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КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE AND FLUORESCENT PROPERTIES OF A 2D CADMIUM COORDINATION POLYMER

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A new 2D cadmium(II) coordination polymer $\{[Cd(MBD)(L)]\cdot(H_2O)_2\}_n$ (**1**) (H_2MBD = 5-methoxycarbonyl-benzene-1,3-dicarboxylic acid, L = 1,3-bis(benzimidazol-l-yl)-2-propanol) is synthesized, in which the starting linker (benzene-1,3,5-tricarboxylic acid) undergoes selective monoesterification during the synthesis. In the structure of complex **1**, each cadmium center is octahedrally coordinated by four O atoms from three carboxylate groups and two N of distinct L ligands. A detailed structural analysis reveales that compound **1** exhibits a unique 2D binodal (3,5)-connected $(4^2.6^7.8)(4^2.6)$ topology structure. Furthermore, the 2D layer is extended into a 3D network through π—π stacking interactions. The solid-state fluorescence properties of **1** are investigated at room temperature.

Keywords: Cd(II), 1,3,5-benzenetricarboxylic acid, binodal(3,5)-connected, π—π stacking interactions.

The rational design and synthesis of coordination polymers have attracted considerable attention, which is propelled by their potential applications as functional materials in adsorption, separation, magnetism, luminescence, catalysis, and so on [1—6]. It is well known that the coordination geometries of the metal centers and the coordination behaviors of the organic ligands are the main keys to achieve the target coordination polymers. Benzene-based multicarboxylic acid ligands as good candidates for the construction of such coordination polymers have been widely used [7—9]. For example, 1,3,5-benzene tricarboxylic acid has been extensively used in the self-assembly process of potentially functional coordination polymers with a peculiar topology due to the versatile coordination ability. On the other hands, flexible bis(benzimidazole) derivatives with the arylaliphatic core have remarkable advantages: (i) the bis(benzimidazole) nitrogen atoms have a strong coordination ability; (ii) benzimidazole ligands contain both imidazole ring and larger conjugated π-system, capable of acting as hydrogen bond donors and for π—π stacking interactions; (iii) the flexible nature of —$(CH_2)_n$— spacers allows the ligand to bend and rotate when it coordinates to metal centers so as to conform to the coordination geometries of metal ions [10—15]. To the best of our knowledge, the coordination polymers based on flexible bis(benzimidazole) and multicarboxylic acid ligands have only been scarcely studied [16—18]. In this report, we focus our continuing efforts on the coordination polymers with flexible bis(benzimidazole) ligands [19—22]. Here we report the crystal structure and fluorescent properties of a novel 2D framework $\{[Cd(MBD)(L)]\cdot(H_2O)_2\}_n$ (L = 1,3-bis(benzimidazol-l-yl)-2-propanol, H_2MBD = 5-methoxycarbonyl-benzene-1,3-dicarboxylic acid).

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 [23]. Elemental analyses were taken on a Perkin-Elmer 240C analyzer. IR spectra (KBr pellet) were

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Table 1

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

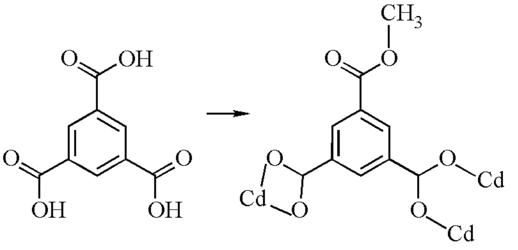
Empirical formula	$CdC_{37}H_{23}N_4O_8$ (**1**)
CCDC number	894682
M	625.88
Temperature, K	295(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions a, b, c, Å; β, deg.	26.7714(17), 10.1898(7), 21.4038(14); 117.3650(10)
Volume, $Å^3$	5185.5(6)
Z	4
d_{calc}, g/cm^3	1.603
μ, mm^{-1}	0.896
$F(000)$	2520
Crystal size, mm	0.22×0.12×0.08
θ range, deg.	1.71 to 25.02
h, k, l range	–31/31, –12/12, –25/16
Reflections collected / unique	12774 / 4573
Max. and min. transmission	0.8084 and 0.7958
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4573 / 0 / 365
Goodness-of-fit on F^2	1.097
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0373$, $wR2 = 0.1216$
R indices (all data)	$R1 = 0.0404$, $wR2 = 0.1240$
Residual peak and hole., $e/Å^3$)	2.789 and –0.621

