



A multi-functional coordination polymer coexisting spontaneous chirality resolution and weak ferromagnetism



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ABSTRACT

A multifunctional homochiral coordination polymer, $[\text{Co}(\text{H}_2\text{O})(\text{BDC})(4,4'\text{-BPY})]\cdot 3\text{H}_2\text{O}$ (**1**) ($\text{H}_2\text{BDC} = 1,2$ -benzenedicarboxylate and $4,4'\text{-BPY} = 4,4'$ -bipyridine), has been successfully isolated from Co(II) ions and mixed ligands (1,2-benzenedicarboxylate and 4,4'-bipyridine). Complex **1**, which exhibits spontaneous chirality resolution and weak ferromagnetism, is built by chiral helices interconnected *via* end-to-end $4,4'\text{-BPY}$ bridges into a two-dimensional (2D) layer structure.

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1. Introduction

Chirality has been receiving intensive research interest due to its fundamental importance in material sciences, pharmacy, as well as in many biological and chemical process related to human life [1–3]. Crystal engineering, as one of the most popular synthetic concepts, has been proven to be effective in preparation of chiral complex materials [4]. Many chiral complex materials have been successfully prepared and most of these materials have shown potential applications as expected [5]. Recently, particular attention has been paid to the isolation of multifunctional chiral materials, and the observation of magnetochiral dichroism is one of the most exciting discoveries. Magnetochiral dichroism is a cross effect between natural optical activity and magnetic optical activity in paramagnetic chiral species [6,7]. It is believed that chiral magnets, which usually have relatively large magnetic moments, may open the prospect for observing stronger magnetochiral dichroism effects [7]. However, current understanding of multifunctional chiral materials, which contain both chirality and magnetism, is still very limited and the design and synthesis of these materials remain a major challenge.

Assembly of multifunctional magnetochiral coordination polymers can only occur if chiral elements and magnetic components coexist. One strategy was to construct helix, which has been proved to be one

of the best methods for introducing chirality into coordination polymers [8], by inorganic magnetic component and organic ligands. In this context, the V-shaped bidentate carboxylate ligands could possibly afford helical coordination polymers [9]. Meanwhile, metal-ligand interactions could spontaneously resolve the polymeric helices and lead to chiral structures [9c]. Therefore, V-shaped BDC^{2-} ligand was selected to build helical motifs and auxiliary $4,4'\text{-BPY}$ to interlink the helical motifs into a higher dimensionality. Herein, the synthesis, crystal structure, chiral and magnetic properties of a 2D cobalt-containing coordination polymer, $[\text{Co}(\text{H}_2\text{O})(\text{BDC})(4,4'\text{-BPY})]\cdot 3\text{H}_2\text{O}$ (**1**) ($\text{H}_2\text{BDC} = 1,2$ -benzenedicarboxylate and $4,4'\text{-BPY} = 4,4'$ -bipyridine), is reported. In the structure of complex **1**, Co(II) ions are covalently bonded with BDC^{2-} ligands to form helices and are further interconnected by $4,4'\text{-BPY}$ into a 2D chiral network. As expected, $4,4'\text{-BPY}$ effectively transfers stereochemical information between neighbouring helices. Meanwhile, spontaneous resolution was demonstrated in complex **1** by the observation of circular dichroism (CD) signals and ferromagnetism was proved by the detection of magnetic measurements.

2. Experimental

2.1. Materials and characterizations

The reagents and solvents were commercially available and used as received. Elemental analyses of C, H, and N were carried

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out on an *Elementar Vario EL III* analyzer. Infrared (IR) spectra were recorded using KBr pellets on a *PerkinElmer Spectrum One* in the range 400–4000 cm^{-1} . Powder X-ray diffractions (PXRD) were recorded on a *Rigaku Dmax 2500* diffractometer equipped with Cu-K α radiation ($\lambda = 1.54056 \text{ \AA}$) over the 2θ range of 5–55° with a scan speed of 5° min^{-1} at room temperature. Thermogravimetric analyses (TGA) were performed under a nitrogen atmosphere with a heating rate of 10° min^{-1} by using a *SDT Q600* thermogravimetric analyzer. Single crystal X-ray diffractions were carried out on *Rigaku Mercury CCD/AFC* diffractometer. The temperature dependence of the magnetic susceptibility was recorded with a *Quantum Design SQUID MPMS-XL*.

2.2. Synthesis

[Co(H₂O)(BDC)(4,4'-BPY)] · 3H₂O (1): A mixture of Co(NO₃)₂ powder (0.037 g, 0.2 mmol), H₂BDC (0.032 g, 0.2 mmol), 4,4'-bipy (0.031 g, 0.2 mmol) in 8 mL deionized water was sealed in a 23 mL Teflon-lined bomb and heated at 160 °C for 3 days, and then slowly cooled to room temperature at a rate of 10 °C h⁻¹. Pink plate crystals of complex **1** suited for single crystal X-ray diffraction analyses were isolated with a yield of approximate 43% (based on Co). Large crystals for circular dichroism (CD) characterization were picked out manually from one batch. IR (KBr, cm^{-1}), 3424 (vs), 1611(s), 1567(vs) 1539(vs), 1494(w), 1399(vs), 1219(m), 1074 (m), 811(s). Anal. calcd for C₁₈N₂O₈H₂₀Co (%): H, 4.47; C, 47.90; N, 6.20; found (%): H, 4.38; C, 47.82; N, 6.15.

