Novel Pillared Layer Structure of the Organically Templated Indium Phosphate $[In_8(HPO_4)_{14}(H_2O)_6](H_2O)_5(H_3O)(C_3N_2H_5)_3$

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An imidazole encapsulating indium phosphate with an In:P ratio of 4:7 and a new pillared layer structure has been synthesized under solvothermal conditions and characterized by single-crystal X-ray diffraction, ^{31}P CPMAS NMR, and thermogravimetric analysis. [Crystal data: $[In_8(HPO_4)_{14}(H_2O)_6](H_2O)_5(H_3O)(C_3N_2H_5)_3$, $M_r = 2686.72$, trigonal, space group $P{-}3c1$ (No. 165), $a = 13.859(2)$ Å, $c = 19.186(8)$ Å, $V = 3193(4)$ Å^3, $Z = 2$, $R = 3.6\%$, $R_w = 3.7\%$ (1650 observed data with $I > 3\sigma(I)$)]. The structure consists of layers assembled from InO_6 and $InO_5(OH_2)$ octahedra and $PO_3(OH)$ tetrahedra which are pillared through additional InO_6 octahedra to produce a three-dimensional framework. The framework contains a two-dimensional array of channels in which imidazolium cations, hydroxonium ions, and water molecules reside. Within the channels are 16-membered rings of alternating In and P polyhedra which have dimensions ~8.6 × 9.7 Å.

Introduction

In the quest for new microporous zeolitic materials, there has recently been much interest in the synthesis of open-framework metal phosphates with exploitable ion-exchange and catalytic properties. A wide range of metals including Be,[1,2] Zn[2,3] and transition metals such as V,[4] Fe,[5] Co,[6] and Mo[7] have been incorporated into phosphates, particularly in the presence of organic templates, and many new structure types have been produced. Within group 13, the research emphasis to date has focused on the phosphates of the lighter elements aluminum and gallium, many of which have structures analogous to those of the aluminosilicate zeolites.[2] For example, AlPO-20[8] and $(pyH)[CoGa_2P_3O_{12}]$[9] have the sodalite and laumontite structures, respectively. A number of AlPOs and GaPOs are also known which have unique structures containing 1-D polymeric chains,[10,11] 2-D layered structures,[12−14] and 3-D open-framework structures.[8,15,16] Little work however has been carried out on the indium phosphates, and to date only the dense phases $InPO_4$,[17] $InPO_4{\cdot}2H_2O$,[18] $Li_3In_2(PO_4)_3$,[19,20] and $NaCdIn_2(PO_4)_3$,[21] and two phases with open structures, $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$[22] and $[NH_3CH_2CH_2NH_3][In_2(HPO_4)_4]$,[23] have been reported in the literature.

Here we report the synthesis and structural and thermal characterization of a new organically templated indium phosphate (InPO), the first to be prepared with

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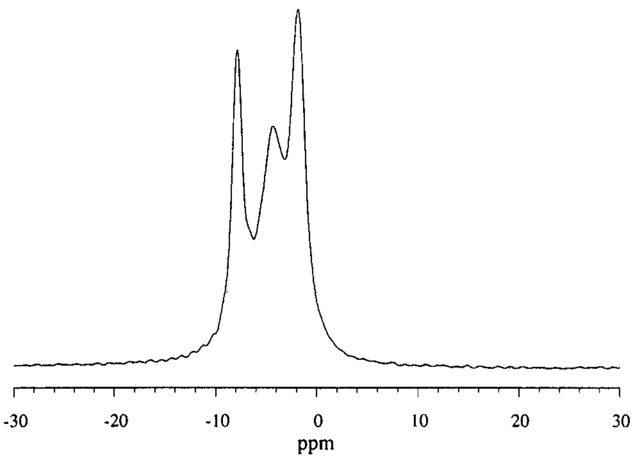

Figure 1. The 81.01 MHz ^{31}P CPMAS NMR spectrum of the title compound. The chemical shift is referenced to pure phosphoric acid.

an In:P ratio of 4:7 and the first to possess a pillared layer structure.

