Mixed Inorganic–Organic Anion Frameworks: Synthesis and Crystal Structure of $Fe_4(PO_4)_2(C_2O_4)(H_2O)_2$

Zoe A. D. Lethbridge and Philip Lightfoot[1]

School of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, United Kingdom

A novel inorganic–organic framework material has been prepared hydrothermally in the iron(II)–phosphate–oxalate system. $Fe_4(PO_4)_2(C_2O_4)(H_2O)_2$ crystallizes in space group $P2_1/n$, $a = 7.974(3)$ Å, $b = 4.817(3)$ Å, $c = 14.169(3)$ Å, $\beta = 94.70(3)°$, $V = 542.4(4)$ Å^3, $Z = 2$, final R, $R_w = 0.023$, 0.025 for 817 observed data ($I > 3\sigma(I)$). The structure consists of sheets of interconnected FeO_6, FeO_5, and PO_4 polyhedra in the ab plane, which are bridged via $C_2O_4^{2-}$ groups along the c-axis to form an infinite three-dimensional network enclosing small cavities into which terminal $FeOH_2$ groups protrude. © **1999 Academic Press**

INTRODUCTION

The hydrothermal chemistry of transition metal phosphates has received much attention in the past few years, mainly driven by the potential for preparing new open-framework and microporous materials related to zeolites and aluminophosphates (1, 2). From the structural chemistry point-of-view, one of the main motivations for this work is the vastly increased diversity of framework topologies possible in transition metal systems, where coordination geometries other than tetrahedral are common. The hydrothermal chemistry of vanadium phosphates, in particular, has yielded a rich variety of new structural types (3). Until very recently, little synthetic work had been carried out hydrothermally in the iron phosphate system. This is surprising given the vast array of known naturally-occurring iron phosphate minerals, including such remarkable open-framework structures as cacoxenite (4). Recent work from several synthetic groups has now begun to redress this imbalance, with reports of several hydrothermally prepared iron phosphates, both with and without organic "structure-directing" agents (5–10). One of our current goals is to widen the scope of hydrothermal chemistry of open-framework materials yet further by incorporating anions of different topology and connectivity into the framework. Recent reports of quite thermally robust metal–organic framework

materials (11–13) prompted us to explore the feasibility of preparing mixed organic–inorganic frameworks by hydrothermal methods. In this way we may hope to retain some of the robustness of the inorganic framework while including the much greater chemical and topological flexibility of the organic framework. One example of this type of structural chemistry is presented here, where we have chosen to use two of the simplest inorganic (phosphate) and organic (oxalate) ions, together with a coordinatively and chemically flexible cation (iron). Transition metal oxalate framework materials themselves have also been found to display interesting magnetic properties (14–16) as well as the ability to include structure-directing agents within open pores and interlayer spaces (17, 18).

EXPERIMENTAL

$Fe_4(PO_4)_2(C_2O_4)(H_2O)_2$ was prepared by hydrothermal reaction of $Fe(C_2O_4) \cdot 2H_2O$, $(NH_4)_2HPO_4$ and $(CH_3)_4NBr$ in water, in a molar ratio 1 : 1 : 1 : 200. The reactants were heated in a Teflon-lined steel autoclave for 22 hours at 160°C. The product was filtered, washed with distilled water, and dried in air. The product consisted of a predominant phase of green powder, identified by X-ray powder diffraction as $NH_4FePO_4 \cdot H_2O$ (19), together with a small amount of orange crystalline material, in the form of thin plates; one of these plates was chosen for the crystal structure analysis presented here. Crystal structure analysis was carried out on a Rigaku AFC7S automated four-circle diffractometer, equipped with $MoK\alpha$ radiation. Details of the data collection and analysis are given in Table 1. The structure was solved using heavy atom methods (20) and expanded using Fourier techniques. All subsequent refinement was carried out using the teXsan package (21), All non-hydrogen atoms were refined anisotropically. Bond valence sum analysis (22) was used to deduce the oxidation states of the two crystallographically independent iron atoms, as well as probable locations of any additional hydrogen atoms. Bond valence sums of 1.83 and 1.98 respectively for Fe(1) and Fe(2) clearly suggest both sites to be divalent.

