

A simple ladder tin phosphate and its layered relative

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A simple ladder tin phosphate built up of the 4-membered cyclic tecton, [Sn₂P₂O₄], is described along with a related layered material.

A variety of open-framework metal phosphate materials have been synthesized and their structures elucidated in the last few years. Of particular interest to us are the recently-discovered open-framework tin(II) phosphates containing trigonal-pyramidal SnO₃ and/or square-pyramidal SnO₄ units linked to tetrahedral PO₄ units.^{1–4} The tin phosphates reported so far possess three-dimensional,^{1,2} layered³ or monomeric structures⁴ and the Sn/P ratios in these materials are generally greater than unity. To our knowledge, a pure tin(II) phosphate with a chain structure has not yet been discovered, although a tin(II) phosphanate with a chain structure is known.⁵ Based on a study of a tin phosphate monomer unit stabilized by hydrogen bonding with the template amine,⁴ we suggested recently that the basic building unit present in all the tin(II) phosphate materials is the [Sn₂P₂O₄] moiety, forming a four-membered ring. We, therefore, considered it important to explore the possibility of synthesizing a simple chain tin(II) phosphate formed by the [Sn₂P₂O₄] tecton. A systematic study of Sn(II) phosphates prepared hydrothermally in the presence of various structure-directing agents has enabled us to obtain two very simple materials with a Sn/P ratio of unity. One of the tin(II) phosphates, **I**, containing only four- and eight-membered rings forms a layered structure, whereas the second material, **II**, contains only four-membered rings forming a ladder structure. We can, however, show how **I** can be generated from **II**, by a mere shifting of Sn–O–P bonds. Furthermore, the ladder structure, **II**, fills the gap left by the absence of one-dimensional chain structures in the tin phosphate family.

Compounds **I** and **II** were synthesized hydrothermally by employing DABCO (1,4-diazobicyclo[2,2,2]octane) and DEED (*N,N'*-diethylethylenediamine) as the structure-directing agents^{6a,b} and characterized by single crystal X-ray diffraction studies,^{7a,b} using the Siemens SMART system. The structure of **I**, [C₆N₂H₁₄]²⁺2[SnPO₄][–]·H₂O, is made up of layers constructed by the networking of SnO₃ and PO₄ units. The connectivity between these units creates 4- and 8-membered rings, forming a layer along the *bc* plane (Fig. 1). The individual layers are held together by the protonated DABCO molecules which occupy spaces in between the layers [Fig. 1(b)] along with a water molecule. This is clearly a simple structure compared to the known Sn(II) phosphates.^{1–4} The tin(II) phosphate, **II**, [C₆N₂H₁₈]²⁺2[SnPO₄][–] formed by DEED, however, is even simpler in that its structure involves edge sharing of 4-membered Sn₂P₂O₄ rings, forming one-dimensional chains in the form of ladders (Fig. 2). The amine molecule is situated between the ladders. Indeed, **II** can be considered to be an inorganic ladderane, not unlike the organic counterpart.⁸ In both **I** and **II**, there are strong hydrogen bond interactions between the anionic framework (layer in the case of **I**, and chain in the case of **II**) and the protonated amine molecules. The Sn–O distances and angles in both the phosphates are as expected for 3-coordinated tin(II) atoms, and the P–O distances and angles are in agreement with those in the

previously reported phosphate structures. The P–O [P(1)–O(4) for **I** and P(1)–O(1) for **II**] distance of *ca.* 1.5 Å corresponds to the P=O double bond which takes part in hydrogen bonding with the amine.

The two structures formed by the Sn₂P₂O₄ tecton described here are the simplest open-framework tin phosphate structures known so far. The layered structure of **I** can be made from the chain structure of **II** by the scheme shown in Fig. 3 [compare this with Fig. 1(a)]. In the proposed transformation, every second alternate 4-membered ring of **II** is broken (Sn–O–P bond—forming a new P=O), accompanied by a simple rotation of the existing P=O group about a P–O single bond giving rise to a Sn–O–P bond and new 4- and 8-membered rings. The broken line in Fig. 3 represents the new Sn–O–P bond formed. Such a formulation is consistent with the doubling of the *b* axis in **I** compared to **II**. In general, *n*-edge-sharing 4-membered rings can give rise to a ring with 4*n* – 2(*n* – 1) atoms. Or, if we add *n* 4-membered rings to a *m*-membered ring, we get a ring with *m* + 2*n* atoms (*m* and *n* represent T atoms; T = Si, P in aluminosilicate zeolites and Sn, P in the present case). We thus

