Synthesis and crystal structure of the first organically templated layered indium phosphate $[C_5H_5NH]^+[In(HPO_4)(H_2PO_4)_2]^-$

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A new templated indium phosphate, prepared as single crystals from a non-aqueous pyridine–butan-2-ol medium, has a unique two-dimensional structure consisting of $[In(HPO_4)(H_2PO_4)_2]^-$ layers held together by hydrogen bonding to generate cavities in which pyridinium cations reside.

In the quest for new microporous zeolitic materials, there has recently been much interest in the synthesis of open-framework metal phosphates. Within group 13, the research emphasis to date has focused on the phosphates of the lighter elements aluminium and gallium, many of which have structures analogous to those of the aluminosilicate zeolites.[1] For example, AlPO-20[2] and $[C_4NH_{10}][CoGaP_2O_8]$[3] have the sodalite and gismondine structures respectively. A number of AlPOs and GaPOs are also known which have unique structures containing one-dimensional polymeric chains,[4] two-dimensional layered structures[5–7] as well as three-dimensional open-framework structures.[8,9] Many of these new materials have come to light through the use of non-aqueous synthetic methods and they are of interest for their potentially exploitable ion-exchange, gas separation and catalytic properties. Little work, however, has been carried out on the indium phosphates (InPOs) and, to date, apart from a few dense phases, only three phases with open structures, namely $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$,[10] $[NH_3CH_2CH_2NH_3][In_2(HPO_4)_4]$,[11] and $[In_8(HPO_4)_{14}(H_2O)_6](H_2O)_5(H_3O)(C_3N_2H_5)_3$,[12] have been described in the literature.

Here we describe the synthesis, structural and thermal characterisation of a new amine encapsulating InPO with an In : P ratio of 1 : 3 which is, to our knowledge, the first layered indium phosphate to be reported.

The title compound was synthesised under solvothermal conditions from a predominantly non-aqueous system. $InCl_3$ (0.5 g) was dispersed in 10 cm^3 of butan-2-ol by stirring and 0.37 cm^3 of pyridine added. Orthophosphoric acid (0.37 cm^3; 85% by weight) was then added to give a gel of overall composition $InCl_3$: 2.4 H_3PO_4 : 25.6 2-BuOH : 2.0 pyridine. The gel was sealed in a Teflon-lined stainless-steel autoclave and heated at 160 °C for 4 days. The solid product, in the form of colourless rectangular plates, was collected by filtration, washed with distilled water and dried at 70 °C. Analytical electron microscopy of a finely ground sample of the product mixture indicated that the product was monophasic with no chlorine present in any of the crystallites examined. The powder X-ray diffraction pattern further confirmed that the product was single phase. C, H, N analysis supported the presence of pyridine in the product (Found: C, 12.22; N, 2.91; H, 2.43. Calc.: C, 12.39; N, 2.89; H, 2.29%). Thermogravimetric analysis of the pure powdered sample in flowing nitrogen over the temperature range 20–600 °C shows one broad weight loss (*ca.* 18.8% by weight over the range 275–350 °C) suggesting complete loss of pyridine (calc. weight loss 16.3%) and possibly some water. A powder X-ray pattern of the final black product indicated that it was amorphous.

A crystal was selected from the original sample for study by single-crystal X-ray diffractometry.†

The structure consists of macroanionic sheets of formula $[In(HPO_4)(H_2PO_4)_2]^-$ with charge balancing pyridinium cations located in cavities between the layers. The sheets are built from InO_6 octahedra and three distinct PO_4 tetrahedra (Fig. 1). Three equatorial coordination sites on the In(1) atom are shared with three $P(3)O_3(OH)$ groups *via* oxygens O(6), O(11) and O(12) to generate ribbons of edge sharing four-membered rings of alternating InO_6 and PO_4 units running parallel to the *a* axis. One axial and one equatorial In(1) site are shared with two $P(1)O_2(OH)_2$ groups *via* oxygens O(1) and O(2) to generate additional eight- and four-membered rings and thereby connect the ribbons into a corrugated sheet (Fig. 2). The second axial coordination site of In(1) is filled by connection through O(7) to a pendant $P(2)O_2(OH)_2$ group. The terminal P(2)–O(8) bond length is reasonably short [1.492(3) Å] suggesting some degree of multiple bond character. Strong hydrogen bonds between O(8) and O(9)H on pendant groups of adjacent layers link the sheets together in an AAA stacking sequence [O(8)···O(9) 2.581(4) Å] and create cavities in which the pyridinium cations reside (Fig. 3). Each pyridinium cation is hydrogen bonded to one of the bridging oxygens of the framework [N(1)···O(6) 3.178(7) Å]. The four remaining P–OH groups are all involved in intralayer hydrogen bonding to framework oxygen atoms, with OH···O distances lying in the range 2.61(1)–2.69(1) Å, and thus play no part in holding the layers together.