[1]Corresponding author.

TABLE 1
Crystal Data and Details of Structure Solution and Refinement

Formula	$Fe_4(PO_4)_2(C_2O_4)(H_2O)_2$
Crystal system	monoclinic
Space group	$P2_1/n$
Cell parameters	$a = 7.974(3)$ Å
	$b = 4.817(3)$ Å
	$c = 14.168(3)$ Å
	$\beta = 94.70(3)°$
Crystal color	orange
Crystal dimensions (mm)	0.20, 0.15, 0.05
Z	2
ρ_{calc} (gcm^{-3})	3.28
μ (Mo$K\alpha$)	56.2 cm^{-1}
2θ (max)'	50.0
Total reflections	1146
Observed reflections ($I > 3\sigma(I)$)	817
No. of variables	109
R, R_w	0.023, 0.025
Max/min difference peak (eÅ^{-3})	0.43, -0.51

A markedly low bond valence sum of 0.41 for O(3) suggested this to be a water molecule. It was then found possible to locate and refine isotropically the two required hydrogen atoms. No further hydrogen atoms were located, either crystallographically or by inference, and the final stoichiometry is compatible with the proposed model.

RESULTS AND DISCUSSION

Final refined atomic parameters are given in Table 2 and selected bond lengths and angles in Table 3. $Fe_4(PO_4)_2(C_2O_4)(H_2O)_2$ is a three-dimensional framework material composed of a linked network of Fe-centered polyhedra, constructed via coordinating PO_4^{3-} and $C_2O_4^{2-}$

TABLE 2
Final Atomic Coordinates and Equivalent Isotropic Temperature Factors for $Fe_4(PO_4)_2(C_2O_4)(H_2O)_2$, Space Group $P2_1/n$, $a = 7.974(3)$ Å, $b = 4.817(3)$ Å, $c = 14.168(3)$ Å, $\beta = 94.70(3)°$

Atom	x	y	z	B(eq)
Fe(1)	0.21197(8)	−0.0365(1)	0.13855(4)	0.71(1)
Fe(2)	0.58907(8)	0.4706(1)	0.19462(4)	0.59(1)
P(1)	0.4992(1)	0.0216(3)	0.30748(8)	0.55(2)
O(1)	0.0559(4)	−0.3609(7)	0.0995(2)	0.71(7)
O(2)	0.0111(4)	0.2056(6)	0.1961(2)	0.69(7)
O(3)	0.2111(5)	0.1623(8)	0.0103(2)	1.00(8)
O(4)	0.3816(4)	0.1604(7)	0.2269(2)	0.73(7)
O(5)	0.4279(4)	0.6936(7)	0.0932(2)	0.77(7)
O(6)	0.6761(4)	0.1277(7)	0.2882(2)	0.70(6)
O(7)	0.6305(4)	0.2653(7)	0.0644(2)	0.94(7)
C(1)	0.5591(5)	0.3771(10)	−0.0076(3)	0.75(10)
H(1)	0.107(7)	0.25(1)	−0.024(4)	4 (1)
H(2)	0.224(6)	0.08(1)	−0.026(3)	0 (1)

TABLE 3
Selected Bond Distances and Angles for $Fe_4(PO_4)_2(C_2O_4)(H_2O)_2$

Fe(1)	O(1)	2.046(3)		Fe(2)	O(7)	2.143(3)
Fe(1)	O(2)	2.192(3)		P(1)	O(1)	1.531(3)
Fe(1)	O(3)	2.053(4)		P(1)	O(2)	1.525(3)
Fe(1)	O(4)	2.005(3)		P(1)	O(4)	1.567(3)
Fe(1)	O(5)	2.291(3)		P(1)	O(6)	1.545(3)
Fe(2)	O(2)	2.126(3)		O(3)	H(1)	1.03(6)
Fe(2)	O(4)	2.303(3)		O(3)	H(2)	0.67(5)
Fe(2)	O(5)	2.137(3)		O(5)	C(1)	1.273(5)
Fe(2)	O(6)	2.195(3)		O(7)	C(1)	1.249(5)
Fe(2)	O(6)	2.016(3)		C(1)	C(1)	1.539(9)

