Crystal structure of *catena*-[diaqua-hexapyridinyl-bis(μ-sulfato)diiron(II)] tetrahydrate, $[Fe(C_5H_5N)_4][Fe(H_2O)_2(C_5H_5N)_2](SO_4)_2 \cdot 4H_2O$

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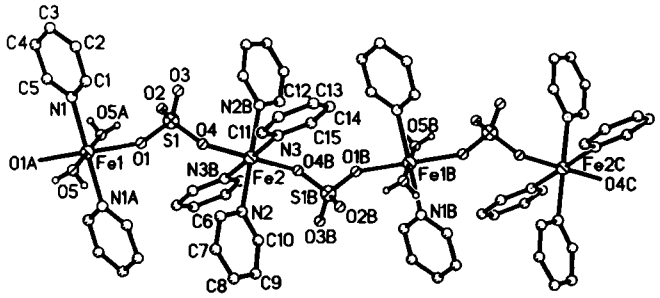

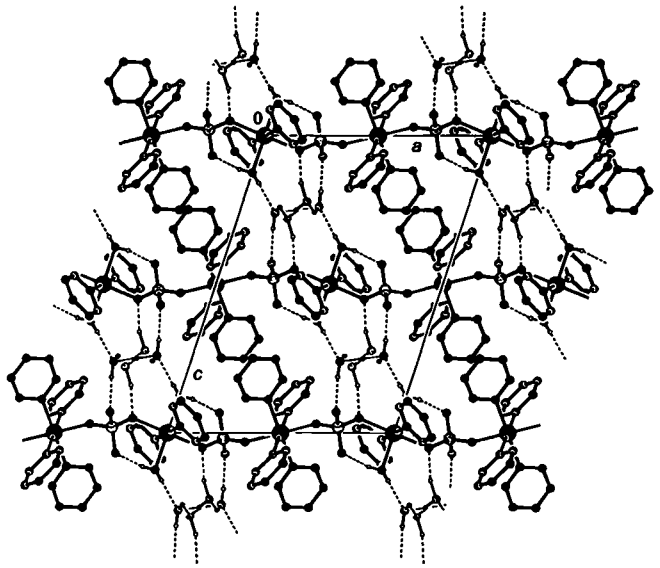

Abstract

$C_{30}H_{42}Fe_2N_6O_{14}S_2$, monoclinic, $P12_1/n1$ (no. 14), $a = 12.470(3)$ Å, $b = 9.498(2)$ Å, $c = 17.043(3)$ Å, $\beta = 108.23(3)°$, $V = 1917.3$ Å^3, $Z = 2$, $R_{gt}(F) = 0.043$, $wR_{ref}(F^2) = 0.086$, $T = 291$ K.

Source of material

A mixture of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot H_2O$, H_3BO_3, tribenzylphosphine, pyridine (py) and water in the molar ratio of 1:3:1:15 was loaded in a thick wall Pyrex tube (7 ml capacity, reactant added to a total volume of 1 ml), which sealed under vacuum and heated at 383 K for 3 days. The compound was initially obtained in an attempt to synthesize hydrothermally organically templated ferric borophosphate, and, therefore, the starting materials included boric acid and tribenzylphosphine. Later, the reaction conditions were optimized, and consisted of $FeSO_4 \cdot (NH_4)_2SO_4 \cdot H_2O$ and pyridine. In fact, higher yield could be obtained in the presence of boric acid. The product was filtered off, washed with distilled water, and dried at RT (yield of 12 % based on Fe).

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Discussion

The structure of the title compound contains only infinite one-dimensionally covalently bonded chains and crystallization water molecules (figure, top). The chain is built up from two different types of octahedrally coordinated iron atoms and sulfate tetrahedra. Each coordinated iron site exhibits a 'two short-two intermediate-two long' octahedral environment.

The coordination Fe1 site is defined by two pyridyl nitrogen donors from two *trans* pyridine ligands with the length of d(Fe1—N1) = 2.198(3) Å, two aqua oxygen donors with the length of d(Fe1—O_{aqua}) = 2.182(3) Å and two oxygen donors of the sulfate anions, whereas the coordination Fe2 site is defined by four pyridyl nitrogen donors from two pairs of *trans* pyridine ligands with the lengths of d(Fe2—N2) = 2.279(3) Å and d(Fe2—N3) = 2.214(3) Å, respectively. The two independent pairs of pyridyl rings in Fe2 site almost are in planar configurations and arranged perpendicular to each other. The sulfates serve as bridges between the different intermolecular Fe centers through strongly coordinated interactions. Two oxygen donors of the sulfate anions are coordinated to Fe centres with the length of d(Fe1—$O_{sulfate}$) = 2.144(2) Å and d(Fe2—$O_{sulfate}$) = 2.070(2) Å. These Fe—$O_{sulfate}$ distances are significantly shorter than those of the known complex containing monodentate analogues and polymer $[Cu(4,4'\text{-bipy})(H_2O)(SO_4)] \cdot 2H_2O$ with Cu–$O_{sulfate}$ groups, indicating a strong Fe-sulfate interaction [1,2].

