

四水合均苯三甲酸二氢钴的合成、结构和磁性

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摘要: 利用水热法在均苯三甲酸、六水氯化钴、甲酸铵和水的体系中合成了四水合均苯三甲酸二氢钴。该化合物晶体属于单斜晶系, 对应的空间群为 $P2_1/c$ 。磁性测量表明该化合物的钴离子之间存在反铁磁的相互作用, 但直至 2 K 时也没有观察到磁有序。

关键词: 均苯三甲酸; 钴; 磁性; 合成; 结构

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Synthesis, Structure, and Magnetic Property of $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$ (H_3BTC =benzene-1,3,5-tricarboxylic acid)

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Abstract: $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$ was synthesized under hydrothermal condition in the system of H_3BTC , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, NH_4CHOO , and water. It crystallizes in monoclinic space group $P2_1/c$ with $a=0.511\ 15(13)$ nm, $b=1.299\ 5(3)$ nm, $c=1.516\ 1(4)$ nm, and $\beta=96.859(6)^\circ$. Magnetic measurements showed that an antiferromagnetic interaction occurred between the $\text{Co}(\text{II})$ ions in $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$, but no antiferromagnetic ordering was found down to 2 K. CCDC: 681478.

Key words: 1,3,5-benzenetricarboxylate; cobalt; magnetic property; synthesis; structure

0 Introduction

The assembly of open framework metal-organic coordination polymers is attracting increasing attention owing to the potential applications in catalysis, non-linear optics, magnetism, sensors and molecular recognition^[1~16]. Hydrogen-bonding has been widely used to construct extended organic solids possessing both

condensed and open structures^[17~22], strategies for their utility in assembling porous metal-organic frameworks also largely explored^[23~26]. The organic ligand 1,3,5-benzenetricarboxylate (H_3BTC) was one of the favorable ligands used in above studies. Many porous metal-organic frameworks with BTC as the ligand were reported^[25,27~30], where the HBTC^{2-} dianion or the BTC^{3-} trianion was frequently found, and the H_2BTC^- anion

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was found in only a few compounds^[31,32]. Here, we report the synthesis, structure, and magnetic property of a new compound $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$ (**1**) with the H_2BTC^- anion as the ligand.

1 Experimental section

1.1 Materials and analyses

All reagents were of analytical grade and were used as obtained 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 Cu radiation at 40 kV, 100 mA. Magnetic data of polycrystalline samples ($H=1\ 000$ Oe) were recorded on 10.84 mg of **1** in the 2~300 K temperature range using a Quantum Design MPMS-5S SQUID Spectrometer. Correction for the sample holder was applied. IR spectra were recorded in the 400~4 000 cm^{-1} range using a Magna-IR 750 FTIR spectrometer. Elemental analyses were carried out on Elementar Vario EL III microanalyzer. TG-MS analysis was performed with a heating rate of $10\ ^\circ\text{C}\cdot\text{min}^{-1}$ using a NETZSCH STA449C instrument.

1.2 Preparation of $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$ (**1**)

A mixture of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (A.R., 0.24 g, 1.0 mmol), NH_4CHOO (A.R., 0.13 g, 2.0 mmol), H_3BTC (A.R., 0.21 g, 1.0 mmol), and H_2O (10.0 mL, 555 mmol) with a mole ratio of 1.0:1.0:2.0:555 was placed in a 23 mL Teflon-

lined stainless steel autoclave, and the autoclave was sealed, heated to $170\ ^\circ\text{C}$ under autogenous pressure for 120 h, and then cooled to room temperature at a rate of $5\ ^\circ\text{C}\cdot\text{h}^{-1}$. Pink crystalline product was filtered, washed with hot distilled water, and dried at ambient temperature to give about 0.24 g of complex **1** (yield 89% based on H_3BTC). Complex **1** is stable in water for about one week and after that it will become cotton-like. Calcd for $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$ (%): C 39.3; H 3.30. Found (%): C 39.3; H 3.17.

