

Large tunnels in the hydrothermally synthesized open-framework iron phosphate $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_2[\text{Fe}_4(\text{OH})_3(\text{HPO}_4)_2(\text{PO}_4)_3]\cdot x\text{H}_2\text{O}$

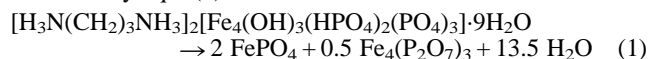
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The synthesis and characterization of a microporous iron phosphate is described; the structure consists of infinite chains of iron–oxygen octahedra linked by phosphate groups to generate large tunnels containing 20-ring windows in which water molecules and the charge-compensating organic cations reside.

A large number of molybdenum and vanadium phosphates with open-framework structures have been synthesized under mild hydrothermal conditions using organic amines as structure-directing agents.^{1,2} These microporous materials are of interest because of their rich structural chemistry and potential applications as molecular sieves, ion-exchange materials and catalysts. Since we had synthesized a large number of ternary iron phosphates and arsenates with a variety of complex crystal structures by a high-temperature, high-pressure hydrothermal method,³ the possibility of preparing three-dimensional frameworks containing large voids filled with cationic organic templates seemed reasonable. Recently, an organically templated iron phosphate $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3]_{0.5}[\text{Fe}(\text{OH})\text{PO}_4]$ was reported.^{4,5} It is isotopic with the layered gallophosphate $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3]_{0.5}[\text{Ga}(\text{OH})\text{PO}_4]$ obtained in ethylene glycol.⁶ We have also synthesized a 1,4-diazabicyclo[2.2.2]octane encapsulating iron phosphate, $[\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH}]_3[\text{Fe}_8(\text{HPO}_4)_{12}(\text{PO}_4)_2(\text{H}_2\text{O})_6]$.⁷ It adopts a pillared layer structure and its framework is closely related to that of an imidazole encapsulating indium phosphate.⁸ To our knowledge, these are the only two examples of organically templated iron phosphates in the literature. Here we describe the synthesis and structural characterization of a 1,3-diaminopropane encapsulating iron phosphate, $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_2[\text{Fe}_4(\text{OH})_3(\text{HPO}_4)_2(\text{PO}_4)_3]\cdot x\text{H}_2\text{O}$ **1**. Its framework structure is unique and contains two-dimensional arrays of large tunnels in which water molecules and the charge-compensating organic cations are located.

Hydrothermal treatment of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (1.5 mmol), H_3PO_4 (7.5 mmol), $\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2$ (7.5 mmol), and water (10 ml) for 3 days at 180 °C yielded a yellow crystalline product. A yellow crystal was used to determine its structure by single-crystal X-ray diffraction.† The material is single phase as judged by comparison of the powder X-ray diffraction of the bulk product to the pattern simulated from the coordinates derived from the single-crystal study. Thermal gravimetric analysis showed mass loss in multiple steps over the temperature range 25–800 °C of 36.73%. Based on powder X-ray diffraction, the final decomposition product at 800 °C is a mixture of FePO_4 and $\text{Fe}_4(\text{P}_2\text{O}_7)_3$.⁹ The observed total mass loss reflects the presence of lattice water molecules and agrees well with that calculated for the loss of 2 $\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2$, 9 H_2O of crystallization and 4.5 H_2O from the decomposition of framework (36.7%), as indicated by eqn. (1).



Samples of **1** appeared to lose water over time if stored in a desiccator. Only four lattice water oxygen sites could be located from the single-crystal X-ray diffraction study. The room-temperature Mössbauer spectrum is a doublet and does not show different Fe components as indicated from the crystal

structure. The spectral parameters are δ (isomer shift) = 0.393 mm s^{-1} (relative to iron foil at 300 K), ΔE_Q (quadrupole splitting) = 0.604 mm s^{-1} , and Γ (full width at half-height) = 0.36, 0.35 mm s^{-1} . The isomer shift is consistent with those for iron(III) phosphates.¹⁰

