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Synthesis and Characterization of Fluorinated Metal Arsenates with a Layer Structure: $(C_4H_{12}N_2)_{1.5}[M_3F_5(HAsO_4)_2(AsO_4)]$ (M = Fe, Ga)

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Two fluorinated metal arsenates, $(C_4H_{12}N_2)_{1.5}[M_3F_5(HAsO_4)_2(AsO_4)]$ (M = Fe, Ga), have been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction, magnetic susceptibility, Mössbauer spectroscopy, and ^{71}Ga NMR spectroscopy. The two compounds are isostructural and crystallize in the monoclinic space group $P2_1/c$ (No. 14) with $a = 8.394(1)$ Å, $b = 21.992(3)$ Å, $c = 10.847(1)$ Å, $\beta = 96.188(2)°$, and $Z = 4$ for the Fe compound, and $a = 8.398(1)$ Å, $b = 21.730(3)$ Å, $c = 10.679(1)$ Å, $\beta = 95.318(2)°$, and $Z = 4$ for the Ga compound. The structure consists of infinite chains of corner-sharing MX_6 (X = O, F) octahedra and dimers of edge-sharing MO_3F_3 octahedra, which are linked into two-dimensional sheets through arsenate tetrahedra with diprotonated piperazinium cations between the sheets. Magnetic susceptibility and Mössbauer spectroscopy confirm the presence of Fe(III). The ^{71}Ga MAS NMR spectrum clearly shows a line shape consisting of three components, corresponding to three crystallographically distinct Ga sites.

Introduction

The synthesis of organically templated transition metal phosphates is a subject of intense research because of their interesting structural chemistry and potential applications as solid catalysts. The first such metallophosphates were prepared with molybdenum and vanadium.[1,2] A large number of organically templated iron phosphates have also been reported.[3,4] These iron phosphates have been prepared in aqueous or predominantly nonaqueous solvents using iron chloride or nitrate as the source of iron.[3] An alternative route using HF as the mineralizer and Fe_2O_3 as the source of iron was initiated by Férey and co-workers.[4] An interesting set of compounds labeled ULM-*n* or MIL-*n* were prepared, in which most of the materials have fluorine directly bonded to iron. The use of HF produced a number of novel microporous phosphate frameworks that do not form in a fluoride-free medium. Little work, however, has been carried out on the arsenate as compared to the phosphate, and to date only several arsenates of gallium, molybdenum, vanadium, and iron have been reported in the literature.[5−11] The synthesis conditions for arsenates are analogous to those for phosphates. Metal chlorides or nitrates have been used as the reactants. Iron metal in its elemental form has also been used for the synthesis of mixed-valence iron arsenates.[9] We therefore extended our search for open frameworks into the metal arsenate systems. By using piperazine as a structure-directing agent and HF as a mineralizer under hydrothermal synthesis conditions, we synthesized a fluorinated iron arsenate and its gallium analogue described below.

Experimental Section

Synthesis and Initial Characterization. The hydrothermal reactions were carried out under autogenous pressure in Teflon-lined stainless steel Parr acid digestion bombs. All chemicals were purchased from Aldrich Chemicals. Arsenic acid was prepared from a reaction of As_2O_3 and H_2O_2. Reaction of $FeCl_3{\cdot}6H_2O$ (1 mmol), H_3AsO_4 (10 mmol), piperazine (10 mmol), HF (40 wt %, 0.5 mL), and water (10 mL) for 3 days at 160 °C followed by slow cooling at 5 °C h^{-1} to room temperature produced $(C_4H_{12}N_2)_{1.5}[Fe_3F_5(HAsO_4)_2(AsO_4)]$, **1**, as pale pink plate crystals in 85% yield based on iron. The pale pink color indicated an iron(III) compound. A crystal was selected for structure determination by single-crystal X-ray diffraction. The bulk product was monophasic as judged by the total consistency of its powder X-ray diffraction pattern with that simulated from the atomic coordinates derived from the single-crystal X-ray study. Electron probe microanalysis on a crystal gave the atomic ratio Fe:F:As = 3:5.15:3.05. Elemental analysis confirmed the stoichiometry. Anal. Found: C, 9.00; H, 2.64; N, 5.18. Calcd: C, 8.84; H, 2.72; N, 5.15. The gallium analogue $(C_4H_{12}N_2)_{1.5}[Ga_3F_5(HAsO_4)_2(AsO_4)]$, **2**, was prepared by heating a mixture of $Ga(NO_3)_3{\cdot}6H_2O$ (1 mmol), H_3AsO_4 (10 mmol), piperazine (10 mmol), HF (40 wt %, 0.5 mL), and water (10 mL) under the same hydrothermal conditions. The bulk product consisted of colorless plate crystals and was monophasic as indicated by powder X-ray diffraction.

