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A Two-Dimensional Iron Phosphate Templated by Ethylenediamine

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Abstract

[Fe(PO₄)(OH)].0.5(ethylenediamine) was synthesized hydrothermally at 453 K. It is isotypic with the layered gallophosphate obtained in ethylene glycol by Jones, Thomas, Qisheng, Hursthouse & Chen [*J. Chem. Soc. Chem. Commun.* (1991), pp. 1520–1522].

Comment

We have investigated the system $FeO(OH)$–$H_3(PO_4)$–HF–en–H_2O (en = ethylenediamine) in order to synthesize oxyfluorinated iron phosphates with open frameworks. By increasing the amine ratio in the mixture, we succeeded in obtaining five different phases, the structures of two of which [ULM-10 (Cavellec, Riou & Férey, 1994) and ULM-11 (Cavellec, Riou & Férey, 1995)] are published elsewhere. The phase described in this paper does not contain fluorine. It corresponds to the formula $0.5(en).[Fe(PO_4)(OH)]$ and is isotypic with the gallophosphate synthesized in ethylene glycol by Jones, Thomas, Qisheng, Hursthouse & Chen (1991). It presents a two-dimensional structure with alternating inorganic and organic layers (Fig. 1). The inorganic sheets (Fig. 2) are built up from chains of edge-sharing $FeO_5(OH)$ octahedra bonded by PO_4 tetrahedra. These polyhedra form a chain of a type already encountered in linarite (Bachmann & Zemann, 1961; Hawthorne, 1990, 1994). Octahedra are linked one to another *via* their O-atom vertices O1 and O3, the O1 atoms belonging to hydroxy groups. The O3 apices are bonded to two Fe atoms and one P atom; they ensure the connection between the chains *via* PO_4 tetrahedra.

The organic layers are made up of ethylenediamine molecules. Strong hydrogen bonds *via* H atoms of the
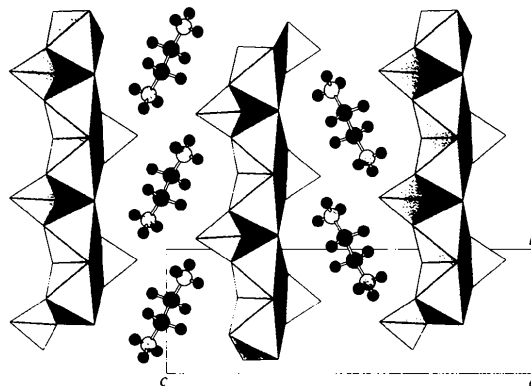

Fig. 1. Projection of the structure along the *a* axis showing its two-dimensional character.
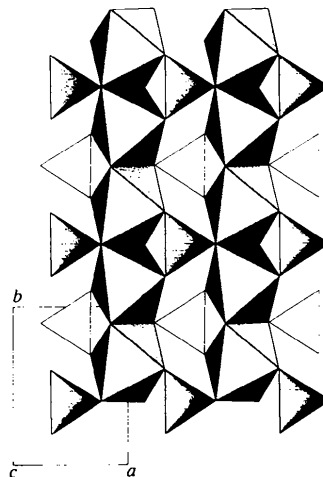

Fig. 2. Projection of an inorganic sheet along the *c* axis.

amino groups and the free vertices of the phosphates are responsible for the cohesion of the structure [e.g. O5···H5 1.82(3), O5···H1 1.98(3)Å (−2 − x, −y, −z)]. To respect the electroneutrality of the structure, the diamine is fully protonated. The formula of the compound can thus be written as $0.5(en)^{2+}.[Fe(PO_4)(OH)]^-$.

Experimental

The title compound was prepared under hydrothermal conditions (453 K, autogenous pressure). The starting mixture was FeO(OH)–H$_3$(PO)$_4$–HF–en–H$_2$O with the molar ratio 2:2:2:x:80. $0.5(en)^{2+}.[Fe(PO_4)(OH)]^-$ appeared as hexagonal greenish yellow platelets, in small amounts, for x varying from 2.5 to 3. A suitable single crystal was isolated by optical microscopy and its quality was tested by Laue photographs before collecting data. The chemical analysis, performed by EDX analysis using a Jeol-2010 TEM equipped with a KEVEX energy-dispersive X-ray spectrometer, confirmed the absence of fluorine in the phase.

