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Notes

Synthesis and Structures of $[In_4(4,4'\text{-bipy})_3(HPO_4)_4(H_2PO_4)_4]\cdot 4H_2O$ and $In_4(4,4'\text{-bipy})_3(HPO_4)_4(H_2PO_4)_4$, Indium Phosphates with a Pillared Layer Structure

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Introduction

Materials with open-framework structures are of great interest due to their catalytic and ion-exchange properties and rich structural chemistry. One class of these materials is aluminophosphates, known as AlPOs.[1] Many of these display new microporous structures; two notable AlPOs are the very large pore materials JDF-20 and VPI-5 containing 20- and 18-membered rings, respectively.[2,3] The replacement of aluminum by gallium has yielded many new structures due to the propensity of gallium to adopt a more variable and expanded coordination environment compared to aluminum.[4] In contrast, much less work has been carried out on the heavier group 13 phosphates. Previously three indium phosphates templated with organic amines have been reported, $[NH_3CH_2CH_2NH_3][In_2(HPO_4)_4]$,[5] $[In_8(HPO_4)_{14}(H_2O)_6](H_2O)_5(H_3O)(N_2C_3H_5)_3$,[6] and $[C_5H_5NH][In(HPO_4)(H_2PO_4)_2]$.[7] Two fluorinated indium phosphates with ethylenediamine as the template were also reported.[8] Macroanionic frameworks were found in all of these compounds. We describe herein the synthesis and characterization of $[In_4(4,4'\text{-bipy})_3(HPO_4)_4(H_2PO_4)_4]\cdot 4H_2O$ (**1**) whose framework structure consists of neutral sheets of indium phosphate which are pillared through 4,4′-bipyridine ligands to form channels in which water molecules are located. The structure of the anhydrous compound, $In_4(4,4'\text{-bipy})_3(HPO_4)_4(H_2PO_4)_4$ (**2**), is also reported.

Experimental Section

Synthesis and Initial Characterization. Hydrothermal reaction of $In(NO_3)_3\cdot 5H_2O$ (1.5 mmol), H_3PO_4 (5 mmol), 4,4′-bipyridine (5 mmol), *n*-butanol (7 mL), and water (1 mL) for 3 days at 170 °C followed by slow cooling at 10 °C h^{-1} to room temperature produced **1** as tan tabular crystals in about 30% yield and an unidentified colorless crystalline material. An optimum set of reaction conditions to prepare a single-phase product of the title compound was not found. The distinct color and shape of the crystals of **1** allowed for hand sorting of a pure sample as judged by comparison of the X-ray powder pattern to the pattern simulated from the atomic coordinates derived from single-crystal study. Chemical analysis confirmed the stoichiometry (Found: C, 19.9; H, 2.47; N, 4.71. Calcd: C, 20.3; H, 2.50; N, 4.74). Thermogravimetric analysis in air showed mass loss in five steps over the temperature range 35−1000 °C of 35.77%. The first weight loss (190 °C, 3.73%) corresponds to the loss of guest water molecules and can be compared with the calculated value of 4.06%. The decomposition product at 1000 °C, which had a nominal composition of $In_4P_8O_{26}$, was poorly crystalline and was not characterized. The observed total mass loss agreed with that calculated for the loss of $2C_{10}N_2H_8$, $4H_2O$ of crystallization and $6H_2O$ from the decomposition of framework (36.61%). A detailed thermal decomposition mechanism was not derived.

