

LETTER TO THE EDITOR

Oxyfluorinated Microporous Compounds

XI. Synthesis and Crystal Structure of ULM-10: The First Bidimensional Mixed-Valence Iron Fluorophosphate with Intercalated Ethylenediamine

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The first oxyfluorinated iron(II, III) phosphate ($\text{Fe}^{3+}\text{Fe}^{2+}\text{F}_2(\text{HPO}_4)_2(\text{H}_2\text{O})_2$, ethylenediamine] with an open structure has been synthesized. It is triclinic (*P*-1 (No. 2), $a = 5.174(2) \text{ \AA}$, $b = 7.518(2) \text{ \AA}$, $c = 8.773(3) \text{ \AA}$, $\alpha = 108.37(1)^\circ$, $\beta = 97.33(2)^\circ$, $\gamma = 109.86(2)^\circ$, $Z = 1$). Its bidimensional structure contains chains of Fe(II) and Fe(III) octahedra, arranged in an ordered way and linked to each other by phosphate groups. © 1994 Academic Press, Inc.

INTRODUCTION

The tremendous amount of work devoted to microporous alumino- and gallophosphates either undoped or partially substituted by transition metals was initiated by Flanigen *et al.* (1). It is only very recently that Soghomonian *et al.* (2) succeeded in obtaining microporous phosphates with only 3d transition metals, instead of Al and Ga. In the same way, we recently showed (3) that microporous oxyfluorinated metallophosphates could be obtained with vanadium in addition to the many compounds that Kessler (4) and our group synthesized with Al and Ga (5). We present here the first compound of this series containing only iron, in the mixed-valence state.

EXPERIMENTAL

$[\text{Fe}^{2+}\text{Fe}^{3+}\text{F}_2(\text{HPO}_4)_2(\text{H}_2\text{O})_2$, ethylenediamine (en)] (ULM-10) was synthesized under hydrothermal conditions. The starting mixture corresponded to the molar ratio $2\text{FeO}(\text{OH}) : 2\text{H}_3\text{PO}_4 : 2\text{HF} : 2$ ethylenediamine : $80\text{H}_2\text{O}$. It was sealed in a Teflon-lined stainless steel autoclave and heated to 453 K for 24 hr under autogenous pressure. The initial pH was 4 and increased to 7 by the end of the reaction. The resulting product consists

TABLE 1
Final Atomic Coordinates ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
P	4686(1)	392(1)	7737(1)	7(1)
Fe(1)	0	0	0	7(1)
Fe(2)	5000	5000	0	11(1)
O(1)	7467(4)	115(4)	8147(3)	16(1)
O(2)(OH)	3486(4)	-728(3)	5803(2)	12(1)
O(3)	2439(4)	-649(3)	8499(3)	13(1)
O(4)	5293(5)	2655(3)	8156(3)	18(1)
F	2218(4)	2938(3)	793(3)	17(1)
O _w	1304(6)	4852(5)	-1685(3)	24(1)
N	2290(5)	2631(4)	5017(3)	15(1)
C	3445(6)	4683(5)	-5028(4)	18(1)

of transparent pink-brown crystalline platelets. They were filtered off and dried in air at room temperature. The fluorine content was determined with a specific electrode and F/Fe and F/P ratios equal to 1 were obtained. A suitable crystal was isolated for the X-ray study on the four-circle diffractometer SIEMENS AED2 ($\lambda_{\text{Mo}} = 0.71073 \text{ \AA}$).

ULM-10 crystallizes in space group *P*-1 (No. 2) with cell parameters $a = 5.174(2) \text{ \AA}$, $b = 7.518(2) \text{ \AA}$, $c = 8.773(3) \text{ \AA}$, $\alpha = 108.37(1)^\circ$, $\beta = 97.33(2)^\circ$, $\gamma = 109.86(2)^\circ$, $V = 293.9 \text{ \AA}^3$, $Z = 1$ for the title formula. Table 1 gives the final atomic coordinates of nonhydrogen atoms. Hydrogen positions, anisotropic thermal parameters, and a list of structure factors can be obtained upon request to the authors.

The ULM-10 structure was solved by the direct method involving SHELXS-86 (6), a program for the refinement of crystal structure determination. Fe and P atoms were first located. All the remaining atoms and the amine skeleton were found by the difference-Fourier map technique. Geometric constraints were applied to hydro-

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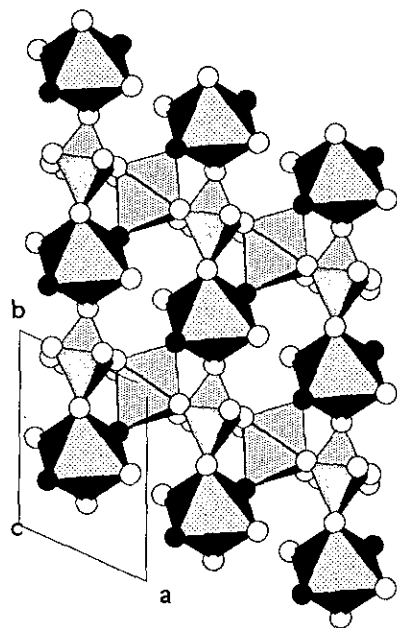