Crystal data

(C$_2$N$_2$H$_{10}$)$_{0.5}$[Fe(PO$_4$)(OH)]
M_r = 198.89
Monoclinic
$P2_1/c$
a = 4.5164(5) Å
b = 6.1355(9) Å
c = 18.515(3) Å
β = 94.58(2)°
V = 511.42(13) Å^3
Z = 4
D_x = 2.583 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 38 reflections
θ = 15–16°
μ = 3.210 mm^{-1}
T = 293 K
Hexagonal platelet
0.304 × 0.247 × 0.034 mm
Yellow

Data collection

Stoe Siemens AED-2 diffractometer
$\omega/2\theta$ scans
Absorption correction:
by integration from crystal shape (Sheldrick, 1990)
T_{min} = 0.111, T_{max} = 0.497
3562 measured reflections
3562 independent reflections

2039 observed reflections
[$I > 2\sigma(I)$]
θ_{max} = 37.47°
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 31$
3 standard reflections
frequency: 60 min
intensity decay: <1%

Refinement

Refinement on F^2
$R(F)$ = 0.0246
$wR(F^2)$ = 0.0641
S = 1.072
2039 reflections
107 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 0.0305P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.008

$\Delta\rho_{max}$ = 0.716 e Å^{-3}
$\Delta\rho_{min}$ = −0.611 e Å^{-3}
Extinction correction: SHELXL93 (Sheldrick, 1993)
Extinction coefficient: 0.0039(9)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe1	0.00329 (4)	0.14314 (3)	0.25372 (1)	0.00757 (5)
P1	−0.50990 (7)	−0.09956 (6)	0.15486 (2)	0.00709 (7)
O1	0.1486 (2)	0.3892 (2)	0.19350 (6)	0.0092 (2)
O2	−0.3239 (2)	0.1051 (2)	0.17538 (6)	0.0106 (2)
O3	−0.7684 (2)	−0.1038 (2)	0.20768 (6)	0.0100 (2)
O4	−0.3286 (2)	−0.3100 (2)	0.16892 (6)	0.0108 (2)
O5	−0.6389 (3)	−0.0845 (2)	0.07721 (6)	0.0156 (2)
N	−1.0561 (4)	0.2345 (3)	0.04778 (8)	0.0178 (2)
C	−1.1061 (4)	−0.4103 (3)	−0.01304 (11)	0.0187 (3)

Table 2. *Selected geometric parameters* (Å, °)

Fe1—O4^i	1.9892 (12)	P1—O5	1.5102 (12)
Fe1—O1^{ii}	1.9901 (11)	P1—O4	1.5397 (11)
Fe1—O2	1.9999 (12)	P1—O2	1.5413 (11)
Fe1—O1	2.0175 (11)	P1—O3	1.5821 (11)
Fe1—O3^{iii}	2.0414 (10)	N—C^v	1.480 (2)
Fe1—O3^{iv}	2.0557 (10)	C—C^{vi}	1.513 (4)
O4^i—Fe1—O1^{ii}	91.35 (5)	O1^{ii}—Fe1—O3^{iv}	80.25 (4)
O4^i—Fe1—O2	178.37 (4)	O2—Fe1—O3^{iv}	88.81 (5)
O1^{ii}—Fe1—O2	90.05 (5)	O1—Fe1—O3^{iv}	97.25 (4)
O4^i—Fe1—O1	92.03 (5)	O3^{iii}—Fe1—O3^{iv}	176.00 (2)
O1^{ii}—Fe1—O1	175.87 (3)	O5—P1—O4	111.83 (7)
O2—Fe1—O1	86.60 (4)	O5—P1—O2	110.24 (7)
O4^i—Fe1—O3^{iii}	90.72 (5)	O4—P1—O2	111.67 (6)
O1^{ii}—Fe1—O3^{iii}	102.38 (4)	O5—P1—O3	110.00 (7)
O2—Fe1—O3^{iii}	88.17 (5)	O4—P1—O3	106.88 (6)
O1—Fe1—O3^{iii}	79.95 (4)	O2—P1—O3	106.00 (6)
O4^i—Fe1—O3^{iv}	92.24 (5)		

Symmetry codes: (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $-1 - x, \frac{1}{2}+y, \frac{1}{2} - z$; (iv) $1+x, y, z$; (v) $-2-x, -y, -z$; (vi) $-2-x, -1-y, -z$.

The structure of the title compound was solved by arguing its isotypy with the phase of Jones *et al.* (1991) mentioned above. H atoms were all located from difference Fourier maps.

Data collection: *DIF4* (Stoe & Cie, 1988a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988b). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *MOLVIEW* (Cense, 1992).

