

# A Metal-Rich Fluorinated Indium Phosphate, 4[NH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>3</sub>]·3[H<sub>3</sub>O]·[In<sub>9</sub>(PO<sub>4</sub>)<sub>6</sub>(HPO<sub>4</sub>)<sub>2</sub>F<sub>16</sub>]·3H<sub>2</sub>O, with 14-Membered Ring Channels

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Received July 22, 1997. Revised Manuscript Received November 5, 1997

The organically templated 3-D open-framework metal-rich phosphate 4[NH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>3</sub>]·3[H<sub>3</sub>O]·[In<sub>9</sub>(PO<sub>4</sub>)<sub>6</sub>(HPO<sub>4</sub>)<sub>2</sub>F<sub>16</sub>]·3[H<sub>2</sub>O] has been synthesized hydrothermally and its structure determined by single-crystal X-ray diffraction. The compound is monoclinic, *P*2<sub>1</sub>/*n*, *a* = 13.616(2) Å, *b* = 9.372(2) Å, *c* = 23.293(4) Å, β = 99.44(2)°, *V* = 2932.1(9) Å<sup>3</sup>, *R* = 0.034, *R*<sub>w</sub> = 0.038. It was characterized further using TGA, <sup>31</sup>P NMR, and elemental analysis, which supported the above formulation. The compound has a complex system of channels, which feature large elliptical 6.5 × 14 Å cavities resulting from 14-membered rings. An unusually high degree of fluorination is found for this compound resulting from use of 8 molar equivalents of HF in its preparation. The fluorides occupy both terminal and bridging environments around the indium. The former are involved in hydrogen bonding to countercations, and the latter are critical to corner sharing of In octahedra to create In<sub>3</sub> polyhedral subunits. The anion framework can be described in terms of a pillared layer structure in which corrugated sheets of formula [In<sub>9</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>16</sub>]<sup>7-</sup> are pillared via the (HPO<sub>4</sub>)<sup>2-</sup> groups.

The use of hydrogen fluoride has been shown to be highly effective in promoting hydrothermal synthesis of microporous inorganic solids, such as zeolites and metal phosphates.<sup>1,2</sup> The fluoride may act solely as a mineralizer or, when stoichiometric quantities of HF are employed, may also become incorporated into the framework.<sup>3–7</sup>

Herein we report the synthesis and structure determination of 4[NH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>3</sub>]·3[H<sub>3</sub>O]·[In<sub>9</sub>(PO<sub>4</sub>)<sub>6</sub>(HPO<sub>4</sub>)<sub>2</sub>F<sub>16</sub>]·3[H<sub>2</sub>O] (**1**), a 3-D open-framework indium phosphate with a high degree of fluoride incorporation. This has a remarkable channel structure of interconnected 8- and 14-membered-ring pores. The higher levels of fluorination are brought about by use of excess HF (8 molar equivalents) compared to the In and P sources.

Synthesis of **1** was carried out using hydrothermal methods starting from a mixture of indium hydroxide, phosphoric acid, 1,3-diaminopropane, and hydrogen fluoride in water. The compound crystallized as long

colorless bars > 1 mm in high yield. Energy-dispersive X-ray analysis of selected crystals of **1** showed the presence of In, P, and F in stoichiometric quantities. Elemental analysis for C, H, and N gave a C/N stoichiometry of 3:2, which indicated the incorporation of intact organic templates. A single-crystal specimen of **1** was subsequently investigated by X-ray structure determination.

On the basis of the crystal structure, the compound is formulated as 4[NH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NH<sub>3</sub>]·3[H<sub>3</sub>O]·[In<sub>9</sub>(PO<sub>4</sub>)<sub>6</sub>(HPO<sub>4</sub>)<sub>2</sub>F<sub>16</sub>]·3[H<sub>2</sub>O] with an anionic open framework (Figures 1, 2, and 3) that is interpenetrated by a network of templating 1,3-propyldiammonium ions, hydroxonium ions, and water molecules.

