Synthesis and Characterization of Four Ethylenediamine-Templated Iron Arsenates

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Four new ethylenediamine-templated iron arsenates and fluoroarsenates have been hydrothermally synthesized from iron metal, hydrofluoric and arsenic acids, and ethylenediamine. $Fe(H_2AsO_4)(HAsO_4)_2{\cdot}enH_2{\cdot}H_2O$ (**1**) is one-dimensional and contains chains, $Fe^{III}Fe^{II}F_2(HAsO_4)(AsO_4){\cdot}enH_2{\cdot}2H_2O$ (**2**) is a layered fluoroarsenate, and $Fe_3(HAsO_4)_6{\cdot}enH_2{\cdot}NH_3{\cdot}NH_4$ (**3**) and $Fe_2F_2(AsO_4)_2(H_2O){\cdot}enH_2$ (**4**) are an arsenate and a fluoroarsenate, respectively, with three-dimensional open-framework type structures. Compounds **1**, **3**, and **4** contain Fe(III) only, while **2** is a mixed-valence compound of Fe(III) and Fe(II). The structures were determined from single-crystal X-ray diffraction. Crystal data: (**1**) $P2_1$, $a = 4.762(1)$ Å, $b = 16.086(3)$ Å, $c = 8.698(2)$ Å, $\beta = 90.65(3)°$, $Z = 2$; (**2**) $P\text{-}1$, $a = 5.289(1)$ Å, $b = 7.573$ (1) Å, $c = 8.888(2)$ Å, $\alpha = 67.32(3)°$, $\beta = 82.77(3)°$, $\gamma = 69.76(3)°$, $Z = 1$; (**3**) $C2/c$, $a = 18.384(3)$ Å, $b = 8.785(1)$ Å, $c = 16.052(2)$ Å, $\beta = 111.11(1)°$, $Z = 4$; (**4**) $Pbca$, $a = 10.490(2)$ Å, $b = 10.090(2)$ Å, $c = 20.540(4)$ Å, $Z = 8$. Strong hydrogen bonding exists between the chains and the layers in **1** and **2**, and between the diprotonated ethylenediamine and the inorganic part of the structures of **1**, **2**, and **4**. The ethylenediamine in **3** is not hydrogen bonded, and as a result it is disordered. The compounds are characterized also by thermogravimetric analysis, infrared spectroscopy, elemental analysis, and magnetic measurements.

Introduction

Open-framework materials are of considerable interest due to their diverse structural chemistry and their application in catalysis and other industrially important areas.[1−6] Furthermore, after the discovery of the first open-framework iron phosphate in 1986,[7] compounds containing transition metals as part of the framework have attracted even greater attention due to their potential for redox catalysis. Thus, numerous transition metal phosphates with novel structures are known today.[8−22] The variety of amines and diamines employed in the hydrothermal synthesis of such open-framework compounds act as the structure-directing templates and also keep the frameworks open.

In contrast to the metal phosphates, only very few arsenates with open-framework structures are known.[23−27] Also, very few such structures containing either reduced or mixed-valent transition metals are known. We have been interested in using transition metals in their elemental form as reactants for the synthesis of such reduced-metal phases. This approach has been successful in the phosphate systems,[8] and here we report on four examples of ethylenediamine-templated iron arsenates and fluoroarsenates synthesized from elemental iron, with mixed-valence iron found in one of them.

Experimental Section

Synthesis and Initial Characterization. The compounds were synthesized hydrothermally in a 23 mL Teflon-lined autoclave under autogenous pressure. All four were made from different mixtures of elemental Fe (Acros), H_3AsO_4 (Alfa Aesar), HF (Alfa Aesar), ethylenediamine (Acros), and distilled H_2O. Compound **1** was made as a major phase mixed with some amounts of compound **3** from a mixture with molar ratio $Fe:H_3AsO_4:HF:en:H_2O = 1:10:7:4:600$ at 180 °C for 5 days. The product is composed of large colorless rods of **1** and a few large colorless crystals of **3** resembling pentagonal bipyramids. Compound **3** can be synthesized in higher yield from a mixture

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Table 1. Crystallographic Data for $Fe(H_2AsO_4)(HAsO_4)_2 \cdot EnH_2 \cdot H_2O$ (**1**), $Fe^{III}Fe^{II}F_2(HAsO_4)(AsO_4) \cdot EnH_2 \cdot 2H_2O$ (**2**), $Fe_3(HAsO_4)_6 \cdot EnH_2 \cdot NH_3 \cdot NH_4$ (**3**), and $Fe_2F_2(AsO_4)_2(H_2O) \cdot EnH_2$ (**4**)

