Three-dimensional Iron Glutarate with Five- and Six-coordinated Iron(II)–Oxygen Networks

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A novel open framework iron(II)–carboxylate was synthesized and characterized. Four crystallographically different iron atoms have five- and six-coordinated geometry giving rise to 1D double metal–oxygen layers. The glutarate ligands link inorganic chains to give an interlocked 3D structure containing water. Magnetic measurement of iron–carboxylate compound shows canted antiferromagnetism around 4 K.

Iron–carboxylate chemistry with di-, trivalent iron and polynuclear iron complexes has been widely investigated owing to relevance as models for protein active sites[1,2] and their magnetic physical properties.[3] Recently, we and other groups tried to diversify the architectures of divalent metal–organic hybrid materials using transition metal and aliphatic-dicarboxylate anions.[4–9] In particular, we reported the preparation of series of iron–dicarboxylate compounds such as iron–succinate,[10] –glutarate,[11] and –adipate[12] with artificial iron(II) oxide geometries, for example, the iron–glutarate[11] compound has the 3D open framework which consists of twelve edge-shared FeO_6. As far, rare iron(II) carboxylates have been structurally characterized, because of their unstable oxidation state under ambient conditions and because Fe^{III} is favored by haloacetates containing heavier halide.[13] Our previous works proved that the hydrothermal method is a useful tool to prepare iron(II)–carboxylate compounds containing Fe–O networks such as FeO_6 or $FeO_5(OH)$ geometry.[10] In this paper, we describe synthesis and characterization of a iron(II)–carboxylate compound, $[Fe_4(OH)_2(C_5H_6O_4)_3](H_2O)$ (**1**) with an unusual FeO_5 geometry.

The hydrothermal reaction of $FeCl_2\cdot4H_2O$, glutaric acid, KOH, and H_2O in a molar ratio of 1:1:1.3:350 (pH 4.9) at 180 °C for 4 days yields needle-like single crystals. Compound **1** is stable both in air and in nonprotic solvents. Pale yellow crystals are stable for several months.

X-ray analysis[14] of a single crystal of **1** revealed iron–glutarates to adopt the mixed FeO_6/FeO_5 geometry depicted in Figure 1. The asymmetric unit contains four independent iron atoms, three crystallographically different glutarate ligands (Figure S1)[25] and two hydroxide ions. Fe(2) and Fe(4) coordinate six oxygen atoms from carboxylate groups and hydroxide ion, on the contrary, the coordination sphere of both Fe(1) and Fe(3) sites have FeO_5 geometry. The trigonal indices[15,16] of Fe(1) and Fe(3) have been calculated 0.55 for Fe(1) and 0.54 for Fe(3), respectively, indicating intermediate states of square pyramid and trigonal bipyramid. The inorganic layers consist of 1D double chains of FeO_6/FeO_5, parallel to the *a* axis, as shown in Figure 2, connected by three crystallographically different glutarate ligands.

The glutarate ligands may have three different conformation modes; gauche/gauche (L1), anti/gauche (L2) and anti/anti (L3) (Figure S2).[17,25] We summarized the conformational analysis of crystal structures of the metal–glutarates; the anti/anti forms give rise to layered structures, and the gauche ones to more compact metal–oxygen geometry such as honeycomb structures. Compound **1** has two types of glutarate ligands, L2 and L3. The conformation variation has been shown to be essential for construction of metal–ligand frameworks depending on different synthetic conditions such as pH and concentration.

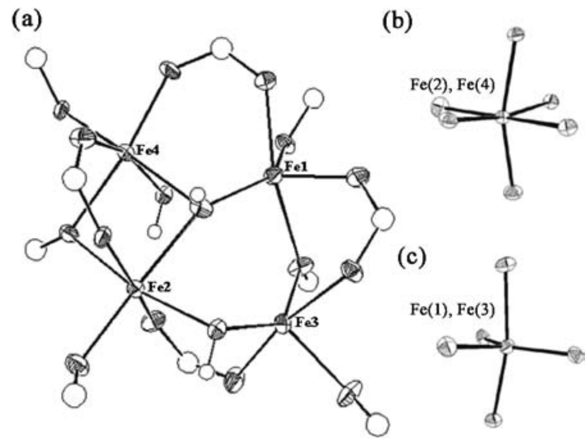

Figure 1. (a) ORTEP diagram of **1** showing 50% thermal ellipsoids for non-hydrogen atoms. For clarity, all atoms of glutarate ligands for except for the carboxylate groups and the α-carbon atoms, were omitted. Presentation of the FeO_x ($x = 5$ or 6) polyhedron as (b) six-coordinated geometry and (c) five-coordinated geometry of iron atoms.

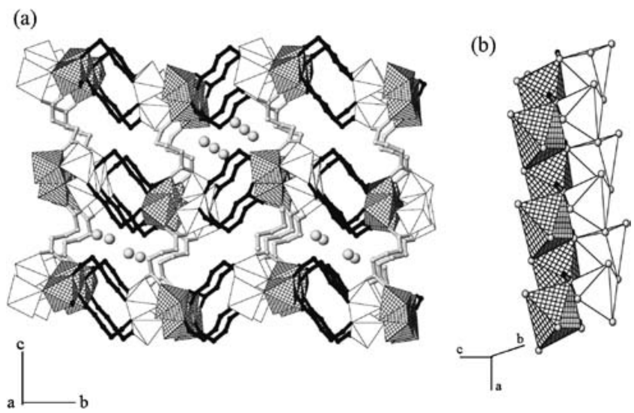

Figure 2. (a) Projection of the three-dimensional structure of **1** along the *a* axis. For clarity, all hydrogen atoms on carbon are omitted. White spheres represent solvated water molecules. (b) A double layer of edge-sharing FeO_6 and corner-sharing FeO_5 unit. Black spheres represent H atoms on hydroxy groups.