O(1)	Fe(1)	O(2)	93.4(1)		O(6)	Fe(2)	O(7)	94.0(1)
O(1)	Fe(1)	O(3)	99.2(1)		O(1)	P(1)	O(2)	112.3(2)
O(1)	Fe(1)	O(4)	153.5(1)		O(1)	P(1)	O(4)	105.8(2)
O(1)	Fe(1)	O(5)	86.9(1)		O(1)	P(1)	O(6)	111.1(2)
O(2)	Fe(1)	O(3)	97.6(1)		O(2)	P(1)	O(4)	112.0(2)
O(2)	Fe(1)	O(4)	89.5(1)		O(2)	P(1)	O(6)	111.8(2)
O(2)	Fe(1)	O(5)	174.3(1)		O(4)	P(1)	O(6)	103.3(2)
O(3)	Fe(1)	O(4)	106.6(1)		Fe(1)	O(1)	P(1)	105.1(2)
O(3)	Fe(1)	O(5)	88.0(1)		Fe(1)	O(2)	Fe(2)	108.5(1)
O(4)	Fe(1)	O(5)	87.7(1)		Fe(1)	O(2)	P(1)	123.9(2)
O(2)	Fe(2)	O(4)	83.2(1)		Fe(2)	O(2)	P(1)	122.2(2)
O(2)	Fe(2)	O(5)	88.9(1)		Fe(1)	O(4)	Fe(2)	130.0(1)
O(2)	Fe(2)	O(6)	94.6(1)		Fe(1)	O(4)	P(1)	125.9(2)
O(2)	Fe(2)	O(6)	96.5(1)		Fe(2)	O(4)	P(1)	91.4(1)
O(2)	Fe(2)	O(7)	165.1(1)		Fe(1)	O(5)	Fe(2)	121.4(1)
O(4)	Fe(2)	O(5)	93.3(1)		Fe(1)	O(5)	C(1)	122.8(3)
O(4)	Fe(2)	O(6)	65.7(1)		Fe(2)	O(5)	C(1)	114.5(4)
O(4)	Fe(2)	O(6)	153.5(1)		Fe(2)	O(6)	Fe(2)	126.8(1)
O(4)	Fe(2)	O(7)	92.0(1)		Fe(2)	O(6)	P(1)	96.2(2)
O(5)	Fe(2)	O(6)	158.0(1)		Fe(2)	O(6)	P(1)	135.0(2)
O(5)	Fe(2)	O(6)	113.2(1)		Fe(2)	O(7)	C(1)	114.3(3)
O(5)	Fe(2)	O(7)	77.3(1)		O(5)	C(1)	O(7)	126.6(4)
O(6)	Fe(2)	O(6)	88.00(8)		O(5)	C(1)	C(1)	115.9(5)
O(6)	Fe(2)	O(7)	96.3(1)		O(7)	C(1)	C(1)	117.5(5)

Hydrogen Bonds

A	H	B	A–H	H ... B	A ... B	A–H ... B
O(3)	H(1)	O(1)	1.03(6)	1.70(6)	2.707(5)	168(6)
O(3)	H(2)	O(7)	0.67(5)	2.12(5)	2.679(5)	142(6)