Experimental Section

Synthesis and Initial Characterization. The title compound was synthesised under solvothermal conditions from a predominantly nonaqueous system. $InCl_3$ (0.50 g) and imidazole (0.31 g) were dispersed in 10 cm^3 of butan-2-ol by stirring. Orthophosphoric acid (0.54 cm^3, 85% by weight) was then added with further stirring to give a gel of overall composition $InCl_3$:2 imidazole:3.5 H_3PO_4:25.6 butan-2-ol. The gel was sealed in a Teflon-lined stainless steel autoclave and heated at 160 °C for 4 days. The solid product was collected by filtration, washed with distilled water, and dried overnight at 70 °C. Examination under the optical microscope revealed large colorless hexagonal prisms as the sole product and one of these was selected for study by single-crystal X-ray diffraction. The crystals are air and moisture stable over at least 5 months.

Energy-dispersive X-ray emission analysis of a finely ground sample of the crystals, determined using a JEOL 2000FX analytical electron microscope, showed that the product was monophasic with a constant phosphorus:indium ratio but no chlorine present in any of the crystallites examined. C, H, and N analysis gave the following result: Found: C, 4.27; H, 2.00; N, 3.31%. Calcd for $[In_8(HPO_4)_{14}(H_2O)_6](H_2O)_5(H_3O)(C_3N_2H_5)_3$: C, 4.02; H, 2.03; N, 3.13%, confirming that imidazole is present in the compound.

A ^{31}P CPMAS NMR spectrum of a finely ground sample packed in a 7 mm zirconia rotor fitted with a Kel-F cap was recorded at 23 °C using a Bruker MSL 200 spectrometer operating at 81.01 MHz (Figure 1). A recycle delay of 2 s was used for 4273 scans with a contact time of 5 ms and the sweep width was 29 kHz. The ^{31}P chemical shift was referenced to pure phosphoric acid (85% by weight).

Thermogravimetric (TGA) measurements carried out under flowing nitrogen on a Stanton Redcroft STA 1500 thermal analyzer over the range 20−400 °C, at a heating rate of 5 °C/min showed a ~9.4% weight loss at 290 °C. An X-ray powder pattern of the white product showed that it was amorphous. C, H, and N analysis indicated that imidazole was still present in the product after heating (found: C, 4.78; H, 0.61; N, 3.52%). The theoretical weight loss for removal of the framework and nonframework water molecules is 8.1%, in reasonable agreement with the measured value, although the possibility exists for dehydration of some of the HPO_4 groups. On further heating, the product melted at ~700 °C to produce a black liquid.

Subsequent reactions showed that the same product could also be synthesized under similar conditions using indium oxide as the source of indium from a gel of composition In_2O_3:2 imidazole:7 H_3PO_4:32 butan-2-ol.

Table 1. Crystallographic Data for $[In_8(HPO_4)_{14}(H_2O)_6](H_2O)_5(H_3O)(C_3N_2H_5)_3$

formula	$In_8P_{14}O_{68}C_9N_6H_{54}$
M_r	2686.72
crystal size (mm)	0.16 × 0.16 × 0.06
crystal habit	colorless hexagonal prism
crystal system	trigonal
space group	$P-3c1$ (No. 165)
a (Å)	13.859(2)
c (Å)	19.186(8)
vol (Å^3)	3193(4)
Z	2
ρ_{calc} (gcm^{-3})	2.79
μ (cm^{-1})	32.83
unique data	2579
obsd data ($I > 3\sigma(I)$)	1650
R_{merg}	0.086
no. of parameters refined	208
R, R_w	0.036, 0.037

