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Formation of a 3D Porous Ferric Arsenate Containing Novel Cubane-like Fe_4F_4 Building Units

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The purely inorganic microporous compound $[H_3O][Fe_4F_4(AsO_4)_3]\cdot 3H_2O$ (**1**), which contains novel cubane-like Fe_4F_4 cages, exhibiting a 3D configuration with channels of dimensions 8 Å × 8 Å running along the [001], [010], and [100] directions, presents antiferromagnetic interactions.

Inorganic compounds possessing open-framework structures continue to be attractive for their potential application in many areas.[1] Since the discovery of organically templated compounds,[1,2] a variety of organically directed transition-metal phosphates, phosphites, and arsenates have mainly been focused on the elimination of the organic templates by heating, with the aim of obtaining true microporous phases. However, amorphous phases were always obtained after calcination of the inorganic frameworks.[3] This is due to the strong ionic and hydrogen-bonding forces that maintain the linking between the templates and the inorganic frameworks, the elimination of which always leads to the collapse of the crystal structure, precluding the attainment of true microporous compounds.

Most of the open-framework compounds are prepared by employing hydrothermal methods. In some cases, HF was used as the mineralizer, which also becomes part of the structure by bridging the metal centers. The use of HF helps to solubilize all of the starting materials in the reaction solvent and produces a number of novel microporous phosphate frameworks that do not form in a fluoride-free medium.[4] Little work, however, has been carried out on the arsenate as compared to the phosphate. To date, only several arsenates of aluminum,[5] gallium,[6] molybdenum,[7] vanadium,[8] zinc,[9] and iron[10] have been reported in the literature, though arsenic belongs to the same group as phosphorus. Open-framework structures based on arsenates are beginning to attract the attention of synthetic chemists because the larger size of As^{5+} (0.335 Å) compared to P^{5+} (0.17 Å) may give rise to novel architectures.[11] The associated toxicity of arsenic is one of the reasons for the lack of a large number of arsenate-based extended structures. In particular, pure inorganic ferric arsenates are scarce.[12]

We are interested in introducing HF into the iron arsenate inorganic open framework and understanding the role of fluorine on the modification of inorganic framework structures. In an effort to further explore the structural diversity of the Fe/F/As system, we have prepared a porous ferric arsenate $[H_3O]Fe_4F_4(AsO_4)_3]\cdot 3H_2O$ (**1**), which represents the first example of a 3D inorganic compound with 1D

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channels employing novel cubane-like Fe_4F_4 cages as building units. Compound **1** presents antiferromagnetic interactions.

The compound $[H_3O][Fe_4F_4(AsO_4)_3]\cdot3H_2O$ (**1**) was prepared[13] by the hydrothermal reaction of $Na_3AsO_4\cdot12H_2O$, $FeCl_3$, HF, and water at 180 °C for 72 h. Light-yellow crystals of complex **1** were obtained, which thus may have been formed by the reaction as summarized in eq 1.

$$3Na_3AsO_4 + 4HF + 4FeCl_3 + 4H_2O \rightarrow$$
$$[H_3O][Fe_4F_4(AsO_4)_3]\cdot3H_2O + 9NaCl + 3HCl \qquad (1)$$

X-ray crystallographic study[14] reveals that compound **1** is a 3D inorganic open framework with 1D channels running in the [001], [010], and [100] directions forming from cubane-like Fe_4F_4 cages interacting with AsO_4 tetrahedra through the corner-sharing mode.

It crystallizes in the cubic space group $P\bar{4}3m$, and there is only one crystallographically distinct As atom as well as one Fe atom in the asymmetric unit. An As atom is located at the special position (0.5, 1, 1), and each O site is half-occupied to form an AsO_4 tetrahedron. For AsO_4, the As−O distance is 1.689(3) Å and the O−As−O angles vary from 107.77(10)° to 112.9(2)°. Each Fe atom completes a distorted octahedral configuration by three O donors from three different AsO_4 tetrahedra and three μ_3-F donors with bond lengths of Fe−O = 1.946(3) Å and Fe−F = 2.081(2) Å, and the angles of O−Fe−F vary from 91.45(12)° to 165.22(15)°. Four FeF_3O_3 octahedra connect with each other through the edge-sharing mode to form a novel cubane-like Fe_4F_4 cage (Figure 1a). To the best of our knowledge, though there is considerable research on cubane-like Fe_4S_4[15] and Fe_4O_4[16] cages, compound **1** represents the first example of a cubane-like cage based on the Fe_4F_4 unit.