Single-Crystal X-ray Diffraction. A tabular crystal of dimensions 0.12 × 0.09 × 0.08 mm was mounted on a Siemens Smart-CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source. Intensity data were collected in 2082 frames with increasing ω (width of 0.30°/frame). The orientation matrix and unit cell dimensions were determined by a least-squares fit of 5375 reflections. Octants collected: $\pm h,\pm k,\pm l$. $2\theta_{max} = 57°$. Of the 5678 unique reflections collected, 4045 reflections were considered observed $[F_o > 4\sigma(F_o)]$ after Lorentz polarization and semiempirical absorption corrections. Agreement between equivalent reflections (R_{int}) = 0.052. The empirical absorption correction was based on 6625 symmetry-equivalent reflections using the SADABS program. The structure was solved by direct methods (SHELXTL-PLUS): the indium and phosphorus atoms were first located, and the carbon, nitrogen, and phosphate oxygen atoms were found in difference Fourier maps. The H atoms were not located. Bond-valence calculations indicated that the In atoms were trivalent, O(4), O(8), O(11), O(12), O(13), O(15), and O(16) had valence sums of 1.07, 1.09, 1.09, 1.19, 1.41, 1.27, and 1.20, respectively, and all other oxygen atoms had values close to 2. The valence sum of O(13) can be satisfied by forming hydrogen bonds. All other O atoms with undersaturated valence sums are hydroxo oxygens. Two lattice water oxygens, Ow(1) and Ow(2), were found in the structural channels. Refinement (383 variables) was performed by using SHELXTL version 5,[9] with anisotropic thermal parameters for all atoms. Neutral-atom scattering factors for all atoms were used.[10] Anomalous dispersion and secondary extinction corrections were applied. $(\Delta\rho)_{max} = 1.16$ e/Å^3, $(\Delta\rho)_{min} = -0.99$ e/Å^3. The reliability factors converged to R1 = 0.0517, wR2 = 0.1163, and GOF = 1.048. The value of the secondary extinction parameter was 0.002 29.

The crystal which was used for structural analysis was heated in air at 190 °C for 5 h and cooled to room temperature by removing the crystal from the oven to a desiccator. The dehydrated crystal was coated with epoxy glue and mounted on the same diffractometer. Peak profile analysis results indicated that the crystal was suitable for structure analysis. The unit cell volume is smaller than that of the tetrahydrate (1229 vs 1252 Å^3). Crystal data: octants collected, $\pm h,\pm k,\pm l$; $2\theta_{max}$,

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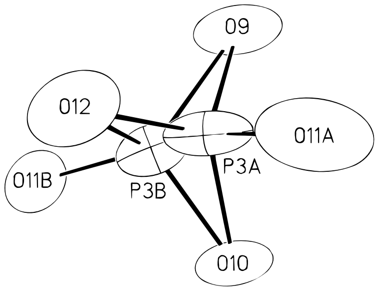

Figure 1. Disorder in the $H_2P(3)O_4$ group in **2**. Thermal ellipsoids are shown at 50% probability.

Table 1. Crystallographic Data for $[In_4(4,4'\text{-bipy})_3(HPO_4)_4(H_2PO_4)_4]\cdot 4H_2O$ (**1**) and $In_4(4,4'\text{-bipy})_3(HPO_4)_4(H_2PO_4)_4$ (**2**)

	1	**2**
empirical formula	$C_{30}H_{44}In_4N_6O_{36}P_8$	$C_{30}H_{36}In_4N_6O_{32}P_8$
fw	1771.75	1699.69
color, habit	tan, tabular	tan, tabular
size, mm	0.12 × 0.09 × 0.08	0.12 × 0.09 × 0.08
cryst syst	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	10.5429(4)	10.4310(2)
b, Å	11.6345(5)	11.4723(2)
c, Å	11.7303(5)	11.7779(2)
α, deg	110.116(1)	112.263(1)
β, deg	100.445(1)	99.093(1)
γ, deg	104.339(1)	102.318(1)
V, Å^3	1251.6(2)	1229.1(2)
Z	1	1
D_{calc}, g cm^{-3}	2.351	2.296
T, °C	23	23
λ(Mo Kα), Å	0.710 73	0.710 73
μ(Mo Kα), cm^{-1}	21.9	22.2
$T_{min,max}$	0.761, 0.915	0.586, 0.928
R1[a]	0.0517	0.0702
wR2[b]	0.1163	0.1864

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. Weight $= 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$, $a = 0.0426$ and b = 3.62 for **1**, and $a = 0.0995$ and $b = 1.24$ for **2**.

