Open-Framework Materials

$(C_4N_2H_{12})[Fe^{II}_{0.86}Fe^{III}_{1.14}(HPO_3)_{1.39}(HPO_4)_{0.47}(PO_4)_{0.14}F_3]$: A Fluoro–Phosphite–Hydrogenphosphate–Phosphate Iron(II,III) Mixed-Valence Organically Templated Compound**

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The search for new open-framework materials has developed with a great interest owing to their potential applications in catalysis, sorption, and ion-exchange processes.[1] Zeolites are one of the best known and widely used open-framework materials, many efforts have been made to introduce transition-metal cations into these compounds, or substitute the silicate anions by other tetrahedral groups, such as the phosphate.[2] In this way, the introduction of organic molecules to the reaction medium as structure-directing agents has led to the hydrothermal synthesis of a great variety of inorganic–organic hybrid phosphates.[3] In particular, iron phosphates, some of them mixed-valent, have shown interesting magnetic behaviors.[4] Recently, the pyramidal hydrogenphosphite $[HPO_3]^{2-}$ oxoanion, has also been incorporated

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into the structural framework of these kinds of compounds, giving rise to new purely inorganic[5] or organically templated[6] phases.

To date, many organically templated mixed valence $Fe^{II,III}$ phosphates are known.[4] However, less exploratory work has been carried out on incorporating a mixed-valent anionic part into the inorganic framework of these organically templated compounds. As far as we are aware, this is the first time in which both the pyramidal phosphite, $[HPO_3]^{2-}$, and the tetrahedral hydrogenphosphate, $[HPO_4]^{2-}$, as well as the phosphate, $[PO_4]^{3-}$, oxoanions form part of the inorganic skeleton of a mixed-valent iron(II,III) phase. This phase has the formula $(C_4N_2H_{12})[Fe^{II}_{0.86}Fe^{III}_{1.14}(HPO_3)_{1.39}(HPO_4)_{0.47}(PO_4)_{0.14}F_3]$ (**1**). Herein we describe the synthesis, crystal structure, Mössbauer and magnetic behavior of this fluoro–phosphite–hydrogenphosphate–phosphate iron(II,III) mixed-valence organically templated compound.

Compound **1** has been prepared under mild hydrothermal conditions from a mixture of phosphorous, phosphoric, and hydrofluoric acids, Fe^{II} and Fe^{III} sulfates, piperazine, ethanol, and water. Dark brown prismatic single-crystals were obtained. Pattern matching analysis of the X-Ray powder diffraction data of the bulk sample provided a good agreement with single-crystal structure data.

The structure consists of $[Fe^{II}_{0.86}Fe^{III}_{1.14}(HPO_3)_{1.39}(HPO_4)_{0.47}(PO_4)_{0.14}F_3]^{2-}$ chains running along the [010] direction (Figure 1 a). The piperazinium cations are in the cavities of the structure delimited by three different chains. These organic cations establish both ionic interactions and hydrogen bonds with the anionic chains, which are surrounded by six piperazinium cations, and hydrogen bonded to four neighboring chains.

The $[Fe^{II}_{0.86}Fe^{III}_{1.14}(HPO_3)_{1.39}(HPO_4)_{0.47}(PO_4)_{0.14}F_3]^{2-}$ chains are formed by a central chain built of $[Fe(2)^{II}O_4F_2]$ edge-sharing octahedra, and two side chains formed by alternating $[Fe(1)^{III}O_3F_3]$ octahedra and $[HP(1)O_{3.11}]$ tetrahedra. The O(3) and F(3) atoms form the common edge of the $[Fe(2)^{II}O_4F_2]$ polyhedra, and are also shared with the $[HP(1)O_{3.11}]$ and $[Fe(1)^{III}O_3F_3]$ polyhedra, respectively. The $[HP(2)O_{3.50}]$ tetrahedra link two edge-sharing $[Fe(2)^{II}O_4F_2]$ octahedra and one $[Fe(1)^{III}O_3F_3]$ octahedron along the chains (Figure 1 b).

