

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE, THERMAL AND FLUORESCENT PROPERTIES OF A 1D Cd(II) COORDINATION POLYMER BASED ON THE BIS(BENZIMIDAZOLE) LIGAND

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A 1D cadmium (II) coordination polymer $\{[\text{Cd}_2(\text{L})_3\text{Cl}_3] \cdot \text{Cl}\}_n$ (**1**) (L = 1,3-bis(benzimidazol-1-yl)-2-propanol) is synthesized by the hydrothermal reaction and characterized by elemental analysis, IR, TG, and X-ray single crystal diffraction. Compound **1** crystallizes in the hexagonal system, space group $P63/m$ with $a = 15.4857(11) \text{ \AA}$, $b = 15.4857(11) \text{ \AA}$, $c = 14.478(2) \text{ \AA}$, $\gamma = 120^\circ$, $V = 3006.8(5) \text{ \AA}^3$, $Z = 2$. In the structure of complex **1**, each cadmium center is hexahedrally coordinated by three chlorine atoms and three nitrogen atoms of three distinct L ligands. A detailed analysis reveals that compound **1** exhibits a 1D chain of beads and the adjacent chains are further linked by C—H \cdots Cl hydrogen bonding to form a 2D supramolecular framework. Furthermore, the solid-state fluorescent property of **1** is investigated at room temperature.

Keywords: cadmium(II), bis(benzimidazole), hydrogen bond, fluorescent property.

The crystal engineering of metal-organic frameworks (MOFs) has grown into a subject that attracts intense attention because the control of the molecular organization in the solid state can lead to materials with novel structures and promising properties [1—6]. Rational design and the synthesis of coordination networks and supramolecular architectures is still a challenge, because the assemble process can be easily influenced by the selection of metal ions with different coordination geometries, ligands, counter anions with different coordination abilities, solvents, etc. [7—9]. One of the efficient routes to complexes is to employ a multifunction ligand to link metal ions so as to give an infinite framework [10—13]. The flexible bis(benzimidazole) ligands which have a strong coordination ability and the imidazole ring capable of acting as hydrogen bond donors are good candidates for the construction of novel complexes [14—18]. For the ongoing works, herein we report the crystal structure, thermal and fluorescent properties of a new one-dimensional cadmium(II) complex $\{[\text{Cd}_2(\text{L})_3\text{Cl}_3] \cdot \text{Cl}\}_n$ (L = 1,3-bis(benzimidazol-1-yl)-2-propanol).

Experimental. Reagents and apparatus. All commercially available starting materials were of analytical grade and used as received. The ligand L was prepared according to the literature method with some modification [19]. Elemental analyses were taken on a Perkin-Elmer 240C analyzer. IR spectra (KBr pellet) were obtained on a FT-IR 170 SX (Nicolet) spectrometer. Thermal gravimetric (TG) studies were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800° under N_2 with a heating rate of $10^\circ/\text{min}$. Fluorescence spectra were measured with a Hitachi F-7000 fluorescence spectrophotometer at room temperature.

X-Ray crystallography. The single crystal X-ray diffraction measurement was carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at $296(2) \text{ K}$. Intensities of reflections were measured using graphite-

Table 1

Crystal data and structure refinement summary for **1**

Empirical formula	C ₅₁ H ₄₈ Cd ₂ Cl ₄ N ₁₂ O ₃
CCDC number	917458
<i>M</i>	1243.61
Temperature, K	296(2)
Wavelength, Å	0.71073
Crystal system	Hexagonal
Space group	<i>P</i> 63/ <i>m</i>
Unit cell dimensions <i>a</i> , <i>b</i> , <i>c</i> , Å; α, β, γ, deg.	15.4857(11), 15.4857(11), 14.478(2); 90, 90, 120
Volume, Å ³	3006.8(5)
<i>Z</i>	2
<i>d</i> _{calc} , g/cm ³	1.374
μ, mm ⁻¹	0.933
<i>F</i> (000)	1252
Crystal size, mm	
θ range, deg.	1.52 to 25.02
<i>h</i> , <i>k</i> , <i>l</i> range	–12/18, –18/17, –17/16
Reflections collected / unique	15367 / 1851
Max. and min. transmission	0.789 and –0.993
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	1851 / 0 / 119
Goodness-of-fit on <i>F</i> ²	0.943
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0431, <i>R</i> 2 = 0.1105
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0670, <i>R</i> 2 = 0.1351
Residual peak and hole., e/Å ³	0.789 and –0.993

monochromatized MoK_α radiation (λ = 0.71073 Å) with a ω scan mode in the range of 1.52 < θ < 25.02°. Unit cell dimensions were obtained with least-squares refinements and semi-empirical absorption corrections were applied using the SADABS program [20]. The structure was solved by a direct method [21] and non-hydrogen atoms were obtained in successive difference Fourier syntheses. The final refinements were performed by full-matrix least-squares methods on *F*² by the SHELXL-97 program package. [22] The summary of the crystallographic data and structure analysis is given in Table 1. CCDC-917458 contains the supplementary crystallographic data for polymer **1**. These data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

