

Hydrothermal Synthesis, Crystal Structure and Fluorescent Property of a New Three-Dimensional Cd(II) Coordination Polymer Based on 1,3-Bis(imidazol-1-ylmethyl)-benzene

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Abstract: A new cadmium(II) coordination polymer, namely $[\text{Cd}(\text{mbix})_3]_n \cdot 2n\text{ClO}_4$ (mbix = 1,3-bis(imidazol-1-ylmethyl)benzene) (1), has been prepared and fully characterized by single-crystal X-ray diffraction, elemental analyses, IR spectroscopy and luminescent property. Of the compound, the Cd(II) center is octahedral coordinated with mbix serving as a bridging ligand by employing six N-donor to coordinate with the Cd(II) center. It exhibits three-dimensional network structure via mbix ligands.

Supporting information: X-Ray (CIF file).

Keywords: Cadmium, hydrothermal synthesis, crystal structure, coordination polymer.

1. INTRODUCTION

Recently, there has been much interest in the construction of coordination compounds due to their versatile structures and interesting topologies [1–4] as well as their potential applications as functional materials in the fields of molecular magnetism, catalysis, gas sorption and optoelectronic devices [5–9]. The most useful building blocks for constructing organic–inorganic hybrid coordination compounds are carboxylate and N-donor ligands. Aromatic carboxylate ligands have been extensively employed in the construction of various dimensional coordination compounds because of their abundant coordination modes and high structural stability for functional materials applications [10–16].

Imidazole and its derivatives are typically heterocyclic ligands with nitrogen as the donor atom. It exhibits a wide variety of pharmacological activities as antihelmintics, anticancer, antifungal and anti-inflammatory agent [17]. Because of this, the coordination chemistry of related ligands has been the subject of numerous investigations. As a good candidate, the conformational flexible ligand 1,3-bis(imidazol-1-yl)butane has been used as an auxiliary ligand because of the free rotation of the two imidazole planes, which results in *cis* or *anti* conformations as

required by the metal coordination geometry in the assembly process [18–21].

To explore the combination effects of this neutral di-imidazole ligand (1,3-bix) and anionic squarate ligands, we synthesize coordination polymers of Cd(II) containing these ligands. Herein, we report the synthesis, characterization of a new cadmium framework, $[\text{Cd}(\text{mbix})_3]_n \cdot 2n\text{ClO}_4$ under hydrothermal conditions.

2. EXPERIMENTAL

2.1 General Procedures

All reagents were purchased commercially and used without further purification. Elemental analyses (C, H and N) were measured on a Perkin-Elmer 2400 CHN Elemental Analyzer. IR spectrum was recorded in the range of $4000 \sim 400 \text{ cm}^{-1}$ on an Alpha Centaur FT/IR Spectrophotometer using a KBr pellet. The fluorescent studies were carried out on a computer-controlled JY Fluoro-Max-3 spectrometer at room temperature.

2.2 Synthesis of $[\text{Cd}(\text{mbix})_3]_n \cdot 2n\text{ClO}_4$

The title compound was prepared from a mixture of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.083 g, 0.2 mmol), 2,4-pyridinedicarboxylic acid (0.055 g, 0.2 mmol), mbix (0.048 g, 0.2 mmol) and H_2O (18 mL) in a 30 mL Teflon-lined autoclave under autogenous pressure at 150°C for seven days. After cooling to room temperature, colorless block crystals were collected by filtration and washed with distilled water in 47% yield (based on Cd). But the 2,4-pyridinedicarboxylic acid ligand was not involved in coordination. Anal. Calcd. (%) for $\text{C}_{42}\text{H}_{42}\text{CdCl}_2\text{N}_{12}\text{O}_8$: C, 49.16; H, 4.13; N, 16.38. Found (%): C, 48.83; H, 3.95; N, 15.87. IR (KBr, cm^{-1}): 3108(m), 2973(w), 2934(w), 2877(w), 1611(w), 1514(s), 1449(m), 1404(w), 1372(w), 1340(w), 1278(m), 1234(s), 1193(w), 1171(w), 1157(w), 1107(s), 1086(s), 1027(m), 980(w), 928(m), 914(w), 862(w), 844(w), 824(w), 751(w), 728(s), 682(w), 657(s), 630(w), 594(w), 503(w), 434(w).

2.3 X-ray Crystallography

Single-crystal X-ray diffraction data for compound **1** was recorded on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure based on F² [22,23]. The hydrogen atom positions on carbon atoms were fixed geometrically at calculated distances and allowed them to ride on the parent atoms. The detailed crystallographic data and structure refinement parameters for **1** are summarized in Table 1.

