

Fe₅(OH)₂(C₄H₄O₄)₄: Hydrothermal Synthesis of Microporous Iron(II) Dicarboxylate with an Inorganic Framework

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The hydrothermal synthesis of inorganic compounds is a very promising route to new extended solids since the nature and temperature of the hydrothermal fluid can be varied over a wide range. Aluminosilicate molecular sieves has been extensively studied because of their utility in commercial processes such as catalysis and gas separation.¹ Recently, there has been considerable efforts on the preparation of three-dimensional open frameworks based on transition metals thanks to their potential applications as catalysts and electronic devices.² This has resulted in the study of noble framework structures based on transition metal phosphates.^{3,4}

In general, the transition metal-carboxylic acid system under ambient conditions gives hydrated compounds and water molecules participate in the coordination with the transition metals. However, hydrothermal condition enhances metal-ligand interactions rather than metal-water coordination, and finally produce three dimensional extended framework.

Compared with metal-carboxylates, the binary oxide of transition metals easily oxidized or reduced to have mixed oxidation states. For instance, Fe(II)O is usually noted as Fe_{1-x}O and impossible to prepare without high pressure treatment. Fe(OH)₂ (two-dimensional)⁵ is also unstable and the hydroxyl group acts as base in aqueous solution. Since carboxylate has medium reduction capability against transition metals, the initial design of the structural analogies of the stoichiometric FeO was in part, the point that the stable Fe(II)-oxygen bonds could be supplied by the carboxylate and hydroxyl anions in such cobalt containing compounds as [Co₃(μ₃-OH)₂(C₄O₄)₂] · 3H₂O⁶, Co₅(OH)₂(O₂CCH₃)₈ · 2H₂O⁷ and Co₅(OH)₂(C₄H₄O₄)₄.⁸

We present here the synthesis and characterization of Fe₅(OH)₂(C₄H₄O₄)₄ (**1**), a new iron carboxylate with a two dimensional array of edge sharing Fe(II)O₆ interconnected by succinate bidentate anions, which is a model compound with the stoichiometric Fe(II)O₆ octahedra.

Experimental Section

Synthesis. FeCl₂ · 4H₂O, succinic acid, KOH and distilled deionized water was used as starting materials. The mixture (Fe : succinic acid : KOH : H₂O = 1 : 1.5 : 3.7 : 60) was heated for 24 hours at 180 °C under autogenous pressure in the teflon coated stainless-steel reaction vessel. The pH of the starting solution was 5.5 and that of the resulting solution was 5.0, respectively. The solid phase was collected by fil-

tration, washed with distilled water and dried at room temperature. The product is insoluble in water and stable in ambient condition. The color of **1** was bright yellow and the yield based on iron was around 35%.

Single crystal X-ray structure determination. One of the crystals of the title compound was glued to a glass fiber and mounted on a Bruker AXS diffractometer using monochromatic molybdenum radiation ($\lambda = 0.71079$). Initial random search on the crystal resulted in twenty four peaks that could be indexed with monoclinic unit cell similar to the final crystallographic results. Data collection was performed accordingly on a hemisphere (*hkl* and *hk-l*). The systematic extinction condition $0k0(k=2n+1)$, $h0l(h+l=2n+1)$ uniquely indicated that the space group is $P2_1/c$ (No.14) which was confirmed by the crystal structure refinement results.

A summary of crystal data is presented in Table 1. The structure was solved by direct methods (SHELX-86)⁹ and

Table 1. Crystal data and structural refinement for Fe₅(OH)₂(C₄H₄O₄)₄

Empirical formula	Fe ₅ (OH) ₂ (C ₄ H ₄ O ₄) ₄
Formula weight	777.55
Measured Temperature	293(2) K
Wave length	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell dimensions	$a = 9.489(2)$ Å $b = 9.429(2)$ Å $c = 12.487(2)$ Å $\beta = 96.77(1)^\circ$
Volume	1109.4(4) Å ³
Z	2
Calculated density	2.328 g · cm ⁻³
Absorption coefficient	3.29 mm ⁻¹
$F(000)$	776
Crystal size	0.2 × 0.3 × 0.2 mm ³
μ (Mo K α)	21.3 cm ⁻¹
Reflections(independent)	1946
Reflection(I>I(2))	1856
Refinement method	Full-matrix least-squares on F ²
Number of parameters	178
θ range for data collection	2.16 - 24.99
Limiting indices	$-11 \leq h \leq 11, 0 \leq k \leq 11, 0 \leq l \leq 14$
Goodness-of-fit on F ²	1.478
Final R indices(I>2 σ (I))	R1=0.0414, wR2=0.1101
R for all data	R1=0.0448, wR2=0.1122