55.3°; 5074 unique reflections collected; 3358 observed reflections [$F_o > 4\sigma(F_o)$]; $R_{int} = 0.0589$. An empirical absorption correction was also applied. The atom labels are the same as those of the tetrahydrate. There is no guest water molecule as observed in the tetrahydrate. Atoms P(3) and O(11) are disordered over two positions with equal occupancy as depicted in Figure 1. O(4), O(8), O(11), O(12), O(13), O(15), and O(16) had valence sums of 1.08, 1.02, 1.04 (average), 1.44 (average), 1.29, 1.41, and 1.21, respectively, and all other oxygen atoms had values close to 2. O(4), O(8), O(11), O(13), and O(16) are hydroxo oxygens. To balance charge it needs one more hydroxo group. O(12) is preferable to O(15); otherwise an unlikely H_3PO_4 group forms. The valence of O(15) may be satisfied by forming the H bond (O(15)···O(13) 2.75 Å). The thermal parameters of all atoms and esd's of bond lengths for **2** are significantly larger than those for **1**, indicating that the crystal quality becomes less satisfactory upon dehydration. It is worthy of note that P(4), O(13), O(15), and O(16) in both compounds have large thermal parameters. $(\Delta\rho)_{max} = 1.57$ e/Å^3, $(\Delta\rho)_{min} = -1.63$ e/Å^3. The reliability factors converged to R1 = 0.0702, wR2 = 0.1864, and GOF = 1.007. The value of the secondary extinction parameter was 0.003 04. The crystallographic data and bond lengths are given in Tables 1 and 2, respectively.

Table 2. Bond Lengths (Å) for $[In_4(4,4'\text{-bipy})_3(HPO_4)_4(H_2PO_4)_4].4H_2O$ (**1**) and $In_4(4,4'\text{-bipy})_3(HPO_4)_4(H_2PO_4)_4$ (**2**)

Compound **1**			
In(1)−O(1)	2.112(5)	In(1)−O(2)	2.112(5)
In(1)−O(5)	2.183(5)	In(1)−O(9)	2.103(5)
In(1)−O(14)	2.156(5)	In(1)−N(1)	2.276(6)
In(2)−O(3)	2.112(4) (2×)	In(2)−O(6)	2.113(5) (2×)
In(2)−N(2)	2.282(5) (2×)	In(3)−O(7)	2.123(5) (2×)
In(3)−O(10)	2.129(5) (2×)	In(3)−N(3)	2.260(6) (2×)
P(1)−O(1)	1.518(5)	P(1)−O(2)	1.517(5)
P(1)−O(3)	1.529(5)	P(1)−O(4)	1.593(5)
P(2)−O(5)	1.537(5)	P(2)−O(6)	1.504(5)
P(2)−O(7)	1.505(5)	P(2)−O(8)	1.595(5)
P(3)−O(9)	1.510(5)	P(3)−O(10)	1.501(5)
P(3)−O(11)	1.581(5)	P(3)−O(12)	1.562(5)
P(4)−O(13)	1.489(7)	P(4)−O(14)	1.489(6)
P(4)−O(15)	1.532(8)	P(4)−O(16)	1.558(8)
N(1)−C(1)	1.353(9)	N(1)−C(2)	1.341(9)
C(1)−C(3)	1.395(9)	C(2)−C(4)	1.395(10)
C(3)−C(5)	1.374(10)	C(4)−C(5)	1.426(10)
C(5)−C(6)	1.472(9)	C(6)−C(7)	1.424(9)
C(6)−C(8)	1.383(10)	C(7)−C(9)	1.377(9)
C(8)−C(10)	1.397(10)	N(2)−C(9)	1.353(9)
N(2)−C(10)	1.357(9)	N(3)−C(11)	1.370(9)
N(3)−C(12)	1.364(9)	C(11)−C(13)	1.385(9)
C(12)−C(14)	1.379(9)	C(13)−C(15)	1.400(9)
C(14)−C(15)	1.401(9)	C(15)−C(15)	1.504(13)
Compound **2**			
In(1)−O(1)	2.120(8)	In(1)−O(2)	2.114(6)
In(1)−O(5)	2.119(8)	In(1)−O(9)	2.109(7)
In(1)−O(14)	2.194(9)	In(1)−N(1)	2.29(1)
In(2)−O(3)	2.089(7) (2×)	In(2)−O(6)	2.118(6) (2×)
In(2)−N(2)	2.274(9) (2×)	In(3)−O(7)	2.126(7) (2×)
In(3)−O(10)	2.134(8) (2×)	In(3)−N(3)	2.205(8) (2×)
P(1)−O(1)	1.521(8)	P(1)−O(2)	1.504(7)
P(1)−O(3)	1.503(7)	P(1)−O(4)	1.589(9)
P(2)−O(5)	1.534(8)	P(2)−O(6)	1.510(6)
P(2)−O(7)	1.507(7)	P(2)−O(8)	1.608(9)
P(3a)-O(9)	1.45(1)	P(3a)-O(10)	1.42(1)
P(3a)-O(11a)	1.66(2)	P(3a)-O(12)	1.52(1)
P(3b)-O(9)	1.62(1)	P(3b)-O(10)	1.43(1)
P(3b)-O(11b)	1.55(2)	P(3b)-O(12)	1.45(1)
P(4)−O(13)	1.52(1)	P(4)−O(14)	1.493(9)
P(4)−O(15)	1.49(2)	P(4)−O(16)	1.55(2)
N(1)−C(1)	1.37(1)	N(1)−C(2)	1.33(1)
C(1)−C(3)	1.40(2)	C(2)−C(4)	1.36(2)
C(3)−C(5)	1.42(2)	C(4)−C(5)	1.42(1)
C(5)−C(6)	1.47(1)	C(6)−C(7)	1.39(1)
C(6)−C(8)	1.39(1)	C(7)−C(9)	1.39(1)
C(8)−C(10)	1.40(2)	N(2)−C(9)	1.36(1)
N(2)−C(10)	1.34(1)	N(3)−C(11)	1.35(1)
N(3)−C(12)	1.37(1)	C(11)−C(13)	1.40(1)
C(12)−C(14)	1.39(1)	C(13)−C(15)	1.40(1)
C(14)−C(15)	1.41(1)	C(15)−C(15)	1.47(2)

