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Organically Templated Inorganic/Organic Hybrid Materials: Synthesis and Structures of $(C_4H_{12}N_2)[Fe^{II}_4(C_2O_4)_3(HPO_4)_2]$ and $(C_5H_{14}N_2)[Fe^{III}_2(C_2O_4)(HPO_4)_3]$

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Recently, a large number of crystalline iron phosphates have been prepared in aqueous or predominantly nonaqueous solution under mild hydrothermal conditions using organic amines as structure directing agents.[1−4] Some of these phosphates exhibit novel open-framework structures. These materials are of interest because of their potential applications in heterogeneous catalysis. Recent reports indicate that open-framework structures can also be prepared by exploiting appropriate metal centers linked through suitable multidentate organic ligands.[5−9] This approach makes possible the rational design and synthesis of coordination polymers with potential interesting properties. To combine the robustness of the inorganic framework with the greater chemical flexibility of the organic ligand, we have attempted to incorporate both inorganic and organic anions into the structure to provide a new route to open-framework materials. We report herein two organically templated inorganic/organic hybrid materials, $(C_4H_{12}N_2)[Fe^{II}_4(C_2O_4)_3(HPO_4)_2]$ (**1**) and $(C_5H_{14}N_2)[Fe^{III}_2(C_2O_4)(HPO_4)_3]$ (**2**), with intersecting tunnel structures. The two compounds are original in that it is the first time that inorganic phosphate and organic oxalate anions, associated with a transition metal, are incorporated into the skeleton of a framework structure templated with an amine. A few compounds were recently published which had the characteristics of the title compounds concerning two anions with metals, namely, the tin compounds $Sn(O_3PCH_3)(C_2O_4)$[10] and $Sn_2(PO_4)(C_2O_4)_{0.5}$[11] and the rare earth compounds $[Ln(H_2O)_2]_2(C_2O_4)_2(CO_3)\cdot 2.5H_2O$ and $[Ln(H_2O)_2]_2(C_2O_4)(CO_3)_2$.[12] However, organic templates are not included in these structures.

Compound **1** was synthesized by heating a homogeneous gel reaction mixture with the millimolar composition 1:5:4:4:555 $FeCl_2\cdot 4H_2O$:piperazine:$H_2C_2O_4\cdot 2H_2O$:H_3PO_4:H_2O in a Teflon-lined autoclave at 165 °C for 3

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days under autogenous pressure. The resulting product, containing orange tabular crystals of **1** and a small amount of black solid, was filtered and washed with water. A suitable orange crystal was selected for single-crystal X-ray analysis.[13] The black solid was manually removed from the bulk product. The experimental and simulated powder X-ray diffraction patterns are in excellent agreement with each other, proving the phase purity of the sample. Chemical analysis also confirms the stoichiometry. (Found: C, 15.72; H, 1.77; N, 3.62. Calcd: C, 15.65; H, 1.84; N, 3.65.) A small black crystal was isolated and indexed on an Enraf-Nonius CAD4 diffractometer. The cell parameters indicate that the black crystal is the synthetic lipscombite, $Fe_{2.95}(PO_4)_2(OH)_2$.[14] Compound **2** was obtained by heating a mixture with the mmolar composition 1.5:6.65:8:13:611 $FeCl_3 \cdot 6H_2O$:2-methylpiperazine:$H_2C_2O_4 \cdot 2H_2O$:H_3PO_4:H_2O at 160 °C for 3 days. The product contained light brown crystals of **2** and a small amount of black solid. A light brown crystal was selected for single-crystal X-ray analysis.[15] The black solid was manually removed. Powder X-ray diffraction and chemical analysis of the light brown solid confirm the phase purity and stoichiometry. (Found: C, 14.23; H, 3.01; N, 4.86. Calcd: C, 14.25; H, 2.91; N, 4.75.) The possible solution ion-exchange behavior of **2** was examined by stirring powder samples (10 mg) in 5 mL of a 4.5 M NH_4Cl aqueous solution for 8 h at room temperature and 50 °C; the samples then filtered out and washed thoroughly with water and ethanol, followed by air-drying. Elemental analysis of the products indicated that the exchange of NH_4^+ for $C_5H_{14}N_2^{2+}$ did not occur. Ion-exchange reactions of **1** with NH_4^+ under the same conditions led to the decomposition of the framework structure, as indicated by powder X-ray diffraction.