Crystal Structure Determination. A crystal suitable for X-ray analysis was obtained from the material synthesized from $InCl_3$ and mounted on a thin glass fiber using cyanoacrylate glue. Intensity data were collected at 293 K on an Enraf-Nonius CAD4 diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.710\ 69$ Å). Lattice parameters $a = 13.859(2)$ and $c = 19.186(8)$ Å were determined from 25 well-centered reflections ($6 < \theta < 14°$). Intensity data were collected using the $\omega-2\theta$ scan technique over the range ($0 < \theta < 28°$). Three standard reflections were measured every hour during the data collection, and no intensity variation was observed. Data were corrected for absorption using ψ scans[24] and further corrected for Lorentz and polarization effects.[25] On the basis of the systematic absence conditions in the reduced data ($h-h0l$, l = odd; $000l$, l = odd) and the successful solution and refinement of the structure, the space group was determined to be $P-3c1$ (No. 165).[26] The structure was solved by direct methods using the program SHELXS-86[27] and the indium, phosphorus and framework oxygen atoms located. The nonframework oxygen, carbon, and nitrogen atoms and the framework hydrogen atoms were progressively located in difference Fourier maps. All Fourier calculations and subsequent full-matrix least-squares refinements were carried out using the CRYSTALS suite of programs.[28]

The hydrogens on the imidazole template were placed geometrically after each cycle of refinement. The hydrogens attached to the nonframework oxygens could not be located and were not placed. In the final cycle, 208 parameters were refined including anisotropic thermal parameters for all non-hydrogen atoms and a correction for secondary extinction.[29] A three-term Chebyshev polynomial was applied as weighting scheme,[30] to give residuals of $R = 0.036$ and $R_w = 0.037$. The final Fourier difference maps revealed residual electron density near the indium atoms (min = −1.3, max = 3.0 e Å^{-3}) but no regions of electron density which could be attributable to additional atomic sites.

Crystal Structure

The atomic coordinates and selected bond lengths and bond angles are given in Tables 2 and 3, respectively,

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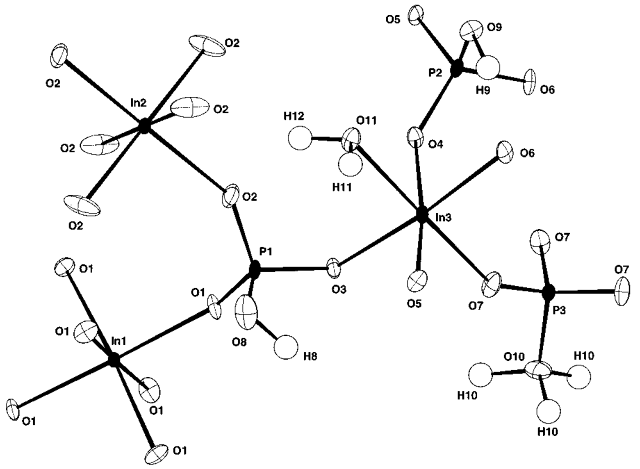

Figure 2. Local coordination of the framework atoms showing the atom-labeling scheme and ellipsoids at 50% probability (drawing package CAMERON[31]).

Table 2. Atomic Positional Parameters, Isotropic Thermal Parameters (Å^2), and Occupancies for $[In_8(HPO_4)_{14}(H_2O)_6](H_2O)_5(H_3O)(C_3N_2H_5)_3$

