A three-dimensional open-framework tin(II) phosphate exhibiting reversible dehydration and ion-exchange properties

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A three-dimensional open-framework tin(II) phosphate, prepared hydrothermally with 1,3-diaminopentane as the template, is shown to exhibit reversible dehydration and ion-exchange properties.

The synthesis of microporous solids with different connectivities and pore chemistry from those obtained in zeolitic materials is of considerable interest because of the potential applications of these materials as catalysts, molecular sieves and ion exchangers.[1,2] Investigations in this direction have led to the discovery of many materials with interesting structures. Recently, open-framework tin(II) phosphates with novel building motifs, such as vertex-sharing trigonal pyramidal SnO_3 units and truncated square-pyramidal SnO_4 units, have been synthesized.[3–5] It would be most desirable to design a more open, three-dimensional network with channels running along the crystallographic axes and to facilitate the formation of such a structure, we have employed a branched diamine as a structure-directing agent, in place of the linear diamines. With 1,3-diaminopentane, we have been able to obtain a tin phosphate with three different channel systems. The structure possesses two molecules of water which can be reversibly intercalated and, more significantly, exhibits remarkable ion-exchange properties reminiscent of aluminosilicate zeolites. Here we describe the synthesis, structure and characterization of this unique open-framework material.

The structure of the new Sn^{II} phosphate‡ involves networking 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 diprotonated organic cation $[NH_3CH_2CH_2CH(NH_3)CH_2CH_3]^{2+}$. There is half a unit of the organic cation per formula unit and the structure contains two molecules of water. Thus, the composition of the material is $[Sn_4P_3O_{12}]^-\{[NH_3CH_2CH_2CH(NH_3)CH_2CH_3]^{2+}\}_{0.5}\cdot 2H_2O$. The asymmetric unit (Fig. 1) contains 27 independent non-hydrogen atoms.

The entire framework structure can be considered to be made from a networking of four-, six-, eight- and twelve-membered rings formed by T atoms (T = Sn, P). The four-, six- and twelve-membered rings are connected to each other in such a way that they form a uniform 8-ring channels bound by 8 T atoms (T = Sn and P) along the *a* and *b* axes [Fig. 2(*a*) and (*b*)]. The widths of these channels are 7.0 × 6.1 Å along the *a* axis and 8.3 × 8.8 Å along the *b* axis (longest and shortest atom–atom contact distances, not including van der Waals radii). The widths of the channels suggest that the eight-membered channels along the *b* axis are more regular [Fig. 2(*b*)]; the amine molecules sit in the middle of these channels. When viewed along the *a* axis, the two water molecules occupy the distorted six- and twelve-membered channels [Fig. 2(*a*)]. The lone pair of electrons of the Sn^{II} protrude into the twelve-membered channel rendering it ineffective for sorption of a guest molecule. Along the *c* axis, the 4-, 6- and 8-rings are connected to form a twelve-membered ring channel which has the appearance of a six-membered channel due to distortion. The amine and the water molecules are both present in this channel. Most of the distortions in the channels arise due to the three coordination of the tin(II) with the oxygens in this structure. The Sn atoms coordinated to three oxygens occupy the vertex of a trigonal pyramid; the lone pair presumably occupies the fourth vertex of the tetrahedron. The M–O bond lengths and O–M–O bond angles (M = Sn, P) are similar to those observed for other tin phosphate materials.

Since the synthesis involved the use of two different optical isomers of the branched organic diamine, we expected the isomers to be resolved and form different channels. We find, however, that the two amine isomers are located at the crystallographic center of inversion in the structure creating a new type of disorder (Fig. 1). A low-temperature single crystal X-ray diffraction study ($T \approx 100$ K) showed no change in the disorder, indicating it to be static rather than dynamic.

Thermogravimetric analysis (TGA) in an oxygen atmosphere showed a mass loss of *ca*. 3.9% at 125 °C due to the removal of two molecules of water present in the channels (calc. 4.1%). Careful experiments showed that the material (heated to 125 °C) reabsorbs the water on cooling and storage for a few hours under atmospheric conditions (typically 4 h). This feature is indeed noteworthy as this is the first time such a complete reversible dehydration–hydration process has been observed in an open-framework tin phosphate material. TGA studies also reveal that the protonated 1,3-diaminopentane is removed at 350 °C. The crystal structure collapsed after the removal of the amine.

