Note

Solvothermal Synthesis and Crystal Structure of a Novel Inorganic-Organic Hybrid Material, $Fe_2O(OH)(C_5H_4NCOO)SO_4$

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A novel inorganic-organic hybrid material, $Fe_2O(OH)(C_5H_4NCOO)SO_4$ was synthesized via solvothermal route using a reaction of $FeCl_3\cdot 6H_2O$, KCNS, and 4-cyanopyridine in aqueous solution of H_2O_2 and ethanol at 130 ℃ for 3 d. The compound crystallized in monoclinic space group $P2_1$, with cell parameters $a = 0.73850(15)$ nm, $b = 0.65100(13)$ nm, $c = 1.0546(2)$ nm, $\beta = 90.36(3)°$, $V = 0.50700(18)$ nm^3 and $Z = 2$. The structure is constructed with inorganic layered $[Fe_2O(OH)SO_4]^+$ cations linked by organic $(C_5H_4NCOO)^-$ anions. The compound is thermally stable up to approximately 240 ℃.

Keywords inorganic-organic hybrid material, ferric isonicotinate-sulphate, solvothermal synthesis, crystal structure

Introduction

There is a tremendous activity for the past years in the area of inorganic-organic hybrid materials in view of their diversified structures and interesting properties.[1,2] The efforts have been made in synthesizing and characterizing the class of materials.[3] The control of inorganic structure by an organic component reveals an interactive structural relation in the materials.[4] Assembly of an inorganic-organic hybrid material can be achieved by selecting organic components (multidentate ligands) and inorganic components (transition metal ions, metal oxides and inorganic acid groups). A multidentate organic ligand coordinates with two or more transition metal centers to construct a polymeric coordination complex cation which serves as a rigid scaffolding for entraining of inorganic component, anionic oxide. The anionic oxide, in general, is simply a discrete charge-compensating guest, but bonded to the cationic framework with one bond as a terminal ligand, or more bonds as a bridging ligand. So far, a few of the inorganic-organic hybrid materials containing sulfate group, $(SO_4)^{2-}$, as multidentate ligand have been reported.[5] Here, we will contribute the synthesis and characterization of a novel inorganic-organic hybrid material containing multidentate $(SO_4)^{2-}$, $Fe_2O(OH)(C_5H_4NCOO)SO_4$.

Experimental

Synthesis

All chemicals and solvents used in the synthesis were of reagent grade and without further purification.

A 23 mL Teflon-lined stainless steel bomb containing $FeCl_3\cdot 6H_2O$ (0.2704 g, 1.0 mmol), KSCN (0.0977 g, 1.00 mmol), 4-cyanopyridine (0.0521 g, 0.50 mmol), and mixed aqueous solution of H_2O_2 (30%, 3 mL) and ethanol (95%, 12 mL) was heated at 130 ℃ for 3 d, and then cooled to room temperature naturally. Orange red granular crystals were isolated from the solid products after filtering. A semi-quantitative analysis for the crystal using SEM-EDS indicated Fe and S elements in a molar ratio of 2:1 in the crystal.

Crystal structure determination

A single crystal (0.18 mm × 0.17 mm × 0.08 mm) was selected for X-ray diffraction measurement. Intensity data were collected using a Rigaku R-AXIS RAPID image plate diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.071073$ nm). The raw data were corrected for Lp factors and empirical absorption. The structure was solved by direct methods and refined by full matrix least-squares refinements on F^2 with *SHELX-97* program package.[6] Hydrogen atoms were placed in the calculated positions. Crystal drawings were generated with the *SCHAKAL92*.[7]

Thermal analysis

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) for the title compound were performed on a Rigaku TG analyzer. The powder sample of 8.90 mg was loaded into an alumina pan and heated in air with a ramp rate of 8 ℃/min from room temperature to 500 ℃. α-Al_2O_3 was selected as the reference.

