# Novel Open-Framework Tin(II) Phosphate Materials Containing Sn−O−Sn Linkages and Three-Coordinated Oxygens

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Two new open-framework tin(II) phosphate materials have been synthesized hydrothermally and their structures elucidated by single-crystal X-ray diffraction. These materials exhibit an entirely new building motif, unknown in phosphate-based materials, viz., vertex-sharing truncated square-pyramidal $SnO_4$ units, in addition to the trigonal-pyramidal $SnO_3$ units. The connectivity between the $SnO_3$, $SnO_4$, and $PO_4$ units is such that Sn−O−Sn linkages are observed for the first time. The networking creates three-coordinated oxygens in the structure. Crystal data for compound **I**, $[Sn_3(PO_4)_2(OH)]^- \cdot 0.5[(NH_3)(CH_2)_6(NH_3)]^+$: monoclinic, $a = 9.315(2)$ Å, $b = 16.806(1)$ Å, $c = 9.513(3)$ Å, $\beta = 111.03(1)°$, $V = 1390.0(5)$, $Z = 4$, $M = 622.13(1)$, $D_{calc} = 2.973$ g cm$^{-3}$, Mo K$\alpha$, $R_F = 0.039$. Crystal data for compound **II**, $[Sn_3(PO_4)_2(OH)]^- \cdot 0.5[(NH_3)(CH_2)_8(NH_3)]^+$: orthorhombic, $a = 10.390(1)$ Å, $b = 16.087(1)$ Å, $c = 18.717(1)$ Å, $V = 2849.3(1)$, $Z = 4$, $M = 636.16(1)$, $D_{calc} = 2.595$ g cm$^{-3}$, Mo K$\alpha$, $R_F = 0.07$.

## Introduction

Hydrothermal methods provide a versatile means of preparing novel, open-framework materials.[1] The best developed class of such materials is the aluminosilicate zeolites, which comprise vertex-sharing tetrahedral $SiO_4$ and $AlO_4$ units, but there is also a wide range of related materials based upon alumino- and gallophosphates in which the Al/Ga coordination may be tetrahedral, pentacoordinated, or octahedral.[2−4] It is becoming increasingly apparent that non-aluminosilicate open-framework materials—essentially based on phosphate-based networks—have an astonishingly diverse structural chemistry. However, the continuing problem in the synthesis of such open-framework materials is that there is a fundamental lack of control in directing a reaction toward a particular framework configuration. The main reason for this difficulty is that most of the syntheses are performed under mild hydro/solvothermal conditions, and the mechanisms of formation are poorly understood.[5] The accepted method for the exploratory synthesis of open-framework materials is often based on *trial and error*. There is, however, considerable incentive to design new molecular sieves, not only with new crystalline architecture but also with different chemical properties, as the possibilities for their use in many areas are immense. Several open-framework materials containing other elements have been synthesized and their structures elucidated by single-crystal X-ray diffraction methods, in recent years. The newly synthesized materials include germanium dioxide[6] and phosphates of iron,[7] cobalt,[8,9] vanadium,[10] molybdenum,[11] and zinc.[12] These are dominated by 4-, 5-, and 6-coordinated cations. We have shown recently that open-framework tin(II) phosphates based upon a new building motif, vertex-sharing trigonal-pyramidal $SnO_3$ units, can be synthesized.[13−15] In common with most open-framework phosphate materials, the tin(II) phosphate compounds are synthesized by the use of organic amines as structure-directing agents. The main structural features of the tin phosphates are the presence of three coordinate Sn(II) atoms which are vertex-linked with $PO_4$ tetrahedra forming channels and cavities wherein lie the organic molecules. It has been found earlier that open-framework structures based on tin-

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(II) phosphonates having $SnO_3$ units can also be made, with these materials showing one-, two-, and three-dimensional architectures.[16,17] However, there are no $SnO_4$ units or Sn−O−Sn linkages in both the phosphate and phosphonate structures reported so far.

In this paper, we present the hydrothermal synthesis and structural characterization of two new tin phosphate materials having identical framework formulas and different crystal structures, obtained by employing 1,6-diaminohexane and 1,8-diaminooctane as the template molecules. These materials contain an entirely novel motif unknown hitherto in phosphate-based materials. The motif involves vertex-sharing truncated square-pyramidal $SnO_4$ units. The connectivity between the $SnO_3$, $SnO_4$, and $PO_4$ units in the two tin phosphate materials is found to give rise to Sn−O−Sn linkages. We believe that this is the first report of such a structural unit.

