

A Novel 2-D Coordination Compound of [Cd(hmt)₂(hbx)₂(H₂O)]

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(Received March 6, 2018; Accepted March 9, 2018)

Key words: Cd(II) complex, Hexamethylenetetramine, Hydrogen bonding, 4-hydroxybenzoic acid

Studies on the novel coordination polymers by self-assembly of multidentate ligands and transition metal ions are of great interest and importance due to their structural diversity and potential applications in catalysts, separation, hydrogen storage, and molecular recognition.^{1–5} To date, a large number of 1-D, 2-D and 3-D extended frameworks have been prepared from the combination of metal ions with linear and/or nonlinear multidentate ligands.⁶ Coordination polymers based on hexamethylenetetramine (hmt) have been extensively studied due to their versatile ligation modes from monodentate to bridging bi-, tri- and tetradentate.⁷ When hmt is combined with carboxylate which can act as monodentate, bridging, and even chelating ligands through their donor atoms, higher dimensional frameworks are also made possible through non-covalent bonding such as hydrogen bond.⁸ Therefore, we have decided to explore the system of Cd²⁺ metal ions with mixed ligands such as linear 4-hydroxybenzoic acid (hbxH) and tetrahedral hexamethylenetetramine. 4-hydroxybenzoate anion (hbx), deprotonated form of hbxH, is linear and a remarkably versatile building block for the construction of coordination polymers due to its versatile ligation modes and possible hydrogen bond formation. Furthermore, the facile variety of coordination configurations around a Cd²⁺ metal ion can offer much opportunities for us to design and synthesize interesting coordination polymers with various architectures and dimensions for exploring new functional materials. Here, we present the synthesis and crystal structure of a 2-D layer compound of [Cd(hmt)₂(hbx)₂(H₂O)] constructed through the hydrogen bonding.

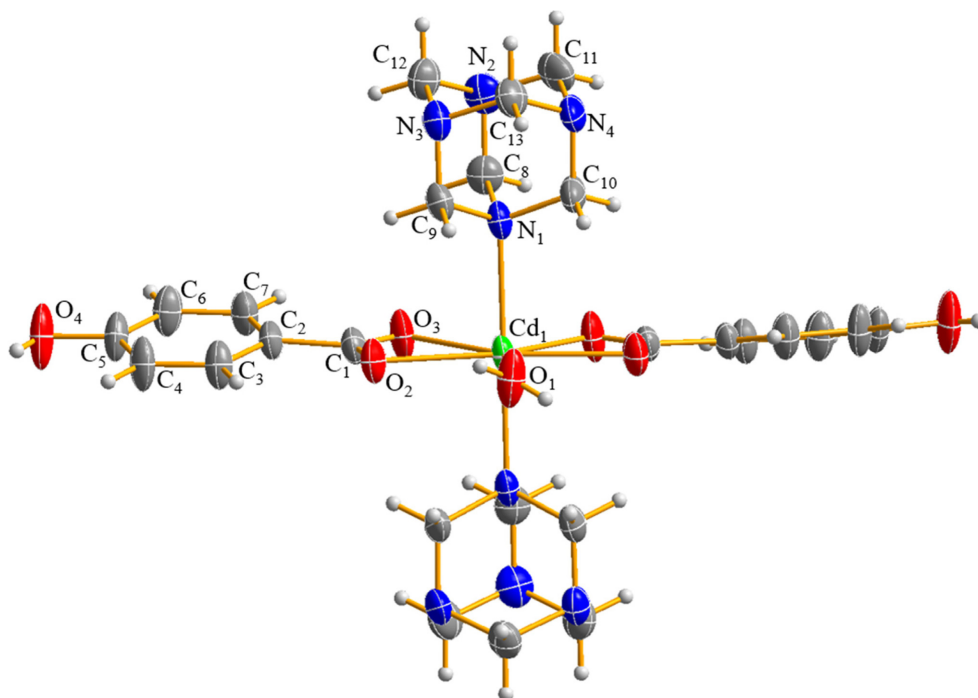
For the synthesis of the title compound, Cd(CH₃COO)₂·2H₂O (0.13 g, 0.50 mmol) dissolved in distilled water (3 mL) was added to aqueous solution (3 mL) of hexamethylenetetramine (0.14 g, 1.0 mmol) followed by slow addition of aqueous solution (3 mL) of 4-hydroxybenzoic acid (0.14 g, 1.0 mmol) mixed with 0.5 M NaOH aqueous solution (1 mL). The solution was stirred for 1 hr. Upon keep-