compd	**1**	**2**	**3**	**4**
fw	556.78	526.7	1104.06	507.68
space group, Z	$P2_1$, 2	P-1, 1	$C2/c$, 4	$Pbca$, 8
unit cell params	$a = 4.762(1)$ Å	$a = 5.289(1)$ Å	$a = 18.384(3)$ Å	$a = 10.490(2)$ Å
	$b = 16.086(3)$ Å	$b = 7.573(1)$ Å	$b = 8.785(1)$ Å	$b = 10.090(2)$ Å
	$c = 8.698(2)$ Å	$c = 8.888(2)$ Å	$c = 16.052(2)$ Å	$c = 20.540(4)$ Å
		$\alpha = 67.32(3)°$		
	$\beta = 90.65(3)°$	$\beta = 82.77(3)°$	$\beta = 111.11(1)°$	
		$\gamma = 69.76(3)°$		
	$V = 666.2(2)$ Å^3	$V = 308.2(1)$ Å^3	$V = 2418.5(6)$ Å^3	$V = 2174.0(8)$ Å^3
radiation, λ (Å)	Mo Kα, 0.7107 3	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
temp (°C)	20	20	20	20
abs coeff (cm^{-1})	85.99	77.62	100.36	87.89
density (g/cm^3)	2.775	2.838	3.014	3.102
R1, wR2 ($I > 2\sigma_I$)[a] (%)	2.44, 5.33	3.71, 9.76	4.49, 12.11	4.35, 7.85
R1, wR2 (all data) (%)	2.83, 5.48	3.82, 9.87	5.36, 12.67	5.73, 8.49

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2F_o2 + (0.0213P)^2]$ for **1**, $1/[\sigma^2F_o^2 + (0.0801P)^2 + 0.1217P]$ for **2**, $1/[\sigma^2F_o^2 + (0.0641P)^2 + 90.6422P]$ for **3**, and $1/[\sigma^2F_o^2 + (0.0383P)^2]$ for **4**, where $P = (F_o^2 + 2F_c^2)/3$.

containing less iron, about 80% of the amount used in the synthesis of **1**. **3** is the major phase in the product, but a small amount of **1** exists as well. Compounds **2** and **4** were made at lower temperatures, 120 °C. A mixture of molar composition $Fe:H_3AsO_4:HF:en:H_2O = 1:3.3:20:4:600$ (pH 2) gives large prismatic crystals of **2** as the only product after 2 days. The color of this compound is deep pink to red and indicates the presence of reduced or mixed-valence iron. Pure compound **4** can be made from a reaction of $Fe:H_3AsO_4:HF:en:H_2O$ in a molar ratio of 1:5:15:4:600 heated at the same temperature for 2 days. It crystallizes as large colorless cubic crystals.

Clearly, the phase-determining factor in these syntheses is the ratio of the two competing ligands, i.e., the ratio $[F^-]/[AsO_4^{3-}]$. The fluoroarsenates **2** and **4** are formed when this ratio is higher than 1, 6 for **2** and 3 for **4**. Notice that doubling the amount of fluoride does not necessarily lead to higher amounts of fluorine in the compound. Actually, the stoichiometries of **2** and **4** differ by only one molecule of water and a proton that accounts for the one reduced iron atom. Also, the reason for reduced iron in **2** is the other important ratio, that of elemental iron to the oxidizing arsenate, which is lower in **2** than in **4**, 1:3 vs 1:5, respectively. Lowering the fluoride/arsenate ratio below 1 to 0.7 as in the synthesis of **1** and **3** leads to the absence of fluorine in the framework.

Powder X-ray diffraction patterns were taken on a Guinier camera with Cu Kα1 radiation for phase identification purposes. FTIR spectra of pellets of the compounds mixed with KBr were recorded on a Perkin-Elmer PARAGON-100. Thermogravimetric analyses were carried out on a CAHN TG-131 under a flow of air (150 mL·min^{-1}) up to 800 °C with a heating rate of 5 °C/min. The magnetizations of 33 mg of **1**, 48 mg of **2**, 54 mg of **3**, and 7 mg of **4** were measured at a field of 3 T over the temperature range of 10−300 K with a step of 10 K on a Quantum Design MPMS SQUID magnetometer. Elemental analyses for fluorine were performed on **2** and **4** (Galbraith Laboratories). The results showed 6.58 and 7.54 wt % for **2** and **4**, respectively. The corresponding theoretical values are 7.23 and 7.48 wt %.

Structure Determination. A few crystals of each compound were selected, mounted on glass fibers, and tested for singularity and quality on a CAD4 single-crystal diffractometer. The best ones were chosen, and data were collected at room temperature with monochromated Mo Kα ($\lambda = 0.710\ 73$ Å) of up to $2\theta_{max} = 50°$. The structures were solved by direct methods and refined on F^2 with the aid of the SHELXTL V5.0 software package. Details of the data collection and structure refinements are given in Table 1, while the atomic parameters and important distances are listed in Tables 2 and 3, respectively.

Results and Discussion

Structure Descriptions. All four compounds are built of octahedrally coordinated iron and tetrahedral AsO_4 units. Also, ethylenediamine templates all four structures. Compounds **1** and **2** are one- and two-dimensional structures, respectively, while both **3** and **4** are three-dimensional.

$Fe^{III}(H_2AsO_4)(HAsO_4)_2 \cdot enH_2 \cdot H_2O$. This compound is isostructural with a vanadium(III) arsenate.[26] It contains one-dimensional chains that are isolated from each other by water and diprotonated ethylenediamine molecules (Figure 1). The chains are built of nearly ideal FeO_6 octahedra, stacked on top of each other along their 3-fold axis and connected by three arsenate groups per pair of octahedra (reminiscent of the building units in the NASICON structure). Each arsenate group shares two corners with two octahedra and has two terminal oxygen atoms (Figure 1a). From the As−O distances, it is quite clear that both terminal oxygens on As3 (O3 and O10) are protonated while only one such atom is protonated for As1 (O12) and for As2 (O1). Thus, the chains carry a charge of 2− per iron octahedron, and it is balanced by the diprotonated diamine. The latter is hydrogen-bonded to the chains with one such bond per nitrogen atom. These hydrogen bonds are with the nonprotonated oxygen atoms from the arsenates, O6 on As1 and O8 on As2. Hydrogen-bonded to the same "naked" oxygen atoms are also the water molecules of the structure. Finally, hydrogen bonds exist between protonated and nonprotonated oxygen atoms of the chains as well.

