

Hydrothermal Synthesis and Crystal Structure of $\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3[\text{In}_2(\text{HPO}_4)_4]$. A Novel Octahedral–Tetrahedral Framework Indium Phosphate with Occluded Organic Cations

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The synthesis and structural characterization by single crystal X-ray diffraction of the first organically templated indium phosphate is reported.

In the past decade a new family of microporous aluminophosphates^{1–3} has been synthesized by using a wide range of organic amines and quarternary ammonium cations as structure-directing agents (templates). Replacement of aluminium by gallium in the framework led to new series of gallophosphates,^{4–8} some of which are analogous to aluminophosphates.^{9–11} These materials have great potential as absorbents and as supports for catalytically active metals, which suggest that framework structures with other compositions and metals will complement that of zeolite (aluminosilicates) molecular sieves. Compared to the immense number of aluminophosphates and gallophosphates synthesized and structurally characterized there is very scant information on the indium

phosphates in the literature. Reported here is the synthesis and X-ray crystal structure of the first example of an organically templated indium phosphate, $\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3[\text{In}_2(\text{HPO}_4)_4]$ **1**, which, to the best of our knowledge, does not have an Al or Ga analogue.

Compound **1** was synthesized as a single-phase product by the hydrothermal method. An aqueous mixture of indium trichloride, 85% (w/w) phosphoric acid and ethylenediamine (en) with the gel composition 1.0 InCl_3 :1 H_3PO_4 :1 en:125 H_2O was heated at 200°C for 2 days in a 23 ml polytetrafluoroethylene coated acid digestion bomb. The transparent crystalline product was filtered off, washed thoroughly with water and dried at room temperature. The presence of

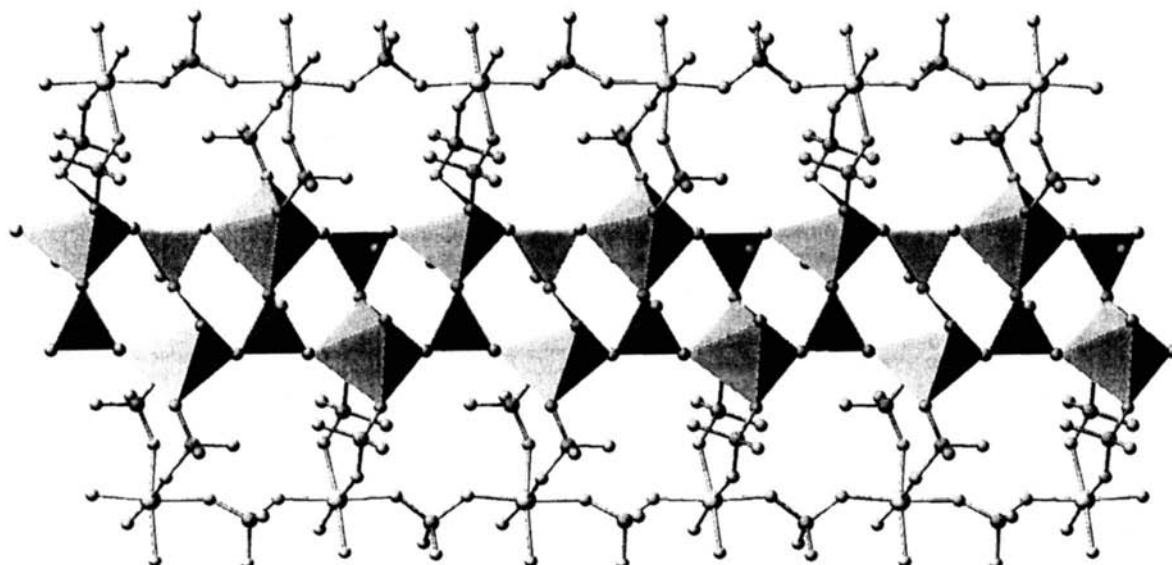


Fig. 1 Polyhedral drawing of a ribbon in the corrugated sheet, showing the interconnection of the indium octahedra and the phosphorus tetrahedra forming the eight- and sixteen-membered rings

the en template in the product was confirmed by IR spectroscopy as six sharp absorptions were observed in the range 1600–1200 cm^{-1} . Thermal gravimetric analysis data show thermal stability up to 450 °C and a sharp weight loss of *ca.* 10%, which corresponds to the calculated weight loss for the organic template (8.9%), in the range 450–575 °C. The sample continued to lose weight slowly up to 800 °C, the highest temperature measured. Suitable single crystals were obtained which allowed the determination of its structure by X-ray diffraction.†

The octahedral–tetrahedral framework of **1** is built up from InO_6 octahedra that contact six HPO_4 tetrahedra, which in turn are coordinated to three different InO_6 octahedra. The In–O bond lengths fall in a narrow range from 2.099 to 2.166 Å. The oxygen atoms of the phosphate groups are linked to three adjacent indium atoms with the fourth coordination site corresponding to a terminal P–OH group which is manifested by the long P–O distance (1.580 and 1.593 Å, respectively). The solid structure can be considered to be array of ribbons, running parallel to (011), that lie in a corrugated sheet as shown in Fig. 1. Two of the axial and one equatorial coordination sites on the indium are shared with three different phosphate groups to constitute the ribbons; two other sites are shared with two structurally distinct phosphate groups to connect the ribbons into the two-dimensional corrugated sheet. The one remaining site on the indium atom is bound to another phosphate group, which along with the