anions. As far as we are aware, this is the first published structure containing both of these anions. One previous report of an open framework iron–phosphate–oxalate material is known to us (23). Coordination around the two iron centers is square pyramidal for Fe(1) and distorted octahedral for Fe(2). Although the overall structure has three-dimensional connectivity, it may be instructional in the first instance to consider it as having *layers* of iron-phosphate in the *ab* plane, which are further linked into three dimensions along *c* via bridging oxalate groups: the projection of an iron–phosphate layer along the *c*-axis is shown in Fig. 1, while the overall connectivity along *b* is shown in Fig. 2. Within the two-dimensional iron phosphate sheet (Fig. 1) there is continuous Fe–O–Fe connectivity via vertex-linking between all FeO_6 and FeO_5 centers. The $C_2O_4^{2-}$ ion
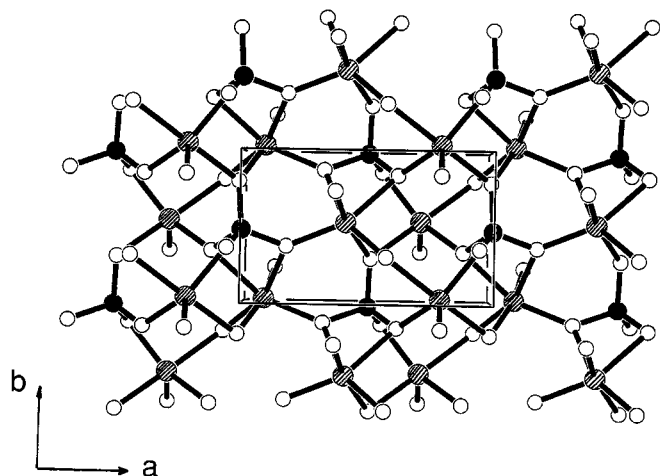
FIG. 1. View of the Fe–O–P two-dimensional network projected along *c*. Three types of polyhedron are present: Fe(1)O$_5$ square pyramids, Fe(2)O$_6$ octahedra and PO$_4$ tetrahedra. Fe and P are shown by hatched and filled circles, respectively.

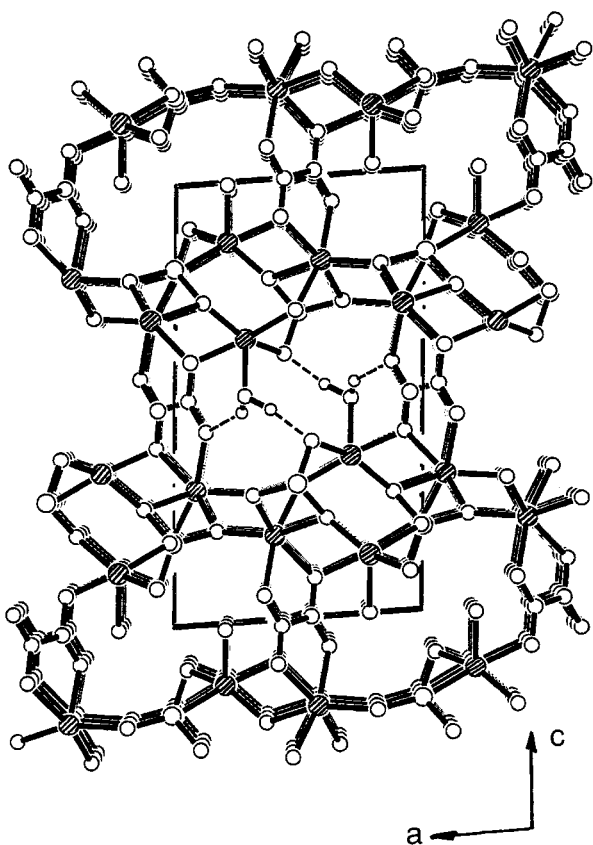**FIG. 3.** ORTEP representation of coordination around the oxalate group.