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Table 1. Crystallographic Data for $(C_4H_{12}N_2)_{1.5}[Fe_3F_5(HAsO_4)_2(AsO_4)]$ (**1**) and $(C_4H_{12}N_2)_{1.5}[Ga_3F_5(HAsO_4)_2(AsO_4)]$ (**2**)

	1	**2**
chemical formula	$C_6F_5H_{20}N_3O_{12}As_3Fe_3$	$C_6F_5H_{20}N_3O_{12}As_3Ga_3$
fw	813.56	855.17
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	8.394(1)	8.398(1)
b, Å	21.992(3)	21.730(3)
c, Å	10.847(1)	10.679(1)
β, deg	96.188(2)	95.318(2)
V, Å^3	1990.8(4)	1940.5(4)
Z	4	4
T, K	295(2)	295(2)
λ(Mo Kα), Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	2.714	2.927
μ(Mo Kα), mm^{-1}	7.22	9.33
R1[a]	0.0290	0.0303
wR2[b]	0.0699	0.0770

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_o^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\mathrm{Max}(F_o,0) + 2(F_c)^2]/3$, where $a = 0.0299$ and $b = 4.77$ for **1** and $a = 0.0317$ and $b = 6.36$ for **2**.

Table 2. Selected Bond Lengths (Å) for $(C_4H_{12}N_2)_{1.5}[Fe_3F_5(HAsO_4)_2(AsO_4)]$ (**1**) and $(C_4H_{12}N_2)_{1.5}[Ga_3F_5(HAsO_4)_2(AsO_4)]$ (**2**)[a]

Compound **1**			
As(1)−O(1)	1.691(3)	As(1)−O(2)	1.677(3)
As(1)−O(3)	1.663(2)	As(1)−O(4)	1.731(3)
As(2)−O(5)	1.674(3)	As(2)−O(6)	1.665(2)
As(2)−O(7)	1.713(3)	As(2)−O(8)	1.671(3)
As(3)−O(9)	1.687(2)	As(3)−O(10)	1.698(2)
As(3)−O(11)	1.694(2)	As(3)−O(12)	1.671(3)
Fe(1)−F(1)	2.052(2)	Fe(1)−F(2)	1.996(2)
Fe(1)−F(4)	1.917(2)	Fe(1)−O(1)	1.956(3)
Fe(1)−O(6)	1.977(2)	Fe(1)−O(9)	1.943(2)
Fe(2)−F(1)	2.014(2)	Fe(2)−F(2)	1.987(2)
Fe(2)−O(3)	1.997(2)	Fe(2)−O(5)	1.971(3)
Fe(2)−O(8)	1.980(3)	Fe(2)−O(12)	1.975(2)
Fe(3)−F(3)	2.011(2)	Fe(3)−F(3)	2.058(2)
Fe(3)−F(5)	1.867(2)	Fe(3)−O(2)	1.925(2)
Fe(3)−O(10)	2.024(2)	Fe(3)−O(11)	1.967(2)
N(1)−C(1)	1.490(5)	N(1)−C(2)	1.491(5)
N(2)−C(3)	1.503(6)	N(2)−C(4)	1.491(6)
N(3)−C(5)	1.449(9)	N(3)−C(6)	1.46(1)
C(1)−C(3)	1.503(6)	C(2)−C(4)	1.507(7)
C(5)−C(6)	1.481(9)	H(1)−O(4)	1.010
H(2)−O(7)	0.960	H(1)···O(10)	1.657
H(2)···F(4)	1.534		
Compound **2**			
As(1)−O(1)	1.700(3)	As(1)−O(2)	1.662(4)
As(1)−O(3)	1.668(3)	As(1)−O(4)	1.738(4)
As(2)−O(5)	1.671(3)	As(2)−O(6)	1.666(3)
As(2)−O(7)	1.711(4)	As(2)−O(8)	1.665(3)
As(3)−O(9)	1.682(3)	As(3)−O(10)	1.699(3)
As(3)−O(11)	1.692(3)	As(3)−O(12)	1.663(3)
Ga(1)−F(1)	2.033(3)	Ga(1)−F(2)	1.964(3)
Ga(1)−F(4)	1.878(3)	Ga(1)−O(1)	1.907(3)
Ga(1)−O(6)	1.937(3)	Ga(1)−O(9)	1.917(3)
Ga(2)−F(1)	1.976(3)	Ga(2)−F(2)	1.952(3)
Ga(2)−O(3)	1.959(3)	Ga(2)−O(5)	1.934(4)
Ga(2)−O(8)	1.948(3)	Ga(2)−O(12)	1.944(3)
Ga(3)−F(3)	1.986(3)	Ga(3)−F(3)	1.998(3)
Ga(3)−F(5)	1.836(3)	Ga(3)−O(2)	1.900(3)
Ga(3)−O(10)	1.970(3)	Ga(3)−O(11)	1.926(3)
N(1)−C(1)	1.488(7)	N(1)−C(2)	1.484(7)
N(2)−C(3)	1.487(8)	N(2)−C(4)	1.478(8)
N(3)−C(5)	1.47(1)	N(3)−C(6)	1.45(1)
C(1)−C(3)	1.500(8)	C(2)−C(4)	1.511(9)
C(5)−C(6)	1.48(1)	H(1)−O(4)	0.951
H(2)−O(7)	0.980	H(1)···O(10)	1.686
H(2)···F(1)	1.562		

