

An unusual two-fold interpenetrating polyrotaxane motif comprised of two interlocked sets of identical diamond nets

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HIGHLIGHTS

- ▶ A novel 3D coordination polymer was synthesized and characterized by X-ray analysis.
- ▶ This compound presents the coexistence of different entangled modes in one structure.
- ▶ The luminescent property of this compound was investigated in the solid state at room temperature.

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ABSTRACT

A novel 3D coordination polymer $[\text{Cd}_2(\text{cca})_2(\text{bib})_3] \cdot 3\text{H}_2\text{O}$ (1, H_2cca = 4-carboxycinnamic acid, bib = 1,4-bis(imidazole)butane) has been synthesized. This compound exhibits an unusual two-fold interpenetrating polyrotaxane-like structure comprised of two interlocked sets of identical diamond nets.

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1. Introduction

Crystal engineering of coordination polymers (CPs) in the last decade has mainly focused on the aesthetics of crystalline architectures and their potential functions, such as magnetism, optics, catalysis, and gas storage [1,2]. Coming from the net-based approach, many coordination networks are particularly intriguing because of the presence of independent motifs entangled together in different ways, which has been discussed in comprehensive reviews by Batten and Robson [3]. Among these, an interesting phenomenon is the coexistence of different entangled modes in one structure. For example, $[\text{Cd}(\mu\text{-tp})(\mu\text{-bpp})(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$ (H_2tp = terephthalic acid, bpp = 1,3-bis(4-pyridyl)propane) is the first example that two (4,4) layers interlock each other to build a 2D → 2D polyrotaxane-like sheet [4]. Wang et al. have reported another interesting polyoxometalate-based coordination polymer, $[\text{Cu}_3^{\text{I}}(\text{L})_3][\{\text{Cu}^{\text{II}}(\text{L})_2\}\{\text{PMo}_{12}\text{O}_{40}(\text{VO})_2\}] \cdot \text{H}_2\text{O}$ (L = 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene), in which loop-containing 2D layers are catenated with a 3D α -Po skeleton into a new type of entangled

framework having polyrotaxane and polycatenane character [5]. Theoretically, a variety of hypothetical species belonging to this theme could be envisaged in view of the multi-types of entanglement, such as polycatenation, polythreading, and polyknotting. However, the reported CPs featuring the structures of mixed entanglements are still quite rare mainly because of the control of entanglement of independent motifs, which is dependent upon the related chemical environment, is still a significant challenge fraught with difficulties.

Nevertheless, the use of long organic spacers to coordinate with transition metals represents a rational strategy to generate entangled topologies [6]. In this paper, we used 4-carboxycinnamic acid (H_2cca) and 1,4-bis(imidazole)butane (bib) as the building blocks (Fig. S1). Compared to common multi-aromatic carboxylic ligands, the little steric hindrance of H_2cca should more favor the generation of entangled frameworks. Furthermore, the conformationally flexible ligand bib , which often shows a supramolecular isomerism by altering the geometry of the ligand, has already proven to be a good candidate to give fascinating entanglements [7]. Thus it may be possible to yield new classes of entangled compounds through combining these two types of different precursors. Following these ideas, we report here an interesting coordination polymer

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[Cd₂(cca)₂(bib)₃·3H₂O (**1**), which exhibits an unusual two-fold interpenetrating polyrotaxane-like structure comprised of two interlocked sets of identical diamond nets.

2. Experimental

2.1. Materials and methods

All the starting materials were of analytic grade and purchased from Aldrich or Fluka. Bib was prepared by the literature method [8]. Elemental analyses (C,H,N) were performed with a Perkin-Elmer 240c elemental analyzer. TGA was performed on a Perkin-Elmer TG-7 analyzer heated from 25 to 650 °C under nitrogen. The luminescent properties of compounds were measured on a HITACHI F-4500 spectrometer. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/M-2200T automated diffractometer (Fig. S2). IR spectra were obtained from KBr pellets on a Perkin-Elmer 580B IR spectrometer in the 400–4000 cm⁻¹ region (Fig. S3).

2.2. Synthesis

A solution of Cd(NO₃)₂·4H₂O (0.0308 g, 0.1 mmol) in H₂O (4 mL) was added to a suspending solution of H₂cca (0.0192 g, 0.1 mmol) in H₂O (7 mL), followed by dropwise addition of a solution of bib (0.0190 g, 0.1 mmol) in DMF (3 mL). Aqueous NH₃ (25%) was then slowly added to the reaction mixture, making sure that the pH value is 7–8. The resulting solution was filtered off. Colorless crystals were obtained with 70% yield based on H₂cca by allowing the filtrate to stand at room temperature for one week. Calcd (%): C, 48.83; H, 4.92; N, 13.67. Found: C, 48.69; H, 4.90; N, 13.79. IR data (KBr, cm⁻¹): 3017 (w), 2987 (w), 2919 (w), 2393 (w), 2172 (m), 1662 (m), 1602 (s), 1556 (s), 1403 (s), 1236 (s), 1098 (s), 1045 (w), 1007 (w), 978 (w), 939 (m), 870 (m), 840 (m), 794 (s), 749 (s), 657 (s), 627 (w), 535 (w), 459 (m).