$Fe^{III}Fe^{II}F_2(HAsO_4)(AsO_4) \cdot enH_2 \cdot 2H_2O$. Compound **2** is isostructural with the corresponding fluorinated iron phosphate ULM-10.[28] Its structure is of the layered type where the layers are built of corner-sharing octahedra and tetrahedra centered by iron and arsenic, respectively (Figure 2). There are two different iron atoms in the structure, Fe(III) and Fe(II), both coordinated by two *trans*-fluorine and four oxygen atoms. The fluorine corners are shared by the two types of iron (Figure 2b) in chains of −Fe(III)−F−Fe(II)−F−Fe(III)− with an angle of 142.7° at the fluorine. Bridging and terminal fluorine atoms have been found in many fluorophosphates synthesized in the past few years.[9,28−33] All four oxygen atoms around Fe(III) are shared with four arsenate groups, while two *trans*-oxygen atoms around Fe(II) are from water molecules. Very similar coordination is observed around Ti(III) in a mixed-valence Ti(III)/Ti(IV) compound.[8a] *trans*-Water molecules seem to stabilize such low-

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **1**−**4**

atom	*x*	*y*	*z*	*U*(eq)
	$Fe(H_2AsO_4)(HAsO_4)_2{\cdot}enH_2{\cdot}H_2O$ (**1**)			
As(1)	0.04146(11)	0.39319(3)	0.38614(6)	0.00885(14)
As(2)	−0.97868(11)	0.61773(3)	0.23382(6)	0.00975(14)
As(3)	0.03794(12)	0.41592(3)	−0.04893(6)	0.01045(14)
Fe	−0.46830(16)	0.47977(5)	0.18212(8)	0.00901(18)
O(1)	−0.1284(10)	0.6484(2)	0.4064(4)	0.0170(10)
O(2)	−0.2206(8)	0.4619(2)	0.3684(4)	0.0120(8)
O(3)	0.2028(9)	0.3227(2)	−0.0819(5)	0.0165(10)
O(4)	−0.7153(8)	0.5574(2)	0.2976(4)	0.0125(8)
O(5)	−0.2258(8)	0.3979(2)	0.0711(4)	0.0125(8)
O(6)	0.1953(8)	0.4071(3)	0.5595(4)	0.0165(9)
O(7)	0.2854(8)	0.3847(2)	0.2521(4)	0.0103(8)
O(8)	−0.8585(9)	0.7041(2)	0.1484(4)	0.0164(9)
O(9)	0.2829(8)	0.4865(2)	−0.0055(4)	0.0129(8)
O(10)	−0.1102(10)	0.4442(3)	−0.2207(5)	0.0223(12)
O(11)	−0.5272(10)	0.7690(3)	0.3870(5)	0.0198(10)
O(12)	−0.1040(9)	0.2945(2)	0.3836(5)	0.0151(9)
O(13)	−0.2240(8)	0.5745(2)	0.1200(4)	0.0124(9)
C(1)	−0.6224(12)	0.6131(4)	0.7053(6)	0.0169(12)
C(2)	−0.4130(14)	0.6691(4)	−0.2103(7)	0.0191(13)
N(1)	−0.4723(11)	0.5477(3)	0.6217(6)	0.0177(11)
N(2)	−0.5626(11)	0.7335(3)	−0.1209(6)	0.0201(12)
	$Fe^{III}Fe^{II}F_2(HAsO_4)(AsO_4){\cdot}enH_2{\cdot}2H_2O$ (**2**)			
As	0.43753(7)	0.03759(5)	0.72407(4)	0.0084(2)
Fe(1)	0.0000	0.0000	0.5000	0.0083(3)
Fe(2)	0.0000	−0.5000	0.5000	0.0113(3)
