Hydrothermal Synthesis, Structure, and Magnetic Properties of a Novel Monodimensional Iron Phosphate: [FeF(HPO$_4$)$_2$,N$_2$C$_3$H$_{12}$,(H$_2$O)$_x$] ($x \approx 0.20$) (ULM-14)

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ULM-14 or [FeF(HPO$_4$)$_2$,N$_2$C$_3$H$_{12}$,(H$_2$O)$_x$] ($x \approx 0.20$) was synthesized by the hydrothermal method (24 h, 453 K) under autogenous pressure. ULM-14 crystallizes in the orthorhombic system (space group *Pmca*, No. 57) with cell parameters $a = 7.221(1)$ Å, $b = 8.655(1)$ Å, $c = 19.329(2)$ Å, and $Z = 4$. Its structure, solved by single-crystal X-ray diffraction, results from isolated single [FeF(HPO$_4$)$_2$]$^{2-}{}_n$ chains of the tancoite type, with diprotonated amines inserted in between. Mössbauer spectrometry clearly evidences the presence of high-spin-state Fe^{3+} ions in octahedral coordination and the remaining water molecules. Both magnetic susceptibility and Mössbauer results indicate that ULM-14 behaves as a paramagnet above 2 K, the intrachains interactions being antiferromagnetic.

Introduction

The ULM-*n* family (for University Le Mans) actually represents a new series of amine-templated oxyfluorinated metallophosphates with open structures. The first compounds we synthesized were mainly gallophosphates.[1] The most representative is ULM-5[2] with 16-membered channels and a free pore aperture of 12.20 Å × 8.34 Å. Many of these structures can be described from hexameric units M$_3$P$_3$(O,F)$_x$. We proposed a hypothesis for the formation of these phases which supposes that the extent of oligomeric condensation of these units in the solution is controlled by the charge density of the amines. This hypothesis ruled out any particular role of Al and Ga in the formation of microporous compounds and claimed that such zeolithic products would exit with 3d transition metals instead of Al and Ga in the framework.

The first 3d oxyfluorinated metallophosphates were obtained with vanadium.[3] This approach was extended to the iron family in which several compounds have already been identified and characterized: bidimensional ULM-10[4] and ULM-11[5] and three-dimensional ULM-12[6] and ULM-15.[7] Beside their structural interest, they provide some of the scarce examples of magnetic microporous compounds far above 4.2 K. Moreover, among them, some are topologically similar to minerals. ULM-14, the compound we present here, has many structural features in common with the mineral tancoite.

Experimental Section

Synthesis, Analysis, and Thermal Behavior. [FeF(HPO$_4$)$_2$,N$_2$C$_3$H$_{12}$,-(H$_2$O)$_x$] ($x \approx 0.20$) was prepared hydrothermally (24 h, 453 K,

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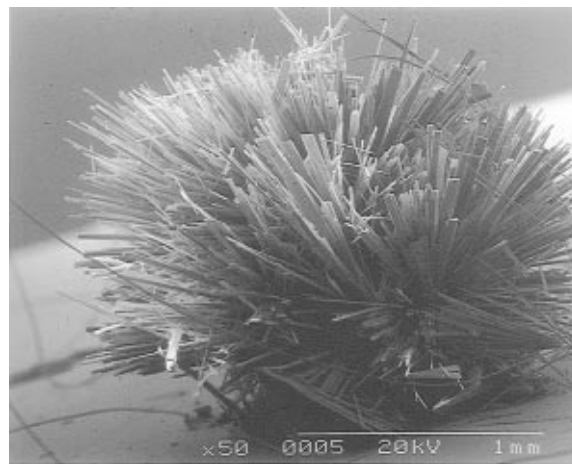(7) Cavellec, M.; Riou, D.; Grenèche, J. M.; Férey, G. *Micropor. Mater.* **1997,** *8(3−4).*

Figure 1. Scanning electronic micrograph of ULM-14.

autogenous pressure) in a Teflon-lined steel autoclave from a starting mixture of Fe$_2$O$_3$ (Aldrich, 99%+), H$_3$PO$_4$ (Prolabo Normapur, 7.5 M), HF (Prolabo Normapur, 4.4 M), 1,3-diaminopropane (Aldrich, 99%+), and H$_2$O. ULM-14 forms in the range of compositions 1:2−4:2:1.5−2:80−160. Whatever the ratio, the final pH was ca. 5. The resulting product was filtered off, washed with distilled water, and dried in air. Many large colorless plateletlike crystals appeared in the preparation. A scanning electronic micrograph performed on a Hitachi S2300 is given in Figure 1. Fluorine was tested by EDX analysis (performed on the mentioned SEM), which confirms its presence in the compound.