ing the clear solution in still place for 7 days, colorless crystals were precipitated. The X-ray single crystal data were collected at room temperature on a Siemens P4 four circle diffractometer with graphite monochromated Mo K α radiation using the ω -2 θ scan mode. The stability of the crystal was monitored by measuring three standard reflections periodically (every 97 reflections) during the course of data collection. No crystal decay was observed. The structure was solved by SHELXT.⁹ All non-hydrogen atoms are refined anisotropically. Hydrogen atoms of water molecule were located in a Difference-Fourier map and refined freely. The other Hydrogen atoms were positioned geometrically and refined using a riding model. The structure was refined by full-matrix least square techniques using SHELXL¹⁰ with Olex2¹¹ program. Graphics of the crystal structures were drawn using DIAMOND.¹² The crystallographic data and detailed information of structure solution and refinement are listed in Table 1. Crystallographic data for the structural analysis have been deposited with CCDC (Deposition No. CCDC-1827076). This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; E-mail: deposit@ccdc.cam.ac.uk.

The structure of [Cd(hmt)₂(hbx)₂(H₂O)] consists of distorted pentagonal bipyramidal cadmium metal centers coordinated by two monodentate hmt, two bidentate hbx, and one water molecule as shown in Fig. 1. Since the cadmium (Cd₁) and oxygen (O₁) of water are located on the two-fold axis, two symmetrically equivalent hmt are bonded to a Cd²⁺ metal ion in trans fashion through N₁ atoms only, and two symmetrically equivalent hbx are bonded to a Cd²⁺ metal ion in bidentate chelating mode through carboxylate oxygens (O₂, O₃). One unique water is also coordinated to the Cd²⁺ metal ion. Therefore, the coordinated five oxygen atoms are all on an equatorial plane and only slightly displaced from their best plane about average 0.028 Å. The central cadmium atom is sitting at the center of the pentagon and bonded to the N atoms which

Table 1. Crystal data and structure refinement for $[\text{Cd}(\text{hmt})_2(\text{hbz})_2(\text{H}_2\text{O})]$

Empirical formula	$\text{C}_{26}\text{H}_{36}\text{N}_8\text{O}_7\text{Cd}$
Formula weight	685.03
Temperature/K	296(2)
Crystal system	monoclinic
Space group	$C2/c$
$a/\text{\AA}$	19.803(4)
$b/\text{\AA}$	6.227(3)
$c/\text{\AA}$	23.877(14)
$\alpha/^\circ$	90
$\beta/^\circ$	100.25(4)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	2897(2)
Z	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.570
μ/mm^{-1}	0.813
$F(000)$	1408
Crystal size/ mm^3	$0.4 \times 0.3 \times 0.3$
Radiation	Mo $K\alpha$ ($\lambda = 0.71073$)
2θ range for data collection/ $^\circ$	4.18 to 50.032
Index ranges	$-23 \leq h \leq 1, -7 \leq k \leq 1, -27 \leq l \leq 28$
Reflections collected	3364
Independent reflections	2560 [$R_{\text{int}} = 0.0285, R_{\text{sigma}} = 0.0347$]
Data/restraints/parameters	2560/0/197
Goodness-of-fit on F^2	1.069
Final R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0336, wR_2 = 0.0894$
Final R indexes [all data]	$R_1 = 0.0374, wR_2 = 0.0924$
Largest diff. peak/hole / $\text{e \AA}^{-3}$	0.70/−0.88

**Figure 1.** A view of a discrete $[\text{Cd}(\text{hmt})_2(\text{hbz})_2(\text{H}_2\text{O})]$ molecule with labelling scheme.

are almost perpendicular to the equatorial plane. The acute bond angles in the equatorial plane around the Cd^{2+} metal ion are ranging from $54.48(9)^\circ$ to $87.56(12)^\circ$. The bond angles between equatorial O atoms and the axial N atoms are ranging from $88.19(10)^\circ$ to $91.76(10)^\circ$. This seven coordinated Cd^{2+} metal ion is found common in the known compounds.^{13,14} The Cd–O bond distances, ranging from $2.325(4)$ Å to $2.442(3)$ Å, are comparable to those of

the known compounds.^{13–15} The Cd–N bond distance of $2.401(3)$ Å is normal and similar to the known monodentate hmt–Cd compounds.^{13,14} Selected bond distances and angles are given in *Table 2*.

