

Hydrothermal Synthesis and Properties of Open-Framework Mixed-valence Iron Phosphates $\text{Fe}_2^{\text{III}}\text{Fe}_{1.5}^{\text{II}}(\text{PO}_4)_3$ with Three-dimensional Structure

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The open-framework iron phosphate $\text{Fe}_2^{\text{III}}\text{Fe}_{1.5}^{\text{II}}(\text{PO}_4)_3$ was hydrothermally synthesized and characterized by elemental analysis, IR, EPR, XPS and single crystal X-ray diffraction analysis. The title compound crystallized in the triclinic, space group $P\bar{1}$ with $a=0.64724(4)$ nm, $b=0.79651(6)$ nm, $c=0.94229(5)$ nm, $\alpha=104.447(2)^\circ$, $\beta=108.919(4)^\circ$, $\gamma=101.741(4)^\circ$, $V=0.42302(5)$ nm³, $Z=1$ and $R_1(wR_2)=0.0307(0.0793)$. Crystal data were collected on a Rigaku R-Axis RAPID IP diffractometer with Mo K α ($\lambda=0.071073$ nm) at 293(2) K in the range of $2.43^\circ < \theta < 27.46^\circ$. The structure of **1** consists of 19 non-hydrogen atoms including three and a half crystallographically independent Fe and three P atoms. Fe(1) connects its symmetrical Fe(1A) through bridging oxygen forming a dimer and the dimers are connected by Fe(4) forming an infinite staircase-like chain. Fe(2) and Fe(3) connect the infinite chains into a layer with bridging oxygen. Layers are interconnected via Fe(4) forming the six-membered and eight-membered channel systems.

Keywords iron phosphate, open framework, three-dimensional structure

Introduction

The metal phosphates have attracted much attention because of their potential applications in catalysis, sorption, and magnetic properties.¹⁻⁵ A large number of metal phosphates⁶⁻¹⁰ with 1-D chain, 2-D layer and 3-D open-framework have been synthesized under mild hydrothermal conditions in the presence of organic amines. Chiral open-framework phosphates have been synthesized in the presence of chiral metal complexes and chiral structure-directing agents.¹¹⁻¹⁵ In the past years, iron phosphates^{16,17} with novel structures occupy an important position owing to their excellent magnetic properties. Iron phosphates reported in the literature are generally synthesized under hydrothermal condition with high temperature and high pressure, and recently long alkyl chain diamines are used as structure-directing agents to construct for large pores.¹⁸ Starting materials are generally single iron salts such as chloride, nitrate, fluoride or acetate resulting in single valence of iron.^{19,20} In some cases, Fe displays mixed valence due to the redox between iron and organic amines.²¹ We attempt to adopt two kinds of iron salts with different valence as starting materials to gain novel mixed-valence iron phosphates with three-dimensional structure. In this

paper, we report the hydrothermal synthesis and properties of open-framework mixed-valence iron phosphate $\text{Fe}_2^{\text{III}}\text{Fe}_{1.5}^{\text{II}}(\text{PO}_4)_3$ (**1**) with three-dimensional structure. Two kinds of iron chlorides (FeCl_2 and FeCl_3) were used as starting materials to prepare mixed-valence iron phosphate. Compound **1** exhibits a six-membered and an eight-membered channel systems between layers. There are channels in the three-dimensional structure without any guest-species.

Experimental

Chemical reagents and methods

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN Elemental analyzer. P and Fe were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectrum was recorded in the range of 400—4000 cm^{-1} on an Alpha Centaur FT/IR spectrophotometer using a KBr pellet. X-ray photoelectron spectroscopic (XPS) analysis was performed on a VG ESCALAB MK II spectrometer with a Mg K α (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber

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was maintained at 6.2×10^{-6} Pa during analysis. EPR spectrum was recorded on a Japanese JES-FE3AX spectrometer at 293 K.

Hydrothermal synthesis of compound 1

The compound **1** was hydrothermally synthesized under autogenous pressure. A mixture of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, FeCl_3 , H_3PO_4 , *o*-phenylenediamine, tartaric acid and H_2O with the molar ratio of 1 : 1 : 2 : 1 : 0.5 : 0.5 : 600 was sealed in a 18 mL Teflon-lined autoclave and heated to 200 °C for 3 d. After slowly cooling to room temperature at the rate of 10 °C/h, black block crystal of **1** was obtained. The crystals were filtered, washed with distilled water and dried in the air. Yield 39% (based on Fe). Anal. calcd for $\text{Fe}_2^{\text{III}}\text{Fe}_{1.5}^{\text{II}}(\text{PO}_4)_3$: Fe 40.69, P 19.34; found Fe 40.61, P 19.60.

