

## A Novel 3-D Network of Fe(II) Glutarate: 2-D Honeycomb-type Edge-shared FeO<sub>6</sub> Layers and Isolated Interlayer FeO<sub>6</sub> Octahedra

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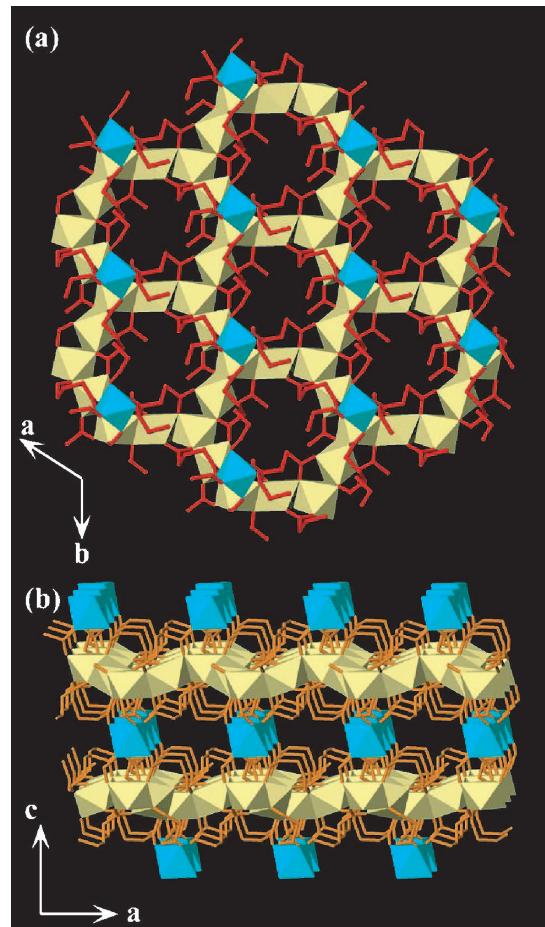
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The 3-D structure of Fe(II) glutarate is built up from 2-D honeycomb layers of 12-membered FeO<sub>6</sub> polyhedra and pillar-like interlayer FeO<sub>6</sub> interconnected by Fe–O–C–O–Fe bridging modes, presenting ferrimagnetic coupling below 5 K.

The design and preparation of organic–inorganic hybrid framework on the basis of transition metals have become widespread over the past decade, and many of them were focused on their specific adsorption properties,<sup>1</sup> and magnetic/optical properties.<sup>2–4</sup> The flexibility of ligand conformations as well as carboxylate bridging modes allow to prepare new open frameworks with corner and/or edge sharing M–O–M polyhedron. Our previous studies on the structural chemistry of the Fe(II) dicarboxylate systems prepared under hydrothermal conditions yield 3-D Fe succinate<sup>5</sup> with 2-D edge-shared FeO<sub>6</sub> layers, and 3-D layered Fe adipate<sup>6</sup> with 1-D edge/corner shared FeO<sub>6</sub> zigzag chain. The succinate and glutarate ligands have *anti* and *gauche* conformations in the reported metal–dicarboxylate compounds.<sup>7–9</sup> For instance, one Ni succinate<sup>8</sup> involves 3-D NiO<sub>6</sub> network formed by the *gauche* one exclusively and another related Ni succinate<sup>9</sup> contains different conformations to produce more compact Ni–O–Ni connectivity. The possible conformations of glutarate ligands can be summarized as three types, *anti/anti* (*L1*), *anti/gauche* (*L2*), and *gauche/gauche* (*L3*). The conformational variation in the crystal structures is strongly related to the synthetic condition and applied metal cations as in the M glutarates, M = Mn (*L1*),<sup>10</sup> Co (*L1*, *L3*)<sup>7c</sup>, and Nd (*L1*, *L2*)<sup>7b</sup>. In this paper, we present the synthesis and magnetic properties of a novel 3-D framework of iron glutarate, Fe(CO<sub>2</sub>–(CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub>), (**1**), containing *L3* exclusively.

