Chem. Mater. **1999,** *11,* 2316−2318

A Hybrid Open-Framework Iron Phosphate−Oxalate with a Large Unidimensional Channel, Showing Reversible Hydration

Amitava Choudhury,[†,‡] Srinivasan Natarajan,[†] and C. N. R. Rao*[,†,‡]

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India and Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

Received June 1, 1999
Revised Manuscript Received July 19, 1999

Among the open-framework metal phosphates, those of transition metals constitute an important family. Thus, there have been several reports in the literature on open-framework iron phosphates exhibiting interesting structural and magnetic properties.[1−4] During the course of our investigations on transition metal phosphates, we have encountered several interesting organic−inorganic hybrid open-framework materials. In particular, we have discovered iron phosphate−oxalates with novel structures and properties, one of them being similar to that reported recently by Lin et al.[5] in this journal. One of the iron phosphate−oxalates synthesized by us consists of continuous sheets of neutral iron phosphate stacked one on top of the other and connected via oxalate units to create large one-dimensional channel bound by 12 T atoms (T = Fe or P) which go through the entire structure in a direction perpendicular to that of the sheets. More significantly, this material also exhibits reversible hydration. In this communication, we describe the structure and properties of this novel hybrid material, **I**, of the composition $[NH_3(CH_2)_2NH_3]_{1.5}[(Fe_3PO_4(HPO_4)_3(C_2O_4)_{1.5}]\cdot xH_2O$ (x = 1.5−2.0), exhibiting antiferromagnetism.

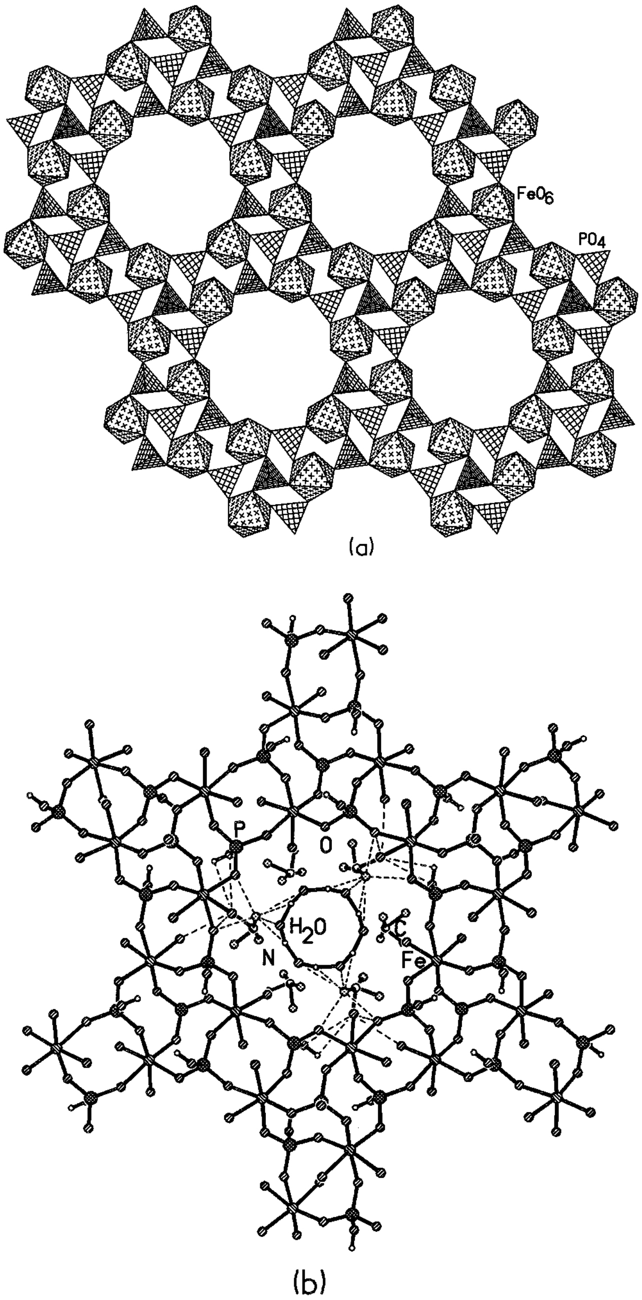

Figure 1. (a) Structure of **I**, $[NH_3(CH_2)_2NH_3]_{1.5}[(Fe_3PO_4(HPO_4)_3(C_2O_4)_{1.5}]$, along the [001] direction showing the 12-membered pore openings For the purpose of clarity, the amine, oxalate, and water molecules are not shown. (b) Structure showing one 12-membered pore with the amine and water molecules. Note that the amine molecules sit at the edge of the ring and the water molecules at the center. (Removal of the capping phosphate units leads to the 4, 6, and 12 net). Dotted lines represent the various possible H-bond interactions.