## Experimental Section

**Synthesis and Initial Characterization.** The two compounds were synthesized from a starting mixture containing 1,6-diaminohexane (compound **I**) and 1,8-diaminooctane (compound **II**) as the structure-directing agent. Tin(II) oxalate (Aldrich), phosphoric acid (85 wt %; Aldrich), 1,6-diaminohexane/1,8-diaminooctane (Aldrich), and water in the ratio $SnC_2O_4$: $0.5P_2O_5$:1.0 diaminohexane/octane:55$H_2O$ were mixed and stirred until a homogeneous mixture was obtained. The mixture was sealed in a PTFE-lined stainless steel autoclave (Parr) and heated at 180 °C for 3 days under autogenous pressure. The resulting product containing predominantly large chunks of crystals for compound **I** and needle-shaped crystals with white powder for compound **II** was filtered and washed thoroughly with deionized water. The powder X-ray diffraction (XRD) pattern on the powdered crystals indicated the products for both the compounds to be a new material. Thermogravimetric analysis (TGA) in air in the range from room temperature to 600 °C has been carried out using a Mettler balance (model no. TGA850).

**Single-Crystal Structure Determination.** A suitable single crystal for each compound was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (superglue) adhesive. 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 Kα radiation, $\lambda$ = 0.710 73 Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with $\omega$ scans (width of 0.30° and exposure time of 20 s/frame). The unit cell constants were determined by a least-squares fit of 2200 reflections for compound **I** and 4413 reflections for compound **II** in the range 5° < $2\theta$ < 46.5°. Pertinent experimental details for the structure determination are presented in Table 1.

The structure was solved by direct methods using SHELXS-86[18] and difference Fourier syntheses. The absorption correction was based on symmetry equivalent reflections using the SADABS[19] program. Other effects such as absorption by glass fiber were simultaneously corrected. The hydrogen atom attached to the oxygen atom was located from difference Fourier map. The other hydrogen atoms on the amine were placed geometrically and held in the riding mode. The last

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**Table 1. Crystal Data and Structure Refinement Parameters for $[Sn_3(PO_4)_2((OH)]^- \cdot 0.5[(NH_3)(CH_2)_6(NH_3)]^+$ and $[Sn_3(PO_4)_2((OH)]^- \cdot 0.5[(NH_3)(CH_2)_8(NH_3)]^+$**

|  | compound **I** | compound **II** |
|---|---|---|
| empirical formula | $Sn_3P_2O_9N_1C_3H_{10}$ | $Sn_3P_2O_9N_1C_4H_{12}$ |
| crystal system | monoclinic | orthorhombic |
| space group | $P2_1/n$ (#14) | $Pbca$ (#61) |
| crystal size (mm) | $0.04 \times 0.1 \times 0.06$ | $0.06 \times 0.06 \times 0.12$ |
| $a$ (Å) | 9.315(2) | 10.390(1) |
| $b$ (Å) | 16.806(1) | 16.087(1) |
| $c$ (Å) | 9.513(3) | 18.717(1) |
| $\beta$ (deg) | 111.03(1) |  |
| volume (Å³) | 1390.0(5) | 2849.3(1) |
| Z | 4 | 4 |
| formula mass | 622.13(1) | 636.16(1) |
| $\rho_{calc}$ (g cm$^{-3}$) | 2.973(1) | 2.595(1) |
| $\lambda$ (Mo Kα) (Å) | 0.71073 | 0.71073 |
| $\mu$ (mm$^{-1}$) | 5.612 | 4.794 |
| $2\theta$ range | 5.0−46.0° | 5.0−46.0° |
| total data collected | 5319 | 10308 |
| index ranges | $-9 \leq h \leq 10$, | $-11 \leq h \leq 9$, |
|  | $-18 \leq k \leq 18$, | $-12 \leq k \leq 16$, |
|  | $-10 \leq l \leq 5$ | $-20 \leq l \leq 20$ |
| unique data | 1996 | 2067 |
| observed data ($\sigma > 4\sigma(I)$) | 1543 | 1770 |
| refinement method | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ |
| $R_{merg}$ | 4.88 | 6.08 |
| $R$ indexes $[I > 2\sigma(I)]$ | $R_F$ = 3.89, | $R_F$ = 6.98, |
|  | $wR_F^2$ = 7.05 | $wR_F^2$ = 8.86 |
| $R$ (all data) | $R_F$ = 6.34, | $R_F$ = 8.84, |
|  | $wR_F^2$ = 7.88 | $wR_F^2$ = 9.28 |
| goodness of fit ($S$) | 1.081 | 1.4 |
| no. of variables | 167 | 177 |
| largest difference map peak and hole (eÅ$^{-3}$) | 0.78 and −0.93 | 0.952 and −0.919 |

**Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for Non-hydrogen Atoms in $[Sn_3(PO_4)_2((OH)]^- \cdot 0.5[NH_3(CH_2)_6NH_3]^{2+}$**

| atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Sn(1) | 1817(1) | 1568(1) | 7084(1) | 19(1) |
| Sn(2) | 5323(1) | 4155(1) | 7794(1) | 23(1) |
| Sn(3) | 6795(1) | 362(1) | 9681(1) | 20(1) |
| P(1) | 4983(3) | 3991(2) | 4172(3) | 17(1) |
| P(2) | 5041(3) | 2260(2) | 9161(3) | 16(1) |
| O(1) | 789(8) | 2594(4) | 5882(7) | 27(2) |
| O(2) | 3268(7) | 2347(4) | 8713(7) | 25(2) |
| O(3) | 5259(8) | 3300(4) | 3231(7) | 24(2) |
| O(4) | 5729(8) | 3762(4) | 5850(7) | 22(2) |
| O(5) | 5610(9) | 2862(4) | 8287(8) | 32(2) |
| O(6) | 2923(10) | 3991(6) | 6698(10) | 29(2) |
| O(7) | 5756(8) | 4737(4) | 3861(7) | 21(2) |
| O(8) | 8249(7) | 907(4) | 8678(7) | 23(2) |
| O(9) | 5362(8) | 1416(4) | 8791(8) | 25(2) |
| N(1) | 7061(10) | 2186(5) | 6042(10) | 31(2) |
| C(1) | 5747(14) | 1604(7) | 5370(14) | 40(3) |
| C(2) | 6337(14) | 866(7) | 4820(14) | 42(3) |
| C(3) | 5139(16) | 191(7) | 4333(12) | 43(3) |

cycles of refinement included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXSTL-PLUS[20] package of programs. The final atomic coordinates, selected bond distances, and bond angles are given in Tables 2−4 for compound **I** and in Tables 5−7 for compound **II**.

## Results and Discussion

The two materials have the same framework architecture. The asymmetric units of $[Sn_3(PO_4)_2(OH)] \cdot 0.5$-

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**Table 3. Selected Interatomic Distances for**
**[Sn$_3$(PO$_4$)$_2$((OH)]$^-$·0.5[NH$_3$(CH$_2$)$_6$NH$_3$]$^{2+}$**

| moiety | distance (Å) | moiety | distance (Å) |
|---|---|---|---|
| Sn(1)−O(1) | 2.101(7) | P(1)−O(3) | 1.543(7) |
| Sn(1)−O(2) | 2.107(6) | P(1)−O(4) | 1.544(6) |
| Sn(1)−O(3) | 2.118(7) | P(1)−O(7) | 1.526(7) |
| Sn(2)−O(4) | 2.122(6) | P(1)−O(8) | 1.522(7) |
| Sn(2)−O(5) | 2.219(7) | P(2)−O(1) | 1.551(7) |
| Sn(2)−O(6) | 2.119(9) | P(2)−O(2) | 1.557(7) |
| Sn(2)−O(7) | 2.412(6) | P(2)−O(5) | 1.520(7) |
| Sn(3)−O(6) | 2.126(9) | P(2)−O(9) | 1.517(9) |
| Sn(3)−O(7) | 2.442(6) | N(1)−C(1) | 1.490(13) |
| Sn(3)−O(8) | 2.124(7) | C(1)−C(2) | 1.52(2) |
| Sn(3)−O(9) | 2.197(6) | C(2)−C(3) | 1.54(2) |
| | | C(3)−C(3) | 1.53(2) |

**Table 4. Selected Bond Angles for**
**[Sn$_3$(PO$_4$)$_2$((OH)]$^-$·0.5[NH$_3$(CH$_2$)$_6$NH$_3$]$^{2+}$**

| moiety | angle (deg) | moiety | angle (deg) |
|---|---|---|---|
| O(1)−Sn(1)−O(2) | 86.4(3) | O(3)−P(1)−O(4) | 107.9(4) |
| O(1)−Sn(1)−O(3) | 86.1(3) | O(3)−P(1)−O(7) | 108.5(4) |
| O(2)−Sn(1)−O(3) | 86.1(3) | O(4)−P(1)−O(7) | 109.7(4) |
| O(4)−Sn(2)−O(5) | 80.4(2) | O(3)−P(1)−O(8) | 106.6(4) |
| O(4)−Sn(2)−O(6) | 91.0(3) | O(4)−P(1)−O(8) | 112.4(4) |
| O(5)−Sn(2)−O(6) | 90.1(3) | O(7)−P(1)−O(8) | 111.7(4) |
| O(4)−Sn(2) −O(7) | 80.5(2) | O(1)−P(2)−O(2) | 107.8(4) |
| O(5)−Sn(2)−O(7) | 152.2(2) | O(1)−P(2)−O(5) | 111.1(4) |
| O(6)−Sn(2)−O(7) | 70.2(3) | O(2)−P(2)−O(5) | 109.4(4) |
| O(6)−Sn(3) −O(7) | 69.4(3) | O(1)−P(2)−O(9) | 109.9(4) |
| O(6)−Sn(3)−O(8) | 89.8(3) | O(2)−P(2)−O(9) | 107.6(4) |
| O(7)−Sn(3)−O(8) | 79.9(4) | O(5)−P(2)−O(9) | 111.0(4) |
| O(6)−Sn(3)−O(9) | 88.3(3) | N(1)−C(1)−C(2) | 110.7(10) |
| O(7)−Sn(3)−O(9) | 151.7(2) | C(1)−C(2)−C(3) | 113.0(10) |
| O(8)−Sn(3)−O(9) | 82.9(3) | C(2)−C(3)−C(3) | 112.3(12) |

