Synthesis of a New Iron(II) Adipate with Layered Inorganic Framework

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The increased activity in the field of metal di- and tricarboxylates[1,2] is primarily due to the wide variety of crystal structures of coordination complex even in similar chemical formulas depending on metal-oxygen coordination and conformation of carbon chains. Carboxylic ligand is part of the framework leading to the formation of neutral network, which results in hybrid open networks with various molecules depending on the size of template ions. In general, the transition metal dicarboxylates prepared under ambient condition give usually complicated solid-state phases with various hydrate water contents. However, hydrothermal reaction could give three-dimensional networks as clearly demonstrated in several dicarboxylate compounds,[1] and also different crystal structures were observed in the coordination solids of manganese(II) 1,3,5-benzenetricarboxylate hydrate and anhydrous.[2] The hydrothermal synthesis of inorganic compounds is a very promising route to new extended coordination solids since the nature and temperature of the hydrothermal fluid can be varied over a wide range.[10]

Recently, we have reported $Mn_2(H_2O)[O_2C(CH_2)_4CO_2]_2$ with a novel structure of well-aligned, closed packed alkyl chains.[4] In this paper, we present the synthesis of $Fe_2(H_2O)[O_2C(CH_2)_4CO_2]_2$ (1), a new iron carboxylate with a two-dimensional array of edge and corner sharing $Fe(II)O_6$ interconnected by adipate bidentate anions. The compound 1 has been characterized by FT-IR spectroscopy, elemental analysis, thermal analysis, X-ray powder and single crystal diffraction, and magnetic susceptibility measurements.

Experimental Section

Iron(II) chloride tetrahydrate, adipic acid and potassium hydroxide were used as received from Aldrich. A mixture of $FeCl_2 \cdot 4H_2O$, adipic acid and of KOH with the molar ratio of 1 : 1 : 3.1 (pH=5.1) was heated along with 90 mL of water in a Teflon-lined reaction vessel at 180 °C for 6 days and then cooled to room temperature. The reaction temperature and initial pH value of the solution are very critical to obtain the title compound. About 2.45 g of 1 was obtained as pale-yellow needle-type crystals after washing with water. Remaining adipic acid was leached out with acetone. The isolated product gave approximately 39% yield based on the $FeCl_2$. The identity of the collected $Fe_2(H_2O)[O_2C(CH_2)_4CO_2]_2$ sample for various characterization was confirmed by matching the powder diffraction pattern to that calculated from the single-crystal structure. Anal. Calcd: Fe, 26.72; C,

34.45; H, 4.31. Found: Fe, 25.92; C, 34.24; H, 4.38. The infrared spectra exhibited the following absorption (KBr pellet): 3500-3000 (s, v br), 2936 (s), 2871 (w), 1558 (vs), 1400 (vs), 1317 (m), 1271 (m), 1075 (m), 811 (m), 706 (m), 655 (s), 548 (m) cm^{-1}.

Single-crystal X-ray data were collected on a Siemens P4 automated four-circle diffractometer equipped with graphite monochromated Mo $K\alpha$ radiation. The orientation matrix and unit cell parameters were determined by least-square analyses of 39 reflections in the range $10.0 < 2\theta < 25.0°$. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorenz and polarization effects. Decay corrections were also made. The pattern of systematic absences observed in the data was consistent with either the space group C2/c or Cc. The centric space group C2/c was assumed and confirmed by the successful solution and refinement of the structure.

A summary of crystal data is represented in Table 1. All calculation was carried out using Siemens SHELXTL program.[5] The structure was solved by the direct method and refined by full-matrix least-squares calculations of F^2s, initially with isotropic and finally with anisotropic temperature fac-

Table 1. Crystal data and structure refinement for 1

Empirical formula	$Fe_2C_{12}H_{18}O_9$
Formula weight	417.96
Temperature	297(2) K
Wavelength	0.71073 Å
Space group	monoclinic, C2/c (No. 15)
Unit cell dimensions	a = 21.496(2) Å
	b = 7.4979(6) Å
	c = 9.0475(5) Å
	β = 108.901(5)°
Volume	1379.6(2) Å^3
Z	4
Calculated density	2.012 mg/m^3
Absorption coefficient	2.152 mm^{-1}
F(000)	856
Crystal size	0.22 × 0.28 × 0.62 mm
θ range for data collection	2.00 to 24.99°
Limiting indices	$-25 \leq h \leq 0, 0 \leq k \leq 8, -10 \leq l \leq 10$
Reflections collected/unique	1253/1219 [R(int) = 0.0265]
Data / restraints / parameters	1216 / 0 / 109
Final R indices [I > 2σ(I)]	R_1 = 0.0241, wR_2 = 0.0675
R indices (all data)	R_1 = 0.0263, wR_2 = 0.0736
Largest diff. peak and hole	0.292 and -0.423 e. Å^{-3}

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|. ^bwR_2 = [\Sigma|w(F_o^2-F_c^2)^2|/\Sigma|w(F_o^2)^2|]^{1/2}. w=[\sigma(F)]^{-1}.$