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for non-hydrogen atoms

Atom	x	y	z	U_{eq}
Fe(1)	8824(1)	2074(1)	1663(1)	12(1)
Fe(2)	11696(1)	3184(1)	3456(1)	12(1)
Fe(3)	1	0	0	12(1)
O(1)	8713(3)	1926(3)	-127(2)	16(1)
O(2)	9492(3)	2276(3)	3373(2)	17(1)
O(3)	11317(3)	2533(3)	1772(2)	16(1)
O(4)	9470(3)	43(3)	1605(2)	13(1)
O(5)	11674(3)	3610(3)	5277(2)	17(1)
O(6)	13580(3)	4224(4)	3474(2)	23(1)
O(7)	6652(3)	1582(3)	1608(2)	22(1)
O(8)	8500(3)	4225(3)	1625(2)	20(1)
O(9)	12528(4)	1259(4)	3904(3)	27(1)
C(1)	7667(4)	4963(4)	988(3)	14(1)
C(2)	8725(4)	2831(4)	-870(3)	14(1)
C(3)	12137(4)	2012(4)	1154(3)	14(1)
C(4)	14066(4)	5465(4)	3470(3)	16(1)
C(5)	13725(5)	2058(5)	1411(4)	21(1)
C(6)	6853(5)	4266(5)	15(3)	20(1)
C(7)	15664(5)	5562(5)	3544(4)	25(1)
C(8)	7784(6)	4105(6)	-898(4)	36(2)

standard difference Fourier techniques (SHELX-97).¹⁰ Iron and oxygen atoms were first located and the carbon atoms were found by difference Fourier maps. Hydrogen positions program generated and included in the refinements as a riding model except for those on hydroxyl group. Absorption corrections were applied using the DIFABS programs.¹¹ Refinements for 178 parameters were performed by full-matrix least-squares analysis, with anisotropic thermal parameters for all non-hydrogen atoms. The reliability factors converged to $R1(F_o) = 0.0414$ and $wR2(F_o^2) = 0.1101$. Fractional atomic coordinates are given in Table 2 and selected bond distances and angles in Table 3. The X-ray powder diffraction pattern is in agreement with that calculated according to the structure determined by single crystal X-ray diffraction analysis.

Characterization. Thermogravimetric analysis was performed with a SDT-2960 (TA instrument) thermal analysis system in nitrogen atmosphere from room temperature up to 1000 °C. IR spectra was recorded on a Nicolet 205 spectrometer using standard KBr methods and magnetic susceptibility in room temperature was measured by the Faraday-type magneto-balance.

Results and Discussion

The structure of **1** can be understood as a three-dimensional network of six-coordinated Fe atoms as shown in Figure 1, in which the Fe-O framework has been drawn as FeO_6 polyhedra, with all C and H atoms contained. The metal-oxygen polyhedra can be described as an infinite square net of edge-sharing FeO_6 units, in which $\text{Fe}(3)\text{O}_6$ occupy the vertices of this octahedra plane. The topology creates loz-

Table 3. Selected bond lengths (\AA) and angles (degree) for $\text{Fe}_3(\text{O}11)_2(\text{C}_8\text{H}_8\text{O}_4)_4$