The atomic labeling scheme for the framework anion of **1** is shown in Figure 1. The asymmetric unit contains three indium atoms at general positions as well as three others sitting on inversion centers. Since there are four phosphate groups at general sites, this gives rise to the In<sub>9</sub>P<sub>8</sub> stoichiometry.

The six indium centers are chemically as well as crystallographically unique, as seen by variation in the number and arrangement of terminal and bridging fluorines. There are four terminal fluorines per asymmetric unit [In–F = 2.037–2.067(5) Å]. In addition, each In atom shares its octahedral coordination sphere with at least one other indium through bent fluoride bridges. [In–F = 2.126–2.156(4) Å; In–F–In = 123.3–134.2°].

The identification of these as F<sup>-</sup> rather than OH<sup>-</sup> bridges is crystallographically difficult; however, refinement of the bridging atoms as oxygens leads to non-

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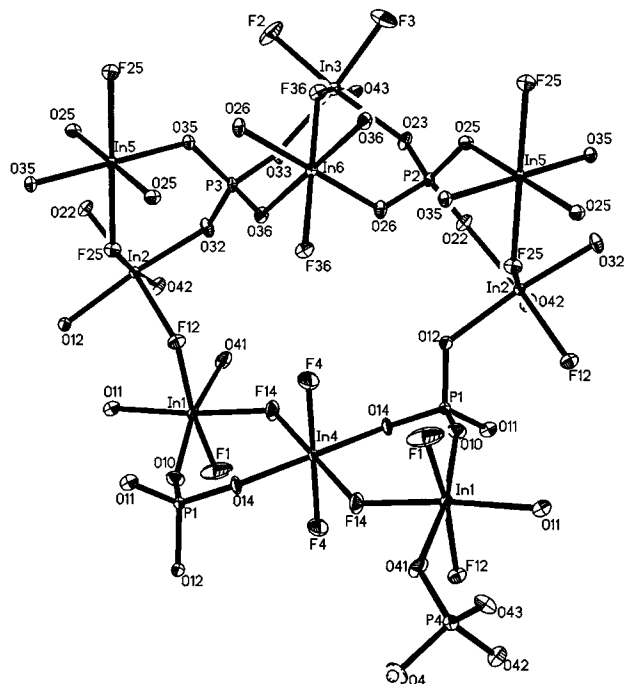
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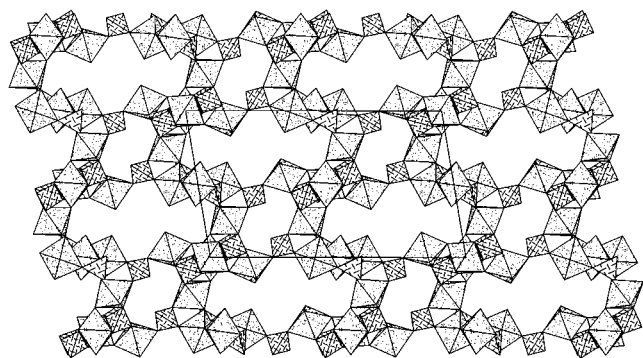
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**Figure 1.** Thermal ellipsoid plot (40% probability) and atomic labeling scheme for the anionic framework of **1**. Distances/angles not mentioned in the text: In–O = 2.078–2.139(5) Å, P–O = 1.515–1.548(5) Å, In–O–P = 122.9–138.3(3)°.



**Figure 2.** Polyhedral representation of the structure of **1**, viewed along the crystallographic *b*-axis [010], showing 14- and 8-membered ring apertures.

positive definite anisotropic thermal parameters. In addition bond valence sum calculations provide strong support for the level of fluorination we propose.<sup>8</sup> If the terminal and bridging atoms are assumed to be fluorides, rather than oxygen-based ligands, the six independent In centers each gave values close to the expected +3 valence. In contrast, calculations for all-oxygen coordination environments lead to considerable deviations from this value.