Synthesis of {[Cd₂(L)₃Cl₃]·Cl}_{*n*} (1**).** A mixture of cadmium(II) chloride (0.3 mmol, 68 mg), the ligand L (0.3 mmol, 89 mg), H₂O (10 ml), and MeOH (5 ml) was placed in a Teflon-lined stainless vessel and heated to 140 °C for 4 days under autogenous pressure, and then cooled to room temperature at a rate of 10 °C/h. The pale crystal of **1** was obtained in 45.8 % yield based on Cd. Anal. calcd. for Cd₂Cl₄C₅₁H₄₈N₁₂O₃ (%): C 49.25; H 3.89; N 13.52. found (%): C 49.48; H 3.74; N 13.68. IR (KBr pellet, cm⁻¹): 3444(s), 1618(m), 1506(s), 1394(m), 1263(m), 1198(m), 1088(w), 913(w), 749(s).

Results and discussion. Syntheses and general methods. The reaction of CdCl₂ and the ligand L in the CH₃OH/H₂O system gave rise to coordination polymer **1** under hydrothermal conditions. IR spectra of **1** show strong absorptions around 1263 cm⁻¹ and 1088 cm⁻¹, which can be assigned to the ν_{C=C}, ν_{C=N} stretching vibrations of the benzimidazole ring in the ligand L. The bands observed at 1198 cm⁻¹ and 3444 cm⁻¹ are related to the ν_{C–O}, ν_{OH} stretching vibrations of alcohol.

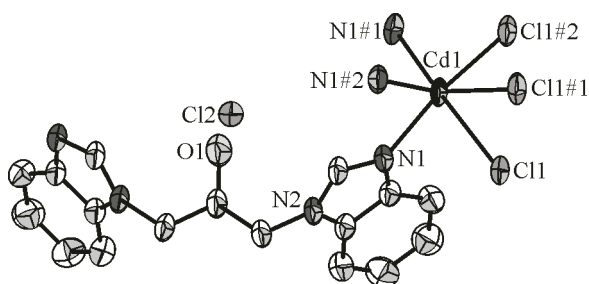


Fig. 1. Metal coordination environment in **1** with the labelling scheme and 30 % thermal ellipsoids. Hydrogen atoms are omitted for clarity. (Symmetry codes: #1 = $-y+1, x-y, z$; #2 = $-x+y+1, -x+1, z$; #3 = $x, y, -z+1/2, -z$; #4 = $x, y, -z+3/2$)

Description of the crystal structure.

The molecular structure of complex **1** is shown in Fig. 1. Principal bond lengths and angles are summarized in Table 2. The Cd(II) center is in a slightly distorted octahedral coordination geometry with three N donor atoms from distinct L ligands and three μ_2 -bridging chlorine atoms. The bond angles around the Cd(II) atoms are in the range of 82.17–168.76°; the Cd—Cl and Cd—N bond lengths are 2.6767(16) Å and 2.338(4) Å, respectively. The Cd(II) atoms are linked into a 1D beaded-like chain through μ_2 -bridge bridging L ligands and chlorine anions alternately. The two adjacent Cd(II) atoms are bridged by three chlorine anions to form binuclear $[\text{Cd}_2\text{Cl}_3]^+$ units with a Cd···Cd distance of 3.4866(10) Å. The adjacent binuclear $[\text{Cd}_2\text{Cl}_3]^+$ units are linked by three L using a bis(monodentate)-bridging mode to form infinite 1D beaded cation chains, as shown in Fig. 2. The 1D chains are further extended into the final 2D supramolecular networks through C—H···Cl weak hydrogen bonding interactions between the ligands L with Cl anions ($\text{C}(8)\cdots\text{Cl}(12) = 3.655(7)$ Å, $\text{C}(8)\text{—H}(8\text{A})\cdots\text{Cl}(1) = 154^\circ$. Symmetry code: A = $1-x, -y, 1/2+z$.) The weak noncovalent interaction is important in the formation of the final supramolecular structure of **1** (Fig. 3).