Fe-O bonds	
Fe(1)-O(4) 2.014(3)	O(4) ^a -Fe(2)-O(3) 100.13(11)
Fe(1)-O(8) 2.052(3)	O(9)-Fe(2)-O(2) 90.11(12)
Fe(1)-O(7) 2.106(3)	O(6)-Fe(2)-O(2) 173.29(12)
Fe(1)-O(2) 2.163(3)	O(4) ^b -Fe(2)-O(2) 80.28(11)
Fe(1)-O(1) 2.229(3)	O(3)-Fe(2)-O(2) 78.55(11)
Fe(1)-O(3) 2.392(3)	O(9)-Fe(2)-O(5) 86.15(12)
Fe(2)-O(9) 2.031(3)	O(6)-Fe(2)-O(5) 90.88(12)
Fe(2)-O(6) 2.038(3)	O(4) ^b -Fe(2)-O(5) 79.78(11)
Fe(2)-O(4) ^c 2.069(3)	O(3)-Fe(2)-O(5) 168.12(11)
Fe(2)-O(3) 2.180(3)	O(2)-Fe(2)-O(5) 89.77(10)
Fe(2)-O(2) 2.250(3)	O(5) ^b -Fe(3)-O(5) ^c 180.00(17)
Fe(2)-O(5) 2.311(3)	O(5) ^b -Fe(3)-O(4) ^d 95.36(11)
Fe(3)-O(5) ^e 2.057(3)	O(5) ^b -Fe(3)-O(4) 84.64(11)
Fe(3)-O(5) ^f 2.057(3)	O(5) ^b -Fe(3)-O(4) ^d 84.64(11)
Fe(3)-O(4) 2.124(3)	O(5) ^b -Fe(3)-O(4) 95.36(11)
Fe(3)-O(4) ^d 2.124(3)	O(4)-Fe(3)-O(4) ^d 180.0(2)
Fe(3)-O(1) ^g 2.184(3)	O(5) ^b -Fe(3)-O(1) 95.96(12)
Fe(3)-O(1) 2.184(3)	O(5) ^b -Fe(3)-O(1) ^g 84.04(11)
	O(4)-Fe(3)-O(1) ^g 98.04(10)
	O(4) ^d -Fe(3)-O(1) ^g 81.96(10)
	O(5) ^b -Fe(3)-O(1) 84.04(11)
	O(5) ^b -Fe(3)-O(1) ^g 95.96(11)
	O(4)-Fe(3)-O(1) 81.96(10)
	O(4) ^d -Fe(3)-O(1) 98.04(10)
	O(1) ^g -Fe(3)-O(1) 180.00(15)
O-Fe-O angles	
O(4)-Fe(1)-O(8) 169.93(12)	
O(4)-Fe(1)-O(7) 95.18(12)	
O(8)-Fe(1)-O(7) 94.21(12)	
O(4)-Fe(1)-O(2) 93.67(11)	
O(8)-Fe(1)-O(2) 87.77(12)	
O(7)-Fe(1)-O(2) 102.91(12)	
O(4)-Fe(1)-O(1) 83.31(11)	
O(8)-Fe(1)-O(1) 92.85(11)	
O(7)-Fe(1)-O(1) 91.33(11)	
O(2)-Fe(1)-O(1) 165.67(11)	
O(4)-Fe(1)-O(3) 82.63(10)	
O(8)-Fe(1)-O(3) 88.08(11)	
O(7)-Fe(1)-O(3) 177.35(11)	
O(2)-Fe(1)-O(3) 75.82(11)	
O(1)-Fe(1)-O(3) 89.89(10)	
O(9)-Fe(2)-O(6) 96.60(14)	
O(9)-Fe(2)-O(4) ^d 162.92(13)	
O(6)-Fe(2)-O(4) ^d 93.26(12)	
O(9)-Fe(2)-O(3) 91.65(12)	
O(6)-Fe(2)-O(3) 100.98(12)	
Fe-O-Fe angles	
Fe(1)-O(1)-Fe(3) 91.11(11)	
Fe(1)-O(4)-Fe(2) 130.04(14)	
Fe(3)-O(4)-Fe(1) 99.12(11)	
Fe(2)-O(4)-Fe(3) 97.70(11)	
Fe(2)-O(5)-Fe(3) 92.38(11)	
Fe(1)-O(3)-Fe(2) 98.95(11)	
Fe(1)-O(2)-Fe(2) 104.00(12)	
Fe-Fe distances	
Fe(1)-Fe(2) 3.702	
Fe(1)-Fe(3) 3.151	
Fe(2)-Fe(3) 3.157	