[a] The N−H and C−H bond lengths are given in the Supporting Information.

Structure Determination. A pale pink crystal of **1** with dimensions 0.25 × 0.1 × 0.1 mm and a colorless crystal of **2** with dimensions 0.35 × 0.15 × 0.15 mm were selected for indexing and intensity data collection on a Siemens SMART CCD diffractometer equipped with a normal focus, 3-kW sealed tube X-ray source. Intensity data were collected at room temperature in 1271 frames with increasing ω (width 0.30° per frame). The 2θ range is 3.7−56.6°. Empirical absorption corrections based on symmetry equivalents were applied ($T_{min/max}$ = 0.522/0.984 for **1**, 0.599/0.951 for **2**).[12] On the basis of the systematic absence conditions in the reduced data and the subsequent successful solution and refinement of the structure, the space groups were determined to be $P2_1/c$ (No. 14). Both structures were solved by direct methods and difference Fourier syntheses. Bond-valence calculations indicate that O(4) and O(7) are hydroxo oxygen atoms.[13] There are one AsO_4^{3-} and two $HAsO_4^{2-}$ groups per asymmetric unit. To balance charge all atoms which connect neighboring metal atoms or coordinate to metal atoms as terminal ligands are fluorine atoms. There are five F atoms per asymmetric unit in accord with the result from electron probe microanalysis. All hydrogen atoms were located in difference Fourier maps. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The atomic positions and isotropic thermal parameters for all hydrogen atoms were fixed. Maximum and minimum peaks in final difference maps were 1.52, −1.05 and 1.14, −1.48 e Å^{-3} for **1** and **2**, respectively. All calculations were carried out with the PC version of the SHELXTL program package. The crystallographic data is given in Table 1, and selected bond distances are provided in Table 2.

Magnetic Susceptibility and Mössbauer Measurements. Variable-temperature magnetic susceptibility $\chi(T)$ data were obtained on 51.5 mg of a polycrystalline sample of **1** from 2 to 300 K in a magnetic field of 5000 G after zero-field cooling using a SQUID magnetometer. Correction for diamagnetism was made according to Selwood.[14] The ^{57}Fe Mössbauer measurements were made on a constant-acceleration instrument at 300 K. Isomer shifts are reported with respect to an iron foil standard.

^{71}Ga NMR Measurements. ^{71}Ga magic angle spinning (MAS) NMR experiments were carried out at room temperature on a Bruker AVANCE−400 spectrometer at ^{71}Ga resonance frequency of 121.84 MHz. The ^{71}Ga MAS NMR spectrum was acquired by using a solid-echo pulse sequence, i.e., $\pi/2-\tau-\pi/2$ acquisition, where τ was set to be the rotor period. A high-speed 2.5 mm probehead for acquiring the ^{71}Ga MAS NMR spectrum at a spinning speed of 30 kHz was used. The applied rf field strength was carefully chosen to be well within the fictitious spin-$^1/_2$ approximation ($\nu \ll \nu_Q$). This was measured on a 1 M gallium nitrate solution that was also used as a reference. The simulation of a ^{71}Ga MAS NMR spectrum was performed with the WINFIT program of the Bruker WINNMR software package.

