

[H₃N(CH₂)₃NH₃]Fe₂O(PO₄)₂: a novel layered iron phosphate containing tetramers of FeO₅ trigonal bipyramids

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The synthesis and characterization of a layered iron phosphate is described; the structure consists of novel Fe₄O₁₆ clusters formed of four FeO₅ trigonal bipyramids, which are linked into two-dimensional sheets through phosphate tetrahedra with propanediammonium cations between the sheets.

A large variety of molybdenum and vanadium phosphates with layered and open frameworks have been synthesized under mild hydrothermal conditions using organic amines as templates.^{1,2} It is reasonable to assume that the formation of these solids will occur with other d-block elements. Iron phosphates exist as minerals and have a rich crystal chemistry. A large number of ternary iron phosphates have been synthesized under high temperature, high pressure hydrothermal conditions.³ Little work, however, has been carried out on the organically templated iron phosphates and, to our knowledge, only three phases, namely [H₃N(CH₂)₂NH₃]_{0.5}[Fe(OH)PO₄],⁴ [HN(CH₂CH₂)₃NH]₃[Fe₈(HPO₄)₁₂(PO₄)₂(H₂O)₆]⁵ and [H₃N(CH₂)₃NH₃]₂[Fe₄(OH)₃(HPO₄)₂(PO₄)₃·xH₂O,⁶ have been synthesized. The latter is particularly interesting because the structure contains large tunnels with 20-ring windows and its framework metal atom density is smaller than the very open faujasite. Here we describe the synthesis and characterization of a novel amine encapsulating FePO, which has a layer structure and contains a hitherto unknown tetramer of FeO₅ trigonal bipyramids.

Hydrothermal treatment of FeCl₃·6H₂O (2.5 mmol), H₃PO₄ (7.5 mmol), H₂N(CH₂)₃NH₂ (14 mmol), *n*-butanol (7 ml) and water (3 ml) for 3 days at 160 °C followed by slow cooling at 5 °C h⁻¹ to room temperature produced [H₃N(CH₂)₃NH₃]Fe₂O(PO₄)₂, **1**, as orange plate crystals and a very small amount of a pale yellow material. The yellow material was [H₃N(CH₂)₃NH₃]₂[Fe₄(OH)₃(HPO₄)₂(PO₄)₃·xH₂O,⁵ as indicated from powder X-ray diffraction measurements. A small orange crystal was used to determine its structure by single-crystal X-ray diffraction.† The orange crystals were manually separated from the yellow material to give pure **1** as judged by visual microscopic examination and by comparison of the X-ray powder pattern to the pattern simulated from the atomic coordinates derived from single-crystal study. The yield of **1** was 94% based on iron. Chemical analysis confirmed the amount of 1,3-diaminopropane (Found: C, 9.22; H, 2.99; N, 7.08. Calc. C, 9.15; H, 3.07; N, 7.11%). The IR spectrum (KBr) showed N–H and C–H stretches at 3090 and 2945 cm⁻¹, respectively. Thermal gravimetry in air showed a mass loss in two steps. In the first step over 280–400 °C a mass loss of 11.0% was observed which corresponded to the release of one mol of C₃H₄ (Calc. 10.2%) due to the decomposition of diprotonated 1,3-diaminopropane. The product contained NH₄⁺ as confirmed by the presence of a band at 3360 cm⁻¹ for the N–H stretch and disappearance of the band at 2945 cm⁻¹ for the C–H stretch in the IR spectrum of the sample heated to 350 °C. A powder X-ray pattern of the sample indicated that it was amorphous. The second step in TG (400–750 °C, mass loss 13.0%) was attributed to the release of one mol of H₂O and two mol of NH₃ (Calc. 13.2%). The final decomposition product at 800 °C was FePO₄. The room-temperature Mössbauer spectrum

of **1** is a doublet with δ (isomer shift) = 0.35 mm s⁻¹ (relative to iron foil at 300 K), ΔE_Q (quadrupole splitting) = 0.92 mm s⁻¹, and Γ (full width at half-height) = 0.32 mm s⁻¹. The isomer shift is consistent for iron(III) phosphates.⁷ Variable-temperature magnetic susceptibility measurements on a powder sample showed that $\chi_M T$ decreased with decreasing temperature and the value at 300 K was only 19% of the spin-only value, indicating large antiferromagnetic interactions so that χ_M is significantly reduced from the expected non-interacting moment even at room temperature.