F	0.0561(5)	−0.2859(4)	0.5704(3)	0.0197(6)
O(1)	0.4182(6)	−0.0824(4)	0.9298(3)	0.0140(6)
O(2)	0.3230(5)	−0.0825(4)	0.6388(3)	0.0125(6)
O(3)	0.7668(5)	0.0078(5)	0.6938(4)	0.0182(7)
O(4)	0.2582(6)	0.2808(4)	0.6851(3)	0.0165(6)
O(5)	0.3526(7)	−0.4964(6)	0.3328(4)	0.0223(7)
N	0.0354(7)	−0.2663(5)	0.0070(4)	0.0167(7)
C	0.1196(9)	−0.4662(7)	−0.0082(6)	0.0191(9)
	$Fe_3(HAsO_4)_6{\cdot}enH_2{\cdot}NH_3{\cdot}NH_4$ (**3**)			
As(1)	0.36116(5)	0.95390(11)	0.24961(6)	0.0077(3)
As(2)	0.36433(5)	0.33928(11)	0.07174(6)	0.0073(3)
As(3)	0.63091(5)	0.41098(11)	0.18905(6)	0.0072(3)
Fe(1)	0.5000	0.2054(2)	0.2500	0.0072(4)
Fe(2)	0.22923(7)	0.21611(15)	0.15760(8)	0.0074(3)
O(1)	0.4103(4)	0.5133(8)	0.1036(5)	0.0170(15)
O(2)	0.5599(4)	0.3877(8)	0.2292(4)	0.0116(14)
O(3)	0.2830(4)	0.3474(8)	0.0961(5)	0.0130(15)
O(4)	0.4245(4)	0.2000(7)	0.1226(4)	0.0113(14)
O(5)	0.6670(4)	0.5875(7)	0.2163(4)	0.0092(13)
O(6)	0.4418(4)	0.0574(8)	0.2933(5)	0.0143(15)
O(7)	0.6965(4)	0.2701(8)	0.2188(4)	0.0110(14)
O(8)	0.5892(4)	0.4015(9)	0.0749(4)	0.0190(16)
O(9)	0.3490(4)	0.3433(8)	−0.0383(4)	0.0127(15)
O(10)	0.3355(4)	0.8948(7)	0.3342(4)	0.0109(14)
O(11)	0.2914(4)	0.0314(8)	0.1615(4)	0.0118(14)
O(12)	0.3915(4)	0.7943(8)	0.2082(5)	0.0179(16)
N(1), 50%	0.5301(11)	0.820(2)	0.4259(12)	0.030(4)
N(2), 50%	0.5709(5)	0.8936(10)	0.4661(6)	0.047(6)
C	0.5060(15)	0.914(3)	0.4932(17)	0.084(7)
N(3′), 70%	0.2192(5)	0.6452(10)	0.0636(6)	0.013(2)
N(3″), 30%	0.1729(5)	0.6563(10)	0.0011(6)	0.021(6)
	$Fe_2F_2(AsO_4)_2(H_2O){\cdot}enH_2$ (**4**)			
As(1)	0.56429(7)	0.09124(5)	0.29496(3)	0.0081(2)
As(2)	0.82226(6)	0.31148(5)	0.44717(3)	0.0079(2)
Fe(1)	0.56094(9)	0.10955(7)	0.45382(4)	0.0078(2)
Fe(2)	0.65905(10)	−0.22596(8)	0.28471(4)	0.0087(2
F(1)	0.5696(3)	0.0398(3)	0.54653(17)	0.0111(8)
F(2)	0.6733(4)	−0.1736(3)	0.19421(18)	0.0184(9)
O(1)	0.8219(5)	−0.1081(4)	0.2951(3)	0.0154(11)
O(2)	0.6759(4)	0.2586(4)	0.4699(2)	0.0129(11)
O(3)	0.5402(5)	−0.0734(4)	0.2950(2)	0.0132(11)
O(4)	0.8082(4)	0.4761(4)	0.4331(2)	0.0113(11)
O(5)	0.7203(5)	0.1205(4)	0.2777(2)	0.0136(11)
O(6)	0.8687(5)	0.2306(4)	0.3792(2)	0.0138(11)
O(7)	0.9218(4)	0.2757(4)	0.5083(2)	0.0131(10)
O(8)	0.4825(4)	0.1544(4)	0.2323(2)	0.0108(10)
O(9)	0.5206(5)	0.1600(4)	0.3655(2)	0.0126(11)
C(1)	0.8070(8)	−0.0919(6)	0.6120(4)	0.0175(17)
C(2)	0.8944(8)	−0.0103(7)	0.5696(4)	0.0243(19)
N(1)	0.8508(6)	−0.2303(5)	0.6178(3)	0.0206(15
N(2)	0.0043(7)	0.0439(6)	0.6076(3)	0.0288(17