FIG. 2. View of the complete structure projected along *b*. Fe–O–P layers in the *ab* plane are bridged by C$_2$O$_4^{2-}$ groups along the *c*-axis, to form a three-dimensional framework. Small void channels along *b* accommodate the terminal Fe-OH$_2$ groups. For clarity, hydrogen atoms and associated H-bonds are shown only in the central cavity. Fe atoms shown as hatched circles.
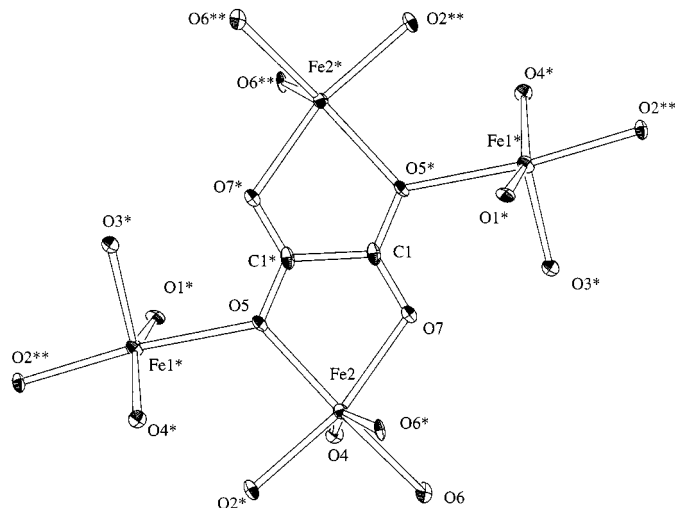
lies on an inversion center in the middle of the C–C bond, and acts as a bis-bidentate ligand to Fe(2) as well as a bis-monodentate ligand to Fe(1) (Fig. 3). The relatively "open" nature of the interlayer bridge provides a mechanism to accomodate the "hanging" water molecule O(3) which coordinates the apical site of the Fe(1) square pyramid and donates H-bonds across the open cavity. An unusual feature of the structure is the sharing of a common edge between the Fe(2)O$_6$ octahedron and the PO$_4$ tetrahedron (Fig. 4). This, together with the μ_2 coordination of Fe(2) by the oxalate, leads to a highly distorted coordination environment for Fe(2), with a very long Fe(2)–O(4) bond length of 2.303(3) Å and small O(4)–Fe(2)–O(6) (65.7(1)°) and O(5)–Fe(2)–O(7) (77.3(1)°) bond angles.

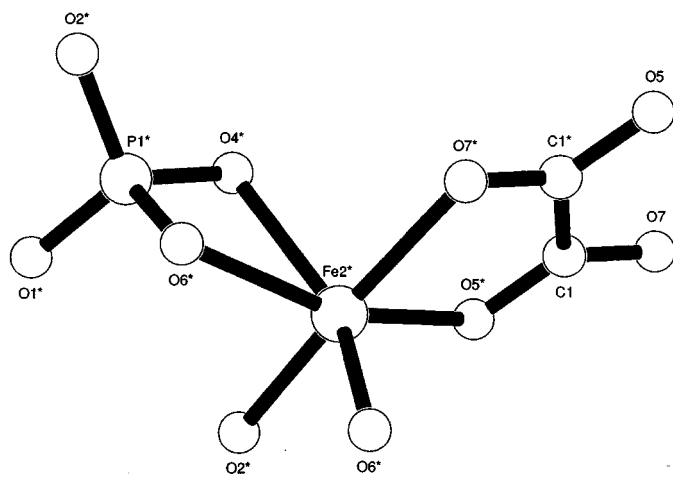**FIG. 4.** The unusual coordination environment of octahedral Fe(2).

Our initial synthesis of this material included $(CH_3)_4NBr$ in the reaction mixture as a possible "template." Since this was not included in the structure obtained, we attempted additional syntheses under very similar conditions but with slightly differing reaction mixtures. The first variation omitted the template cation and was merely a reaction of a 1 : 1 molar mixture of $(NH_4)_2HPO_4$ and $Fe(C_2O_4) \cdot 2H_2O$ in water. The second variation was to replace the $(CH_3)_4NBr$ template with an equivalent amount of $(CH_3CH_2CH_2)_4$ NBr. Both of these reactions produced a mixture of the title phase plus an unidentified black polycrystalline material. In the former case a significantly improved yield was obtained, however this was unfortunately still insufficient to carry out further chemical or physical characterization of the material. Clearly this new phase is preferred over any phases templated by either NH_4^+, Me_4N^+, or $^iPr_4N^+$ under these conditions. Further work is ongoing in order to encourage formation of a templated product.