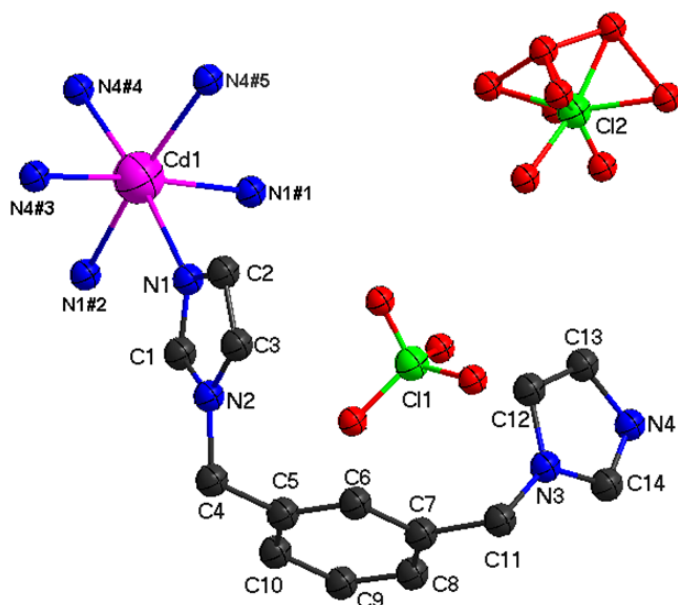


Figure 1. View of the coordination environment of Cd(II) in the titled complex.

TABLE 1

Crystallographic data for compound **1**

Empirical formula	C ₄₂ H ₄₂ CdCl ₂ N ₁₂ O ₈
Fw	1026.12
Crystal system	Trigonal
Space group	R3
<i>a</i> [Å]	12.625(2)
<i>b</i> [Å]	12.625(2)
<i>c</i> [Å]	25.786(10)
α [°]	90.00
β [°]	90.00
γ [°]	120.00
Volume [Å ³]	3559.4(16)
Z	3
D _c (g/cm ³)	1.436
GOF	1.113
RefIns collected/unique	6204 / 2785
<i>R</i> _{int}	0.0221
<i>R</i> 1 [I > 2 σ (I)]	0.0442

3. RESULTS AND DISCUSSION

3.1. IR analysis

The infrared spectrum of the cadmium complex has been recorded and some important assignments are shown above. No strong IR band from –COOH appeared at nearly 1600 cm⁻¹, indicating that the carboxylate ligands are not existed in it, and peak at 3108 cm⁻¹ could be assigned to characteristic peak of the C–H stretching mode of mbix ligand. Peaks at 1514 and 1449 cm⁻¹ could be attributed to $\nu(\text{C}=\text{C})$ vibration of mbix ligand. The peak at 1372 cm⁻¹ is ascribed to the $\nu(\text{C}=\text{N})$ vibration of mbix. The peak at 1107 cm⁻¹ could be assigned to characteristic peak of ClO₄⁻. These IR results are coincident with the crystallographic analyses.

3.2 Description of the crystal structure

Selected bond lengths and angles for **1** are listed in Table 2. A single-crystal X-ray diffraction study reveals that compound **1** crystallizes in trigonal system with space group *R*3 and the molecular structure contains one Cd(II) atom, three mbix ligands and two free ClO₄⁻, as shown in Figure 1. In Figure 1, there are eight oxygen atoms around one atom of Cl, illustrate that the chlorine atom is disorder. Cd(1) is six coordinated with slightly distorted octahedral coordination geometry defined by six nitrogen donors (N1, N1#1, N1#2, N4#3, N4#4, N4#5) from six different mbix ligands. Four nitrogen atoms (N1#1, N1#2, N4#3, N4#4) define an equatorial plane, while the axial coordination sites are occupied by two nitrogen atoms (N1, N4#5) too. The bond distances of Cd–N in compound **1** fall in the 2.344(5) ~ 2.362(5) Å range, which are in the normal range and the coordination angles around Cd(II) atom are in the range 85.66(18)

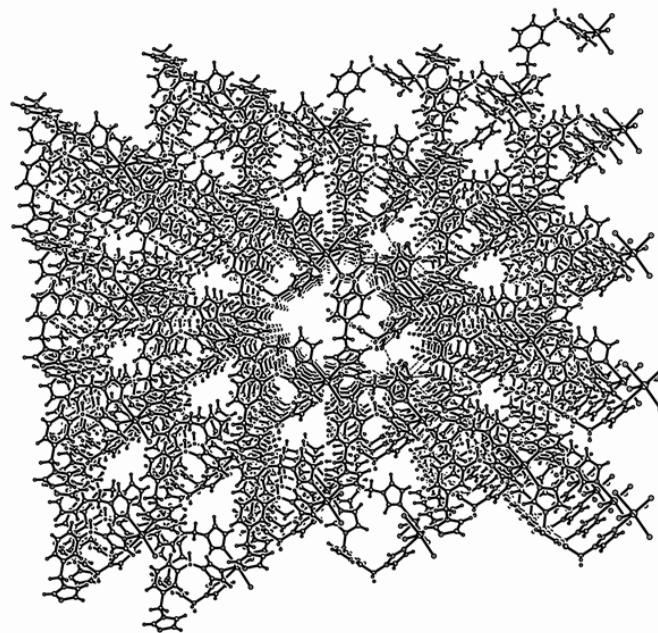


Figure 2: View of the 3D framework of the title complex.