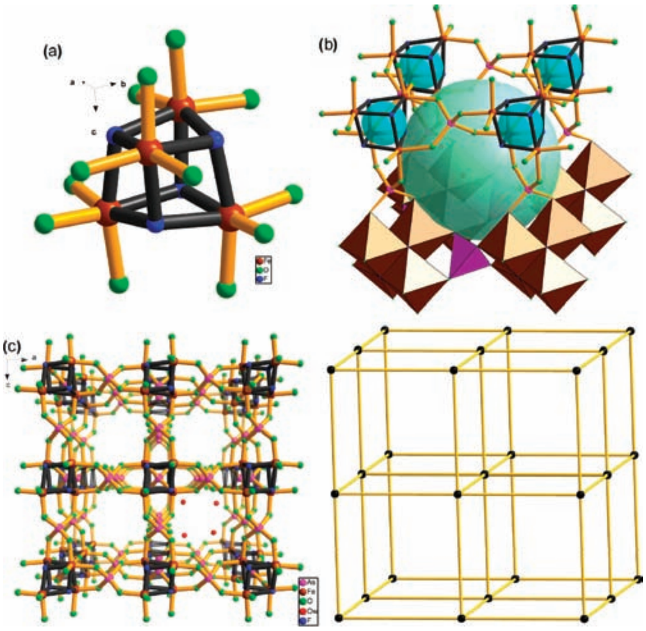

Figure 1. (a) Novel cubane-like Fe_4F_4 cage in compound **1**. (b) Cubic lattice fragment in **1**. (c) View down the [010] direction of the 3D porous inorganic framework and its related schematic illustration.

It is worth noting that, with metal centers providing rigid lattice points to support robust crystal structures, AsO_4 tetrahedral spacers play significant roles in the formation of the 3D porous framework. In detail, each Fe_4F_4 unit is octahedrally coordinated by six AsO_4 units, each AsO_4 unit is linearly bridging two Fe_4F_4 units to form a cubic lattice (Figure 1b), and propagation of the cubic lattices leads to the overall 3D open framework with 1D channels along the [001], [010], and [100] directions (Figure 1c). The protonated free water molecules occupy channels that balance the charge on the anionic framework. Alternatively, one FeF_3O_3-distorted octahedron connects with three AsO_4 tetrahedra, and each AsO_4 tetrahedron interacts with four FeF_3O_3-distorted octahedra from two Fe_4F_4 cages via the corner-sharing mode to form a 3D framework with 1D channels. The channels have a diameter of ca. 8.0 Å, delimited by four SBU-7 units. As calculated by *PLATON*,[17] compound **1** possesses large solvent-accessible volumes of 45.3% of the unit cell volume.

Using the Brown−Altermatt formalism[18] for the bond length/bond valence relationship for Fe−O and As−O, bond-order sums for the cations and anions were calculated (S-Table 1 in the Supporting Information). The calculated bond-order sums for both cations and anions are in agreement with the formal oxidation states of 3+, 5+, and 2− for Fe, As, and O atoms, respectively.

Variable-temperature magnetic susceptibility (4−300 K) measurement of **1** has been carried out on a powdered sample in a field of 1000 Oe. At room temperature, the χ_mT value is equal to 17.36 emu K mol^{-1} (Figure 2), which is lower than the expected values of 17.50 emu K mol^{-1} for four high-spin Fe^{III} (S = $^5/_2$, g = 2.0) magnetic centers. The molar magnetic susceptibility increases with decreasing temperature and reaches a sharp maximum at ca. 14 K. After that, the susceptibility decreases continuously. This result, together

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[13] Mild hydrothermal synthesis (453 K, 3 days) was carried out in a Teflon-lined autoclave, in which a previously stirred mixture of $Na_3AsO_4\cdot12H_2O$ (0.14 g, 0.31 mmol), $FeCl_3$ (0.17 g, 1.02 mmol), and HF (0.3 mL) in 15 mL of water was placed. The pH value was adjusted to ca. 4 with ethylenediamine. The light-yellow block crystals **1** were collected after the mixture was cooled to room temperature. Yield: 0.036 g (18% based on Fe). The elemental percentages in the product were calculated by inductively coupled plasma atomic emission spectroscopy, the with fluorine content requiring the use of a selective electrode. The hydrogen elemental percentage was determined using a Perkin-Elmer 2400 series IICHNS/O elemental analyzer. Anal. Calcd for $Fe_4F_4As_3O_{16}H_9$: Fe, 28.30; F, 9.63; As, 28.48; H, 1.15. Found; Fe, 28.50; F, 10.30; As, 28.73; H, 1.13. FT-IR (KBr, cm^{-1}): 3418 (m), 2926 (w), 2850 (w), 1633 (s), 1114 (m), 800 (s), 408 (s).