The thermogravimetric analysis (Figure 2) performed on a Setaram gear under argon flow indicates a tiny weight loss in the 150−200 °C range and an important one occurring at about 320 °C. The first loss corresponds to the dehydration of the compound (% theor = 1.14, % exptl = 1.1(1)); the second loss fits with the destruction of the amine (% theor = 21.9, % exptl = 21.9(1)). X-ray diffraction experiments prove that the latter leads to the amorphization of the structure.

Structural Determination. A suitable single crystal of ULM-14 was isolated and tested by a Laüe photograph. It was mounted on a Siemens AED2 four-circle diffractometer. The conditions of data measurements are summarized in Table 1. The data were corrected for Lorentz−polarization effects, and then an absorption correction based on the crystal morphology was applied.

The iron and phosphorus atoms were first located by direct methods (option TREF20 of the SHELXS-86 program[8]) on three special positions P1(4d), P2(4d), and Fe(4a), leading to a Fe/P ratio equal to 1:2. All

Figure 2. TGA curve of ULM-14.

Table 1. Crystallographic Data for ULM-14
($[FeF(HPO_4)_2,N_2C_3H_{12},(H_2O)_x]$ ($x \approx 0.20$))

$a = 7.2213(8)$ Å	$T = 20$ °C
$b = 8.6546(7)$ Å	λ(Mo Kα) = 0.710 73 Å
$c = 19.329(2)$ Å	$\rho_{obs} = 1.90$ g·cm^{-3}
$V = 1208.0(2)$ Å^3	$\rho_{calcd} = 1.907$ g·cm^{-3}
$Z = 4$	$\mu = 15.94$ cm^{-1}
$M_r = 346$	$R_1(F_o)^a = 0.029$
$Pmca$ (No. 57)	w$R_2(F_o^2)^b = 0.081$

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} w$R_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

the remaining atoms except hydrogen were deduced from Fourier-difference maps supplied by the SHELXL-93 program.[9] Geometrical constraints were applied to localize hydrogen atoms of the HPO_4 groups and of the diprotonated amine.

Fluorine and hydroxyl sites were attributed by considering the chemical analysis of fluorine, the bond-valence calculations,[10] and their respective thermal parameter values.

After refinements, an important residual peak remained (2.18 e$^-$/Å^3). Another refinement using another set of data collected on a different single crystal led to the same result. It is the Mössbauer study (see below) which led us to attribute this peak to a site partially filled by a water molecule. The occupancy was refined to 22%. The presence of water, which is reversible, was confirmed by TG measurements.

All non-H atoms were refined with individual anisotropic temperature factors. The final cycle of least-squares refinement led to $R_1(F_o) = 0.029$ and w$R_2(F_o^2) = 0.081$. The calculated X-ray diffraction pattern is in very good agreement with the experimental one.

Atomic coordinates and selected bond distances and angles are listed in Tables 2 and 3, respectively.

Magnetic Measurements and Mössbauer Spectroscopy. The temperature dependence of the magnetic susceptibility was followed using a Quantum Design Squid device. Mössbauer experiments were carried out at 300, 77, 4.2, and 2 K using a constant-acceleration spectrometer and a ^{57}Co source diffused into a Rh matrix. The values of isomer shifts are quoted here relative to α-Fe foil at 300 K. The hyperfine parameters were refined using a least-squares fitting procedure of the MOSFIT program.[11]

Description of the Structure

The ULM-14 or $[FeF(HPO_4)_2,N_2C_3H_{12},(H_2O)_x]$ ($x \approx 0.20$) structure is built up from isolated infinite $[FeF(HPO_4)_2]^{2-}_n$ chains running along the [100] direction with diprotonated

