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Synthesis and Structural Characterization of a New Open-Framework Tin(II) Phosphate: $[Sn_4(PO_4)_3]^- \cdot 0.5[C_4N_2H_{12}]^{2+}$

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Introduction

In the past two decades, a large number of open-framework metal phosphates have been synthesized in the presence of an organic amine as the template.[1−5] For their potential applications in catalysis, ion exchange, and separation, these metal phosphate materials have attracted great attention. Recently, a series of organically templated tin(II) phosphates, which exhibit a considerable structural and compositional diversity, were synthesized under hydrothermal conditions.[6−12] Among these newly discovered tin(II) phosphate compounds, a few have structural features similar to microporous crystalline materials (e.g., zeolites). The building units in these compounds are SnO_3 and PO_4 groups, and they are alternately connected by sharing their vertices to form open frameworks with channels and/or cages. The amine molecules (mostly in protonated form) reside in the channels as guest species. Unlike most metal phosphate frameworks which are built up from MO_4, MO_5, and MO_6 units, the tin(II) phosphates contain a unique building motif of trigonal-pyramidal SnO_3 units. This is due to the effect of the lone pair on the Sn(II) cation. The Sn atoms are coordinated with three oxygen atoms and occupy the vertex of a trigonal pyramid, whereas the lone pair presumably occupies the fourth vertex of a tetrahedron formed by the three O atoms and the lone pair itself around the Sn(II) atom. The composition of the inorganic part for the 3D open-framework tin phosphates reported in the literature is usually $[Sn_4P_3O_{12}]^-$ with the negative charges being balanced by the protonated amine cations located in the framework channels. In this paper, we present the synthesis and structural characterization of a new three-dimensional tin phosphate templated by piperazine. This compound has a framework composition of $[Sn_4P_3O_{12}]^-$ as well but the connection of the building units in the framework is rather unique.

Table 1. Crystallographic Data for $[Sn_4(PO_4)_3]^- \cdot 0.5[C_4N_2H_{12}]^{2+}$

chemical formula	$[Sn_4(PO_4)_3]^- \cdot 0.5[C_4N_2H_{12}]^{2+}$
fw	803.75
space group	$P2_1/c$
a, Å	7.088(2)
b, Å	23.336(4)
c, Å	9.043(2)
β, deg	103.34(1)
V, Å^3	1455.5(5)
Z	4
μ, cm^{-1}	71.75
ρ_{calcd}, g cm^{-3}	3.668
λ, Å	0.71073
T, °C	20
R1 $[I > 2\sigma(I)]$[a]	0.0289
wR2 $[I > 2\sigma(I)]$[b]	0.0678

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Experimental Section

Synthesis. The title compound was hydrothermally synthesized using tin(II) chloride dihydrate, phosphoric acid (85 wt %), and piperazine ($C_4H_{10}N_2$) as the starting materials. The molar composition of the initial mixture was $SnCl_2$:$2H_3PO_4$:$2C_4H_{10}N_2$:$168H_2O$. Thus, 1.1 g of $SnCl_2 \cdot 2H_2O$ was first dispersed in 15 mL of distilled water with stirring, followed by hydrolysis to form a white gel. To the gel were successively added 0.8 g of piperazine and 0.7 mL of H_3PO_4 with stirring. The final reaction mixture was stirred further until homogeneous, sealed in a Teflon-lined stainless steel autoclave and heated at 453 K for 10 days under autogenous pressure. The solid product (in about 80% yield based on the Sn source) consisting of colorless prismatic single crystals was recovered by filtration, washed thoroughly with distilled water, and dried at room temperature.

Characterization. The powder X-ray diffraction (XRD) data were obtained using a Siemens D5005 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The step size was 0.02°, and the count time was 4 s. The element analyses were performed on a Perkin-Elmer 2400 element analyzer, and the inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300 DV ICP instrument. The IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted on a Perkin-Elmer TGA 7 thermogravimetric analyzer and a Perkin-Elmer DTA 1700 differential thermal analyzer, respectively, with a heating rate of 20 °C min^{-1}.