The structure consists of anionic sheets of formula [Fe₂O(PO₄)₂]²⁻ in the *bc*-plane with charge compensating propanediammonium cations between the sheets (Fig. 1). The sheets are constructed from tetramers of FeO₅ trigonal bipyramids, which are joined to four other tetramers by the bridging phosphate ligands as shown in Fig. 2. Each sheet has a double-layered structure. Within a layer, FeO₅ trigonal bipyramids share corners with PO₄ tetrahedra, in an alternating manner to form eight-sided windows. Infinite tunnels are formed along the [100] direction, in which the organic molecules are located. The molecules are locked in their positions by hydrogen bonds to phosphate oxygens [$d_{N(1)-O(5)} = 2.81$, $d_{N(2)-O(1)} = 2.84$, $d_{N(2)-O(4)} = 2.83$ Å]. The tetramer contains a dimer of edge-sharing trigonal bipyramids which further links at the shared

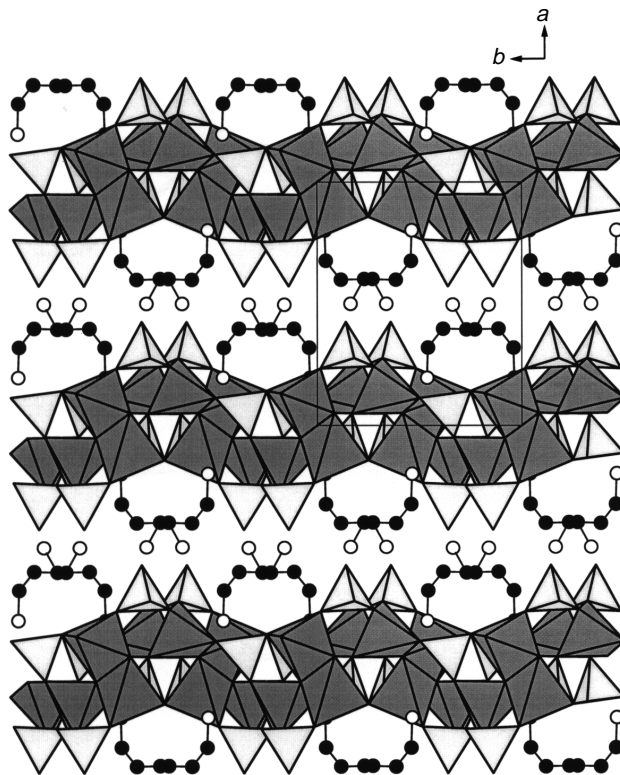


Fig. 1 Polyhedral view of the structure of **1** along the [001] direction. Polyhedra with darker shade, FeO₅ trigonal bipyramids; tetrahedra with lighter shade, PO₄; solid circles, C atoms; open circles, N atoms.

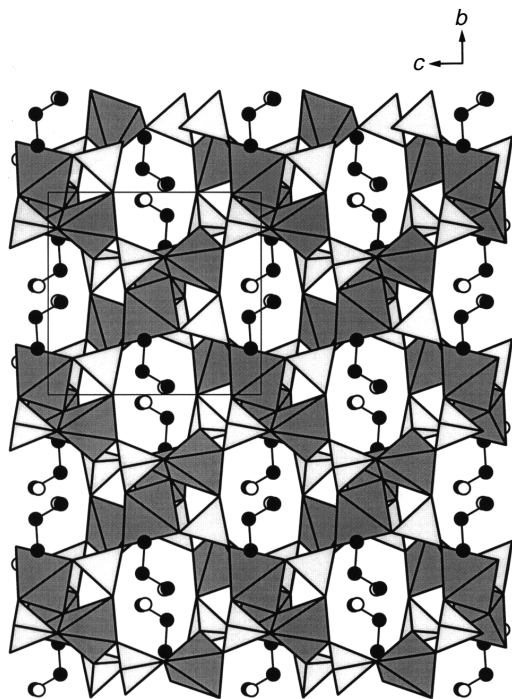


Fig. 2 Section of a sheet in **1** showing the connectivity between the iron-oxygen clusters

corners to two other trigonal bipyramids forming a Fe_4O_{16} cluster (Fig. 3). The tetramer possesses $\bar{1}$ symmetry located at the midpoint of the shared edge. The $\text{P}(1)\text{O}_4$ group is tetradentate. Two of the phosphate oxygens bond to two Fe atoms of a cluster in a bridging mode, while the other two bridge to two Fe atoms of an adjacent cluster. The $\text{P}(2)\text{O}_4$ group coordinates to three Fe atoms of two different clusters through three oxygen donors; the fourth oxygen, O(5), is present as a pendant $\text{P}=\text{O}$ unit and projects into the interlamellar region. Average Fe–O and P–O bond lengths are typical for their polyhedra, with Fe(1)–O 1.934, Fe(2)–O 1.949, P(1)–O 1.538 and P(2)–O 1.542 Å, in accord with the sum of ionic radii, $r(\text{VFe}^{3+}) = 0.58$, $r(\text{IVP}^{5+}) = 0.17$ and $r(\text{III}\text{O}^{2-}) = 1.36$ Å.⁸