The structure of **1** consists of a three-dimensional covalently bonded framework built up from FeO_6 octahedra and phosphate tetrahedra. The fundamental building unit is an octahedral tetramer, which is shown in Fig. 1. The unit involves an edge-sharing $\text{Fe}(2)_2\text{O}_{10}$ dimer which further links at the shared corners to two $\text{Fe}(1)\text{O}_6$ octahedra forming a Fe_4O_{20} tetramer. A topologically identical cluster exists in the iron phosphate mineral leucophosphate, $\text{K}_2[\text{Fe}_4(\text{OH})_2(\text{H}_2\text{O})_2(\text{PO}_4)_4]\cdot 2\text{H}_2\text{O}$.¹¹ The tetramer in **1** possesses $\bar{1}$ symmetry located at the midpoint of the shared edge. $\text{Fe}(2)\text{O}_6$ is more distorted than $\text{Fe}(1)\text{O}_6$ because of edge-sharing. The μ_3 - and μ -oxo atoms, O(11) and O(12), which coordinate to Fe atoms only, are the hydroxo oxygens. The H atoms are not involved in hydrogen bonding. Each tetramer is joined by corner-sharing, *via* $-\text{O}(12)-\text{Fe}(1)-\text{O}(12)-$ bonds, to two other tetramers forming orthogonal, but non-intersecting infinite chains parallel to the $\langle 100 \rangle$ directions. One may regard the infinite chain as a column. In a unit cell, there are four layers of columns with z values equal to 0, 1/4, 1/2 and 3/4, respectively. Each column lies in an a -glide plane and columns in adjacent layers are 4_1 -screw axis related. The columns are interlinked by phosphate tetrahedra generating large tunnels running parallel to $\langle 100 \rangle$, in which the diprotonated 1,3-diaminopropane and water molecules reside (Fig. 2). The amine molecules are well ordered, which can be attributed to the formation of extensive hydrogen bonds. Within tunnels are 20-ring windows formed by the edges of ten iron-oxygen octahedra and ten phosphate tetrahedra in an alternating manner. The $\text{P}(1)-\text{O}(4)\text{H}$ groups project into the tunnels at a nearest $\text{O}(4)\cdots\text{O}(4)$ distance of 7.35 Å. The long side of the ring has a free dimension (minimum $\text{O}\cdots\text{O}$ distance less one O diameter of 2.6 Å) of 10.4 Å. The framework also contains open

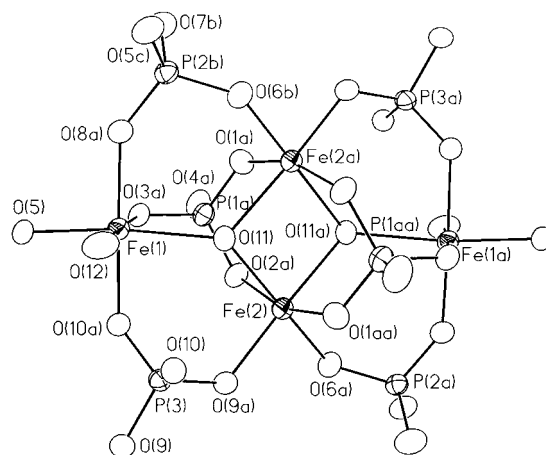


Fig. 1 The tetranuclear iron cluster in compound **1**: thermal ellipsoids are shown at 60% probability

windows delimited by four infinite chains, through which they connect orthogonal, non-intersecting tunnels. The presence of large open windows is also reflected in the very low framework metal atom density. For **1**, there are 10.5 M atoms (M = Fe, P) per 1000 Å³ compared with the value of 12.7 atoms per 1000 Å³ for the very open faujasite (M = Si),¹² 12.1 atoms per 1000 Å³ (M = Fe, P) for the phosphate mineral cacoxenite which contains enormous channels,¹³ and 9.3 atoms per 1000 Å³ for [HN(CH₂CH₂)₃NH]K_{1.35}[V₅O₉(PO₄)₂] \cdot xH₂O (M = V, P) which is among the lowest framework density materials known.²