Results and Discussion

Structural Description. The asymmetric unit consists of 32 unique non-hydrogen atoms. All atoms are at general positions. One of the two crystallographically distinct piperazinium cations sits on an inversion center. The Fe (or Ga) and As atoms are six- and four-coordinated, respectively. The three F atoms in $M(1)O_3F_3$ and $M(3)O_3F_3$ are in facial and meridional configuration, respectively. The two F atoms in $M(2)O_4F_2$ are cis to each other. All three octahedra are distorted, and the extent of distortion can be estimated by using the equation $\Delta = (1/6)\sum[(R_i - R_{av})/R_{av}]^2$, where R_i = individual bond lengths and R_{av} = average bond length.[15] The calculation results show that the

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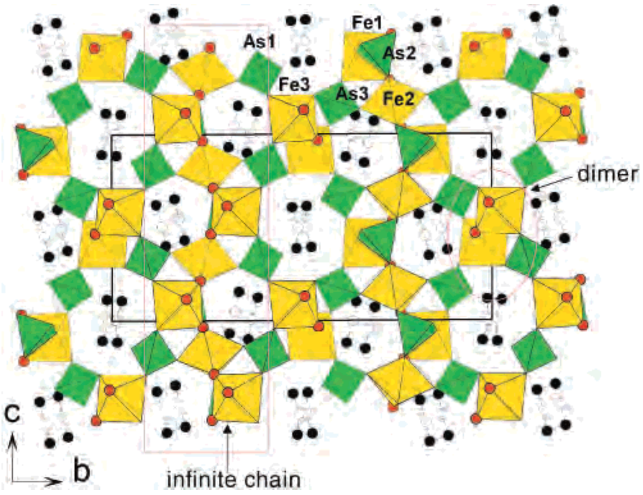

Figure 1. Polyhedral view of the structure of **1** along the [100] direction. FeX_6 (X = O, F) octahedra and arsenate tetrahedra are shown in yellow and green, respectively. Black circles: C atoms. Open circles: N atoms. Red circles: F atoms.

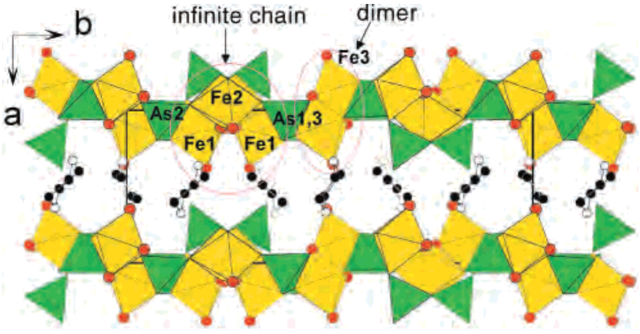

Figure 2. Structure of **1** viewed along the [001] direction.

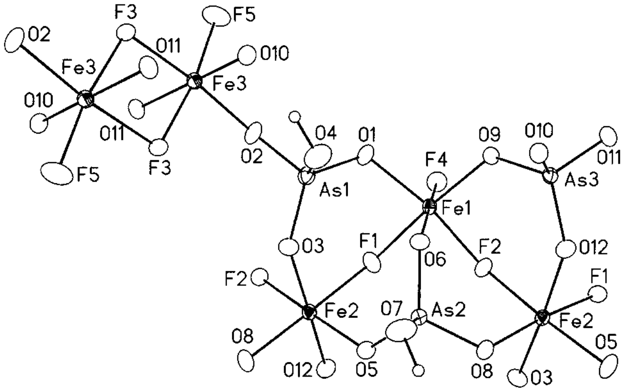

Figure 3. A fraction of an anionic sheet in **1** showing the connectivity and labeling of atoms. Thermal ellipsoids are shown at 50% probability. Small open circles represent hydrogen atoms.

order of increasing distortion is $M(2)O_4F_2$, $M(1)O_3F_3$, and $M(3)O_3F_3$ ($10^4\Delta = 0.4$, 6.5, and 8.4 for Ga(2), Ga(1), and Ga(3), respectively). The largest distortion in $M(3)O_3F_3$ can be ascribed to an edge-sharing octahedral dimer (vide infra). In the following only the structure of **1** will be discussed in detail because the two compounds are isostructural.

