Synthesis and structural characterisation of two- and three-dimensional fluorinated indium phosphates

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Hydrothermal synthesis of two new fluorinated indium phosphates [InPO$_4$F(Hen)] and [In$_5$P$_4$F$_3$O$_{16}$(en)$_3$(OH$_2$)$_2$] is carried out in the system In$_2$O$_3$–P$_2$O$_5$–en–HF–H$_2$O (en = ethylenediamine); these have two- and three-dimensional inorganic frameworks respectively, with the latter having ten-membered ring channels spanned by coordinated en; the fluorides bridge exclusively between indium ions and may be linear or bent.

The synthesis of new classes of inorganic microporous solids, with different architectures and pore chemistry to classical zeolite-related materials, remains an active area.[1–3] Extensive use of organic amines as structure directing agents promotes microporous solid formation, with frequent inclusion of the amine in the microporous channel. Using this approach, a rich chemistry has already been established for group 13 phosphates of Al[4–6] and Ga[7–10] and work is now emerging on the indium phosphate family. Previously three indium phosphates templated by organic amines have been reported, [H$_2$en]-[In(HPO$_4$)$_2$][11] [In$_8$(HPO$_4$)$_{14}$(H$_2$O)$_6$](H$_2$O)$_5$(H$_3$O)(N$_2$C$_3$H$_5$)$_3$[12] and [C$_5$H$_5$NH][In(HPO$_4$)(H$_2$PO$_4$)$_2$].[13]

The presence of fluoride as a mineraliser in hydrothermal synthesis frequently has a pronounced effect on the microporous phases produced[14] and may even result in the incorporation of fluoride into the inorganic framework, as observed for certain alumino-[15] and gallo-phosphates.[16] We report herein the synthesis and structure of two fluorinated indium phosphates, [InPO$_4$F(Hen)] **1** and [In$_5$P$_4$F$_3$O$_{16}$(H$_2$O)$_2$(en)$_3$] **2**, using ethylenediamine (en) as the organic structure directing agent in a fluoride-containing system.

Compounds **1** and **2** were synthesized hydrothermally. An aqueous mixture of indium hydroxide, 85% (m/m) phosphoric acid, ethylenediamine and 40% (m/m) hydrofluoric acid with the gel molar composition 1.0 In(OH)$_3$: 1.0 H$_3$PO$_4$: 1.0 en : 2.0 HF : 80 H$_2$O was heated at 180 °C for 20 days under autogeneous pressure in a Teflon-lined stainless-steel autoclave. The resulting crystalline products were filtered off, washed thoroughly with water and dried at room temp. Microscopic examination revealed two phases, predominantly compound **1** which formed tablets of maximum dimension 150 µm, together with a small amount (*ca.* 10%) of a second phase, compound **2**, as small rectangular blocks of maximum dimension 60 µm. X-Ray photoelectron spectroscopy on the product mixture indicated the presence of In, P and stoichiometric amounts of fluorine. Energy dispersive X-ray analysis on selected single crystals of the two compounds confirmed the presence of these elements in both phases. Their structures were then determined by single-crystal X-ray diffraction.†

[InPO$_4$F(Hen)] **1** is a two-dimensional network with monoprotonated ethylenediamine groups (Hen)$^+$ pendant to InPO$_4$F layers through coordination of one amino group to the indium. A view perpendicular to the layer is shown in Fig. 1. The two-dimensional sheet has chains of corner-shared indium octahedra which are linked to other chains by phosphate bridges forming In$_4$P$_2$ six-membered rings. The corner-sharing of the In octahedra is due to fluoride ions which bridge symmetrically in a bent manner between the In atoms [In–F 2.121, 2.129(5) Å,

In–F–In 133.2(2)°]. Although crystallographically it is difficult to distinguish µ-F from µ-OH, this bridging position is the only chemically reasonable location for the fluorine which must be present in this compound. The phosphate groups point alternately above and below the layer and have three oxygen atoms forming In–O–P bridges and one terminal P–O$^-$ functionality. This is hydrogen bonded to three pendant ammonium NH$_3$R$^+$ chains of the adjacent layer, which serves to organise the overall packing of the structure.