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Notes

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Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3)

	x	y	z	U(eq)^a
Fe	5224(1)	2976(1)	9596(1)	12(1)
O(1)	4343(1)	2019(2)	9824(2)	20(1)
O(2w)	5000	1009(3)	7500	17(1)
O(3)	5727(1)	791(2)	11022(2)	16(1)
O(4)	4574(1)	5185(2)	8511(2)	14(1)
O(5)	4050(1)	3895(2)	6226(2)	16(1)
C(1)	4054(1)	4818(3)	7384(2)	12(1)
C(2)	3409(1)	5449(3)	7520(2)	16(1)
C(3)	2801(1)	5129(3)	6101(2)	18(1)
C(4)	2164(1)	5487(3)	6448(2)	18(1)
C(5)	4069(1)	523(3)	9590(2)	13(1)
C(6)	3446(1)	272(3)	9996(2)	17(1)
H(2A)	3443(1)	6719(3)	7737(2)	20
H(2B)	3342(1)	4862(3)	8413(2)	20
H(3A)	2803(1)	3903(3)	5759(2)	21
H(3B)	2820(1)	5899(3)	5254(2)	21
H(4A)	2174(1)	6691(3)	6849(2)	22
H(4B)	2133(1)	4670(3)	7253(2)	22
H(6A)	3432(1)	1143(3)	10778(2)	20
H(6B)	3445(1)	-907(3)	10436(2)	20
H(1)	4718(14)	308(41)	7775(36)	46(9)

^{a}The iron, oxygen, carbon (except hydrogen) atoms were refined anisotropically and given in the form of the equivalent displacement parameters defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond lengths (Å) and angles (°) for **I**

Fe-O(5)^a	2.0524(14)
Fe-O(1)	2.099(2)
Fe-O(4)^b	2.1317(14)
Fe-O(3)	2.1478(14)
Fe-O(4)	2.1843(14)
Fe-O(2w)	2.3259(14)
O(1)-Fe-O(3)	88.52(6)
O(1)-Fe-O(4)	80.58(5)
O(1)-Fe-O(2w)	84.72(5)
O(3)-Fe-O(2w)	86.41(5)
O(4)-Fe-O(2w)	100.42(5)
O(5)^a-Fe-O(4)^b	95.36(6)
O(1)-Fe-O(4)^b	95.56(6)
O(4)^b-Fe-O(3)	94.52(5)
O(5)^a-Fe-O(4)	91.93(5)
O(4)^b-Fe-O(4)	78.72(5)
O(5)^a-Fe-O(2w)	84.21(5)
Fe-O(2w)-Fe^a	101.30(8)
Fe^b-O(4)-Fe	101.28(5)

Symmetry transformations used to generate equivalent atoms: ^{a}-x+1, y, -z+3/2. ^{b}-x+1, -y+1, -z-2

tors for all non-hydrogen atoms. Iron and oxygen atoms were first located and the carbon atoms were found by dif-

ference Fourier maps. Positions of all hydrogen atoms attached to carbons are included in the refinements as a riding model. The hydrogen on water molecule was refined separately according to electron density difference. The reliability factors converged to $R_1(F_0)$=0.0241 and $wR_2(F_0^2)$= 0.0675. Fractional atomic coordinates are given in Table 2 and selected bond distances and angles in Table 3.

Results and Discussion

The powder X-ray diffraction pattern supports the preferred crystal growth along bc plane since (200) peak is strongly enhanced compared with other (hkl) ones according to the intensity calculation. As shown in Figure 1, the structure of **I** is two-dimensional layered structure, consisting of chains of edge-sharing FeO$_6$ polyhedra cross-linked by carboxylate groups. Fe atoms coordinate with six oxygen atoms donated by the five adipate ions and one water molecule. The organic and inorganic layers are stacked along a axis, where the interlayer spacing is 10.17 Å. It is worth pointing out that adipate ligands have all *anti* conformation and two carboxylate groups in an adipate ligand rotated by 90° with respect to one another. We note that iron(II) succinate, Fe$_5$(OH)$_2$(CO$_2$(CH$_2$)$_2$CO$_2$)$_4$[1d] has both *anti* and *gauche* conformation of alkyl chain in the crystal structure as previously reported. All adipates are surrounded by six other chains with regular distance of about 4.1 Å. The hydrophobic characteristic of alkyl-chains may induce self-assembly to give parallel alignment of alkyl chains. The unit cell volume of **I** is smaller than that of Mn$_2$(H$_2$O)[O$_2$C(CH$_2$)$_4$CO$_2$]$_2$[4] presumably because the ionic radius of Fe(II) is smaller than that of Mn(II) in high spin configuration for both ions.