X-ray crystallography

The crystal structure of compound **1** was determined by the single crystal X-ray diffraction analysis. A suitable single crystal with dimensions 0.317 mm \times 0.267 mm \times 0.069 mm was affixed on a glass fiber stick. Data were collected on a Rigaku R-Axis RAPID IP diffractometer with Mo K α ($\lambda=0.071073$ nm) at 293(2) K in the range of $2.43^\circ < \theta < 27.46^\circ$ with ω -scan technique. A total of 3036 (1909 unique, $R_{\text{int}}=0.0237$) reflections were measured ($-8 \leq h \leq 8$, $-10 \leq k \leq 10$, $-12 \leq l \leq 11$). The structure was solved by the direct method using SHELXL 97 program^{22,23} and refined by the full-matrix least-squares method on F^2 . All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from different Fourier maps. Structure solution and refinement based on 1909 independent reflections with $I > 2\sigma(I)$ and 169 parameters gave $R_1=0.0307$ ($wR_2=0.0793$). Crystal data and structure refinement are summarized in Table 1. Selected bond lengths and angles are provided in Table 2 and Table 3, respectively.

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Results and discussion

Structure description

The asymmetric unit contains 19 non-hydrogen atoms as shown in Figure 1. There are three and a half crystallographically independent Fe atoms and three P atoms. The Fe(4) occupies special position with a site occupancy of 0.5. Fe(1), Fe(2) and Fe(4) are octahedrally coordinated by six oxygen atoms with Fe—O bond length in the range of 0.2024—0.2242 nm (average Fe—O bond length: Fe(1)—O 0.2076 nm, Fe(2)—O 2.090 nm, Fe(4)—O 2.175 nm). The angles of O—Fe—O vary from 77.04° to 180°, which shows that the FeO_6 octahedra are disordered. Fe(3) bonds with five oxygen atoms forming trigonal bipyramid with Fe—O distance in the range of 0.2022—0.2171 nm (average Fe—O bond length: Fe(3)—O 0.2092 nm). The bond angles of O—Fe—O vary from 80.40° to 167.65°. The phosphorus atoms are tetrahedrally coordinated by four

oxygen atoms with P—O bond length being in the range of 0.1515—0.1552 nm. All oxygen atoms are bridging

Table 1 Crystal data and structure refinement for compound **1**

Empirical formula	$\text{Fe}_7\text{O}_{24}\text{P}_6$
Formula weight	960.77
Temperature	293(2) K
Wavelength	0.071073 nm
Crystal system	Triclinic
Space group	$P\bar{1}$
	$a=0.64724(4)$ nm
	$b=0.79651(6)$ nm
	$c=0.94229(5)$ nm
Unit cell dimensions	$\alpha=104.447(2)^\circ$
	$\beta=108.919(4)^\circ$
	$\gamma=101.741(4)^\circ$
Volume, Z	$0.42302(5)$ nm ³ , 1
Density (calculated)	3.771 Mg/m ³
Absorption coefficient	6.541 mm ⁻¹
Crystal size	$0.317 \times 0.267 \times 0.069$ mm ³
θ range for data collection	2.43° to 27.46°
Reflections collected	3036
Independent reflection	1909 ($R_{\text{int}}=0.0237$)
Completeness to $\theta=27.46^\circ$	98.5%
Absorption correction	Empirical
Data/restraints/parameters	1909/0/169
Final R indices [$I > 2\sigma(I)$]	$R_1=0.0307$, $wR_2=0.0793$
R indices (all data)	$R_1=0.0329$, $wR_2=0.0805$

