*Inorg. Chem.* **2001,** *40,* 5691−5694

# Notes

## A New Three-Dimensional Inorganic−Organic Hybrid Fluorinated−Iron(III) Arsenate: $(C_6H_{14}N_2)[Fe_3(HAsO_4)_2(AsO_4)F_4]0.5H_2O$. Hydrothermal Synthesis, Crystal Structure, and Spectroscopic and Magnetic Properties

**Begoña Bazán, José L. Mesa, José L. Pizarro,[†]
A. Goñi, L. Lezama, María I. Arriortua,[†] and
Teófilo Rojo***

Departamento de Química Inorgánica and Departamento de
Mineralogía-Petrología, Facultad de Ciencias, Universidad
del País Vasco, Apdo. 644, E−48080 Bilbao, Spain

*Received April 9, 2001*

### Introduction

Work on the synthesis and characterization of new microporous materials continues apace, revealing an ever increasing variety of framework composition topologies. In this way, much research has been devoted to the hydrothermal synthesis of new 3d transition metal open-framework compounds.[1] Most of these compounds are mixed organic−inorganic phases in which amine molecules act as templating agents. In past years, a large number of transition metal phosphates with open architectures have been synthesized.[2−7] The incorporation of transition elements is particularly fascinating due to the possibility of the variation in coordination environment around the metal ion and the possibility of observing interesting magnetic properties.[7−9] Among these materials, iron phosphates occupy a first position because they have given rise to a rich structural chemistry.[2,8−13] The open-framework iron phosphates are sometimes synthesized hydrothermally employing fluorine ions, which often get incorporated as a part of the framework and act as a bridge between the iron centers.[10−13]

Since phosphorus and arsenic belong to the same group in the periodic table, arsenates are also interesting anions, in comparison with the phosphates, for use in the attainement of compounds with occluding organic amines. In this sense, some arsenates of aluminum, gallium, zinc, vanadium, molibdenum, and iron have been reported in the literature.[14−17] To exploit more possibilities in open-framework metal arsenates, we performed mild hydrothermal reactions in the iron(III)−diamine−arsenate system. In this work, we present a new three-dimensional hybrid inorganic−organic iron(III)−fluorinated arsenate, $(C_6H_{14}N_2)[Fe_3(HAsO_4)_2(AsO_4)F_4]0.5H_2O$, synthesized using 1,4-diazabicyclo[2.2.2]octane as a structural directing agent.

### Experimental Section

**Synthesis and Initial Characterization.** The compound was synthesized hydrothermally under autogenous pressure from the reaction of $As_2O_5{\cdot}3H_2O$ (3.70 mmol), 1,4-diazabicyclo[2.2.2]octane (8.85 mmol), $FeCl_3{\cdot}6H_2O$ (0.56 mmol), and HF (57.5 mmol) in ca. 30 mL of water. The reaction mixture with pH of ca. 1.5 was stirred to homogeneity and then sealed in a PTFE-lined stainless steel pressure vessel (fill factor 75%); the mixture was heated at 170 °C for 5 days. The pH did not show any appreciable change during the hydrothermal reaction. The resulting product consists of prismatic, light green single-crystals as the only product, in a yield of 80% based on iron. The powder X-ray diffraction pattern of the bulk product was in good agreement with the calculated diffractogram based on the results from single-crystal X-ray diffraction. Chemical analysis by inductively coupled plasma atomic emission spectroscopy (ICP−AES), performed with an ARL Fisons 3410 spectrometer, confirmed the amount of the iron and arsenic elements. C, H, N elemental analysis was carried out with a Perkin−Elmer Model 240 automatic analyzer. Fluorine content was determined using quantitative chemical analysis. Found: Fe, 21.1; As, 28.3; C, 9.0; H, 2.0; N, 3.4; F, 9.0%. Calcd: Fe, 21.3; As, 28.6; C, 9.2; H, 2.2; N, 3.6; F, 9.7%.