atom	x	y	z	*U*(iso)	occ[a]
In(1)	0.0000	0.0000	0.2500	0.0097	
In(2)	0.0000	0.0000	0.0000	0.0105	
In(3)	−0.14543(3)	−0.44067(3)	0.04952(2)	0.0116	
P(1)	−0.0453(1)	−0.1937(1)	0.12831(8)	0.0142	
P(2)	−0.3661(1)	−0.4960(1)	−0.04915(8)	0.0114	
P(3)	−0.3333	−0.6667	0.1449(1)	0.0120	
C(1)	0.347(2)	0.008(3)	0.2032(9)	0.0423	0.5000
C(3)	0.370(2)	−0.028(3)	0.315(1)	0.0699	0.5000
C(5)	0.451(3)	0.019(4)	0.205(2)	0.0575	0.5000
N(2)	0.308(2)	−0.011(2)	0.2680(6)	0.0446	0.5000
N(4)	0.457(2)	−0.002(3)	0.273(1)	0.0611	0.5000
O(1)	−0.0793(4)	−0.1473(4)	0.1882(2)	0.0205	
O(2)	−0.0474(6)	−0.1447(4)	0.0599(3)	0.0318	
O(3)	−0.1226(4)	−0.3187(4)	0.1251(2)	0.0175	
O(4)	−0.2893(4)	−0.4371(3)	0.0125(2)	0.0180	
O(5)	0.0124(3)	−0.4224(4)	0.0753(2)	0.0170	
O(6)	−0.1671(4)	−0.5512(4)	−0.0334(3)	0.0180	
O(7)	−0.2259(4)	−0.5664(4)	0.1237(3)	0.0239	
O(8)	0.0759(5)	−0.1713(5)	0.1404(4)	0.0359	
O(9)	−0.2943(4)	−0.4989(4)	−0.1119(2)	0.0218	
O(10)	−0.3333	−0.6667	0.2275(4)	0.0309	
O(11)	−0.0555(4)	−0.3094(4)	−0.0314(3)	0.0226	
O(100)	0.281(2)	0.399(4)	0.240(1)	0.0606	0.61(9)
O(101)	0.284(3)	0.452(5)	0.249(1)	0.0666	0.39(9)
H(8)	0.063(8)	−0.237(5)	0.168(4)	0.05	
H(9)	−0.241(6)	−0.522(8)	−0.094(5)	0.05	
H(10)	−0.32(2)	−0.58(1)	0.25(1)	0.05	0.3333
H(11)	0.020(4)	−0.302(8)	−0.027(5)	0.05	
H(12)	−0.045(8)	−0.234(4)	−0.021(5)	0.05	

[a] Occupancy of site is unity unless stated.

and the local coordinations of the framework atoms are shown in Figure 2. The indium atoms In(1), In(2), and In(3) are located in three distinct sites with point symmetries S_6, D_3, and C_1, respectively. All but one of the In−O distances in the InO_6 octahedra lie in the narrow range 2.089−2.139 Å and are in good agreement with bond lengths seen in other compounds containing In−O−P bridges; for example, in $[NH_3CH_2CH_2NH_3][In_2(HPO_4)_4]$, $In-O_{br}$ = 2.099−2.166 Å[23] and in $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$, $In-O_{br}$ = 2.088−2.180 Å.[22] The exception is the In(3)−O(11) distance, which is rather longer at 2.237 Å. Bond-valence calculations[32] indicate that O(11) has unsatisfied valence which can be satisfied by its assignment as an OH_2 group. Both protons attached to O(11) were subsequently located in Fourier maps to give the unit $In(3)O_5(OH_2)$. In−O distances of 2.205 and 2.28 Å have been reported for In−OH_2 groups in $Cs[In_2(PO_4)(HPO_4)_2(H_2O)_2]$[22] and $InPO_4{\cdot}2H_2O$,[18] respectively.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[In_8(HPO_4)_{14}(H_2O)_6](H_2O)_5(H_3O)(C_3N_2H_5)_3$