Direct methods[7] were employed to solve the structure, and refined by the full-matrix least-squares method based on F^2, by using the SHELXL 97[8] computer program belonging to the WINGX software package.[9] Throughout solution and refinement processes only three oxygen atoms near P(1) and four near P(2) were found. Finally, a 2 e Å^3 peak near P(1) appeared in the difference electron-density map that was assigned to the phosphite hydrogen atom. At the end of the refinement, the P(1)–H separation (1.54 Å) was much greater than the theoretical value (1.30 Å) and the isotropic thermal factor was extremely low. Instead, the isotropic thermal factor of the O(8) oxygen atom, which is not coordinated to any metal atom and belongs to the $(HP(2)O_4)$ group, was very high.

The presence of both phosphite and hydrogenphosphate groups in the two P(1) and P(2) phosphorus sites was considered. The P(1)–H separation was fixed to the theoretical value, 1.30 Å, and the site occupation factor of the O(8) atom was considered as a variable. After some refinement cycles the peak near P(1) was assigned to the fourth oxygen atom O(7) from the hydrogenphosphate unit. Finally, the protons corresponding to the hydrogenphosphate groups were geometrically placed and the H- and HO- groups were treated as disordered groups with complementary occupation factors.

After convergence was achieved, we found that all thermal factors shown reasonable values, and the phosphorus–oxygen separations were in excellent agreement with those expected for the hydrogenphosphate groups. The final occupation factors were 0.11 for the hydrogenphosphate in

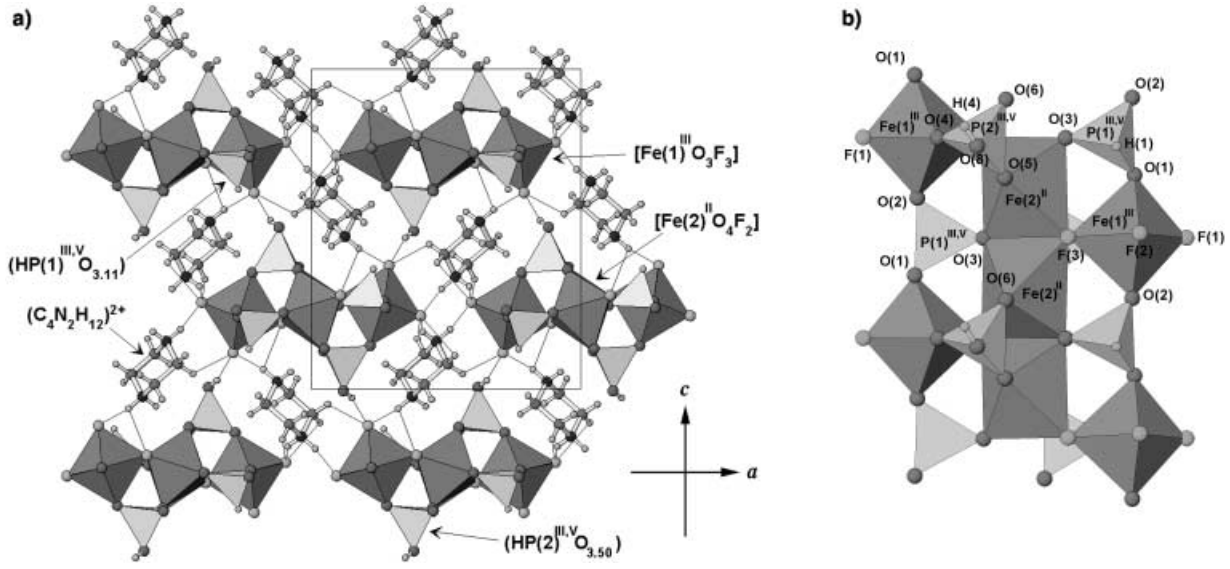

Figure 1. a) Polyhedral view of **1** along the [010] direction. b) Detailed polyhedral view of the anionic triple chain. Both phosphite and hydrogenphosphate–phosphate groups are present in two phosphorus crystallographic sites, only those with site occupation factors equal or greater than 0.50 have been represented.