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Table 2. Atomic Coordinates($\times 10^4$, Except for Hydrogen Atoms $\times 10^3$) and Equivalent Isotropic Thermal Parameters (Å$^2 \times 10^3$)^a

atoms	x	y	z	$U_{eq}{}^b$
Fe	0	0	0	14(1)
P(1)	2500	1517	1240(1)	15(1)
P(2)	2500	−2687(1)	779(1)	16(1)
O(1)	2500	−4407(2)	669(1)	29(1)
O(2)	767(2)	1273(2)	802(1)	29(1)
O(3)	770(2)	−1917(2)	477(1)	26(1)
O(4)	2500	520(2)	1880(1)	36(1)
O(5)h	2500	3224(2)	1519(1)	26(1)
O(6)h	2500	−2430(2)	1584(1)	33(1)
F	−2500	−225(2)	415(1)	18(1)
Ow	0	−4150(3)	2500(1)	65(6)
N(1)	−2500	1380(1)	1763(1)	30(1)
N(2)	2500	3707(2)	−477(1)	27(1)
C(1)	−2500	3852(3)	1123(1)	32(1)
C(2)	−2500	−4436(4)	1172(2)	46(1)
C(3)	2500	3087(3)	3175(1)	32(1)
H(1)h	221(1)	381(1)	121(1)	47(3)
H(2)h	284(8)	−155(2)	167(1)	47(3)
H(3)	−159(5)	109(1)	148(1)	47(3)
H(4)	−358(1)	107(1)	159(3)	47(3)
H(5)	−233(8)	96(1)	218(1)	47(3)
H(6)	351(7)	313(9)	−43(2)	47(3)
H(7)	150(7)	312(9)	−43(2)	47(3)
H(8)	249(13)	444(1)	−15(1)	47(3)
H(9)c	−141(1)	352(1)	87(1)	47(3)
H(10)c	−359(1)	−410(1)	143(1)	47(3)
H(11)c	141(1)	341(1)	292(1)	47(3)

^{a} w indicates a water molecule, h a hydroxyl group, and c a CH_2 group. $^b U_{eq}$ is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Interatomic Distances (Å) and Angles (deg) (Italics)

HP(1)O$_4$ Tetrahedron

P(1)	O(4)	O(2)	O(2)	O(5)h
O(4)	**1.508(2)**	2.517(2)	2.517(2)	2.442(3)
O(2)	*112.13(8)*	**1.526(1)**	2.503(2)	2.517(2)
O(2)	*112.13(8)*	*110.2(1)*	**1.526(1)**	2.517(2)
O(5)h	*104.9(1)*	*108.64(6)*	*108.64(6)*	**1.572(2)**

$\langle P-O \rangle = 1.533(2)$ Å

HP(2)O$_4$ Tetrahedron

P(2)	O(1)	O(3)	O(3)	O(6)h
O(1)	**1.504(2)**	2.518(2)	2.518(2)	2.461(3)
O(3)	*112.16(6)*	**1.531(1)**	2.499(2)	2.517(2)
O(3)	*112.16(6)*	*109.4(1)*	**1.531(1)**	2.517(2)
O(6)h	*106.2(1)*	*108.38(8)*	*108.38(8)*	**1.573(2)**

$\langle P-O \rangle = 1.535(2)$ Å

FeF$_2$O$_4$ octahedron

Fe	O(3)	O(3)	O(2)	O(2)	F	F
O(3)	**1.978(1)**	3.956(3)	2.832(2)	2.767(2)	2.781(2)	2.823(2)
O(3)	*180.0*	**1.978(1)**	2.767(2)	2.832(2)	2.823(2)	2.781(2)
O(2)	*91.32(6)*	*88.68(6)*	**1.981(1)**	3.962(2)	2.794(2)	2.815(2)
O(2)	*88.68(6)*	*91.32(6)*	*180.0*	**1.981(1)**	2.815(2)	2.794(2)
F	*90.87(5)*	*89.13(5)*	*90.41(5)*	*89.59(5)*	**1.985(1)**	3.970(1)
F	*89.13(5)*	*90.87(5)*	*89.59(5)*	*90.41(5)*	*180.0*	**1.985(1)**

$\langle Fe^{3+}-F \rangle = 1.985(1)$ Å $\langle Fe^{3+}-O \rangle = 1.979(1)$ Å

molecules of 1,3-DAP (1,3-diaminopropane) and water molecules inserted between (Figure 3).

Each $[FeF(HPO_4)_2]^{2-}_n$ chain is built up from a central core constituted by a string of $Fe^{III}O_4F_2$ octahedra linked by their trans fluorine apices. On this octahedral unit, HPO_4 tetrahedra are grafted in such a way that each octahedron shares its four oxygen atoms with four distinct tetrahedra and that two consecutive octahedra are linked by two distinct tetrahedra.