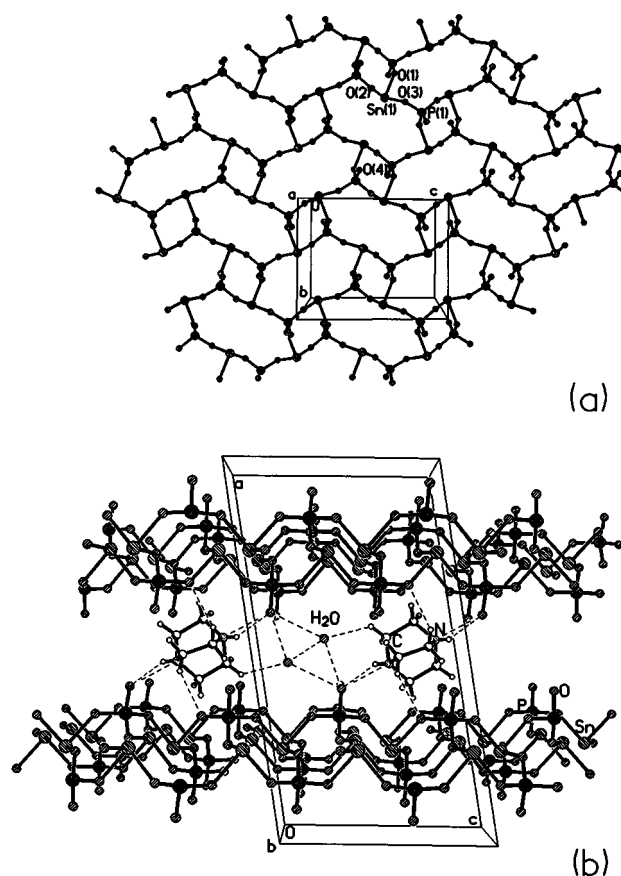


Fig. 1 Structure of **I**, [C₆N₂H₁₄]²⁺2[SnPO₄][–]·H₂O showing (a) the 4- and 8-membered rings and the connectivity within the layer, and (b) the arrangement of anionic layers, the amine and the water molecules

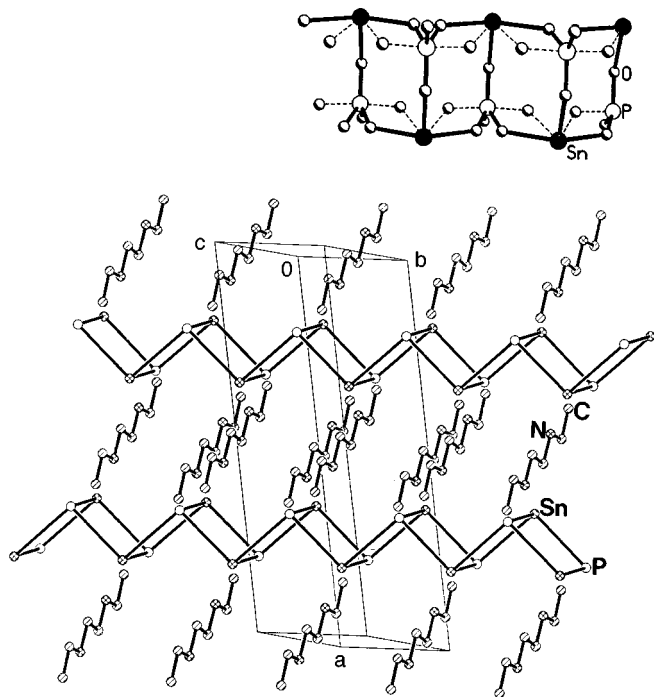


Fig. 2 Structure of **II**, $[\text{C}_6\text{N}_2\text{H}_{18}]^{2+}2[\text{SnPO}_4]^-$ showing the ladders and the amine (inset shows oxygen positions and the dotted lines represent the bonding with the disordered oxygens)

see how 6-, 8-, 10- and 12-membered rings can be formed from the 4-membered units.