P(1) and 0.50 for the phosphite in P(2). Bond-valence calculations[10] for the P(1) and P(2) phosphorus atoms treated as a part of the hydrogenphosphate groups provided values of 4.86 and 4.77, respectively. However, when these calculations were made by treating both phosphorus atoms as belonging to phosphite[11] groups we obtained 4.08 for the $HP(1)^{4+}$ and 4.00 for $HP(2)^{4+}$ groups. Bond-valence sum calculations were also carried out for the iron atoms, which gave values of 3.06 and 2.04 for Fe(1) and Fe(2), respectively. Finally, the electroneutrality of the formula of this compound also requires the existence in the chemical composition of the $[PO_4]^{3-}$ oxoanion in an amount of 0.14 ions per formula. The presence of this anion was confirmed by IR spectroscopy where a band at approximately 1010 cm^{-1} appears. Bands corresponding to the $[HPO_4]^{3-}$ and $[HPO_3]^{2-}$ oxoanions were also observed.

The Mössbauer spectrum shows the presence of pure electric hyperfine interactions, and seems to be formed by two doublets corresponding to the Fe^{III} and Fe^{II} ions in the Fe(1) and Fe(2) sites, respectively (Figure 2). The simulation for Fe^{II}

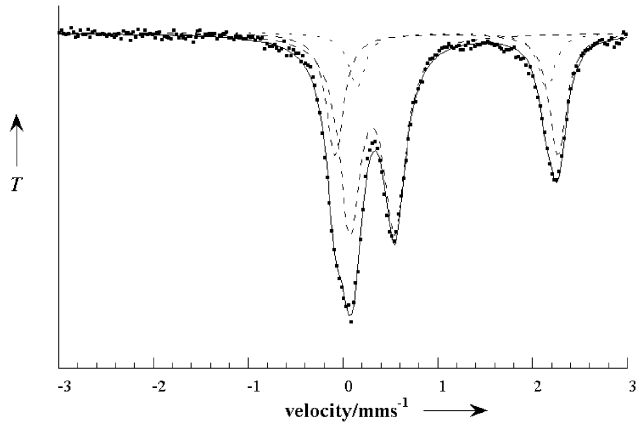

Figure 2. Simulation (-----) of the Mössbauer spectrum employing three doublets. (● data points, —— fit.)

in the Fe(2) site was performed by using a convolution of doublets with the same line-width, isomer shift, and intensity distribution over a quadrupole splitting interval. A distribution with two maxima was obtained. This result was attributed to the presence of slightly different chemical environments for Fe(2) related to the substitution of phosphite (P^{III}) by hydrogen-phosphate (P^{V}) in the P(2) neighboring position. In this way, the best simulation was made considering two doublets for the Fe^{II} ions in Fe(2)a and Fe(2)b positions (see Table 1) taking into account the two chemical environments, and one doublet for the Fe^{III} ions in Fe(1), allowing us to obtain a reasonably good fit (Figure 2). Attempts to simulate the spectrum by employing only two doublets corresponding to the Fe^{II} and Fe^{III} cations gave unsatisfactory results.

The isomer-shift and quadropole-spliting values are in good agreement with those expected for Fe^{III} and Fe^{II} ions in octahedral coordination environments (Table 1). Oxidation states are trapped in their positions and evidence of Fe^{III}/Fe^{II} substitution is not observed, which is in good agreement with

Table 1: Values of isomer shift (IS), quadrupolar splitting (QS), area percentage, and assignation of each doublet in the final simulation of the Mössbauer spectrum.

