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-ethanediyl)*bis*(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, $Z = 2$, $F(000) = 594$, $\text{Goof} = 0.997$, $R1 = 0.0358$, $wR2 = 0.0881$. 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-benzimidazoly)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-ethanediyl)*bis*(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-ethanediyl)*bis*(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 formyl oxy. (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 ($\text{N}(3)\text{--H}(111)\text{--O}(1\text{W})^{\text{i}} = 2.749(5)$, $\text{N}(1)\text{--H}(222)\text{--O}(1)^{\text{ii}} = 2.782(4)$, $\text{O}(4)\text{--H}(66)\text{--O}(3)^{\text{iii}} = 2.723(4)$, $\text{O}(4)\text{--H}(77)\text{--O}(2)^{\text{iv}} = 2.733(4)$, $\text{O}(1\text{W})\text{--H}(333)\text{--O}(2\text{W})^{\text{v}} = 2.771(11)$, $\text{i} = x, y, -1+z$, $\text{ii} = -x, -y, -z$, $\text{iii} = -x, 1-y, 1-z$, $\text{iv} = 1-x, 1-y, 1-z$, $\text{v} = 1-x, -y, 1-z$).

TABLE-1
SELECTED BOND LENGTHS (nm) AND ANGLES ($^\circ$)

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).. ⁱ O(3)	0.82	1.94	160	2.723(4)
O(4)–H(77).. ⁱⁱ O(2)	0.83	1.98	151	2.733(4)
N(3)–H(111).. ⁱⁱⁱ O(1W)	0.91	1.85	168	2.749(5)
N(1)–H(222).. ^{iv} O(1)	0.93	1.97	145	2.782(4)
O(1W)–H(333).. ^v O(2W)	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 the 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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REFERENCES

- O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae and M. Eddaoudi, *J. Kim. Nat.*, **423**, 705 (2003).
- A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M.A. Withersby and M. Schröder, *Coord. Chem. Rev.*, **183**, 117 (1999).
- Y.-P. Hu, C.-P. Tan, S.-F. Wang and X.-B. Meng, *Asian J. Chem.*, **25**, 1137 (2013).
- Z.Q. Jiang, *Asian J. Chem.*, **25**, 2353 (2013).
- R. Wang, L. Han, F. Jiang, Y. Zhou, D. Yuan and M. Hong, *Cryst. Growth Des.*, **5**, 129 (2005).
- (a) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim (1995); (b) J.W. Steed and J.L. Atwood, *Supramolecular Chemistry*, Wiley, New York (2000).
- (a) J.C. MacDonald, P.C. Dorrestein, M.M. Pilley, M.M. Foote, J.L. Lundburg, R.W. Henning, A.J. Shultz and J.L. Manson, *J. Am. Chem. Soc.*, **122**, 11692 (2000); (b) J.C. Noveron, M.S. Lak, R.E. Del Sesto, A.M. Miller and P.J. Stang, *J. Am. Chem. Soc.*, **124**, 6613 (2002).
- J.Y. Lu and V. Schauss, *Inorg. Chem. Commun.*, **6**, 1332 (2003).
- Y.-B. Wang, X.-J. Zheng, W.-J. Zhuang and L. Jin, *Eur. J. Inorg. Chem.*, 1355 (2003).
- V. Arora, M. Gupta and P. Mathur, *Indian J. Chem.*, **38**, 1219 (1999).
- G.A. van Albada, M.T. Lakin, N. Veldman, A.L. Spek and J. Reedijk, *Inorg. Chem.*, **34**, 4910 (1995).
- G.A. van Albada, N. Veldman, A.L. Spek and J. Reedijk, *J. Chem. Crystallogr.*, **30**, 69 (2000).
- L. Jiang, Z.X. Li and Z.M. Su, *Inorg. Chem. Commun.*, **14**, 1077 (2011).
- V.A. Blatov, L. Carlucci, G. Ciani and D.M. Proserpio, *Cryst. Eng. Comm.*, **6**, 378 (2004).
- M. Du, X.J. Jiang and X.J. Zhao, *Inorg. Chem.*, **45**, 3998 (2006).
- L.Y.W. Lilian and M.J. Madeleine, *J. Am. Chem. Soc.*, **79**, 5706 (1957).
- T. Higashi, Program for Absorption Correction, Rigaku Corporation, Tokyo, Japan, (1995).
- SHELXTL, Version 5.1, Siemens Industrial Automation, Inc. (1997).
- G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structure, University of Göttingen, Germany (1997).
- I.P. Santos and L.M.L. Marzan, *Langmuir*, **15**, 948 (1999).