Results and Discussion

The structure of **1**, viewed along the [001] and [010] directions, is shown in Figures 2 and 3. It consists of neutral sheets of indium phosphate in the *ac*-plane, which are linked through 4,4′-bipyridine pillars to generate channels along the [001] direction, in which the water molecules reside. The tunnel has a rhomboidal window (ca. 10 × 5 Å) formed by four octahedra, two tetrahedra, and two 4,4′-bipyridine molecules. It should be noted that a phosphate group protrudes from the indium phosphate layer. Each indium is octahedrally coordinated. In(1) is bonded to five oxygens [In−O (av) 2.133(5) Å] and one nitrogen [In−N 2.276(6) Å]. In(2) and In(3), which are located at inversion centers, are bonded to four oxygens [In(2)−O (av) 2.112(5) Å, In(3)−O (av) 2.126(5) Å] and two nitrogens [In(2)−N (av) 2.282(5) Å, In(3)−N (av) 2.260(6) Å]. The two nitrogens are in trans positions. Each oxygen on the indiums is linked to a phosphorus, whereas the 4,4′-bipyridine ligands bridge the In^{3+} cations in adjacent layers. There are two unique 4,4′-bipyridine molecules. One is planar and sits on an inversion center. The other one is not planar; rather the rings are twisted at an angle of 22°. The P−OH groups of $HP(1)O_4$,

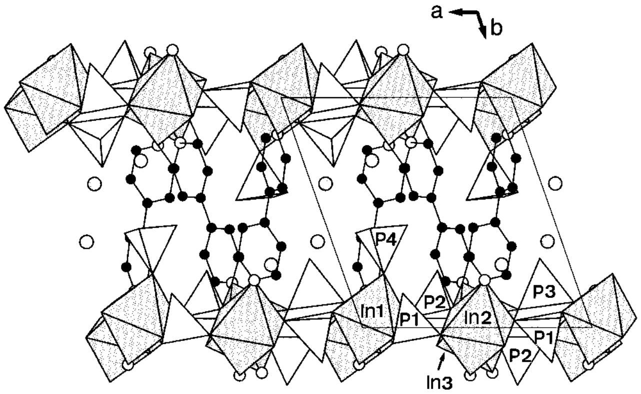

Figure 2. Polyhedral view of the structure of **1** viewed along the [001] direction. Polyhedra with darker and lighter shades are In−(O,N) octahedra and phosphate tetrahedra, respectively. Solid circles: C atoms. Open circles: N atoms. Stippled circles: water oxygen atoms.

