

由三核铁构筑成的新型的二维网状超分子化合物的合成、结构与性质

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Synthesis, Structure and Magnetic Properties of a Novel 2-D Supramolecular Network Formed by the Fe_3O Building Unit through Three Hydrogen Bonds

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A novel 2-D supramolecular network formed by the Fe_3O building unit through three hydrogen bonds [$\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_2\text{OC}_6\text{H}_5)_6(3\text{H}_2\text{O})\text{NO}_3 \cdot 2\text{H}_2\text{O}$ (**1**)] are presented. The title complex crystallizes in monoclinic, space group $P2_1/n$, with $a=1.709\ 3(2)$ nm, $b=3.152\ 9(3)$ nm, $c=1.021\ 2(2)$ nm, $V=5.503\ 5(14)$ nm³, $Z=4$, $D_{\text{(calc)}}=1.500\ \text{g}\cdot\text{cm}^{-3}$, $F(000)=2\ 564$. Each Fe_3O unit is connected by three NO_3^- ions and inversely each NO_3^- ion is surrounded by three Fe_3O moieties. It shows that the well-known Fe_3O unit is a potential three H-donors and may be able to be a three-connected linker. This complex displays weak anti-ferromagnetic coupling between Fe(III) centers. Electrochemical experiments were carried out to obtain the character of its redox reaction. CCDC: 222011.

Keywords: 2-D supramolecular network Fe_3O H-bonding

0 Introduction

Self-assembly of discrete units into supramolecular aggregates and networks is a prominent field in contemporary chemistry^[1]. Usual approaches in this area were making use of donor-containing ligands and heterocycles to connect different metal centers together or self-organizing pure organic donor and acceptor together by H-bonding and other weak interactions. Moreover, this decade has witnessed the rapid development of the iron-oxo complexes since the discovery that they can behave as nano-magnets and show mag-

netic bi-stability of pure molecular origin^[2]. For example, a serial of poly-iron clusters containing bridging oxygen-centers, such as Fe_2 , Fe_3 , Fe_6 , Fe_8 , have been synthesized and its interesting magnetic properties have been investigated. However, iron-oxo cluster-based arrays are still rare.

We are interested in the exploration of the new iron-oxo complexes and novel iron-oxo cluster-based supramolecular networks with physical properties^[3]. In the present work, we report a novel 2-D supramolecular network, [$\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_2\text{OC}_6\text{H}_5)_6(3\text{H}_2\text{O})\text{NO}_3 \cdot 2\text{H}_2\text{O}$

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(1). Furthermore, its structure and magneto-chemical properties have been investigated.

1 Experimental

1.1 Synthesis

Complex (1) was prepared as follows. To a solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.515 g, 3.75 mmol) and phenoxy-acetic acid (0.19 g, 1.25 mmol) in water (10 mL), a solution of NaOH (0.06 g, 1.5 mmol) in ethanol (10 mL) was added and a red precipitate appeared instantly. 2 h later, the product was collected by filter, washed with water (3×5 mL) and dried under vacuum. Deep red crystals were obtained by slow evaporation of the filtrate at room temperature over three weeks. The yield is 28%. Anal. Calcd(%): $\text{Fe}_3\text{O}_{27}\text{C}_{48}\text{H}_{52}\text{N}$: C, 46.45; H, 4.62. Found(%): C, 46.42, H, 4.59. FT-IR (KBr, 400~4 000 cm^{-1}): 3 445.93 cm^{-1} (w), 1 627.78 cm^{-1} (vs), 1 600.23 cm^{-1} (vs), 1 589.40 cm^{-1} (s), 1 497.20 cm^{-1} (m), 1 466.03 cm^{-1} (m), 1 427.00 cm^{-1} (m), 1 384.26 cm^{-1} (m), 1 234.02 cm^{-1} (m), 1 071.77 cm^{-1} (w), 725.51 cm^{-1} (m), 582.77(m), FT-IR (KBr, 400~4 000 cm^{-1}) (Phenoxy-acetic acid): 2 919.97(w), 1 735.25 (s), 1 699.80 (s), 1 598.43 (m), 1 499.62(m), 1 437.64(ms), 1 234.95 (s), 1 094.12, 755.35(s), 688.90(s), 510.37(m).