**Table 5. Atomic Coordinates (×10$^4$) and Equivalent**
**Isotropic Displacement Parameters (Å$^2$ × 10$^3$) for**
**Non-Hydrogen Atoms in**
**[Sn$_3$(PO$_4$)$_2$((OH)]$^-$·0.5[NH$_3$(CH$_2$)$_8$NH$_3$]$^{2+}$**

| atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Sn(1) | 5095(1) | 7540(1) | 1520(1) | 16(1) |
| Sn(2) | −1518(1) | 8516(1) | 641(1) | 17(1) |
| Sn(3) | 1926(1) | 8854(1) | 676(1) | 18(1) |
| P(1) | 166(3) | 9479(2) | −928(2) | 13(1) |
| P(2) | 2504(3) | 8049(2) | 2434(2) | 14(1) |
| O(1) | 3397(8) | 7315(6) | 2136(5) | 21(2) |
| O(2) | 6123(7) | 7652(6) | 2520(5) | 18(2) |
| O(3) | 5371(8) | 6157(6) | 1585(5) | 23(2) |
| O(4) | 291(10) | 8157(7) | 1051(7) | 17(3) |
| O(5) | −1269(8) | 9850(6) | 960(5) | 20(2) |
| O(6) | −2084(9) | 8342(6) | 1812(5) | 28(3) |
| O(7) | 218(8) | 8947(6) | −213(5) | 19(2) |
| O(8) | −1155(8) | 9913(6) | −1027(5) | 19(2) |
| O(9) | 2507(8) | 8820(5) | 1899(4) | 15(2) |
| N(1) | 2772(10) | 5517(7) | 2572(6) | 25(3) |
| C(1) | 3849(14) | 5308(10) | 3057(8) | 29(4) |
| C(2) | 4131(17) | 6048(10) | 3588(8) | 38(4) |
| C(3) | 5119(16) | 5818(11) | 4166(8) | 45(5) |
| C(4) | 4680(14) | 5019(11) | 4635(8) | 36(4) |

**Table 6. Selected Interatomic Distances for**
**[Sn$_3$(PO$_4$)$_2$((OH)]$^-$·0.5[NH$_3$(CH$_2$)$_8$NH$_3$]$^{2+}$**

| moiety | distance (Å) | moiety | distance (Å) |
|---|---|---|---|
| Sn(1)−O(1) | 2.118(8) | P(1)−O(3) | 1.546(9) |
| Sn(1)−O(2) | 2.115(8) | P(1)−O(5) | 1.530(9) |
| Sn(1)−O(3) | 2.109(9) | P(1)−O(7) | 1.528(9) |
| Sn(2)−O(4) | 2.224(9) | P(1)−O(8) | 1.532(9) |
| Sn(2)−O(5) | 2.111(9) | P(2)−O(1) | 1.543(9) |
| Sn(2)−O(6) | 2.092(11) | P(2)−O(2) | 1.557(9) |
| Sn(2)−O(7) | 2.467(8) | P(2)−O(4) | 1.503(10) |
| Sn(3)−O(6) | 2.110(10) | P(2)−O(9) | 1.516(9) |
| Sn(3)−O(7) | 2.405(9) | N(1)−C(1) | 1.46(2) |
| Sn(3)−O(8) | 2.123(9) | C(1)−C(2) | 1.51(2) |
| Sn(3)−O(9) | 2.305(8) | C(2)−C(3) | 1.51(2) |
| | | C(3)−C(4) | 1.54(2) |
| | | C(4)−C(4) | 1.49(3) |