When extended bonding such as hydrogen bond is considered, the molecular units are further linked together to form a 2-D fat layer as shown in *Fig. 2*. The hydrogen bond between the water molecule (O_1) and carboxylate

Table 2. Selected bond lengths [Å] and angles [$^\circ$] for $[\text{Cd}(\text{hmt})_2(\text{hbx})_2(\text{H}_2\text{O})]$

Cd ₁	O ₁	2.325(4)	Cd ₁	O ₃ ¹	2.442(3)		
Cd ₁	O ₂ ¹	2.336(3)	Cd ₁	N ₁ ¹	2.401(3)		
Cd ₁	O ₂	2.336(3)	Cd ₁	N ₁	2.401(3)		
Cd ₁	O ₃	2.442(3)					
O ₁	Cd ₁	O ₂	81.76(6)	O ₂ ¹	Cd ₁	N ₁	89.32(10)
O ₁	Cd ₁	O ₂ ¹	81.76(6)	O ₂ ¹	Cd ₁	N ₁ ¹	90.69(10)
O ₁	Cd ₁	O ₃ ¹	136.22(6)	O ₂	Cd ₁	N ₁ ¹	89.32(10)
O ₁	Cd ₁	O ₃	136.22(6)	O ₂	Cd ₁	N ₁	90.69(10)
O ₁	Cd ₁	N ₁	90.03(7)	O ₃ ¹	Cd ₁	O ₃	87.56(12)
O ₁	Cd ₁	N ₁ ¹	90.03(7)	N ₁ ¹	Cd ₁	O ₃	88.19(10)
O ₂	Cd ₁	O ₂ ¹	163.53(13)	N ₁ ¹	Cd ₁	O ₃ ¹	91.75(10)
O ₂	Cd ₁	O ₃	54.48(9)	N ₁	Cd ₁	O ₃ ¹	88.19(10)
O ₂ ¹	Cd ₁	O ₃	141.98(9)	N ₁	Cd ₁	O ₃	91.76(10)
O ₂ ¹	Cd ₁	O ₃ ¹	54.48(9)	N ₁	Cd ₁	N ₁ ¹	179.93(13)
O ₂	Cd ₁	O ₃ ¹	141.98(9)				