Table 3. Important Distances (Å) for Compounds **1**−**4**

	$Fe(H_2AsO_4)(HAsO_4)_2{\cdot}enH_2{\cdot}H_2O$ (**1**)		
As(1)−O(7)	1.661(4)	As(3)−O(3)	1.719(4)
As(1)−O(2)	1.673(4)	Fe−O(4)	1.995(4)
As(1)−O(6)	1.684(4)	Fe−O(13)	1.995(4)
As(1)−O(12)	1.732(4)	Fe−O(5)	2.006(4)
As(2)−O(13)	1.674(4)	Fe−O(9)	2.009(4)
As(2)−O(4)	1.675(4)	Fe−O(2)	2.014(4)
As(2)−O(8)	1.679(4)	Fe−O(7)	2.025(4)
As(2)−O(1)	1.741(4)	C(1)−C(2)	1.525(8)
As(3)−O(5)	1.667(4)	C(1)−N(1)	1.470(7)
As(3)−O(9)	1.668(4)	C(2)−N(2)	1.482(7)
As(3)−O(10)	1.707(4)		
	$Fe^{III}Fe^{II}F_2(HAsO_4)(AsO_4){\cdot}enH_2{\cdot}2H_2O$ (**2**)		
As−O(4)	1.671(3)	Fe(1)−O(2)	2.007(3)
As−O(2)	1.672(3)	Fe(2)−O(4)	2.054(3)
As−O(3)	1.677(3)	Fe(2)−O(4)	2.054(3)
As−O(1)	1.708(3)	Fe(2)−F	2.067(3)
Fe(1)−F	1.930(3)	Fe(2)−F	2.067(3)
Fe(1)−F	1.930(3)	Fe(2)−O(5)	2.235(3)
Fe(1)−O(3)	1.996(3)	Fe(2)−O(5)	2.235(3)
Fe(1)−O(3)	1.996(3)	N−C	1.478(5)
Fe(1)−O(2)	2.007(3)	C−C	1.492(8)
	$Fe_3(HAsO_4)_6{\cdot}enH_2{\cdot}NH_3{\cdot}NH_4$ (**3**)		
As(1)−O(6)	1.664(7)	As(3)−O(5)	1.681(6)
As(1)−O(10)	1.672(6)	As(3)−O(8)	1.714(7)
As(1)−O(11)	1.674(7)	Fe(1)−O(6)	1.963(7)
As(1)−O(12)	1.728(7)	Fe(1)−O(6)	1.963(7)
As(2)−O(4)	1.655(7)	Fe(1)−O(4)	2.016(6)
As(2)−O(3)	1.679(6)	Fe(1)−O(4)	2.016(6)
As(2)−O(9)	1.686(6)	Fe(1)−O(2)	2.038(7)
As(2)−O(1)	1.732(7)	Fe(1)−O(2)	2.038(7)
As(3)−O(2)	1.663(6)	Fe(1)−Fe(1)	3.181(2)
As(3)−O(7)	1.674(7)	Fe(2)−O(11)	1.971(6)
Fe(2)−O(3)	1.998(6)	Fe(2)−O(5)	2.061(6)
Fe(2)−O(10)	2.002(6)	C−N(1)	1.52(3)
Fe(2)−O(9)	2.007(6)	C−N(2)	1.40(2)
Fe(2)−O(7)	2.021(6)	C−C	1.59(4)
	$Fe_2F_2(AsO_4)_2(H_2O){\cdot}enH_2$ (**4**)		
As(1)−O(9)	1.671(4)	Fe(1)−F(1)	2.032(4)
As(1)−O(8)	1.672(4)	Fe(1)−F(1)	2.036(3)
As(1)−O(3)	1.680(4)	Fe(2)−F(2)	1.938(4)
As(1)−O(5)	1.700(5)	Fe(2)−O(8)	1.945(4)
As(2)−O(7)	1.673(4)	Fe(2)−O(3)	1.992(4)
As(2)−O(6)	1.689(4)	Fe(2)−O(5)	2.005(5)
As(2)−O(2)	1.691(5)	Fe(2)−O(6)	2.011(4)
As(2)−O(4)	1.692(4)	Fe(2)−O(1)	2.093(5)
Fe(1)−O(9)	1.931(4)	Fe(1)−Fe(1)	3.180(2)
Fe(1)−O(2)	1.956(4)	C(1)−C(2)	1.508(10)
Fe(1)−O(4)	1.970(4)	C(1)−N(1)	1.455(8)
Fe(1)−O(7)	2.019(4)	C(2)−N(2)	1.495(10)

oxidation states by completing the octahedral coordination spheres and being neutral ligands at the same time. As expected, the distances around Fe(II) are quite longer than those around Fe(III). The corresponding valence sums are 2.12 and 3.04 for Fe(II) and Fe(III), respectively, and clearly confirm the valence assignments.

There is only one type of arsenate tetrahedron in the structure. It has three shared oxygen atoms and one terminal oxygen atom. The terminal oxygen is at somewhat longer distance from the arsenic compared to the other three, and this suggests that perhaps it is protonated to a hydroxyl group. These groups, together with the water molecules from the Fe(II) coordination spheres, point outward from the layers into the interlayer space where the ethylenediamine templates are positioned (Figure 2a). To keep the charges balanced, either the latter are monoprotonated and all arsenates are monoprotonated as $HAsO_4^{2-}$, or the templates are diprotonated and the arsenates are AsO_4^{3-} and $HAsO_4^{2-}$ in an equimolar ratio. This, of course, is next to impossible to tell from X-ray diffraction. Furthermore, the exact

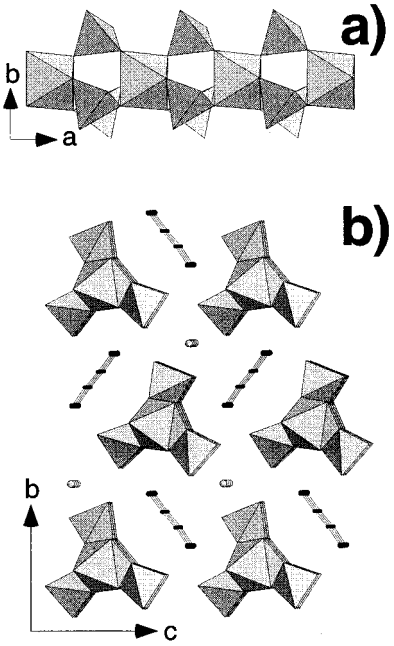

Figure 1. Two polyhedral views of the structure of compound **1**: (a) A chain of iron-centered octahedra connected via three arsenic-centered tetrahedra per pair of octahedra. (b) A general view of the structure along the direction of the chains with the water molecules (isolated spheres) and the ethylenediamine shown.

