

Assembly of 1D Cadmium(II) Coordination Polymer with *Bis*(2-benzimidazole) and 1,3-Benzenedicarboxylic Acid Mixed Ligands

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A novel one-dimensional cadmium(II) compound: $\{[\text{CdL}(\text{H}_2\text{C}_2\text{EIm})(\text{H}_2\text{O})](\text{H}_2\text{O})_2\}_n$ (**1**) with 1,3-benzene dicarboxylic acid (H_2L) and 2,2'-(1,2-ethanediy)l**is**(1*H*-benzimidazole) ($\text{H}_2\text{C}_2\text{EIm}$) has been synthesized by means of hydrothermal method and characterized by X-ray single-crystal diffraction. The crystal belongs to the triclinic system triclinic, space group P-1 with $a = 1.0189(5)$ nm, $b = 1.1204(5)$ nm, $c = 1.2319(5)$ nm, $\alpha = 115.824(5)^\circ$, $\beta = 98.363(5)^\circ$, $\gamma = 102.654(5)^\circ$, $V = 1.1878(9)$ nm³, $D_c = 1.649$ g cm⁻³, $Z = 2$, $F(000) = 594$, $\text{Goof} = 0.997$, $R_1 = 0.0358$, $wR_2 = 0.0881$. The compound **1** shows a novel one-dimensional (1D) chain structure along the c axis and further extended into a 1D double chain structure through π - π packing interactions. The intermolecular hydrogen bonds contribute to the formation of the three-dimensional supramolecular architecture and stabilize the crystal structure.

Key Words: Cadmium(II) polymer, Crystal structure, *bis*-(1*H*-benzimidazole).

INTRODUCTION

Known metal-organic frameworks has been aroused more and more people's interests because of variety of intriguing architectures and topologies and their potential applications in microelectronics, non-linear optics and catalysis¹⁻⁴. Many of metal-organic frameworks are constructed by assembly of metal ions with an appropriate organic ligand, especially a bridging ligand containing nitrogen, oxygen, or sulfur atoms⁵. Strong metal-ligand coordination bonds, weak hydrogen bonds and π - π interactions have been a general protocol to afford multidimensional metal-organic supramolecular entities^{6,7}. The *bis*(2-benzimidazoles) and some substituted *bis*(2-benzimidazolyl)alkanes containing N-donors are widely used as the bridging ligand in the construction of metal-organic frameworks due to their suitable flexible skeletons and two bridging moieties, which can lead to various modes of connections with metal ions^{8,9}. Indeed, mononuclear¹⁰, dinuclear¹¹, a 1D chain structures¹² and 2D sheet¹³ made of *bis*(2-benzimidazole) ligands have been reported. Comparatively, The 1,3-benzene dicarboxylic acid (H_2L), as a family rigid organic O-donors are especially interesting because of their rigidity and various coordination numbers to metal ions¹⁴ and their abilities to act as H-bond acceptors and donors to assemble various supramolecular structures¹⁵. Based on these studies, we report syntheses and crystal structure of a new coordination polymer

$\{[\text{CdL}(\text{H}_2\text{C}_2\text{EIm})(\text{H}_2\text{O})](\text{H}_2\text{O})_2\}_n$ based on the mixed ligands of aromatic carboxylates, 1,3-benzenedicarboxylic acid (H_2L) and N-donor ligands, 2,2'-(1,2-ethanediy)l**is**(1*H*-benzimidazole) ($\text{H}_2\text{C}_2\text{EIm}$).

EXPERIMENTAL

All chemical reagents were of analytical grade and used without further purification. The $\text{H}_2\text{C}_2\text{EIm}$ ligand was prepared according to the reported method¹⁶. The emission/excitation spectra were recorded on a Varian Cary eclipse spectrometer. The single-crystal structure of the compound **1** was determined on a Bruker APXII CCD diffractometer.