In summary, we have shown that new materials can be made in which both inorganic and organic anions occur within the same framework. The scope for the preparation of new materials using variations on this theme is clearly very promising. It would be interesting to establish, as this area develops, whether the type of "segregation" of the two anionic species which occurs here, viz. *intralayer* PO_4^{3-} units and *interlayer* $C_2O_4^{2-}$ units, is a common feature of these structures. If so, it is simple to envisage how the structural and electronic/magnetic properties of such frameworks could be tailored by varying the size, shape, and connectivity of the organic anion moieties.

ACKNOWLEDGMENTS

REFERENCES

1. M. E. Davis and R. F. Lobo, *Chem. Mater.* **4,** 756 (1992).
2. S. L. Suib, *Chem. Rev.* **93,** 803 (1993).
3. M. I. Khan, L. M. Meyer, R. C. Haushalter, A. L. Schweitzer, J. Zubieta, and J. L. Dye, *Chem. Mater.* **8,** 43 (1996).
4. P. B. Moore and J. Shen, *Nature* **306,** 356 (1983).
5. J. R. D. DeBord, W. M. Reiff, C. J. Warren, R. C. Haushalter, and J. Zubieta, *Chem. Mater.* **9,** 1994 (1997).
6. J. R. D. DeBord, W. M. Reiff, R. C. Haushalter, and J. Zubieta, *J. Solid State Chem.* **125,** 186 (1996).
7. K.-H. Lii and Y.-F. Huang, *Chem. Commun.,* 839 (1997).
8. K.-H. Lii and Y.-F. Huang, *J. Chem. Soc. Dalton Trans.,* 2221 (1997).
9. M. Cavellec, D. Riou, and G. Ferey, *J. Solid State Chem.* **112,** 441 (1994).
10. M. Cavellec, D. Riou, J.-M. Greneche, and G. Ferey, *Inorg. Chem.* **36,** 2187 (1997).
11. O. M. Yaghi, G. Li, and H. Li, *Nature* **378,** 703 (1995).
12. S. O. H. Gutschke, M. Molinier, A. K. Powell, and P. T. Wood, *Angew. Chem. Int. Ed. Engl.* **36,** 991 (1997).
13. C. J. Kepert and M. J. Rosseinsky, *Chem. Commun.,* 31 (1998).
14. S. Decurtins, H. W. Schmalle, P. Schneuwly, J. Ensling, and P. Gutlich, *J. Amer. Chem. Soc.* **116,** 9521 (1994).
15. H. Tamaki, Z. J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto, and H. Okawa, *J. Amer. Chem. Soc.* **114,** 6974 (1992).
16. M. Clemente-Leon, E. Coronado, J.-R. Galan-Mascaros, and C. J. Gomez-Garcia, *Chem. Commun.,* 1727 (1997).
17. R. P. Farrell, T. W. Hambley, and P. A. Lay, *Inorg. Chem.* **34,** 757 (1995).
18. C. Mathoniere, C. J. Nuttall, S. G. Carling, and P. Day, *Inorg. Chem.* **35,** 1201 (1996).
19. S. G. Carling, P. Day, and D. Visser, *Inorg. Chem.* **34,** 3917 (1995).
20. P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel, and J. M. M. Smits, "The DIRDIF-94 program system," Technical Report of the Crystallography Laboratory, University of Nijmegen, Netherlands (1994).
21. teXsan Crystal Structure Analysis Package, Molecular Structure Corporation (1992).
22. I. D. Brown and D. Altermatt, *Acta Crystallogr. Sect. B* **41,** 244 (1985).
23. P. Lightfoot, Thesis, University of Oxford (1987).