The carboxylate groups chelate two neighboring octahedra in a FeO$_6$ layer, consisting of thin hydrophilic layer between
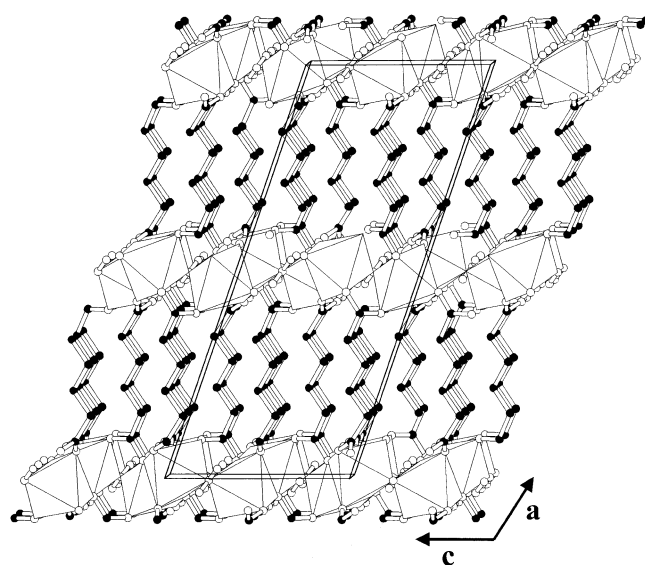

Figure 1. Views of the framework along the b direction. Polyhedra represent the FeO$_6$ octahedra and black sphere corresponds to carbon atoms. Oxygen of water molecule locates between two FeO$_6$ polyhedra in the same plane.
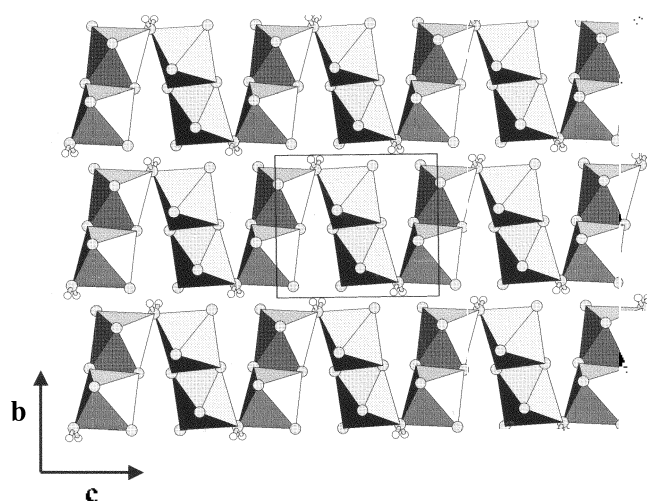
Figure 2. Zigzag chains of FeO$_6$ octahedra in the layer of *bc* plane.

thick hydrophobic crystalline alkyl-chain overlays. Figure 2 shows the layer of FeO$_6$ octahedra in **1**, illustrating the details of the FeO$_6$ linkage in the inorganic layer. The metal oxide framework can be described as an infinite zigzag chains of edge- and corner-sharing. FeO$_6$ octahedra are strongly distorted with five short Fe-O bond distances (2.052(2)-2.184(2) Å), one long (2.326(2) Å). The oxygen atom of water, O(2w), is shared between two Fe atoms with the largest Fe-O bond length. We assign O(2w) to coordinated water for a charge-balanced compound, and O(2w) has a bond valence sums[6] of 0.44 (excluding the hydrogen) while the values for other oxygens range from 1.66 to 1.87. The coordinated water formulation is also consistent with TGA behavior (*vide infra*) and the appearance of broad O-H stretches in the IR spectra. Only that noticeable hydrogen bond linkage exists in the crystal structure, a bond between the hydrogen atom of the water and an oxygen atom of neighboring octahedron. The O-H bond distances of [O(2w)-H(1)···O(3)] linkage 0.90 and 1.86 Å, respectively. The Fe···Fe separations in the structure are 3.34 Å and 3.60 Å in the edge-shared and in the corner shared bioctahedra, respectively. None of these distances is sufficiently short to imply any metal-metal bonding.

The room temperature effective magnetic moment (μ_{eff}) is 5.35μ_B per mole of Fe, which is generally observed in high-spin Fe(II)($3d^6$) centers (5.1-5.7)[7] and is close to 5.27μ_B, the value reported for Fe$_5$(OH)$_2$(C$_4$H$_4$O$_4$)$_4$ polycrystalline.[1d] The effective magnetic moment is also in agreement with bond valence calculation[6] which give 1.96.

Thermogravimetric analysis of **1** was performed in a nitrogen atmosphere. Two distinct mass loss regions were observed around 230 and 290 °C. At 230 °C, the observed mass loss of 4.4% corresponds to 1.02 equivalent of H$_2$O per formula unit. The next mass loss (290 °C) corresponds to loss of coordinated adipate, giving FeO and carbon. The observed remained weight percent of 35.3% (at ca. 700 °C) approximates 34.4 wt % of the expected value for FeO and equivalent elementary carbon.

In conclusion, a new layered iron(II) adipate compound was synthesized as a single crystal by hydrothermal method and the crystal structure involves a single layer of FeO$_6$ polyhedra chains separated by close packed *anti* alkyl-chains. Various dicarboxylate ligands as building blocks for inorganic framework is now under investigation.

Supporting Information Available: X-ray crystallographic file, in CIF format, for the structural determination of Fe$_2$(H$_2$O)[O$_2$C(CH$_2$)$_4$CO$_2$]$_2$ will be given upon your request to the correspondence author (Duk-Young Jung).

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