The thermal behavior was studied by thermogravimetric analysis, which was carried out on a SDC 2960 Simultaneous DSC−TGA TA Instrument under a flow of air up to 800 °C with a heating rate of 2.5 °C/min. Time-resolved X-ray thermodiffractometry was performed in an air atmosphere with a PHILIPS X′PERT automatic diffractometer (Cu Kα radiation) equipped with a variable-temperature stage (Anton Paar HTK16) and a Pt sample holder. The thermal decomposition curve reveals a continuous weight loss (ca. 25.0%) between ca. 180 and 320 °C, which can be attributed to the simultaneous loss of the water molecule, the 1,4-diazabicyclooctane dication, and the fluorine ions present in the compound (calc. 25.6%). In the ca. 380−400 °C range a weight loss (ca. 25%) occurs, which can be assigned to a partial decomposition of the arsenate anions and a sublimation process giving $As_2O_3$ and/or $As_2O_5$.[18] The decomposition product obtained below ca. 540 °C is amorphous. In the ca. 540−645 °C range, the X-ray patterns show peaks which cannot be identified with phases given in the PDF base data.[19] Above ca. 645 °C the diffractograms indicate the existence

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* To whom correspondence should be addressed. Telephone: 34−946012458. Fax: 34−944648500. E-mail: qiproapt@lg.ehu.es.

[†] Departamento de Mineralogía-Petrología, Universidad del País Vasco.

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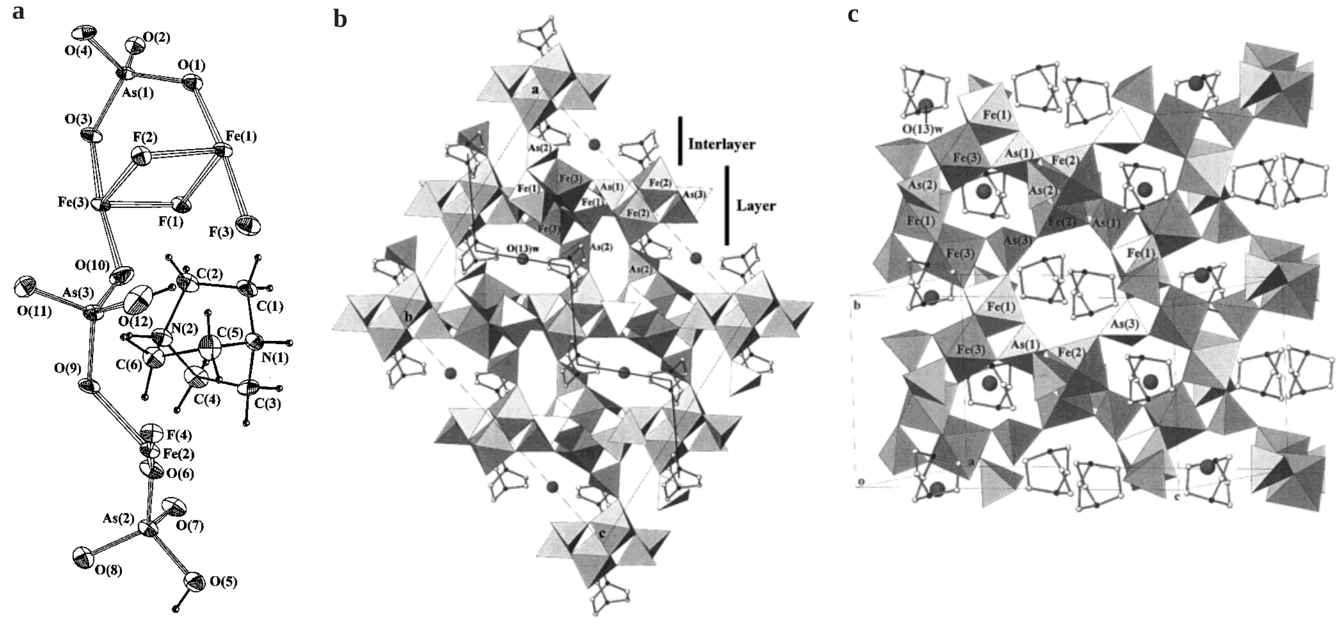