In(1)−O(1)	2.130(4)	P(1)−O(1)	1.503(5)
In(2)−O(2)	2.111(5)	P(1)−O(2)	1.485(5)
In(3)−O(3)	2.127(4)	P(1)−O(3)	1.517(4)
In(3)−O(4)	2.139(4)	P(1)−O(8)	1.565(6)
In(3)−O(5)	2.130(4)	P(2)−O(4)	1.527(4)
In(3)−O(6)	2.122(4)	P(2)−O(5)	1.497(4)
In(3)−O(7)	2.089(5)	P(2)−O(6)	1.504(4)
In(3)−O(11)	2.237(5)	P(2)−O(9)	1.575(5)
		P(3)−O(7)	1.498(4)
C(1)−N(2)	1.33(1)	P(3)−O(10)	1.585(8)
N(2)−C(3)	1.34(1)		
C(3)−N(4)	1.33(1)		
N(4)−C(5)	1.34(1)		
C(5)−C(1)	1.36(4)		
O(1)−In(1)−O(1)	92.0(2)	O(1)−P(1)−O(2)	113.5(3)
O(1)−In(1)−O(1)	175.8(3)	O(1)−P(1)−O(3)	109.1(3)
O(1)−In(1)−O(1)	91.1(3)	O(2)−P(1)−O(3)	108.8(3)
O(1)−In(1)−O(1)	85.0(3)	O(1)−P(1)−O(8)	109.7(3)
		O(2)−P(1)−O(8)	107.8(4)
O(2)−In(2)−O(2)	180	O(3)−P(1)−O(8)	107.9(3)
O(2)−In(2)−O(2)	93.2(2)		
O(2)−In(2)−O(2)	86.8(2)	O(4)−P(2)−O(5)	112.3(2)
O(2)−In(2)−O(2)	86.8(2)	O(4)−P(2)−O(6)	112.1(3)
		O(5)−P(2)−O(6)	111.6(3)
O(3)−In(3)−O(4)	88.7(2)	O(4)−P(2)−O(9)	109.0(3)
O(3)−In(3)−O(5)	90.6(2)	O(5)−P(2)−O(9)	105.9(3)
O(4)−In(3)−O(5)	170.8(2)	O(6)−P(2)−O(9)	105.5(3)
O(3)−In(3)−O(6)	174.4(2)	O(7)−P(3)−O(7)	112.9(2)
O(4)−In(3)−O(6)	88.3(2)	O(7)−P(3)−O(10)	105.8(2)
O(5)−In(3)−O(6)	91.5(2)		
O(3)−In(3)−O(7)	90.2(2)	C(5)−C(1)−N(2)	107.5(23)
O(4)−In(3)−O(7)	97.5(2)	C(1)−N(2)−C(3)	115.2(23)
O(5)−In(3)−O(7)	91.7(2)	N(2)−C(3)−N(4)	96.7(25)
O(6)−In(3)−O(7)	94.9(2)	C(3)−N(4)−C(5)	119.8(38)
O(3)−In(3)−O(11)	91.5(2)	N(4)−C(5)−C(1)	100.1(34)
O(4)−In(3)−O(11)	84.1(2)		
O(5)−In(3)−O(11)	86.8(2)		
O(6)−In(3)−O(11)	83.5(2)		
O(7)−In(3)−O(11)	177.7(2)		
In(1)−O(1)−P(1)	135.5(3)		
In(2)−O(2)−P(1)	147.9(4)		
In(3)−O(3)−P(1)	132.5(3)		
In(3)−O(4)−P(2)	130.8(2)		
In(3)−O(5)−P(2)	140.2(3)		
In(3)−O(6)−P(2)	136.2(3)		
In(3)−O(7)−P(3)	145.9(3)		

The three distinct phosphorus atoms are all tetrahedrally coordinated and linked through oxygen to three adjacent indium atoms ($P(1)-O_{av}$, 1.502 Å; $P(2)-O_{av}$, 1.509 Å; $P(3)-O_{av}$, 1.498 Å), with the fourth coordination site in each case corresponding to a terminal P−OH group as shown by the longer P−O distances (P(1)−O(8) = 1.565 Å, P(2)−O(9) = 1.575 Å, and P(3)−O(10) = 1.585 Å). These findings are consistent with those from the ^{31}P CPMAS NMR spectrum (Figure 1) which shows three distinct, yet similar, tetrahedral phosphorus sites.

