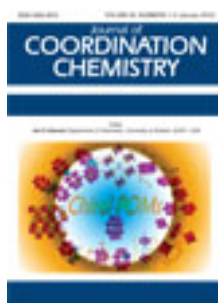


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A (3,6)-connected metal-organic framework consisting of chair-like {Fe₆} clusters and BTC linkers

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A 2-D framework composed of a chair-like {Fe₆} cluster and BTC linkers, [Fe₆(BTC)₂(HCOO)₆(DMF)₆] (1, BTC = 1,3,5-benzenetricarboxylate), has been synthesized under solvothermal conditions and characterized by elemental analysis, infrared spectroscopy, thermal gravimetric analysis, and single-crystal X-ray diffraction analysis. The {Fe₆} cluster contains six iron ions and six formate ligands, with each formate coordinating with three iron ions to construct the hexa-nuclear iron wheel. The {Fe₆} wheels are further connected *via* BTC ligands resulting in the first example of a 2-D framework based on {Fe₆} clusters and BTC linkers. A magnetic study indicates that intramolecular antiferromagnetic interactions exist in the hexa-nuclear iron cluster.

Keywords: Polynuclear aggregate; Iron; Magnetism; Framework

1. Introduction

The design and synthesis of 3-D transition-metal clusters are of great interest owing to potential applications in chemical bionics, catalysis, energy storage, and multifunctional materials [1–3]. Ferric systems represent an important subfamily in polynuclear aggregates and attract much attention owing to relevance as model complexes for protein active sites and as molecular species with unusual magnetic properties [4, 5]. Up to now, a series of polynuclear ferric aggregates with nuclearities including 3, 6, 7, 8, 9, and up to 22, 64, and Fe₁₆₈ aggregates have been reported [6–10]. Numerous synthetic efforts indicate that the preparation of ferric aggregates is highly dependent on the assistance of the carboxylate-based ligands owing to versatile abilities in coordinating with transition-metal cations and mediating efficient magnetic coupling among magnetic metal sites. Powell *et al.* synthesized several {Fe₁₉} wheels by the reaction of carboxylate-based ligands with Fe³⁺ [6e, 6f]. Christou *et al.* reported the reaction of Fe³⁺ and acetates, resulting in a particularly thermodynamically stable high-nuclearity ferric cluster Fe₂₂ and a giant Fe₁₈ wheel [6c, 6d]. Recently, Gao *et al.* reported a {Fe₆₄} cubic cage that incorporates propeller-like Fe₈^{III} Apices and formate edges [9a].

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Based on such a strategy, we have obtained two nanosized $\{\text{Fe}_{28}\}$ wheels by the introduction of tartrate ligands into Fe^{3+} -acetate systems [10a]. Two protein-sized chiral $\{\text{Fe}_{168}\}$ cages were also obtained by the reaction of Fe^{3+} ions, L- and D-tartrate ligands, and formate ligands [10b].

Polymetallic clusters, as one kind of classic metal oxide cluster with abundant structures and interesting properties, have been considered as excellent building blocks to construct functional framework materials [11]. However, such polynuclear iron cluster-based framework materials were rarely observed up to now [12]. Polycarboxylate ligands have been proven to be effective linking units to form framework materials in a previous report [13]. Based on the above consideration, we employ 1,3,5-benzenetricarboxylic acid (H_3BTC) and formic acid ligands to react with Fe^{3+} ions under solvothermal conditions to synthesize the polynuclear iron cluster-based framework materials. In this work, we report a new (3,6)-connected framework structure composed of the chair-shape $\{\text{Fe}_6\}$ clusters and BTC linkers $[\text{Fe}_6(\text{BTC})_2(\text{HCOO})_6(\text{DMF})_6]$ (**1**).