1.2 Crystal Structure Determination

A well-shaped 0.2 mm × 0.3 mm × 0.2 mm individual crystal was chosen for X-ray data collection which performed on a SMART APEX CCD diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.071\,073\text{ nm}$) at room temperature. The title complex crystallizes in monoclinic, Space group $P2_1/n$, with $a = 1.709\,3(2)\text{ nm}$, $b = 3.152\,9(3)\text{ nm}$, $c = 1.021\,2(2)\text{ nm}$, $V = 5.503\,5(14)\text{ nm}^3$, $Z = 4$, $D_{\text{(calc)}} = 1.500\text{ g} \cdot \text{cm}^{-3}$, $F(000) = 2\,564$. A total of 28 832 intensity data were collected in the range $2.1^\circ \leq \theta \leq 26.0^\circ$, of which 10 784 were unique. The structure was solved by direct methods and the all non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. Hydrogen atoms of water molecules were found in the Fourier difference map and other hydrogen atoms were added geometrically and were not refined^[4]. The finally R_1 and wR_2 was 0.053 8, and 0.130 0 respectively, $w = 1/[\sigma^2(F_o^2) + (0.080\,0P)^2 + 1.550\,0P]$ where $P = (F_o^2 + 2F_c^2)/3$. The key crystallographic data and structure refinement for the complex are given in Table 1.

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Table 1 Crystal Data and Structure Refinement Details for $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_2\text{OC}_6\text{H}_5)_6(3\text{H}_2\text{O})]\text{NO}_3 \cdot 2\text{H}_2\text{O}$

formula	$\text{C}_{48}\text{H}_{52}\text{Fe}_3\text{O}_{27}\text{N}$
formula weight	1 242.46
crystal system	monoclinic
space group	$P2_1/n$ (No.14)
a / nm	1.709 3(2)
b / nm	3.152 9(3)
c / nm	1.021 2(2)
$\beta / (^\circ)$	90.210(10)
V / nm^3	5.503 5(14)
Z	4
$D_{\text{(calc)}} / (\text{g} \cdot \text{cm}^{-3})$	1.500
μ / mm^{-1}	0.869
$F(000)$	2 564
crystal size / mm^3	0.20 × 0.20 × 0.30
temperature / K	293
$\theta_{\text{min}}, \theta_{\text{max}} / (^\circ)$	2.1, 26.0
index range	$-21 \leq h \leq 18$, $-38 \leq k \leq 38$, $-12 \leq l \leq 11$
reflections unique	1 0784 ($R_{\text{int}} = 0.038$)
observed reflections [$I > 2\sigma(I)$]	7 883
R_1, wR_2	$R_1 = 0.053\,8$, $wR_2 = 0.130\,0$
GOF	1.06

2 Results and Discussion

2.1 IR Spectra and Description of the Structure

The Δ value ($\nu(\text{C}=\text{O}) - \nu(\text{C}-\text{O}) = 27.55\text{ cm}^{-1}$) of title complex is smaller than that of free ligand anion (35.45 cm^{-1}) which indicates that the phenoxy-acetic acid coordinates to Fe as the bi-chelating mode^[5]. Furthermore, the characteristic band at 582.77 cm^{-1} identifies the existence of the Fe_3O core^[5].

The phenoxy group was introduced into this well-known $[\text{Fe}_3\text{O}(\text{RCOO})_6\text{L}_3]^+$ species (where L is H_2O or pyridine and R is an alkyl or aryl group). The asymmetry unit of the complex is depicted in Fig.1.

