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Synthesis and Characterization of an Open-Framework Antimony(III) Phosphate: $[H_3N(CH_2)_2NH_3]_{1.5}[(SbO)_2(SbF)_2(PO_4)_3]$**

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Nanoporous aluminosilicate zeolites find technological applications in areas such as catalysis, separations, and ion exchange.[1] After Flanigen et al. reported a series of open-framework aluminophosphates ($AlPO_4$s),[2] others successfully incorporated transition and other main group metals into open frameworks.[3] Unlike the zeolites and many $AlPO_4$s, which are based upon corner-sharing $[XO_4]$ tetrahedra, many of the newer materials are based on other polyhedra that give rise to new topologies. For example, several open-framework tin(II) phosphates[4] were prepared in which the stereochemically active electron lone pair associated with each Sn^{II} center leads to trigonal $[SnO_3]$ and square pyramidal $[SnO_4]$ units. One of these materials[4f] is truly nanoporous and exhibits reversible dehydration and ion-exchange properties. We therefore extended the search for open frameworks into the Sb_2O_3/P_2O_5 system.

Open frameworks containing Sb^{III} include the antimony(III) sulfides[5] and the mineral cetineite and related synthetic phases.[6] While a number of Sb^{V} [7] and mixed-valent Sb^{III}/Sb^{V} [8] phosphates have been made, until recently the only known materials based solely on $[Sb^{III}O_x]$ and $[P^{V}O_4]$ polyhedra were condensed $SbPO_4$[9] and layered $SbO(H_2PO_4)\cdot H_2O$.[10] Layered antimony(III)fluoride phosphates have also been synthesized: $KSbF_2(HPO_4)$[11] and $MSbFPO_4\cdot n\,H_2O$ ($M = NH_4$, Na, K, Rb, Cs, CN_3H_6, $n = 0 - 1.5$)[12, 13], as well as a chain-type structure: $CsSbF_3(H_2PO_4)$.[13] The three-dimensional structure of a new Sb^{III}-based material, $NaSb_3O_2(PO_4)_2$,[14] although not microporous, suggested that Sb^{III} could be incorporated into an open framework phosphate. By using a structure-directing agent (SDA) under hydrothermal synthesis conditions[15] we synthesized the material described below.

The asymmetric unit of $[H_3N(CH_2)_2NH_3]_{1.5}[(SbO)_2(SbF)_2(PO_4)_3]$ contains 29 crystallographically independent non-hydrogen atoms (Figure 1). As in many other open frameworks for which fluorine is used as a mineralizer,[16–19] fluorine is incorporated into the structure. This framework is based upon a network containing: 1) pseudo-octahedral $[SbO_5E]$ and $[SbO_4FE]$ units (E = lone pair), 2) pseudo-trigonal-bipyramidal $[SbO_4E]$ and $[SbO_3FE]$ units (the lone pairs of electrons occupy axial and equatorial positions in the

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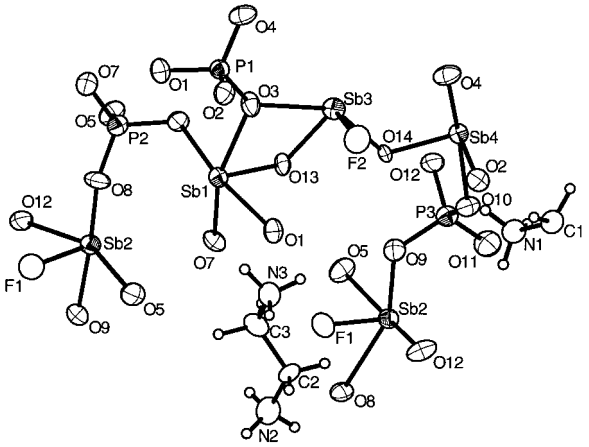

Figure 1. Asymmetric unit of $[H_3N(CH_2)_2NH_3]_{1.5}[(SbO)_2(SbF)_2(PO_4)_3]$ (50% probability thermal ellipsoids).

octahedra and bipyramids, respectively, when Sb–O bonds up to 2.7 Å are taken into account), and 3) tetrahedral $[PO_4]$ units. The bond lengths and angles agree with those of reported Sb^{III} phosphates and fluoride phosphates (av P–O 1.537 Å, av O-P-O 109.51°; for SbX_5E, av Sb–O 2.202 Å, av adjacent X-Sb-X 85.1°; for SbX_4E, av Sb–O 2.135, av adjacent X-Sb-X 83.4°; av Sb–F = 1.964 Å).[9–14]

The polyhedra combine to form layers built from four-rings, which are made from two Sb and two P atoms bridged by oxygen atoms (an Sb_2P_2 ring), and six-rings (Sb_3P_3) (Figure 2). $[SbO_3FE]$ polyhedra connect the layers by sharing the axial