2. Experimental

2.1. Materials and methods

All reagents were purchased commercially and used without purification. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN elemental analyzer and a PLASMA – SPEC (I) ICP atomic emission spectrometer (Fe). Infrared (IR) spectra were obtained on an Alpha Centaur FTIR spectrometer from 400 to 4000 cm^{-1} with KBr pellets. The thermal gravimetric analysis (TG) was performed on a Perkin-Elmer TGA7 instrument with a heating rate of $10^\circ\text{C min}^{-1}$. Magnetic susceptibility data were collected over the temperature range of 2–300 K at a magnetic field of 1000 Oe on a Quantum Design MPMS-5 SQUID magnetometer.

2.2. Synthesis

Synthesis of 1: A mixture of $\text{FeCl}_3\cdot 4\text{H}_2\text{O}$ (0.3 mmol, 0.04 g), H_3BTC (0.45 mmol, 0.1 g), formic acid (1.5 mL), and DMF (4.5 mL) was sealed in a Teflon-lined autoclave and heated at 150°C for 36 h, followed by slow cooling at 10°C h^{-1} . After being washed with DMF several times, light-yellow block crystals were obtained (yield *ca* 67.4% (based on Fe)). Anal. Calcd for **1** (%): Fe, 23.07; C, 34.74; H, 3.33; N, 5.78. Found (%): Fe, 23.12; C, 34.81; H, 3.45; N, 5.84.

2.3. X-ray crystallography

Single-crystal X-ray data for **1** was collected on a Rigaku R-AXIS RAPID IP diffractometer equipped with a normal focus 18 KW sealed tube X-ray source (Mo- $\text{K}\alpha$ radiation, $\lambda = 0.71073\text{ \AA}$) operating at 50 kV and 200 mA. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL-97 software [14]. Further details of the X-ray structural analysis are given in table 1.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	C ₄₂ H ₄₈ Fe ₆ N ₆ O ₃₀
Formula mass	1451.96
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Hexagonal
Space group	<i>P</i> -3
Unit cell dimensions (Å)	
<i>a</i>	14.049(2)
<i>b</i>	14.049(2)
<i>c</i>	8.1607(16)
Volume (Å ³), <i>Z</i>	1394.9(4), 1
Calculated density (g cm ⁻³)	1.728
Absorption coefficient (mm ⁻¹)	1.616
<i>F</i> (000)	738
Data/restraints/parameters	2137/0/127
Goodness-of-fit on <i>F</i> ²	0.932
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^{a,b}	<i>R</i> ₁ = 0.0300, <i>wR</i> ₂ = 0.1059

$$^a R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; \quad ^b wR_2 = \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]^{1/2}.$$

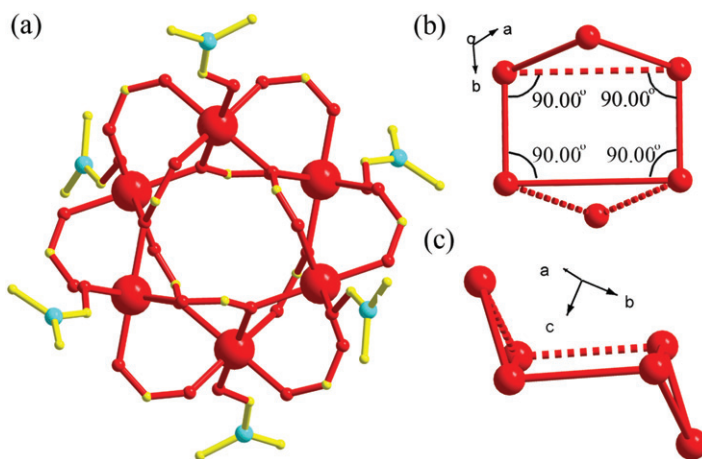


Figure 1. (a) The polyhedral and ball-and-stick view of the {Fe₆} cluster of **1** and (b), (c) simplified views of the {Fe₆} cluster. Codes: big dark ball, Fe; small dark ball, O; white small ball, C; middle white ball, N.