Symmetry transformation used to generate equivalent atoms: ^a-x, 2-y+1, 2-z; ^b-x, 2-y-1/2, -z-1/2; ^cx, -y+1/2, z-1/2; ^d-x, 2-y, -z.

enge-shaped nets made from 12 edge-sharing octahedra in which two of four succinates are located (Figure 1(a)). The infinite two-dimensional arrays of edge-sharing iron octahedra along *bc* plane are covalently linked by other two succinate anions (Figure 1(b)). The layers are stacked along the *a* axis and the interlayer spacing is 9.38 Å. It should be emphasized that although there appear to be large channels

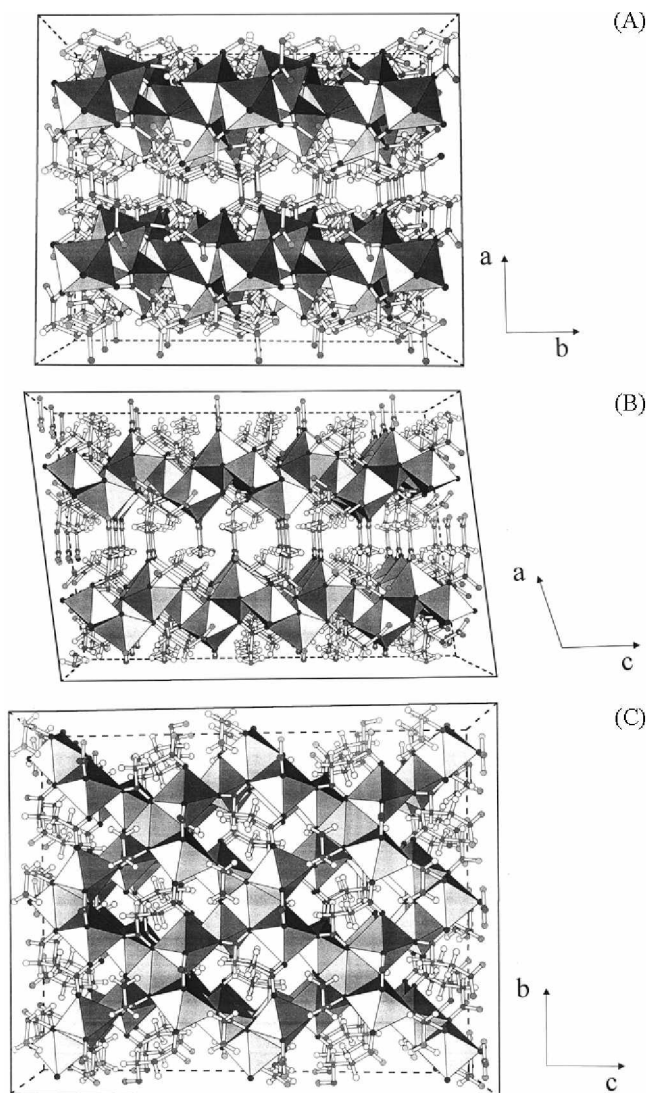


Figure 1. Views of the framework along the crystallographic axis *a*(a), *b*(b) and *c*(c). Black sphere represents oxygen atoms in the FeO_6 octahedra. Grey sphere correspond to the carbon atoms in the succinate ion linking two octahedra in the same FeO_6 one or different layers. Empty sphere are hydrogen atoms in the succinate ions.

along *a* axis, they are actually filled by hydrocarbon of the succinate ligands (*intra*-layer, see below). On the contrary, the view along *b* and *c* axes gives empty window surrounded by hydrogen of ethylene groups between two FeO_6 layers, as shown in Figure 1(b) and 1(c), resulting in the hydrophobic channels.