Compound **2**, has a three-dimensional open framework with a 5 : 4 In : P ratio. Its structure is complex featuring ten-membered rings (In$_6$P$_4$) which are spanned by en bridges between opposite indium atoms (Fig. 2). In addition en acts as a simple chelate to one indium centre. Once more, the fluorides are assigned to bridging environments between In atoms but may be linear or bent. The bent bridges have similar geometry to those found for **1** [bent In–F 2.136, 2.135(5) Å, In–F–In 125.9(2)°]. The linear bridges are also assigned to be fluoride, rather than oxide, on the basis of charge balance. Linear In–F–In linkages are well established, and occur in several condensed phases including [InOF].[17] The shorter In–F bond [linear In–F 2.068(1) Å] found for the linear case, is expected due to involvement of the fluoride lone pairs in π bonding and the smaller radius of sp hybridised fluorine. All phosphate oxygen atoms form In–O–P bridges and the coordination environments of the indium atoms are completed by aqua ligands [In–O 2.295(9) Å].†
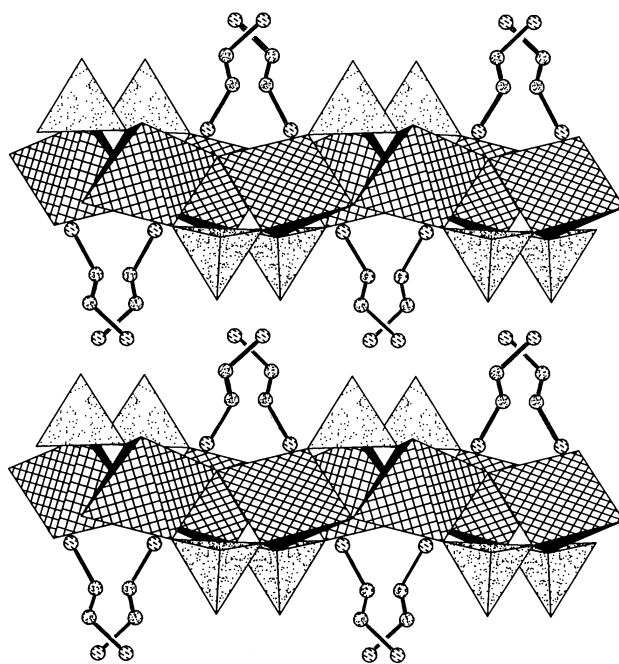

Fig. 1 Projection of **1** along the *c*-axis showing a side view of the sheets with pendant [Hen] groups
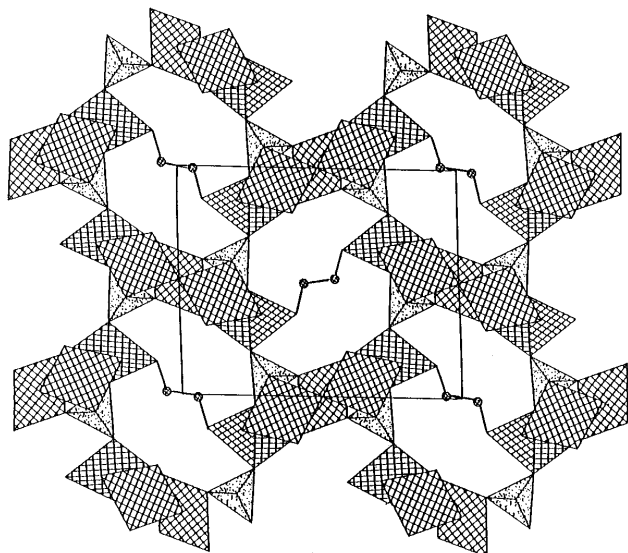
Fig. 2 Polyhedral representation of **2** projected down [001]

Whilst use of stoichiometric levels of fluoride in these syntheses can result in F⁻ incorporation, the use of lesser amounts can still promote crystallisation of indium phosphate phases not containing fluoride itself.[18] For example, in the same system for the synthesis of **1** and **2**, the use of 0.2 mol equiv. HF results in two other phases:[19] a two-dimensional layer compound 0.5[H₂en][InPO₄(OH)] (*ca.* 80%) and a chiral three-dimensional phase [H₃O][InPO₄(OH)] (3%), which is isostructural with Rb[InPO₄(OH)].[20]

The In/P ratios in **1** and **2** are unity or indium rich, in contrast to the previously reported indium phosphates containing template counterions, which are phosphorus rich.[11–13] Fluoride bridges and coordinated ethylenediamine groups exclusively occupy the surplus coordination sites of the octahedral indium atoms. This means that fewer phosphate groups are required than for constructing solely In–O–P linked systems, or that fewer oxygens need be in relatively unfavourable three-coordinate environments compared to InPO₄ itself. In conclusion, we believe more diverse stuctural types will continue to be found for mixed octahedral–tetrahedral framework materials and that use of fluoride may be a useful synthetic strategy to assist in their formation.

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