



Syntheses, structures and magnetic properties of Mn(II), Co(II) and Ni(II) metal–organic frameworks constructed from 1,3,5-benzenetricarboxylate and formate ligands

Ying Fu^a, Jie Su^a, Sihai Yang^b, Guobao Li^{a,*}, Fuhui Liao^a, Ming Xiong^c, Jianhua Lin^{a,*}

^a Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China

^b School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK

^c X-ray Laboratory, China University of Geoscience, Beijing 100083, PR China

ARTICLE INFO

Article history:

Received 19 August 2009

Received in revised form 10 November 2009

Accepted 13 November 2009

Available online 20 November 2009

Keywords:

Metal–organic framework

Carboxylate ligands

Magnetic property

Nickel

Manganese

Cobalt

ABSTRACT

Three compounds, $[(\text{CH}_3)_2\text{NH}_2][\text{M}_3(\text{BTC})(\text{HCOO})_4(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ ($\text{M} = \text{Mn}$ (**1**), Co (**2**), Ni (**3**), $\text{H}_3\text{BTC} = 1,3,5$ -benzenetricarboxylic acid), were synthesized under hydrothermal conditions and were characterized by single crystal and powder X-ray diffraction, IR spectra, elemental analysis, coupled TG-MS and magnetic measurements. Compounds **1–3** are isostructural analogues and crystallize in monoclinic space group $P2_1/c$. Each metal ion in these compounds connects to six oxygen atoms to form a MO_6 octahedron. Six MO_6 octahedra link to each other to form a corner-shared hexameric M_6 cluster, which is linked by BTC ligands to form two-dimensional layers. The two-dimensional layers are further connected by formic ions to form a three-dimensional network with channels, where $(\text{CH}_3)_2\text{NH}_2^+$ ions and water molecular are located. Magnetic measurements indicate that anti-ferromagnetic ordering occurs at low temperature for these compounds.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The design and synthesis of metal–organic frameworks (MOFs) on the basis of the assembly of metal ions and multifunctional organic ligands is a rapidly expanding research area due to their intriguing aesthetic structures and promising properties in gas adsorption, separation, catalysis, magnetism and nonlinear optics [1–12]. The construction of molecular architecture is influenced by the combination of several factors: medium, temperature, metal–ligand ratio, template, counterion and sometimes hydrogen bonding and π – π interactions [5,13–15]. The selection of metal ions and organic ligands is very important in the control of organic–inorganic frameworks in the self-assembly process [16–18]. Different ligands or metal ions have been used to synthesize MOFs with complex structures or multi-functions [19–23]. Such a trend has been followed by us, and several new results have been obtained. Here, we report the syntheses, structures and magnetic properties of metal–organic frameworks: $[(\text{CH}_3)_2\text{NH}_2][\text{M}_3(\text{BTC})(\text{HCOO})_4(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ ($\text{M} = \text{Mn}$ (**1**), Co (**2**), Ni (**3**)), which adopt three-dimensional framework structures consisting of edge-sharing MO_6 octahedra with BTC and formate as ligands.

2. Experimental

2.1. Materials and characterizations

All solvents and reagents for the syntheses were of analytical grade and were used as received from commercial sources without further purification. Powder X-ray diffraction data of the studied samples were collected on a Rigaku D/Max-2000 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV, 100 mA and a graphite monochromator at the secondary beam. Magnetic data of polycrystalline samples were measured on a Quantum Design MPMS-5S SQUID Spectrometer in the 2–300 K temperature range. Correction for the sample holder was applied. IR spectra were recorded on a Magna-IR 750 FTIR spectrophotometer in the region of 4000 – 650 cm^{-1} . Elemental analyses for C, H and N were carried out on Elementar Vario EL III microanalyzer. TG-MS analyses were performed in air atmosphere with a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ from 50 to $800 \text{ }^\circ\text{C}$, using a NETZSCH STA449C instrument. Electron paramagnetic resonance (EPR) spectrums of the studied samples were recorded on a powdered sample at X band at 300 K on the Bruker ESP300 Electron Spin Resonance Spectrometer.

2.2. Syntheses

Identical synthetic procedures were used to prepare the three compounds. To synthesize **1**, a mixture of $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ (3.0 mmol,

* Corresponding authors. Tel.: +86 10 62750342; fax: +86 10 62753541 (G. Li).
E-mail addresses: liguobao@pku.edu.cn (G. Li), jhlin@pku.edu.cn (J. Lin).

