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Two novel CPs with double helical chains based rigid tripodal ligands: Syntheses, crystal structures, magnetic susceptibility and fluorescence properties

Xiao Wang [a, b], Xiang-Yang Hou [a, *], Quan-Guo Zhai [b, **], Man-Cheng Hu [b]

[a] Department of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Chemical Reaction Engineering, Yan'an University, Yan'an, Shaanxi 716000, PR China
[b] Key Laboratory of Macromolecular Science of Shaanxi Province, School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an, Shaanxi 710062, PR China

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ABSTRACT

Two three-dimensional coordination polymers (CPs), namely $[Cd(bpydb)\text{-}(H_2bpydb)]_n \cdot 0.5nH_2O$ (**1**), and $[Cu_2(bpydb)_2]_n$ (**2**) (2,6-di-p-carboxyphenyl-4,4'- bipyridine1 = H_2bpydb), containing a novel double-helical chains, which have been solvothermal synthesized, characterized, and structure determination. CPs **1**-**2** reveal the new (3,5)-net and (3,6)-net *alb* topology, respectively. The fluorescence properties of CPs **1**-**2** were investigated, and magnetic susceptibility measurements indicate that compound **1** has dominating antiferromagnetic couplings between metal ions.

1. Introduction

Rapid development of CPs has been made in recent years not only their fascinating architectures [1] but also potential applications as functional materials, such as Photocatalytic [2], electrochemical [3], luminescence [4], magnetism [5], porosity properties [6], etc. Luminescence is the term used to describe the process in which light is produced through the absorption of energy. Which contains two basic forms, fluorescence and phosphorescence. Fluorescence refers to the emitting of light between energy states of the same spin multiplicity, and the process lasts no more than 10 ns So far, many of luminescent CPs have been reported, and the luminescence can exist in several forms [7]. There are four different types of luminescence mechanism, which are ligand-based luminescence, lanthanide metal-centered luminescence, charge-transfer luminescence (ligand-to-metal charge transfer (LMCT) and metal-toligand charge transfer (MLCT)), and guest-induced luminescence. The magnetic properties of the metal complexes Is the most studied molecular magnets. Generally, which center atoms is transition metal, rare earth metal ions and transition-rare earth metal ions, and mononuclear, dinuclear or polynuclear as its basic building blocks, through intermolecular interactions that can get a one-dimensional, two-dimensional and three-dimensional molecular magnets [8]. Metal complexes have good magnetic properties, must meet the following conditions: 1)larger spin ground state; 2)ignore the magnetic properties of the opposite sex; 3)the lower level of spin excited states; 4)the weaker ferromagnetic interactions; 5)high levels of metal ions. However, helicity, as an important factor of crystal engineering, has also been successfully introduced into complexes architectures field [9]. Although, helicity-CPs containing of one or several factors, such as discrete helices, single spiral chain, double helix chain, multi-helical-array, have been reported [10]. However, especially assembly of the helical units into a multi-helical-array is still a great challenge. About higher interest is the nexploratio of symmetrical rigid tripodal ligands, which may adopt various coordination modes to satisfy the requirements of assembly process and lead to interesting architectures. Along with our work of assembly of CPs based upon symmetrical rigid tripodal ligand [11]. Herein, we have focused on H_2bpydb, a rigid tripodal ligand reported two unprecedented three-dimensional architectures $[Cd(bpydb)(H_2bpydb)]_n \cdot 0.5nH_2O$

* Corresponding author.
** Corresponding author.
E-mail addresses: houxiangyang7@126.com (X.-Y. Hou), zhaiqg@snnu.edu.cn (Q.-G. Zhai).

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(**1**), and [Cu_2(bpydb)$_2$]n (2), with weaving double - helical chains from a versatile rigid tripodal ligand H_2bpydb and Cd^{2+} and Cu^{2+} ions. Moreover, solid-state photoluminescence measurements show **1** and **2** are good candidates for luminescence materials, and magnetic susceptibility measurements indicate that **1** has strong dominating antiferromagnetic couplings between Cu^{2+} metal ions.

2. Experimental

2.1. General

All available solvents and starting materials of analytical grade in the experiments was purchased from Sigma-Aldrich. The typical PXRD patterns were recorded using Cu-Kα radiation on a PANalytical X'Pert PRO diffractometer. The infrared spectra were measured between 4000 and 400 cm^{-1} on a Bruker EQUINOX-55 spectrophotometer using KBr pellets. Elemental analysis(C, H, N) was determined on a Perkin-Elmer 2400 type elemental analyzer. The thermogravimetric analyses were performed in platinum crucibles on a NETZSCH STA449C thermogravimetric analyzer under a atmosphere with a heating rate of 10 °C min^{-1}. The solid samples photoluminescence analyses were performed on Edinburgh Instrument FLS920 fluorescence spectrometer at ambient temperature. Magnetic measurement was performed of **1** using a MPMS-XL-7 magnetometer under an applied field of 1000 Oe over the temperature range of 1.8–300 K.

2.2. Synthesis of 1

Synthesis of [Cd(bpydb)(H_2bpydb)(H_2O)]$_n$ (1): A mixture of $CdCO_3$ (0.05 mmol, 0.009 g), H_2bpydb (0.05 mmol, 0.020 g) was dissolved in 5 mL distilled water. The resulting solution was stirred for about 60 min at room temperature, sealed in a 20-mL Teflon-lined stainless steel autoclave under autogenous pressure at 180 °C for 4 days to yield 12 mg yellow sheet-shaped crystals. Anal. Calcd (Found) for $C_{96}H_{62}Cd_2N_8O_{17}$: C, 63.22 (63.20); H, 3.41 (3.43); N, 6.17 (6.14).