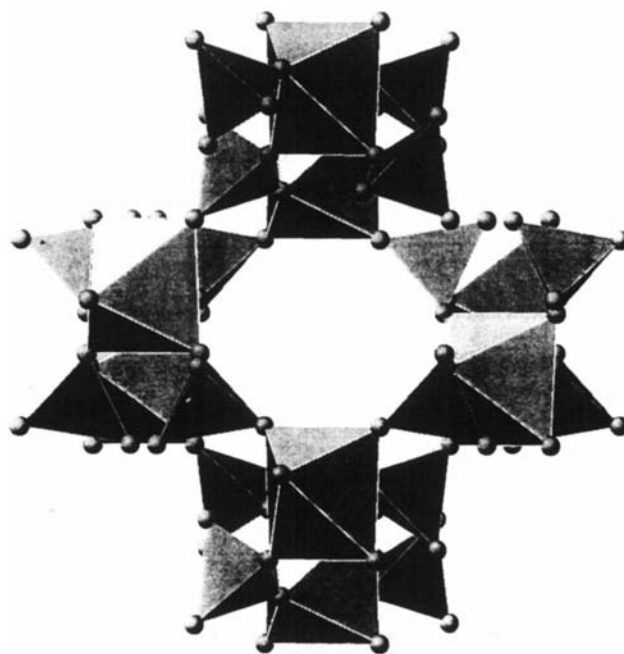


Fig. 2 Polyhedral view of the one-dimensional channels and the pore opening of *ca.* 6 Å with the cavity diameter of *ca.* 10 Å. The view is perpendicular to the (101) plane.

† Crystal data for $\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3[\text{In}_2(\text{HPO}_4)_4]$ **1**, monoclinic, space group $P2_1/n$ (No. 13); $a = 9.444(2)$, $b = 9.156(2)$, $c = 9.756(2)$ Å, $\beta = 117.459(9)^\circ$, $V = 748.6(2)$ Å³, $Z = 2$, $D_c = 2.997$ g cm^{-3} , $\mu(\text{Mo-K}\alpha) = 36$ cm^{-1} , $\lambda = 0.7107$ Å, crystal dimensions 0.10 × 0.10 × 0.10 mm, $R = 0.044$, $R_w = 0.056$. The data were collected on a Rigaku AFC7R four-circle diffractometer at 22 °C in the range of $5^\circ < 2\theta < 50^\circ$ using an ω - 2θ scan technique. A total of 1499 reflections were measured of which 1047 reflections with $I \geq 3\sigma(I)$ were considered. An empirical absorption correction using the program DIFABS was applied. The structure was solved by direct methods (SIR88) and refined using the teXsan crystallographic software package of Molecular Structure Corporation. The In, P, C and N atoms were refined anisotropically and the O atoms isotropically. The hydrogen atoms associated with the en were included in geometrically ideal positions. The two hydrogens on the phosphate groups were found in the final difference Fourier map. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

previous two phosphate groups interact with the layers above and below thus leading to an extended framework. This mode of connectivity generates four different sets of eight-membered rings, each consisting of two indium, two phosphorus and four oxygen atoms. The aforementioned ribbons are generated by the repetition of the four eight-membered rings fused together. The two phosphate groups that connect the ribbons also generate two eight-membered rings which stack alternately one on top of the other in the same (011) direction as the one dimensional ribbons as shown in Fig. 1.

The two different stackings of the eight-membered rings generate a larger sixteen-membered ring, which constitutes the one-dimensional channels in the structure that are normal to the crystallographic (101) plane. The channels are not of a regular diameter but consist of wide cavities which communicate to each other through pore openings *ca.* 6 Å (atom-to-

atom) in size. The tunnels in which the $\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3$ cations reside are shown in Fig. 2 and the cavities are an average of 10 Å wide (O atom-to-O atom). It is reasonable to consider the ethylenediamine molecules are dications, that is, diprotonated, and thus balance the anionic charge of the framework. These cations are hydrogen bonded to the framework with distances ranging from 2.89 to 3.24 Å.

The same framework stoichiometry as found in the title compound has been seen in a number of vanadium(III) phosphates. The structure of **1** has some resemblance to that of $\text{Ba}[\text{V}^{\text{III}}_2(\text{HPO}_4)_4](\text{H}_2\text{O})^{12}$ which also has eight- and sixteen-membered rings, and has the Ba cations in cavities. The same stoichiometry is also displayed in α - and β - $\text{Rb}[\text{V}^{\text{III}}(\text{HPO}_4)_2]^{13}$, $\text{Na}[\text{V}^{\text{III}}(\text{HPO}_4)_2]^{13}$ and $\text{NH}_4[\text{V}^{\text{III}}(\text{HPO}_4)_2]^{13}$ which exhibit unusual open-framework structures.

In summary, this structure is the first member of a new family of organic templated open-framework indium phosphates.

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