**Figure 1.** (a) ORTEP drawing (50% thermal ellipsoids) of the asymmetric unit of $(C_6H_{14}N_2)[Fe_3(HAsO_4)_2(AsO_4)F_4]0.5H_2O$ with detailed labeling of the atoms. (b) Polyhedral view of $(C_6H_{14}N_2)[Fe_3(HAsO_4)_2(AsO_4)F_4]0.5H_2O$ showing the three-dimensional structure. (c) Polyhedral representation of a layer of $(C_6H_{14}N_2)[Fe_3\ (HAsO_4)_2(AsO_4)F_4]0.5H_2O$.

of $Fe(AsO_4)$, $Fe_3(AsO_7)$, and $Fe_2O_3$ in its hematite synthetic form;[19] $Fe(AsO_4)$ is the majority phase.

The IR spectrum (KBr pellet) was obtained with a Nicolet FT−IR 740 spectrophotometer. The spectrum shows the bands of the stretching and bending modes of the water molecule at 3420 and 1640 $cm^{-1}$, respectively. Bands above 3500 $cm^{-1}$ were not observed, in accordance with the absence of $(OH)^-$ groups in the crystal structure.[20] The asymmetrical stretching mode of the arsenate anion appears as a broad band centered at ca. 820 $cm^{-1}$. The symmetrical stretch is detected at 735 $cm^{-1}$. The asymmetrical deformation vibration is observed at 500 $cm^{-1}$. The bands at 2325 and 1210 $cm^{-1}$ are assigned to the stretching and bending modes of the HO−As bonds from the hydrogenarsenate groups.[17,20] The vibrations of the organic skeleton of the 1,4-diazabicyclooctane dication appear in the 1500−1300 $cm^{-1}$ range.

**Single-Crystal X-ray Diffraction.** Intensities of the diffraction data were collected on an Nonius KappaCCD equipped with a Cu anticatode, $\lambda$ radiation 1.5418 Å. A single crystal with dimensions 0.24 × 0.12 × 0.08 mm was used. Crystallographic data are reported in Table 1. 3428 reflections were collected in the whole Ewald sphere for $4.46° \leq \theta \leq 69.86°$, all were independent. The intensity data were corrected for Lorentz and polarization effects.[21] Absorption corrections were also performed using the XRED program.[22] The structure was solved by direct methods (SHELXS 97 program[23]) and refined by the full-matrix least-squares method based on $F^2$, using the SHELXL 97 computer program.[24] The atomic scattering factors were taken from the international tables for X-ray crystallography.[25] All non-hydrogen atoms were assigned anisotropic thermal parameters. Hydrogen atoms were geometrically placed except for those of the water molecule, which were not located. The least-squares refinement led to the final reliability factors, R1 = 0.062 and wR2 = 0.158, obtained by fitting 278 parameters. The final difference Fourier map had maximum and minimum peaks of 2.07 and −1.70 $eÅ^{-3}$. All drawings were made using the ATOMS program.[26] Selected bond distances and angles are given in Table 2.

**Table 1.** Crystallographic Data for $(C_6H_{14}N_2)[Fe_3(HAsO_4)_2(AsO_4)F_4]0.5H_2O$

| | |
|---|---|
| formula | $C_6H_{17}As_3F_4Fe_3N_2O_{12.5}$ |
| *a*, Å | 18.323(1) |
| *b*, Å | 10.118(1) |
| *c*, Å | 20.623(1) |
| $\beta$, ° | 106.03(1) |
| *V*, Å$^3$ | 3674.6(2) |
| *Z* | 8 |
| formula weight (g mol$^{-1}$) | 785.53 |
| space group | *C*2/*c* (no. 15) |
| *T*, K | 200(2) |
| radiation, $\lambda$(Cu K$\alpha$), Å | 1.5418 |
| $\rho_{obsd.}$, $\rho_{calcd.}$, g cm$^{-3}$ | 2.83(3), 2.840 |
| $\mu$ (Mo K$\alpha$), mm$^{-1}$ | 25.812 |
| $R\ [I > 2\sigma(I)]^a$ | R1= 0.062 wR2= 0.158 |
| $R$ [all data]$^a$ | R1= 0.064 wR2= 0.161 |

[a] $R1 = [\Sigma(|F_o| - |F_c|)]/\Sigma|F_o|$; $wR2 = [\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]]^{1/2}$ ; $w = 1/[\sigma^2|F_o|^2 + (xp)^2\ ]$; where $p = [|F_o|^2 + 2|F_c|^2]/3$; $x = 0.1385$.