1.3 Crystal structure determination

Intensity data were collected on a Bruker SMART APEX CCD using graphite-monochromated $\text{Mo } K\alpha$ ($\lambda = 0.071\ 073\ \text{nm}$) radiation at room temperature. The absorption correction was applied based on symmetry-equivalent reflections using the ABSOR program^[33]. The structure was solved with direct methods and refined on F^2 with full-matrix least-squares methods using SHELXS-97 and SHELXL-97 programs, respectively^[34,35]. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were added in the riding model and refined isotropically with $\text{O-H}=0.082\ \text{nm}$. The crystallographic data and structural refinement parameters are summarized in Table 1, selected bond lengths are listed in Table 2.

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Table 1 Crystallographic and Structure Refinement Parameters for $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$

Formula	$\text{C}_{18}\text{H}_{18}\text{CoO}_{16}$	Goodness-of-fit (F^2)	1
Formula weight	549.25	T / K	298
Crystal system	Monoclinic	$\mu(\text{Mo } K\alpha) / \text{nm}$	0.071 073
Space group	$P2_1/c$	μ / mm^{-1}	0.95
a / nm	0.511 15(13)	Reflections collected	8 438
b / nm	1.299 5(3)	Indepeudent reflections	3 619
c / nm	1.516 1(4)	Independent reflections $[I > 2\sigma(I)]$	2 532
$\beta / (^\circ)$	96.859(6)	$R_1 [I > 2\sigma(I)]^a$	0.0458
V / nm^3	0.999 8(4)	wR_2 (all data) ^a	0.112 3
Z	2		

$$^a R_1 = \sum (|F_o| - |F_c|) / \sum |F_o|, wR_2 = [\sum (F_o^2 - F_c^2)^2 / \sum (F_o^2)^2]^{1/2}, w = 1 / [\sigma^2(F_o^2) + (0.050\ 5P)^2 + 0.00P], \text{ where } P = (F_o^2 + F_c^2) / 3.$$

Table 2 Selected bond distances (nm) for $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$

Co1-O1×2	0.211 0(1)	O4-C14	0.125 6(2)	C9-C11	0.139 2(3)	C12-C16	0.138 5(3)
Co1-O2×2	0.211 1(1)	O6-C17	0.131 9(2)	C10-C12	0.140 0(3)	C13-C16	0.139 1(3)
Co1-O5×2	0.207 4(2)	O7-C15	0.121 3(2)	C10-C17	0.148 9(3)	C15-C16	0.149 8(3)

Continued Table 2

O1-C14	0.126 8(2)	O8-C15	0.130 8(3)	C11-C13	0.138 9(3)
O3-C17	0.121 5(2)	C9-C10	0.139 4(3)	C11-C14	0.150 5(3)

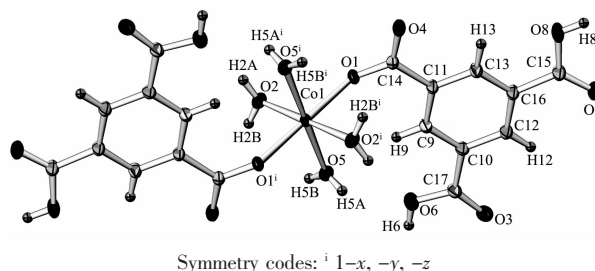
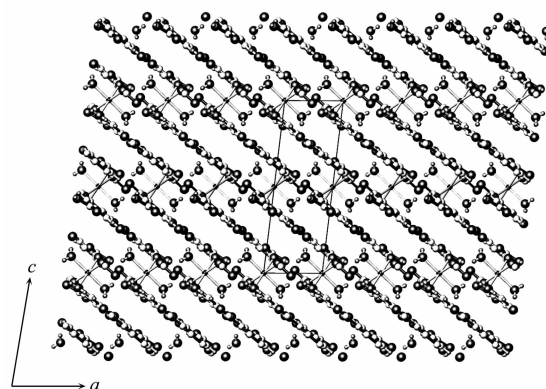
2 Results and discussion