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$(C_2N_2H_{10})_{0.5}[Fe(PO_4)(OH)]$

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{Tris[4-(2-pyridyl)-3-aza-3-butenyl]-amine}iron(II) Bis(hexafluorophosphate), [Fe(py₃tren)](PF₆)₂

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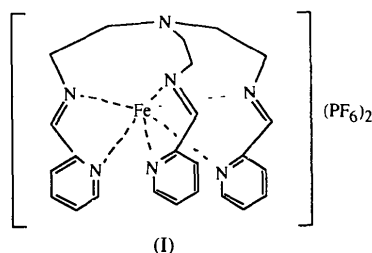
Abstract

The coordination polyhedron of the Fe^{II} ion in the title compound, $[Fe(C_{24}H_{27}N_7)](PF_6)_2$, is best described as a trigonal antiprism twisted 6° towards a trigonal prism. The tris[4-(2-pyridyl)-3-aza-3-butenyl]amine ligand coordinates to the metal centre through the three pyridine and three imino N atoms, each set of atoms forming two parallel ideal equilateral triangles; the metal ion is located between these two planes. The average values for the Fe—$N_{pyridine}$ and the Fe—N_{imino} bond lengths are 1.981 and 1.950 Å, respectively. The tripodal bridging amine N atom lies on the pseudo ternary axis of the molecule and is situated 3.427 (7) Å from the Fe centre.

Comment

The potentially heptadentate tripodal ligand tris[4-(2-pyridyl)-3-aza-3-butenyl]amine (py₃tren) has been found to form iron(II) and manganese(II) complexes characterized by sixfold coordination of the metal ion (Kichner *et al.*, 1987). As part of our continuing studies involving such hindered polydentate ligands and our general interest in their complexes, which may be proposed as iron or manganese superoxide mimics, we have found that the complex [Fe(py₃tren)](PF₆)₂ can be formed in two different ways: (*a*) by the direct mixing of py₃tren with FeCl₂ and NH₄PF₆ in methanol to give

compound (I), and (*b*) by the reaction of a methanolic solution of FeCl₃ with the polyamine ligand tris[*N*-(2-pyridylmethyl)-2-aminoethyl]amine (TPAA), in the presence of NH₄PF₆, under an air atmosphere to give compound (II). This reaction involves the oxidation of the TPAA ligand through a metal-assisted oxidative dehydrogenation.

(I)

We have shown recently that TPAA can form a heptadentate manganese(II) complex (MnTPAA) and have performed the first crystallographic characterization of the structure of this ligand (Deroche *et al.*, 1995). In the present paper, we report the crystal structure of (I). An *ORTEP*II (Johnson, 1976) plot of the [Fe(py₃tren)]²⁺ ion is shown in Fig. 1. The coordination polyhedron of the iron(II) ion is best described as a trigonal antiprism twisted 6° towards a trigonal prism. The Fe atom is bonded to three pyridine N atoms [Fe—N2, Fe—N4 and Fe—N6 are 1.983 (3), 1.980 (4) and 1.979 (3) Å, respec-
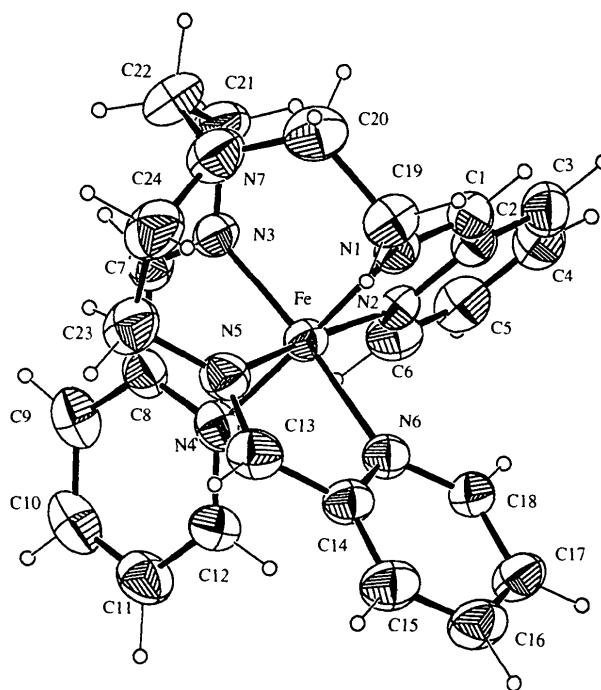

Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the [Fe(C₂₄H₂₇N₇)]²⁺ cation with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.