The structure consists of two-dimensional anionic sheets of fluorinated iron arsenate in the *bc*-plane with charge-compensating diprotonated piperazinium cations between the sheets (Figures 1 and 2). The connectivity between iron atoms with the labeling scheme is shown in Figure 3. The anionic sheets are constructed from infinite chains of cis-corner-sharing $Fe(1)O_3F_3$ and $Fe(2)O_4F_2$ octahedra and dimers of edge-sharing $Fe(3)O_3F_3$ octahedra, which are joined by arsenate ligands. Each infinite chain sits on a *c*-glide plane. All the bridging atoms within a chain are F atoms. Fe(1) is also bonded to a terminal F atom, F(4). Each dimer resides on an inversion center with two bridging F and two terminal F atoms. There are three distinct arsenate groups. $HAs(1)O_4$ and $As(3)O_4$ link the infinite chains with dimers while $HAs(2)O_4$ forms a bridge over three Fe atoms within a chain. The topology of the chain can be described with a pentameric secondary building unit (SBU) which consists of the connection of two octahedra and three tetrahedra by corner-sharing. An alternative description of the chain is two types of SBU. One is SBU-6 (3 AsO_4 + 3 FeX_6) and the other is SBU-2 (1 AsO_4 + 1 FeX_6). Both of them have been observed in ULM-*n* phases.[4] The dimeric edge-shared dioctahedra have not been observed in iron phosphates but were observed in aluminophosphates such as ULM-6 and MIL-27.[16,17] Within a layer in **1** the Fe−O(F) octahedra share corners with arsenate tetrahedra in alternating manner to form eight- and six-sided windows. Consecutive layers are stacked one exactly above another so that infinite tunnels are formed along the [100] direction, in which the organic cations are located. The cations are locked in their positions by hydrogen bonds to framework oxygen or fluorine atoms. The cation which sits on an inversion center forms weaker hydrogen bonds with the arsenate relative to the cation at general position, as indicated from a comparison of the N···O (or N···F) distances and the thermal parameters.

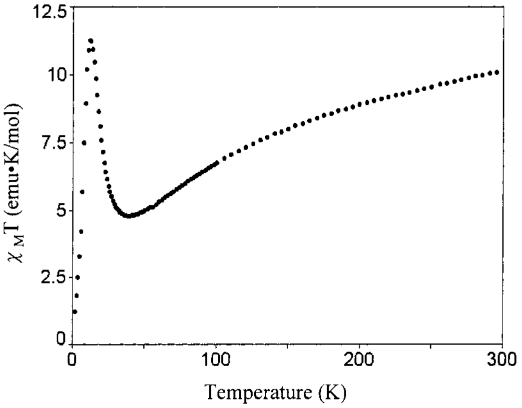

Figure 4. $\chi_M T$ versus *T* of **1**.

Magnetic Susceptibility and Mössbauer Spectroscopy. As shown in Figure 4, the $\chi_M T$ value decreases with decreasing temperature in the range 50−300 K, indicating that the main magnetic intereactions between Fe atoms are antiferromagnetic. In particular, the effective magnetic moment at 300 K is only 5.19 μ_B/Fe as compared with 5.92 μ_B/Fe expected for spin-only and noninteracting Fe^{3+} ions. The inverse magnetic susceptibility followed the Curie−Weiss law in the paramagnetic state (for $T > 50$ K), and the Weiss temperature θ_p is strongly negative ($\theta_p = -91.6$ K), which is consistent with strong antiferromagnetic interactions. The calculated Curie constant (13.1) based on three Fe^{3+} per formula unit is in good agreement with the experimental value (13.0). The ferromagnetic rise in $\chi_M T$ at ~12 K can be interpreted as canted antiferromagnetism. At lower temperatures the magnetic moments of different spin lattices reach equivalency and the net moment diminishes.

The room temperature ^{57}Fe Mössbauer spectrum of **1** was least-squares fitted by one doublet (Figure 5). The obtained parameters are δ (isomer shift) = 0.403 mm/s, ΔE_Q (quadrupole

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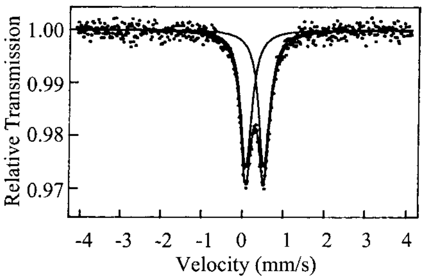

Figure 5. Mössbauer spectrum of **1** at 300 K.

