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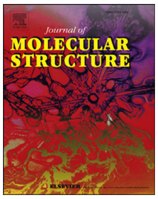

Two Co(II) compound constructed by phthalic acid and 3-Cl-phthalic acid: Synthesis, structure, and magnetic properties

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ABSTRACT

In this paper, we obtained two novel 2D layered cobalt coordination polymers, namely [(Co(o-BDC)]$_n$ (**1**) and (Co(3-Cl-o-BDC)]$_n$ (**2**), through solvothermal method with acetone as solvent based on phthalic acid (o-H_2BDC) and 3-chloro-phthalic acid (3-Cl-o-H_2BDC) respectively. Due to the steric hindrance effect of chloric substituent, the two ligands revealed different coordination modes. And cobalt centers of **1** and **2** showed CoO_6 octahedral and CoO_4 tetrahedral configurations respectively. As a result, **1** and **2** revealed different layered constructions: a 5-connected topology with $4^8.6^2$ Schläfli symbol for **1**, and a 4-connected topology with $4^4.6^2$ Schläfli symbol for **2**, respectively. Besides, Compound **1** and **2** reveal ferromagnetic and antiferromagnetic behaviors, respectively.

1. Introduction

Metal–organic coordination polymers have recently attracted great interest not only because of their versatile intriguing architectures and topologies but also because of their potential applications as functional materials [1]. Thus, a series of studies in this field have mainly focused on the design and preparation, as well as the structure–property relationships [2]. Among the reported studies, much efforts have been focused on the rational design and controlled synthesis of coordination polymers using multidentate ligands such as polycarboxylate and *N*– heterocyclic ligands [3]. Besides, some cheap, readily available building blocks have also been widely reported, such as formic acid [4], oxalic acid [5], and so on [6]. Phthalic acid and its derivatives are also excellent multi-connection building blocks to construct various supramolecular coordination complexes together with various 2-connected linkers [7]. While, supramolecular coordination complexes constructed by only phthalic acid as ligand are scarcely reported.

In this paper, two novel 2D layered cobalt coordination polymers, namely [(Co(o-BDC)]$_n$ (**1**) and (Co(3-Cl-o-BDC)]$_n$ (**2**), based on phthalic acid (o-H_2BDC) and 3-chloro-phthalic acid (3-Cl-o-H_2BDC), respectively were constructed successfully. Although the two carboxylic acid ligands are very similar, the steric hindrance effect of chloric substituent is non-negligible. The relative rotation angle of the two carboxyl groups in **1** and **2** is 61.85(1) ° and 97.20(1) °, respectively (Scheme 1). As a result, compound **1** and **2** reveal different layered constructions based on CoO_6 octahedral and CoO_4 tetrahedral configurations respectively.

2. Experimental section

2.1. Materials and physical measurements

All reagents and solvents for synthesis and analysis were commercially available and used as received. IR spectra were taken on a Perkin-Elmer spectrum One FT-IR spectrometer in the 4000-400 cm^{-1} region with KBr pellets. Elemental analyses for C, H were carried out on a Model 2400 II, Perkin-Elmer elemental analyzer. Powder X–Ray diffraction (XRD) intensities were measured on a Rigaku D/max diffractometer (Cu–Kα, λ = 1.54056 Å). The single–crystalline powder samples were prepared by crushing the crystals and scanned from 2 to 50° with a step of 5° min^{-1}. Calculated patterns of the complexes were generated with PowderCell. The magnetic susceptibility measurements of the polycrystalline

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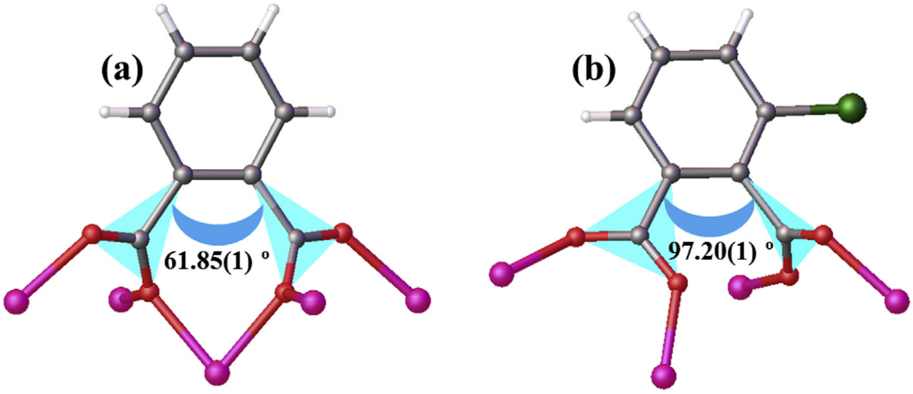

Scheme 1. The versatile coordination modes of *o*-BDC (a) in **1** and 3-Cl-*o*-BDC (b) in **2** used in this work.

samples were measured over the temperature range of 2–300 K with a Quantum Design MPMS-XL7 SQUID magnetometer using an applied magnetic field of 1000 Oe. A diamagnetic correction to the observed susceptibilities was applied using Pascal's constants. TG-DTA tests were performed on a Perkin-Elmer thermal analyzer from room temperature to 1000 °C under N_2 atmosphere at a heating rate of 5 °C min^{-1}.