The succinate anions of **1** present two different conformations, which are *gauche* and *anti* form. The *gauche* succinate links FeO_6 units in a *bc* plane (*intra*-layer) and the *anti* one bridges cross-linked two FeO_6 layers along the *a* axis (*inter*-layer). The oxygens of the *intra* succinate connect four different iron atoms in the same FeO_6 layer. One of the carboxyl group of the *intra* succinate bounds two pairs of iron octahedra through $\text{Fe}-\mu_2-\text{O}[\text{O}(1), \text{O}(2)]$ and the other links two iron octahedra through $\text{Fe}-\mu_1-\text{O}[\text{O}(8) \text{ and } \text{O}(9)]$. The *inter* succinate also has $\text{Fe}-\mu_2-\text{O}[\text{O}(3), \text{O}(5)]$ and $\text{Fe}-\mu_1-$

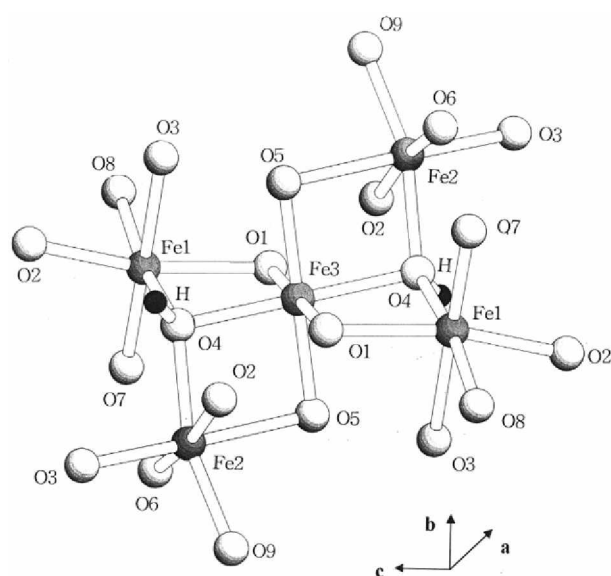


Figure 2. Schematic representation of the coordination of the $\text{Fe}_3\text{O}_{23}(\text{OH})_2$ framework and numbering scheme used in the tables. The O(4) shows μ_3 -bridging bond and hydroxyl group.

$\text{O}[\text{O}(6) \text{ and } \text{O}(7)]$, in which stands up along the *a* axis, as shown in Figure 1(b). The bond distances of the $\text{Fe}-\mu_2-\text{O}$ for the different succinates give larger values than the $\text{Fe}-\mu_1-\text{O}$, presumably because metal-oxygen bond distances of $\text{M}-\mu_2-\text{O}$ generally are larger than those of $\text{M}-\mu_1-\text{O}$.

Iron atoms occupy three different crystallographic sites surrounded by six oxygen atoms. Figure 2 shows a portion of FeO_6 layer, illustrating the details of the $\text{Fe}-\text{O}$ bonding and the local symmetry for three $\text{Fe}(\text{II})$ ions. The $\text{Fe}-\text{O}$ bond lengths range from 2.031(3) to 2.392(3) Å and the average value of all the $\text{Fe}-\text{O}$ distances is 2.16 Å. The $\text{Fe}-\mu_3-\text{O}(\text{H})$ bonds of O(4) is shared among three iron atoms with bond distance between 2.01 and 2.12 (average is 2.08 Å), indicating the strong $\text{Fe}-\text{O}(\text{H})$ bonding compared with $\text{Fe}-\text{O}(\text{succinate})$. The $\text{Fe}(1)\text{O}_6$ and $\text{Fe}(2)\text{O}_6$ octahedra are strongly distorted, with two short $\text{Fe}-\text{O}$ bonds (2.01-2.05 Å), two intermediates (2.11-2.18 Å) and two long ones (2.23 and 2.39 Å). $\text{Fe}(3)$ occupying an inversion center and cross-linking two $\text{Fe}(1)$ s and two $\text{Fe}(2)$ s, has a relatively regular octahedral geometry with $\text{Fe}(3)-\text{O}$ bonds of 2.12 ± 0.06 Å. It is noted that the average bond distance of $\text{Fe}(3)-\text{O}$ presented smallest value among the three different FeO_6 octahedra.