All phosphate oxygens bridge to the In atoms, with the exception of one, which we have identified as a terminal P–OH functionality on the basis of its long associated bond length [P(4)–O(4) = 1.583(5) Å].

The main feature of the channel structure of the compound is the presence of 8- and 14-membered-ring apertures running parallel to the *b*-axis [010]. These are featured in Figure 2, which is a polyhedral representation of the framework anion viewed along the

*b*-axis. The 14-membered-ring opening is highly elliptical with approximate maximum dimensions of 14.0 × 6.5 Å. It is noteworthy that the ring itself is not composed of alternating In and P polyhedra but has an In<sub>8</sub>P<sub>6</sub> arrangement. The channels that are parallel to [010] are intersected by other eight-membered-ring channels which run continuously along the [110] and  $\bar{1}\bar{1}0$  directions. Hence a 2-D channel network is formed in the *ab*-plane.

Identification of the moieties within the channels was not completely straightforward. However, two 1,3-propyldiammonium ions could be discerned. One was well-ordered and associated with the eight-membered-ring channel along [010], whereas the other sits in the larger 14-membered-ring channel and appears to have several different orientations. It was refined with split occupations of one NH<sub>3</sub> end group and partial occupancy of the major orientation of the propylene chains.

Charge balance of the structure dictates that three further cations must be found over two asymmetric units. No peaks were found located at, or near, centers of inversion, but three other major peaks of electron density could be located in crystallographic general positions. All three were within the 14-membered-ring channels, at hydrogen-bonded distances from various oxygen and fluorine atoms of the framework anion, and were compatible with being either water or hydroxonium ions. Although hydrogen atoms could not be located, we believe the additional protons are distributed over these sites, giving a formulation of three [H<sub>3</sub>O]<sup>+</sup> and three [H<sub>2</sub>O] for the two asymmetric units. Frequently ammonium ions have been generated in hydrothermal syntheses from partial decomposition of organoamine templates; however the presence of [NH<sub>4</sub>]<sup>+</sup> in this case is not supported by the CHN analysis. In addition, the high yield found for **1** would seem inconsistent with inclusion of intact templates along with products of their break-down.

Further support for the formulation of **1** comes from thermal gravimetric analysis. This showed a total weight loss of 26%. About 4 wt % weight loss occurred between 170 and 320 °C, in agreement with loss of six molecules of water per formula unit. Loss of the water at these relatively high temperatures is consistent with the partial hydroxonium ion formulation that we propose. A similar case is found for [H<sub>3</sub>O]·[InPO<sub>4</sub>(OH)] in which loss of H<sub>2</sub>O from the channel hydroxonium ion occurs between ca. 170 and 400 °C.<sup>9</sup> Decomposition of four template molecules corresponds to a weight loss of 12%, which fits well with the loss over the range 320–550 °C. Finally a further 10% loss is found upon heating to 1000 °C, which is consistent with elimination of 13 molar equivs of hydrogen fluoride, which would be necessary to remove all acidic protons from the material.

The use of indium, like many other heavier framework elements, necessitates a change from the classical all tetrahedral frameworks found for ALPOs and zeolites, since coordination numbers are expanded. Addition of fluoride to the preparative mixtures can assist network formation for phosphates of larger metals by coordination to surplus metal sites and allowing polyhedral connectivities between these metals through bridging as found for **1**. Incorporation of F<sup>−</sup> in more limited degrees has been seen previously in a number

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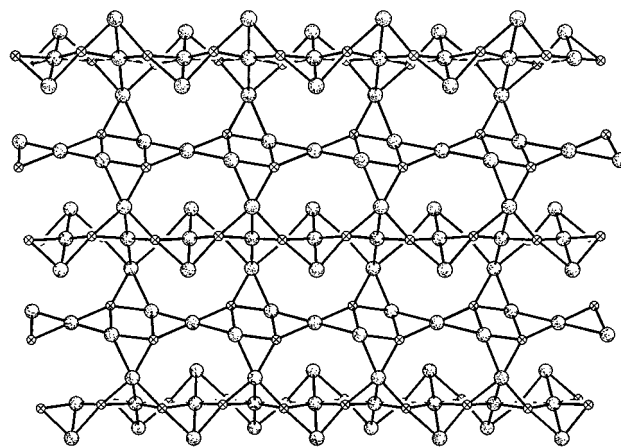
of interesting open-framework phases, notably in cloverite, a fluorinated gallophosphate with a large-pore 20-membered-ring structure.<sup>3</sup> Other recent reports of fluorinated metal phosphates include  $M = \text{Al},^4 \text{Fe},^5 \text{V},^6$  and  $\text{Zr}.$ <sup>7</sup>