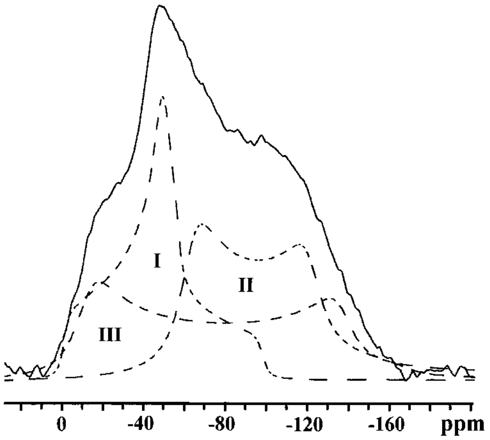

Figure 6. Experimental ^{71}Ga MAS NMR spectrum of **2** with its deconvolution shown in dashed lines.

splitting) = 0.444 mm/s, and Γ (full width at half-height) = 0.33 mm/s. The isomer shift is characteristic of high-spin Fe^{III}. According to Menil, the usual ranges of isomer shifts in oxides are 0.29−0.50 and 1.03−1.28 mm/s for Fe^{III} and Fe^{II} in 6-coordination, respectively.[18] Therefore, the valence of the iron atoms in **1** is confirmed by Mössbauer spectroscopy.

^{71}Ga MAS NMR. Figure 6 shows the experimental ^{71}Ga MAS NMR spectrum of **2** at 9.4 T, together with the simulation. To retrieve isotropic chemical shifts and EFG (electric field gradient) tensors, the observed ^{71}Ga NMR line shape was fitted with three components in an area ratio of 0.34:0.34:0.32 in accord with three unique Ga sites. The deconvoluted spectrum as shown in dashed lines, neglecting CSA (chemical shift anisotropy), yields NMR parameters for three ^{71}Ga sites: site I, $\delta_{CS} = -1.0 \pm 5.0$ ppm, C_Q (quadrupolar coupling constant) $= 4.5 \pm 0.2$ MHz, η (asymmetry parameter) $= 0.95 \pm 0.02$; site II, $\delta_{CS} = -45.8 \pm 5.0$ ppm, $C_Q = 5.4 \pm 0.2$ MHz, $\eta = 0.05 \pm 0.02$; site III, $\delta_{CS} = 24.0 \pm 5.0$ ppm, $C_Q = 7.8 \pm 0.2$ MHz, $\eta = 0.02 \pm 0.02$. Site III is indicated from a comparison with quadrupolar coupling constant to be assigned to Ga(3), which has the most distorted coordination environment due to edge-sharing. The C_Q values for the other two sites are about the same, although the octahedral distortion of Ga(1) appears considerably larger than that of Ga(2) on the basis of the Ga−O(F) bond lengths. Bradley et al. indicated that the presence of a fluoride ion rather than an oxygen in the first coordination sphere of a gallium atom would exert a deshielding influence, thus causing a downfield shift.[19] Hence, site I and site II are assigned to Ga(1) and Ga(2), respectively, as inferred from a comparison of the number of fluorine atoms bonded to Ga atoms.

Concluding Remarks

Although a large number of organically templated metal phosphates have been reported, only a few arsenates are known. This work reports the synthesis and single-crystal X-ray structure of a layered iron arsenate and its gallium analogue. Each layer consists of infinite chains of corner-sharing MX_6 (X = O, F) octahedra and dimers of edge-sharing MO_3F_3 octahedra, which are linked by arsenate groups. It is a new structural type which has not been observed in phosphates. Magnetic susceptibility and Mössbauer spectroscopy measurements are in good agreement with the existence of high-spin Fe(III) cations in **1**. ^{71}Ga MAS NMR spectroscopy of **2** confirms the presence of three unique metal sites. The three resonances are assigned according to the extent of octahedral distortion and the number of fluorine atoms bonded to Ga atoms. The hydrothermal synthesis conditions for arsenates are analogous to those for phosphates. The use of HF as a mineralizer appears particularly useful to the crystal growth of arsenates. Many other new compounds in the metal arsenate systems with or without fluorine in the inorganic frameworks have been prepared and will be reported elsewhere.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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