Trans $\text{O}-\text{Fe}-\text{O}$ bond angles range from $162.9(1)$ to $180.0(1)^\circ$, and *cis* angles vary from $75.8(1)$ to $102.9(2)^\circ$. The shortest $\text{Fe}\cdots\text{Fe}$ separation in the structure is 3.151 Å for $\text{Fe}(1)\cdots\text{Fe}(3)$ between edge-shared octahedra. The distance of $\text{Fe}(2)\cdots\text{Fe}(3)$ (3.157 Å) is close to the $\text{Fe}(1)\cdots\text{Fe}(3)$ distance (3.151 Å) but smaller than the $\text{Fe}(1)\cdots\text{Fe}(2)$ (3.702 Å). $\text{Fe}(1)$ and $\text{Fe}(2)$ share only one vertex of $\text{O}(4)(\text{OH})$ and other two $\text{Fe}\cdots\text{Fe}$ combinations linked two different oxygen (μ_2 - and μ_3 -O) atom. None of these $\text{Fe}\cdots\text{Fe}$ distances is sufficiently short to imply any metal-metal bonding.

We assigned O(4) to the hydroxyl ligand rather than μ_3 -oxo since hydrogen can exist within hydrogen bond distance to O(10) of a nearby other succinate anion, resulting in a

Table 4. Bond valence sums for compound **1** from X-ray crystallography

Fe-O bond	bond length	v_{ij}	bond valence sum	average bond length
Fe(1)-O(4)	2.014	0.469	2.00	2.16
Fe(1)-O(8)	2.052	0.423		
Fe(1)-O(7)	2.106	0.364		
Fe(1)-O(2)	2.163	0.314		
Fe(1)-O(1)	2.229	0.262		
Fe(1)-O(3)	2.392	0.169		
Fe(2)-O(9)	2.031	0.448	2.05	2.15
Fe(2)-O(6)	2.038	0.440		
Fe(2)-O(4)	2.069	0.404		
Fe(2)-O(3)	2.180	0.300		
Fe(2)-O(2)	2.250	0.248		
Fe(2)-O(5)	2.311	0.210		
Fe(3)-O(5)	2.057	0.418	2.13	2.12
Fe(3)-O(5)	2.057	0.418		
Fe(3)-O(4)	2.124	0.349		
Fe(3)-O(4)	2.124	0.349		
Fe(3)-O(1)	2.184	0.296		
Fe(3)-O(1)	2.184	0.296		
O(4)-Fe(1)	2.014	0.469	1.22	2.07
O(4)-Fe(2)	2.069	0.404		
O(4)-Fe(3)	2.124	0.349		

charge-balanced compound even though the Fourier map difference in the X-ray diffraction drives less reliable certainty. All iron atoms have bond valence sum around 2.1 indicating Fe(II) as summarized in Table 4. The O(4) has a valence sum of 1.22 when the hydrogen is excluded, and the calculated valence sums for other oxygen range from 1.74(5) to 2.01.¹² The hydroxide formulation is also consistent with absence of weight loss below 300 °C in the TG analysis and appearance of medium O-H stretching band in the IR spectra (3330 cm⁻¹). Consequently, water molecule is excluded in **1** although it was synthesized in the aqueous solution.

The magnetic measurement at 291 K gives 5.28 μ_B (Bohr magneton) per mole of iron, which is typical of high-spin Fe(II) centers (5.10-5.70 μ_B).¹³ This is in good agreement with bond valence calculation for Fe(II). Study of details on magnetic property in low temperature is currently in progress.

Thermogravimetric measurements under nitrogen atmosphere showed a weight loss of 50.2% around 320 °C characteristic of the pyrolysis of the succinate group. The

resulting product after the TG analysis has mixed phases of Fe_{1-x}O characterized by the powder X-ray diffraction spectra.

In conclusion, we have shown that hydrothermal synthesis is a powerful technique for preparing new coordination solid state compounds containing transition metals, especially unstable oxidation state such as iron(II). Dicarboxylic acid as chelating ligands controls the oxidation state of transition metal and builds the skeleton of inorganic framework both as a part of the oxide sheet and pillars between layers. The three dimensional framework of transition metal carboxylate opens a new series of transition metal complexes for engineering tailored materials.

Supporting Information Available. Tables giving details of X-ray data collection parameters, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, hydrogen atomic parameters; table of observed and calculated structure factors are available.

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