3. Results and discussion

3.1. Synthesis and structure

Compound **1** was obtained by the reaction of FeCl₃, H₃BTC, and formate in DMF at 150°C for 36 h. Parallel experiments showed the ratio of formic acid and DMF plays an important role in the formation of **1**, which could be synthesized in the ratio range from 1:2.5 to 1:3. Single-crystal X-ray structural analysis reveals that **1** exhibits a 2-D framework structure that consists of hexameric {Fe₆} clusters and BTC linkers (figure 1). Each {Fe₆} cluster is composed of six corner-sharing FeO₆ octahedra,

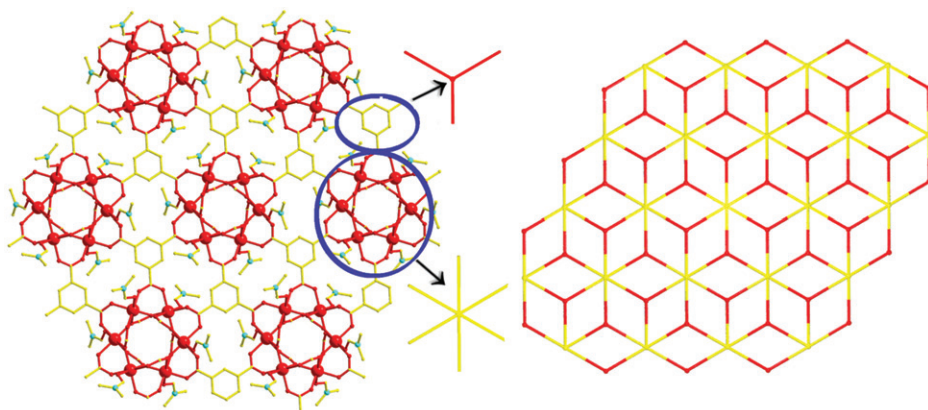


Figure 2. The polyhedral and ball-and-stick view of the 2-D network of **1** and simplified view of the scheme of **1** along the *c*-axis. Codes: big dark ball, Fe; small dark ball, O; small white ball, C; middle white ball, N.

six formate ligands, and six coordinated DMF molecules. As shown in figure 1(a), all iron ions are hexa-coordinate completed by three carboxylate oxygen atoms from three HCOO ligands, one oxygen atom of DMF, and two carboxylate oxygen atoms from two different BTC ligands. In the $\{\text{Fe}_6\}$ cluster, the six iron ions can be divided into three groups according to different positions. As shown in figure 1(b), the first group includes four iron ions, which makes an approximately rectangular plane, and the other groups contain one Fe ion, respectively. The ions are located at the underside and upside to constitute a chair-like structure (figure 1c). Further, each $\{\text{Fe}_6\}$ cluster connects with six BTC linkers, and each BTC linker bridges three $\{\text{Fe}_6\}$ clusters, resulting in a 2-D network parallel to the *ab* plane (figure 2). As shown in figure 2, the six carboxylate carbons of BTC in the $\{\text{Fe}_6\}$ cluster serve as points-of-extension that define the vertexes of a hexangular building unit, and the BTC also represents the triangular building unit. Therefore, the structure of **1** can be simplified into a 2-D (3,6)-connected network, which was first observed in the $\{\text{Fe}_6\}$ cluster-based framework materials. The structure of **1** is analogous to that of Co-containing compound MOF-CJ14 except some differences in the coordination environments of metals [15]. The bond lengths of Fe–O are in the range 2.058(1)–2.178(1) Å and Fe–O_{DMF} distance is 2.182(1) Å. Valence sum calculation indicates that Fe in **1** is in the +2 oxidation state [16].

3.2. FT-IR spectroscopy

The IR spectrum of **1** exhibits absorptions of the asymmetric and symmetric vibrations of carboxyl at 1626, 1570, 1415, and 1337 cm^{-1} (figure S1). The $\Delta\nu$ ($\nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$) is 211 and 233 cm^{-1} , which suggests bidentate bridge coordination of carboxylate [17]. An additional broad strong band near 2971 cm^{-1} is attributed to the N–H vibration for dimethylamine [18].