In our effort to remove the template molecule from the open-framework structure by other methods, we employed soft chemical routes, including ion-exchange. Since the structure is open and the framework is anionic, we used an NaCl (1.0 M) solution for the ion-exchange with the expectation that the Na^+ cations might exchange for the protonated diamine. After 4 days of continuous stirring at room temperature (the solution was

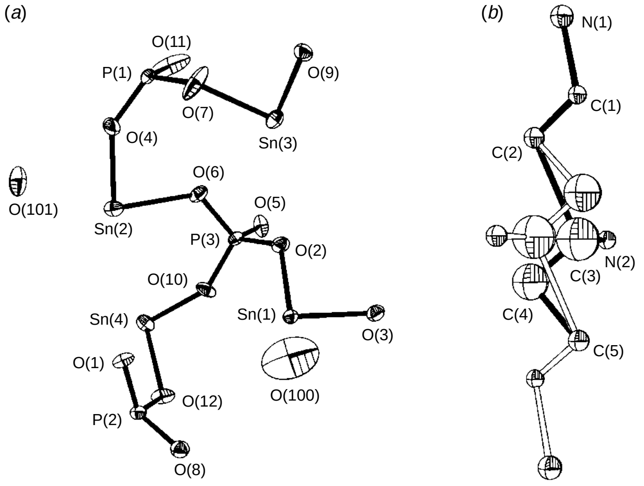

Fig. 1 ORTEP plots of (*a*) the framework along with the water molecule and (*b*) the organic template molecule showing the disorder

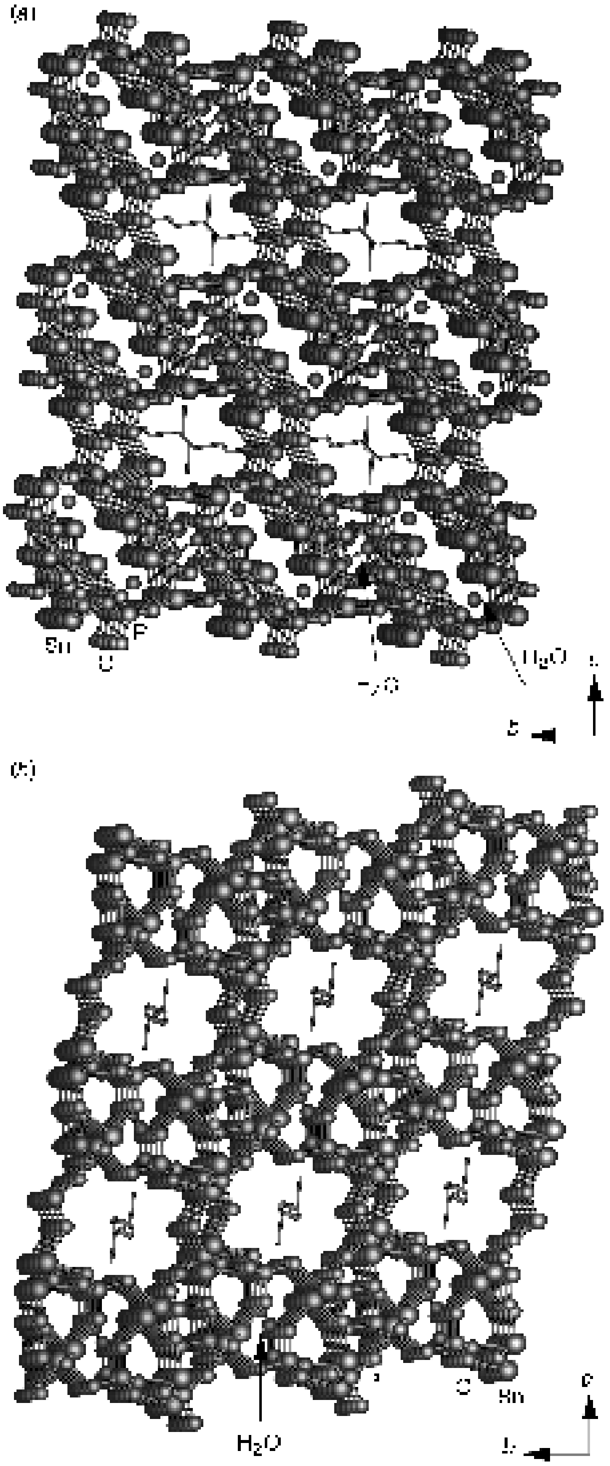

Fig. 2 Structures of $[Sn_4P_3O_{12}]^-\{[NH_3CH_2CH_2CH(NH_3)CH_2CH_3]^{2+}\}_{0.5}\cdot 2H_2O$ viewed down the *a* axis (*a*) and *b* axis (*b*). Note that the amine and the water molecule occupy different channels in both cases.