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Notes and References

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- 6 (a) 2.06 g of tin(II) oxalate were dispersed in 10 ml of water and 1.8 g of 85 wt% H_3PO_4 were added to the mixture under continuous stirring. 2 g of DABCO were added to the above and stirred until homogeneous. The composition of the mixture was $\text{SnC}_2\text{O}_4 : 1.5\text{H}_3\text{PO}_4 : 1.8\text{DABCO} : 45\text{H}_2\text{O}$. The mixture was heated initially at 150 °C for 2 days and finally at 180 °C for 2 days and the product contained large quantities of plate-

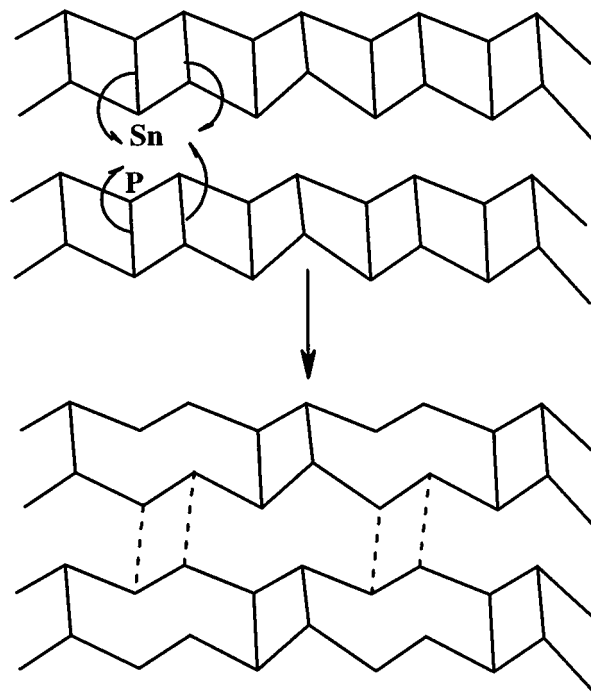


Fig. 3 Conversion of the chain (**II**) into the layered structure shown schematically. Note that the 4-membered rings are broken to form the 8-membered rings. The dotted lines represent the new 4- and 8-membered rings that are formed due to the Sn–O–P bonding and subsequently the layer (oxygen atoms are not shown).

like single crystals. (b) 2.06 g of tin(II) oxalate, 2.81 ml of DEED, 5 ml of water and 5 ml of ethylene glycol were mixed together and stirred for 10 min. To this mixture 1.53 g of 85 wt% H_3PO_4 were added and the mixture homogenized and heated at 150 °C for 2 days. The final composition of the mixture was $\text{SnC}_2\text{O}_4 : 1.95\text{DEED} : 27.5\text{H}_2\text{O} : 8\text{glycol} : 1.3\text{H}_3\text{PO}_4$.

- 7 (a) Crystal data for **I**: $[\text{C}_6\text{N}_2\text{H}_{14}]^{2+}2[\text{SnPO}_4]^- \cdot \text{H}_2\text{O}$, $M = 559.4$, monoclinic, space group $C2/c$, $a = 18.539(2)$, $b = 8.105(1)$, $c = 10.203(1)$ Å, $\beta = 98.9(2)^\circ$, $V = 1514.4(1)$ Å³, $Z = 4$, $D_c = 2.52$ g cm⁻³, $T = 298$ K, $\mu(\text{Mo-K}\alpha) = 3.57$ mm⁻¹, $R = 0.068$, $R_w = 0.076$ for 717 data with $F \geq 3\sigma(F)$. (b) Crystal data for **II**: $[\text{C}_6\text{N}_2\text{H}_{18}]^{2+}2[\text{SnPO}_4]^-$, $M = 271.4$, monoclinic, space group $C2/m$, $a = 17.938(1)$, $b = 4.883(1)$, $c = 10.814(1)$ Å, $\beta = 116.9(1)^\circ$, $V = 844.3(1)$ Å³, $Z = 2$, $D_c = 2.15$ g cm⁻³, $T = 298$ K, $\mu(\text{Mo-K}\alpha) = 3.2$ mm⁻¹, $R = 0.057$, $R_w = 0.14$ for 834 data with $F \geq 2\sigma(F)$; two of the oxygens bonded to the phosphorous are disordered with a site occupancy factor of 0.5. CCDC 182/1004.
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