The complex is tri-nuclear with the central oxygen atom O(7) lying approximately in the plane of the

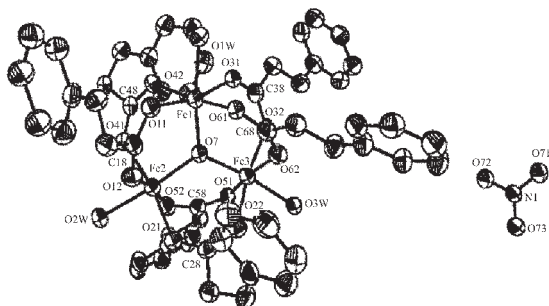


Fig.1 Asymmetry unit structure of complex (1)

three irons. Every Fe atom is octahedral coordinated by six O atoms in which one is the central O, the other from water molecules, and the next four from bridging phenoxy-acetic acid groups. The average Fe-O(7)-Fe angle is 120° , and distance is 0.192 5 nm. The average values for the other four Fe(1,2,3)-O bond distances are Fe(1)-O=0.203 1 nm; Fe(2)-O=0.200 2 nm; Fe(3)-O=0.203 5 nm; Fe(1)-O1w=0.208 4 nm. The bond angles of central O-Fe(n)-O from carboxylate group are $94.81(9)^\circ$ (Fe(1)), $95.05(9)^\circ$ (Fe(2)), $94.70(9)^\circ$ (Fe(3)), respectively. The bond angles of central O-Fe-O

from the solvent molecules are all nearly $173.25(9)^\circ$. The average O-Fe-O (carboxylate group) angles are $144.89(9)^\circ$ (O-Fe(1)-O(carboxylate)), $116.03(9)^\circ$ (O-Fe(2)-O(carboxylate)) and $116.39(9)^\circ$ (O-Fe(3)-O(carboxylate)) respectively. Bond lengths and angles within the trinuclear cluster are consistent with values found for other iron basic carboxylate structures^[6]. The other bond lengths and angles for the complex are listed in the Table 2.

The most striking feature of this system is that three iron-coordinated waters and nitrate ions form a novel planar array the oxygen atoms of nitrate (O71, O72, O73) and coordinated water (O1w, O2w, O3w) almost lie in the plane of the three irons by three bonds, O3W-H3WA...O73_#1, 0.272 7(3) nm, 146.0° ; O1W-H1WA...O72_#2, 0.276 5 (3) nm, 121.4° ; O2W-H2WA...O71_#3, 0.287 3(3) nm, 157.8° , respectively. (Fig.2). Each Fe_3O unit is connected by three NO_3^- ions and inversely each NO_3^- ion is surrounded by three Fe_3O moieties. This complex shows

Table 2 Selected Bond Lengths (nm) and Angles ($^\circ$)