Thermal gravimetric analysis. Complex **1** is air-stable and retains the crystalline integrity at ambient conditions. The TG curve of complex **1** shows that it is stable until 290 °C (Fig. 4). The weight loss step from 290 °C to 732 °C is attributed to the loss of the ligands L. The weight loss is about 71.9 %, in correspondence with the calculated value of 70.52 %. The remaining weight (28.1 %) indicates that the final product should be CdCl_2 (calcd. 29.48 %).

Table 2

Selected bond lengths (Å) and angles (deg.) for complex **1**

Cd(1)—N(1)	2.338(4)	N(1)—Cd(1)—N(1)#1	89.36(15)	N(1)#2—Cd(1)—Cl(1)#1	168.76(11)
Cd(1)—N(1)#2	2.338(4)	N(1)—Cd(1)—N(1)#2	89.36(15)	Cl(1)#2—Cd(1)—Cl(1)#1	82.17(5)
Cd(1)—Cl(1)#1	2.6767(16)	N(1)#1—Cd(1)—N(1)#2	89.36(15)	N(1)—Cd(1)—Cl(1)	87.76(11)
Cd(1)—N(1)#1	2.338(4)	N(1)—Cd(1)—Cl(1)#2	168.76(11)	N(1)#1—Cd(1)—Cl(1)	168.76(11)
Cd(1)—Cl(1)#2	2.6767(16)	N(1)#1—Cd(1)—Cl(1)#2	101.47(12)	N(1)#2—Cd(1)—Cl(1)	101.47(12)
Cd(1)—Cl(1)	2.6767(16)	N(1)#2—Cd(1)—Cl(1)#2	87.76(11)	Cl(1)#2—Cd(1)—Cl(1)	82.17(5)
		N(1)—Cd(1)—Cl(1)#1	101.47(12)	Cl(1)#1—Cd(1)—Cl(1)	82.17(5)
		N(1)#1—Cd(1)—Cl(1)#1	87.76(11)	Cd(1)#3—Cl(1)—Cd(1)	81.28(6)

Symmetry codes: #1 = $-y+1, x-y, z$; #2 = $-x+y+1, -x+1, z$; #3 = $x, y, -z+1/2, -z$; #4 = $x, y, -z+3/2$.

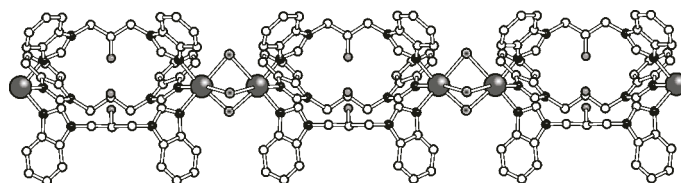


Fig. 2. 1D chain of beads in complex **1**

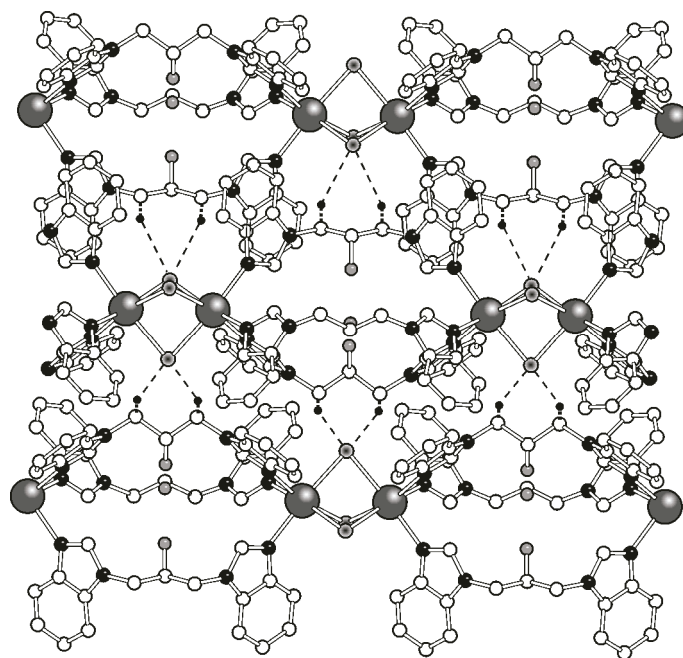


Fig. 3. 2D supramolecular networks of **1** made by C—H...Cl weak hydrogen bonding