Such octahedral files are well-known in ULM compounds and also in minerals where the fluorine atoms are often substituted by hydroxyl groups. The number of tetrahedra and

Table 4. Hyperfine Parameters in the Temperature Range (4.2−300 K)[a]

		major doublet[b]				minor doublet[b]			
	T (K)	IS, mm/s ($\pm$0.02)	Γ, mm/s ($\pm$0.02)	QS, mm/s ($\pm$0.02)	% ($\pm$1)	IS, mm/s ($\pm$0.02)	Γ, mm/s ($\pm$0.02)	QS, mm/s ($\pm$0.02)	% ($\pm$1)
(a)	4.2	0.56	0.33	0.92	86	0.52	0.31	0.24	14
	77	0.55	0.27	0.92	84	0.54	0.26	0.25	16
	300	0.44	0.26	0.96	81	0.42	0.33	0.21	19
(b)	77	0.55	0.26	0.92	90	0.52	0.26	0.32	10

[a] (a) for ULM-14; (b) after partial dehydration of ULM-14. [b] Abbreviations: IS, isomer shift; Γ, linewidth; QS, quadrupolar splitting; %, contribution.
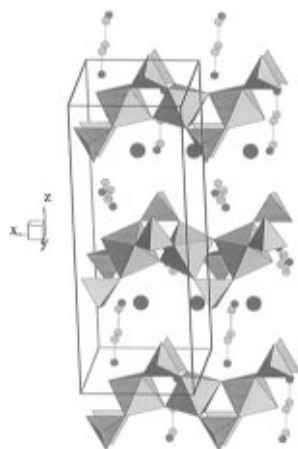
Figure 3. Perspective view of ULM-14. Black circles correspond to the (4c) site partially occupied by water molecules (see text).
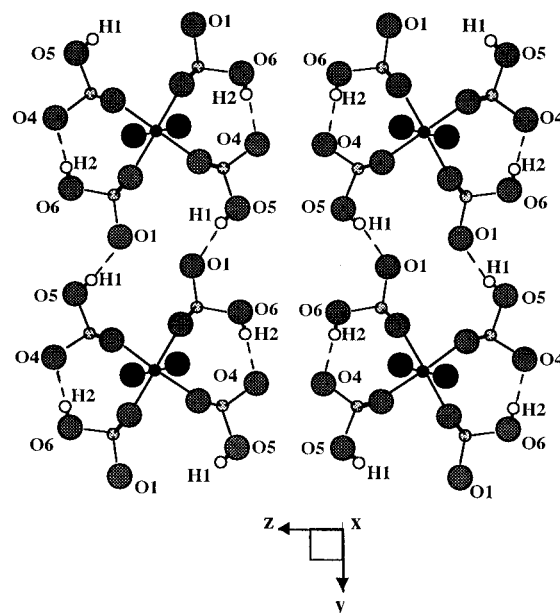

Figure 4. Projection of ULM-14 along [100]. Hydrogen bonds are represented by dashed lines. Iron and fluorine atoms are represented by small and large black circles, respectively.

their type of connection on the iron files define different types of chains already referenced in the litterature: (i) In ULM-10 and ULM-11,[5] adjacent octahedra are bridged by one tetrahedron thus leading to the laueite type chain. (ii) In ULM-14 and ULM-15,[7] adjacent octahedra are bridged by two tetrahedra; this $[M(T\phi_4)_2\phi]_n$ chain (M and T are cations of different coordination, ϕ = O, OH, F) is encountered in the mineral tancoite [LiNa$_2$HAl(PO$_4$)$_2$(OH)] discovered by Hawthorne[12] and the synthetic aluminophosphate [Na$_4$Al(PO$_4$)$_2$(OH)],[13] both based on $[Al(PO_4)_2(OH)]^{4-}{}_n$ chains. In these chains, AlO$_4$(OH)$_2$ octahedra share their trans (OH) vertices.