Although the structure described above is unique, it has a number of features in common with the open three-dimensional structure of $[NH_3CH_2CH_2NH_3][In_2(HPO_4)_4]$.[11] The latter framework is also constructed from InO_6 and HPO_4 polyhedra linked to form ribbons of four-membered rings which in turn link through further HPO_4 units to generate corrugated layers similar to those identified here. The main difference between the two structures is that in the $[In_2(HPO_4)_4]^-$ compound, additional HPO_4 groups bridge adjacent corrugated layers to

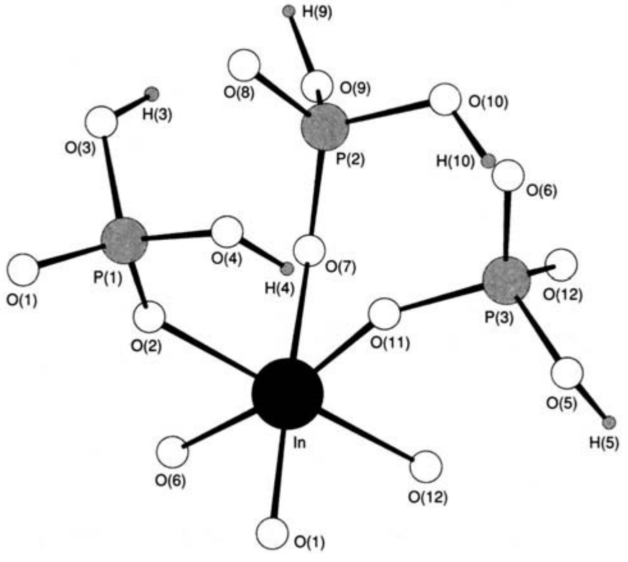

Fig. 1 Local coordination of the InPO framework. In–O bond lengths lie in the range 2.116(3)–2.175(3) Å and average P–O bond lengths in In–O–P bridges and P–OH groups are 1.52(2) and 1.567(8) Å respectively. The P(2)–O(8) bond length is 1.492(3) Å.

form an extended three-dimensional framework, whereas in the present compound, the crosslinking is terminated by the pendant $PO_2(OH)_2$ groups and a network of hydrogen bonds holds the discrete layers together.

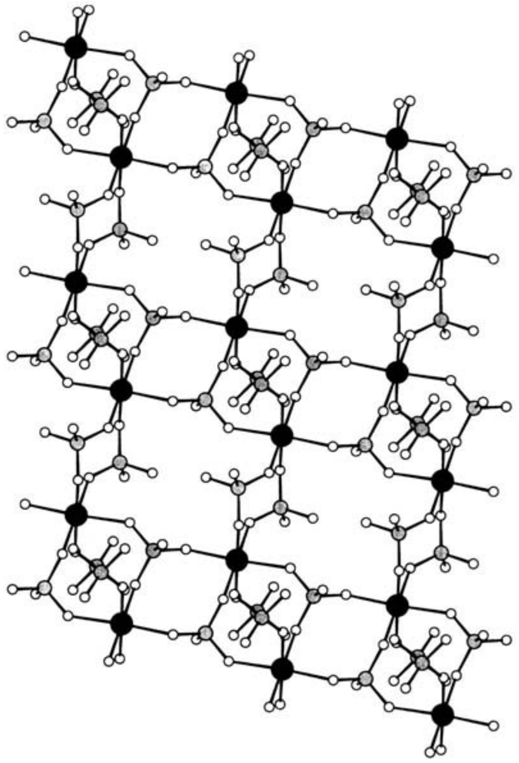

Fig. 2 View along the *c* axis showing the corrugated sheet structure constructed from ribbons of edge-sharing four-membered rings of alternating InO_6 and PO_4 units linked *via* $P(1)O_2(OH)_2$ groups. O···O separations across the diagonals of the four- and eight-membered rings lie in the ranges 3.09–4.68 and 3.09–7.59 Å respectively (hydrogen atoms have been omitted for clarity).