0.5937 g), H₃BTC (1.0 mmol, 0.2101 g), DMF (*N,N*-dimethylformamide) (5.0 ml) and distilled water (5.0 ml) was placed in a 23 ml Teflon-lined stainless autoclave. The autoclave was sealed, heated to 120 °C at a rate of 10 °C/h, kept at 120 °C under autogenous pressure for 5 days, and then cooled to room temperature at a rate of 5 °C/h. Colorless crystals were filtered, washed with DMF and distilled water and then dried in air to give about 0.53 g of **1** (yield 84% based on H₃BTC). The (CH₃)₂NH₂⁺ and HCOO⁻ were generated via decomposition of DMF. *Anal. Calc.* for C₁₅H₁₉NO₁₆Mn₃ (Fw: 634.13): C, 28.41; H, 3.02; N, 2.21. Found: C, 28.42; H, 2.69; N, 2.17%.

The cobalt analogue **2** was prepared by an identical procedure to that described for **1**, and then purple crystals were obtained (yield 73% based on H₃BTC). *Anal. Calc.* for C₁₅H₁₉NO₁₆Co₃ (Fw: 646.10): C, 27.88; H, 2.96; N, 2.17. Found: C, 27.76; H, 2.64; N, 2.08%. The nickel analogue **3** was prepared as light green crystals (yield 71% based on H₃BTC) using the similar procedure as that for **1**. *Anal. Calc.* for C₁₅H₁₉NO₁₆Ni₃ (Fw: 645.44): C, 27.91; H, 2.97; N, 2.17. Found: C, 27.64; H, 3.17; N, 2.27%.

2.3. Crystallographic studies

Suitable single crystals of **1**, **2** and **3** were carefully selected under an optical microscope and glued to thin glass fibers with epoxy resin. X-ray single-crystal diffraction data of **1** and **2** were collected

Table 1
Crystallographic data and structural refinement parameters for **1–3**.

	1	2	3
Formula	C ₁₅ H ₁₉ NO ₁₆ Mn ₃	C ₁₅ H ₁₉ NO ₁₆ Co ₃	C ₁₅ H ₁₉ NO ₁₆ Ni ₃
Formula weight	634.13	646.10	645.44
T (K)	298(2)	298(2)	120(2)
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a (Å)	9.756(2)	9.616(2)	9.540(2)
b (Å)	14.139(3)	13.904(3)	13.783(3)
c (Å)	15.733(3)	15.346(3)	15.154(3)
β (°)	90.96(3)	91.18(3)	91.02(3)
V (Å ³)	2170.0(8)	2051.4(7)	1992.2(7)
Z	4	4	4
D _{calc} (g cm ⁻³)	1.941	2.092	2.152
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073
μ (mm ⁻¹)	1.803	2.487	2.898
Goodness-of-fit on F ²	1.000	1.002	1.001
R _{int}	0.0454	0.0538	0.0520
R ₁ , wR ₂ [I > 2σ (I)]	0.0613, 0.1659	0.0379, 0.1159	0.0421, 0.1435
R ₁ , wR ₂ (all data)	0.0666, 0.1713	0.0458, 0.1233	0.0536, 0.1576

Table 2
Selected bond distances (Å) for **1–3**.

Bond	1 (M = Mn)	2 (M = Co)	3 (M = Ni)
M1–O3	2.136(3)	2.052(2)	2.022(3)
M1–O5	2.194(3)	2.136(2)	2.093(3)
M1–O8	2.194(3)	2.091(3)	2.069(3)
M1–O11	2.194(3)	2.091(3)	2.051(3)
M1–O13	2.226(3)	2.133(2)	2.090(3)
M1–O15	2.184(3)	2.108(2)	2.067(3)
M2–O1	2.137(3)	2.085(2)	2.054(3)
M2–O4	2.184(3)	2.085(2)	2.042(3)
M2–O6	2.176(3)	2.104(3)	2.074(3)
M2–O9	2.225(3)	2.134(2)	2.084(3)
M2–O12	2.199(3)	2.133(2)	2.074(3)
M2–O13	2.175(3)	2.079(2)	2.041(3)
M3–O2	2.172(3)	2.103(2)	2.077(3)
M3–O7	2.200(3)	2.118(3)	2.061(3)
M3–O9	2.199(3)	2.100(2)	2.062(3)
M3–O10	2.203(3)	2.134(2)	2.096(3)
M3–O11	2.210(3)	2.124(2)	2.073(3)
M3–O14	2.118(3)	2.035(2)	2.000(3)

