

Organically templated inorganic/organic hybrid materials: hydrothermal synthesis and structural characterization of $[C_4H_{12}N_2][In_2(C_2O_4)(HPO_4)_3]\cdot H_2O$

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The synthesis and characterization of a novel inorganic/organic hybrid material is described; the 3-D framework consists of InO_6 octahedra which are linked by inorganic phosphate and organic oxalate anions to generate intersecting tunnels in which piperazinium cations and water molecules reside.

Recently considerable attention has been focused on the organically templated metal phosphates because of their rich structural chemistry and potential applications in heterogeneous catalysis, adsorption, and ion exchange. While phosphate structures constructed from aluminium and gallium represent the most well developed classes of materials, hydrothermal chemistry of phosphates containing transition metals¹⁻⁶ or the heavier Group 13 element, In,⁷⁻⁹ has also yielded a large variety of new structures. Another approach to microporous materials has exploited appropriate metal centers that are linked through suitable multidentate organic ligands.¹⁰⁻¹⁴ The structures of these coordination polymers have the potential for more precise rational design, through control of the shape, size and functionalization of the pores. As part of our general investigations of the synthesis of oxide phases, we have sought to incorporate both inorganic and organic anions into the framework to provide a new route to open-framework materials. This expectation has been realized in the synthesis and characterization of the organically templated three-dimensional solid $[C_4H_{12}N_2][In_2(C_2O_4)(HPO_4)_3]\cdot H_2O$ **1**. The material is original in the sense that it is the first time that inorganic phosphate and organic oxalate anions, associated with Group 13 elements, belong to the skeleton of an open framework structure templated with an amine. A few compounds were recently published which had the characteristics of compound **1** containing two anions with metals, namely, the tin compound $Sn(O_3PCH_3)(C_2O_4)$ ¹⁵ and the rare earth compounds $[Ln(H_2O)_2](C_2O_4)_2(CO_3)\cdot 2.5H_2O$ and $[Ln(H_2O)_2](C_2O_4)(CO_3)$.¹⁶ However, organic templates are not included in these structures.

Hydrothermal treatment of $In(NO_3)_3\cdot 5H_2O$ (1 mmol), H_3PO_4 (5 mmol), oxalic acid (4 mmol), piperazine (6 mmol), and water (10 ml) for 3 days at 165 °C yielded a colorless crystalline product. A colorless bladed crystal was used for single-crystal X-ray diffraction.† The product is pure **1** as judged by comparison of the X-ray powder pattern of the bulk product to that simulated from the coordinates derived from the single-crystal study. The yield of **1** was almost quantitative based on indium. Chemical analysis confirmed the stoichiometry (Found: C, 10.18; H, 2.26; N, 3.90. Calc. C, 10.12; H, 2.41; N, 3.94). Thermal gravimetric analysis in flowing oxygen showed a mass loss in two steps in the region 30–700 °C and a sequential decomposition above 800 °C. The first step (≈ 240 °C) shows a mass loss of 2.75%, which corresponds to the loss of guest water (calc. 2.53%). The second step (≈ 410 °C, mass loss 17.65%) is correlated to the decomposition of oxalate anion, dehydration of HPO_4 groups and deprotonation of piperazinium dication. The decomposition at higher temperatures corre-

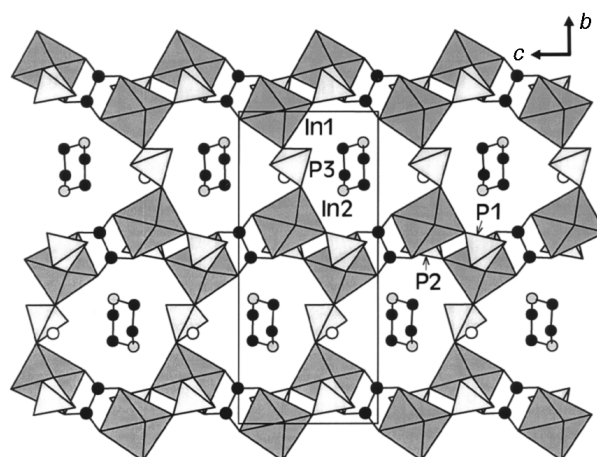


Fig. 1 Structure of **1** viewed along the [100] direction. Polyhedra with darker and lighter shading are InO_6 octahedra and phosphate tetrahedra, respectively. Solid circles, C atoms; stippled circles, N atoms; open circles, water oxygens.

sponds to the release of the organic component. Powder X-ray diffraction of the decomposition product at 600 °C shows it to be amorphous. The final decomposition product at 950 °C is essentially pure $InPO_4$.¹⁷ A detailed thermal decomposition mechanism has not been derived.