2.3. Crystallography

Data were collected on a *Rigaku Mercury CCD/AFC* diffractometer equipped with graphite-monochromated Mo K α radiation (wavelength 0.71073 Å) by using the ω -scan technique. The organic hydrogen atoms were positioned geometrically and the hydrogen atoms bonded to water molecules were not located. All absorption corrections were performed using the *CrystalClear* program [10a]. Structures were solved by direct methods and refined on F^2 by full matrix least-squares using the SHELXL-97 program package [10b]. The crystallographic data for complex **1** is listed in Table S1 and selected bonds and angles are listed in Table S2 (CCDC-682626).

3. Results and discussion

3.1. Structural descriptions

The hydrothermal reaction of cobalt salt with H₂BDC and 4,4'-bipy at 160 °C gave rise to pink crystals of **1**. Complex **1** is air stable and insoluble in water and common organic solvents. Single-crystal X-ray analysis reveals that complex **1** crystallizes in monoclinic space group $P2_1$. The crystallographically independent cobalt atom is defined by three O donors from two different BDC²⁻ ligands, one O donor of aqua ligand, and two N donors from two different 4,4'-BPY ligands to complete the octahedral coordination geometry. Co–N/O distances are in the normal range of 2.068(2) Å–2.170(2) Å, which are comparable to the ones in cobalt coordination polymers [11]. The Co(II) centres are jointed *via* BDC²⁻ ligand, leading to the formation of right-handed helical chain subunits along the crystallographic 2_1 axis (Fig. 1, right). The two carboxyl groups on a BDC²⁻ ligand show mono- and bis-bidentate coordination mode, respectively. The helical chains are further linked through the 4,4'-BPY into a 2D layered coordination polymer (Fig. 1, left). Packing of the 2D layers results in a supramolecular structures with O–H...O hydrogen bonding (H-bonds) interactions among the coordinated and/or uncoordinated

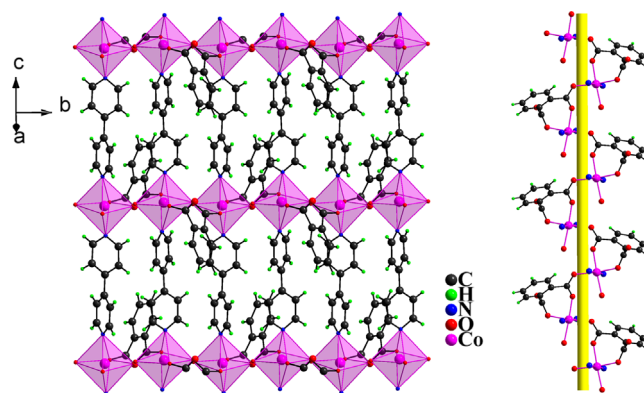


Fig. 1. View of the 2D layer structure (left); and the helical chain subunit along the 2_1 axis in complex **1** (right).

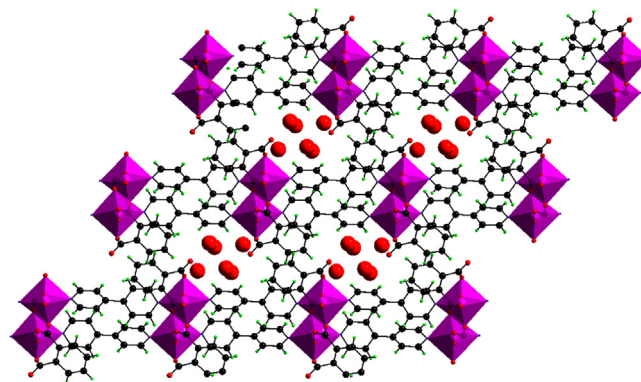


Fig. 2. View of the 3D packing of complex **1**.

water molecules (Fig. 2). The primary H-bonds between coordinated and uncoordinated water molecules are 2.741(1) Å and 2.854(2) Å; whereas the secondary H-bonds between uncoordinated water molecules range from 2.758(6) Å to 3.003(7) Å. These supramolecular interactions offer auxiliary molecular forces to stabilize the overall network structure.

3.2. X-ray powder diffraction and thermal analysis

Phase purity of complex **1** was identified by powder X-ray diffraction (PXRD) study. The experimental PXRD pattern matches perfectly with the one simulated from the single crystal data indicating the batch products were phase-pure (Fig. 3). Thermogravimetric analysis (TGA, Fig. S1) of complex **1** shows multi-step of weight losses. The first weight loss of ca. 17.6% before 220 °C is assigned to the release of three uncoordinated and one coordinated water molecules per formula unit (calculated 16.0%). The second weight loss of ca. 33.1% between 380 °C and 580 °C is attributed to the release of 4,4'-BPY ligands (calculated 34.5%). Further weight loss belongs to the decomposition of BDC²⁻ ligands and the oxide residue was unidentified.

3.3. Circular dichroism

Solid-state CD spectra of large single crystals prepared in a same batch were recorded (Fig. 4). The single crystals crystallize as either *M* (**1a**) or *P* (**1b**) enantiomer, confirming the chirality of complex **1**. The enantiomeric excess *ee* value based on the CD measurement of 20 single crystals is calculated to be about zero, which indicates the formation of *M* and *P* enantiomers in about 1:1 ratio through spontaneous resolution during the crystallization and racemization of the product. We thus assume that a chiral

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