The compound $\{[\text{CdL}(\text{H}_2\text{C}_2\text{EIm})(\text{H}_2\text{O})](\text{H}_2\text{O})_2\}_n$ (**1**) was prepared by the mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.154 g, 0.5 mmol), 2,2'-(1,2-ethanediy)l**is**(1*H*-benzimidazole) ($\text{H}_2\text{C}_2\text{EIm}$) (0.106 g, 0.5 mmol), 1,3-benzene dicarboxylic acid (H_2L) (0.083 g, 0.5 mmol) and H_2O (16 mL) was heated at 160 °C for 3 days in a 25 mL Teflon-lined stainless steel vessel under autogenous pressure. After the reaction mixture was slowly cooled down to room temperature, colourless block crystals were obtained. Yield: 75 %.

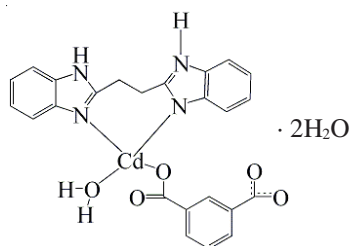
Structure determination: A colourless block single crystal of compound **1** with 0.42 mm × 0.31 mm × 0.21 mm was carefully selected under a polarizing microscope and were mounted on a glass fiber and used for X-ray diffraction analyses. Single crystal structure determination by X-ray diffraction

measurements were performed using a Bruker APXII CCD diffractometer with graphite monochromated $\text{MoK}\alpha$ ($k = 0.71069 \text{ \AA}$) radiation in the range of $1.91 \leq \theta \leq 28.20^\circ$ ($-11 \leq h \leq 13$, $-14 \leq k \leq 13$, $-15 \leq l \leq 16$) at 293 K. Absorption corrections were applied using the multi-scan technique¹⁷. A total of 7295 reflections including 5288 unique ones were collected, of which 5288 with $I > 2\sigma(I)$ were considered as observed and used in the succeeding refinements. The structure was solved by the direct method and refined by full-matrix least-square techniques on F2 using SHELXL-97¹⁸. All of the non-hydrogen atoms were refined anisotropically¹⁹. The H atoms attached to C atoms were positioned geometrically, with Uiso values derived from Ueq values of the corresponding C atom. The final $R = 0.0358$ and $wR = 0.0881$, $S = 0.997$, $(\Delta\rho)_{\text{max}} = 0.600$ and $(\Delta\rho)_{\text{min}} = -0.777 \text{ e/\AA}^3$.

Crystallographic data for the structural analysis(es) have been deposited with the Cambridge Crystallographic Data Centre, CCDC No.: 838278 for the compound **1**.

RESULTS AND DISCUSSION

The molecular structure, ORTEP drawing, 1D chain structure and the 2-D network of the compound **1** are illustrated in **Scheme-I** and Figs. 1-3, respectively. Selected bond distances and angles for the complex are shown in Table-1. The single crystal X-ray analysis shows that the asymmetrical unit of the compound **1** contains one Cd(II) ion, one $\text{H}_2\text{C}_2\text{EIm}$ ligand, one H_2L molecule. As shown in Fig. 1, the one Cd(II) sites show a distorted octahedral geometry, being connected by three O atoms from two H_2L ligands and one coordinated water molecule. The remaining two coordination sites are occupied by two N atoms from one $\text{H}_2\text{C}_2\text{EIm}$ ligand. The Cd-O bond lengths are in the range 2.246(2)-2.518(3) Å and the Cd-N bond lengths are in the range 2.219(3)-2.355(3) Å. The Cd(II) atoms are bridged by H_2L ligand with an intramolecular Cd---Cd distance of 10.189 Å. A number of cases were reported in which a proton transferred from a carboxylic acid to an amine to form some novel proton transfer compounds²⁰. In the crystal structure, to balance the charge, the H_2L as a proton donor was transferred to the N-ring atom of *bis*-benzimidazoles.