The InO_6 and $PO_3(OH)$ polyhedra are connected together in an alternating manner to give a novel open-framework structure of composition $[In_8(HPO_4)_{14}(H_2O)_6]^{4-}$ (Figure 3). The framework consists of layers containing the $PO_3(OH)$ tetrahedra and $In(2)O_6$ and $In(3)O_5(OH_2)$ octahedra linked to form 4- and 6-membered rings. The layers are stacked in an ABAB sequence and linked through $In(1)O_6$ pillars to generate a two-dimensional array of channels (Figure 4). The P(3)−O(10)H groups project into the channels at a nearest separation of 8.05

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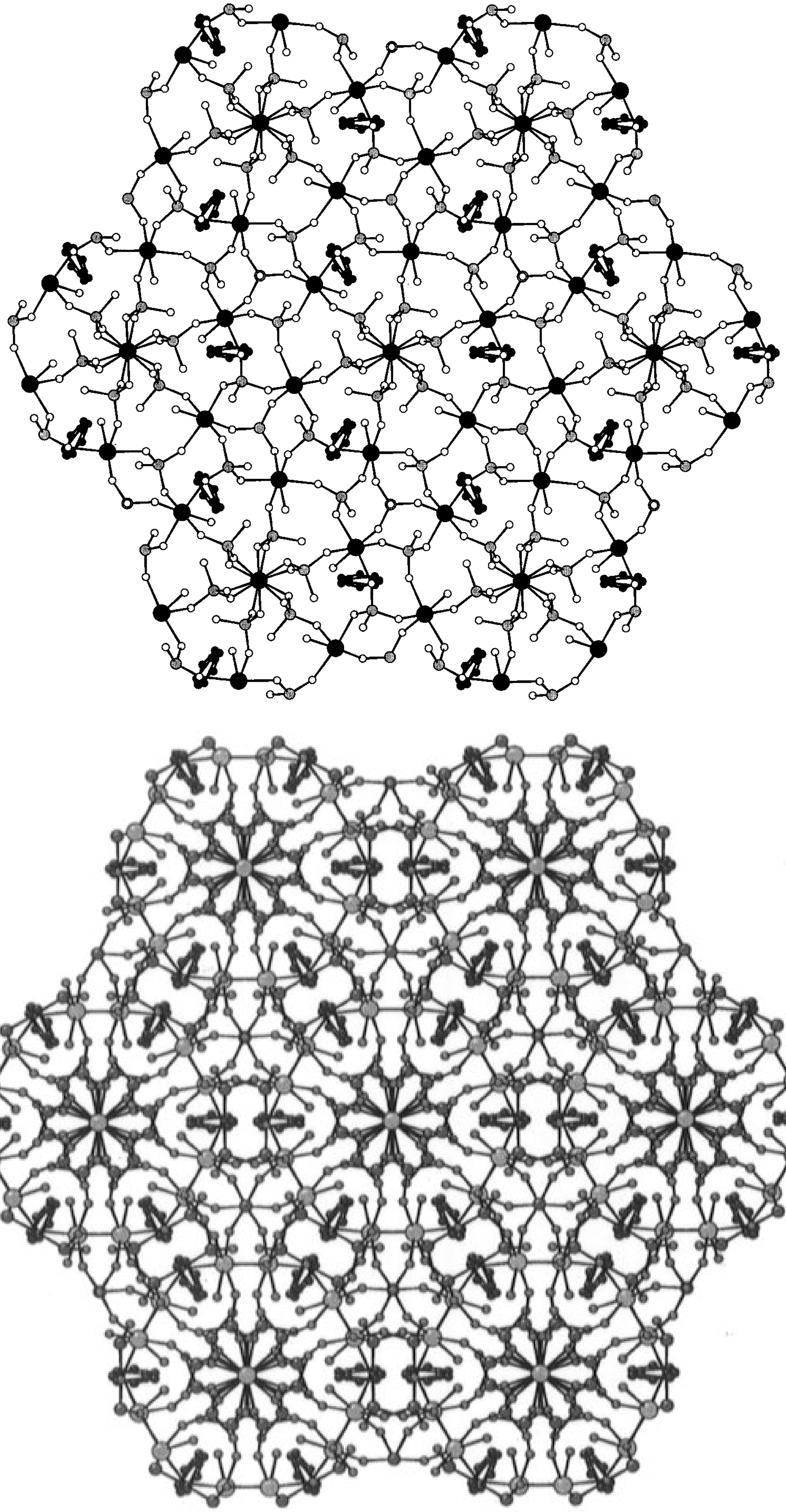

Figure 3. (a, top) View along the *c* axis of one layer with associated imidazolium ions. Key: large black spheres = indium, shaded spheres = phosphorus, open spheres = oxygen, small black spheres joined into rings = imidazolium cations. (b, bottom) View of unit cell along the *c* axis showing stacking of layers. N. B. Nonframework water molecules have been omitted for clarity.