In summary, the synthesis and structure of an iron phosphate, [H₃N(CH₂)₃NH₃]₂[Fe₄(OH)₃(HPO₄)₂(PO₄)₃] \cdot xH₂O is reported. The incorporation of H₃N(CH₂)₃NH₃ cations extends the iron phosphate framework into a large pore size range. The structures are very sensitive not only to the nature of the templates incorporated but also to reaction conditions. When 1,4-diazabicyclo[2.2.2]octane is used instead of diaminopropane, a different compound with a composition of [HN(CH₂CH₂)₃NH]₃[Fe₈(HPO₄)₁₂(PO₄)₂(H₂O)₆] with a pillared layer structure is formed.⁷ Other hydrothermally prepared iron phosphates with microporous structures have been prepared and will be reported elsewhere.

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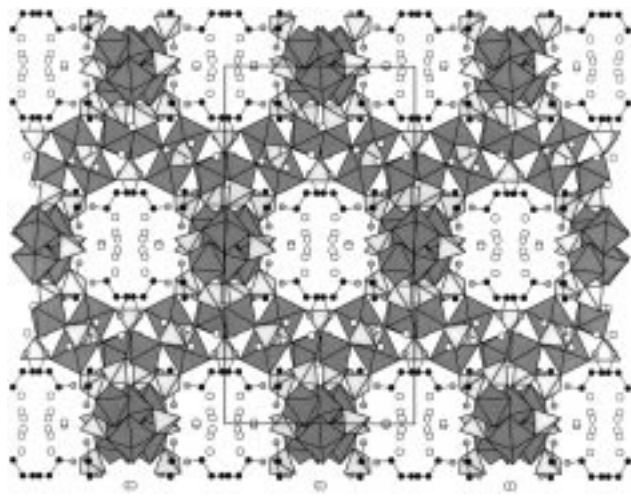


Fig. 2 Polyhedral view of the structure of **1** along the *b* axis. Solid circles, C atoms; stippled circles, N atoms; open circles, water oxygen sites.

Footnotes

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† *Crystal data* for [H₃N(CH₂)₃NH₃]₂[Fe₄(OH)₃(HPO₄)₂(PO₄)₃] \cdot xH₂O: tetragonal, space group *I*4₁/*a*; *a* = 15.4017(3), *c* = 28.9421(4) Å, *U* = 6840.1(8) Å³, *Z* = 8, *M_r* = 903.58, *D_c* = 1.755 g cm⁻³, μ(*Mo-Kα*) = 19.8 cm⁻¹, λ = 0.71073 Å, graphite monochromator, crystal dimensions: 0.18 × 0.12 × 0.12 mm. The crystal 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 1200 frames with increasing ω (width of 0.30° per frame). Of the 4115 unique reflections collected (2θ_{max} = 57.5°), 2939 reflections were considered observed [*I* > 3.0σ(*I*)] after Lorentz polarization and semiempirical absorption corrections using the SHELXTL-PC program package (*T_{min,max}* = 0.725, 0.761).¹⁴ The structure was solved by direct methods: the Fe and P atoms were first located and the C, N, and O atoms were found in the final difference Fourier map. The H atoms were not located. Bond-valence calculations¹⁵ indicated that both Fe atoms were trivalent, O(4), O(7), O(11) and O(12) had valence sums of 1.26, 1.15, 1.02 and 1.11, respectively, and all other oxygen atoms had values between 1.71 and 1.92. O(4), O(11) and O(12) are hydroxo oxygens. The valence sum of O(7) is satisfied by forming hydrogen bonds [O(7)⋯N(1) = 3.06, O(7)⋯O(4) 2.58 Å]. Four lattice water sites were located in the structural tunnels. Each site is partially occupied. Refinement (212 variables) was performed by full-matrix least-squares analysis, with isotropic thermal parameters for water oxygens and anisotropic thermal parameters for all other atoms. (Δρ)_{max,min} = 1.17, -0.80 e Å⁻³. The reliability factors converged to *R*(*F*) = 0.052, *R_w*(*F*) = 0.058 and GOF = 1.78. 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 182/424.

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