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Template synthesis and characters of the 2D 6^3 honeycomb-type nets

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Abstract

Compound **1**, namely $Fe_2(ox)_3(L)_2$ (L = *N*,*N*′-dimethylcyclohexylamine, ox = oxalate dianion), was hydrothermally synthesized via different temperatures under the direction of the organic template L, characterized by the 2D (6,3) honeycomb-type nets and a strong antiferromagnetic behavior with $\theta = -106$ K between high-spin Fe(III) ions ($S = 5/2$). Compound **1** belongs to orthorhombic system, space group *Pbca*, $a = 9.4262(13)$ Å, $b = 16.641(2)$ Å, $c = 16.825(2)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2639.3(6)$ Å^3, $Z = 4$, $R_1 = 0.0447$, $\omega R_2 = 0.1074$, $S = 1.031$.

Keywords: 6^3 nets; ox; Hydrothermal synthesis; Antiferromagnetic interaction; Template synthesis

1. Introduction

Extensive research work has been carried out in the last few years on the synthesis and characterization of several families of open-framework materials, including aluminosilicates [1], phosphates [2], and carboxylates [3]. The intense interest in these materials is driven to a large extent by their interesting properties and potential in various applications, such as electrical conductivity [4], magnetism [5], photomechanism [6], host–guest chemistry, ion exchange, shape specificity [7] and catalysis [8,9], high-temperature, and flame-resistant fibers [10].

The oxalate ion acts as a rigid bidentate ligand that can facilitate the formation of extended structures by bridging metal centers. Many metal oxalate structures are reported in the literature [3]. A property of oxalate ions that has been of specific interest is their ability to mediate electronic effects between paramagnetic metal ions [11]. The oxalate moiety also acts as a linker between metal centers to yield open structures with dimensionalities ranging from zero to three [12]. And the 2D honeycomb structure is the most common for the oxalates, however it is believed that this structure allows for large variations in molecule type and pore functionalization if different organic templates were selected [13]. Herein, we report another oxalate coordination compound showing the 2D (6,3) honeycomb structure, directed by the novel organic template L formed *in situ*.

2. Experimental

2.1. Materials and methods

All reagents were bought from commercial sources without further purification. Analyses for C, H and N were carried out on a Perkin-Elmer analyzer. Thermal gravimetric analyses were completed on a NETZSCH TG 209 instrument. IR (KBr pellets) spectra were recorded in the 400–4000 cm^{-1} range using a Perkin-Elmer Spectrum One FTIR spectrometer.

2.2. Synthesis of 1

Compound **1** was obtained hydrothermally from the mixture of $FeCl_3$/dichloroacetic acid/cyclohexylamine in water. In addition, further experiments were made: (a) equivalent Fe(III) salt such as $Fe_2(SO_4)_3$ and Fe(II) salts from $FeCl_2$ and $FeSO_4$ were chosen to replace $FeCl_3$, resulted in the same product, which suggests that the type

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of the ferric salt has no effect on the formation of **1**, interestingly, on the other hand, the Fe(II) salts from $FeCl_2$ and $FeSO_4$ were also chosen to replace $FeCl_3$ to lead to the same product, along with the oxidation of Fe(II) to Fe(III) in air; (b) in addition, based on the $FeCl_3$ salt, compound **1** furnished hydrothermally under different temperatures (120, 140, 160, 180 °C), respectively, which suggests the temperature has no obvious effect on the formation of **1**; (c) oxalic acid was directly employed to replace dichloroacetic acid, resulted in no product, which suggests the hydrolyzation of dichloroacetic acid is responsible for the formation of organic template L *in situ*; (d) aniline was chosen to replace cyclohexylamine, resulted in no product, possibly due to the effect on the amido from the aromatic phenyl (Scheme 1). Elemental analysis (%) calcd. for **1**: Anal. Found (%): C, 42.03; N, 4.56; H, 5.36. Calcd: C, 41.93; H, 5.44; N, 4.45. IR (KBr pellet): $v = 488$(v), 586(v), 950(w), 998(w), 1029(w), 1057(w), 1174(m), 1218(m), 1614(vs), 2732(s), 2863(m), 2934(ms) cm^{-1}.

