Synthesis and structure of an open-framework tin phosphate, $[H_3N(CH_2)_4NH_3]_{0.5}{}^{2+}[Sn_4P_3O_{12}]^-$, containing intersecting channels

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A novel open-framework tin phosphate made of strictly alternating SnO_3 and PO_4 moieties contains two intersecting channels; the protonated 1,4-diaminobutane molecules are situated in one of the channels and the lone pairs of Sn^{II} extend into the other, preventing access to the channel.

The use of structure-directing agents (templates) in the synthesis of new solids exhibiting open-framework structures has gained prominence, following the seminal work at Mobil in the late 1960s and early 1970s.[1] It is now well established that for the synthesis of new micro- and meso-porous materials, an organic structure-directing agent can be used to steer the process of crystallization to form open architectures.[2–5] Not only is it possible to synthesize materials resembling naturally occurring zeolites,[6–8] but new aluminosilicate and phosphate materials with interesting structures have been synthesized and studied in great detail.[9–11] The organic moiety is normally accommodated within the cavities and channels of these open structures and, in many cases, can be removed by post-synthesis treatments such as calcination or chemical extraction (leaching). In the course of a programme[12–15] aimed at producing new open-framework structures, we have recently shown that open-framework tin phosphate compounds can be synthesized with the aid of organic structure-directing molecules.[16] We now report the synthesis and structure of a new tin phosphate with the same composition as that reported previously,[16] but synthesized in the presence of a different organic molecule: 1,4-diaminobutane rather than ethylenediamine. A new open-framework architecture is thereby created.

The title compound was synthesised from a starting tin phosphate gel containing 1,4-diaminobutane as the structure directing agent. Tin(II) oxalate (Aldrich), phosphoric acid (85 mass%, Aldrich), 1,4-diaminobutane $[H_2N(CH_2)_4NH_2$, Aldrich] and water in the ratio $SnC_2O_4 : 0.5P_2O_5 : 1.0H_2N(CH_2)_4NH_2 : 55H_2O$ were mixed and stirred until homogeneous. The mixture was sealed in a Teflon lined stainless steel autoclave (Parr, USA) and heated at 170 °C for 2 days under autogeneous pressure. The resulting product, containing a mixture of powder and colourless single crystals, was filtered and washed thoroughly with deionised water. The single crystals were separated easily by ultrasonication. The powder X-ray diffraction indicated that the product was a new material; the pattern is entirely consistent with the structure determined by single-crystal X-ray diffraction. Thermogravimetric analysis (TGA) under an oxygen atmosphere in the range from room temperature to 700 °C show only one mass loss in the region 400–475 °C. The mass loss corresponds to about 4.97% of the total mass of the sample and can be directly correlated to the decomposition of the occluded organic cation, diprotonated diaminobutane (calc. 5.3%). The powder X-ray diffraction pattern of the decomposed sample indicated the presence of another new phase.

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 framework with the formula $[Sn_4P_3O_{12}]^-$. Charge neutrality is achieved by the incorporation of the template in its diprotonated form; there are $0.5[H_3N(CH_2)_4NH_3]^{2+}$ ions per framework formula unit. The asymmetric unit contains 22 independent non-hydrogen atoms [Fig. 1(*a*)]: three phosphate goups are linked *via* oxygens to four tin atoms to form the building block of the framework. All the P–O distances are in the range 1.495–1.544 Å (av. 1.526 Å) and the bond angles are in the range 105.5–113.5° (av. 109.5°), which is in good agreement with those previously observed.[12–15] All the Sn atoms are three-coordinated with respect to oxygen with Sn–O distances in the range 2.075–2.206 Å (av. 2.118 Å) and the Sn–O bond angles are in the range 81.5–93.59° (av. 86.87°). These values are typical of three-coordinated Sn in the 2+ oxidation state and are in excellent agreement with other previously known tin phosphates in the literature.[16–20] The three oxygen atoms form a trigonal pyramid around the Sn with the lone pair of electrons on the Sn atoms presumably occuping the base vertex of a tetrahedron. The lone pair of electrons associated with Sn^{II} opens up the possibility of using this material, or others like it, in base-catalysed reactions; zeolites and aluminophosphates are normally used for acid-catalysed processes.

The entire framework structure can be considered to be built from the networking of four-, six-, eight- and twelve-membered rings. The four- and six- (slightly distorted) membered rings are so connected as to form a one-dimensional eight-membered

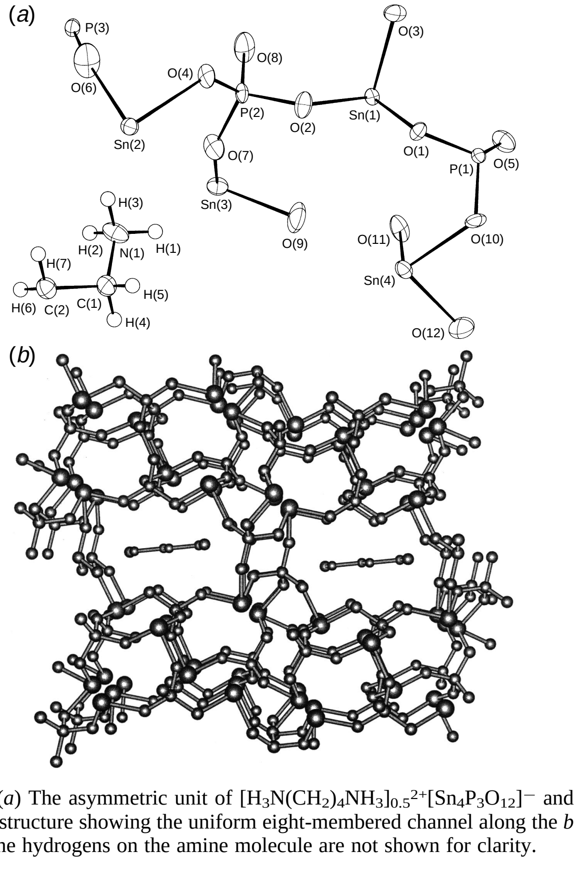

Fig. 1 (*a*) The asymmetric unit of $[H_3N(CH_2)_4NH_3]_{0.5}{}^{2+}[Sn_4P_3O_{12}]^-$ and (*b*) the structure showing the uniform eight-membered channel along the *b* axis. The hydrogens on the amine molecule are not shown for clarity.

