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An open-framework iron phosphate with large voids, exhibiting spin-crossover

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A novel iron phosphate, $[(C_4N_3H_{16})(C_4N_3H_{15})]^{5+}$-$[Fe_5F_4(H_2PO_4)(HPO_4)_3(PO_4)_3]^{5-}\cdot H_2O$, consisting of a Fe–O/F–Fe network crosslinked by PO_4 groups is shown to possess unusually large elliptical voids of 24 T atoms (T = Fe, P) and to exhibit a gradual low- to high-spin transformation.

Amongst the variety of open-framework metal phosphates investigated in recent years, those of transition metals are of particular interest not only because of the novelty in their structures, but also because of their properties of potential value. One of the important objectives in synthesizing open-framework transition metal phosphates is the possibility of obtaining new solids with novel magnetic properties. Several open-framework iron phosphates have been synthesized and characterized in recent years,[1–3] but most of them order antiferromagnetically with the exception of one, which shows ferrimagnetic behavior at low temperatures.[4] Open-framework cobalt phosphates also order antiferromagnetically.[5] We have synthesized a new iron phosphate, exhibiting spin-crossover, which is rather unusual in an oxidic material. The material also has several noteworthy structural features which include the presence of infinite Fe–O/F–Fe chains, large voids formed by 24 T atoms (T = Fe, P), crosslinking by PO_4 tetrahedra.

The new iron phosphate $[(C_4N_3H_{16})(C_4N_3H_{15})]^{5+}[Fe_5F_4(H_2PO_4)(HPO_4)_3(PO_4)_3]^{5-}\cdot H_2O$ **I**, was prepared by employing hydrothermal methods in the presence of diethylenetriamine (DETA).† The light green colored crystals of **I** belonged to the monoclinic space group $P2_1/n$ and since the asymmetric unit of **I** contains 59 non-hydrogen atoms and it is convenient to describe the structure in terms of small building blocks. The three-dimensional structure of **I** can be considered as made from layers along the [001] direction, consisting of a network of FeO_6, FeO_5F and FeO_4F_2 octahedra and PO_4 tetrahedra (Fig. 1). The framework has the formula $[Fe_5F_4(H_2PO_4)(HPO_4)_3(PO_4)_3]^{5-}$. Charge neutrality is achieved by the presence of the organic structure-directing amine (DETA) in its protonated form. There are two molecules of DETA in the unit cell, one triply protonated and the other doubly protonated. The layers are connected to each other *via* phosphate groups, completing the three-dimensional architecture (Fig. 2). This connectivity creates large elliptical voids bound by 24 T atoms (T = Fe, P) forming one-dimensional channels along the [010] direction, within which the DETA and water molecules reside. The width of the channels is 15.3 × 4.5 Å (longest and shortest atom—atom contact distances, not including van der Waals radii). To our knowledge, this is the first open-framework iron phosphate material with such large voids. The layers themselves contain pores bound by 8 T atoms (T = Fe, P) and the H_2PO_4 groups protrude into this opening rendering the pores inaccessible. Along the [100] direction, the structure has another narrow channel bound by 16 T atoms and the protruding H_2PO_4 and HPO_4 moieties occupy this channel.

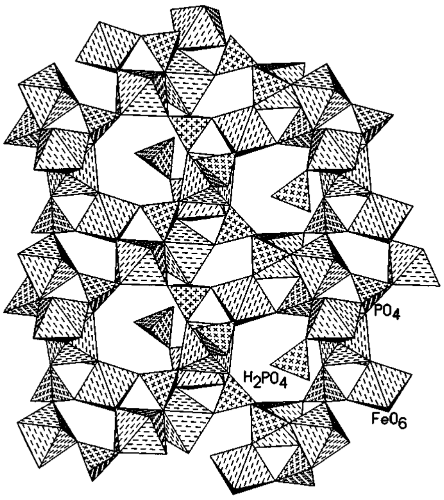

Fig. 1 Layer type arrangement in **I** along the [001] direction. Note that the H_2PO_4 moieties project into the eight-membered pores within the layers.