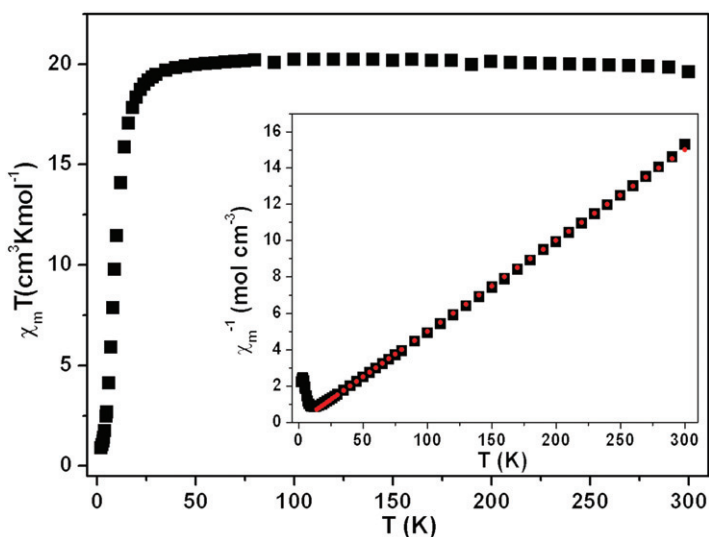


Figure 3. Plot of $\chi_M T$ vs. T for **1** and (inset) temperature dependence of reciprocal magnetic susceptibility χ_m^{-1} for **1**.

3.3. TG analysis

The TG curve of **1** displays two continuous weight loss processes (figure S2). The first of 44.3% from 160°C to 425°C could be assigned to the loss of DMF molecules and coordinated HCOO^- (Calcd 48.7%). The continuous weight loss of 22.3% is caused by the release of BTC ligands (Calcd 18.0%). The decomposition process is completed at 480°C giving black iron oxide as the final decomposition product, which constituted 32.6% of the initial weight (Calcd 33.0%).

3.4. Magnetic properties

The magnetic susceptibility of **1** was measured from 2 to 300 K in a 0.1 T magnetic field and plotted as χT versus T as shown in figure 3. The $\chi_M T$ value decreases from 19.58 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 300 K to 0.89 $\text{cm}^3 \text{mol}^{-1} \text{K}$ at 2 K, revealing principally antiferromagnetic interaction between the iron ions in **1**. The $\chi_M T$ value at 300 K (19.58 $\text{cm}^3 \text{mol}^{-1} \text{K}$) is marginally higher than the expected value (18 $\text{cm}^3 \text{mol}^{-1} \text{K}$, assuming $g=2.0$ for Fe^{2+}) for six independent spin-only Fe(II) ions ($S=2$), which can be attributed to spin-orbit effects of the octahedral Fe(II). They are fitted well by the Curie-Weiss law above 2 K with the Curie and Weiss constants: $C=19.99 \text{ cm}^3 \text{K mol}^{-1}$ and $\theta=-0.307 \text{ K}$, respectively. The negative Weiss constant confirms the presence of antiferromagnetic interaction between Fe(II) ions in the $\{\text{Fe}_6\}$ cluster.

4. Conclusions

Introduction of H_3BTC into the Fe^{3+} /formic acid solvothermal system leads to a chair-type $\{\text{Fe}_6\}$ wheel, which were connected by BTC into a (3,6)-connected

2-D network. The studies of **1** not only expand the family of polynuclear aggregates from a structural point of view, but also afford an effective method for constructing polynuclear iron cluster-based framework materials. Future research will focus on iron cluster-based framework materials, aiming to synthesize 3-D porous frameworks composed of the giant metal-oxide cluster and the polycarboxylate ligands.

Supplementary material

TG curve and IR spectrum and additional figures, X-ray crystallographic information file (CIF) are available for **1**. Further details on the crystal structure investigations may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223 336408; Email: support@ccdc.cam.ac.uk) on quoting the depository number CCDC-843668.

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