Single-Crystal X-ray Diffraction. A prismatic crystal of approximate dimensions 0.16 × 0.06 × 0.04 mm^3 was mounted on a glass fiber on a Siemens Smart CCD diffractometer equipped with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Intensity data were collected in 1271 frames with increasing ω (width of 0.3° per frame). A total of 2921 reflections were collected at 293 K with 1997 unique reflections ($R_{int.} = 0.0657$), of which 1750 were considered to be observed with $I > 2\sigma(I)$. Data processing was accomplished with the SAINT processing program.[13] The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL version 5.1.[14] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the amine were placed geometrically ($d_{N-H} = 0.90$ Å, $d_{C-H} = 0.97$ Å) and allowed to ride on the atoms to which they were attached with fixed isotropic thermal parameters. The detailed crystallographic data are listed in Table 1.

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Table 2. Gel Compositions and Crystallization Conditions for $[Sn_4(PO_4)_3]^- \cdot 0.5[C_4N_2H_{12}]^{2+}$

	reactants (molar ratio)				crystallization conditns			
run	SnO	P_2O_5	H_2O	piperazine	pH	time (days)	T (°C)	product[a]
1	1.0	1.0	168	1.25	2	8	180	$SnHPO_4$
2	1.0	1.0	168	2.00	4	8	180	SnPO-P
3	1.0	1.0	168	2.25	5	10	180	SnPO-P
4	1.0	1.0	168	2.50	6	10	180	SnPO-P + PPZ
5	1.0	1.0	168	2.75	6	8	180	SnPO-P + PPZ
6	1.0	1.0	168	3.50	7	6	180	PPZ
7	1.0	1.0	168	4.25	8−9	6	180	PPZ
8	1.0	1.0	168	5.00	9	6	180	PPZ
9	1.0	1.0	168	6.25	9−10	6	180	PPZ
10	1.0	1.0	168	7.50	10	10	180	no solid product
11	1.0	0.8	168	2.00	5	10	180	SnPO-P
12	1.0	1.0	168	2.00	5	10	180	SnPO-P
13	1.0	1.2	168	2.00	5	10	180	SnPO-P
14	1.0	1.3	168	2.00	4	10	180	SnPO-P

[a] SnPO-P = $[Sn_4(PO_4)_3]^- \cdot 0.5[C_4N_2H_{12}]^{2+}$, PPZ = $C_4N_2H_{12} \cdot HPO_4 \cdot H_2O$.

Results and Discussion

Synthesis. The gel compositions and the crystallization conditions for the title compound are presented in Table 2. It is seen that the content of the organic amine piperazine is an important factor for the formation of the product. The content of the piperazine directly influences the pH value of the initial gel. At pH = 2 (run 1), the crystallization product is the known compound $SnHPO_4$, whereas, when the pH is raised to above 4 (run 2), the title compound forms. If the pH value ranges from 6 to 10 (runs 5−9), another crystalline phase $C_4N_2H_{12} \cdot HPO_4 \cdot H_2O$ is obtained. At pH > 10, a clear solution without any solid product is formed. Therefore, the suitable pH range for the crystallization of the title compound is in the region 4−6.

It is interesting to note that the alkylammonium phosphate can also be obtained hydrothermally in the $SnO-P_2O_5-H_2O-$piperazine system. Riou et al. reported the structure of piperazinium monohydrogen phosphate monohydrate obtained in a hydrothermal fluoroaluminophosphate reaction system containing piperazine.[15] Recently, Oliver et al. also reported three alkylammonium phosphate structures formed in aluminophosphate synthesis mixtures.[16] It seems that the presence of a metal phosphate facilitates the crystallization of alkylammonium phosphates under appropriate reaction conditions.

