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Synthesis and characterization of alkali-metal tin(II) phosphates: $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$ and $K_2SnP_2O_7$

Sheng-Feng Weng, Kuei-Bo Chen, Chi-Shen Lee*

Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, 1001 Ta-Hsueh Road, Hsinchu 30010, Taiwan

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Abstract

Two new alkali-metal tin(II) phosphates – $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$ (**1**) and $K_2SnP_2O_7$ (**2**) – were synthesized by high-temperature reactions and structurally characterized by single-crystal X-ray diffraction. $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$ crystallized in the noncentrosymmetric space group $P\text{-}62c$ (No. 190) with $a = 9.6445(1)$ Å, $b = 9.6445(1)$ Å, $c = 34.059(6)$ Å, $V = 2743.6(7)$ Å^3 and $Z = 1$. $K_2SnP_2O_7$ crystallized in the monoclinic space group $P2_1/n$ with $a = 9.856(3)$ Å, $b = 6.7244(1)$ Å, $c = 12.225(3)$ Å, $\beta = 108.240(5)^\circ$, $V = 769.5(3)$ Å^3 and $Z = 4$. Both structures exhibit a novel open-framework structure. The crystal structure of **1** contains SnO_3 and SnO_4 polyhedra sharing corners with $[HPO_4]^{2-}$, $[PO_4]^{3-}$ and $[P_2O_7]^{4-}$ groups, which form tunnels of six rings filled with Na^+ cations and parallel to the c-axis, which are connected via O–Sn–O bridges to form a three-dimensional open framework. The crystal structure of **2** contains SnO_4 seesaw polyhedra sharing corners with diphosphate groups to form a three-dimensional $[SnP_2O_7]^{2-}$ framework that exhibits a tunnel structure of 10- and 12-membered rings expanding along [011] and [100] with four arrays of K^+ cations located in channels of the framework.

Keywords: Tin(II) phosphate; Crystal structure; Noncentrosymmetric; Channel structure

1. Introduction

Metal phosphates exhibit varied structural types that have been the subject of intensive research [1–4]. Much attention has been devoted to the synthesis of open-framework metal phosphates, which might produce large void volumes for prospective applications such as chemical sensors and receptors for selective catalysis [5]. Many main-group metals, such as group III (Al, Ga, In), IV (Ge, Sn, Pb), and V (As–Sb–Bi) can cooperate with phosphate units to form open-framework structures [1]. Among these compounds, tin phosphates are rare compared to other phosphate compounds [1]. Several authors have shown that tin(II) phosphates are interesting inorganic materials for lithium-ion battery and catalysts [5–8]. The Sn^{2+} cation contains nonbonded 5s electron pairs, which tend to coordinate with ligands in an acentric environment. Tin phosphates have thus become appealing in this regard as they offer interesting open-framework structures with possible noncentrosymmetric crystal structures showing a nonlinear optic property. Many tin phosphates have been structurally characterized [9–22]. Despite many efforts that show hydrothermal synthesis to be the most effective synthetic route to prepare open-framework tin(II) phosphates [23–36], the solid-state method tends to form a robust structure, which makes the compound capable of undertaking ion exchange and a large ionic conductivity. Our group has demonstrated that A_2HPO_4 and metal can serve as reducing and oxidizing reagents to synthesize metal phosphates, and several known compounds, such as $A_2MP_2O_7$ (A = Na, K; M = Pb, Zn) and $KZnBP_2O_8$, have been successfully synthesized [37–39]. We extended this research to the tin phosphate system and two new tin phosphates with unprecedented structural types were synthesized. As confirmed by measurements on single crystals, the synthesis of $K_2SnP_2O_7$ is presented as follows:

$$4K_2HPO_4 + 3Sn + SnO_2 + 2P_2O_5 \rightarrow 4K_2SnP_2O_7 + 2H_2$$

* Corresponding author. Tel.: +886 3 5131332; fax: +886 3 5723764.
E-mail address: chishen@mail.nctu.edu.tw (C.-S. Lee).

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In a reaction in which Na replaced K, a new phase $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$ was synthesized.

The compounds described here, with a channel structure, are interesting examples of tin phosphates prepared according to the solid-state synthetic route. Here we report the synthesis, structure and characterization of two new tin phosphates.

2. Experiments

2.1. Synthesis

$Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$ (**1**) and $2K_2SnP_2O_7$ (**2**) were synthesized by solid-state methods. The starting reagents were A_2HPO_4 (A = Na, K, 99.999%, Sigma), Sn (99.9%, Alfa), SnO_2 (99.9%, Sigma) and P_2O_5 (99.999%, J.T. Baker). In a typical reaction, precursors in stoichiometric proportions were mixed in an Ar-filled glove box (total mass ~ 0.5 g), placed in a silica tube, sealed under vacuum ($P \sim 10^{-4}$ torr), and heated slowly to 600 °C over 48 h, followed by cooling in the furnace to 22 °C on switching off the power. To avoid a possible explosion due to the formation of gaseous hydrogen, the length of reaction tube was kept about 7–8 cm (id = 0.9 cm). The products contain colorless and transparent crystals, rod- and plate-shaped for **1** and **2**, respectively. According to powder X-ray diffraction, the synthesis of **1** has a byproduct $Na_5P_3O_{10}$, and the reaction of **2** yields an impure KPO_3. Attempts to synthesize analogues using K^+ in **1** and Na^+ in **2** failed.

