Synthesis and Crystal Structure of New Sulfate-Bridged Coordination Polymer, $\{(4,4'\text{-bpyH}_2)[Fe_3(4,4'\text{-bpy})_3(SO_4)_4(H_2O)_6]\cdot 10H_2O\}_n$ (4,4'-bpy = 4,4'-Bipyridine). Three-Dimensional Network with Microporous Channels

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A new sulfate-bridged coordination polymer, $\{(4,4'\text{-bpyH}_2)[Fe_3(4,4'\text{-bpy})_3(SO_4)_4(H_2O)_6]\cdot 10H_2O\}_n$, was synthesized and crystallographically characterized. This complex shows a novel three-dimensional (3-D) *log-cabin* type structure constructed from one-dimensional (1-D) $[Fe(4,4'\text{-bpy})(H_2O)_2]_n$ cationic chain, free protonated 4,4'-bpy, and sulfate dianion. This structure shows channel-like cavities with dimensions of about 3 Å x 4 Å.

Synthesis of coordination polymers with a channel structure is of great current interest due to unique functionalities such as molecule adsorption,[1-4] heterogeneous catalysis,[5] and ion exchange.[6-8] Recent efforts have been focused on the crystal engineering of 3-D coordination polymers with robust channel structures. A relevant synthetic strategy for the channel structures is to use a rod-like bridging ligand, 4,4'-bipyridine (4,4'-bpy). Although a number of coordination polymers with channel structures have been prepared from divalent metal ions and 4,4'-bpy,[9] this crystal engineering has been facing with difficulties because of i) the formation of interpenetrating structures, ii) the occupation of channels by counter anions, and iii) the decay of channel after the removal of guest molecules. Use of a counter dianion as a linking ligand is one of the useful synthetic strategies for the construction of coordination networks of transition metal cations. The resulting coordination polymers with dianion coordination links could be robust and free from both the interpenetration and the occupation of channels by counter anions. Since a sulfate dianion has a tetrahedral geometry with four oxygen atoms, providing multi-linking sites, this anion can give rise to a well-associated network with metal-4,4'-bpy modules. A few examples constructed from 4,4'-bpy and sulfate have been reported.[10-12] However, the sulfate dianions are found to act as a monodentate, and thus no channel structure is formed. We have first succeeded in the synthesis and structural characterization of a sulfate-bridged porous coordination polymer, $\{(4,4'\text{-bpyH}_2)[Fe_3(4,4'\text{-bpy})_3(SO_4)_4(H_2O)_6]\cdot 10H_2O\}_n$, in which the sulfate anion acts as an effective connector between the Fe centers, providing a new 3-D network with the channels.

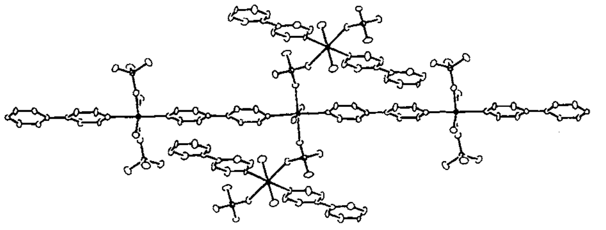

Figure 1. A view of the $[Fe(SO_4)]_n$ undulating chain that serves to interconnect $[Fe(4,4'\text{-bpy})]_n$ linear chains.

The compound was prepared by the reaction of $FeSO_4\cdot 7H_2O$ and 4,4'-bpy. An ethanol solution (20 ml) of 4,4'-bpy (312 mg, 2 mmol) was added to an aqueous solution (20 ml) of $FeSO_4\cdot 7H_2O$ (278 mg, 1 mmol). The obtained yellow solution was filtered, and diffusion of acetone in the filtrate gave orange single crystals after a few weeks.