replenished every 24 h), *ca*. 50% of the amine was exchanged, as indicated by FTIR and TGA studies. The powder XRD pattern of the ion-exchanged sample was consistent with that of the parent material. Gravimetric adsorption studies were carried out on the parent material and the Na^+-exchanged sample after dehydration at 175 °C, by employing N_2 and MeOH as adsorbants. Methanol exhibits a Langmuir type I isotherm corresponding to about 1 molecule per unit cell (at higher pressures, $p/p_o \geqslant 0.8$, the results indicate some type II component as well) and N_2 shows a type IV isotherm for the dehydrated Na^+-exchanged sample (Fig. 3). The parent material, however, showed no significant adsorption of these molecules. This study suggests that there is considerably greater free volume in the dehydrated Na^+-exchanged sample. Further experiments on the ion-exchange properties of this novel three dimensional tin(II) phosphate material and its catalytic properties are currently in progress and the results will be reported elsewhere.

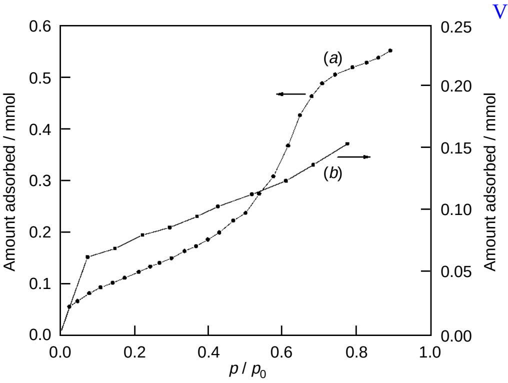

Fig. 3 Sorption isotherms (at 77 K) for (*a*) nitrogen and at room temp. for (*b*) methanol (p/p_o ratio of partial pressure of sorbate to its saturated vapour pressure)

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Notes and References

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‡ The title compound was synthesized from a starting tin phosphate gel containing a mixture of the two optical isomers of 1,3-diaminopentane as the structure directing agent. Tin(II) oxalate (Aldrich), phosphoric acid (85 wt%, Merck), 1,3-diaminopentane (DYTEK, Aldrich) and water in the ratio $SnC_2O_4 : 0.5\ P_2O_5 : 1.0$ 1,3-diaminopentane : 55 H_2O were mixed, sealed and heated at 170 °C for 3 days under autogeneous pressure. The resulting product, containing a mixture of white powder and a few colorless single crystals, was filtered and washed thoroughly with deionised water. The single crystals were separated easily under a polarizing microscope. The powder X-ray diffraction patterns taken independently on both the white powder and the single crystals were found to be identical indicating that the product was a new material. A suitable, needle-like single crystal (0.06 × 0.05 × 0.04 mm) was selected and mounted at the tip of a glass fiber using cyanoacrylate adhesive. Crystal structure determination by X-ray diffraction was performed on a Siemens Smart-CCD diffractometer (Mo-Kα radiation, $\lambda = 0.71073$ Å). A hemisphere of intensity data was collected at room temperature in 1321 frames with ω scans (width of 0.30° and exposure time of 30 s per frame).

Crystal data for the title compound: triclinic, space group $P\bar{1}$ (no. 2), $a = 9.417(1)$, $b = 9.754(1)$, $c = 11.002(1)$ Å; $\alpha = 80.51(1)$, $\beta = 71.64(2)$, $\gamma = 61.68(1)°$, $U = 844.2(2)$ Å^3, $Z = 2$, $M = 861.85(1)$ and $\rho_{calc} = 3.39(1)$ g cm^{-3}. A total of 3352 reflections were collected in the range $-8 \leqslant h \leqslant 10$, $-8 \leqslant k \leqslant 10$, $-12 \leqslant l \leqslant 11$. These were merged to give 2383 unique data ($R_{merg} = 2.3$). The absorption correction was based on symmetry equivalent reflections using the SADABS[6] program. Because of the heavy disorder on the carbon and nitrogen atoms of the amine molecule, hydrogen atoms though found on the Fourier map were not used for refinement purposes. The last cycles of refinement included atomic positions, anisotropic thermal parameters for all the atoms. Final $R = 0.0397$, $R_w = 0.0937$ and $S = 1.04$ were obtained for 215 parameters. The final Fourier map minimum and maximum: -1.26 and 1.68 e Å^{-3}. The structure was solved and refined using the SHELXSTL-PLUS[7,8] package of programs. CCDC 182/895.

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