2.2. Single-crystal X-ray diffraction

Single crystals of compounds **1** ($0.3 \times 0.4 \times 0.85$ mm^3) and **2** ($1.3 \times 0.25 \times 0.2$ mm^3) were mounted on glass fibers with epoxy glue; intensity data were collected on a diffractometer (Bruker APEX CCD) with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. The distance from crystal to detector was 5.038 cm. Data were collected with a scan 0.3° in groups of 600 frames each at ϕ settings 0° and 60°. The duration of exposure was 30 and 20 s/frame for **1** and **2**, respectively. The 2θ values varied between 2.40° and 56.48°. Diffraction peaks obtained from all frames of reciprocal space images were used to determine the unit-cell parameters. The data were integrated using the Siemens SAINT program and were corrected for Lorentz and polarization effects [40]. Absorption corrections were based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements of numerous reflections. The structural model was obtained by direct methods and refined by full-matrix least-square refinement based on F^2 using the SHELXTL package [41]. The rod-shaped crystal of **1** revealed a hexagonal unit cell ($a = 9.6445(1)$ Å, $c = 34.059(6)$ Å, $V = 2743.6(7)$ Å^3) and the systematic absence conditions were consistent with space groups *P*-31*c* (No. 163), *P*31*c* (No. 159), *P*6$_3$*mc* (No. 186), *P*6$_3$/*mmc* (No. 194), and *P*-62*c* (No. 190). An initial model of the crystal structure was built in the centrosymmetric space groups. However, the diffraction data refinements indicate that the structure was not centrosymmetric and the noncentrosymmetric space group *P*-62*c* (No. 190) was found to be correct during structure refinement. The hydrogen atoms for **1** were observed with difference Fourier maps. Atomic positions were refined with anisotropic displacement parameters except O5 and O11 sites; fixed isotropic displacement parameters 0.02 was applied for H atom. Final structural refinements produced $R1/wR2 = 0.039/0.0886$. The plate-shaped crystal of **2** revealed a monoclinic unit cell ($a = 9.856(3)$ Å, $b = 6.7244(1)$ Å, $c = 12.225(3)$ Å, $V = 769.5(3)$ Å^3); systematic absences indicated space group $P2_1/n$ (No. 14). Final structural refinements produced $R1/wR2 = 0.0170/0.0431$. Crystallographic data and selected bond distances for **1** and **2** are given in Tables 1–3. Further details of the crystal-structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD-419265 for $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)12$ (**1**) and CSD-419264 for $K_2SnP_2O_7$ (**2**).

2.3. Characterizations

X-ray powder diffraction data of the products were measured at 22 °C on a powder diffractometer (Bruker D8 Advance Bragg–Brentano-type, operated at 40 kV and 40 mA; Cu Kα, $\lambda = 0.15418$ nm). For phase identification, XRD data were collected in a 2θ range from 5° to 70° with a step interval 0.02°. Infrared spectra were recorded on a spectrometer (BIO-RAD FTS 165 FT-IR) in the range 400–4000 cm^{-1}, with the sample pressed between two KBr pellets. Differential scanning calorimetry (DSC) was performed with a thermal analyzer (Setaram Labsys DSC131). A powder sample (approximately 20 mg) was placed in an alumina crucible and Al_2O_3 powder served as a reference sample. The sample was heated to 800 °C at 5 °C min^{-1} under flowing N_2.

3. Results and discussion

3.1. Structure of $Na_{10}Sn_{31}(HPO_4)_6(P_2O_7)_6(PO_4)_{12}$

Analysis of single-crystal X-ray diffraction data for **1** initially revealed 11 unique sites for Na, Sn and P and 11 unique sites for O atoms. The charge balance of the structure dictates that six further hydrogen cations must be found in one asymmetric unit, which were observed with a differential Fourier map; they were located in crystallographic general positions close to O11, giving a formulation of six $[HPO_4]^{2-}$ for the asymmetric unit. The structural analysis yielded a charge-balanced formula $Na^+_{10}Sn^{2+}_{31}(HPO_4)^{2-}_6(P_2O_7)^{4-}_6(PO_4)^{3-}_{12}$. The structure of **1** consists of $[HPO_4]^{2-}$, $[PO_4]^{3-}$ and $[P_2O_7]^{4-}$ layers stacked along the *c*-axis with a repeat sequence of four layers $[HPO_4]^{2-}$–$[PO_4]^{3-}$–$[P_2O_7]^{4-}$–$[PO_4]^{3-}$, which are connected to each other by Sn(II) atoms to form a three-dimensional framework. The structure contains channels running along the [001] direction with Na cations located in