The three-dimensional anionic framework of **1** consists of InO_6 octahedra connected *via* coordinating HPO_4^{2-} and $C_2O_4^{2-}$ anions to form intersecting tunnels parallel to the [100] and [001] directions. Diprotonated piperazinium cations are located at the intersections of these tunnels. The tunnel parallel to [100] has a window formed by the edges of six InO_6 octahedra, four phosphate tetrahedra and two oxalate anions (Fig. 1). The other type of tunnel has an eight-membered window formed by four octahedra and four tetrahedra. An alternative way of describing the structure is that it contains puckered layers of indium phosphate parallel to the (001) plane, which are further connected into a three-dimensional framework *via* bridging oxalate ligands. The indium phosphate layer is shown in Fig. 2. Each indium atom is coordinated by a bidentate $C_2O_4^{2-}$ anion and four HPO_4^{2-} anions. The μ coordination of the oxalate leads to highly distorted coordination polyhedra for both In(1) and In(2), as indicated by the wide range of In–O bonds [2.05–2.21 Å for In(1), 2.09–2.24 Å for In(2)] and the small O–In–O bond angles [76.0° for In(1), 75.9° for In(2)] subtended by the oxalate ligand. The oxalate anion acts as a bis-bidentate ligand to In(1) and In(2). Both $HP(1)O_4$ and $HP(2)O_4$ groups coordinate to three In atoms with the hydroxo group being unshared. $HP(3)O_4$ bonds to two In atoms with a pendant P–O unit being strongly H-bonded to the lattice water molecule. The loss of lattice water molecules in TG analysis occurs well above the boiling point of water, which can be attributed to the extensive

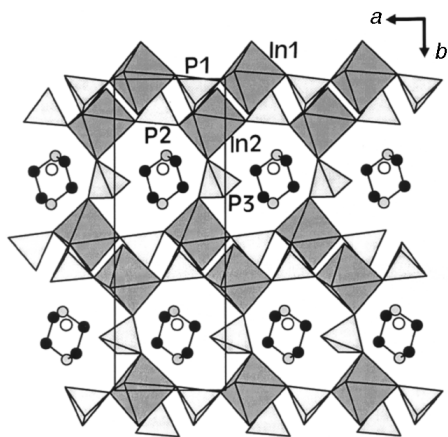


Fig. 2 Section of an indium-phosphate layer in **1** viewed along the [001] direction. Oxalate groups are not shown.

hydrogen bonding holding the water in the crystal lattice [Ow...O(10), 2.45; Ow...O(8), 2.62; Ow...O(9) 2.63 Å]. The piperazinium cation is H-bonded to the phosphate oxygens, as inferred from the N...O distances [N(1)...O(6), 2.83; N(1)...O(10), 3.043; N(2)...O(3), 2.83; N(2)...O(12), 2.91 Å].

The most important feature of the structure of **1** is that it is the first member of a new class of organically templated inorganic/organic hybrid materials. Both phosphate and oxalate anions occur within the same framework. In the structure, large cavities are occupied by C₄H₁₂N₂ counter cations and waters of crystallization. This new compound provides a new route for open-framework materials. A series of related materials involving transition metals have been prepared. Also, it may be possible to replace oxalate with extended analogues such as squarate (3,4-dihydroxy-3-cyclobutene-1,2-dionate) and 1,3,5-benzenetricarboxylate. Further work on this theme is in progress.

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Notes and references

† Crystal data for [C₄H₁₂N₂][In₂(C₂O₄)(HPO₄)₃]·H₂O: monoclinic, space group *P*2₁, *a* = 6.5052(2), *b* = 17.5005(2), *c* = 8.1811(2) Å,

$\beta = 107.656(1)^\circ$, $U = 887.50(5) \text{ \AA}^3$, $Z = 2$, $M_r = 711.76$, $D_c = 2.663 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 29.7 \text{ cm}^{-1}$, $\lambda = 0.71073 \text{ \AA}$, graphite monochromator, crystal dimensions $0.12 \times 0.05 \times 0.01 \text{ mm}$. Of the 3644 unique reflections collected ($2\theta_{\text{max}} = 55.7^\circ$), 3151 reflections were considered observed [$F_o > 4\sigma(F_o)$] after empirical absorption correction. Bond-valence calculations¹⁸ indicated that both In atoms are trivalent, O(4), O(6), O(10) and O(11) had valence sums of 1.20, 1.21, 1.27 and 1.11, respectively, and all other oxygen atoms had values between 1.76 and 1.94. A lattice water site, Ow, was located in the structural tunnel. Atoms O(4), O(6) and O(11) are hydroxo oxygens. The valence sum of O(10) can be satisfied by forming a strong hydrogen bond with Ow [O(10)...Ow 2.45 Å]. Refinement (271 parameters) was performed by full-matrix least-squares analysis, with anisotropic thermal parameters for all atoms. ($\Delta\rho$)_{max,min} = 0.90, -0.83 e Å⁻³. The reliability factor converged to $R1 = 0.0435$, $wR2 = 0.1012$ and $S = 0.999$. CCDC reference number 186/1228. See <http://www.rsc.org/suppdata/dt/1998/4085/> for crystallographic files in .cif format.

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