on a Rigaku AFC6S diffractometer by using the ω-2θ scan method at room temperature. Their PSI absorption corrections were applied using the TEXSAN program [24]. The intensity data of **3** were collected at 120 K on a Bruker NONIUS X-ray diffractometer, equipped with an APEX-CCD area detector. The data absorption correction of **3** was applied using the SADABS program [25]. The structures were solved by the direct method and refined on F² with full-matrix least-squares methods using the SHELXS-97 and SHELXL-97 programs, respectively [26]. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added in the riding model and refined isotropically with O–H = 0.82 Å, N–H = 0.90 Å and C–H = 0.93 Å (in BTC or formate) or C–H = 0.96 Å (in (CH₃)₂NH₂⁺). The crystallographic data and structural refinement parameters are presented in Table 1, and the selected bond lengths are listed in Table 2.

3. Results and discussion

3.1. Infrared (IR) spectra

FT-IR spectra of these compounds are shown in Fig. 1. The broad absorption bands of the asymmetric and symmetric stretching vibrations of water appear at 3612–3081 cm⁻¹ [13,27–29]. The bands at 1650–1547 cm⁻¹ and 1442–1336 cm⁻¹ correspond to the asymmetric and symmetric stretching vibrations of the bound carboxylic groups (CO₂M), respectively [13,27–31]. And the bands at 863–807 cm⁻¹ and 798–714 cm⁻¹ are related to the stretching vibrations of C–C groups and the out-of-plane deformation vibrations of the C–H groups in the benzene ring [27–29]. The absence of the absorption bands from 1680–1800 cm⁻¹ indicates the complete deprotonation of BTC ligands [30]. A group of bands at 2917–2779 cm⁻¹ is due to the asymmetric and symmetric stretching vibrations of H₂N⁺ groups.

3.2. Crystal structure

Compounds **1–3** are isostructural analogues with slight differences in the lattice parameters. They crystallize in the monoclinic space group P2₁/c. Here **1** is taken as an example to present and discuss the structure in detail. In the asymmetric unit of **1** (Fig. 2a), there are three crystallographic independent Mn(II) ions (Mn(1), Mn(2) and Mn(3)), one BTC ligand, four formate ligands, one terminal water molecule, one (CH₃)₂NH₂⁺ ion, and one free water molecular. Each Mn(II) ion is six coordinated to form a distorted octahedron with Mn–O bond distances in the range of 2.118–2.225 Å and O–Mn–O angles from 83.51° to 98.63° or 168.30° to 176.64°. The Mn(1) ion is coordinated with two carboxyl oxygen atoms (O3, O5) from two BTC ligands, three carboxyl oxygen atoms (O11, O13, O15) from formate ligands in a 3.21 (*syn, syn, anti*) mode [32–34] (here, the symbol “(n + m).nm (*syn* or *anti, syn* or *anti, anti* or *syn*)”, means that (n + m) metal ions link to a formate, n metal ions connect to one oxygen atom of the formate, and m metal ions connect to the another oxygen atom of the formate; *syn* or *anti* means the mode of the connection of a metal ion to the formate is *syn* or *anti*), and one oxygen atom (O8) from a terminal water molecule. The Mn(2) ion is bound with two BTC (O1, O4), three 3.21 (*syn, syn, anti*) formates (O9, O12, O13) and one 2.11 (*anti, anti*) formate (O6). The Mn(3) ion links with two BTC linkers (O2, O14), three 3.21 (*syn, syn, anti*) formates (O7, O9ⁱⁱ, O11) and one 2.11 (*anti, anti*) formate (O10).

In **1**, each bridging BTC is completely deprotonated, binding to six separate Mn(II) ions. The formates have two bridging modes: the 2.11 (*anti, anti*) and the 3.21 (*syn, syn, anti*) bridging configurations. By the six carboxyl oxygen atoms of the 3.21 (*syn, syn, anti*) formates, six MnO₆ octahedra link to each other to form a corner-

Download English Version:

<https://daneshyari.com/en/article/1311226>

Download Persian Version:

<https://daneshyari.com/article/1311226>

[Daneshyari.com](https://daneshyari.com)