**Physical Measurements.** A Bruker ESP 300 spectrometer was used to record the ESR polycrystalline spectra. The temperature was stabilized by an Oxford Instrument (ITC 4) regulator. The magnetic field was measured with a Bruker BNM 200 gaussmeter, and the frequency inside the cavity was determined using a Hewlett−Packard 5352B microwave frequency counter. Magnetic measurements of the powdered sample were obtained in the temperature range 4.2−300 K using a Quantum Design MPMS-7 SQUID magnetometer. The magnetic field was 0.1 T, which is within the range of linear dependence of magnetization versus magnetic field even at 5.0 K.

## Results and Discussion

The asymmetric unit of $(C_6H_{14}N_2)[Fe_3(HAsO_4)_2(AsO_4)F_4]0.5H_2O$ is shown in Figure 1a. The structure consists of a three-dimensional framework formed by $[Fe_3(HAsO_4)_2(AsO_4)F_4]^{2-}$

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**Table 2.** Selected Bond Distances (Å) for $(C_6H_{14}N_2)[Fe_3(HAsO_4)_2\ (AsO_4)F_4]0.5H_2O$ (E.S.D. in Parentheses)[a]

| $Fe_1O_6$ octahedron | | $Fe_2O_6$ octahedron | | $Fe_3O_6$ octahedron | |
|---|---|---|---|---|---|
| Fe(1)−O(1) | 1.940(4) | Fe(2)−O(6) | 1.932(5) | Fe(3)−F(3)$^{v}$ | 1.943(4) |
| Fe(1)−O(7)$^{i}$ | 1.943(4) | Fe(2)−O(4)$^{ii}$ | 1.951(4) | Fe(3)−O(8)$^{vi}$ | 1.960(5) |
| Fe(1)−O(11)$^{ii}$ | 1.953(5) | Fe(2)−O(9) | 1.969(4) | Fe(3)−O(10) | 1.969(5) |
| Fe(1)−F(3) | 1.987(4) | Fe(2)−O(2)$^{iii}$ | 1.988(5) | Fe(3)−O(3) | 1.999(5) |
| Fe(1)−F(1) | 2.025(3) | Fe(2)−F(4)$^{iv}$ | 2.016(4) | Fe(3)−F(1) | 2.002(4) |
| Fe(1)−F(2) | 2.028(4) | Fe(2)−F(4) | 2.044(3) | Fe(3)−F(2) | 2.010(4) |
| | | intradimer | | | |
| Fe(1)−Fe(3) | 3.126(2) | Fe(2)−Fe(2) | 3.148(2) | | |
| | | interdimer | | | |
| Fe(1)−Fe(3) | 3.608(2) | | | | |
| $As(1)O_4$ tetrahedron | | $As(2)O_4$ tetrahedron | | $As(3)O_4$ tetrahedron | |
| As(1)−O(4) | 1.670(4) | As(2)−O(6) | 1.649(4) | As(3)−O(10) | 1.653(5) |
| As(1)−O(1) | 1.679(4) | As(2)−O(8) | 1.666(5) | As(3)−O(9) | 1.659(4) |
| As(1)−O(3) | 1.679(4) | As(2)−O(7) | 1.677(4) | As(3)−O(11) | 1.670(4) |
| As(1)−O(2) | 1.692(4) | As(2)−O(5) | 1.723(5) | As(3)−O(12) | 1.720(5) |
| | | $(C_6H_{14}N_2)^{2+}$ | | | |
| N(1)−C(1) | 1.471(9) | N(1)−C(3) | 1.508(8) | N(1)−C(5) | 1.518(9) |
| N(2)−C(2) | 1.483(8) | N(2)−C(4) | 1.492(8) | N(2)−C(6) | 1.504(8) |
| C(1)−C(2) | 1.512(9) | C(3)−C(4) | 1.54(1) | C(5)−C(6) | 1.543(9) |