Scheme-I: Molecular structure of the compound **1**

It is noticeable that H_2L anion in compound **1** shows two types of coordination modes with Cd ions through the carboxylate groups, as shown in **Scheme-II**, (i) The monodentate H_2L ligand links Cd atom with the carboxylate groups of the formylxy. (ii) The H_2L ligand coordinates adjacent cadmium atom, in which one carboxylate group containing O(3) and O(5) interacts with one Cd atom through a bidentate-chelating mode. Owing to the special coordination modes, each H_2L

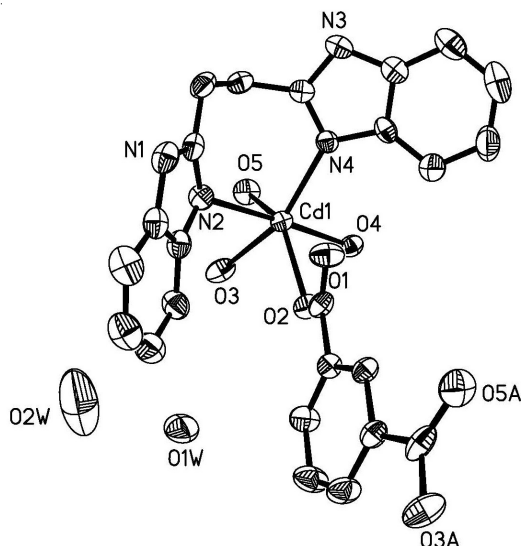


Fig. 1. Coordination environment of Cd(II) atom in compound (50 % thermal ellipsoids). Symmetry code: A: $-1+x, y, z$

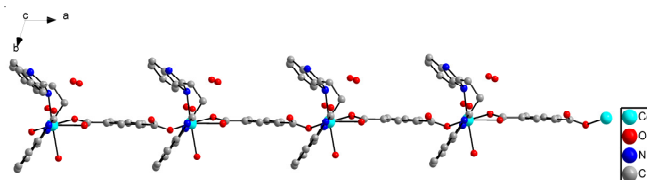


Fig. 2. Views of the 1D chain structure of compound **1** viewed down along the c-axis. Colour code: Zn, teal; C, gray; N, blue; O, red

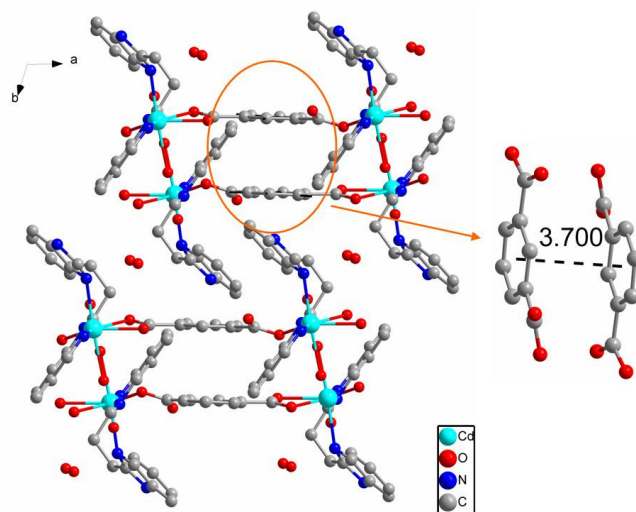
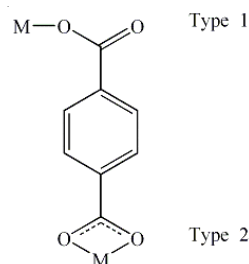


Fig. 3. View of the 2D double chain structure and the p-p packing interaction in compound **1**. Colour code: Zn, teal; C, gray; N, blue; O, red



Scheme-II: The coordination modes of the H_2L with metals. Type 1 (monodentate), Type 2 (bidentate-chelating mode)