Table 2 Selected bond lengths (nm) for compound **1**

Fe(1)—O(10)#1	0.2040(2)	Fe(1)—O(12)#2	0.2045(2)
Fe(1)—O(2)#3	0.2064(2)	Fe(1)—O(5)	0.2069(2)
Fe(1)—O(1)	0.2116(2)	Fe(1)—O(5)#4	0.2122(2)
Fe(2)—O(3)#5	0.2024(2)	Fe(2)—O(6)	0.2075(2)
Fe(2)—O(11)#5	0.2084(2)	Fe(2)—O(8)#6	0.2093(2)
Fe(2)—O(6)#5	0.2094(2)	Fe(2)—O(9)	0.2171(2)
Fe(3)—O(4)#1	0.2022(2)	Fe(3)—O(8)#6	0.2051(2)
Fe(3)—O(1)#7	0.2106(2)	Fe(3)—O(9)	0.2108(2)
Fe(3)—O(12)#3	0.2171(2)	Fe(4)—O(7)#8	0.2096(2)
Fe(4)—O(7)#1	0.2096(2)	Fe(4)—O(11)	0.2186(2)
Fe(4)—O(11)#9	0.2186(2)	Fe(4)—O(4)	0.2242(2)
Fe(4)—O(4)#9	0.2242(2)	P(1)—O(3)	0.1515(2)
P(1)—O(4)	0.1528(2)	P(1)—O(1)	0.1532(2)
P(1)—O(2)	0.1549(2)		

Table 3 Selected bond angles (°) for compound **1**

O(10)#1-Fe(1)-O(12)#2	103.13(9)	O(10)#1-Fe(1)-O(2)#3	91.18(9)
O(12)#2-Fe(1)-O(2)#3	91.74(9)	O(10)#1-Fe(1)-O(5)	90.87(9)
O(12)#2-Fe(1)-O(5)	165.57(9)	O(2)#3-Fe(1)-O(5)	84.39(9)
O(10)#1-Fe(1)-O(1)	81.85(9)	O(12)#2-Fe(1)-O(1)	79.50(9)
O(2)#3-Fe(1)-O(1)	167.18(10)	O(5)-Fe(1)-O(1)	106.34(9)
O(10)#1-Fe(1)-O(5)#4	164.45(9)	O(12)#2-Fe(1)-O(5)#4	89.72(8)
O(2)#3-Fe(1)-O(5)#4	97.23(9)	O(5)-Fe(1)-O(5)#4	77.04(10)
O(1)-Fe(1)-O(5)#4	92.11(9)	O(3)#5-Fe(2)-O(6)	178.47(9)
O(3)#5-Fe(2)-O(11)#5	96.69(9)	O(6)-Fe(2)-O(11)#5	84.69(8)
O(3)#5-Fe(2)-O(8)#6	89.77(9)	O(6)-Fe(2)-O(8)#6	90.46(8)
O(11)#5-Fe(2)-O(8)#6	106.43(8)	O(3)#5-Fe(2)-O(6)#5	94.08(9)
O(6)-Fe(2)-O(6)#5	85.22(9)	O(11)#5-Fe(2)-O(6)#5	91.52(8)
O(8)#6-Fe(2)-O(6)#5	161.09(8)	O(3)#5-Fe(2)-O(9)	98.50(9)
O(6)-Fe(2)-O(9)	80.07(8)	O(11)#5-Fe(2)-O(9)	164.19(8)
O(8)#6-Fe(2)-O(9)	78.05(8)	O(6)#5-Fe(2)-O(9)	83.07(8)
O(4)#1-Fe(3)-O(8)#6	139.69(9)	O(4)#1-Fe(3)-O(1)#7	125.28(9)
O(8)#6-Fe(3)-O(1)#7	92.05(9)	O(4)#1-Fe(3)-O(9)	106.21(8)
O(8)#6-Fe(3)-O(9)	80.40(8)	O(1)#7-Fe(3)-O(9)	97.11(8)
O(4)#1-Fe(3)-O(12)#3	85.95(8)	O(8)#6-Fe(3)-O(12)#3	88.91(8)
O(1)#7-Fe(3)-O(12)#3	76.96(8)	O(9)-Fe(3)-O(12)#3	167.65(8)
O(7)#8-Fe(4)-O(7)#1	180.00(1)	O(7)#8-Fe(4)-O(11)	87.56(8)
O(7)#1-Fe(4)-O(11)	92.44(8)	O(7)#8-Fe(4)-O(11)#9	92.44(8)
O(7)#1-Fe(4)-O(11)#9	87.56(8)	O(11)-Fe(4)-O(11)#9	180.00(1)
O(7)#8-Fe(4)-O(4)	92.79(9)	O(7)#1-Fe(4)-O(4)	87.21(9)
O(11)-Fe(4)-O(4)	93.34(8)	O(11)#9-Fe(4)-O(4)	86.66(8)
O(7)#8-Fe(4)-O(4)#9	87.21(9)	O(7)#1-Fe(4)-O(4)#9	92.79(9)
O(11)-Fe(4)-O(4)#9	86.66(8)	O(11)#9-Fe(4)-O(4)#9	93.34(8)
O(4)-Fe(4)-O(4)#9	180.00(1)	O(3)-P(1)-O(4)	110.14(13)
O(3)-P(1)-O(1)	110.41(13)	O(4)-P(1)-O(1)	111.20(12)
O(3)-P(1)-O(2)	108.37(14)	O(4)-P(1)-O(2)	110.34(13)
O(1)-P(1)-O(2)	106.28(13)		