This compound consists of a 1-D chain of $[Fe(4,4'\text{-bpy})(H_2O)_2]_n$, protonated 4,4'-bpy, and sulfate dianion. The aspect of the sulfate-linking is shown in Figure 1.[13] In the crystal, there are three independent Fe atoms, which sit on the crystallographic inversion center and have similar distorted

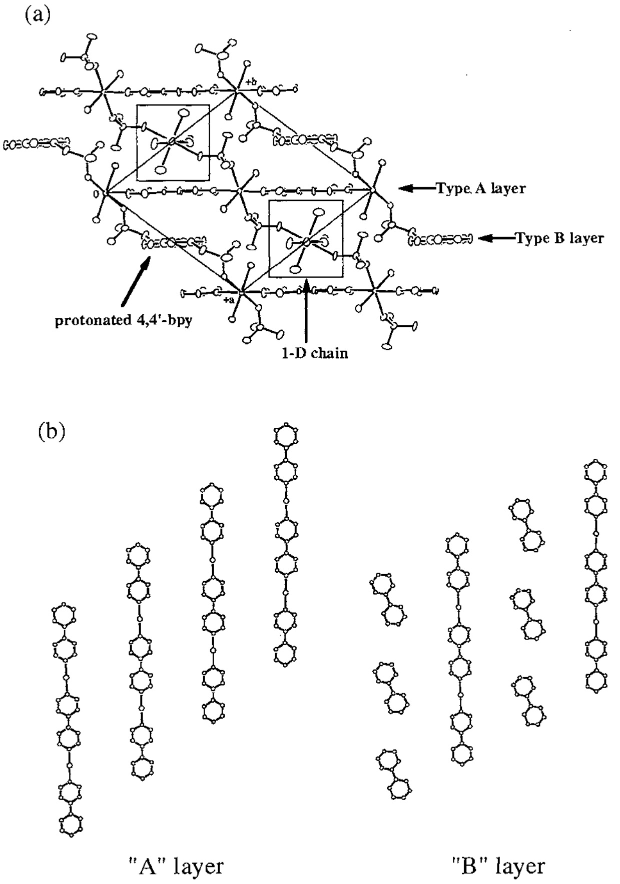

Figure 2. (a) ORTEP view of the crystal cell of the compound along the *c*-axis. (b) Structural aspects of two types of layers; the coordinated sulfate dianion and H_2O are omitted for clarity.

octahedral coordination environment. Each Fe is coordinated by two pyridine nitrogen donors (Fe-N = av. 2.194 Å), two sulfate oxygen donors (Fe-O = av. 2.136 Å), and two water molecules (Fe-O = av. 2.135 Å). Each of the pair of donor atoms (two pyridine nitrogens, two sulfate oxygens, and two water oxygens) occupies *trans* position to each other, and the *trans* N-Fe-N and O-Fe-O bond angles are crystallographically linear. The *cis* N-Fe-O and O-Fe-O bond angles are slightly deviated from 90 ° (range from 84.4 to 90.4 °). The two pyridine rings of each 4,4'-bpy ligand are co-planar.

The crystal structure affords a 3-D porous framework. In the crystal, two types of layers (A and B) are formed as shown in Figure 2. Type A layer consists of only linear $[Fe(4,4'\text{-}bpy)(H_2O)_2]_n$ cationic chains. On the other hand, type B layer consists of linear $[Fe(4,4'\text{-}bpy)(H_2O)_2]_n$ cationic chains, which run parallel along the *c*-axis, and protonated 4,4'-bpy. The directions of these two types of chains are mutually oriented at 53 °. Both A and B layers are perpendicular to the *ab* plane and these planes alternatively stack as shown in Figure 2a.

