diffraction. Similar products are formed when other alkyl amines are used. However, no new material like that reported here has been formed in the absence of such usage of the amine in the synthesis mixture.

   A suitable colorless needle-shaped single crystal ($0.05 \times 0.05 \times 0.125$ mm) was carefully selected under a polarizing microscope and glued to the tip of a glass fiber using Superglue (cyanoacrylate). Crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. A hemisphere of intensity data were collected in 1321 frames with ω scans (width of 0.30 and exposure time of 10 s per frame). The lattice parameters are $a = 4.712(1)$; $b = 5.862(1)$; $c = 22.242(2)$ Å; $\beta = 95.77(1)°$; $V = 611.3 (1)$ Å^3; space group $= P2_1/n$ (No. 14); and $Z = 4$. The pertinent experimental conditions are listed in Table 1.

   The structure was solved by direct methods using SHELXS-86 (8) and difference Fourier syntheses. The absorption correction was based on symmetry equivalent reflections using the SADABS (9) program. Other effects such as absorption by the glass fiber were simultaneously corrected. The last cycles of refinement included atomic positions and anisotropic thermal parameters for all atoms. Full-matrix least-squares structure refinement against $|F|$ was carried out using the CRYSTALS (10) package of programs. The applied weighting scheme was based on Tukey and Prince with a three term modified Chebyshev polynomial (11). The final Fourier map had minimum and maximum peaks of -0.96 and 0.89 e Å^{-3}, respectively. Final R values,

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TABLE 1
Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for $Sn_2(PO_4)(C_2O_4)_{0.5}$

Formula	$Sn_2(PO_4)(C_2O_4)_{0.5}$
Crystal system	Monoclinic
Space group	$P2_1/n$ (No. 14)
Crystal size	$0.05 \times 0.05 \times 0.125$ mm
a	4.712(1) Å
b	5.862(1) Å
c	22.242(2) Å
β	95.77(1)°
Volume	611.3(1) (Å^3)
Z	4
Formula mass	376.4(1)
ρ	4.09 (g cm^{-3})
λ (MoKα)	0.71073 (Å)
μ	8.43 (mm^{-1})
2θ range	5.0°–46.0°
Total data collected	2250
Index ranges	$-6 \leq h \leq 6, 0 \leq k \leq 7, 0 \leq l \leq -29$
Unique data	1442
Observed data ($\sigma > 3\sigma(I)$)	1077
R_{merg}	3.25
R	2.65
R_w	2.93
Goodness of fit (S)	1.1
Number of variables	92

$R = 2.65$ and $R_w = 2.93$, and $S = 1.11$, were obtained for a total of 92 parameters. The atomic coordinates are given in Table 2.

TABLE 2
Atomic Coordinates and Isotropic Displacement Parameters for $Sn_2(PO_4)(C_2O_4)_{0.5}$

Atom	x/a	y/b	z/c	U_{eq}/U_{iso}
Sn(1)	0.06611(9)	0.65931(7)	0.81664(2)	0.0162
Sn(2)	0.15610(9)	0.12645(8)	0.93162(2)	0.0182
P(1)	$-0.1019(3)$	0.7636(3)	0.67339(7)	0.0138
O(1)	0.034(1)	0.5885(8)	0.7240(2)	0.0220
O(2)	0.4611(9)	0.4939(8)	0.8113(2)	0.0206
O(3)	$-0.0737(9)$	0.3121(8)	0.8373(2)	0.0175
O(4)	0.499(1)	0.2116(8)	1.0185(2)	0.0254
O(5)	0.208(1)	0.5130(8)	0.9444(2)	0.0226
O(6)	0.5178(9)	0.1627(8)	0.8862(2)	0.0190
C(1)	0.582(1)	0.412(1)	1.0215(3)	0.0177