**Table 7. Selected Bond Angles for**
**[Sn$_3$(PO$_4$)$_2$((OH)]$^-$·0.5[NH$_3$(CH$_2$)$_8$NH$_3$]$^{2+}$**

| moiety | angle (deg) | moiety | angle (deg) |
|---|---|---|---|
| O(1)−Sn(1)−O(2) | 88.8(3) | O(3)−P(1)−O(5) | 106.1(5) |
| O(1)−Sn(1)−O(3) | 85.7(3) | O(3)−P(1)−O(7) | 109.0(5) |
| O(2)−Sn(1)−O(3) | 87.9(3) | O(5)−P(1)−O(7) | 110.7(5) |
| O(4)−Sn(2)−O(5) | 83.2(3) | O(3)−P(1)−O(8) | 107.4(5) |
| O(4)−Sn(2)−O(6) | 82.3(4) | O(5)−P(1)−O(8) | 112.5(5) |
| O(5)−Sn(2)−O(6) | 92.2(4) | O(7)−P(1)−O(8) | 110.8(5) |
| O(4)−Sn(2) −O(7) | 145.8(3) | O(1)−P(2)−O(2) | 107.3(5) |
| O(5)−Sn(2)−O(7) | 80.3(3) | O(1)−P(2)−O(4) | 111.1(5) |
| O(6)−Sn(2)−O(7) | 68.6(4) | O(2)−P(2)−O(4) | 109.1(5) |
| O(6)−Sn(3) −O(7) | 69.6(4) | O(1)−P(2)−O(9) | 109.0(5) |
| O(6)−Sn(3)−O(8) | 92.0(4) | O(2)−P(2)−O(9) | 109.4(5) |
| O(7)−Sn(3)−O(8) | 82.6(3) | O(4)−P(2)−O(9) | 111.0(5) |
| O(6)−Sn(3)−O(9) | 83.6(4) | N(1)−C(1)−C(2) | 112.1(13) |
| O(7)−Sn(3)−O(9) | 147.5(3) | C(1)−C(2)−C(3) | 114.1(13) |
| O(8)−Sn(3)−O(9) | 80.1(3) | C(2)−C(3)−C(4) | 111.3(13) |
| | | C(3)−C(4)−C(4) | 113.0(2) |

open structure, akin to those found by us in another tin phosphate.[15] From the Fourier map, we note that the oxygen atom forming the Sn−O−Sn units has a proton attached with it. Bond valence sum calculations[21] performed on the framework confirm the presence of the proton on the oxygen involved in forming the Sn−O(H)−Sn linkages. Bonding involving two metal atoms and an −OH group has been reported in alumino[22] and gallo[23] phosphates. However, this is the first time such bonding has been observed in a tin phosphate material.

There are two crystallographically distinct phosphorus sites and three distinct tin sites present in the asymmetric unit in both compounds **I** and **II**. Of the two independent phosphorus atoms, each P is four-coordinated with respect to oxygen with the P−O distances in the range 1.503−1.557 Å (av 1.533 Å) and the O−P−O angles in the range 106.1−112.5° (av 109.5°). These values are in good agreement with those reported earlier.[2−4,13−15,22,23] Of the three independent Sn atoms in the asymmetric unit, Sn(1) is three-coordinated with respect to oxygen while Sn(2) and Sn-(3) are four-coordinated. The Sn(1)−O distances are in the range 2.101−2.118 Å (av 2.111 Å), and the O−Sn-(1)−O bond angles are in the range 85.7−88.8° (av 86.8°). The M−O (M = Sn(2), Sn(3)) distances are in the range 2.092−2.467 Å (av 2.225 Å), and the O−M−O (M = Sn(2), Sn(3)) bond angles are in the range 68.6−152.2° (av 93.1°). These values are also in agreement