Sulfate dianion shows an important role for the construction of the 3-D network. The 1-D chains in the adjacent A and B layers are linked by coordination bonds of sulfate bridges (see Figures 1 and 2a). In addition, the sulfate dianion of the 1-D chains in the A layer is hydrogen-bonded to both the coordinating water molecule in the next A layer and the protonated 4,4'-bpy in the adjacent B layer; the O (SO_4) - O (H_2O) and O (SO_4) - N ($4,4'\text{-}bpyH_2$) distances are 2.71 and 2.67 Å, respectively. As a result, the 3-D framework is built up. This unique structure is described as *log-cabin* type network (Figure 3a). In the 3-D network, parallel π-π interaction (ca. 3.4 Å) is observed between all 4,4'-bpy molecules in the adjacent layers.

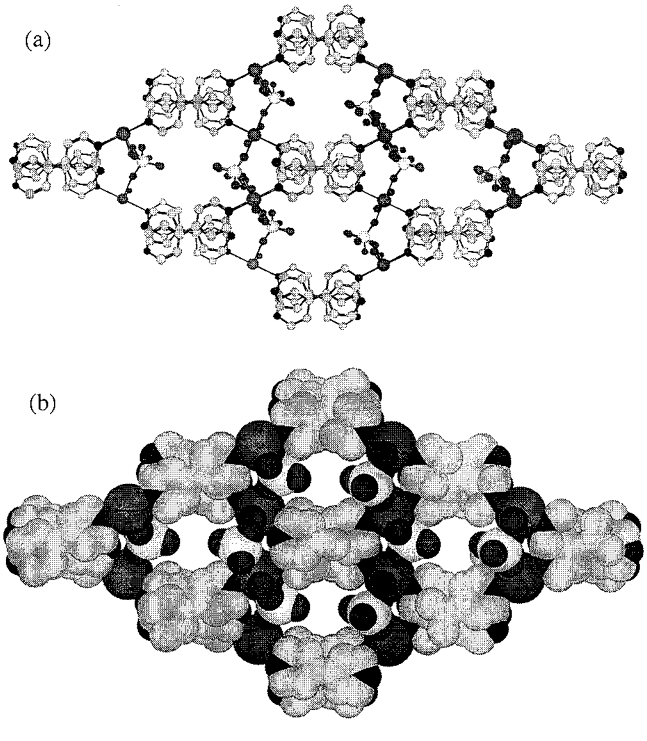

Figure 3. (a) A view of the *log-cabin* type structure. (b) A space-filling model of the *log-cabin* type structure, indicating the small channel structure.

The framework of this complex creates the channels along the (a - b) vector with dimensions of about 3 Å x 4 Å. The aspect is illustrated in Figure 3b. The cavities are occupied with crystallized water molecules, which are hydrogen bonded to the sulfate oxygen atoms (O-O = ca. 2.9 Å) and coordinated water oxygen atoms (O-O = ca. 2.8 Å). Thermogravimetric analysis reveals that this compound loses these guest waters in the region 70 - 130 °C and has no remarkable weight loss up to 350 °C. This result may indicate that the production of vacant cavities (ca. 3 Å x 4 Å) after removal of the guest molecules.

In this work, we demonstrate the first example of a sulfate-bridged porous coordination polymer, $\{(4,4'\text{-}bpyH_2)[Fe_3(4,4'\text{-}bpy)_3(SO_4)_4(H_2O)_6]\cdot 10H_2O\}_n$. Unique sulfate bridges not only between 1-D chains of $[Fe(4,4'\text{-}bpy)(H_2O)_2]_n$, but also between protonated 4,4'-bpy and the 1-D chains produce a 3-D framework with channels.

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13 Crystal data : $C_{40}H_{66}Fe_3N_8O_{32}S_4$, formula weight = 1466.78, triclinic, space group $P\bar{1}$ (no. 2), a = 12.000(3), b = 12.611(4), c = 11.526(3) Å, α = 115.75(2), β = 106.99(2), γ = 69.34(2) °, V = 1449.9(8) Å^3, Z = 1, D_{calcd} = 1.680 g/cm^3, R (R_w) = 0.078 (0.097) for 2706 diffraction data with $I > 3\sigma(I)$ and 410 variables.