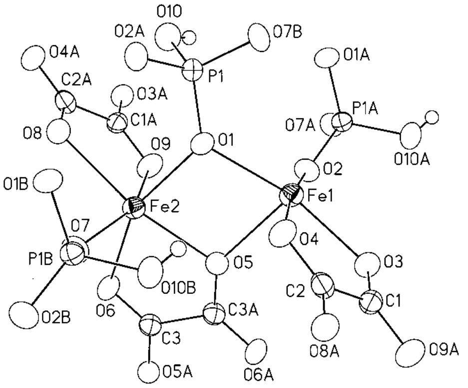

Figure 1. The dinuclear iron cluster in $(C_4H_{12}N_2)[Fe_4(C_2O_4)_3(HPO_4)_2]$; thermal ellipsoids are shown at 60% probability

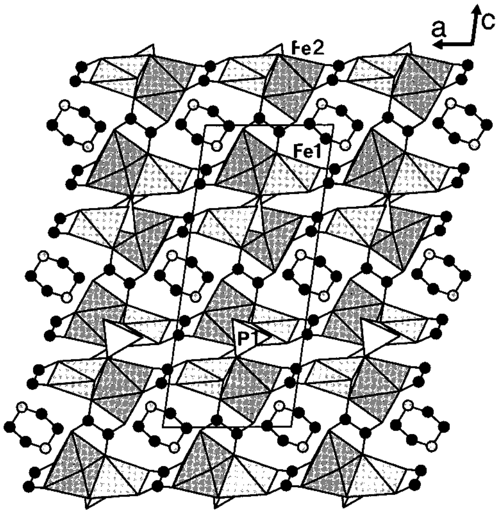

Figure 2. Polyhedral view of the structure of $(C_4H_{12}N_2)[Fe_4(C_2O_4)_3(HPO_4)_2]$ along the *b* axis. Solid circles, C atoms; stippled circles, N atoms

The basic structural feature of **1** is an edge-sharing dimer formed of two Fe^{II}-centered polyhedra (Figure 1). The coordination around the two iron centers is square pyramidal for Fe(1) and octahedral for Fe(2). The oxygen atoms involved in the shared edge serve as corners for HPO_4 and $C(3)_2O_4$ ligands. The dimer alternates with the HPO_4 group, and each HPO_4 shares corners with three dimers, thus forming a double chain parallel to the *b*-axis (Figure 2). Each double chain is linked to others by oxalate anions to generate a three-dimensional framework with intersecting tunnels parallel to the [010] and [100] directions. Diprotonated piperazinium cations, which possess $\bar{1}$ symmetry, are located at the intersections of these tunnels. The tunnel parallel to [010] has a window formed by the edges of two FeO_5, two FeO_6, and four oxalate anions. The other type of tunnel has an eight-membered window formed by two FeO_5, two FeO_6, two HPO_4, and two oxalate anions. The $C(1)C(2)O_4^{2-}$ anion acts as a bis-bidentate ligand to Fe(1) and Fe(2). The $C(3)_2O_4^{2-}$ anion has $\bar{1}$ symmetry and is a bis-bidentate ligand to Fe(2) as well as a bis-monodentate ligand to Fe(1). The μ_2 coordination by the oxalate leads to a highly distorted coordination polyhedra for both Fe(1) and Fe(2), as indicated by the wide range of Fe−O bonds lengths [1.97−2.21 Å for Fe(1), 2.00−2.26 Å for Fe(2)] and the small O−Fe−O bond angles [77.8° for Fe(1), 76.8° for Fe(2)] subtended by the oxalate ligands. The piperazinium cation is H-bonded to framework oxygens.

The structure of **2** consists of $Fe^{III}O_6$ octahedra connected by coordinating HPO_4^{2-} and $C_2O_4^{2-}$ anions to form intersecting tunnels parallel to the [100] and [010] directions with the diprotonated 2-methylpiperazine cations being nested at the intersections of these tunnels via hydrogen bonds to the phosphate oxygens (Figure 3). The (*R*)-enantiomer of 2-methylpiperazine is segregated from the (*S*)-enantiomer in different

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(13) Crystal data for **1**, $(C_4H_{12}N_2)[Fe^{II}_4(C_2O_4)_3(HPO_4)_2]$, M = 767.57: monoclinic, $P2_1/c$, a = 7.5573(4) Å, b = 7.8188(4) Å, c = 18.0421(9) Å, β = 98.710(1)°, V =1053.8(1) Å^3, Z = 2, D_{calc} = 2.419 Mg m^{-3}, λ = 0.71073 Å, $F(000)$ = 764, 1685 absorption corrected reflections with $F_o > 4\sigma(F_o)$ out of 2237 unique reflections ($2\theta_{max}$ = 55.1°) measured at 23 °C for an orange crystal of dimension 0.05 × 0.05 × 0.14 mm on a Siemens Smart-CCD diffractometer on convergence gave final values of R_1 = 0.0467 and wR_2 = 0.1073. Bond valence sums of oxygen atoms were calculated to help locate the hydrogen atom. All non-hydrogen atoms were anisotropically refined and hydrogen atoms were found in difference Fourier maps and were refined isotropically. All calculations were carried out with PC version of the SHELXTL program package.