In compound **1**, the fluorines not only create the novel stoichiometry which is metal-rich ( $\text{In}_9\text{P}_8$ ) but also play key roles in the unusual framework and channel architectures found for the compound. Compound **1** is a rare example of a fluorinated metal phosphate with fluorine/metal ratio greater than unity and in which the F atoms are coordinated to all metal atoms of the structure with both terminal and bridging environments. By occupying bridging sites, they allow the indium polyhedra to connect together, helping to create special  $\text{In}_3\text{P}_2$  subunits within the structure. In addition, the terminal fluorides are not merely spectator ligands, but they are involved in the formation of a hydrogen bond network to the channel counterions.

Following the success in synthesis of open-framework alumino- and gallophosphates, work has been emerging on the indium phosphate family,<sup>10–13</sup> with indications of expanded rings and variable stoichiometries. Recently we reported that use of stoichiometric amounts of fluoride in organo-templated syntheses of indium phosphates has resulted in formation of the neutral 2-D and 3-D fluorinated compounds  $[\text{In}(\text{PO}_4)\text{F}(\text{enH})]$  and  $[\text{In}_5(\text{PO}_4)_4\text{F}_3(\text{en})_6(\text{H}_2\text{O})_2]$ .<sup>13</sup> The latter is notable in also being metal-rich and again has fluorination, this time with linear and bent F bridges between In atoms. This chemistry further supports our identification of the bridges in **1** as  $\text{F}^-$  rather than  $\text{OH}^-$  since the two phases above have bridging but no terminal fluorides present.

A 3-D pillared layer structure  $3(\text{C}_3\text{N}_2\text{H}_5) \cdot (\text{H}_3\text{O}) \cdot [\text{In}_8(\text{HPO}_4)_{14}(\text{H}_2\text{O})_6] \cdot 5(\text{H}_2\text{O})$  was reported by Chippindale et al., which possessed large 16-membered-ring cavities and for which  $[\text{InO}_6]$  octahedra acted as the pillars.<sup>12</sup> Compound **1** may also be described as having a pillared layer structure. Corrugated sheets of formula  $[\text{In}_9(\text{PO}_4)_6\text{F}_{16}]$  with three independent  $[\text{In}_3\text{P}_2]$  subunits can be identified in **1** (Figure 3). Each has one In at the inversion center and two In at general positions in a trans (linear) arrangement. The sheet may then be considered to be pillared by the  $[\text{HPO}_4]$  groups to form the 3-D anion framework.

The search for new microporous solids with pore architectures and channel chemistry complementary to the existing zeolite and aluminophosphate families remains highly active. We believe that use of large excess  $\text{F}^-$  in the reaction mixture, as for **1**, may allow more extensive fluorination of metal phosphates than typically seen and that more unusual stoichiometries and open-framework structures are to be expected from this approach.



**Figure 3.** Corrugated sheet of **1** of formula  $[\text{In}_9(\text{PO}_4)_6\text{F}_{16}]$ , showing In and P positions only with polyhedral connectivity within the sheet.