2.1 Infrared (IR) spectra

The IR spectrum of **1** was obtained. In comparison with the characteristic absorption of the functional groups in known compounds, one may assign the main absorption bands in the spectra. The bands from 3 514 to 3 024 cm^{-1} are due to the asymmetric and symmetric stretching vibrations of the water in **1**^[36], and the band 1 662 cm^{-1} is related to the bending vibrations of the water. The 1 612, 1 550, 1 423, 1 396, and 1 373 cm^{-1} bands correspond to the asymmetric and symmetric stretching vibrations of the bound carboxylate group (CO_2M)^[36]. The band at 1 709 cm^{-1} is due to stretching vibrations of C=O groups. And carboxylic group COOH give strong absorption band at 1 234 cm^{-1} corresponds to stretching vibrations of C-OH group. The bands at 899 and 852 cm^{-1} may be related to the stretching vibrations of C-C^[37], and the bands around 744 and 683 cm^{-1} are due to the out-of-plane deformation vibrations of the C-H group in the benzene ring^[36].

2.2 Structural description

$\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$ is centrosymmetric in the monoclinic system with the space group $P2_1/c$, the centre of inversion is lain on the Co atoms. The asymmetric unit of **1** corresponds to half of the molecular formula, including half a cobalt(II) atom, one H_2BTC^- ligand, two water molecules. As shown in Fig.1, the cobalt(II) atom binds to four oxygen atoms from four water molecules, and two oxygen atoms from two H_2BTC^- ligands to form a regular CoO_6 octahedron with the bond length of Co-O in the range of 0.207 to 0.211 nm, a very common geometry in cobalt(II) compounds^[25,38,39]. The CoO_6 octahedron links to two H_2BTC^- ions and four water molecules to form a neutral clusters $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$ (see Fig.1). With the help of hydrogen bonding (listed in Table 3), the neutral cluster $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$ connect to each other to form a three dimensional structure. Fig. 2 shows the packed structures of **1** along different axes. Small channels were formed along the b -axis.

Fig.1 An asymmetric unit in the structure of **1**Fig.2 Packed structure of $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$ along different axesTable 3 Selected hydrogen bond distances in $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$

D-H...A	D...H / nm	H...A / nm	D-H...A / nm
O2-H2A...O4 ^a	0.082 0	0.192 0	0.272 3(2)
O2-H2B...O3 ^b	0.082 0	0.218 0	0.291 2(2)
O5-H5A...O1 ^c	0.082 0	0.196 0	0.274 2(2)
O5-H5B...O3 ^b	0.082 0	0.193 0	0.273 6(3)
O6-H6...O7 ^b	0.082 0	0.181 0	0.262 7(2)
O8-H8...O4 ^d	0.082 0	0.181 0	0.258 6(2)

Symmetry code: ^a $-x, -y, -z$; ^b $-x+2, y-1/2, -z+1/2$; ^c $x+1, y, z$; ^d $-x, -y+1, -z$.

In the literature, a similar compound $[\text{Co}(\text{H}_2\text{O})_4]_3(\text{BTC})_2$ (**2**) was reported^[25], which is composed of zigzag chains of tetra-aqua cobalt (II) benzenetricarboxylate that are hydrogen-bonded to yield a tightly held 3D network. From the structural point of view, the compounds **1** and **2** are very different, which may be due to their different synthesis condition. The compound **1** shows another possibility to form a new compound in the system of Co^{2+} , water and H_3BTC . More new

compounds may be expected when the synthesis conditions are changed.