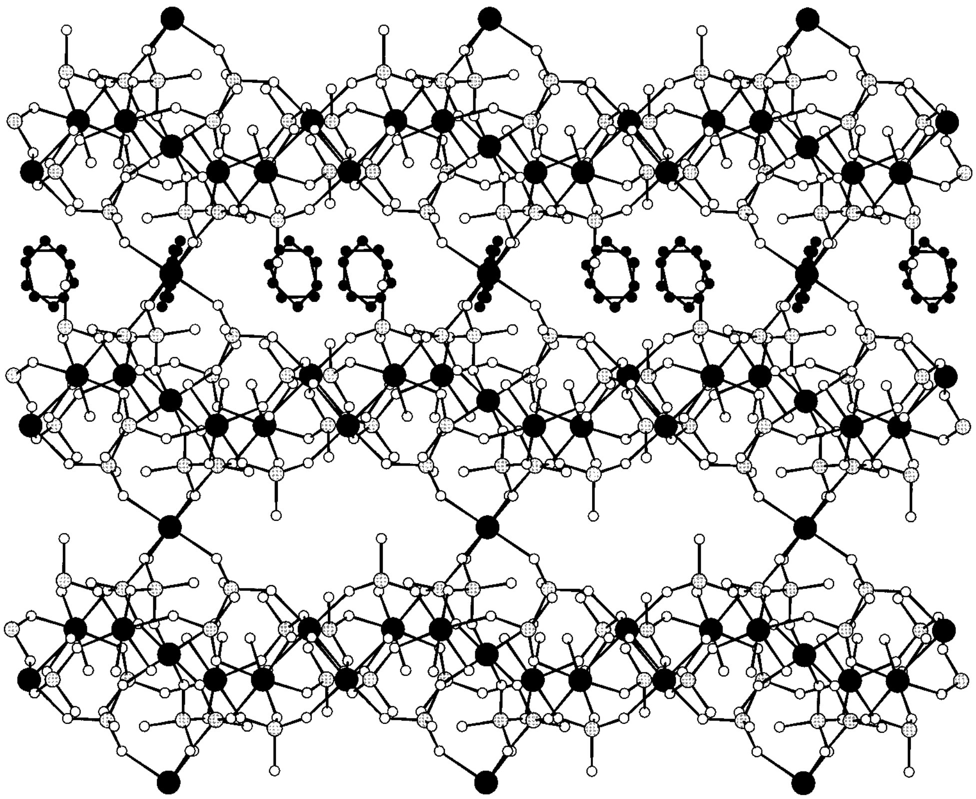

Figure 4. View along the *a* axis showing the layers containing In(2), In(3), and P-based polyhedra pillared by In(1)O_6 octahedra. The In(1) pillars are spaced ~13.86 Å apart. The imidazolium ion positions are shown in one channel. Key as for Figure 3a.

Table 4. List of O···O and O···N Contacts (Å) Indicating Possible Hydrogen Bonds[a]

O(8)−H(8)···O(100)	2.679(49)	O(100)···O(100)	2.882(58)
O(9)−H(9)···O(6)[b]	2.679(6)	O(100)···O(3)	2.837(16)
O(10)−H(10)···O(101)	2.736(69)	O(101)···O(7)	2.794(34)
O(11)−H(11)···O(4)[b]	2.714(6)	O(101)···O(3)	2.905(38)
O(11)−H(12)···O(2)[b]	2.835(7)	N(2)−H(2)···O(1)	2.978(20)

[a] N. B.: no other O···O or O···N contacts exist at distances less than 3 Å. [b] Intralayer hydrogen bonds.

