Hydrothermal Synthesis and Crystal Structure of A Three-Dimensional Open-Framework Tin(II) Phosphate, $[H_2DACO]_{0.5}^{2+}[Sn_4(PO_4)_3]^-$

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Open-framework materials, especially those of metal phosphates, have been of great interest in the past few years because of their potential applications in catalysis, sorption, ion-exchange processes and other areas, and also due to the fascinating structural features exhibited by them.[1-6] Continued research in this area has shown that these materials are generally prepared under hydrothermal conditions in the presence of structure-directing organic amines (templates).[7-11] It is well established that open-framework tin(II) phosphate compounds can be synthesized with the aid of organic structure-directing amines.[12-14] From the perspective of structure, a tin atom will link with either three oxygen atoms to form a trigoanl pyramidal SnO_3 or four oxygen atoms to form a square pyramidal SnO_4, and a phosphorus atom will link with four oxygen atoms to form a tetrahedron PO_4. Either SnO_3 or SnO_4 units connect with PO_4 by common vertex to form the anion structures ranging from isolated anions to infinite chains, two-dimensional layers, and three-dimensional extended networks.[15-18] The organic amines could act as a structure-directing agent, or merely fill the available voids and stabilize the structures through hydrogen bonding and other interactions.[9,17,18]

In this paper, we report the synthesis and crystal structure of a new three-dimensional open-framework tin(II) phosphate, $[H_2DACO]_{0.5}^{2+}[Sn_4(PO_4)_3]^-$, having a Sn:P ratio of 4:3, prepared under hydrothermal conditions in the presence of 1,5-diazacyclooctane (DACO) as the structure-directing agent.

Experimental Section

General Remarks. With the exception of 1,5-diazacyclooctane dihydrobromide (DACO·2HBr) which was synthesized according to the literature method,[19] all solvents and chemicals required for syntheses were commercially available and employed without further purification. X-ray powder diffraction data were measured on a DMAX2500 diffractometer. Element analyses of carbon, hydrogen and nitrogen were performed with a Vario EL III element analyzer. Thermogravimetric analysis was performed on a Netzsch Sta449C thermoanalyzer under N_2 atmosphere in the range of 30-1000 °C at a heating rate of 10 °C/min. The crystal structure was determined by a Rigaku Mercury CCD area-detector diffractometer and SHELXL crystallographic software of molecular structure.

Synthesis of the Complex $[H_2DACO]_{0.5}^{2+}[Sn_4(PO_4)_3]^-$ (1). The complex **1** was synthesized hydrothermally under autogenous pressure. A mixture of tin(II) oxalate (1.03 g, 5 mmol), 85 wt.-% aqueous phosphoric acid (0.58 g, 5 mol), DACO·2HBr (1.38 g, 5 mmol), Na_2CO_3 (0.53 g, 5 mmol), H_2O (14 mL) and EtOH (1 mL) was stirred at room until a homogeneous mixture was obtained. The mixture was sealed in a Teflon-line autoclave and heated 170 °C for 5 days and then cooled to room temperature. Colorless crystals were recovered by filtration, washed with distilled water, and dried in air (62% yield based on tin). Anal. Calcd for **1** (dried) (%): C, 4.41; H, 0.99; N, 1.71. Found: C, 4.33; H, 1.15; N, 1.83. The X-ray powder diffraction pattern for the bulk product is in fair agreement with the pattern based on single-crystal X-ray solution in position, indicating the phase purity of the as-synthesized sample of the complex **1** (Figure 1). The difference in reflection intensities between the simulated and experimental patterns was due to the variation in preferred orientation of the powder sample during collection of the experimental XRD data.

X-ray Crystal Determination. A colorless prismatic single crystal of complex **1** with dimensions of 0.30 mm × 0.10 mm × 0.10 mm was mounted on a glass fiber. X-ray diffraction intensity data were collected on a Rigaku Mercury CCD area-detector equipped with a graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) by using an ω-2θ scan mode