[14] Compound **1** was studied on a Rigaku R-AXIS-RAPID image plate area detector using graphite-monochromated Mo Kα diffraction (λ = 0.710 73 Å) at room temperature. Data collection was in the range 3.59° ≤ 2θ ≤ 27.43°. The structure was solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using *SHELXTL-97* crystallographic software package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of water were not located. Crystal data for **1**: crystal dimens 0.05×0.02×0.01 mm^3, cubic, space group $P\bar{4}3m$, $a = b = c$ = 8.0163(9) Å, V = 515.14(10) Å^3, Z = 1, ρ_{calcd} = 2.544 g cm^{-3}, M = 789.23, μ(Mo Kα) = 7.619 mm^{-1}; 5097 reflections were measured, and 260 [$I \geq 2\sigma(I)$] unique reflections were used in all calculations. Final R1 = 0.0179, wR2 = 0.0469, GOF = 1.009.

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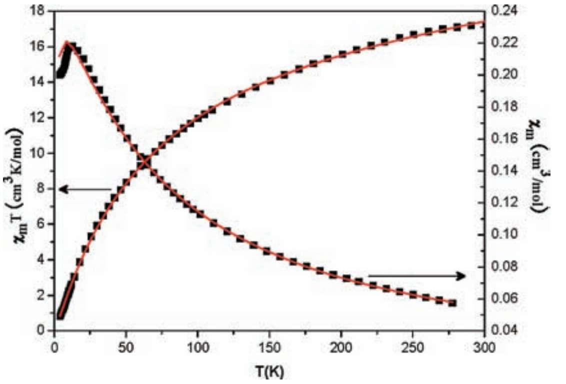

Figure 2. Temperature dependence of magnetic susceptibility in the form of χ_m versus T and $\chi_m T$ versus T. The solid lines represent the best fits.

with the decrease of the magnetic moment from 17.36 emu K mol^{-1} at room temperature to 0.85 emu K mol^{-1} at 4 K, indicates the presence of an antiferromagnetic interaction within the $\{Fe^{3+}{}_4\}$ unit in **1**.

In general, the effect of weak spin interactions on the magnetic susceptibility may be treated by the molecular field approximation. To fit the magnetic data to a theoretical model and to obtain the J exchange parameter, the 3D magnetic ordering can be understood by considering that the crystal structure is formed by [Fe_4F_4] cubane cores interconnected by AsO_4 groups. Because the Fe···Fe distance in the [Fe_4F_4] cubane core [3.225(1) Å] is shorter than that between two neighboring cubane cores [6.172(1) Å], we considered the system to be a $\{Fe^{III}{}_4\}$ cluster; the magnetic susceptibility data of **1** was fitted by means of least squares using the Heisenberg−Dirac−van Vleck Hamiltonian $\hat{H}$ for an isotropic exchange interaction with $S_1 = S_2 = S_3 = S_4 = {}^5/_2$.

$$\hat{H} = -J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_4 + \hat{S}_4\hat{S}_1 + \hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_4) \quad (2)$$

$$\chi_M = \frac{Ng^2\beta^2}{3kT}\,\frac{\sum S_T(S_T+1)(2S_T+1)e^{-E(S_T)/kT}}{\sum(2S_T+1)e^{-E(S_T)/kT}} + \mathrm{TIP} \quad (3)$$

The total spin state (S_T) values and their energies [$E(S_T)$], can be obtained using the vector-coupling method of Kambe.[19] χ_M is the molar magnetic susceptibility of the paramagnetic center; N, k, T, and β have their usual meanings. The best fit is obtained with values of $g = 2.02 \pm 0.01$, $J = -2.08 \pm 0.03$ cm^{-1}, and $\chi_{TIP} = 0.0075 \pm 0.0005$ cm^3 mol^{-1}, and the agreement factor R is 6.4×10^{-3} ($R = \sum[(\chi_M)^{obs} - (\chi_M)^{calc}]^2/[(\chi_M)^{obs}]^2$). The negative J value suggests that an antiferromagnetic coupling between Fe^{III} centers exists in the cubane core. The magnetic exchange interactions inside the Fe_4F_4 edge-sharing cubane core are propagated through the F atoms with an Fe−F−Fe bond angle of 101.6(3)°. Similar behaviors have also been observed and reported in other fluoroarsenate iron(III) compounds.[20]

In summary, a novel 3D porous inorganic compound containing the first examples of cubane-like Fe_4F_4 cages has been synthesized by a hydrothermal method. This work represents the family of inorganic microporous compounds formed without organic templates. Extended researches are underway to reveal the synthetic rules and explore attractive properties.

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Supporting Information Available: Table of bond valence sums, details of the experimental procedures and thermogravimetric decomposition, CIF file, IR spectrum, TGA curve, and table of bond lengths and angles for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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