[a] Symmetry codes: $i = x, -y + 1, z - 1/2$; $ii = -x + 1/2, y - 1/2, -z + 1/2$; $iii = x + 1/2, -y + 3/2, z + 1/2$; $iv = -x + 1, -y + 1, -z + 1$; $v = -x + 1/2, y + 1/2, -z + 1/2$; $vi = -x + 1/2, -y + 3/2, -z + 1$.

inorganic layers extended along the (10−1) plane and interconnected by hydrogenarsenate groups. The 1,4-diazabicyclooctane dications compensate for the anionic charge of the sheets and are placed together with the water molecule in the interlayer space (Figure 1b).

The layers are formed by $Fe(1)Fe(3)O_6F_4$ and $Fe(2)_2O_8F_2$ dimeric edge-sharing octahedra. The first dimers are linked through a vertex, giving rise to chains running along the *b* axis (Figure 1c). The chains and the $Fe(2)_2O_8F_2$ dimeric units are connected through the $As(1)O_4$−arsenate and $HOAs(3)O_3$−hydrogenarsenate anions. Two types of cavities can be distinguished in the structure. The cavities of six members are delimited by two $Fe(3)O_3F_3$ and one $Fe(1)O_3F_3$ octahedra, which are linked by the $As(1)O_4$ and $HOAs(3)O_3$ groups to the $Fe(2)O_4F_2$ octahedra. The cavities of eight members are formed by two $Fe(1)O_3F_3$ and two $Fe(2)O_4F_2$ octahedra linked in an alternate way by the $As(1)O_4$ and $HOAs(3)O_3$ anions. The 1,4-diazabicyclooctane dications are located above and below the mean plane determined by these cavities at a distance of ca. 6.6 Å. Another organic dication appears in every side of the sheet, which is placed at a distance of ca. 6.4 Å with respect to the above position (Figure 1b). The layers are interconnected by the $HOAs(2)O_3$−hydrogenarsenate groups. The O(7) and O(8) oxygen atoms of this anion are linked to the $Fe(1)O_3F_3$ and $Fe(3)O_3F_3$ octahedra, respectively, whereas the O(6) atom is linked to the $Fe(2)O_4F_2$ octahedra (Figure 1b). The water molecule is placed between two $HOAs(2)O_3$ anions at a distance of ca. 3.6 Å from every hydrogenarsenate.

The $HOAs(2)O_3$ and $HOAs(3)O_3$ hydrogenarsenate anions establish hydrogen bonds with the water molecule at 1.86(1) Å and with the O(3) oxygen from the $Fe(3)O_3F_3$ octahedra at 2.47(1) Å. The 1,4-diazabicyclooctane dication forms, through the N(1) atom, bifurcated hydrogen bonds with both the F(2) ion and O(5) atom from the $HOAs(2)O_3$ hydrogenarsenate anion at distances of 2.61(1) and 2.08(1) Å, respectively. Finally, the N(2) atom of the organic molecule establishes a strong hydrogen bond at 1.92(1) Å with the O(2) atom belonging to the $Fe(2)O_4F_2$ octahedra.

The ESR spectra of $(C_6H_{14}N_2)[Fe_3(HAsO_4)_2(AsO_4)F_4]0.5H_2O$, performed at X-band on a powdered sample at room temperature and 5.0 K, exhibit isotropic signals with a *g* value of 2.01(1), which remains unchanged with variation in temperature. These results are in good agreement with the presence of high spin Fe(III) cations in octahedral symmetry.