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Results and discussion

Synthesis

Hydrothermal reaction was adopted to prepare the title compound, $Fe_2O(OH)(C_5H_4NCOO)SO_4$, which is composed of Fe^{3+}, $(SO_4)^{2-}$ and $(C_5H_4NCOO)^-$ ions. However, no $(SO_4)^{2-}$ and $(C_5H_4NCOO)^-$ ions were added in the initial reactants. The $(SO_4)^{2-}$ and $(C_5H_4NCOO)^-$ ions were supposed to result from oxidization of KSCN and hydrolysis of 4-cyanopyridine under the hydrothermal conditions, respectively.[8] Then, the crystal was assembled, in control, as slowly releasing $(SO_4)^{2-}$ from oxidation of KSCN and $C_5H_4NCOO^-$ from hydrolysis of 4-cyanopyridine, respectively. It should be advantageous to assembly of the crystal framework that instantaneous concentrations of the component ions were appropriately controlled during packing the ions in order. We have demonstrated that $Fe_2O(OH)(C_5H_4NCOO)SO_4$ could not be formed by a direct reaction of $Fe_2(SO_4)_3$ with $C_5H_4NCOONa$ under the same conditions.

Description of the crystal structure

$Fe_2O(OH)(C_5H_4NCOO)SO_4$ crystallizes in monoclinic space group $P2_1$. The crystallographic data, atomic coordinates and selected bond lengths and angles are listed in Tables 1, 2 and 3, respectively.

The single crystal structure determination revealed a three-dimensional framework as shown in Fig. 1, which was constructed with $[Fe^{III}(1)O_5N]$ and $[Fe^{III}(2)O_6]$ octahedra, $[S^{VI}O_4]$ tetrahedra, and $C_5H_4NCOO^-$, isonicotinate ligands (Fig. 2).

The structure can be regarded as $[Fe_2O(OH)SO_4]^+$, inorganic cationic layers parall to (001) plane as depicted in Fig. 3, linked by $(C_5H_4NCOO)^-$, organic anionic ligands along the c axis direction to form a 3-D covalent framework.

In the $[Fe_2O(OH)SO_4]^+$ cationic layer, the slightly distorted $[Fe(1)O_5N]$ octahedra with mean Fe—O distance of 0.2111 nm and Fe—N 0.2342(3) nm are alternately connected with $[SO_4]$ tetrahedra with mean S—O distance of 0.1470 nm by sharing the corner O(6) and O(7) atoms to form $[Fe(1)SO_7HN]$ chains extending along the b-axis direc-

Table 1 Details of data collection, processing and structure refinement

Molecular formula	$C_6H_5Fe_2NO_8S$
Molecular weight	362.87
Color and habit	Orange red, granular
Crystal size	0.18 mm × 0.17 mm × 0.08 mm
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell parameters	$a = 0.73850(15)$ nm $\alpha = 90.00°$
	$b = 0.65100(13)$ nm $\beta = 90.36(3)°$
	$c = 1.0546(2)$ nm $\gamma = 90.00°$
	$V = 0.50700(18)$ nm^3
Z	2
$F(000)$	360
Density (calcd)	2.377 g·cm^{-3}
Diffractometer	Rigaku R-AXIS RAPID image plate diffractometer
Radiation	Graphite-monochromatized Mo Kα, $\lambda = 0.071073$ nm
Temperature	(295 ± 2) K
Data collection range	$0 \leqslant h \leqslant 9$, $0 \leqslant k \leqslant 8$, $-13 \leqslant l \leqslant 13$; $\theta_{max} = 27.5°$
Reflections measured	Total: 1256; Observed [$I \geqslant 2\sigma(I)$]: 1115
Absorption coefficient	3.102 mm^{-1}
No. of variables, p	164
R_1	0.0707 (for all reflections) 0.0622 (for observed data)
wR_2	0.1095 (for all reflections) 0.1079 (for observed data)
Goof = S	1.007
Largest and mean Δ/σ	0.067, 0.004
Residual extrema in final difference map	−995 to 1603 e·nm^{-3}