RESULTS AND DISCUSSION

The Sn(II) phosphate material synthesized in the present study was found to contain oxalate groups, giving rise to the structure formula $Sn_2(PO_4)(C_2O_4)_{0.5}$. The structure of this material is based on a network of pyramidal SnO_3, truncated square-pyramidal SnO_4, and tetrahedral PO_4 units. The asymmetric unit contains nine independent nonhydrogen atoms (Fig. 1). The SnO_3 and PO_4 units are vertex linked to form four-membered rings, which are connected to each other forming a one-dimensional chain along the b axis (Fig. 2). These one-dimensional chains are, in turn, connected to each other through the four-coordinated Sn(11)
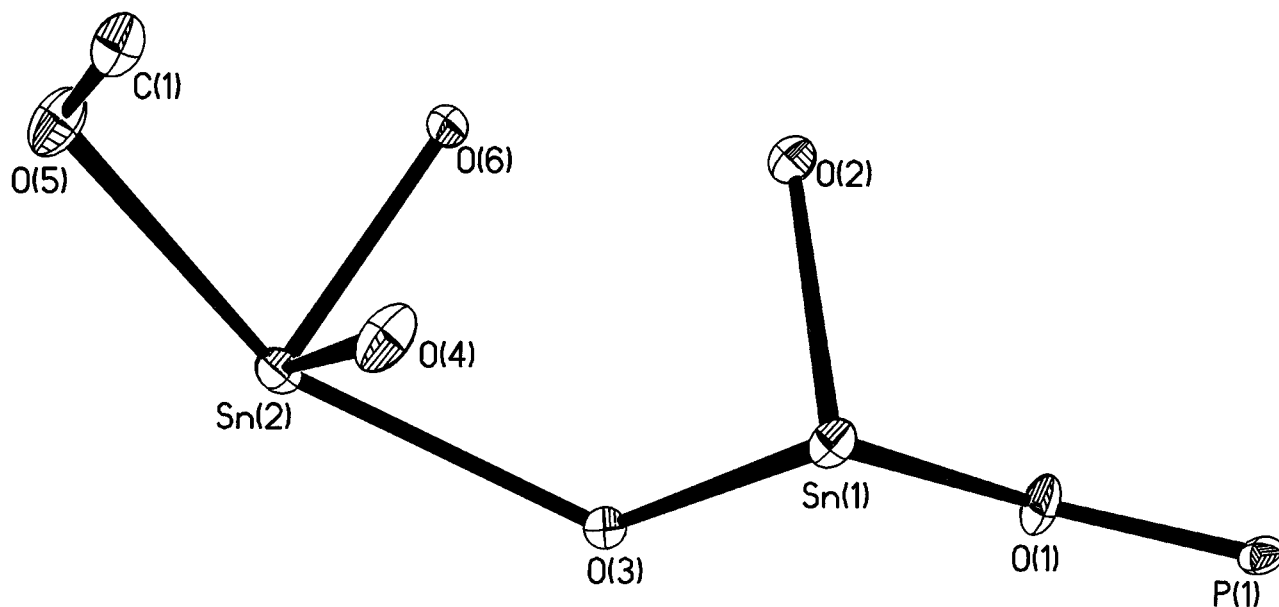
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FIG. 1. Asymmetric unit of $Sn_2(PO_4)(C_2O_4)_{0.5}$. Thermal ellipsoids are shown at 30% probability.
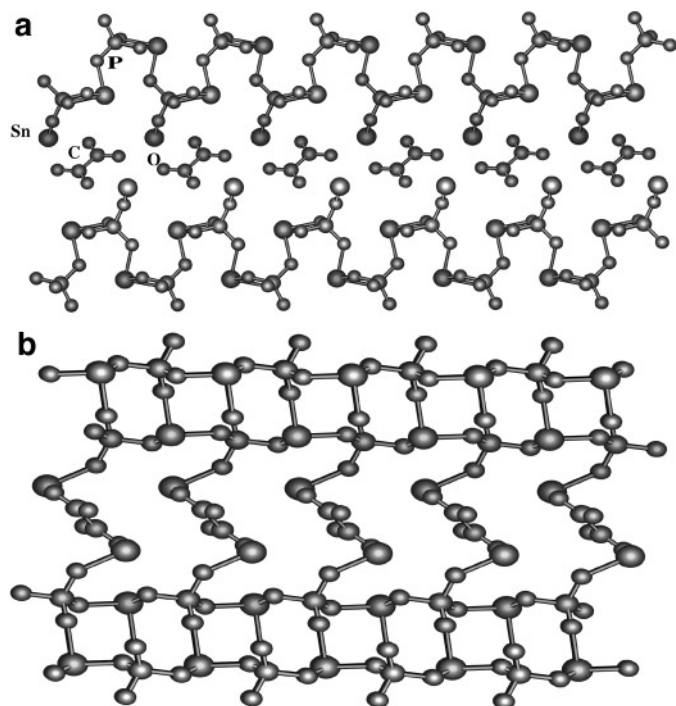
FIG. 2. (a) Connectivity within the chain and the position of the oxalate unit along the *a* axis. (b) Connectivity within the chain and with the adjacent ones via the oxalate group along the *b* axis.