Table 2: Selected bond distances (Å) and angles (deg) for **1**

Cd(1)-N(1)	2.344(5)	Cd(1)-N(1)#1	2.344(5)
Cd(1)-N(1)#2	2.344(5)	Cd(1)-N(4)#3	2.362(5)
Cd(1)-N(4)#4	2.362(5)	Cd(1)-N(4)#5	2.362(5)
N(1)-Cd(1)-N(1)#1	85.90(18)	N(1)-Cd(1)-N(2)#2	85.90(18)
N(1)#1-Cd(1)-N(1)#2	85.90(18)	N(1)-Cd(1)-N(4)#3	94.8(2)
N(1)#1-Cd(1)-N(4)#3	171.5(2)	N(1)#2-Cd(1)-N(4)#3	85.66(18)
N(1)-Cd(1)-N(4)#4	171.5(2)	N(1)#1-Cd(1)-N(4)#4	90.6(2)
N(1)#2-Cd(1)-N(4)#4	94.8(2)	N(4)#3-Cd(1)-N(4)#4	94.8(2)
N(4)#3-Cd(1)-N(4)#4	93.75(17)	N(1)-Cd(1)-N(4)#5	85.66(18)
N(1)#1-Cd(1)-N(4)#5	94.8(2)	N(1)#2-Cd(1)-N(4)#5	171.5(2)
N(4)#3-Cd(1)-N(4)#5	93.75(17)	N(4)#4-Cd(1)-N(4)#5	93.75(17)

Symmetry transformations used to generate equivalent atoms:

#1 $-x+y+2, -x+1, z$; #2 $-y+1, x-y-1, z$; #3 $-y+2/3, x-y-5/3, z+1/3$; #4 $-x+y+8/3, -x+4/3, z+1/3$; #5 $x-1/3, y+1/3, z+1/3$

$\sim 171.5(2)^\circ$. The mbix ligand adopts *cis*-conformation bridging mode with a dihedral angle between the two imidazole rings of 78.41° . The Cd(II) center forms a type of 6N mixed neutrality complex, and are interconnected by the bridging mbix ligands to generate 3D framework (Figure 2).

3.2 Photoluminescent properties

Luminescence property is very important in photochemistry and photophysics [24, 25]. So in this study, the solid-state photoluminescence spectra of **1** (Figure 3) and mbix ligands were investigated at room temperature. Excited by 355 nm, coordination polymer **1** gives wide green emission with the maximum

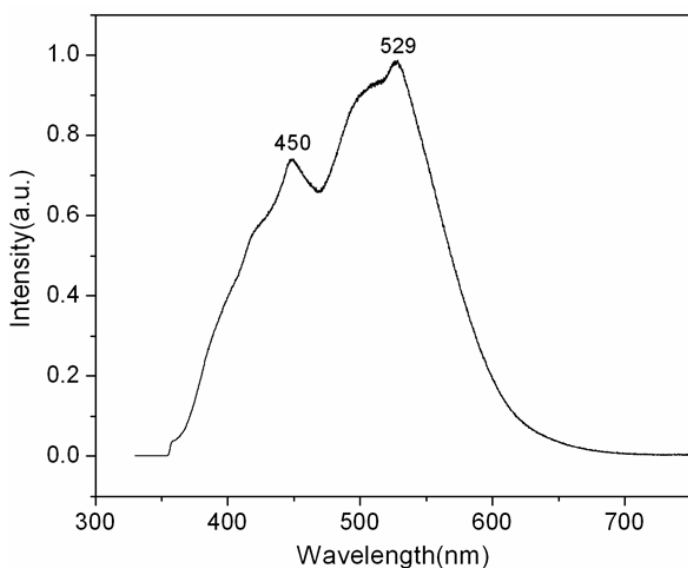


Figure 3: Solid-state emission spectrum of **1** at room temperature.

peak at 529 nm plus shoulder peak at 450 nm. The main emission peak of ligand mbix is at 430 nm. The significant phenomenon of the fluorescence emission of **1** here could be tentatively assigned to the ligand-to-metal charge transfer (LMCT) [26]. For possesses strong fluorescent intensity, it appears to be good candidates for novel hybrid inorganic-organic photoactive materials.

Supplementary materials

CCDC 934231 contains the supplementary crystallographic data. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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