$R_1 = \frac{\sum||F_o| - |F_c||}{\sum|F_o|}$, $wR_2 = \sqrt{\frac{\sum[w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2}}$, $S = \sqrt{\frac{\sum[w(F_o^2 - F_c^2)^2]}{n - p}}$. Weighting scheme $w = \frac{1 - \exp[-0.8(\sin\theta/\lambda)^2]}{\sigma^2(F_o^2) + (0.001P)^2 + 0.4000P}$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2 Atomic coordinates and equivalent isotropic temperature factors U_{eq}[a] (× 10^2 nm^2)

Atom	*x*	*y*	*z*	U_{eq}
Fe(1)	0.12525(5)	0.14520(12)	0.16885(3)	0.01057(7)
Fe(2)	0.49618(11)	0.38831(10)	-0.00227(8)	0.00925(7)
S(1)	-0.12346(7)	0.1491(2)	-0.10652(5)	0.01046(11)
O(1)	0.3925(2)	0.1417(7)	0.09803(14)	0.0126(2)
O(2)	-0.1504(2)	0.1572(6)	0.23116(16)	0.0175(2)
O(3)	0.3721(2)	0.3178(3)	-0.18076(15)	0.0039(2)
O(4)	0.3820(3)	-0.0233(4)	-0.1721(2)	0.0207(2)
O(5)	0.0335(2)	0.1532(6)	-0.02316(15)	0.0143(2)
O(6)	0.1229(3)	0.4678(3)	0.19312(18)	0.0114(2)
O(7)	0.1211(3)	-0.1685(3)	0.1823(2)	0.0149(2)
O(8)	0.7041(2)	0.1348(6)	-0.03154(15)	0.0133(2)
N(1)	0.2124(3)	0.1539(7)	-0.62796(17)	0.0141(5)
C(1)	0.3552(3)	0.1523(8)	-0.22966(19)	0.0101(2)
C(2)	0.2999(3)	0.1475(11)	-0.3699(2)	0.0138(2)
C(3)	0.3562(4)	-0.0212(5)	-0.4475(3)	0.0154(2)
C(4)	0.3101(4)	-0.0131(6)	-0.5746(3)	0.0188(2)
C(5)	0.1543(4)	0.2882(5)	-0.5515(3)	0.0191(2)
C(6)	0.1966(5)	0.2983(6)	-0.4224(3)	0.0231(2)

[a] U_{eq} defined as one third of the trace of the orthogonalized U tensor.

Table 3 Selected bond lengths (× 10 nm) and bond angles (°)

Fe(1)—O(7)	2.047(2)	S(1)—O(5)	1.4509(18)
Fe(1)—O(1)	2.1150(17)	S(1)—O(6)[d]	1.492(2)
Fe(1)—O(6)	2.116(2)	S(1)—O(8)[e]	1.5062(18)
Fe(1)—O(5)	2.1318(17)	O(1)—Fe(2)[f]	2.104(4)
Fe(1)—O(2)	2.1445(19)	O(3)—C(1)	1.201(5)
Fe(1)—N(1)[a]	2.2342(19)	O(4)—C(1)	1.309(5)
Fe(2)—O(1)	2.072(4)	N(1)—C(5)	1.266(5)
Fe(2)—O(1)[b]	2.104(4)	N(1)—C(4)	1.420(5)
Fe(2)—O(4)[b]	2.122(3)	C(1)—C(2)	1.532(3)
Fe(2)—O(3)	2.1382(19)	C(2)—C(6)	1.359(6)
Fe(2)—O(8)[b]	2.213(3)	C(2)—C(3)	1.433(6)
Fe(2)—O(8)	2.276(3)	C(3)—C(4)	1.381(4)
S(1)—O(7)[c]	1.432(3)	C(5)—C(6)	1.397(5)
O(7)-Fe(1)-O(1)	91.61(15)	O(3)-Fe(2)-O(8)	90.62(7)
O(7)-Fe(1)-O(6)	169.00(8)	O(8)[b]-Fe(2)-O(8)	178.50(4)
O(1)-Fe(1)-O(6)	93.54(14)	O(7)[c]-S(1)-O(5)	108.08(18)
O(7)-Fe(1)-O(5)	94.90(12)	O(7)[c]-S(1)-O(6)[d]	108.32(12)
O(1)-Fe(1)-O(5)	87.51(7)	O(5)-S(1)-O(6)[d]	112.36(17)
O(6)-Fe(1)-O(5)	95.04(12)	O(7)[c]-S(1)-O(8)[e]	110.93(17)
O(7)-Fe(1)-O(2)	90.03(12)	O(5)-S(1)-O(8)[e]	110.99(9)
O(1)-Fe(1)-O(2)	176.82(10)	O(6)[d]-S(1)-O(8)[e]	106.15(16)
O(6)-Fe(1)-O(2)	85.32(12)	Fe(2)-O(1)-Fe(2)[f]	102.46(7)
O(5)-Fe(1)-O(2)	89.63(7)	Fe(2)-O(1)-Fe(1)	121.37(19)
O(7)-Fe(1)-N(1)[a]	87.89(14)	Fe(2)[f]-O(1)-Fe(1)	123.10(19)
O(1)-Fe(1)-N(1)[a]	94.32(7)	C(1)-O(3)-Fe(2)	127.83(19)
O(6)-Fe(1)-N(1)[a]	82.03(13)	C(1)-O(4)-Fe(2)[f]	134.5(2)
O(5)-Fe(1)-N(1)[a]	176.63(15)	S(1)-O(5)-Fe(1)	145.39(11)