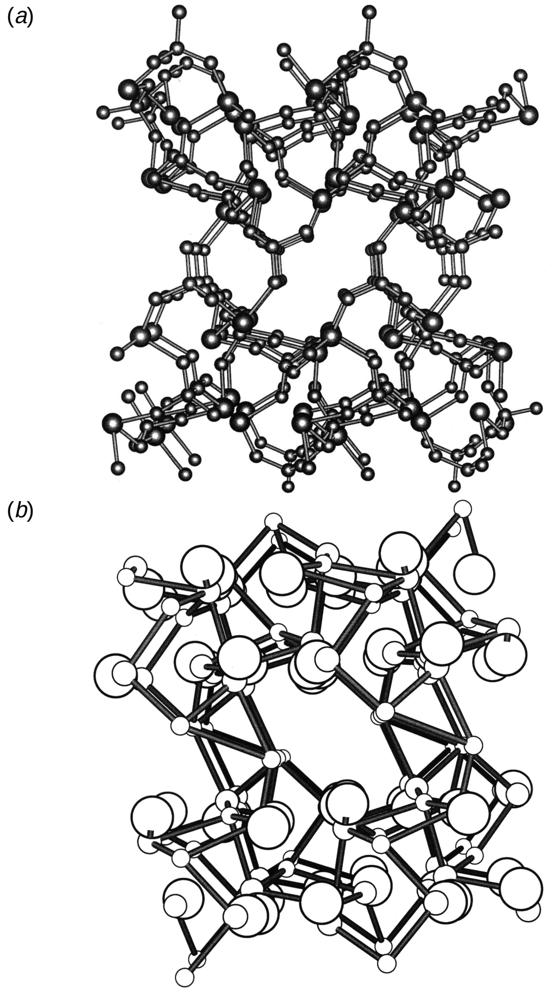

Fig. 2 (*a*) View showing the staggered twelve-membered ring channel along the *c* axis. The amine molecule is not shown for clarity. (*b*) View showing the staggered twelve-membered ring channel along with the lone pair of electrons on the Sn atoms. The amine molecule and the oxygens are not shown.

channel along the *b* axis. The width of this channel is 9.4 × 6.2 Å. The template molecule sits in the middle of this channel [Fig. 1(*b*)]. Along the *c* direction, there is another channel delineated by twelve-membered rings. However, the twelve-membered rings are staggered and, in projection, create the appearance of a compressed eight-membered ring channel of width 9.6 × 5.1 Å [Fig. 2(*a*)]. The lone pair of electrons of the Sn^{II} atoms extend into this channel and prevent access completely for any guest molecules [Fig. 2(*b*)]. The intersection of these two channels forms a cage which can be considered to be a pseudo-cube. The organic template is located at this intersection.

Presently, our efforts to remove the organic molecule by thermal methods to render the material microporous were not successful and we are pursuing softer chemical techniques (*e.g.* Soxhlet extraction) for this step. Our continuing research on tin phosphates indicates that further open-framework structures are formed under hydrothermal conditions using other structure directing agents.

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Footnotes

† A suitable single crystal (0.04 × 0.04 × 0.10 mm) was carefully selected under a polarizing microscope. *Crystal data* for $[H_3N(CH_2)_4NH_3]_{0.5}^{2+}[Sn_4P_3O_{12}]^-$: M = 804.75(3), monoclinic, space group $P2_1/c$ (no. 14), a = 10.0163(14), b = 7.8878(4), c = 20.1187(33) Å, β = 101.24(2)°, U = 1558.84(1), Z = 4, graphite-monochromated Cu-Kα radiation, λ = 1.5418 Å, T = 293 K, D_c = 3.428(1) g cm^{-3}. Data collection was performed on an Enraf-Nonius CAD4-MACH four-circle diffractometer equipped with a Rigaku rotating anode using ω–2θ scans with the width of $\Delta\omega$ = (1.0 + 0.15tanθ)° extending 25% on each side for background measurement. The unit-cell constants were determined from 25 well centred reflections within the 2θ range 29.3–64.9°. A total of 4154 reflections were collected. These were merged to give 2955 unique data (R_{merg} = 5.27) of which 2569 were considered to be observed with $I > 3\sigma(I)$. The structure was solved by direct methods using SHELX-86[21] and difference Fourier syntheses. The absorption correction was carried out using DIFABS calculation routine. Hydrogen atoms on the amine molecules were placed geometrically and held in the 'riding' mode. Final R_F = 0.0414 and R_w = 0.0485 (unit weights), S = 1.04, were obtained for a total of 200 parameters. The final Fourier map had a minimum and maximum of −1.36 and 1.55 e Å^{-3} respectively. Full-matrix least-squares structure refinement was carried out using the CRYSTALS[22] package of programs. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/440.

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