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(15) Crystal data for **2**, $(C_5H_{14}N_2)[Fe^{III}_2(C_2O_4)(HPO_4)_3]$, M = 589.84: triclinic, $P\bar{1}$, a = 6.3948(3) Å, b = 9.1419(4) Å, c = 16.1585(7) Å, α = 98.758(1)°, β = 93.443(1)°, γ = 108.488(1)°, V = 879.50(7) Å^3, Z = 2, D_{calc} = 2.227 Mg m^{-3}, λ = 0.71073 Å, $F(000)$ = 596, 3204 absorption corrected reflections with $F_o > 4\sigma(F_o)$ out of 3802 unique reflections measured at 23 °C for a light brown crystal of dimension 0.05 × 0.18 × 0.18 mm ($2\theta_{max}$ = 56.2°) on convergence gave final values of R_1 = 0.0383 and wR_2 = 0.0927. Bond valence sums of oxygen atoms were calculated to help locate hydrogen atoms. All non-hydrogen atoms were anisotropically refined and hydrogen atoms were found in difference Fourier maps and were refined isotropically. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited.

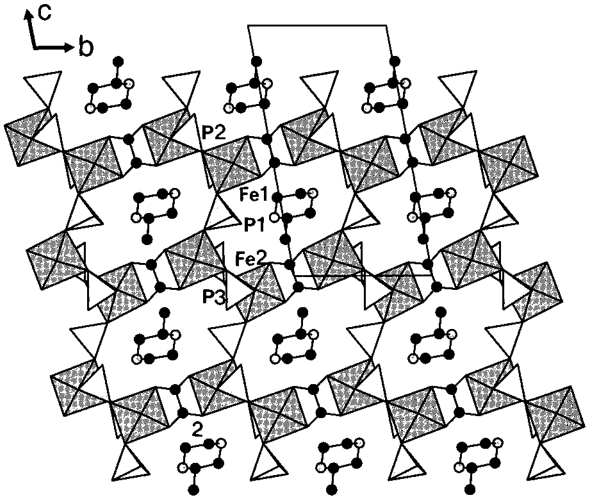

Figure 3. Polyhedral view of the structure of $(C_5H_{14}N_2)[Fe_2(C_2O_4)(HPO_4)_3]$ along the *a* axis. Solid circles, C atoms; stippled circles, N atoms

tunnels. The organic amines are found to be ordered. The tunnel parallel to [100] has a window formed by the edges of six FeO_6 octahedra, four phosphate tetrahedra, and two oxalate anions. The other type of tunnel has an eight-membered window formed by four octahedra and four tetrahedra. An alternative way of describing the structure is that it contains puckered layers of iron phosphate parallel to the (010) plane, which are further connected into a three-dimensional framework via bridging oxalate ligands. Each iron atom is coordinated by a bidentate $C_2O_4{}^{2-}$ anion and four $HPO_4{}^{2-}$ anions. The FeO_6 octahedra are also highly distorted due to the μ_2 coordination by the oxalate ligands [Fe(1)−O, 1.90−2.14 Å; Fe(2)−O, 1.92−2.16 Å; ∠O(13)−Fe(1)−O(14), 78.2°; ∠O(15)−Fe(2)−O(16), 76.8°]. Both $HP(2)O_4$ and $HP(3)O_4$ groups coordinate to three Fe atoms with the hydroxo group being unshared. $HP(1)O_4$ bonds to two Fe atoms through two oxygen donors; the hydroxo group and the pendant P−O(2) project into the tunnel. All hydroxo groups are involved in hydrogen bonding.

In conclusion, two compounds have been synthesized under hydrothermal conditions. Their structures are featured by the presence of both phosphate and oxalate anions in the same framework. They are the first members of a new class of organically templated inorganic/organic hybrid materials. These two compounds provide potential for further exploration. For example, it may be possible to increase the size of the channels by replacing oxalate with extended analogues such as squarate and 1,3,5-benzenetricarboxylate. Further work on this theme is in progress.

Acknowledgment. We thank the National Science Council and Chinese Petroleum Corp. of Taiwan for support.

Supporting Information Available: Tables of experimental details and crystal data, atomic coordinates, anisotropic temperature factors, bond lengths and angles, and hydrogen atom positions for **1** and **2** (9 pages); tables of structure factors (15 pages). Ordering information is given on any current masthead page.

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