Fe1-O1W	0.208 4(2)	Fe1-O7	0.198 2(2)	Fe1-O11	0.201 9(2)
Fe1-O32	0.200 3(2)	Fe1-O42	0.203 4(2)	Fe1-O61	0.207 0(2)
Fe2-O2W	0.210 3(2)	Fe2-O7	0.191 1(2)	Fe2-O12	0.201 7(2)
Fe2-O21	0.199 1(2)	Fe2-O41	0.201 1(2)	Fe2-O52	0.198 7(2)
Fe3-O3W	0.206 3(2)	Fe3-O7	0.188 3(2)	Fe3-O22	0.203 4(2)
Fe3-O51	0.205 8(2)	Fe3-O31	0.204 8(2)	Fe3-O62	0.200 1(2)
O1W-Fe1-O7	174.49(10)	O21-Fe2-O52	95.54(9)	O1W-Fe1-O11	84.95(9)
O41-Fe2-O52	88.81(9)	O1W-Fe1-O32	85.35(9)	O3W-Fe3-O7	172.88(9)
O1W-Fe1-O42	83.88(9)	O3W-Fe3-O22	88.78(9)	O1W-Fe1-O61	87.23(9)
O3W-Fe3-O31	82.10(9)	O7-Fe1-O11	91.00(9)	O3W-Fe3-O51	88.98(9)
O7-Fe1-O32	98.16(9)	O3W-Fe3-O62	82.04(9)	O7-Fe1-O42	92.88(9)
O7-Fe3-O22	96.23(9)	O7-Fe1-O61	97.20(9)	O7-Fe3-O31	92.97(9)
O11-Fe1-O32	86.49(9)	O7-Fe3-O51	96.37(9)	O11-Fe1-O42	96.52(9)
O7-Fe3-O62	93.23(9)	O11-Fe1-O61	169.83(9)	O22-Fe3-O31	88.32(9)
O32-Fe1-O42	168.51(9)	O22-Fe3-O51	86.25(9)	O32-Fe1-O61	86.41(9)
O22-Fe3-O62	170.17(9)	O42-Fe1-O61	89.08(9)	O31-Fe3-O51	169.65(9)
O2W-Fe2-O7	172.39(9)	O31-Fe3-O62	93.87(9)	O2W-Fe2-O12	86.87(9)
O51-Fe3-O62	90.06(9)	O2W-Fe2-O21	83.46(9)	O2W-Fe2-O41	90.00(9)
O2W-Fe2-O52	80.34(9)	O7-Fe2-O12	98.60(9)	O7-Fe2-O21	91.44(9)
O7-Fe2-O41	95.59(9)	O7-Fe2-O52	94.59(9)	Fe1-O7-Fe2	120.32(11)
O12-Fe2-O21	87.66(9)	Fe1-O7-Fe3	118.84(12)	O12-Fe2-O41	86.43(9)
Fe2-O7-Fe3	120.80(11)	O12-Fe2-O52	166.35(9)	O21-Fe2-O41	171.42(9)

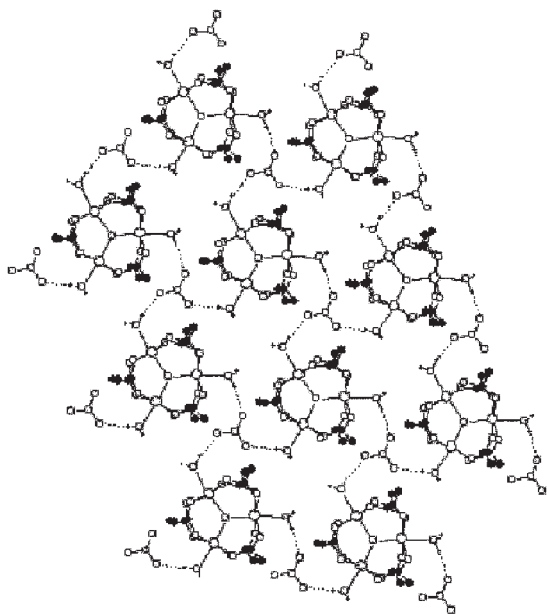


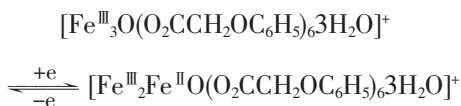
Fig.2 View of the planar network of the complex (1) along the *b* axis

(For clarity, the PhOCH_2 groups and the H atoms except the H1wa, H1wb, H2wa, H2wb, H3wa, and H3wb were omitted)

that the well-known Fe_3O unit is a potential three H-donors and may be able to be a three-connected linker.

2.2 Electro-chemistry

The cyclic voltammetry reveals a quasi-reversible reduction process due to $\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$ couple (Fig.3) which can be explained^[6,7] in terms of the simple equilibrium shown in the equation.



Cyclic voltammogram of the complexes shows a second oxidation wave close to 0.45 V as depicted in Fig.3. This may be the oxidation wave of the ligand which has been confirmed by the graph of pure ligand in acetonitrile.