Continued

O(2)-Fe(1)-N(1)[a]	88.47(8)	S(1)[c]-O(6)-Fe(1)	135.31(12)
O(1)-Fe(2)-O(1)[b]	177.81(8)	S(1)[d]-O(7)-Fe(1)	142.06(14)
O(1)-Fe(2)-O(4)[b]	85.61(10)	S(1)[g]-O(8)-Fe(2)[f]	134.2(2)
O(1)[b]-Fe(2)-O(4)[b]	92.22(9)	S(1)[g]-O(8)-Fe(2)	126.9(2)
O(1)-Fe(2)-O(3)	97.21(8)	Fe(2)[f]-O(8)-Fe(2)	92.98(6)
O(1)[b]-Fe(2)-O(3)	84.97(8)	C(5)-N(1)-C(4)	116.7(2)
O(4)[b]-Fe(2)-O(3)	176.66(10)	C(5)-N(1)-Fe(1)[h]	122.1(3)
O(1)-Fe(2)-O(8)[b]	103.31(12)	C(4)-N(1)-Fe(1)[h]	120.2(3)
O(1)[b]-Fe(2)-O(8)[b]	76.83(11)	O(3)-C(1)-O(4)	124.7(2)
O(4)[b]-Fe(2)-O(8)[b]	86.78(9)	O(3)-C(1)-C(2)	117.3(4)
O(3)-Fe(2)-O(8)[b]	90.82(7)	O(4)[b]-Fe(2)-O(8)	91.80(9)
O(1)-Fe(2)-O(8)	76.06(11)	O(1)[b]-Fe(2)-O(8)	103.74(11)

Symmetry transformation codes: a (x, y, $1+z$), b ($1-x$, $0.5+y$, $-z$), c ($-x$, $0.5+y$, $-z$), d ($-x$, $-0.5+y$, $-z$), e ($-1+x$, y, z), f ($1-x$, $-0.5+y$, $-z$), g ($1+x$, y, z), h (x, y, $-1+z$).

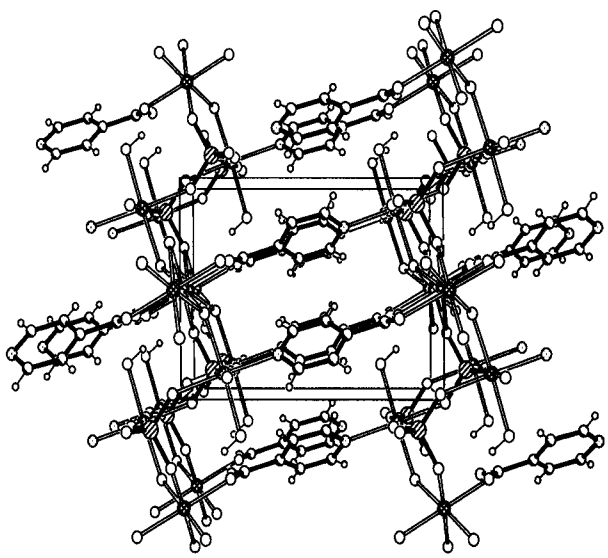

Fig. 1 A packing view along the b direction with double shaded circles for Fe, single shaded circles for S, open circles for O, black circles for C and the rest for N atoms. Unit cell is outlined.