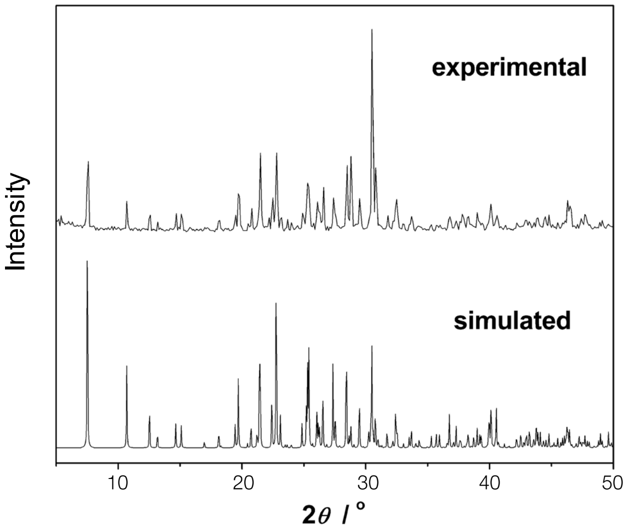


Figure 1. Experimental and simulated X-ray powder diffraction patterns of complex **1**.

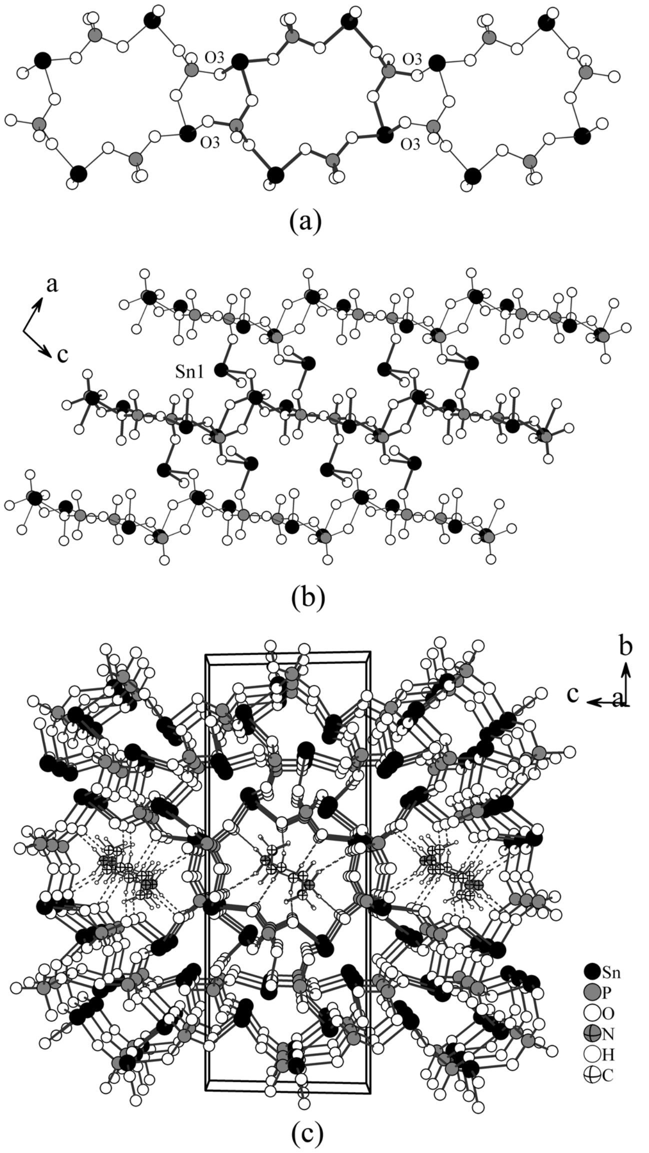
Table 1. Crystallographic data and structure refinement parameters for complex **1**

Formula	$C_3H_8NO_{12}P_3Sn_4$	β (°)	103.633(7)
Fw	817.77	V (Å^3)	1495.7(10)
Crystal system	Monoclinic	Z	4
Space group	$P2_1/c$	D_{calcd}, (g cm^{-3})	3.632
a (Å)	7.209(3)	μ (mm^{-1})	6.985
b (Å)	23.499(9)	GOF on F^2	1.043
c (Å)	9.085(4)	R_1, wR_2	0.0255, 0.0614

in the range of $2.89 \le \theta \le 27.48^{\circ}$ at 293(2) K with the index ranges $-9 \le h \le 9$, $-29 \le k \le 30$, $-11 \le l \le 9$. A total of 11220 independent reflections were measured, of which 3427 were unique ($R_{\text{int}} = 0.03$) and 3130 were observed ($I > 2\sigma(I)$) and used in the subsequent structure determination. Absorption correction was performed by the CrystalClear program.[20] The structure was solved by direct methods using SHELXS-97 program and refined by full-matrix least-squares refinement on F^2 with the aid of SHELXL-97 program.[21,22] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located geometrically. The final $R = 0.0255$ and $wR = 0.0614$ ($w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 0.3P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.043$, $(\Delta/\sigma)_{\max} = 0.002$, $(\Delta\rho)_{\max} = 0.835$ and $(\Delta\rho)_{\min} = -1.042$ e/Å^3. Some refinement details and crystal data are gathered in Table 1.