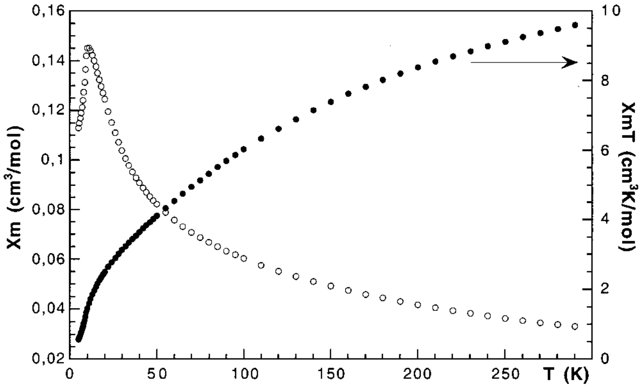

**Figure 2.** Thermal evolution of the $\chi_m$ and $\chi_m T$ curves of $(C_6H_{14}N_2)[Fe_3(HAsO_4)_2(AsO_4)F_4]0.5H_2O$.

Variable-temperature magnetic susceptibility measurements of $(C_6H_{14}N_2)[Fe_3(HAsO_4)_2(AsO_4)F_4]0.5H_2O$ have been carried out on a powdered sample in the range from 5.0 to 300 K. Plots of the $\chi_m$ and $\chi_m T$ versus *T* curves are shown in Figure 2. The molar magnetic susceptibility increases with decreasing temperature and reaches a sharp maximum at ca. 11.2 K, indicating that a long-range magnetic ordering is established at this temperature. After that, the susceptibility decreases continuously. This result together with the decrease of the magnetic moment from 9.60 cm$^3$ K/mol at room temperature to 0.55 cm$^3$K/mol at 5.0 K indicates the presence of antiferromagnetic interactions.

The three-dimensional magnetic ordering can be understood by considering the crystal structure is formed by $[Fe_3(HAsO_4)_2(AsO_4)F_4]^{2-}$ inorganic layers interconnected by hydrogenarsenate groups. To fit the magnetic data to a theoretical model and to obtain the *J* exchange parameter, we considered the system as a simple cubic network. In this sense, the high temperature series expansion developed by Rushbrooke and Wood for a simple cubic antiferromagnetic system with $S = 5/2$ was used.[27] Only the low temperature magnetic data, in the proximity of the maximum, can be reasonably fitted to a value of $|J/K| = 0.41$ K. From the magnetic point of view, another approximation to the problem could be the use of the molecular field theory for a three-dimensional antiferromagnetic system.[28] In this way, the $J$ exchange parameter is estimated by the following expression:

$$\chi_{\max} = (N\beta^2 g^2/4zJ)$$

where $\chi_{\max}$ is the maximum value of the magnetic susceptibility, $N$ is Avogadro's number, $\beta$ is the Bohr magneton, and $z$ is the magnetic coordination number of a lattice site. The $|J/K|$ value calculated is 0.44 K, taking $z = 6$ and $g = 2.01$, as obtained from the ESR spectra. The value of the $J$ exchange parameter obtained from both procedures is in a reasonable accordance. This fact allows us to confirm the three-dimensional character of the magnetic interactions at low temperature in this compound.

The magnetic exchange interactions inside the $Fe(2)_2O_8F_2$ edge-sharing dimeric entities are propagated through the fluorine atoms with an Fe(2)−F(4)−Fe(2) bond angle of 101.8(1)°. The $Fe(1)Fe(3)O_6F_4$ dimers in the chains exhibit Fe(1)−F(1)−Fe(3) and Fe(1)−F(2)−Fe(3) bond angles of 101.8(1) and 101.4(1)°, respectively, whereas the connection between these dimers is established with an Fe(1)−F(3)−Fe(3) angle of 133.3(2)°. These bond angles together with those established by the arsenate anions linking to the iron(III) ions should favor the antiferromagnetic interactions observed in this compound.[29]

**Acknowledgment.** This work was financially supported by the Ministerio de Educación y Ciencia and Universidad del País Vasco/EHU (grants PB97-0640 and 169.310-EB149/98, respectively), which we gratefully acknowledge. We thank S. Garcia−Granda and C. Alvarez−Rua from the Universidad de Oviedo for X-ray diffraction data measurements. B. Bazán thanks the UPV/EHU for a doctoral fellowship.

**Supporting Information Available:** Four X-ray crystallographic files, in CIF format, are available. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0103796

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