Site	IS [mm s^{-1}]	QS [mm s^{-1}]	Ox. State	Area percentage	
Fe(1)	0.419	0.474	+3	57.1	
Fe(2)a	1.202	2.352	+2	29.9	42.9
Fe(2)b	1.255	2.003	+2	13.0	

the bond-valence calculations. The ratio between Fe(1) and Fe(2) is close to 1, which is in accord with their multiplicities.

Magnetic measurements on powdered samples have been performed from room temperature to 5.0 K. The thermal evolution of $1/\chi_m$ follows the Curie–Weiss law for temperatures higher than 130 K, with $C_m = 8.00\ cm^3\,K\,mol^{-1}$ and $\theta = -65.2$ K. Considering, $g = 2$ and $S = 5/2$ for Fe^{III} and the Fe^{III}/Fe^{II} ratio obtained from the Mössbauer spectrum, an effective magnetic moment of 5.30 μ_B per Fe^{II} ion was calculated, in good agreement with those usually found for octahedral high-spin Fe^{II} ions. The molar susceptibility increases from room temperature with decreasing temperature and reaches a maximum at approximately 22 K, which indicates the existence of antiferromagnetic interactions, with a magnetic ordering at temperatures below 22 K. The complexity of this system prevented us from modeling the magnetic behavior.

In conclusion, the new organically templated phase synthesized by using mild hydrothermal conditions exhibits a mixed-valence nature and the phosphite and hydrogenphosphate–phosphate oxoanions are both present together.

Experimental Section

Hydrothermal synthesis (443 K, 5 days) was carried out in a PTFE-lined stainless steel pressure vessel in which a previously stirred mixture of H_3PO_3 (15 mmol), H_3PO_4 (85%; 5.2 mmol), HF (48%), $Fe(SO_4)\cdot 7H_2O$ (1.5 mmol), $Fe_2(SO_4)_3\cdot 5H_2O$ (0.75 mmol), $C_4N_2H_{10}$ (37 mmol) ethanol, and water was placed. The percentage of the elements in the product was calculated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and elemental analysis. Fluoride content was measured with an ion-selective electrode. A chemical analysis confirmed the existence of two oxidation states for iron (Fe^{II}:Fe^{III} close to 1). Calcd (%) for $(C_4N_2H_{12})[Fe^{II}_{0.86}Fe^{III}_{1.14}(HPO_3)_{1.39}(HPO_4)_{0.47}(PO_4)_{0.14}F_3]$: C 11.1, H 3.3, N 6.5, F 13.1, Fe 25.7, P 14.8; found: C 10.7, H 3.0, N 6.4, F 13.0, Fe 25.5,P 14.5.

Mössbauer measurements were recorded at room temperature in the transmission geometry using a conventional constant-acceleration spectrometer with a $^{57}CoRh$ source. The fit of the Mössbauer spectrum has been performed using the NORMOS program.[12] Magnetic measurements on powdered sample were performed at temperatures between 5.0–300 K, using a Quantum Design MPMS-7 SQUID magnetometer. The magnetic field was 0.1, 0.05, and 0.01 T, values in the range of linear dependence of magnetization versus magnetic field, even at 5.0 K.

Crystal data of $C_4H_{13.86}F_3Fe_2N_2O_{6.61}P_2$: $M = 426.57$, orthorhombic, $P2_12_12_1$, $a = 12.790(2)$, $b = 6.440(1)$, $c = 15.167(1)$ Å, $V = 1249.3(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.268\ g\,cm^{-3}$, $D_M = 2.25(1)\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 2.646\ mm^{-1}$, 2049 total (2049 independent) reflections, $2.08 < \theta < 29.94$, $R = 0.045$ and $R_w = 0.113$ for 1822 reflections with $I > 2\sigma(I)$, absolute structure parameter 0.05(3). Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax:

(+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-413223.

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