The hydrothermal reaction of FeCl<sub>2</sub>·4H<sub>2</sub>O, glutaric acid, KOH and H<sub>2</sub>O in a molar ratio of 1:1:1.3:350 (pH = 4.1) at 180 °C for 4 days afforded a large single crystal sample. Elemental analysis (%). Calcd for C<sub>5</sub>H<sub>6</sub>FeO<sub>4</sub> : C, 32.26; H, 3.23. Found: C, 32.60; H, 3.34.

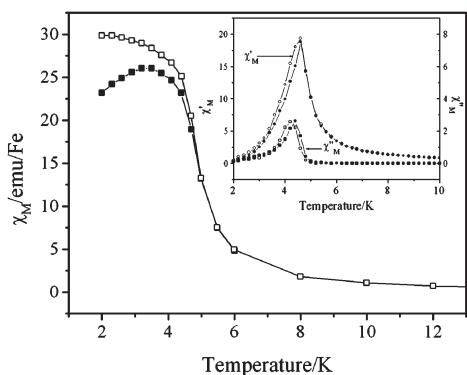
A single crystal X-ray diffraction study<sup>11</sup> reveals that **1** is a 3-D open framework with edge-sharing FeO<sub>6</sub> octahedral layers propagating along the *ab* plane (Figure 1). The honeycomb-type 2-D layer consists of 12-membered rings, six Fe(1)s in apexes and six Fe(2)s in sides, respectively. The glutarate ligands interconnected the 2-D FeO<sub>6</sub> sheets (yellow) and the pillar-like FeO<sub>6</sub> polyhedra (Fe(3), blue in Figure 1) between the layers to form a 3-D network. The resulting 2-D FeO<sub>6</sub> layers are stacked in hexagonal packing. It should be noted that the honeycomb layers in **1** are connected by the Fe–O–C–O–Fe modes without direct Fe–O–Fe bond, which is compared with Ni succinate compound involving direct Ni–O–Ni bonding mode along the *c* axis.<sup>8</sup> The



**Figure 1.** Projection along the *c* axis (a) and *b* axis (b) shows the 3-D open framework of **1**. The 2-D FeO<sub>6</sub> network (yellow) and the pillar-like FeO<sub>6</sub> (blue) between the sheets are shown. All hydrogen atoms have been omitted for clarity.

Fe–O bond lengths of **1** range from 2.030(2) to 2.200(2) Å, and *cis* O–Fe–O angles range from 76.89(7) to 103.80(6)°.

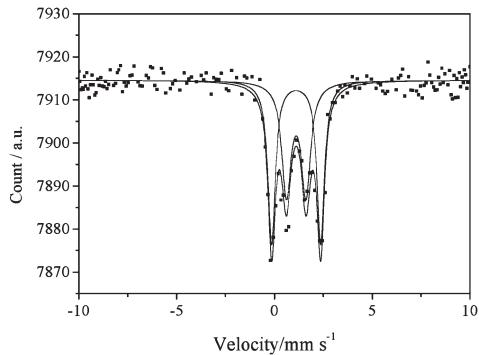
The Fe(2)O<sub>6</sub> shows the most strongly distorted octahedral environments and the Fe(3)O<sub>6</sub> coordinates six different dicarboxylate ligands leading to a nearly ideal octahedral geometry. The shortest Fe–Fe separation in **1** is 3.28 Å for the Fe(1)–Fe(2) of edge-sharing octahedral in 12-membered 2-D framework, which is smaller than those found in Fe succinate (3.33 Å)<sup>5</sup> and in Fe adipate (3.47 Å).<sup>6</sup> All the glutarate ligands of **1** present unique *gauche* (*L3*) conformation with torsional angles of 63° and 71°,<sup>7d</sup> which is ascribed at least partially to the



**Figure 2.** Field-cooled (□) and zero-field cooled (■) magnetization curves at  $H = 0.01$  T. Inset shows the plot of the real ( $\chi_M'$ ) and imaginary ( $\chi_M''$ ) ac magnetic susceptibility vs temperature for the compound **1**. Data were collected under zero magnetic field at the frequencies of 100(○), 1000(●) Hz.

condensed Fe–O network formation in hydrothermal crystallization.