2.3. X-ray crystallography

The diffraction data of **1** were collected on a Bruker Apex II CCD area-detector diffractometer (Mo K α , λ = 0.71073 Å) [9]. Absorption correction was applied by using multiscan program SADABS [10]. The structure was solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package [11]. Anisotropic thermal parameters were applied to all non-hydrogen atoms of **1**. The positions of H atoms were generated geometrically, assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of refinement. The vibration of cca²⁻ ligands makes some hydrogen atoms of aromatic rings could not be added. The selected bond

Table 1
Selected bond distances (Å) and angles (°) for **1**.

Cd(1)–N(1)	2.312(3)	Cd(1)–N(3)	2.364(3)
Cd(1)–N(5)	2.347(3)	Cd(1)–O(1)	2.387(3)
Cd(1)–O(2)	2.511(3)	Cd(1)–O(3)	2.388(4)
Cd(1)–O(4)	2.580(3)		
N(1)–Cd(1)–N(5)	104.30(12)	N(1)–Cd(1)–N(3)	89.35(13)
N(5)–Cd(1)–N(3)	163.97(12)	N(1)–Cd(1)–O(1)	83.82(12)
N(5)–Cd(1)–O(1)	84.29(11)	N(3)–Cd(1)–O(1)	88.98(12)
N(1)–Cd(1)–O(3)	130.93(13)	N(5)–Cd(1)–O(3)	90.97(12)
N(3)–Cd(1)–O(3)	86.16(13)	O(1)–Cd(1)–O(3)	144.75(13)
N(1)–Cd(1)–O(2)	135.55(11)	N(5)–Cd(1)–O(2)	84.64(11)
N(3)–Cd(1)–O(2)	79.68(11)	O(1)–Cd(1)–O(2)	53.34(11)
O(2)–Cd(1)–O(3)	91.48(12)	N(1)–Cd(1)–O(4)	82.15(12)
N(5)–Cd(1)–O(4)	85.92(12)	N(3)–Cd(1)–O(4)	104.52(12)
O(1)–Cd(1)–O(4)	160.35(12)	O(3)–Cd(1)–O(4)	52.26(12)
O(2)–Cd(1)–O(4)	142.29(11)		

Table 2
Crystal data and structure refinement for **1**.

Empirical formula	Cd ₂ O ₁₁ N ₁₂ C ₅₀ H ₆₀
Formula weight	1229.90
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	9.0012(10)
<i>b</i> (Å)	9.7513(11)
<i>c</i> (Å)	15.6798(18)
α (°)	101.428(2)
β (°)	92.161(2)
γ (°)	90.812(2)
<i>V</i> (Å ³)	1347.7(3)
<i>Z</i>	1
<i>D</i> _{calc} (Mg m ⁻³)	1.515
<i>F</i> (000)	628
Goodness-of-fit on <i>F</i> ²	1.106
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0378, <i>wR</i> ₂ = 0.1079
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	<i>R</i> ₁ = 0.0425, <i>wR</i> ₂ = 0.1140

distances and bond angles are listed in Table 1, and the crystal data is given in Table 2.

3. Results and discussion

3.1. Crystal structure

Single crystal X-ray diffraction study revealed that compound **1** crystallizes in a triclinic space group *P*-1. In the structure, there are one crystallographically unique Cd²⁺ atom, two unique cca²⁻ ligands, and three unique bib ligands (Fig. 1). The Cd²⁺ atom adopts a high distorted pentagonal bipyramid geometry and is coordinated by four O atoms from two cca²⁻ ligands (Cd–O 2.387(3)–2.580(3) Å) and three N atoms from three bib ligands (Cd–N 2.312(3)–2.364(3) Å). All chemical bonds are within the normal range. Two cca²⁻ ligands act as a bridge to link two Cd²⁺ atoms through two chelate carboxylate groups. The three bib ligands exhibit two kinds of space configuration: two adopt cis-conformation and connect with two Cd²⁺ atoms to generate a Cd₂(bib)₂ ring; the other one shows trans-conformation to link two adjacent Cd₂(bib)₂ rings. In the structure, Cd²⁺ atoms are connected by five linear ligands (including two cca²⁻ and three bib) extending into a 3D network, and the free water molecules occupy some void space.

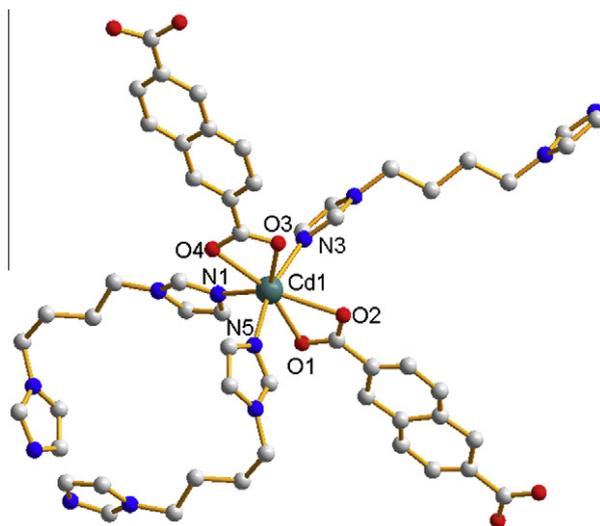


Fig. 1. Molecular structure of **1** showing the geometry of the Cd²⁺ ions. Hydrogen atoms are omitted for clarity.

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