2.2. Preparation

[(Co(*o*-BDC)]$_n$ (1). A mixture containing $CoCl_2 \cdot 6H_2O$ (238 mg, 1 mmol), *o*-BDC (49.2 mg, 0.3 mmol), acetone (15 mL) and triethylamine (0.25 mL) was sealed in a Teflon-lined stainless steel vessel (25 mL), which was heated at 160 °C for 3 days and then cooled to room temperature at a rate of 5 ℃/h. Ianthinus sheet crystals of **1** were obtained and picked out, washed with distilled water and dried in air. Yield: 30% (based on Co(II)). Anal. Calcd. (%) for $C_8H_4CoO_4$: C, 43.08; H, 1.81. Found: C,43.02; H, 1.75. IR (KBr, cm^{-1}): 3420(m), 1543(s), 1482(w), 1417(s), 1359(m), 1255(w), 1138(w), 1086(w), 1041(w), 957(w), 853(w), 801(w), 730(s), 691(m), 594(s), 490(m), 432(m).

[(Co(3-Cl-*o*-BDC)]$_n$ (2). The same synthetic procedure as that for **1** was used except that *o*-BDC (49.2 mg, 0.3 mmol) was replaced by 3-Cl-*o*-BDC (77.1 mg, 0.3 mmol) giving blue block X-ray-quality crystals of **2** in a 39% yield (based on Co(II)). Anal. Calcd. (%) for $C_8H_3ClCoO_4$: C, 37.32; H, 1.17. Found: C, 37.67; H, 1.10. IR (KBr, cm^{-1}): 3672(w), 3067(m), 1534(s), 1474(m), 1397(s), 1169(w), 1117(w), 1059(w), 870(m), 754(s), 623(w), 507(w), 474(m).

2.3. X-ray crystallographic determination

Both reflection data were collected on an Agilent Supernova diffractometer (Mo, $\lambda = 0.71073$ Å) at room temperature. A semi-empirical absorption correction by using the SADABS program was applied, and the raw data frame integration was performed with SAINT [8]. The crystal structures were solved by the direct method using the program SHELXS-97 [9] and refined by the full-matrix least-squares method on F^2 for all non-hydrogen atoms using SHELXL-97 [10] with anisotropic thermal parameters. All hydrogen atoms were located in calculated positions and refined isotropically. The details of the crystal data were summarized in Table 1, and selected bond lengths and angles for compounds **1**–**2** are listed in Table S1. The crystallographic data of **1**–**2** in CIF format has been deposited in the Cambridge Crystallographic Data Center (CCDC reference number: 1574334–1574335).

2.4. PXRD results

To confirm whether the crystal structures are truly representative of the bulk materials, powder X-ray diffraction (PXRD) experiments have also been carried out for **1**–**2**. The PXRD experimental and computer-simulated patterns of the corresponding complexes are shown in ESI, Fig. S1. Although the experimental patterns have a few unindexed diffraction lines and some are slightly broadened in comparison with those simulated from the single crystal models, it can still be considered favorably that the bulk synthesized materials and the as-grown crystals are homogeneous for **1**–**2**.

3. Results and discussion

3.1. Description of the crystal structure

[(Co(*o*-BDC)]$_n$ (1). Single-crystal X-ray structural analysis shows that compound **1** crystallizes in space groups of *P*2/*c*, and the asymmetric unit contains one crystallographically independent Co atom and one *o*-BDC anionic. As illustrated in Fig. 1a, Co1 lying on a symmetry plane is coordinated by six O atoms (O1, O1A, O2B, O2C, O2D, O2E, symmetry codes: A −x, y, −z+1/2; B −x+1, −y+1, −z+1; C x−1, −y+1, z−1/2; D x−1, y, z; E −x+1, y, −z+1/2.) from five *o*-BDC ligands to yield a distorted O_6 octahedron geometry. Interestingly, the positions of O1 and O1A, O2B and O2C, O2D and O2E are mirror-symmetric. And the Co–O distances fall in the range 2.020 (4)–2.202 (4) Å. The adjacent Co units are connected by the bis-(*cis-trans-μ*-O,O′-carboxylato) and the bis-(*μ*-oxo) bridges (Co1B–O2–Co1D = 104.3(2) °) of the *o*-BDC ligands extend along different directions (Fig. 1b and c) with the separation of 4.478 (1) Å and 3.382 Å, respectively, to form a 2D layer structure (Fig. 1d). A topological analysis reveals that both the Co unit and the *o*-BDC ligand serve as a 5- connected node to link each other. According to Wells' topology definition [11], an interesting topology with the short Schläfli symbol of $4^8.6^2$ as being estimated by OLEX [12] is formed (Fig. 1e).

[(Co(3-Cl-*o*-BDC)]$_n$ (2). Single-crystal X-ray structural analysis shows that compound **2** crystallizes in space groups of $P2_1/c$, and the asymmetric unit contains one crystallographically independent Co atom and one 3-Cl-*o*-BDC anionic. As illustrated in Fig. 2a, Co1 lying on a symmetry site is coordinated by four O atoms (O1, O2A, O3B, O4C, symmetry codes: A x, y+1, z; B −x+1, y+1/2, −z+1/2; C x, −y−1/2, z+1/2.) from four 3-Cl-*o*-BDC ligands to yield a distorted O_4 tetrahedron geometry. The Co–O distances fall in the range 1.929 (1)–1.976 (1) Å. The adjacent Co units are connected by the bis-(*cis-cis-μ*-O,O′-carboxylato) bridge of the *o*-BDC ligands with the separation of 3.790 (1) Å, to form a Co_2 subunit (Fig. 1b). The