The magnetization measurements between 2.0 and 300 K were carried out using a SQUID magnetometer. The room temperature effective magnetic moment ( $\mu_{\text{eff}}$ ) of **1** is  $5.43 \mu_B$  per iron, which is generally observed in high-spin Fe(II)( $3d^6$ ) centers ( $5.10$ – $5.70 \mu_B$ )<sup>12</sup> and is close to  $5.77 \mu_B$ , the value reported for other Fe(II) dicarboxylates.<sup>5,6</sup> The best linear fit of the reciprocal magnetic susceptibility  $\chi^{-1}(T)$  data above 50 K for **1** yields  $C = 3.71 \text{ emu/mol}$  and  $\theta_p = -11 \text{ K}$ , which suggests the antiferromagnetic interactions. Below 5 K, magnetization values depend on field-cooled and zero-field-cooled measurements, as illustrated in Figure 2. The canted antiferromagnetic ordering is confirmed by the peaks at around 4.5 K in the in-phase ( $\chi_M'$ ) and out-of-phase component ( $\chi_M''$ ) in ac susceptibility measurements (inset in Figure 2). Within the honeycomb layers, stronger spin coupling through  $90^\circ$  superexchange interactions may occur because both Fe(1)O<sub>6</sub> and Fe(2)O<sub>6</sub> share their edges, according to the Goodenough's theory.<sup>13</sup> The intralayer spin couplings may be predominant rather than interlayer ones and the contribution from the Fe(3)O<sub>6</sub>.



**Figure 3.** Mössbauer spectra of compound **1** at 300 K.

<sup>57</sup>Fe Mössbauer spectra of **1**, performed at 300 K, are in agreement with the structural results and the oxidation state of iron(II) in high spin octahedral coordination. (Figure 3) The spectra could be refined with two doublets (49% for  $\Gamma_1$  IS =  $1.12 \text{ mm s}^{-1}$ , QS =  $0.99 \text{ mm s}^{-1}$ , FWHM =  $0.57 \text{ mm s}^{-1}$  and 51% for  $\Gamma_2$  IS =  $1.11 \text{ mm s}^{-1}$ , QS =  $2.51 \text{ mm s}^{-1}$ , FWHM =

$0.79 \text{ mm s}^{-1}$ ) in agreement with the expected ratio of two kinds of iron site, one belong to 2/6 Fe(1) and 1/6 Fe(3), the other to 3/6 Fe(2), respectively, based on the different multiplicities of the three sites. The Fe(2) is assigned to  $\Gamma_2$  because of its strong distortion of octahedron environments.<sup>14</sup>

The present work shows that a 3-D framework with 2-D honeycomb network and pillar-like FeO<sub>6</sub> is built from glutarate ligand. The flexible ligand conformations may create structural diversity and also open the conformational isomerism in the supramolecular structures.

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#### References and Notes

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- 11) Crystal data for **1** :  $C_5H_6FeO_4$ , rhombohedral, space group  $R\bar{3}$ ,  $a = 11.043(2)$ ,  $b = 11.043(2)$ ,  $c = 29.209(6) \text{ \AA}$ ,  $V = 3085.0(10) \text{ \AA}^3$ ,  $Z = 18$ ,  $D_{\text{calcd}} = 1.802 \text{ Mg m}^{-3}$ , Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), 724 reflections collected, 721 independent ( $R_{\text{int}} = 0.0437$ ). The data collection was performed on a Siemens P4 automated four-circle diffractometer. The structure was refined by direct methods using SHELX-97 program with the final residual  $R_1(I > 2\sigma(I)) = 0.0287$ ,  $wR_2(I > 2\sigma(I)) = 0.0739$ . Crystallographic data (excluding structure factors) for **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 209391. Copies of the data can be obtained free of charge in application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).
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