obtained on a FT-IR 170 SX (Nicolet) spectrometer. 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 293(2) K. Intensities of reflections were measured using graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) with a ω scan mode in the range $1.71 < \theta < < 25.02°$. Unit cell dimensions were obtained with least-squares refinements, and semi-empirical absorption corrections were applied using the SADABS program [24]. The structure was solved by a direct method [25] 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 using the SHELXL-97 program package [26]. Water H atoms were located in a difference Fourier map; other hydrogen atoms were included in calculated positions and refined with fixed thermal parameters riding on their parent atoms. In the structure of **1**, one and a half lattice water molecules are disordered, thus this structure was refined by the SQUEEZE routine of the PLATON program [27]. The summary of the crystallographic data and structure analysis is given in Table 1.

The atomic coordinates and other parameters of structure have been deposited with the Cambridge Crystallographic Data Centre (NO. 894682); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.)

Synthesis of [Cd(MBD)(L)(H_2O)$_2$]$_n$ (1). A mixture of cadmium(II) chloride (0.3 mmol, 69 mg), the ligand L (0.3 mmol, 89 mg), 1,3,5-benzenetricarboxylic acid (0.3 mmol, 63 mg), H_2O (10 ml), and MeOH (5 ml) was placed in a Teflon-lined stainless vessel and heated to 140 °C for 4 days under



Scheme 1. Coordination mode and monomethyl esterification of the 1,3,5-benzenetricarboxylic acid ligand

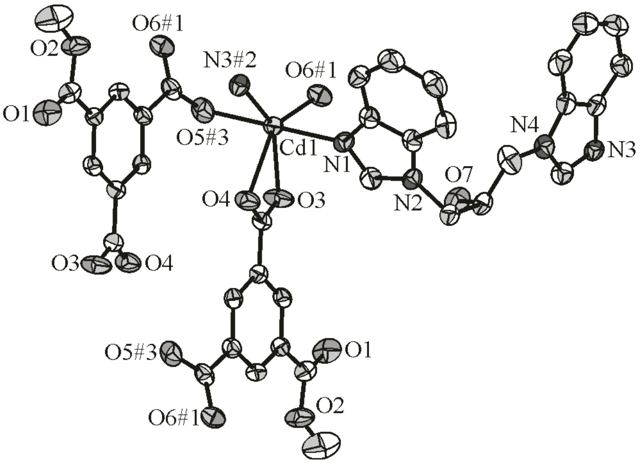


Fig. 1. Coordination environment of Cd^{II} in **1** with the labelling scheme and 30 % thermal ellipsoids. Hydrogen atoms are omitted for clarity. (Symmetry codes: #1 = x, y+1, z; #2 = x, $-y$+2, z–1/2; #3 = $-x$+2, $-y$+1, $-z$)

autogenous pressure, and then cooled to room temperature at a rate of 10°C/h. The resulting colorless block crystals of **1** were obtained by filtration, washed with distilled water and dried at ambient temperature; 37.6 % yield based on Cd. Anal. calcd. for $CdC_{27}H_{25}N_4O_9$ (%): C 48.99; H 3.81; N 8.46. Found (%): C 48.67; H 3.64; N 8.30. IR (KBr pellet, cm^{-1}): 3387(s), 1698(m), 1615(s), 1668(s), 1510(m), 1439(m), 1371(s), 1265(m), 1198(w), 1099(w), 747(s), 695(w), 526(w).