FIG. 1. Projection of $[\text{Fe}^{2+}\text{Fe}^{3+}\text{F}_2(\text{HPO}_4)_2(\text{H}_2\text{O})_2, \text{en}]$ along the [001] axis. Fe^{2+} octahedra are dark, and those of Fe^{3+} are lighter. Fluorine atoms are represented as black circles. Phosphorus tetrahedra link iron chains.

gen in the hydroxyl and the amino groups in order to accurately locate them. Refinements were performed by the full-matrix least-squares analysis (SHELXL-93 (7)), with anisotropic thermal parameters for all nonhydrogen atoms. An identical isotropic thermal parameter was applied to hydrogen. The reliability factor converges to $R = 0.045$, $wR_2 = 0.117$, for 2294 reflections ($I \geq 2\sigma(I)$).

DISCUSSION

The ULM-10 network is bidimensional (Fig. 1). Inorganic and organic layers alternate along the [001] direction. The inorganic layers are built up from HPO_4 phosphorus tetrahedra ($\langle \text{P}-\text{O} \rangle = 1.523$ to 1.537 Å, $\langle \text{P}-\text{OH} \rangle = 1.565$ Å) which link two types of octahedra: FeO_4F_2 and $\text{FeO}_2\text{F}_2(\text{H}_2\text{O})_2$. The Fe–F distances are $\langle \text{Fe}(1)-\text{F} \rangle = 1.946$ Å and $\langle \text{Fe}(2)-\text{F} \rangle = 2.093$ Å; the bond valence calculations (8) and a preliminary Mössbauer spectroscopy experiment indicate that iron exhibits two oxidation states: Fe(1) corresponds to Fe^{3+} , and Fe(2) to Fe^{2+} . This mixed-valence state is also reflected by the Fe–O distances: $\langle \text{Fe}^{3+}-\text{O} \rangle = 1.997$ to 2.001 Å and $\langle \text{Fe}^{2+}-\text{O} \rangle = 2.048$ Å. Moreover,

on the Fe^{2+} octahedron, water molecules are terminal ($\langle \text{Fe}^{2+}-\text{O}_w \rangle = 2.210$ Å).

To satisfy electroneutrality, the diamine must be half-protonated; the formula of ULM-10 is therefore $[\text{Fe}^{3+}\text{Fe}^{2+}\text{F}_2(\text{HPO}_4)_2(\text{H}_2\text{O})_2], \text{en}$.

Fe^{2+} and Fe^{3+} octahedra share their fluorine vertices to form *trans* chains along [110]. Two chains are linked by two HPO_4 tetrahedra whose OH group points toward the intercalated amine. This connection provides P– Fe^{3+} –P– Fe^{3+} chains along [100] and therefore ensures the formation of the inorganic layer. Strong hydrogen bonds between the amino group of the organic layer and the OH group of the HPO_4 tetrahedra are responsible for the cohesion of the structure.

This structure is interesting from three points of view: (i) it is one of the rare examples involving half-protonation of a linear diamine, in agreement with the final pH of the solution; (ii) magnetically, two ways of superexchange exist in the layers, 180° superexchange via F^- along [110] between Fe^{2+} and Fe^{3+} octahedra as well as supersuperexchange along [100] via the oxygens of HPO_4 groups which involve exclusively Fe^{3+} – Fe^{3+} interactions (a complete magnetic and Mössbauer study is in progress to elucidate the magnetic properties of this compound); and (iii) this compound probably represents a unique example of a solid synthesized from the solution which might be formed by the infinite condensation of monophosphate complexes of iron(II) and iron(III). The study of the formation mechanism of ULM-10 starting from the nature of the complex species in the solution is in progress. The corresponding results should shed some light on the mechanisms of the formation of solid species from the solution.

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REFERENCES

1. S. T. Wilson, B. M. Lok, C. A. Messina, and E. M. Flanigen, *J. Am. Chem. Soc.* **104**, 1146 (1982).
2. V. Soghomonian, Q. Chen, R. C. Haushalter, J. Zubieta, C. J. O'Connor, and Y. S. Lee, *Chem. Mater.* **5**, 1690 (1993); V. Soghomonian, Q. Chen, R. C. Haushalter, and J. Zubieta, *Chem. Mater.* **5**, 1595 (1993).
3. D. Riou and G. Férey, *J. Solid State Chem.* **111**, 422 (1994).
4. M. Estermann, L. B. McCusker, C. Baerlocher, A. Merrouche, and H. Kessler, *Nature* **352**, 320 (1991).
5. T. Loiseau and G. Férey, *J. Solid State Chem.* **111**, 403 (1994).
6. G. M. Sheldrick, *Acta Crystallogr. Sect. A* **46**, 467 (1990).
7. G. M. Sheldrick, SHELXL-93, University of Göttingen, Germany (1993).
8. N. Brese and M. O'Keeffe, *Acta Crystallogr. Sect. B* **47**, 192 (1991).