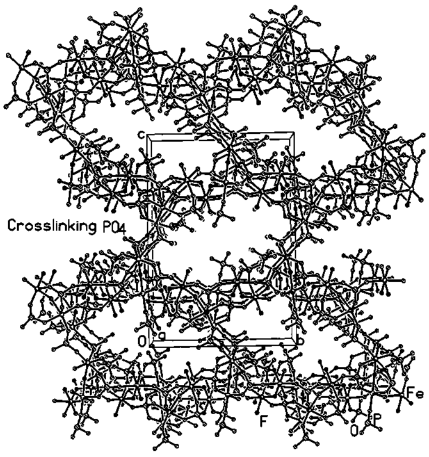

Fig. 2 Structures of **I**, showing large elliptical tunnels along the [010] direction. Note that the walls of the tunnels are composed of PO_4 tetrahedra. Amine and water molecules are not shown for clarity.

The most striking aspect of the structure of **I** is the cationic sub-network of Fe atoms. The connectivity between the various iron–oxygen(fluorine) octahedra is such that infinite Fe–O/F–Fe polymeric chains are formed as shown in Fig. 3(a). This network results from the presence of three-coordinate oxygen atoms and fluorine bridges in the structure. The Fe–O/F–Fe polymeric chains and the phosphate tetrahedra are so connected as to give rise to channels which appear as though they are decorated by PO_4 tetrahedra. This material may, thus, be considered to be an infinite iron–oxy fluoride network, $Fe_2O_{3-x}F_x (x \leqslant 0.4)$, crosslinked by the phosphate groups. Pillaring of layers in framework solids is not common, the only such material being an indium phosphate,[6] where the pillaring is by InO_6 octahedra. The crosslinking by PO_4 tetrahedra found in **I** is analogous to the pillaring in the indium phosphate.[6]

Besides its novel structural features, the iron phosphate **I** also exhibits unusual magnetic properties. Magnetic susceptibility measurements show that the magnetic moment increases gradually from 2.0 μ_B around 20 K to *ca.* 6.0 μ_B around 250 K [Fig. 3(b)]. The low-temperature moment corresponds to that of low-spin Fe^{III} $(^2T_{2g})$ and the high-temperature moment to that of

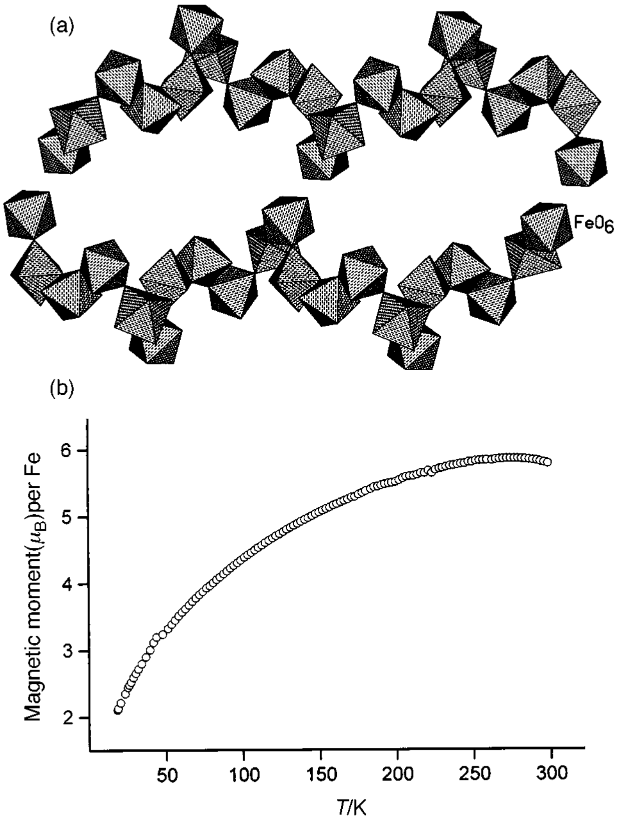

Fig. 3 Network of Fe–O/F octahedra along the [100] direction. The network shows strong anisotropy and is crosslinked by PO_4 tetrahedra (not shown). (b) Temperature variation of the magnetic moment.