anion acts as a μ_2 -bridge linking two Cd atoms into one-dimensional (1D) chain structure along the *c* axis. By reason of the π - π stacking interactions ($d_{\text{face to face}} = 3.700$) among $\text{H}_2\text{C}_2\text{EIm}$ ligands, the 1D chain is linked to form a double chain network (Fig. 3.). Moreover, owing to the multiple nitrogen atoms in the $\text{H}_2\text{C}_2\text{EIm}$ ligand, hydrogen-bonding interactions are formed. As a result, the 1D double chain structure is further linked to form a three-dimensional network with the features a quasi-bedded structure by the intermolecular hydrogen bonds ($\text{N}(3)\text{-H}(111)\text{-O}(1\text{W})^i = 2.749(5)$, $\text{N}(1)\text{-H}(222)\text{-O}(1)^{ii} = 2.782(4)$, $\text{O}(4)\text{-H}(66)\text{-O}(3)^{iii} = 2.723(4)$, $\text{O}(4)\text{-H}(77)\text{-O}(2)^{iv} = 2.733(4)$, $\text{O}(1\text{W})\text{-H}(333)\text{-O}(2\text{W})^v = 2.771(11)$, $i = x, y, -1+z$, $ii = -x, -y, -z$, $iii = -x, 1-y, 1-z$, $iv = 1-x, 1-y, 1-z$, $v = 1-x, -y, 1-z$).

TABLE-1
SELECTED BOND LENGTHS (nm) AND ANGLES (°)

Bond Length	nm	Angles	Degree
Cd(1)-N(4)	2.219(3)	N(4)-Cd(1)-O(5)	95.51(9)
Cd(1)-O(2)	2.246(2)	O(2)-Cd(1)-O(5)	135.82(9)
Cd(1)-N(2)	2.355(3)	N(2)-Cd(1)-O(5)	97.14(10)
Cd(1)-O(5)	2.358(3)	N(4)-Cd(1)-O(4)	90.25(9)
Cd(1)-O(4)	2.462(3)	O(2)-Cd(1)-O(4)	79.60(8)
Cd(1)-O(3)	2.518(3)	N(2)-Cd(1)-O(4)	175.47(9)
O(1)-C(23)	1.240(4)	O(5)-Cd(1)-O(4)	79.46(9)
C(24)-O(5)i	1.236(5)	N(4)-Cd(1)-O(3)	148.97(9)
C(24)-O(3)i	1.274(4)	O(2)-Cd(1)-O(3)	86.77(9)
O(1W)-H(333)	0.8756	N(2)-Cd(1)-O(3)	88.92(10)
N(3)-H(111)	0.9136	O(5)-Cd(1)-O(3)	53.57(9)
N(1)-H(222)	0.9271	O(4)-Cd(1)-O(3)	86.64(9)
O(4)-H(77)	0.8274	N(4)-Cd(1)-O(2)	123.00(9)
O(4)-H(66)	0.8171	N(4)-Cd(1)-N(2)	93.07(10)
O(2)-C(23)	1.284(4)	O(2)-Cd(1)-N(2)	101.10(9)

Symmetry code: ⁱ $x-1, y, z$

TABLE-2
DISTANCE (nm) AND ANGLES OF HYDROGEN
-BONDING FOR COMPOUND

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)
O(4) H(66)..O(3) ⁱ	0.82	1.94	160	2.723(4)
O(4) H(77)..O(2) ⁱⁱ	0.83	1.98	151	2.733(4)
N(3)-H(111)..O(1W) ⁱⁱⁱ	0.91	1.85	168	2.749(5)
N(1) -H(222)..O(1) ^{iv}	0.93	1.97	145	2.782(4)
O(1W)-H(333)..O(2W) ^v	0.88	1.96	154	2.771(11)

Symmetry code: ⁱ $x, 1-y, 1-z$, ⁱⁱ $1-x, 1-y, 1-z$, ⁱⁱⁱ $x, y, -1+z$, ^{iv} $x, -y, -z$, ^v $1-x, -y, 1-z$

Conclusion

In summary, a novel one-dimensional (1D) cadmium(II) coordination polymer with the ligand ($\text{H}_2\text{C}_2\text{EIm}$) and aromatic ligand (H_2L) has been synthesized in hydrothermal reaction condition. Single crystal X-ray diffraction analyses revealed

that the distorted octahedral Cd(II) centers are bridged by $\text{H}_2\text{C}_2\text{EIm}$ and H_2L ligands through the different coordination mode. It is found that the special coordination mode plays a very important role in building the 1D chain structure along the *c* axis. The successful syntheses of the compounds indicate that the π - π packing interactions and the hydrogen-bonding interactions existing in the compound not only stabilize the crystal structure, but also confirm the significant potential of constructing high-dimensional network.

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