Results and discussion. Syntheses and general methods. The reaction of $CdCl_2$, the ligand L, and 1,3,5-benzenetricarboxylic acid in the CH_3OH/H_2O system gave rise to coordination polymer **1** under hydrothermal conditions. It is interesting that 1,3,5-benzenetricarboxylic acid has been esterified during the synthesis reaction to form selectively the mono-methyl derivative (Scheme 1). In the IR spectra of **1**, the band of the uncoordinated carboxylate group was observed at 1750 cm^{-1}, suggesting the strong stretching vibration of ester in the carboxylate group [28], which was further confirmed by single crystal X-ray diffraction. **1** shows strong absorptions around 1265 cm^{-1} and 1099 cm^{-1}, which can be assigned to the $\nu_{C=C}$, $\nu_{C=N}$ stretching vibration of the benzimidazole ring in the ligand L. The bands observed at 1193 cm^{-1} and 3387 are assigned to the $\nu_{C—O}$, ν_{OH} stretching vibrations of alcohol. The strong bands at 1698 cm^{-1} and 1615 cm^{-1} can be assigned to the $\nu_{C=O}$ asymmetrical and symmetrical stretching vibrations of 1,3,5-benzenetricarboxylic acid.

Description of the crystal structure. The single crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the monoclinic space group $C2/c$. The asymmetric unit consists of one crystallographically independent Cd(II) ion, one MBD dianion, and one ligand L. As shown in Fig. 1, each Cd(II) center is coordinated by four oxygen atoms from the carboxylate groups of three different MBD

Table 2

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

Cd(1)—O(6)#1	2.243(3)	O(6)#1—Cd(1)—N(3A)#2	125.81(11)	O(6)#1—Cd(1)—N(1)	85.17(11)
Cd(1)—N(1)	2.356(3)	N(3A)#2—Cd(1)—N(1)	95.59(12)	O(6)#1—Cd(1)—O(4)	139.15(10)
Cd(1)—O(3)	2.407(3)	N(3A)#2—Cd(1)—O(4)	94.77(10)	N(1)—Cd(1)—O(4)	86.52(11)
Cd(1)—N(3A)#2	2.283(3)	O(6)#1—Cd(1)—O(3)	85.87(11)	N(3A)#2—Cd(1)—O(3)	147.97(11)
Cd(1)—O(4)	2.370(3)	N(1)—Cd(1)—O(3)	91.38(12)	O(4)—Cd(1)—O(3)	54.43(9)
Cd(1)—O(5)#3	2.438(3)	O(6)#1—Cd(1)—O(5)#3	91.34(10)	N(3A)#2—Cd(1)—O(5)#3	88.60(11)
		N(1)—Cd(1)—O(5)#3	175.61(10)	O(4)—Cd(1)—O(5)#3	94.44(10)
		O(3)—Cd(1)—O(5)#3	85.72(11)	C(18)—O(4)—Cd(1)	93.0(2)

Symmetry codes: #1 = x, y+1, z; #2 = x, $-y$+2, z–1/2; #3 = $-x$+2, $-y$+1, $-z$; #4 = x, y–1, z; #5 = x, $-y$+2, z+1/2.