Characterization. The ICP analysis indicates that the title compound contains 58.13 wt % Sn and 11.45 wt % P, in good agreement with the values 59.08 wt % Sn, 11.57 wt % P based on the single-crystal structure analysis. This gives rise to a Sn:P ratio of 4:3. The elemental analysis shows that the C, H, and N contents are 3.04, 0.81, and 1.76 wt % (calculated: 2.99 wt % C, 0.74 wt % H, 1.74 wt % N), respectively, corresponding to an empirical molar ratio of C:H:N = 1.0:3.2:0.5. These analysis results indicate that the solid sample of the title compound is a pure phase.

The IR spectrum of the $[Sn_4(PO_4)_3]^- \cdot 0.5[C_4N_2H_{12}]^{2+}$ compound is assigned as follows: The bands at 3400−3000 cm^{-1} are typically attributed to H-bonded N−H groups. The bands at 1103 and 958 cm^{-1} are associated with the asymmetric stretching vibrations of PO_4 units. There appear absorptions at 617, 534, and 459 cm^{-1} as well due to bending vibrations of PO_4 groups. The bands at 1600, 1455, and 1392 cm^{-1} are attributable to δ_{N-H}, ν_{C-H}, ν_{C-C}, and/or ν_{C-N} vibrations of the protonated piperazine cations occluded in the structure of the title compound.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[Sn_4(PO_4)_3]^- \cdot 0.5[C_4N_2H_{12}]^{2+}$

atoms	x	y	z	U(eq)[a]
Sn(1)	2391(1)	2421(1)	4066(1)	20(1)
Sn(2)	2437(1)	4222(1)	640(1)	21(1)
Sn(3)	3559(1)	6668(1)	2577(1)	20(1)
Sn(4)	2039(1)	8520(1)	2369(1)	18(1)
P(1)	4168(3)	3695(1)	4044(2)	17(1)
P(2)	2314(3)	5616(1)	160(2)	17(1)
P(3)	844(3)	7450(1)	4154(2)	17(1)
O(1)	2712(8)	3310(2)	4585(6)	23(1)
O(2)	3149(8)	4200(2)	3081(6)	26(1)
O(3)	3314(8)	5072(3)	895(6)	32(2)
O(4)	375(7)	5485(2)	−971(6)	21(1)
O(5)	3626(7)	5937(2)	−678(6)	23(1)
O(6)	1849(8)	6000(2)	1442(6)	24(1)
O(7)	4409(7)	6058(2)	4557(5)	20(1)
O(8)	1264(8)	6844(2)	3652(6)	21(1)
O(9)	656(7)	7447(2)	5822(5)	20(1)
O(10)	−1142(7)	7667(2)	3233(5)	21(1)
O(11)	2486(7)	7858(2)	3998(6)	23(1)
O(12)	4777(8)	8330(2)	1925(5)	22(1)
N(1)	1495(11)	5198(3)	4308(8)	37(2)
C(2)	−409(14)	5473(4)	3967(10)	35(2)
C(1)	1938(14)	4934(4)	5844(10)	36(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Selected Bond Lengths (Å) for $[Sn_4(PO_4)_3]^- \cdot 0.5[C_4N_2H_{12}]^{2+}$

Sn(1)−O(1)	2.128(6)	Sn(2)−O(3)	2.077(6)
Sn(1)−O(10)[a]	2.142(5)	Sn(2)−O(2)	2.148(5)
Sn(1)−O(9)[b]	2.207(5)	Sn(2)−O(4)[c]	2.192(5)
Sn(3)−O(6)	2.093(5)	Sn(4)−O(11)	2.106(5)
Sn(3)−O(8)	2.118(5)	Sn(4)−O(12)	2.117(5)
Sn(3)−O(7)	2.259(5)	Sn(4)−O(5)[d]	2.253(5)
P(1)−O(1)	1.532(6)	P(2)−O(3)	1.529(6)
P(1)−O(12)[e]	1.534(5)	P(2)−O(4)	1.543(5)
P(1)−O(7)[f]	1.538(5)	P(2)−O(6)	1.558(6)
P(1)−O(2)	1.543(6)	P(2)−O(5)	1.525(6)
P(3)−O(11)	1.535(6)	N(1)−C(2)	1.461(12)
P(3)−O(8)	1.537(6)	N(1)−C(1)	1.485(12)
P(3)−O(9)	1.545(5)	C(1)−C(2)[b]	1.480(13)
P(3)−O(10)	1.546(5)		