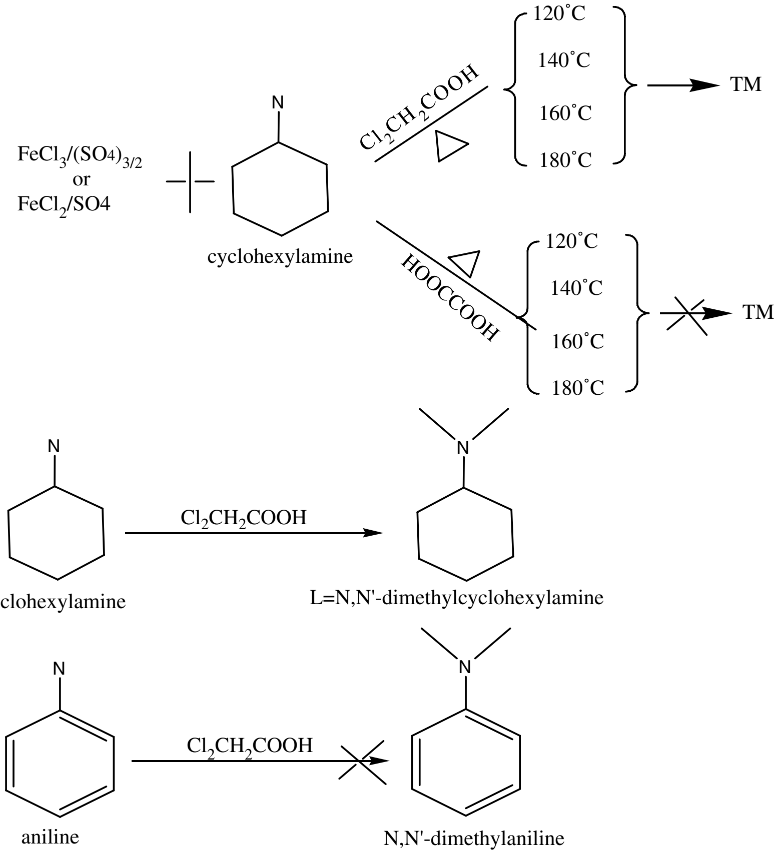
2.3. Crystallographic measurements on *1*

A yellow clear single crystal was selected for the diffraction Analysis. Data collection is performed on a Bruker SMART 1000 CCD bidimensional detector using Mo-Kα radiation. Data were integrated and corrected for absorption using the Bruker programs SAINT SADABS and SMART [14]. The structure of **1** was resolved by direct methods and refined using SHELXL-97. All non-hydrogen atoms (iron, oxygen, carbon, nitrogen) were located first in difference Fourier maps, whereas hydrogen atom positions were found and firmed in calculated positions. Crystal data and experimental details are summarized in Table 1. Selected bond length and angle are listed in Table 2.

3. Results and discussion

3.1. Crystal structure of *1*

Single-crystal X-ray analysis revealed that compound **1** crystallizes in the space group Pbca and exhibits the 2D (6,3) honeycomb structure with the edges of 5.533 Å. The Fe(III) atom located at an inversion center defines a slightly distorted octahedral $[FeO_6]$ coordination core with the axis elongated, whose equatorial positions are occupied by O1, O2, O4 and O5 atoms from ox-bridging groups, while the remaining apical positions are occupied by O3 and O6 atoms of ox-bridging groups. By and large, the axial Fe—O bonds (Fe—O3/2.2.134 Å and Fe—O6/2.164 Å) are longer than those of the equatorial positions (Fe—O2/2.118 Å, Fe—O5/2.120 Å, Fe—O1/2.124 Å, Fe—O4/2.183 Å). And the distortion parameter 1.31×10^{-4} of the FeO_6 polyhedron with an average Fe—O distance 2.141 Å is calculated using the formula of $\Delta = (1/N)\sum_{n=1,N}\{(d_n - \langle d\rangle)/\langle d\rangle\}^2$, in which the d_n and $\langle d\rangle$ are the single Fe—O and overage Fe—O bond lengths, respec-



Scheme 1. Schematic description of the whole process of experiments.