The most remarkable structural feature of $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]\text{Fe}_2\text{O}(\text{PO}_4)_2$ is the presence of a novel Fe_4O_{16} cluster formed of four FeO_5 trigonal bipyramids. Although five-coordination with trigonal-bipyramidal geometry is frequently found in iron phosphates, iron-oxygen clusters formed of only FeO_5 trigonal bipyramids are very rare. To our knowledge, Fe_3PO_7 is the only other iron phosphate which contains clusters

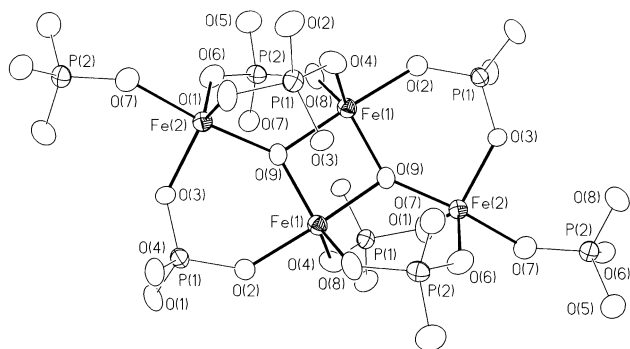


Fig. 3 The tetranuclear iron cluster in **1**; thermal ellipsoids are shown at 60% probability

of FeO_5 trigonal bipyramids.⁹ The Fe_3PO_7 structure consists of Fe_3O_{10} clusters of edge-sharing FeO_5 trigonal bipyramids. The polyhedral linkage in the octahedral tetramers in the mineral leucophosphate, $\text{K}_2[\text{Fe}_4(\text{OH})_2(\text{H}_2\text{O})_2(\text{PO}_4)_4] \cdot 2\text{H}_2\text{O}$ ¹⁰ and the organically templated iron phosphate $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_2[\text{Fe}_4(\text{OH})_3(\text{HPO}_4)_2(\text{PO}_4)_3] \cdot x\text{H}_2\text{O}$ ⁵ is similar to that in **1**. The tetranuclear Fe_4O_{16} core in the iron arsenate $\text{Cs}_3\text{Fe}_5\text{O}(\text{OH})(\text{AsO}_4)_5$ ¹⁰ has the same structure as that of the molecular tetramer $[\{\text{Ti}(\text{OEt})_4\}]$,¹² in which four MO_6 octahedra are joined by shared edges. This new phosphate, $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]\text{Fe}_2\text{O}(\text{PO}_4)_2$, further expands the variety of structures in the iron phosphate phase space which contain clusters of Fe–O polyhedra linked *via* phosphate tetrahedra. The incorporation of bulky organic templates, as compared to cations like the alkali metals, apparently increases the size and complexity of the framework. We are continuing the exploratory synthesis of new FePO frameworks with structure directing organic templates.

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Footnotes

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† *Crystal data* for $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]\text{Fe}_2\text{O}(\text{PO}_4)_2$: monoclinic, space group $P2_1/c$, $a = 11.6591(8)$, $b = 9.5718(7)$, $c = 10.1158(7)$ Å, $\beta = 99.963(2)^\circ$, $U = 1111.9(2)$ Å³, $Z = 4$, $M_r = 393.79$, $D_c = 2.352$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 29.4$ cm⁻¹, $\lambda = 0.71073$ Å, graphite monochromator, crystal dimensions: $0.075 \times 0.075 \times 0.012$ 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 2603 unique reflections collected ($2\theta_{\text{max}} = 57.5^\circ$), 1770 reflections were considered observed [$I > 3.0\sigma(I)$] after Lorentz polarization and semiempirical absorption corrections using the SHELXTL-PC program package ($T_{\text{min, max}} = 0.773, 0.912$).¹³ 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. Refinement (164 variables) was performed by full-matrix least-squares analysis, with anisotropic thermal parameters for all atoms. $(\Delta\rho)_{\text{max, min}} = 0.90, -0.80$ e Å⁻³. The reliability factors converged to $R(F) = 0.055$, $R_w(F) = 0.063$ and GOF = 1.39. CCDC 182/508.

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