In ULM-14, all tetrahedra are occupied by HPO$_4$ groups. As indicated in Tables 2 and 3, each tetrahedron presents an hydroxyl group (O5−H1 for HP(1)O$_4$ and O6−H2 for HP(2)-O$_4$) and a free oxygen vertex (O4 for HP(1)O$_4$ and O1 for HP-(2)O$_4$). As a result, O1 and O4 develop strong hydrogen bonds to ensure their valence: d(O1−H1) = 1.867 Å, d(O4−H2) = 1.849 Å (inter- and intrachain hydrogen bonds, respectively). This is illustrated in Figure 4.
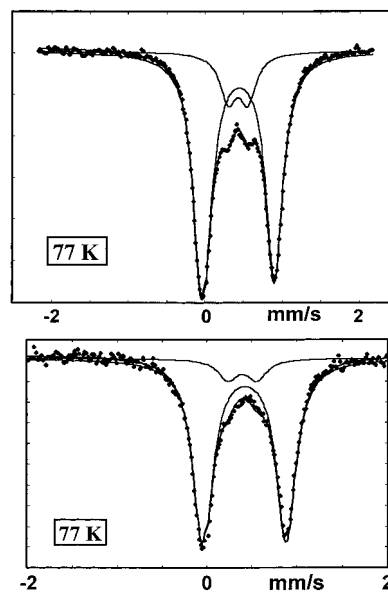
Usual strong hydrogen bonds between some oxygen atoms of the anionic inorganic chains and some hydrogen atoms of the diprotonated amines are also observed: d(O1−H8) = 1.879 Å, d(O2−H3) = 2.156 Å, d(O3−H7) = 1.941 Å.

Magnetic Study

Mössbauer spectra recorded on ULM-14 at 300, 77, 4.2, and 2 K exhibit similar hyperfine structures resulting only from the presence of pure quadrupolar interactions. As illustrated in Figure 5a, the 77 K Mössbauer spectrum consists of two quadrupolar components with narrow lines. The refined values of the hyperfine parameters are listed in Table 4. The isomer shift values are consistent with the presence of octahedrally coordinated Fe^{3+} sites in a high-spin state. The main component

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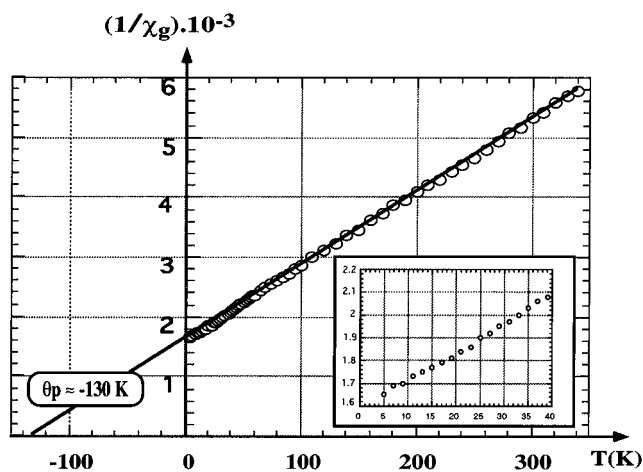

Figure 5. (a) Top: 77 K Mössbauer spectrum of ULM-14. The two doublets are represented. (b) Bottom: 77 K Mössbauer spectrum of ULM-14 after dehydration. A decrease of the minor doublet is observed.

is unambiguously attributed to the presence of Fe^{3+} ion located in the FeO$_4$F$_2$ octahedron. The presence of water molecules (Ow) randomly distributed at the (4c) site located in the vicinity of iron sites modifies the electric field gradient originating the minor quadrupolar doublet. We checked such an interpretation by performing Mössbauer experiments on the dehydrated ULM-14 sample: As shown in Figure 5b, the sizable decrease of the

Figure 6. Thermal variation of the inverse magnetic susceptibility of ULM-14 (uem/g).

minor doublet confirms previous attribution. However, the relatively rapid rehydration of the compound during sampling prevents one from having a pattern of a fully dehydrated compound.

The temperature dependence of the inverse magnetic susceptibility illustrated in Figure 6 shows that as prepared ULM-14 consistently behaves as a paramagnet, according to the Mössbauer data. The decrease (see insert of Figure 6) would suggest a very low temperature magnetic ordering. The Curie—Weiss temperature ($\Theta_p \approx -130$ K) is consistent with the presence of antiferromagnetic interactions. Indeed, they derive from direct superexchange interactions via F^- ligands between FeO_4F_2 octahedra within tancoite type chains. The values of the superexchange angle (Fe−F−Fe = 131°) favor the presence of weak antiferromagnetic interactions, according to the Goodenough rules.[14] One can expect only magnetic ordering at lower temperatures, because of its structural behavior (1D) and the rather weak interchain magnetic coupling.

Supporting Information Available: Tables S1−S3, listing experimental crystallographic details, anisotropic thermal parameters, and the bond lengths within the amine (2 pages). Ordering information is given on any current masthead page.

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