high-spin Fe^{III} ($^6A_{1g}$). The variation of the magnetic moment [Fig. 3(b)] is characteristic of a gradual spin-crossover similar to that found in some iron(III) complexes.[7] Mössbauer spectra recorded at 298 and 50 K show the presence of the high- and low-spin Fe^{III} ions, respectively, with characteristic differences in the isomer shift and the quadruple splitting (δ = 0.32, 0.1 and ΔE_Q = 0.34, 1.03 mm s^{-1}). The occurrence of spin-crossover in Fe^{III} ions in an oxide material is rather unusual and suggests that the possibility of internal pressure being exerted on the Fe–O polyhedra.

In summary, the synthesis of a novel open-framework iron phosphate with interesting structure and magnetic properties has been accomplished. The presence of Fe–O/F–Fe chains and large one-dimensional channels decorated by phosphate groups are two of the novel features of the material. The occurrence of a smooth magnetic spin-crossover as a function of temperature is noteworthy in that iron(III) oxides generally have Fe^{III} in the high-spin state.

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Notes and references

† The title compound was synthesized from an iron phosphate gel containing DETA as a structure-directing agent. iron(III) chloride, phosphoric acid (85 wt%), DETA, HF and water in a ratio 1:6:3:1:200 were mixed and stirred until homogeneous. The mixture was sealed in a 23 ml Teflon-lined, stainless steel autoclave (Parr, USA) and heated at 180 °C for 72 h. The resulting product, containing predominantly light green crystals, was filtered off and washed thoroughly with deionized water. A suitable single crystal (0.06 × 0.06 × 0.08) was carefully selected under a polarizing microscope. The crystal structure determination was performed on a Siemens SMART CCD diffractometer equipped with a normal focus, 2.4 kW sealed-tube X-ray source (Mo-Kα radiation, λ = 0.71073 Å) operating at 50 kV and 40 mA. A hemisphere of intensity data were collected in 1321 frames with ω scans (width of 0.30° and exposure time of 30 s per frame).

Crystal data for $[(C_4N_3H_{16})(C_4N_3H_{15})]^{5+}[Fe_5F_4(H_2PO_4)(HPO_4)_3(PO_4)_3]^{5-}\cdot H_2O$, **I**: monoclinic, space group $P2_1/n$ (no. 14), a = 9.670(1), b = 15.618(1), c = 22.563(1), β = 90.82(1)°, V = 3407.1(1) Å^3, Z = 4, M = 1254.1, μ = 1.915 mm^{-1} and D_c = 1.836(1) g cm^{-3}. A total of 13848 reflections were collected at 298 K in the θ range 1.59–23.19° and merged to give 4844 unique data (R_{int} = 0.065) of which 3635 with $I > 2\sigma(I)$ were considered to be observed. The structure was solved by direct methods with SHELXS-86[8] and difference Fourier synthesis. Final R = 0.06, R_w = 0.13 and S = 1.13 were obtained for 541 parameters. Part of the hydrogen atoms were located initially in the difference Fourier maps and for the final refinements, hydrogen atoms for both the framework as well as the amine molecules were placed geometrically and held in the riding mode. Final Fourier map minimum and maximum: −1.009 and 0.908. Full-matrix least-squares structure refinement against $|F^2|$ were carried out with SHELXTL-PLUS program package.[9]

CCDC 182/1280. See: http://www.rsc.org/suppdata/cc/1999/1305/ for crystallographic files in .cif format.

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