[(NH$_3$)(CH$_2$)$_6$(NH$_3$)]$^+$ (compound **I**) and [Sn$_3$(PO$_4$)$_2$(OH)]$^-$·0.5 [(NH$_3$)(CH$_2$)$_8$(NH$_3$)]$^+$ (compound **II**) are shown in Figure 1a,b. The Sn atoms present two different coordination environments with oxygen in this structure: the three-coordinated trigonal-pyramidal SnO$_3$ and the four-coordinated truncated square-pyramidal SnO$_4$. The SnO$_3$, SnO$_4$, and PO$_4$ moieties are vertex-linked forming the three-dimensional framework. Of the nine bridging oxygen atoms in the asymmetric unit, seven are respectively bound to a Sn and a P. Of the remaining two oxygens, one bonds two Sn atoms and a P atom giving rise to (Sn$_2$P)−O units while the other oxygen bonds two Sn atoms forming Sn−O−Sn units. Thus, there are three-coordinated oxygen atoms in this
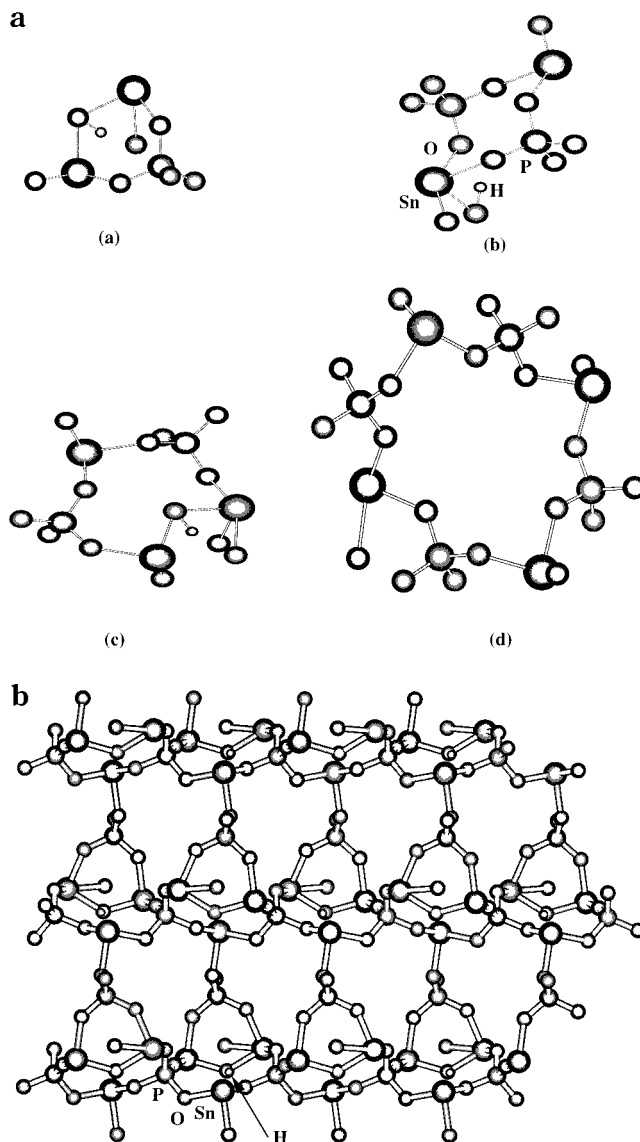
(21) Brown, I. D.; Aldermatt, D. *Acta Crystallogr. Sec. B* **1984**, *41*, 244.

(22) Natarajan, S.; Gabriel J.-C. P.; Cheetham, A. K. *J. Chem. Soc., Chem. Commun.* **1996**, 1415.

(23) Gabriel, J.-C. P.; Natarajan, S.; Cheetham, A. K. *J. Solid State Chem.* **1997**, submitted.

**a**



**b**
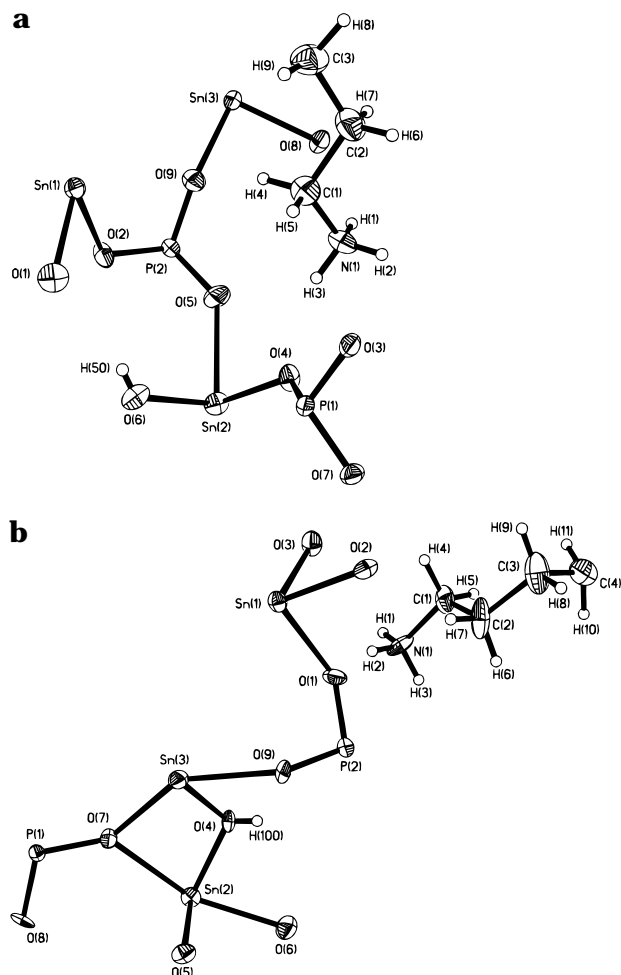


**Figure 1.** (a) Asymmetric unit of compound **I**, $[Sn_3(PO_4)_2(OH)]^- \cdot 0.5[(NH_3)(CH_2)_6(NH_3)]^+$. Thermal ellipsoids are shown at 50% probability. (b) Asymmetric unit of compound **II**, $[Sn_3(PO_4)_2(OH)]^- \cdot 0.5[(NH_3)(CH_2)_8(NH_3)]^+$. Thermal ellipsoids are shown at 50% probability.