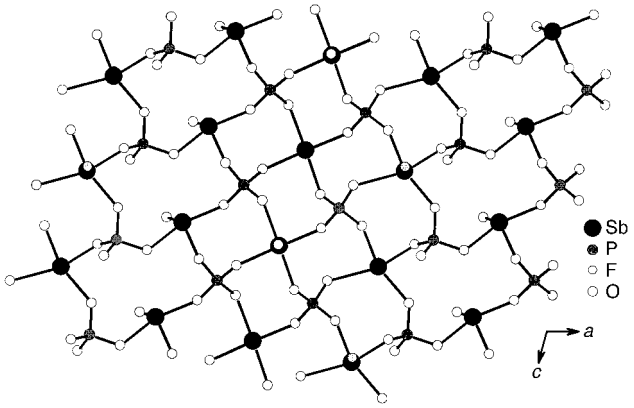

Figure 2. View of $[H_3N(CH_2)_2NH_3]_{1.5}[(SbO)_2(SbF)_2(PO_4)_3]$ down the *b* axis, showing the four- and six-rings that make up the layers.

oxygen atoms of the $[SbO_5E]$ polyhedra to give eight- and twelve-ring channels that run along the [100] and [001] directions, respectively (Figure 3). Diprotonated ethylenediamine (en) resides in the channels and provides for charge compensation. Each N atom of the en dication is within 3 Å of two framework O atoms (av 2.841 Å); this distance is indicative of hydrogen bonding. Fluorine atoms are directed into both channels: the F atoms of $[SbO_4FE]$ lie in the twelve-rings and those of $[SbO_3FE]$ in the eight-rings. Sb_2P_2 rings are also found in layered Sb^{III} fluoride phosphates, in which $[SbO_3F_2E]$[9] or $[SbO_4FE]$[10, 11] octahedra and $[PO_4]$ polyhedra combine to form layers separated by small cations.

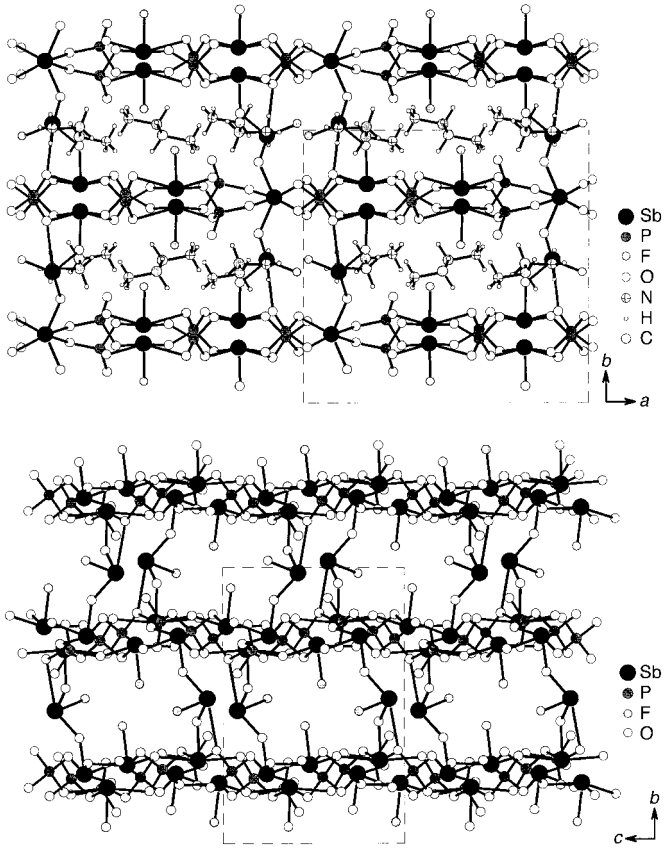

Figure 3. Top: View of $[H_3N(CH_2)_2NH_3]_{1.5}[(SbO)_2(SbF)_2(PO_4)_3]$ down the *c* axis, showing the twelve-ring channels and diprotonated en. The unit cell is outlined. Bottom: View of $[H_3N(CH_2)_2NH_3]_{1.5}[(SbO)_2(SbF)_2(PO_4)_3]$ down the *a* axis, showing the eight-rings lined with fluorine atoms (en omitted for clarity).