oxygen and are divided into two types of μ_2 -O [O(2), O(3), O(7), O(10)] and μ_3 -O [O(1), O(4), O(5), O(6), O(8), O(9), O(11), O(12)]. Valence bond calculations²⁴ show that all the phosphorus sites display +5 valence [P(1), 5.05; P(2), 4.97; P(3), 4.94;], Fe(1), Fe(2) display +3 valence and Fe(3), Fe(4) display +2 valence [Fe(1), 2.56; Fe(2), 2.47; Fe(3), 1.92; Fe(4), 1.85].

Fe(1) connects its symmetrical Fe(1A) through bridging oxygens O(5) and O(5A) forming a dimer (shown in Figure 2). It is interesting that there is a square ring composed of two Fe atoms [Fe(1) and Fe(1A)] and two O atoms between two six-membered polyhedral rings. Each of the six-membered polyhedral rings is constructed by alternation of three P atoms and three Fe atoms. The dimers are connected by Fe(4) forming an infinite staircase-like chain. The FeO₆ octa-

hedra of Fe(1) and Fe(1A) are connected by sharing edge oxygen, FeO₆ octahedra and PO₄ tetrahedra are connected by sharing corner oxygen as shown in Figure 3. Fe(2) and Fe(3) connects the infinite chains into a layer with bridging oxygen [O(8), O(9)]. The eight-membered polyhedral ring between four dimers is constructed by alternation of four Fe atoms and four P atoms. The connection between Fe(2)O₆ octahedra and Fe(3)O₅ trigonal bipyramid via edge-sharing. The most interesting aspect of this iron phosphate is that the layers are interconnected via Fe(4) forming the six-membered and eight-membered channel systems as shown in Figure 4. The arrangement of six- and eight-membered polyhedral rings is regular and there are channels in the three-dimensional structure without any guest-species.

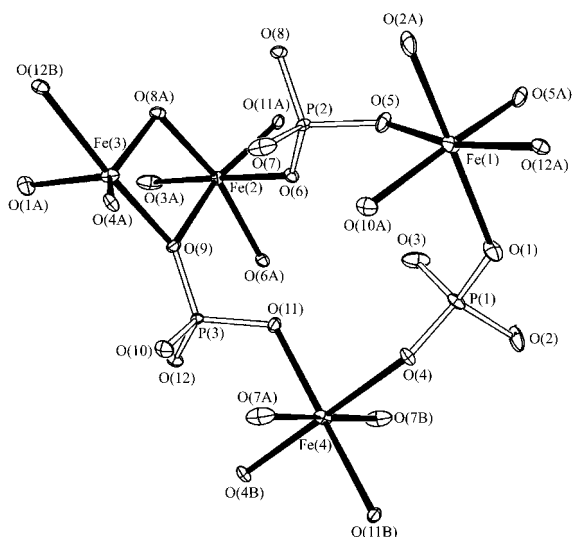


Figure 1 ORTEP plot of $\text{Fe}_2^{\text{III}}\text{Fe}_{1.5}^{\text{II}}(\text{PO}_4)_3$ (**1**), showing the structural unit. Thermal ellipsoids are given at 50% probability.

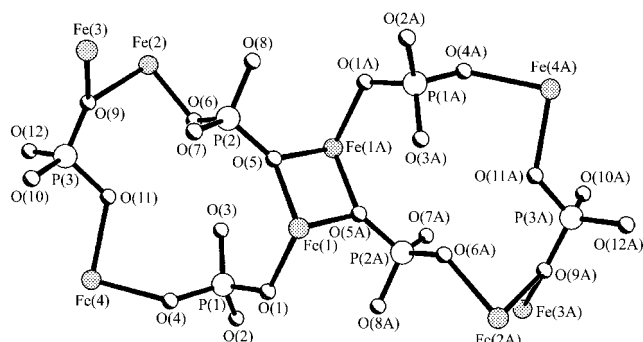


Figure 2 An asymmetric unit connecting its mirror image forming a dimer.