with those observed before,[13-15] but we find the longest Sn−O distance in the present structures (2.442 Å for compound **I** and 2.467 Å for compound **II**) as well as the largest O−Sn−O bond angle (152.2° for compound **I** and 147.5° for compound **II**) involves 3-coordinated oxygen. Such lengthening of bond distances is known to occur in other materials with 3-coordinate oxygen atoms.[24]
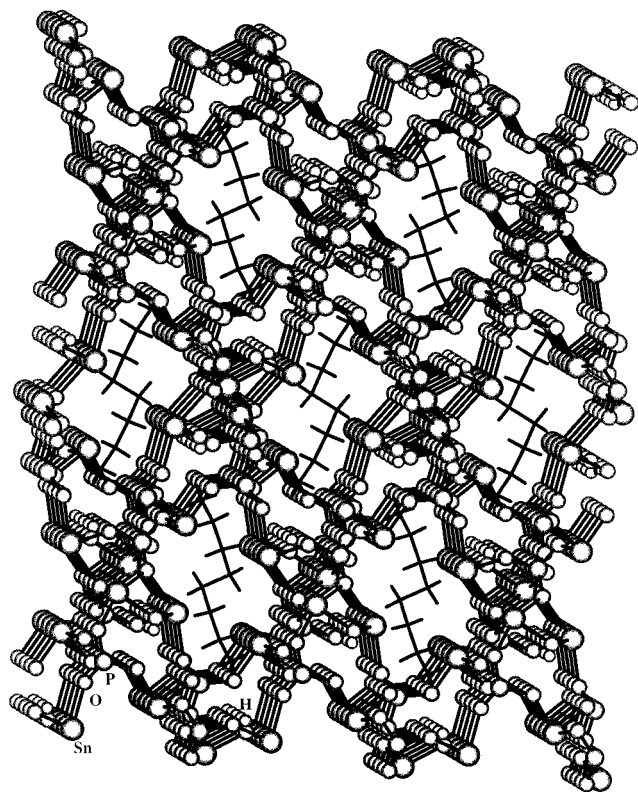
The structures of compounds **I**, $[Sn_3(PO_4)_2(OH)]^- \cdot 0.5[(NH_3)(CH_2)_6(NH_3)]^+$, and **II**, $[Sn_3(PO_4)_2(OH)]^- \cdot 0.5[(NH_3)(CH_2)_8(NH_3)]^+$, can be considered to be built up from the networking of three-, four-, five-, and eight-membered rings which are shown independently in Figure 2a. The three-, five-, and eight-membered rings are connected with each other forming a layer type of arrangement along the *b* axis for compound **I** and along the *c* axis for compound **II** (Figure 2b). These layers are connected to each other via the four-membered rings forming the three-dimensional network. In the case of the former, the layers are stacked one upon another in an identical fashion forming a one-dimensional eight-membered elliptical-shaped channel along the *a* axis. The width of this channel is 8.9 × 6.1 Å (longest and

(24) Song, T.; Hursthouse, M. B.; Chen, J.; Xu, J.; Abdul Malik, K. M.; Jones, R. H.; Xu, R.; Thomas, J. M. *Adv. Mater.* **1994**, *6*, 679.

**a**



**b**



**Figure 2.** (a) Basic building units for compounds **I** and **II**: (a) three-, (b) four-, (c) five-, and (d) eight-membered rings. Sn atoms form four-coordinated truncated square-pyramidal arrangement. (b) Structure of compound **I**, $[Sn_3(PO_4)_2(OH)]^- \cdot 0.5[(NH_3)(CH_2)_6(NH_3)]^+$, viewed along the *b* axis. The organic amine molecule is not shown for clarity.

shortest atom−atom contact distances, not including the van der Waals radii) (Figure 3). The position and arrangement of the amine molecule inside the eight-membered channel indicate that the rest of the space is occupied by the lone pair of electrons of Sn(II). The intramolecular N−N distance in the amine is 8.2 Å which just fits within the major axis of the elliptical channel, which is 8.9 Å. The ammonium groups of the amine molecule, however, protrude into the side pockets of the main channel. In the case of compound **II**, however, the layers are stacked one over the other translated by one-half of a unit cell, rendering the channels along the *b* axis completely inaccessible. Figure 4 shows the eight-membered star-shaped cavity along with the amine in the absence of the overlapping layer. The structures of **I** and **II** can also be described as built up of five-membered rings, which are arranged in a zigzag fashion forming a tape (see Figures 2b,3, and 4). These tapes are connected with each other via