[a−f] The following symmetry transformations were used to generate equivalent atoms. [a] $-x, y - {}^1/_2, -z + {}^1/_2$. [b] $-x, -y + 1, -z + 1$. [c] $-x, -y + 1, -z$. [d] $x, -y + {}^3/_2, z + {}^1/_2$. [e] $-x + 1, y - {}^1/_2, -z + {}^1/_2$. [f] $-x + 1, -y + 1, -z + 1$.

The TGA curve shows that the weight loss of $[Sn_4(PO_4)_3]^- \cdot 0.5[C_4N_2H_{12}]^{2+}$ is ca. 5.9% from 369 to 451 °C, in accordance with the calculated amount of 5.47% for the decomposition of the template. The DTA curve exhibits one endothermic peak at ca. 415 °C corresponding to this decomposition. After calcination at 500 °C for 2 h, the structure of $[Sn_4(PO_4)_3]^- \cdot 0.5[C_4N_2H_{12}]^{2+}$ collapses and converts to an amorphous phase. Above 700 °C the amorphous phase recrystallizes to form a poorly crystalline $Sn_2P_2O_7$ phase [JCPDS: 35−28], which is confirmed by powder X-ray diffraction. It is likely that an amorphous phase with a Sn:P ratio greater than 4:3 is also present.

Description of the Structure. The atomic coordinates and selected bond lengths are given in Table 3 and Table 4, respectively. The structure of the title compound is based on a network of strictly alternating SnO_3 and PO_4 units with all the vertices being shared. The framework has a formula of $[Sn_4(PO_4)_3]^-$, which is identical to that for the open-framework

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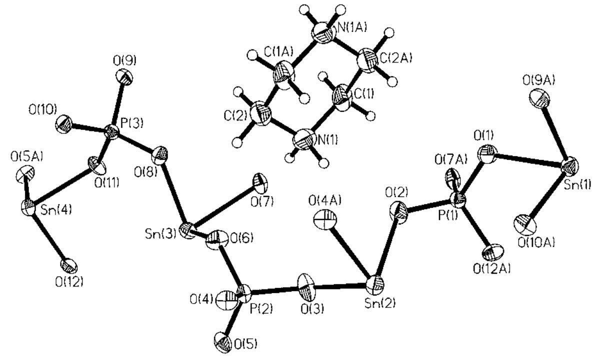

Figure 1. ORTEP view of the $[Sn_4(PO_4)_3]^{-}\cdot 0.5[C_4N_2H_{12}]^{2+}$ structure showing the atom-labeling scheme (50% thermal ellipsoids).

tin(II) phosphates reported earlier.[9−11] The negative charges of the inorganic part of the title compound are balanced by diprotonated piperazine cations located in the channels of the open-framework structure. The atom-bonding scheme of $[Sn_4(PO_4)_3]^{-}\cdot 0.5[C_4N_2H_{12}]^{2+}$ is shown in Figure 1. It contains four crystallographically distinct tin sites and three distinct phosphorus sites. Of the three independent phosphorus atoms, each is four-coordinated by oxygen atoms with the P−O distances varying between 1.525 and 1.558 Å (1.538 Å on average) and the O−P−O angles in the range 104.7−112.1° (109.5° on average). These bond distances and angles are close to those observed previously for other metal phosphates.[8−10] All the Sn atoms are three-coordinated by oxygen, and the Sn−O distances fall in the range 2.077−2.259 Å (2.165 Å on average). The Sn−O bond angles vary from 79.47 to 89.0° (85.11° on average). The Sn−O bond lengths and O−Sn−O bond angles are within the typical ranges reported for other tin phosphate materials.[7−12]