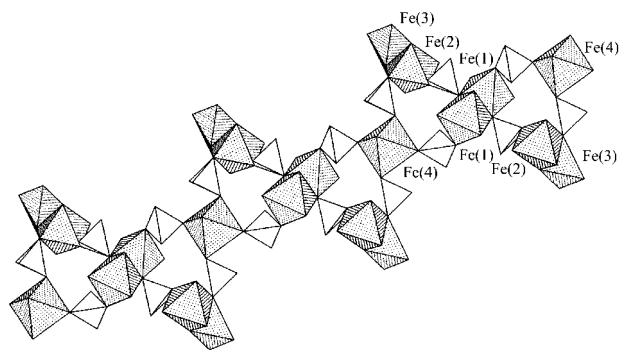


Figure 3 The polyhedral figure of the infinite staircase-like chain. Some Fe atoms are labeled.

IR, EPR, XPS spectrum

In the IR spectrum of compound **1**, the strong bands at 1121, 1042 cm^{-1} are attributed to the vibrations of P—O bonds. The broad band of 551.82 cm^{-1} is due to the $\nu(\text{Fe—O})$ vibrations.

EPR spectrum at room temperature only shows Fe^{3+} signal with $g=1.9976$ and $\Delta H_{\text{pp}}=60$ G as shown in Figure 5. XPS supports the mixed-valence Fe in the energy regions of $\text{Fe}2\text{p}_{1/2}$ and $\text{Fe}2\text{p}_{3/2}$ in accordance with

the valence sum calculation. The XPS spectrum shown in Figure 6 gives two overlapped peaks at 712.2 and 726.1 eV attributed to Fe^{3+} and Fe^{2+} respectively. These spectra further confirm the mixed valence of Fe atoms.

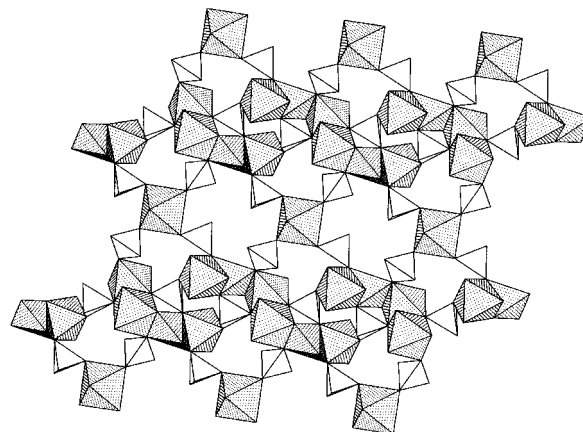


Figure 4 The polyhedral figure of compound **1**. Note the 6-membered and 8-membered channels.

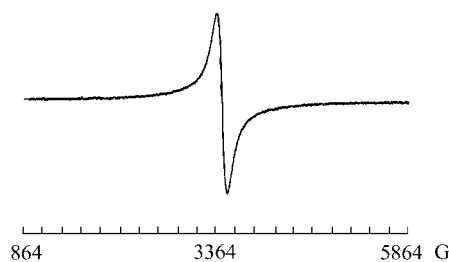


Figure 5 EPR spectrum of compound **1**.

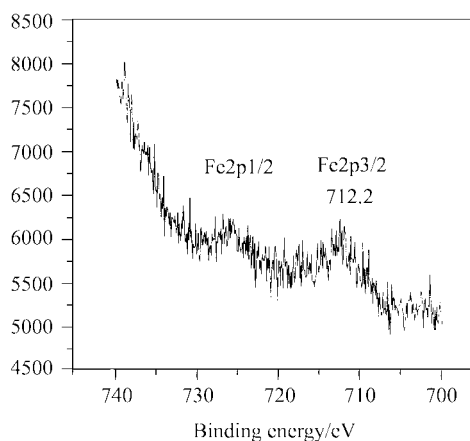


Figure 6 XPS spectrum of compound **1**.

Conclusion

In summary, the compound $\text{Fe}_2^{\text{III}}\text{Fe}_{1.5}^{\text{II}}(\text{PO}_4)_3$ has been hydrothermally synthesized using two iron salts FeCl_2 and FeCl_3 as starting material to obtain a novel three-dimensional structure. Compound **1** exhibits a six-membered and an eight-membered channel systems between layers. There are channels in the three-dimen-

sional structure without any guest-species.

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