**Table 8. Important Hydrogen-Bonding Distances and Angles Present in Compounds I and II**

| moiety | distance (Å) | moiety | angle (deg) |
|---|---|---|---|
| | | Compound **I** | |
| O(4)−H(2) | 2.145 | N(1)−H(2)−O(4) | 144.9 |
| O(2)−H(3) | 1.708 | N(1)−H(3)−O(2) | 163.4 |
| O(9)−H(4) | 2.524 | C(1)−H(4)−O(9) | 151.4 |
| | | Compound **II** | |
| O(9)−H(1) | 2.001 | N(1)−H(1)−O(9) | 160.0 |
| O(1)−H(2) | 2.059 | N(1)−H(2)−O(1) | 157.0 |
| O(3)−H(3) | 2.209 | N(1)−H(3)−O(3) | 160.0 |



**Figure 3.** Structure of $[Sn_3(PO_4)_2(OH)]^-\cdot 0.5[(NH_3)(CH_2)_6(NH_3)]^+$ viewed along the *a* axis showing the eight-membered ring channels and the organic amine molecule (big spheres = Sn, medium spheres = P, small spheres = O, and smallest spheres = H).
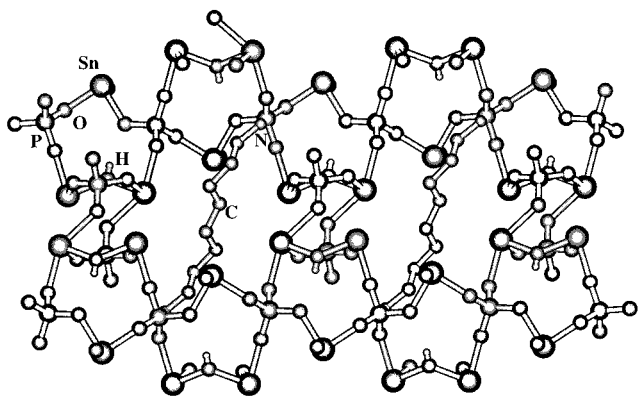


**Figure 4.** Structure of compound **II**, $[Sn_3(PO_4)_2(OH)]^-\cdot 0.5[(NH_3)(CH_2)_8(NH_3)]^+$, viewed along the *b* axis showing the eight-membered ring cavity and the organic molecule. Hydrogens on the amine molecule are not shown for clarity.

the three- and four- membered rings forming the eight-ring cavity.

Strong interaction between the organic structure-directing agent and the framework oxygens via multi-point hydrogen bonding enhances the inherent stability of the open-framework structures investigated here. The important hydrogen-bonding distances and angles for compounds **I** and **II** are presented in Table 8. In both

these materials, we have not been able to remove the occluded organic molecule completely.

Thermogravimetric analysis (TGA) of compounds **I** and **II** was carried out in the presence of flowing air from room temperature up to 600 °C. The results show a sharp mass loss in the region 350−380 °C in the case of **I**. The mass loss corresponds to about 9% of the total mass of the sample and can be directly related to the decomposition of the occluded organic amine (calcd: 9.2%). There is a further small step in the 400−425 °C region accompanied by the decomposition of the sample. In the case of compound **II** also a sharp mass loss occurs, at a lower temperature, in the 250−300 °C region corresponding to about 13% of the total mass. This can be related to the decomposition of some of the adsorbed water and the occluded amine (calcd: 11.5%). There is another small step in the region 350−380 °C, accompanied by the decomposition of the sample. The powder XRD patterns of the decomposed samples indicated poorly crystalline phases in both cases, with the majority of the lines corresponding to crystalline $Sn_2P_2O_7$ [JCPDS:35-28]. It is also likely that an amorphous phase with a Sn:P ratio > 3:2 is also present.

In conclusion, we have established the synthesis and structures of two novel tin phosphate materials with a new structural motif, involving truncated square-pyramidal $SnO_4$ units and Sn−O−Sn linkages along with trigonal-pyramidal $SnO_3$ units. The structure illustrates the role of organic structure-directing agents (amines in the present structures) and of multipoint hydrogen bonding in the design and synthesis of open-framework materials. Our efforts to remove the organic molecule by thermal methods to render these materials microporous have not been successful, and we are pursuing soft chemical approaches to accomplish this. Our ongoing research on the tin phosphates suggests that further novel open-framework structures can be formed under hydrothermal conditions, by the use of different structure-directing agents.