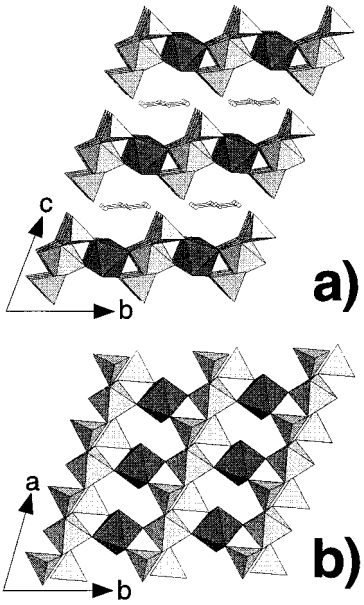

Figure 2. Polyhedral views of the structure of the layered mixed-valence compound **2** with the Fe(II)- and Fe(III)-centered octahedra shown in dark and light gray, respectively: (a) A view parallel to the layers with the ethylenediamine molecules shown between the layers. (b) A view of one layer. The terminal corners of the Fe(II)-octahedra are water molecules, and the shared corners between the two types of octahedra are fluorine atoms.

positioning of a proton is not of such great importance in this case. Nevertheless, there are a couple of clues suggesting the whereabouts of the proton. First, the templates are hydrogen-bonded to terminal oxygens of the arsenate, and second, terminal oxygens from different layers are hydrogen-bonded to each other through a unusually short O−O distance of only 2.47 Å. The latter suggests a symmetrical H-bond involving a hydrogen atom at half the distance between the two oxygens. This, on the other hand, would suggest that only half of the terminal oxygens

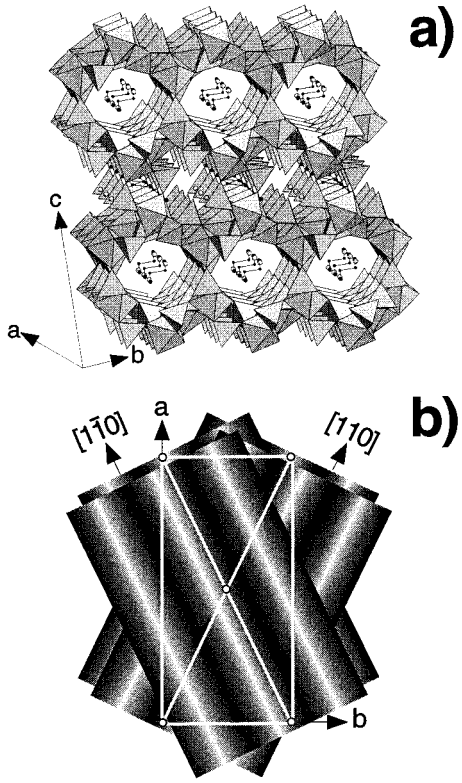

Figure 3. Structure of compound **3**: (a) A polyhedral view along [110] of the C-centered monoclinic cell. The ammonia (isolated spheres) and ethylenediamine molecules are shown. (b) A schematic representation of the two sets of equivalent channels along [110] and [1$\bar{1}$0] shown as cylindrical tubes. The view is normal to the centered *a*,*b*-face (outlined in white). The directions of the channels alternate along the *c* direction.

should be counted as protonated. Thus, the formula is better written as $Fe^{III}Fe^{II}F_2(HAsO_4)(AsO_4)\cdot enH_2\cdot 2H_2O$, where the ethylenediamine is diprotonated rather than as the one given for the analogous phosphate, $Fe^{III}Fe^{II}F_2(HPO_4)_2\cdot enH\cdot 2H_2O$, where the ethylenediamine is monoprotonated.[28]

$Fe_3(HAsO_4)_6\cdot enH_2\cdot NH_3\cdot NH_4$. The structure of compound **3** is a three-dimensional open framework (Figure 3). All iron atoms are octahedrally coordinated by oxygen atoms, while the arsenic atoms are tetrahedrally coordinated by three oxygen atoms and a terminal hydroxyl group, $AsO_3(OH)$. All oxygen atoms, except those of the OH groups (O2, O8, O12), are 2-bonded and shared by one tetrahedron and one octahedron. As expected, the As−O distances of the hydroxyl oxygen atoms, 1.728(7), 1.732(7), and 1.714(7) Å, are quite longer than those of the shared oxygen atoms, 1.672 Å on average. There is one type of one-dimensional opening in the framework formed of four octahedra and four tetrahedra. These channels run along two different but otherwise equivalent directions in the structure, [110] and [1$\bar{1}$0]. Figure 3b shows a view of the C-centered cell normal to the *a*,*b*-plane (outlined). The channels are represented schematically by cylindrical tubes. Their directions alternate on going along the *c* axis. Figure 3a is along one set of channels, [110], seen at the bottom and top of the picture, while the other set, [1$\bar{1}$0], runs in the middle of the picture but at angle of 51.08° from the view direction.