The one-dimensional –SO_4–Fe(py)$_2$(H_2O)$_2$–SO_4–Fe(py)$_4$–SO_4– chains run along the a axis, being identical with the isotypic Cr(II) structure [3]. Parallel {[Fe(py)$_2$(H_2O)$_2$](SO_4)$_2$[Fe(py)$_4$]} chains are connected to each other via π-π interactions. Along the b axis the structure contains channels, encompassing rhombic type patterns (figure, bottom). The rhombic grids are surrounded by borders formed from the organic amine molecules and the chains, of which there are two Fe2 sites, two sulfate sites and a Fe1 site. The size of the space is larger than those of the square meshes of the known coordination polymers {M(bipy)$_2$}X_2 [4]. The enlargement of the channel size maybe adjust some behavior on the dimension-controlled properties for new inorganic/organic hybrid coordination polymers. The formation of large cavities within the crystalline lattice have been proven to be useful in guest exchange and selective catalytic activity related to zeolites. The crystallized water molecules are located within the rhombic grids. Through hydrogen bonds between the chains and the crystallized water molecules, a three-dimensional structure is constructed.

Table 1. Data collection and handling.

Crystal:	yellow, prismatic, size 0.18 × 0.20 × 0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.38 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID IV, ω/φ
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4969, 2893
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2608
$N(param)_{refined}$:	262
Programs:	SHELXS-97 [5], SHELXL-97 [6]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
O(6)	4e	0.2820(3)	−0.0168(3)	0.2224(2)	0.0596(8)
O(7)	4e	0.3419(3)	−0.2976(4)	0.2398(2)	0.0549(8)
H(1A)	4e	0.0790	−0.2491	0.1236	0.042
H(2B)	4e	0.0298	−0.4703	0.1537	0.053
H(3B)	4e	−0.1301	−0.5753	0.0640	0.057
H(4A)	4e	−0.2363	−0.4526	−0.0513	0.054
H(5B)	4e	−0.1816	−0.2302	−0.0752	0.045
H(6A)	4e	0.4077	0.1307	0.1398	0.044
H(7A)	4e	0.4107	0.3283	0.2170	0.058
H(8A)	4e	0.5046	0.5263	0.1940	0.066
H(9A)	4e	0.5938	0.5186	0.0927	0.060
H(10A)	4e	0.5837	0.3166	0.0176	0.043
H(11A)	4e	0.4991	−0.0933	0.1783	0.046
H(12A)	4e	0.6016	−0.2148	0.2925	0.052
H(13A)	4e	0.7736	−0.3110	0.2970	0.057
H(14A)	4e	0.8372	−0.2798	0.1837	0.061
H(15A)	4e	0.7307	−0.1517	0.0728	0.050
H(5E)	4e	−0.063(4)	0.095(5)	0.113(3)	0.08(2)
H(5F)	4e	0.042(3)	0.100(4)	0.159(3)	0.04(1)
H(6E)	4e	0.230(7)	−0.04(1)	0.160(3)	0.29(5)
H(6F)	4e	0.245(6)	0.079(5)	0.250(5)	0.18(3)
H(7E)	4e	0.329(6)	−0.311(8)	0.188(5)	0.17(3)
H(7F)	4e	0.330(3)	−0.234(5)	0.259(3)	0.06(1)