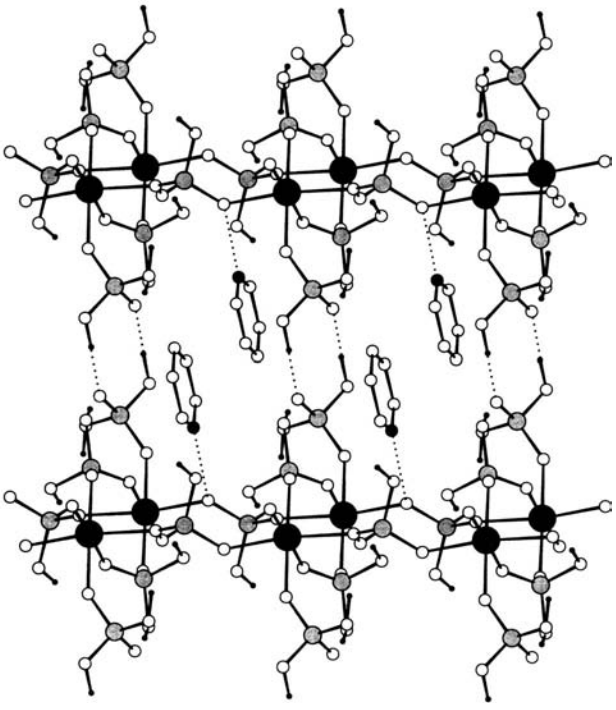

Fig. 3 View along the *b* axis showing the location of the pyridinium cations between the InPO sheets. The interlayer hydrogen bonding [O(9)–H···O(8), 2.581(4) Å] and the hydrogen bonding of the pyridinium cation to the InPO framework [N(1)···O(6), 3.178(7) Å] are represented by dotted lines.

Although a number of layered aluminium and gallium phosphates containing octahedrally coordinated metal ions have been characterised,[7,16,17] to date no Al or Ga analogue of $[C_5H_5NH][In(HPO_4)(H_2PO_4)_2]$ is known. The two-dimensional AlPO, $[C_5H_5NH][H_2Al_2P_3O_{12}]$,[5] which also contains pyridinium cations, has a rather different layered structure containing Al in tetrahedral and trigonal-bipyramidal coordination sites.

The authors thank A. R. Cowley for his practical assistance and one of us (A. M. C.) thanks the University of Oxford for a Glasstone Research Fellowship.

Footnote

† A crystal suitable for X-ray analysis (size 0.096 × 0.16 × 0.22 mm) was obtained from the synthesised material. *Crystal data* for $C_5H_{11}InNO_{12}P_3$, M = 484.88, triclinic, space group $P\bar{1}$, a = 6.615(1), b = 9.629(1), c = 11.553(1) Å, α = 75.19(1), β = 86.74(1), γ = 73.90(1)°, U = 683.4 Å^3, Z = 2, μ(Cu-Kα) = 181.97 cm^{-1}, D_c = 2.36 g cm^{-3}. Data were collected at room temperature on an Enraf-Nonius MACH3 diffractometer using the ω–2θ technique, for the range $2.12 < 2\theta < 140°$. The total number of reflections measured was 2862, of which 2463 were unique and 2451 had $I > 3\sigma(I)$. The structure was solved by direct methods (SHELX-86).[13] All atoms were located easily in Fourier maps apart from the hydrogens on the carbon atoms of the template which were placed geometrically. Refinement of 218 variables was by full-matrix least-squares analysis (CRYSTALS)[14] to give final residuals R and R_w of 0.037 and 0.042 respectively. Bond-valence calculations further supported the assignment of the P–OH groups in the structure.[15] 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 182/299.

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Received, 9th August 1996; Com. 6/05564H