tion. Two $[Fe(1)SO_7HN]$ chains set up a $[Fe(1)SO_5HN]_2$ ladder-type chain through corner-bridged O(5) atoms. While each Fe(2) is octahedrally coordinated by six oxygen atoms with Fe—O distances in the range from 0.2072(4) nm to 0.2276(3) nm. The $[Fe(2)O_6]$ octahedra are linked to form a $[Fe(2)O_4]$ chain extending also along the b-axis direction by sharing O(1)—O(8) edges. The $[Fe(2)O_4]$ chains and $[Fe(1)SO_5HN]_2$ chains alternate to construct a $[Fe_2O(OH)SO_4N]^+$ layer in (001) plane by sharing O(1) and O(8) corner atoms.

In $[Fe_2O(OH)SO_4N]^+$ layer, N, O(3) and O(4) atoms are all from isonicotinate ligands. Carboxyl group of an isonicotinate ligand coordinates to two adjacent Fe(2) centers of this Layer, respectively, through two carboxyl oxygen atoms, O(3) and O(4), while pyridyl N atom of the isonicotinate ligand coordinates to Fe(1) center of the adjacent layer. The coordinated O(3) and O(4) atoms of a Fe(2)

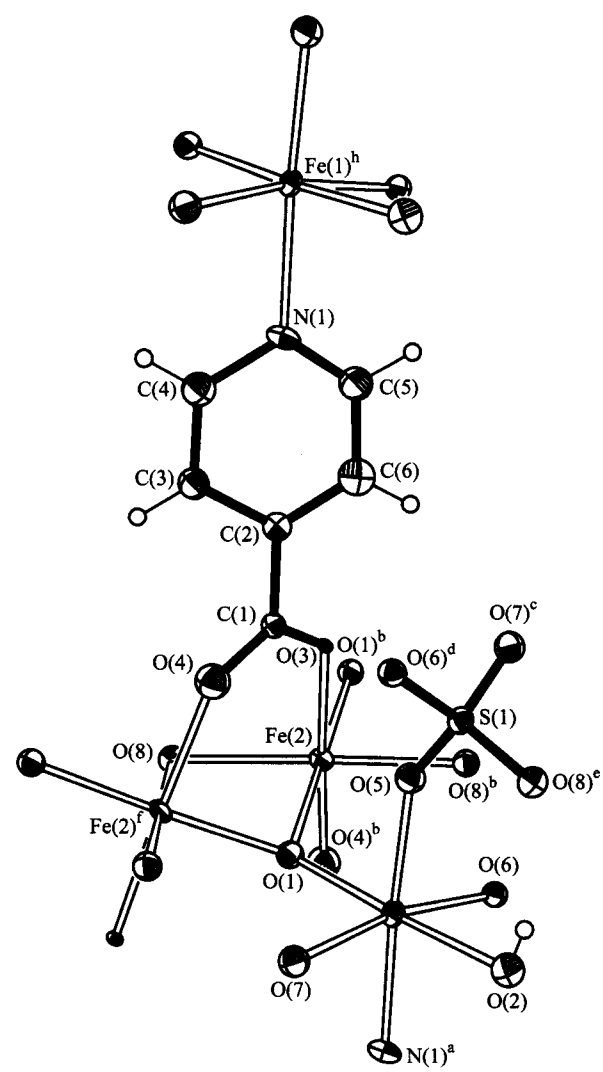

Fig. 2 ORTEP drawing for $Fe_2O(OH)(C_5H_4NCOO)SO_4$ with 60% probability ellipsoids, showing the atomic numbering scheme. Symmetry transformation codes: a (x, y, $1+z$), b ($1-x$, $0.5+y$, $-z$), c ($-x$, $0.5+y$, $-z$), d ($-x$, $-0.5+y$, $-z$), e ($-1+x$, y, z), f ($1-x$, $-0.5+y$, $-z$), g ($1+x$, y, z), h (x, y, $-1+z$).