Compound, **I**, was synthesized under hydrothermal conditions.[18] A X-ray diffraction study of a single crystal[19] of the material shows that the structure consists of a network of FeO_6, PO_4, and HPO_4 polyhedra. While the FeO_6 vertexes are shared (av Fe − O = 2.018 Å), only three of the vertexes of the PO_4 units are shared, (av P − O = 1.535 Å), the remaining having a P═O or a P—OH bond. Connectivity between the polyhedra leads to a neutral inorganic layer of formula $Fe_3P_4O_{13}(OH)_3$ with the FeO_6 octahedra and PO_4 tetrahedra strictly alternating within the layer. The layers are porous, encompassing a circular 12-membered ring shown in Figure 1a. The 12-membered rings are surrounded by a series of four-membered ones, of which there are two distinct types. In one set of these rings, the phosphorus atoms are part of the wall of the 12-membered ring, while in the other, a phosphoryl group caps a six-membered ring and alternates above and

---

* Corresponding author, e-mail: cnrrao@jncasr.ac.in.
† Jawaharlal Nehru Centre for Advanced Scientific Research.
‡ Indian Institute of Science.

(1) Cavellec, M.; Riou, D.; Greneche, J. M.; Fèrey, G. *Inorg. Chem.* **1997**, *36*, 2187.

(2) DeBord, J. R. D.; Reiff, W. M.; Warren, C. J.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1997**, *9*, 1994.

(3) Lii, K.-H.; Huang, Y.-F.; Zima, V.; Huang, C.-Y.; Lin, H.-M.; Jiang, Y.-C.; Liao, F.-L.; Wang, S.-L.; *Chem. Mater.* **1998**, *10*, 2599 and references therein.

(4) Mgaidi, A.; Boughzala, H.; Driss, A.; Clerac, R.; Coulon, C. *J. Solid State Chem.* **1999**, *144*, 163.

(5) Lin, H.-M.; Lii, K.-H.; Jiang, Y.-C.; Wang, S.-L. *Chem. Mater.* **1999**, *11*, 519. Lethbridge, Z. A. D.; Lightfoot, P. *J. Solid State Chem.* **1999**, *143*, 58.

10.1021/cm9903430 CCC: $18.00

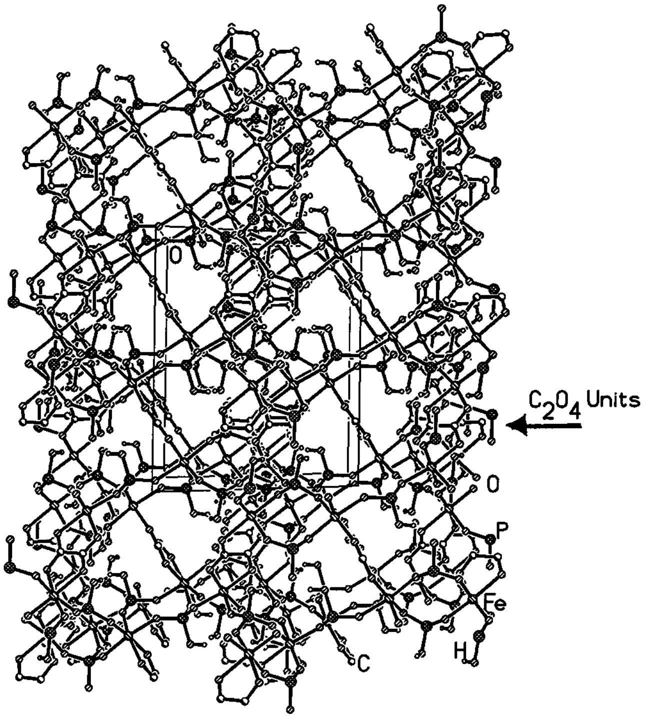

Figure 2. Structure of **I** along the [010] direction. Oxalate units acting as pillars holding the layers apart and together, can be seen.

below the plane of the 12-membered ring (P(1)) as shown in Figure 1b. The layers are held in position by the oxalate units bonded to the iron centers (Figure 2). Thus, the oxalate moieties act as pillars holding the layers apart, and together.