2.3 Thermal properties

The TG curve and the corresponding MS curves of **1** were shown in Fig.3. **1** firstly loses weight about 12.6wt% up to about 250 °C, which may be attributed to the loss of four water molecules of $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$ (the calculated value is 13.1wt%) as confirmed by the MS curves. Then a dramatic weight-loss of about 71.9wt% occurs from 250 to 700 °C, which may correspond to the decomposition of H_2BTC^- ligands. Correspondingly, CO_2 , CO, O, CH_3 and C_2H_4 are observed in the mass spectra of the gas phase. A trace of N_2 in the transformation gas Ar is also observed.

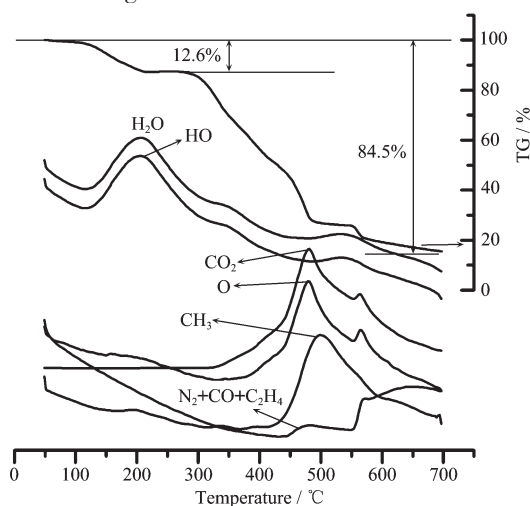


Fig.3 TG curve of **1** (top) and variation of the species (mass spectra) in the gas phase during the heating for **1** (bottom)

2.4 Magnetic property

Magnetic measurements of $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$ (**1**) were performed on a powdered sample from 2 K to room temperature. The thermal evolution of χ_m and χ_m^{-1} curves under an applied field of 1 000 Oe, are shown in Fig.4. The thermal variation of the molar magnetic susceptibility follows the Curie-Weiss law [$\chi_m = C_m / (T - \theta)$] above *ca.* 60 K with values of the Curie and Curie-Weiss constants of 1.75(1) $\text{emu} \cdot \text{K} \cdot \text{Oe}^{-1} \cdot \text{mol}^{-1}$ and $-25.5(1)$ K, respectively. The former corresponds to the calculated Curie constant of 1.88 $\text{emu} \cdot \text{K} \cdot \text{Oe}^{-1} \cdot \text{mol}^{-1}$ for a spin-only system with $S=3/2$ and $g=2$, which is scare to see for the compound of $\text{Co}(\text{II})$ ^[40,41]. The later shows an antiferromagnetic interaction occur between the $\text{Co}(\text{II})$ ions.

However, no antiferromagnetic ordering was found down to 2 K.

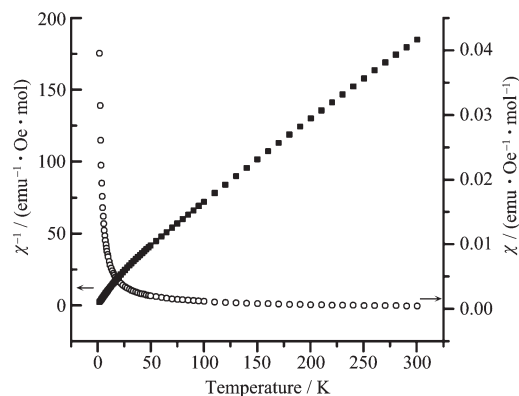


Fig.4 Thermal evolution of χ_m and χ_m^{-1} curves of the $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$ compound

3 Conclusion

In summary, a new compound, $\text{Co}(\text{H}_2\text{BTC})_2(\text{H}_2\text{O})_4$ (**1**), has been synthesized under hydrothermal condition. In the compound **1**, four water molecules, two H_2BTC^- ions, and one Co^{2+} ion connect together by CoO_6 octahedra to form a neutral cluster, which indicates that the compound **1** is a molecular compound similar as ice, where hydrogen bonding is extensive. Magnetic measurements show that antiferromagnetic interactions occur between the Co^{2+} ions in the compound **1**.

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