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	2a	0	0	0	0.0183(3)	0.0227(3)	0.0253(3)	−0.0015(3)	0.0077(2)	−0.0015(3)
Fe(2)	2b	½	0	0	0.0173(3)	0.0235(3)	0.0228(3)	−0.0022(3)	0.0079(2)	0.0007(3)
S(1)	4e	0.25461(6)	−0.13891(8)	0.01969(5)	0.0178(3)	0.0219(4)	0.0234(4)	−0.0021(3)	0.0082(3)	−0.0021(3)
O(1)	4e	0.1757(2)	−0.0516(2)	0.0500(1)	0.019(1)	0.032(1)	0.029(1)	0.000(1)	0.0091(9)	−0.007(1)
O(2)	4e	0.2015(2)	−0.1730(3)	−0.0674(1)	0.031(1)	0.045(2)	0.025(1)	0.004(1)	0.0061(9)	−0.012(1)
O(3)	4e	0.2853(2)	−0.2653(2)	0.0702(2)	0.047(1)	0.025(1)	0.045(2)	0.005(1)	0.018(1)	0.008(1)
O(4)	4e	0.3566(2)	−0.0525(2)	0.0300(1)	0.023(1)	0.037(1)	0.037(1)	−0.010(1)	0.014(1)	−0.004(1)
O(5)	4e	−0.0005(2)	0.0497(3)	0.1248(2)	0.030(1)	0.046(2)	0.031(2)	0.003(1)	0.008(1)	−0.010(1)
N(1)	4e	−0.0462(2)	−0.2165(3)	0.0219(2)	0.026(1)	0.029(2)	0.035(2)	−0.003(1)	0.011(1)	−0.001(1)
N(2)	4e	0.4973(2)	0.2019(3)	0.0715(2)	0.027(1)	0.029(2)	0.029(2)	0.004(1)	0.008(1)	−0.002(1)
N(3)	4e	0.6033(2)	−0.1100(3)	0.1130(2)	0.028(1)	0.032(2)	0.027(2)	0.002(1)	0.009(1)	0.003(1)
C(1)	4e	0.0143(3)	−0.2903(4)	0.0882(2)	0.030(2)	0.037(2)	0.036(2)	−0.001(2)	0.009(2)	0.001(2)
C(2)	4e	−0.0140(3)	−0.4233(4)	0.1067(2)	0.048(2)	0.038(2)	0.046(2)	0.004(2)	0.016(2)	0.014(2)
C(3)	4e	−0.1089(3)	−0.4851(4)	0.0536(3)	0.056(2)	0.025(2)	0.063(3)	−0.007(2)	0.022(2)	0.002(2)
C(4)	4e	−0.1719(3)	−0.4124(4)	−0.0148(3)	0.040(2)	0.036(2)	0.056(3)	−0.014(2)	0.009(2)	−0.008(2)
C(5)	4e	−0.1384(3)	−0.2790(4)	−0.0287(2)	0.033(2)	0.030(2)	0.044(2)	−0.005(2)	0.004(2)	0.002(2)
C(6)	4e	0.4460(3)	0.2098(4)	0.1303(2)	0.037(2)	0.039(2)	0.038(2)	−0.002(2)	0.017(2)	−0.004(2)
C(7)	4e	0.4470(3)	0.3279(4)	0.1769(2)	0.058(2)	0.050(3)	0.042(2)	0.003(2)	0.023(2)	−0.011(2)
C(8)	4e	0.5024(4)	0.4449(5)	0.1632(3)	0.069(3)	0.036(2)	0.056(3)	0.003(2)	0.017(2)	−0.019(2)
C(9)	4e	0.5552(4)	0.4406(4)	0.1030(3)	0.056(3)	0.030(2)	0.064(3)	−0.006(2)	0.019(2)	−0.005(2)
C(10)	4e	0.5493(3)	0.3183(4)	0.0588(2)	0.036(2)	0.031(2)	0.042(2)	0.003(2)	0.016(2)	0.003(2)
C(11)	4e	0.5684(3)	−0.1307(4)	0.1793(2)	0.035(2)	0.049(2)	0.034(2)	0.005(2)	0.014(2)	0.011(2)
C(12)	4e	0.6293(3)	−0.2040(4)	0.2482(2)	0.049(2)	0.054(3)	0.028(2)	−0.001(2)	0.012(2)	0.009(2)
C(13)	4e	0.7309(3)	−0.2607(4)	0.2510(2)	0.048(2)	0.050(3)	0.034(2)	0.007(2)	−0.003(2)	0.013(2)
C(14)	4e	0.7686(3)	−0.2416(5)	0.1840(2)	0.033(2)	0.067(3)	0.048(3)	0.019(2)	0.006(2)	0.008(2)
C(15)	4e	0.7035(3)	−0.1654(4)	0.1172(2)	0.032(2)	0.056(3)	0.038(2)	0.008(2)	0.012(2)	0.008(2)

References

1. Hagrman, D.; Hammond, R. P.; Haushalter, R.; Zubieta, J.: Organic/Inorganic Composite Materials: Hydrothermal Syntheses and Structures of the One-, Two-, and Three-Dimensional Copper(II) Sulfate-Organodiamine Phases $[Cu(H_2O)_3(4,4'\text{-bipyridine})(SO_4)] \cdot 2H_2O$, $[Cu(bpe)_2][Cu(bpe)(H_2O)_2(SO_4)_2] \cdot 2H_2O$, and $[Cu(bpe)(H_2O)(SO_4)]$ (bpe = *trans*-1,2-Bis(4-pyridyl)ethylene). Chem. Mater. **10** (1998) 2091-2100.
2. Ezuhara, T.; Endo, K.; Hayashida, O.; Aoyama, Y.: Metal-ion induced alignment of an orthogonal anthracene-pyrimidinederivative. Cooperation of metal coordination, hydrogen bonding, and aromatic stacking in the buildup of one-, two- and three-dimensional networks. New J. Chem. **22** (1998) 183-188.
3. Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Zuniga, L. A.: The aqueous chromium sulfate-pyridine system – X-ray structural characterization of chain and tetranuclear compounds. Eur. J. Solid State Inorg. Chem. **31** (1994) 535-544.
4. Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K.: Preparation, Clathration Ability, and Catalysis of a Two-Dimensional Square Network Material Composed of Cadmium (II) and 4,4'-Bipyridine. J. Am. Chem. Soc. **116** (1994) 1151-1152.
5. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
6. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.