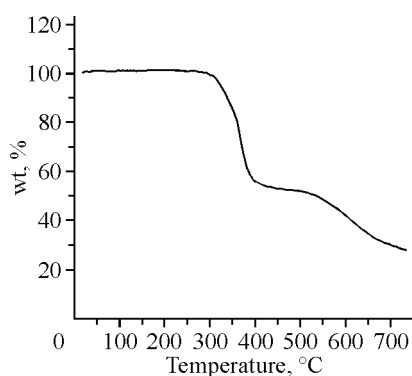


Fig. 4. TG curve of **1**

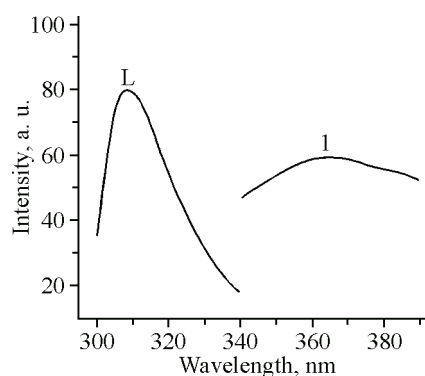


Fig. 5. Solid-state fluorescence spectra of L and **1**

Fluorescence of 1. The luminescent behaviors of coordination polymer **1** and the free ligand L were studied in the solid state at room temperature; emission spectra are shown in Fig. 5. The free ligand L displays luminescence with an emission band at 308 nm (under 309 nm excitation). Meanwhile, the emission for complex **1** can be observed, where the emission bands appear at 363 nm (under 315 nm excitation). In comparison to that of the free ligand, there is a red shift of 99 nm in **1**. These emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT), and can probably be assigned to the intra-ligand ($\pi-\pi^*$) emission [24].

REFERENCES

1. Zhang J., Wojtas L., Larsen R.W. // *J. Amer. Chem. Soc.* – 2009. – **131**. – P. 17040 – 17041.
2. Pramanik S., Zheng C., Emge T.J. // *J. Amer. Chem. Soc.* – 2011. – **133**. – P. 4153 – 4155.
3. Deng H., Doonan C.J., Furukawa H. // *Science*. – 2010. – **327**. – P. 846 – 850.
4. Geng J.C., Qin L., Du X. // *Z. Anorg. Allg. Chem.* – 2012. – **638**. – P. 1233 – 1238.
5. Yaghi M., Li G., Li H. // *Nature*. – 1995. – **378**. – P. 703 – 706.
6. Li H., Davis C.E., Groy T.L. // *J. Amer. Chem. Soc.* – 1998. – **120**. – P. 2186 – 2187.
7. Geng J.C., Qin L., He C.H. // *Transition Met Chem.* – 2012. – **37**. – P. 579 – 585.

8. *Geng J.C., Cui G.H., Jiao C.H.* // *J. Chin. Chem. Soc.* – 2012. – **59**. – P. 704 – 709.
9. *Ma L.F., Qin J.H., Wang L.Y.* // *RSC Advances.* – 2011. – **1**. – P. 180 – 183.
10. *Gandolfo C.M., LaDuca R.L.* // *Cryst. Growth&Des.* – 2011. – **11**. – P. 1328 – 1337.
11. *Jiao C.H., He C.H., Geng J.C.* // *J. Coord. Chem.* – 2012. – **65**. – P. 2852 – 2861.
12. *Cui G.H., He C.H., Jiao C.H.* // *CrystEngComm.* – 2012. – **14**. – P. 4210 – 4216.
13. *Jiao C.H., Geng J.C., He C.H.* // *J. Mol. Struct.* – 2012. – **1020**. – P. 134 – 141.
14. *Zheng S.T., Zhang J., Li X.X.* // *J. Amer. Chem. Soc.* – 2010. – **132**. – P. 15102 – 15103.
15. *Yang E.C., Liu Z.Y., Shi X.J.* // *Inorg. Chem.* – 2010. – **49**. – P. 7969 – 7975.
16. *Liu Q.X., Zhao Z.X., Zhao X.J.* // *Cryst. Growth Des.* – 2011. – **11**. – P. 4933 – 4942.
17. *Horike S., Bureekaew S., Kitagawa S.* // *Chem. Commun.* – 2008. – P. 471 – 473.
18. *Wang X.L., Yang S., Liu G.C.* // *Inorg. Chim. Acta.* – 2011. – **375**. – P. 70 – 76.
19. *Chang Q., Meng X.R., Song Y.L., Hou H.W.* // *Chinese J. Chem.* – 2005. – **23**. – P. 725.
20. *Sheldrick G.M.* SADABS, Program for Empirical Absorption Correction of Area Detector Data, Univ. Göttingen, Germany, 1996.
21. *Sheldrick G.M.* SHELXLS-97, Program for X-ray Crystal Structure Solution, Univ. Göttingen, Germany, 1997.
22. *Sheldrick G.M.* SHELXL-97, Program for X-ray Crystal Structure Refinement, Univ. Göttingen, Germany, 1997.
23. *Cui Y., Yue Y., Qian G., Chen B.* // *Chem. Rev.* – 2012. – **112**. – P. 1126 – 1162.