When ethylene glycol (eg) is replaced by water in the present synthesis, an unreported material forms: $[H_3N(CH_2)_2NH_3]_{0.5}SbF(PO_4)$ (monoclinic, space group $P2_1/c$, $a = 6.5417$, $b = 14.9877$, $c = 9.2193$ Å, $\beta = 134.769°$). This material, which will be described in detail elsewhere, contains diprotonated en between inorganic layers that are identical to those found in the $M[SbFPO_4]\cdot n H_2O$ family.[12, 13]

The product of the present synthesis appears pure, as determined by comparing the experimental with the simulated X-ray powder diffraction pattern. However, elemental analysis results (Sb 51.9, P 9.1 (Sb/P 1.46), F 5.2, C 4.1, N 4.7, H 2.0%; calcd: Sb 56.2, P 9.9 (Sb/P 1.33), F 4.1, C 3.9, N 4.5, H 1.6%) do not rule out the possibility of the presence of an impurity phase. Differential thermogravimetric analysis was performed under flowing O_2. An exothermic peak and a mass loss of about 10% at about 300 °C corresponds to the removal of the organic substance (calcd 9.9%). This is immediately followed by a mass loss of about 14%, accompanied by an exothermic peak, which is complete by around 500 °C. Powder diffraction indicates the final material to be mainly $SbPO_4$, with a small amount of Sb_2O_3 (Sb/P = 1.25 from elemental analysis). We have so far been unable to remove the organic component without loss of the open framework, but are investigating ion-exchange methods to achieve this end.

The small number of reported materials based on Sb^{III}/P^V[9, 10, 14] or $Sb^{III}/P^V/F$[13–15] contain a large variety of polyhedra

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([SbO_5E], [SbO_4FE], [SbO_3F_2E], [SbO_2F_3E], [SbO_4E], [SbO_3FE]) and secondary building units (Sb_2P,[14] Sb_2P_2,[9, 11–14] Sb_4P_2,[10, 14] Sb_3P_3,[14] and Sb_5P_3[14] rings), as well as the new Sb_6P_2 and Sb_8P_4 rings of the title compound. We have recently discovered additional molecular, chain, layered, and three-dimensional materials belonging to this large family. In addition to their novel architectures, Sb^{III}-based materials, unlike closed-shell zeolites and $AlPO_4$s, may have redox behavior or other interesting properties associated with their lone pairs of electrons.

Experimental Section

Hydrofluoric acid (49 wt%, Fisher) was added to antimony(III) oxide (Aldrich), and the mixture was stirred to give a clear solution. Phosphoric acid (85 wt%, Fisher), en (Aldrich), eg (Fisher), and water, were added with stirring to give a mixture with composition 1 Sb:0.6 P:3.1 F:1.0 en:11 H_2O:37 eg. This was sealed in a PTFE-lined stainless steel autoclave and heated at 135 °C under autogeneous pressure for 5 d. The crystalline product was filtered, washed with ethanol, and dried at 90 °C in air. A single crystal ($0.08 \times 0.04 \times 0.03$ mm) was mounted on a glass fiber, and room temperature X-ray diffraction data were collected with a Siemens SMART CCD diffractometer equipped with a normal focus 2.4-kW sealed X-ray tube ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) operating at 45 kV and 35 mA. About 1.3 hemispheres of intensity data were collected in 1321 frames with ω scans (width 0.30°, exposure time 10 s per frame). A total of 8328 reflections were collected in the range $2.8 < 2\theta < 46.6°$ and merged to give 2648 unique reflections. Unit cell parameters were determined by a least-squares fit of 1724 reflections: monoclinic, space group $P2_1/c$ (no. 14), $a = 14.8222(14)$, $b = 13.7657(13)$, $c = 9.3022(9)$ Å, $\beta = 105.341(2)°$, $V = 1830.4(3)$ Å^3, $Z = 2$, $M = 935.09$, $\rho_{calcd} = 3.393$. Absorption correction was performed with the program SADABS.[20] Positions of Sb and P atoms were determined by direct methods with SHELXS-97.[21] Other non-hydrogen atoms were located in subsequent difference Fourier maps. Bond-valence parameters[22] unambiguously distinguished bridging atoms. The final structure model was established by full-matrix least-squares refinement against $|F|^2$ with SHELXTL-PLUS.[21] The hydrogen atoms were placed in calculated positions and held in the riding model. The final reliability factors obtained in the fitting of 265 parameters with 1809 independent reflections with $I > 2.0\sigma(I)$ were $R_1(F) = 0.0387$, $wR(F^2) = 0.0843$, $S = 0.985$. The final difference Fourier map had maximum and minimum peaks of 0.936 and -1.325 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133133. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A $p(O_2)$-Responsive MRI Contrast Agent Based on the Redox Switch of Manganese(II/III) – Porphyrin Complexes

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Contrast in magnetic resonance imaging (MRI) is largely determined by differences in the relaxation times of protons in tissues. Therefore, contrast agents (CAs) for this diagnostic methodology have mainly been sought among the coordination compounds of metal ions with several unpaired electrons,

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