atoms and the oxalate group (Fig. 2). This type of linkage creates Sn–O–Sn (involving O(3)) bonding in this structure. Along the *ab* plane the network forms a sheet made entirely of six-membered rings (Fig. 3), which are again connected to the adjacent ones by the oxalate group.
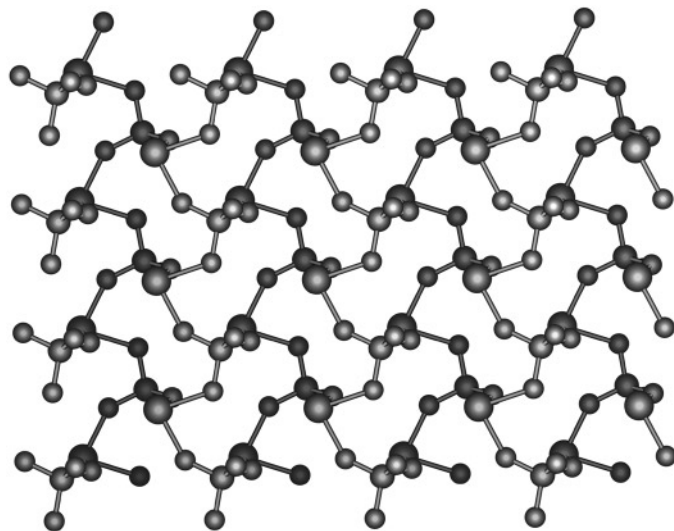

FIG. 3. Structure of a single layer along the *ab* plane. For clarity the oxalate units are not shown. Large spheres = Sn; medium spheres = P; smaller spheres = O.

All the Sn–O bond distances lie in the range 2.080 to 2.507 Å (average, 2.249 Å), and the O–Sn–O bond angles are in the range 69.3° to 140° (average, 87.6°); this is typical of three- and four-coordinated Sn in 2+ oxidation state. The values are in excellent agreement with other tin(II) phosphates previously reported (5–7, 12, 13). However, the longest bond distance [Sn(2)–O(3) = 2.507 Å] and the largest bond angle (O(5)–Sn(2)–O(3)) are observed for oxygens involved in Sn–O–Sn linkages. However, the shortest bond angle [O(4)–Sn(2)–O(5) = 69.3°] are observed for the oxygen atom coordinating with the carbon atom in this structure. The P–O distances are within the range 1.527 to 1.550 Å (average, 1.537 Å), and the O–P–O bond angles are in the range 105.8° to 112.8° (average, 109.5°). These values, too, are comparable to other P–O distances and angles found in many of the alumino- and gallophosphates reported in the literature (5–7, 14–16).

Thermogravimetric analysis (TGA) of the tin phosphooxalate material was carried out in the presence of flowing air from room temperature up to 700°C. The results show a single sharp weight loss in the region 450–500°C, after which the sample decomposes. The weight loss corresponds to about 7.5% of the total mass of the sample and can be directly correlated to the decomposition and the oxalate group (calc., 7.2%). The powder X-ray diffraction pattern of the decomposed sample indicates a very poorly crystalline phase, with most of the lines corresponding to the crystalline phase $Sn_2P_2O_7$ (JCPDS: 35-28); it seems likely that an amorphous phase with a Sn:P ratio >2:1 is also present.

The structure of the title compound is unique and novel in that the oxalate group provides the link between the two tin phosphate chains, the oxalate group having formed by the decomposition of the tin oxalate used in the starting mixture as the tin source. The structure has some similarities to the previously reported structure of stannous hydroxide phosphate, $Sn_2(OH)PO_4$ (13). In the structure of stannous hydroxide phosphate the SnO_3 and PO_4 units are connected via –OH groups. Four-membered zigzag chains are present in the structure along the *b* axis, while the layers formed along the *ab* plane are held together by the lone pair of electrons of the Sn(II) atoms. In the present structure, however, the layers are held together by the oxalate group and the four-membered chains are more regular in nature and do not involve any hydroxyl groups (Fig 2). Also, the presence of Sn–O–Sn bonding along with the oxalate linkages makes this material unique. The other tin phosphate materials reported in the literature (5–7, 12, 13) contain only phosphate groups attached to the tin atoms. Thus, the present study is the first report wherein another anion, viz., oxalate, is part of the framework giving rise to the tin phosphatooxalate structure. At present, efforts are underway to introduce other anions as part of the frame-work to create new structures based on tin and phosphorus.

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