The templates, diprotonated ethylenediamine and ammonia or ammonium cations, are positioned in the channels of the structure. In the structure refinement they all appear disordered with two positions, N1 and N2, for each amino group of the ethylenediamine, and two positions, N3 and N4, for the ammonia. Such disorder is quite typical for many amino-

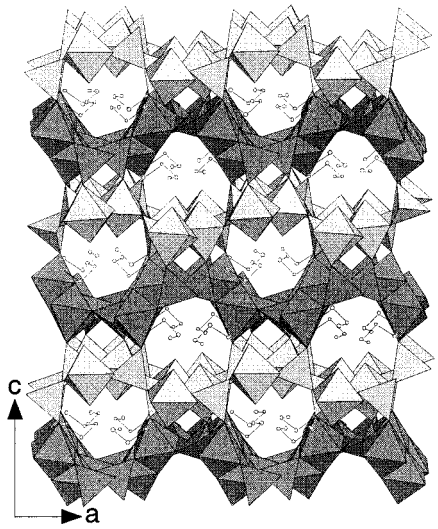

Figure 4. A general view of the structure of compound **4** along the direction of the channels. The structure can be described as built of two types of puckered out-of-phase layers (darker and lighter polyhedra) that are connected at the areas of close approach. The ethylenediamine molecules are positioned off the centers of the channels.

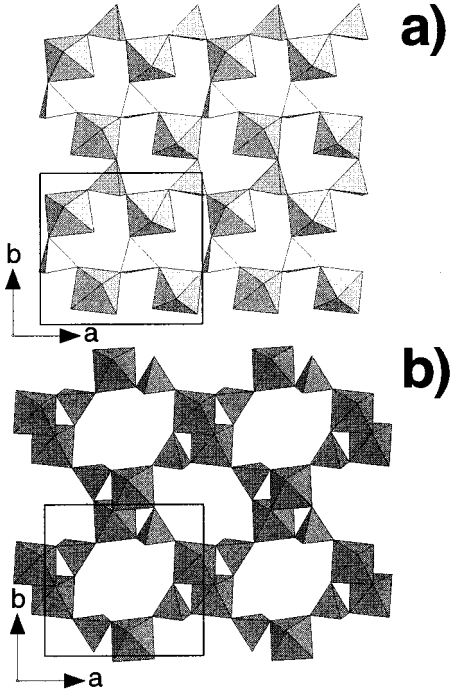

Figure 5. Views normal to the two types of puckered layers of compound **4** (the unite cell is outlined). (a) The in-layer terminal vertexes of the iron octahedra are water molecules, while those pointing away are fluorine atoms. (b) The dimers of edge-sharing octahedra are clearly visible.

templated frameworks, especially when the templates are not hydrogen-bonded to framework atoms as in this case. None of the nitrogen atoms of the ethylenediamine are near oxygen atoms or hydroxyl groups. One of the ammonia positions, N3, is hydrogen-bonded to two oxygen atoms, O3 and O7, at 2.83 and 2.88 Å, respectively, but the second ammonia nitrogen has no close oxygen neighbors. At the same time all three hydroxyl oxygens are hydrogen bonded to framework oxygen atoms by extremely short bonds, O1 to O2 at 2.76 Å, O8 to O9 at 2.67 Å, and O12 to O5 at 2.61 Å.

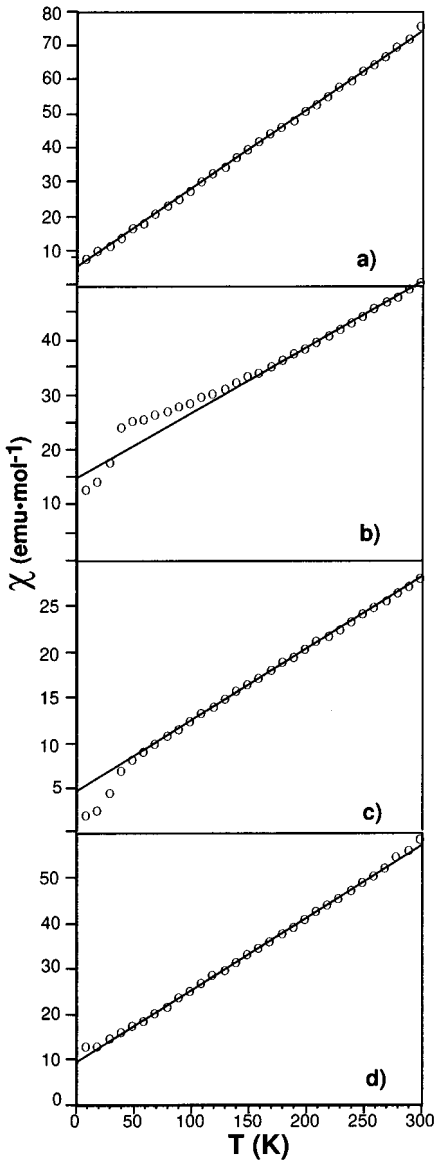

Figure 6. Molar magnetic susceptibilities for compounds (a) **1**, (b) **2**, (c) **3**, and (d) **4**. The ferrimagnetic ordering temperature for both **2** and **3** is around 40 K.