2.3. Synthesis of 2

[Cu_2(bpydb)$_2$]n (2): A mixture of $CuCl_2 \cdot 2H_2O$ (0.06 mmol, 0.010 g), H_2bpydb (0.06 mmol, 0.024 g) was dissolved in 5 mL distilled water. The resulting solution was stirred for about 60 min at room temperature, sealed in a 20-mL Teflon-lined stainless steel autoclave under autogenous pressure at 140 °C for 6 days to yield 8 mg light blue block crystals. Anal. Calcd (Found) for $C_{48}H_{28}Cu_2N_4O_8$: C, 62.28 (62.95); H, 3.12 (3.08); N, 6.09 (6.12).

2.4. X-ray structural determinations

Data were collected with a Bruker APEX II CCD using Cu-Kα radiation and corrected for absorption with SADABS. The structure was solved by the direct methods and successive Fourier difference syntheses, and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXTL Version 5.1). All hydrogen atoms were added according to theoretical models. Crystal structures and packing figures were drawn with the program diamond 3.1. The crystallographic refinement data are listed below.

1: $C_{96}H_{56}Cd_2N_8O_{17}$: $Mr = 1818.29$, Monoclinic, space group C2/*c*, $a = 26.865(6)$ Å, $b = 12.937(3)$ Å, $c = 23.858(5)$, $\alpha = 90$, $\beta = 109.57$, $\gamma = 90$, $V = 7813(3)$ Å^3, Z = 4, $D_{calcd} = 1.546$ g cm^{-3}, $F(000) = 3680$, $R_1 = 0.0566$, $wR_2 = 0.0914$ ($I > 2\sigma(I)$), $F^2 = 0.907$.

2: $C_{48}H_{28}Cu_2N_4O_8$, $Mr = 915.82$, Monoclinic, space group C2/*c*, $a = 26.2445(8)$ Å, $b = 13.4325(4)$ Å, $c = 22.7810(7)$, $\alpha = 90$, $\beta = 108.676(3)$, $\gamma = 90$, $V = 7608.1(4)$ Å^3, Z = 8, $D_{calcd} = 1.599$ g cm^{-3}, $F(000) = 3728$, $R_1 = 0.0734$, $wR_2 = 0.2205$ ($I > 2\sigma(I)$), $F^2 = 1.039$.

3. Results and discussion

3.1. Structure description of 1

The single-crystal X-ray analysis reveals that complexe **1** crystallizes in the Monoclinic space group *C2/c*. The asymmetric unit of complexe **1** consists of one $Cd1^{2+}$ center, one completely deprotonated $bpydb^{2-}$ ligand, one H_2bpydb ligand, and half of lattice water molecule. As shown in Fig. 1, the structure consists of one kind coordination mode of $Cd1^{2+}$ center, each $Cd1^{2+}$ center is seven coordinated by one nitrogen (N1a) from a $bpydb^{2-}$ ligand, and six carboxyl oxygens (O1, O2, O3c, O4, O7b, O8b) from two $bpydb^{2-}$ and H_2bpydb ligands, respectively, to form a distorted single-cap octahedron geometry of Cd[NO_7] moieties (Fig. S1), in which O1, O2, O4, and N1a occupied the equatorial plane position, O3c located in the side of the plane, O7b and O8b in the other side of the plane, Cd^{2+} ion lies in the center. The Cd–O/N bond lengths vary from 2.269(4) to 2.528(4) Å, and the O–Cd–O/N bond angle vary from 53.40(19) to 155.97(19) °. The $Cd1^{2+}$ center is alternately coordinated by $bpydb^{2-}$ and H_2bpydb ligands to generate a double-1D chains along the **b** axis direction (Fig. S2 and Fig. 2). The most striking feature of double-1D chain is novel interweaving helical chain formed by the tripodal $bpydb^{2-}$, H_2bpydb ligands, and metal $Cd1^{2+}$ centers. Four carboxylate groups from $bpydb^{2-}$ and H_2bpydb ligands are bonded to three $Cd1^{2+}$ centers in bidentate chelating and monodentate fashion, giving rise to infinite right-handed and left-handed helical chain (-Cd-H_2bpydb-Cd-$bpydb^{2-}$-Cd-)$_n$, which

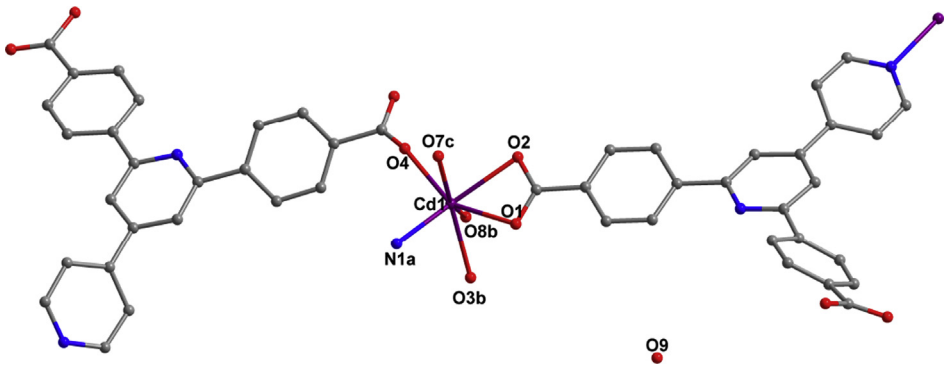

Fig. 1. View of the basic coordination environments of CPs 1. Symmetry codes: a:0.5 + x,1.5-y, 0.5 + z; b:x,1-y,0.5 + z; c: x,3-y,-0.5 + z.