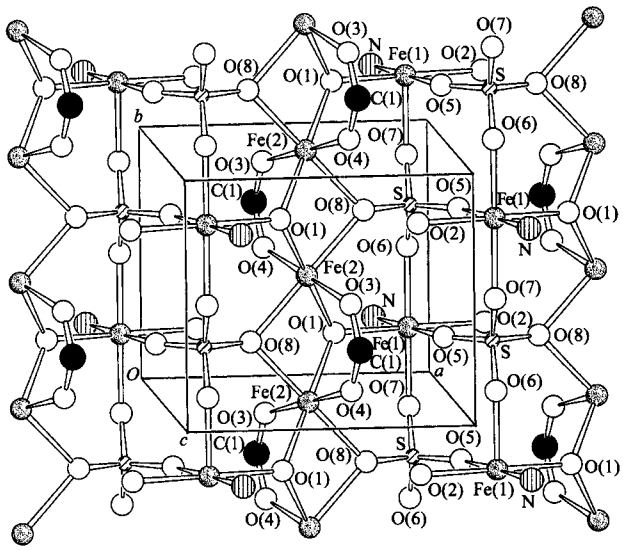

Fig. 3 Structure of inorganic layer, $[Fe_2O(OH)SO_4]^+$, where N and C(1) atoms are pyridyl nitrogen atom and carboxyl carbon atom of isonicotinate group, respectively.

center are from two isonicotinate ligands located, respectively, at two sides of this layer. N atom coordinating to Fe(1) center in this layer is pyridyl nitrogen atom of another isonicotinate ligand, of which, carboxyl group coordinates to two adjacent Fe(2) centers of the adjacent layer. In this way, the inorganic $[Fe_2O(OH)SO_4N]^+$ layers are connected by the organic $(C_5H_4NCOO)^-$ ligands along the *c* axis direction via O—Fe(2) and N—Fe(1) coordination bonds to build up a three dimensional framework (Fig. 1). Only O(2) atoms in $(OH)^-$ groups are terminal ligands of Fe(1) centers.

$Fe_2O(OH)(C_5H_4NCOO)SO_4$ has a novel 3-D framework in which the inorganic anionic oxide, $(SO_4)^{2-}$ as a tetradendate ligand is bonded by four Fe centers in the framework so that the crystal structure is quite stable up to 240 ℃ as exhibited in thermal analysis (Fig. 4).

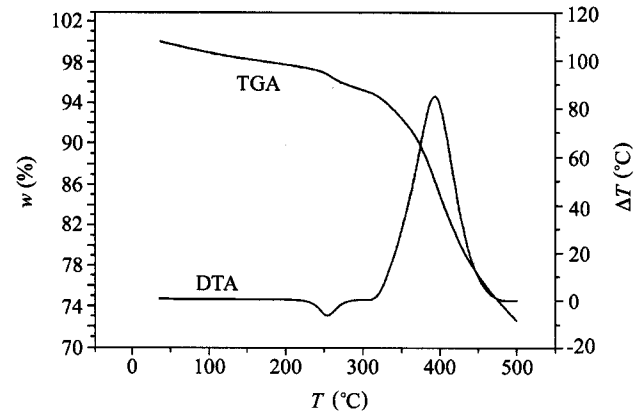

Fig. 4 TGA and DTA curves for $Fe_2O(OH)(C_5H_4NCOO)SO_4$.

The first thermal effect occurred at 240 ℃, where the coordination bonds between the inorganic $[Fe_2O(OH)SO_4N]^+$ layers and the organic $(C_5H_4NCOO)^-$ ligands were broken resulting in an endothermic event and an associated ~3% weight loss due to the volatilization of a few anionic organic ligands. The second thermal effect, about 30% weight loss and a large associated exothermic event exhibited in the temperature range from 310 to 450 ℃ because of oxidization of the organic ligand (calculated 33.64 wt%) in the air.

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