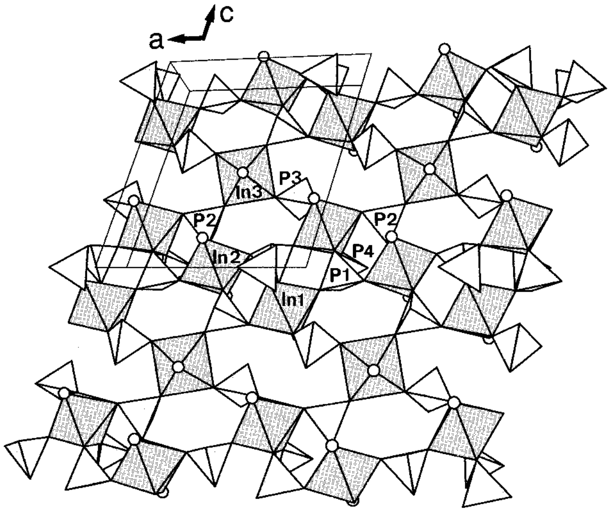

Figure 3. Section of a sheet in **1** viewed along [010]. Open circles are N atoms.

$HP(2)O_4$, and $H_2P(3)O_4$ are directed toward the interlayer region. $H_2P(4)O_4$ has only one oxygen, O(14), bridging to indium and extends away from the layer as a pendant group, which accounts for the large thermal parameters for P(4), O(13), O(15), and O(16). Of the three remaining P(4)−O bonds, one receives hydrogen bonds from a neighboring $H_2P(3)O_4$ group and a water molecule [O(13)···O(12) 2.51 Å, O(13)···Ow(2) 2.71 Å], while the other two with longer bonds [P(4)−O(15) 1.532(8) Å, P(4)−O(16) 1.558(8) Å] constitute P−OH groups. $HP(1)O_4$ and $HP(2)O_4$ groups bridge adjacent In(1) and In(2) atoms to form zigzag ribbons of four-membered rings which in turn link to In(3) through $HP(2)O_4$ and $H_2P(3)O_4$ groups to generate additional six- and eight-membered rings. The title compound has structural features in common with the layer structure of $[C_5H_5NH][In(HPO_4)(H_2PO_4)_2]$.[7] The latter layer is constructed from linear ribbons of four-membered rings which are similar to those identified here. The main difference between the two structures is that, in the title compound, 4,4′-bipyridine ligands bridge adjacent neutral layers to form a three-dimensional framework, whereas in $[C_5H_5NH][In(HPO_4)(H_2PO_4)_2]$, the linkage is terminated by the pendant H_2PO_4 groups and a network of hydrogen bonds holds the discrete layers together to create cavities in which the pyridinium cations reside.

The framework structure of **2** is identical to that of **1** except that $H_2P(3)O_4$ in **2** is disordered, O(13) is a hydroxo oxygen, and O(15) forms a pendant P═O group. In contrast, O(13) in **1** forms a pendant P═O group and O(15) is a hydroxo oxygen. O(13) in **1** is strongly H-bonded to O(12)H and Ow(2), as indicated by the short O(13)···O(12) and O(13)···Ow(2) distances. The O(13)···O(12) distance in **2** is considerably longer than that in **1** (2.775 vs 2.504 Å), indicating that O(12) of $H_2P(3)O_4$ is not strongly H-bonded to the neighboring phosphate group. Therefore, the $H_2P(3)O_4$ group in **2** is loosely bound and disordered over two positions.

In summary, the synthesis and structures of an indium phosphate tetrahydrate and the anhydrous compound are reported. The framework structure of the tetrahydrate is essentially unchanged after removal of the guest water molecules. They have a unique structure in which the neutral two-dimensional framework of indium phosphate is pillared through 4,4′-bipyridine ligands. In contrast macroanionic frameworks were found in other organically templated indium phosphates. To our knowledge, no aluminum or gallium analogue of the title compound is known. In $[In_8(HPO_4)_{14}(H_2O)_6](H_2O)_5(H_3O)(N_2C_3H_5)_3$,[6] the indium phosphate layers are held together only by the InO_6 pillars. The 4,4′-bipyridine ligand not only completes the In^{3+} octahedra but also increases the interlayer separation and produces larger channels. To further increase the size of the channels extended analogues of 4,4′-bipyridine can be employed. Further work on this theme is in progress.

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Supporting Information Available: TGA of $[In_4(4,4'\text{-bipy})_3(HPO_4)_4(H_2PO_4)_4]\cdot 4H_2O$. An X-ray crystallographic file in the CIF format for $[In_4(4,4'\text{-bipy})_3(HPO_4)_4(H_2PO_4)_4]\cdot 4H_2O$ and $In_4(4,4'\text{-bipy})_3(HPO_4)_4(H_2PO_4)_4$ is available. This material is available free of charge via the Internet at http://pubs.acs.org.

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