Results and Discussion

The complex **1** was synthesized from the reaction mixtures of SnC_2O_4, H_3PO_4, DACO·2HBr, Na_2CO_3, H_2O, and EtOH in the mole ratio of 1:1:1:1:155:4 at 170 °C by the hydrothermal technique. In this system, Na_2CO_3 was added to adjust the pH value of the reaction mixture. And it was found that crystals suitable for X-ray single-crystal analysis were obtained only with this ratio. In general, syntheses of the metal phosphates are not only closely related to the geometry and the number of coordination sites provided by metal ions or oxygen atoms, but also controlled by the environment conditions (such as: reactants, metal-to-phosphorus ratio, organic amine, pH value, solvents, temperature, *etc*.). Thus, this preparation may mainly depend on the choices of both reactants and their stoichiometric ratio.



(a)

(b)

(c)

Figure 2. (a) Chain composed of eight-membered rings $[(SnO_3)_4(PO_4)_4]$. (b) Linkage of the chains and $Sn(1)O_3$ trigonal pyramids. (c) Packing diagram of complex **1** along the *a* axis, showing eight-membered ring channels occupied by diprotonated DACO molecules in the same direction. The dotted lines represent possible hydrogen-bonding interactions.

The structure, which was solved by single-crystal X-ray diffraction, is based on a network of strictly alternating SnO_3 and PO_4 units in which all the vertices are shared. The SnO_3 and PO_4 units form a three-dimensional open framework with the formula $[Sn_4(PO_4)_3]^-$. Charge neutrality is achieved by the incorporation of the template in its diprotonated form; there are $0.5[H_2DACO]^{2+}$ ions per framework formula unit. The asymmetric unit contains 23 independent non-hydrogen atoms: three phosphate groups are linked *via* oxygens to four tin atoms to form the building block of the framework. All the Sn atoms are three-coordinated with oxygen atoms with Sn–O bond lengths in the range of 2.092(3)-2.256(3) Å (*av*. 2.147 Å) and the O–Sn–O bond angles are in the range of 80.74(12)-88.21(13)° (*av*. 85.35°). These values are typical of three-coordinated Sn in the 2+ oxidation state and are in excellent agreement with values for other previously known tin phosphates in the literatures.[18,23,24] The three oxygen atoms form a trigonal pyramid around the Sn atom, with the lone pair of electrons on the Sn atoms presumably occupying the base vertex of a tetrahedron. All the P atoms in the complex feature tetrahedral coordination sphere of four oxygen atoms with P–O bond lengths varying from 1.528(3) to 1.553(3) Å (*av*. 1.538 Å) and O–P–O bond angles lying between 104.58(18) and 112.13(19)° (*av*. 109.31°), which are in close with those previously observed.[7,9,10] All the twelve oxygen atoms are μ-O which are connected with Sn atoms and P atoms. The bond valence sum calculations carried out on both frameworks indicate that the individual bond valences of Sn, P, and O are

Table 2. Hydrogen bonding distances (Å) and angles (°) for complex **1**

D–H···A	*d*(D-H)	*d*(H···A)	*d*(D-A)	∠(DHA)
N(1)–H(1A)···O(3)#1	0.90	2.32	3.167(10)	156
N(1)–H(1B)···O(2)#2	0.90	2.03	2.926(11)	172
C(2)–H(2A)···O(6)	0.97	1.95	2.904(10)	169
C(2)–H(2B)···O(5)#2	0.97	2.01	2.944(10)	161

Symmetry codes: #1 1 + *x*, y, 1 + *z*; #2 1 − *x*, 1 − *y*, 1 − *z*.

2+, 5+, and 2−, respectively.