The fine tuned hydrothermal reaction gave the new type iron(II)–glutarate with FeO_6/FeO_5 geometry supported by L2 and L3.

The structure of **1** consists of infinite double inorganic layers producing rectangular channels along the *a* axis. The rectangles possess two L2 and one L3 ligands along *b* and *c* axis, respectively. The two carboxylate groups of L2 are bound to six iron atoms, one with three-edge-shared FeO_6 and the other with three-corner-shared FeO_5. The L3 connects with four iron centers which consist of two-corner-shared units (Figure S1).

Five coordination Fe(II)–O distances are in the range 1.987(5)–2.241(5) Å (bond valence calculations:[18,19] 1.96 v.u. for Fe(1), 2.00 v.u. for Fe(3)) and that of FeO_6 in the range from 1.999(5) to 2.214(5) (bond valence calculations: 2.01 v.u. for Fe(2), 2.06 v.u. for Fe(4)). The trans bond angle of O–Fe(1)–O is 168.3(2)° and that of O–Fe(3)–O is 169.6(2)°. The bond angles in the equatorial plane O–Fe(1)–O and O–Fe(3)–O angle range from 107.2(2) to 137.0(2)°.

The shortest Fe···Fe separation is 3.08 Å for the Fe(2)···Fe(4) of edge-shared FeO_6 which is smaller than the corner-shared Fe(1)···Fe(3) of 3.29 Å. The short Fe···Fe distance of edge-shared octahedral is even smaller than those found in other iron–glutarates (3.28 Å).[11] The shortest interchain Fe^{II} in FeO_6···Fe^{II} in FeO_5 separation is around 7.3 Å. Residual electron density of approximately 1 e/Å^3, most likely arising from highly disordered water molecules, was not assigned. The solvate water molecule (OW) shows hydrogen bonding[20] with carboxylate oxygens, with distances of 3.1 Å. The distance of water (O(W)···O(W)) is 2.9 Å, which may involve a weak hydrogen-bonding network. TGA of **1** displays the first weight loss of the one solvated water at about 110 °C and completion at 200 °C.

The room-temperature effective magnetic moment of **1** is 4.99 μ_B per iron, smaller than those for other iron(II)–dicarboxylates (5.77 μ_B).[10–12,21] The best linear fit of the reciprocal magnetic susceptibility $\chi^{-1}(T)$ data above 150 K for **1** yields $C = 4.65$ emu/mol and $\theta_p = -150$ K, which suggests the strong antiferromagnetic interactions. Canted antiferromagnetic ordering behavior is suggested by the peaks at around 4 K in AC susceptibility measurement in Figure 3. The maxima of both χ' and χ'' appeared at 4.2 K. Unfortunately, the magnetic data could not exclusively reveal the existence of $Fe^{II}O_5$.[16,22,23]

In summary, a novel mixed FeO_6/FeO_5 iron(II)–dicarboxylate compound **1** was characterized. All iron atoms have five or six oxygen atoms giving rise to an uncommon 1D double metal oxide layer. The glutarate ligands construct 1D inorganic chains to give an interlocked 3D structure containing water molecules. The detailed magnetic properties of **1** is currently under investigation.

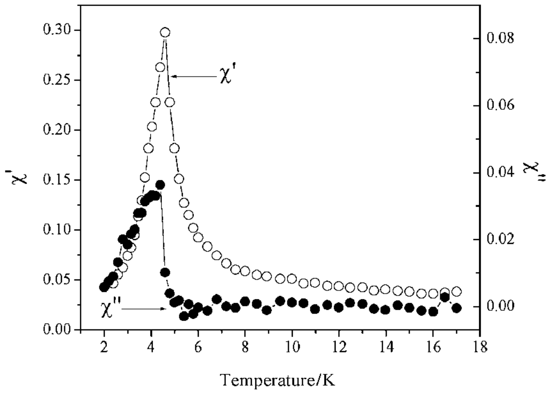

Figure 3. Plot of the real (χ_M') and imaginary (χ_M'') AC magnetic susceptibility vs. temperature for compound **1**.

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References and Notes

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14 Crystal and structure refinement parameters, **1**: $C_{15}H_{20}Fe_4O_{15}$, $T = 296$ K, $P2_1/n$, $Z = 4$, $a = 4.996(3)$, $b = 20.072(5)$, $c = 20.034(6)$ Å, $\beta = 93.36(3)°$, $V = 2006(2)$ Å^3, $R_1 = 0.0481$, $wR_2 = 0.0957$. Data were collected on a Siemens P4 four-circle diffractometer using graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Structures were solved by direct methods (SHELXS-86) and refined by full matrix least-squares based on Fo2 (SHELXL-97).[24] CCDC reference numbers 643304.
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25 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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