2.3 Magnetic Properties

The magnetic susceptibility data for complex (1) were measured over the 75~300 K ranges. From the Fig.4, it can be seen that $\chi_m T$ decreases on cooling from $2.4 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 300 K and tends to $0.8 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 75 K which indicates an overall anti-ferro-

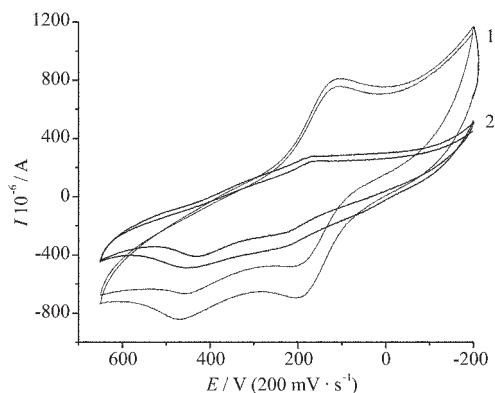


Fig.3 (1) complex (1) in acetonitrile; (2) pure ligand in acetonitrile

$E_{\text{ap}}=0.196$; $E_{\text{cp}}=0.082$; $\Delta E=0.114$; $E_{1/2}=0.139$;
 $I_{\text{a}}/I_{\text{c}}=0.8655$; $\Delta E=E_{\text{ap}}-E_{\text{cp}}$; $E_{1/2}=1/2(E_{\text{ap}}+E_{\text{cp}})$;
 E_{ap} : anodic peak potential; E_{cp} : cathodic peak potential

magnetic behavior in the higher temperature range. If it is assumed that the three $\text{Fe}(\text{III})$ ions are equivalent, a theoretical expression for the molar magnetic susceptibility can be derived by using the Kambe vector-coupling method and the Van Vleck equation. The exchange magnet constant J was fitted by eqs.1~2 which are shown as follows:

$$\chi_m = \frac{Ng^2\beta^2 A}{4kTB} \quad (1)$$

Where

$$A = 1 + 20\exp(3x) + 105\exp(8x) + 210\exp(15x) + 330\exp(24x) + 429\exp(35x) + 455\exp(48x) + 340\exp(63x),$$

$$B = 1 + 4\exp(3x) + 9\exp(8x) + 10\exp(15x) + 10\exp(24x) + 9\exp(35x) + 7\exp(48x) + 4\exp(63x),$$

$x = J / kT$ and

$$\chi' = \frac{\chi_m''}{1 - (2zJ'/Ng^2\beta^2)\chi_m''} \quad (2)$$

where $\chi_m'' = \chi_m(1-\rho) + \rho \frac{4.38}{T}$.

Equation (2) considers inter-cluster interaction with molecular field model^[8,9] which involves inter-cluster coupling constant zJ' and impurity like monomer paramagnetic impurity by the percents ρ . The fitting gave the results that $J = -59.14 \text{ cm}^{-1}$, $g = 2.10$, $\rho = 0.081$, $zJ' = -3.07 \text{ cm}^{-1}$ and $R = 2.05 \times 10^{-4}$ ($R = \sum (\chi_m^{\text{exp}} - \chi_m^{\text{cal}})^2 / \sum (\chi_m^{\text{exp}})^2$)

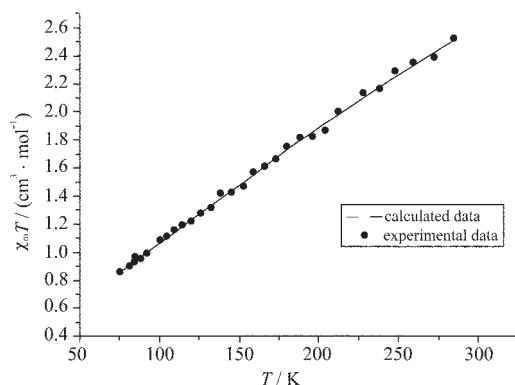


Fig.4 Temperature dependence of $\chi_m T$

and the fitting line was shown in Fig.4.

In conclusion, we have reported a novel planar supramolecular network based on the Fe_3O cluster, demonstrated that the Fe_3O cluster can be utilized as a 3-connected linking unit to construct supramolecule arrays by hydrogen bond. In addition, its magnetic property has been investigated in details.

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