### Experimental Procedure

Synthesis of **1** was from a mixture with gel composition of 1.0  $\text{In}(\text{OH})_3$ :1.0  $\text{H}_3\text{PO}_4$ :1.7 1,3-PDA:8.0 HF:120  $\text{H}_2\text{O}$ . Heating for 6 days at 180 °C yielded long colorless bars of 2 mm maximum dimension as the major phase (ca. 80% based on In). Trace amounts of  $[\text{H}_3\text{O}] \cdot [\text{InPO}_4(\text{OH})]$  are formed; however this is predominant if lesser amounts (2 molar equivs) of HF are used.<sup>9</sup>

Elemental anal. Calcd for  $\text{C}_{12}\text{H}_{65}\text{F}_{16}\text{In}_9\text{N}_8\text{O}_{38}\text{P}_8$ : C 5.72, H 2.58, N 4.45. Found C: 5.75, H 2.86, N 4.57. Experimental mole ratio C/N: 1.0:0.68.

A separate indium/phosphorus analysis found In 43.88%, P 10.28%, giving a mole ratio of 1.15 (expected 1.125 for 9:8).

The extent of fluorination was experimentally determined semiquantitatively from energy-dispersive X-ray emission analysis. This was carried out using a JEOL 6300F scanning electron microscope. Analysis for different crystals of compound **1** as well as different selected areas of the same crystal gave consistent results with stoichiometric In, P, and F (typical mole ratio 5:5:8).

<sup>31</sup>P CP MAS NMR:  $\delta$  2.05;  $-0.70$  ppm (ca. 3:1 ratio by deconvolution simulation), 85%  $\text{H}_3\text{PO}_4$  as external standard. Recorded at 23 °C using a JEOL EX400 spectrometer operating at 161.8 MHz. A recycle delay of 2 s was used for 4901 scans with a contact time of 5 ms.

The thermal gravimetric curve was measured on a Perkin-Elmer TGA7 instrument under flowing  $\text{N}_2$  over the range 24–1000 °C at a heating rate of 5 °C/min. This showed a total weight loss of 26%, which occurred continuously between 170 and 1000 °C. Three major sections between 170 and 320, 320 and 550, and 550 and 1000 °C are consistent with loss of channel water, organo-template, and hydrogen fluoride, respectively.

Bond valence sum calculations for **1** based on the method of Brown and Altermatt,<sup>8</sup> using  $r_0(\text{In}-\text{F}) = 1.792$  Å and  $r_0(\text{In}-\text{O}) = 1.902$  Å, gave the following valence sums for In atoms: (values in parentheses for all-oxygen coordination)  $\text{In}(1) = +3.00$  (3.44),  $\text{In}(2) = 3.04$  (3.38),  $\text{In}(3) = 3.05$  (3.53),  $\text{In}(4) = 2.95$  (3.56),  $\text{In}(5) = 2.98$  (3.24),  $\text{In}(6) = 3.01$  (3.29).

Crystal structure analysis of **1**: Siemens P4-RA four-circle diffractometer, Mo  $K\alpha$  radiation, 293 K, monoclinic,  $P2_1/n$ ,  $a = 13.616(2)$  Å,  $b = 9.372(2)$  Å,  $c = 23.293(4)$  Å,  $\beta = 99.44(2)^\circ$ ,  $V = 2932.1(9)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calc}} = 2.85$  g cm<sup>-3</sup>,  $2\theta_{\text{max}} = 55^\circ$ , reflections (measured/independent) 6859/6578; 5202 with  $I > 2\sigma(I)$ ;  $\mu = 3.84$  mm<sup>-1</sup>, crystal dimensions 0.1 × 0.15 × 0.35 mm, absorption correction using psi scans, max/min transmission 0.93/0.74, structure solution and refinement using SHELXL suite of X-ray programs (G. M. Sheldrick, Siemens Analytical Instruments, 1993) 393 parameters,  $R = 0.034$ ,  $R_w = 0.038$  for observed data,  $R = 0.048$ ,  $R_w = 0.043$  for all data,

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with GOF 1.31; residual e.d.  $\pm 1.2 \text{ e \AA}^{-3}$  in the region of disordered template ions. Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany).

**Acknowledgment.** This work was supported by Research Grants Council of Hong Kong (681/96P) and the National Natural Science Foundation of China.

CM970521U