¹1–X,+Y,3/2–Z

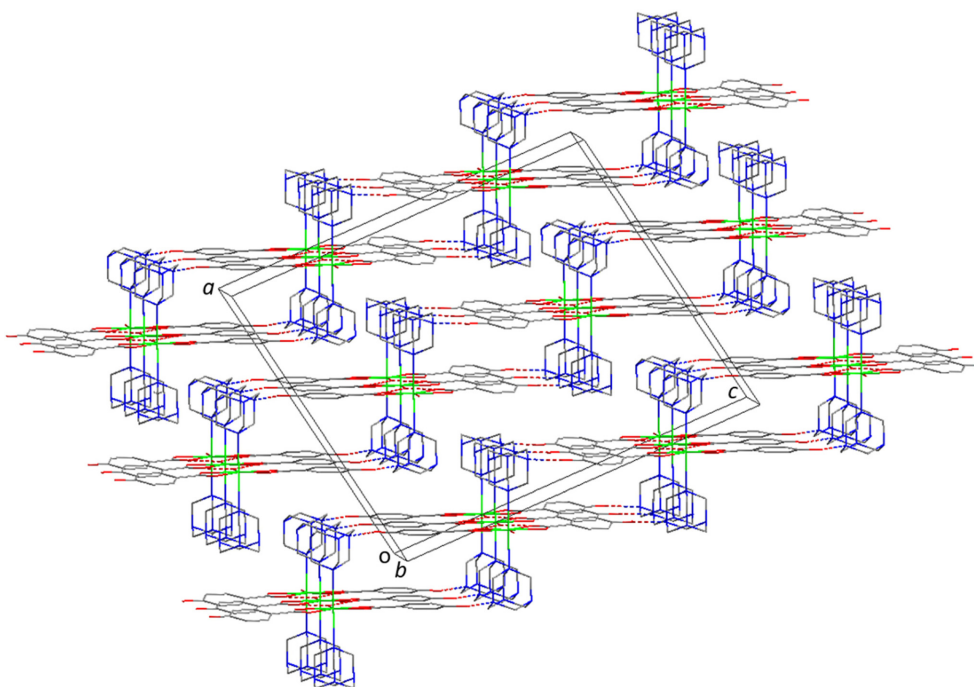


Figure 2. Packing diagram of $[\text{Cd}(\text{hmt})_2(\text{hbx})_2(\text{H}_2\text{O})]$ molecules connected through hydrogen bonding (dotted line) revealing 2-D fat layer framework with the formation of 1-D tunnels along the crystallographic *b* axis (H atoms are omitted for clarity).

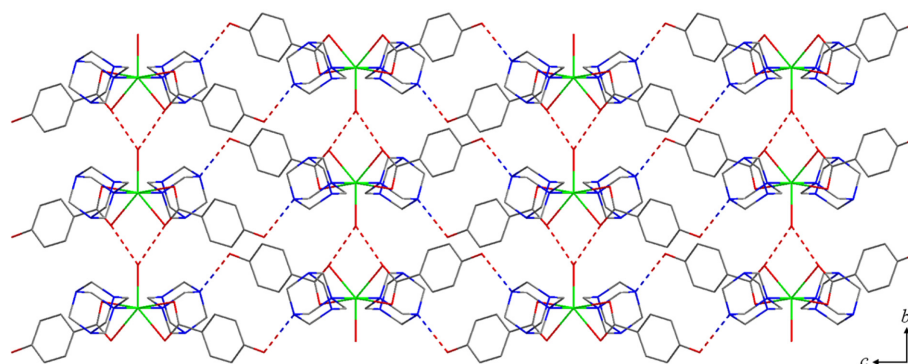


Figure 3. Projection view of one layer formed through hydrogen bonding (dotted line) on *bc* plane.

Table 3. Hydrogen bonds for [Cd(hmt)₂(hbm)₂(H₂O)] [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O ₁ -H ₁ ...O ₃ ¹	0.78(4)	2.06(4)	2.726(4)	144(4)
O ₄ -H ₄ ...N ₃ ²	0.82	1.99	2.786(4)	163.8

¹1-X, -1+Y, 3/2-Z; ²+X, 1-Y, -1/2+Z

groups (O₃), with an O–O separation of 2.726(4) Å, extends the molecular units to an infinite chain along the crystallographic *b* axis. The neighboring Cd–Cd distance along the chain is 6.227(3) Å, the length of *b* axis. The other hydrogen bond found between hydroxyl groups (O₄) and hmt units (N₃), with an O–N separation of 2.876(4) Å, extends 1-D chains into a 2-D fat layer with the formation of 1-D tunnels with rectangular shape openings. The fat layer has stairway like features as shown in the Fig. 2. The 2D sheets are stacked on top of each other slipped half unit to secure their packing with each other. The projection view of this 2-D layer on *bc* plane is shown in Fig. 3. However, it is worth noting that there exist non-covalent interactions between the layers through –CH₂...N interactions, with an C₁₁–N₄ separation of 3.594(5) Å. This is not rare in the known hmt coordination compounds.¹³ If this weak interaction is counted, then the structure can be viewed as a 3-D network structure by connecting each stacked layer through –CH₂...N interactions between the neighboring hmt ligands.

The result presented here further illustrates the structural diversity induced by non-direct chemical bond such as hydrogen bonding. At present, the controlling and designing of the interactions between the coordination environments and the ligation modes associated with multidentate ligands are not well understood. However, using the well-designed synthetic strategy, we are expecting novel structural compounds and their structure related properties, otherwise impossible in the other system.

Acknowledgments. This work was supported by research fund of Chungnam National University.

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