In this open-framework structure, four SnO_3 trigonal pyramids are linked alternately with four PO_4 tetrahedra to form distorted eight-membered ring $[(SnO_3)_4(PO_4)_4]$ (Figure 2a); these rings are connected each other by common vertex (O(3)) to form one-dimensional chain (Figure 2a); adjacent chains are joined by $Sn(1)O_3$ trigonal pyramids to form two-dimensional structure extending along the *ac* plane (Figure 2b). On the other hand, $Sn(4)O_3$ trigonal pyramids are linked alternately with $P(2)O_4$ tetrahedra to form wave-shape chain along the *c* axis. And then these chains connect with those two-dimensional structures to construct three-dimensional open-framework structure (Figure 2c). The structure can also 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. Along the *a* axis there are eight-membered ring channels composed of $[(SnO_3)_4(PO_4)_4]$ rings with the width of 7.119 × 5.280 Å (longest and shortest atom-atom distances not including the van der Waals radii). The diprotonated DACO molecules with the chair configuration locate in the middle of the eight-membered ring channels (Figure 2c). The lone pair of electrons of the Sn atoms do not protrude into the eight-membered ring channels rendering it effective for sorption of diprotonated DACO molecules.

Although the framework formula $[Sn_4(PO_4)_3]^-$ has also been observed in another three tin(II) phosphates,[12-14] the framework structure of the complex **1** is different from those for the previously reported materials. The framework of $[NH_3CH_2CH(NH_3)CH_3]_{0.5}^{2+}[Sn_4(PO_4)_3]^-\cdot H_2O$ has eight-membered ring channels which are constructed by four- and six-membered rings.[12] $[NH_3(CH_2)_4NH_3]_{0.5}^{2+}[Sn_4(PO_4)_3]^-$ contains interesting eight- and twelve-membered ring channels, and its basic building units are four- and six-membered rings.[13] $[NH_3CH_2CH_2CH(NH_3)CH_2CH_3]_{0.5}^{2+}[Sn_4(PO_4)_3]^-\cdot 2H_2O$ exhibits uniform eight-membered ring channels along the *a* and *b* axis, and there are twelve-membered ring channels along the *c* axis.[14]

Strong interactions between the organic structure-directing agent and the framework oxygens *via* multipoint hydrogen bonding enhance the inherent stability of the three-dimensional open-framework structure investigated here. The important hydrogen bonding distances and angles for complex **1** are presented in Table 2. The present complex thus provide good example of multipoint hydrogen bonding and illustrate the importance of them in the structural stability of three-dimensional materials.

To study the stability of this material, thermogravimetric analysis (TGA) was performed on polycrystalline sample of this complex (Figure 3). TGA revealed that it is stable up to *ca.* 296 °C, and then a sharp weight loss of *ca.* 6.84% occurred between *ca.* 296 and 397 °C, corresponding to the removal of the organic templates (calc. 7.11%). In the following weight loss, this complex continued to decompose gradually, and the resulting white unknown residue was found after complete decomposition.

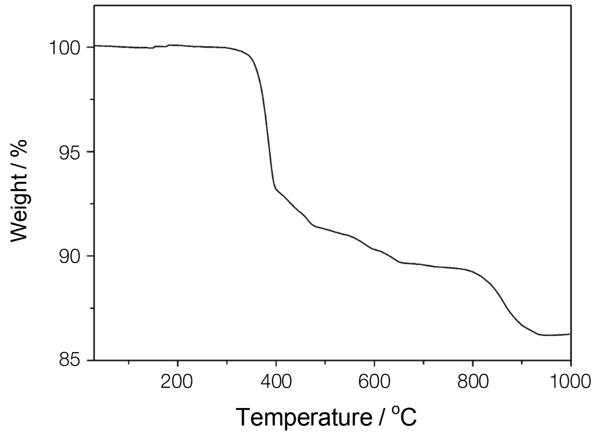


Figure 3. TGA curve of complex **1**.

In conclusion, using 1,5-diazacyclooctane as template, a new three-dimensional open-framework tin(II) phosphate has been obtained and characterized structurally by X-ray crystallography. The structure contains eight-membered ring channels occupied by the protonated template molecules which interact with the framework through hydrogen bonding. It pays to continue to synthesize open-framework tin(II) phosphates using other organic amines as structure-directing agent and investigate the relation of their structures and properties.

Supplementary Material. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC706438. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336-033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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