It is noteworthy that the inorganic layer in the iron phosphate–oxalate, **I**, is neutral and the negative charge required to neutralize the positive charge of the diprotonated amine is provided by the oxalate pillars. This is in contrast to the situation that is generally obtained in open-framework layered phosphates where the layers are usually anionic.[7–13] Another remarkable feature of the structure of **I** is that within each iron phosphate sheet there is a supermesh of apertures of ~5 Å free diameter (Figure 1). The oxalate and the organic amine units are so positioned that a unidimensional channel is created through the structure, in a direction perpendicular to the sheets. This results in a solid with unidimensional pores similar to those in aluminosilicate zeolites,[14] in certain detemplated aluminophosphates,[15] and in the supramolecularly assembled channel structures formed between trithiocyanuric acid and 4,4′-bipyridyl.[16] The inorganic part of the framework in **I**, $Fe_3P_4O_{13}(OH)_3$, is essentially identical to the macroanion $[Al_3P_4O_{16}]^{3-}$ present in many layered aluminophosphates[7–13] where the AlO_4 and PO_4 units form a four-membered rings surrounding eight-membered ones or structures similar to **I**. An alternative way to describe the topology of the 2D net in **I**, is by removing the capping PO_4 group (Figure 1b). We then see a 4.6.12 net (viz., 82a in the nomenclature of Smith et al.[17]) commonly observed in aluminosilicate zeolites. The water molecules occupy the empty channels formed by the network and the amine molecules are positioned toward the edge of the 12-membered pore (Figure 1b).

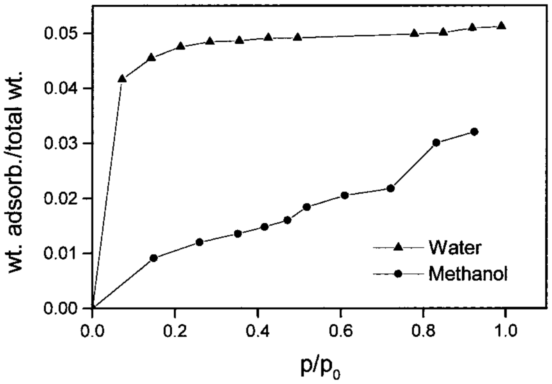

Figure 3. Room-temperature adsorption isotherms for H_2O and CH_3OH in a dehydrated sample of **I**.

---

[6] Sheldrick, G. M. *SHELXTL-PLUS Program for Crystal Structure solution and refinement*; University of Gottingen: Gottingen, 1993.

[7] Jones, R. H.; Thomas, J. M.; Xu, R.; Huo, Q.; Cheetham, A. K.; Powell, A. V. *J. Chem. Soc., Chem. Commun.* **1991**, 1266. Chippindale, A. M.; Natarajan, S.; Thomas, J. M.; Jones, R. H. *J. Solid State Chem.* **1994**, *111*, 18.

[8] Bruce, D. A.; Wilkinson, A. P.; White, M. G.; Bertrand, J. A. *J. Chem. Soc., Chem. Commun.* **1995**, 2059. Williams, I. D.; Gao, Q.; Chen, J.; Ngai, L.-Y.; Lin, Z.; Xu, R. *Chem. Commun.* **1996**, 1781.

[9] Oliver, S.; Kuperman, A.; Lough, A.; Ozin, G. A. *Inorg. Chem.* **1996**, *35*, 6373; *Chem. Commun.* **1996**, 1761; *Chem. Mater.* **1996**, *8*, 2391.

[10] Morgan, K.; Gainsford, G.; Milestone, N. *J. Chem. Soc., Chem. Commun.* **1995**, 425. Gray, M. J.; Jasper, J. D.; Wilkinson, A. P.; Hanson, J. C. *Chem. Mater.* **1997**, *9*, 976.

[11] Thomas, J. M.; Jones, R. H.; Xu, R.; Chen, J.; Chippindale, A. M.; Natarajan, S.; Cheetham, A. K. *J. Chem. Soc., Chem. Commun.* **1992**, 929. Barrett, P. A.; Jones, R. H.; *J. Chem. Soc., Chem. Commun.* **1995**, 1979.

[12] Kuperman, A.; Nadimi, S.; Oliver, S.; Ozin, G. A.; Garces. J. M.; Olken, M. *Nature* **1993**, *365*, 239.