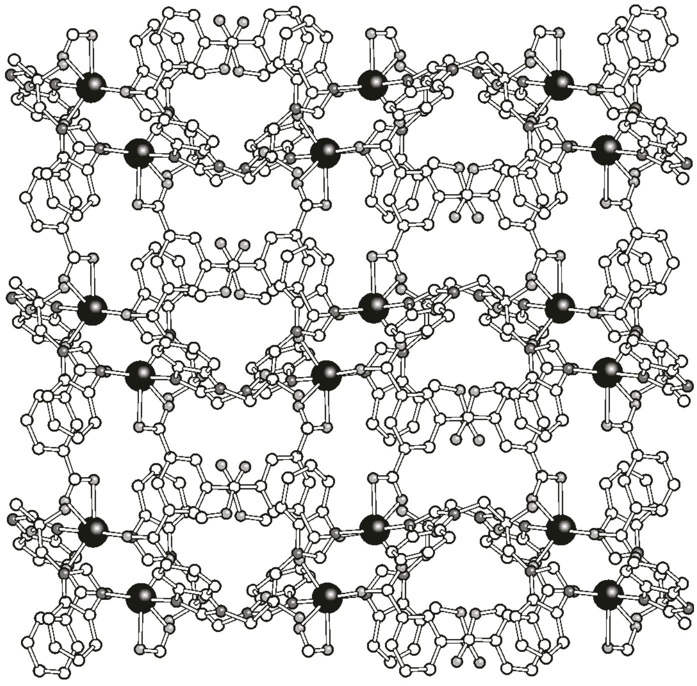


Fig. 2. 2D layer of **1**

ligands with the Cd—O bond lengths varying from 2.243(3) Å to 2.438(3) Å, and two nitrogen atoms of individual ligands L with Cd—N distances of 2.283(3) Å and 2.356(3) Å, forming a distorted octahedral coordination sphere. The two carboxylate groups of the MBD dianions adopt two different coordination modes; one displays a chelating mode, another adopts a bridging bidentate arrangement. Each MBD ligand bridges three cadmium(II) ions to form a 1D ladder chain. Further, the ligands L link two adjacent Cd(II) atoms with a Cd—Cd distance of 11.132 Å, forming a 2D network (Fig. 2).

From the view of topology, Cd(II) atoms are linked by three MBD, and two ligands L act as a 5-connected node; the ligands L are considered as a linker, while μ_3-bridging MBD should be simplified as a 3-connected node (Scheme 1). The network of **1** can be described with the point symbol of $(4^2.6^7.8)(4^2.6)$, being a rare example of a (3,5)-connected binodal topology (Fig. 3), which has been deposited in the TOPOS database (http://www.topos.samsu.ru) as cgh5. To the best of our knowledge, this is the first example of MOF with such a connected topology.

It should be noted that there are three kinds of intermolecular face-to-face π—π stacking interactions between the imidazole-benzene rings and the benzene-benzene rings with a centroid-centroid distance of 3.798(2) Å, 3.665(2) Å, and 3.792(2) Å, respectively. Thus, the 2D layer is further extended

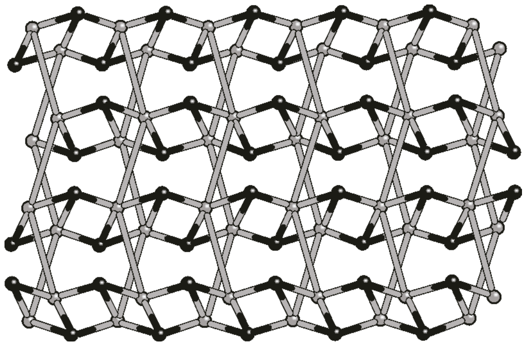


Fig. 3. Binodal (3,5)-connected topology network of **1**

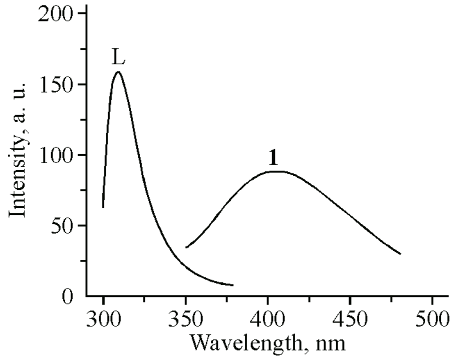


Fig. 4. Solid-state fluorescence spectra of L and **1**

into a 3D supramolecular framework by these π—π stacking interactions. The existence of the intermolecular π—π stacking interaction is more conducive to the stability of the structure of the complex.

Fluorescence of 1. The photoluminescent properties of **1**, together with L, were studied in the solid state at room temperature; emission spectra are shown in Fig. 4. Blue emission for **1** and L can be observed, where the maximum emission wavelength are at 308 nm (under 309 nm excitation) for L and 407 nm (under 400 nm excitation) for **1**. In comparison to that of the free ligand, a red shift of 99 nm in **1** with a lower intensity is a result of the ligand-to-metal charge transfer (LMCT) [29]. The photoluminescence shows that the coordination anions may contribute to the fluorescense emission of the Cd(II) coordination polymers.

Conclusions. A new 2D network coordination polymer $\{[Cd(MBD)(L)]\cdot(H_2O)_2\}_n$ based on the 1,3-bis(benzimidazol-l-yl)-2-propanol ligand and 1,3,5-benzenetricarboxylic acid has been hydrotherthermally prepared and structurally characterized by the single crystal X-ray diffraction analysis. The topology analysis shows that complex **1** is a 2D binodal (3,5)-connected network. The results demonstrate that 1,3,5-benzenetricarboxylic acid is a good candidate for constructing interesting coordination frameworks. The fluorescence of **1** is also investigated.

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