Å. P−OH groups protruding into cavities have been observed previously in cloverite[16] and JDF-20.[15]

The channels also contain imidazolium cations and water molecules. The former are disordered over two symmetry-related positions, while the latter are disordered over two nonequivalent positions (refined occupancies of O(100) and O(101) are 0.61(9) and 0.39(9), respectively) separated by 0.72 Å, and thus precluding their simultaneous occupation. One-sixth of the nonframework water molecules must be protonated to achieve charge balance with the framework, although the H_2O and H_3O^+ units cannot be distinguished in the X-ray experiment.

Within the channels are 16-membered rings containing eight indium octahedra and eight phosphate tetrahedra (Figure 5). The imidazolium cations lie in the plane of these rings.

Hydrogen bonding plays an important role in linking the amine cations and water/hydroxonium ions to the framework (Table 4). Intralayer hydrogen-bonded interactions also exist involving two bonds from the In(3)−O(11)H_2 unit and one from the P(2)−O(9)H to O(2), O(4), and O(6), respectively. It should be noted that none of the hydrogen bonds cross-link the indium−phosphate layers; the layers are held together only by the In(1)O_6 pillars, which are 13.86 Å apart.

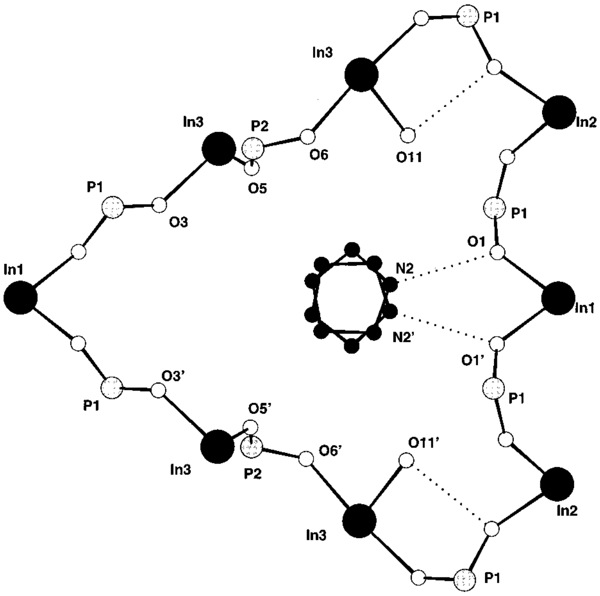

Figure 5. View of 16-membered ring containing imidazolium cation disordered over two symmetry-equivalent sites. Hydrogen-bonding interactions within the ring are shown as dotted lines. Intra-ring distances are as follows: O3···O1′, 9.70 Å; O5···O11′, 8.59 Å; O6···O6′, 9.23 Å; N2···O1, 2.98 Å. Key as for Figure 3a.

Discussion

The compound described here, with its unique pillared-layer structure, is the first indium phosphate (InPO) to be prepared under predominantly nonaqueous conditions and the first to incorporate an aromatic amine. Such synthesis conditions and aromatic-amine templates have been used in the recent past for the preparation of new AlPOs and GaPOs; for example, pyridine in butan-2-ol produces a layered AlPO, (PyH)-

$[Al_2P_3O_{12}H_2]$,[12] and imidazole/pyridine in butan-1-ol produces a 3-D CoGaPO (TH)$[CoGa_2P_3O_{12}]$ (T = py,[9] imidazole[33]), but this is their first reported use in indium chemistry. The InPO is also unusual in that the In:P ratio is 4:7; the only other organically templated InPO reported to date, $[NH_3CH_2CH_2NH_3][In_2(HPO_4)_4]$, has In:P in the ratio 1:2.[23] There are no known AlPOs or GaPOs with this metal:phosphorus ratio.

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Supporting Information Available: Tables listing anisotropic thermal parameters for non-hydrogen atoms (2 pages); observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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(33) Cowley, A. R.; Chippindale, A. M., unpublished results.