[13] Chippindale, A. M.; Cowley, A. R.; Huo, Q.; Jones, R. H.; Law, A. D.; Thomas, J. M.; Xu, R. *J. Chem. Soc., Dalton Trans.* **1997**, 2639.

[14] *Atlas of Zeolite Structure Types*, Meier, W. H., Olson, D. H., Baerlocher, Ch., Eds.; Elsevier: Boston, MA, 1996.

[15] Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146.

[16] Pedireddi, V. R.; Anupama, T. R.; Chatterjee, S.; Rao, C. N. R. *J. Am. Chem. Soc.* **1997**.

[17] Smith, J. V. *Am. Mineral.* **1978**, *63*, 960. Bennett, J. V.; Smith, J. V. *Z. Kristallogr.* **1986**, *171*, 65.

[18] In a typical synthesis 0.458 g of ferric chloride was added to a solution containing 0.23 mL of phosphoric acid (85 wt %) and 0.418 g of boric acid in 6.1 mL of H_2O. To the above were added 0.427 g of oxalic acid and 0.23 mL of ethylenediamine (*en*), and the mixture was homogenized for 30 min. The final reaction mixture (pH = 2.0), with a composition 1.0 $FeCl_3 \cdot 6H_2O:2H_3PO_4:2H_2C_2O_4:4H_3BO_3:2en:200H_2O$, was sealed in a Teflon-lined stainless steel autoclave and heated at 150 °C for 70 h under autogenous pressure. We have found that addition of boric acid facilitates the formation of the phosphate–oxalate. The material is not readily formed otherwise. The resulting product consisting of large quantities of single crystals was filtered, washed thoroughly with deionized water, and dried in air at ambient temperature. The crystals were easily separated under an optical microscope and used for further characterization. EDAX analysis gave an Fe:P ratio of 1:1.33 which matches with the composition obtained from the single-crystal X-ray study and the XPS studies indicated the absence of boron.

[19] A suitable colorless rodlike single crystal was carefully selected under a polarizing microscope (0.04 × 0.04 × 0.12 mm). Crystal data: $[NH_3(CH_2)_2NH_3]_{1.5}[(Fe_3PO_4(HPO_4)_3(C_2O_4)_{1.5}]$; trigonal; space group = $P3c1$; $a = 13.630(3)$, $c = 14.739(4)$ Å; $V = 2371.3(1)$ Å^3; $Z = 4$; $D_c = 2.00$ g cm^{-3}; μ(Mo Kα) = 3.68 mm^{-1}; $R = 0.058$; wR2 = 0.17. Data were collected on a Siemen's SMART-CCD diffractometer equipped with a normal focus. A total of 9245 reflections were collected in the range $1.73 \leq \theta \leq 23.3°$ and were merged to give 1150 unique reflections ($R_{merg} = 5.6\%$) of which 975 were considered to be observed ($I \geq 2\sigma(I)$). The structure was solved by direct methods. Hydrogen atoms were geometrically placed. The nitrogen atoms of the amine molecule are disordered (SOF = 0.85). The water molecules located in the channels also included in the refinement. Final refinement (125 parameters) was performed by full-matrix least-squares analysis, with anisotropic thermal parameters for all the non-hydrogen atoms using SHELXTL-PLUS suite of program.[6] The final Fourier maximum and minimum: 1.674 and −0.749 eÅ^{-3}.

Magnetic susceptibility measurements reveal that **I** undergoes an antiferromagnetic transition with a Neel temperature of 31 K. The asymptotic Curie−Weiss temperature is −60 K, revealing the predominant presence of antiferromagnetic interactions. The experimental effective magnetic moment of iron is 5.9 μB which corresponds to the theoretical high-spin Fe^{III} value (5.89 μB).

Thermogravimetric analysis of **I** shows the loss of water at 110 °C (∼4%) with the sample decomposing in the region 350−450 °C (loss of oxalate and amine from the structure, ∼31%). The final product is a condensed iron phosphate, $FePO_4$ (JCPDS: 29-0715). The loss of water is completely reversible. We have carried out gravimetric adsorption studies on the dehydrated material, by using a Cahn electric balance. The dehydrated sample of **I** adsorbs water and methanol and exhibits Langmuir type I adsorption isotherms (Figure 3). The observed weight changes at 25 °C in the case of water and methanol correspond respectively to 2.2 and 1.0 molecules per unit cell.

Acknowledgment. A.C. thanks the Council of Scientific and Industrial Research (CSIR), Government of India for the award of a research fellowship.

CM9903430