The framework of $[Sn_4P_3O_{12}]^{-}$ is three-dimensional and has a one-dimensional eight-membered T-ring (T stands for Sn or P) channel along the *a* axis (Figure 2). The structure can be considered to be built up from the network of four-, six-, eight-, and ten-membered rings. The four-, six-, eight-, and ten-membered rings are so connected as to form an open-framework structure. The width of the 8-ring channel is 7.420 × 4.564 Å (longest O−O and shortest O−O distances) with the diprotonated piperazine molecules being located in the middle of the channel.

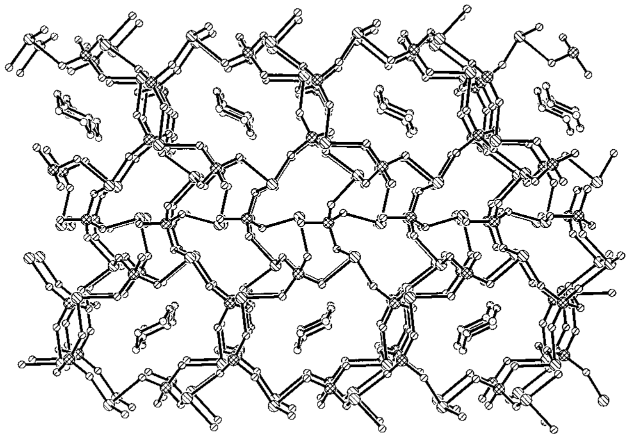

Figure 2. The structure of $[Sn_4(PO_4)_3]^{-}\cdot 0.5[C_4N_2H_{12}]^{2+}$ viewed along the *a* axis showing the eight-membered-ring channels and the piperazine molecules. Hydrogens on the amine molecule are not shown for clarity.

Although the framework formula $[Sn_4P_3O_{12}]^{-}$ has also been observed in another three tin phosphates,[9−11] the framework structure of the title compound is different from those for the previously reported materials. The framework of $[Sn_4P_3O_{12}]^{-}\cdot 0.5[H_3N(CH_2)_2NH_3]^{2+}$ is constructed from cages that are stacked to form 8-ring channels.[9] $[Sn_4P_3O_{12}]^{-}\cdot 0.5[H_3N(CH_2)_4NH_3]^{2+}$ contains intersecting 8- and 12-membered-ring channels, and its basic building units are four- and six-membered rings.[10] $[Sn_4P_3O_{12}]^{-}\cdot 0.5[H_3NCH_2CH_2CH(NH_3)CH_2CH_3]^{2+}\cdot 2H_2O$ has uniform 8-ring channels along the *a* and *b* axes, and there are 12-ring channels along the *c* axis.[11]

There are strong H-bonding interactions between the organic amine and the framework oxygen atoms [N(1)···O(7) = 2.851(9) Å, N(1)···O(2) = 2.938(10) Å], and these interactions are believed to be conducive to the formation of the open-framework structure.

In summary, a three-dimensional open-framework tin(II) phosphate with occluded diprotonated piperazine has been prepared under hydrothermal conditions from the $SnO-P_2O_5-H_2O-$piperazine reaction system. X-ray structural analysis shows that the structure is built up from strictly alternating SnO_3 and PO_4 units. The protonated piperazine molecules are entrapped in the eight-membered-ring channels, and they have strong interactions via hydrogen bonding with the framework oxygen atoms. The successful synthesis of the title compound indicates that, by variation of the template molecule, 3D open-framework tin phosphates with new structural features are able to crystallize.

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Supporting Information Available: An X-ray crystallographic file in CIF format for $[Sn_4(PO_4)_3]^{-}\cdot 0.5[C_4N_2H_{12}]^{2+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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