$Fe_2F_2(AsO_4)_2(H_2O)\cdot enH_2$. Compound **4** is a three-dimensional fluoroarsenate (Figure 4) with a somewhat unusual structure. Again, all iron and arsenic atoms center corner-sharing octahedra and tetrahedra, respectively, but some of the former share edges made of fluorine atoms and form dimers of $O_4Fe(F_2)FeO_4$ (Figure 5). The structure is of the open-framework type with channels running along the *b*-axis of the orthorhombic cell (Figure 4). For easier visualization the structure can be described as assembled of two types of puckered layers that are stacked alternatingly along the *c*-axis. The puckering of the layers is "out of phase", and they are connected at the areas of close approach by sharing corners of the polyhedra. The two layers are shown in Figure 5, where the dimers of edge-sharing octahedra centered by Fe1 are clearly distinguishable in the second layer. This layer is built of such dimers and tetrahedra centered by As2. The tetrahedra of the first layer are centered by As1, while the octahedra are centered by Fe2 and are made of four oxygen atoms, a coordinated water molecule, O1, and a fluorine atom, F2, cis to the water. The fluorine and the water molecule are terminal ligands, and therefore the octahedron is connected to only four arsenates (Figure 5a). Often, the identity

of such terminal ligands is unclear due to the number of available possibilities: H_2O, OH, O, or F. Support for the fluorine and water assignments in our case comes from the distances and the elemental analysis for fluorine. Thus, the long distance of 2.093 Å to O1 and the short distance of 1.938 Å to F2 suggest that they are water and fluorine, respectively. Also, the analysis of 7.54 wt % fluorine in the compound compares well with the calculated 7.48 wt % for two fluorine atoms per formula, i.e., per $Fe_2F_2(AsO_4)_2(H_2O)\cdot enH_2$. In Figure 5a the water molecule is the vertex that is within the "plane" of the layer, while the fluorine corners are alternating above and below that plane. The latter point toward the middle of the channels as it can be seen in Figure 4, and are hydrogen-bonded to the templates at very short distances, 2.622 Å to N1 and 2.889 Å to N2. The shared fluorine, F1, and the water molecule on Fe2 are also in the walls of the channels and are exposed and hydrogen-bonded to the templates at distances of 2.867 Å to N1 and 2.781 Å to N2 for F1 and O1, respectively. The ethylenediamine molecules are not at the center of the channels but are rather closer to the walls.

Magnetic Properties. Magnetic measurements were carried out mainly to confirm the oxidation state(s) of the iron atoms (Figure 6). The magnetization of the chain compound **1** is of the Curie−Weiss type within the measured temperature range of 10−300 K with $\Theta = -12$ K indicative of antiferromagnetic interactions between the iron centers (Figure 6a). The effective magnetic moment derived from this measurement, 6.04 μ_B, is in good agreement with the expected 5.9−6.0 μ_B for weak-field octahedral coordination and five unpaired electrons as in Fe(III). Compound **4** (Figure 6d) is also of the Curie−Weiss type at temperatures higher than 25 K with $\Theta = -50$ K and $\mu_{eff} = 8.41$ μ_B. The latter is also in good agreement with two Fe(III) centers per formula unit (calculated spin-only moment of 8.37 μ_B). Below 25 K the magnetization shows the beginning of antiferromagnetic ordering. Compound **3**, on the other hand, orders ferrimagnetically below 40 K. Above this temperature it is paramagnetic with $\Theta = -53$ K and $\mu_{eff} = 10.05$ μ_B, the latter in good agreement with the calculated spin-only moment for three high-spin octahedral Fe(III) centers, 10.25 μ_B.

The magnetization of the mixed-valence compound **2** is nearly identical with that of the corresponding phosphate, ULM-10.[28,34] It shows Curie−Weiss behavior at higher temperatures with effective moment 8.32 μ_B (8.10 μ_B for ULM-10), which is somewhat higher than the calculated spin-only 7.68 μ_B for one Fe(II) and one Fe(III) in high-spin octahedral environments. The asymptotic Curie temperature for the fit is −127 K (−133 K for ULM-10), and indicates strong antiferromagnetic interactions. Below 40 K the two sublattices order ferrimagnetically (30 K for ULM-10).[34]

Thermogravimetric and IR Analysis. All compounds lose weight up to about 600 °C but become amorphous above about 300 °C as a result of losing part of the weight. Samples heated to 800 °C recrystallize to simple iron orthoarsenate, $FeAsO_4$. The ratio As: Fe in compounds **1** and **3** is larger than 1, and part of the weight loss in these compounds is due to As_2O_5. On the other hand, part of the weight loss in compounds **2** and **4** is due to HF. All compounds also lose ethylenediamine and water. Thus, the measured weight loss for **1** is 62.4%, and it compares well with the theoretical 65.0% for As_2O_5 + en + $4H_2O$. Compound **3** loses 43.9%, and the calculated loss for $1.5As_2O_5$ + en + $2NH_3$ + $4.5H_2O$ is 47.1%. Both compounds lose the weight in multiple steps. Compounds **2** and **4** lose the weight in single steps at around 160 °C. The weight losses are 28.1% and 25.5% for **2** and **4**, respectively, while the corresponding theoretical values are 26.4% for 2HF + en + $2.5H_2O$ in **2** and 23.3% for 2HF + en + H_2O in **4**.

The IR spectra of all four compounds exhibit the "signature" vibrations of ethylenediamine, doublets at 1500−1550 and 1600−1650 cm^{-1}.

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

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