

配位聚合物 $[\text{Cd}_2(\text{BDC})_2(\text{obix})_2] \cdot \text{H}_2\text{O}$ 的合成、晶体结构和荧光性质

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摘要: 用水热合成方法得到 1 个新的配位聚合物 $[\text{Cd}_2(\text{BDC})_2(\text{obix})_2] \cdot \text{H}_2\text{O}$ (H_2BDC =对苯二甲酸, obix =1,2-(二亚甲基)咪唑)。配合物晶体属三斜晶系, $P\bar{1}$ 空间群。晶体结构表明: 镉原子与 3 个对苯二甲酸上的 5 个氧原子, 2 个 1,2-(二亚甲基)咪唑中的 2 个氮原子配位形成扭曲的五角双锥配位构型。2 个 $\text{Cd}(\text{II})$ 原子通过两个羧基桥联形成一个双核 Cd_2 单元, 再通过配体连接成二维层状结构, 层与层之间通过 $\text{C}-\text{H} \cdots \text{O}$ 氢键和弱的 $\pi-\pi$ 相互作用形成三维超分子结构。室温下配合物具有较强的荧光发射光谱。

关键词: 镉的配位聚合物; 晶体结构; 荧光性质

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Synthesis, Crystal Structure and Luminescent Property of Coordination Polymer $[\text{Cd}_2(\text{BDC})_2(\text{obix})_2] \cdot \text{H}_2\text{O}$

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Abstract: The coordination polymer $[\text{Cd}_2(\text{BDC})_2(\text{obix})_2] \cdot \text{H}_2\text{O}$ (**1**) (H_2BDC =1,4-benzenedicarboxylic acid and obix =1,2-bis((1*H*-imidazol-1-yl)methyl)benzene) has been prepared hydrothermally and characterized by IR spectroscopy, elemental analysis and single-crystal X-ray diffraction structure analysis. Complex **1** has two-dimensional (2D) sheet structure and displays strong luminescent emission at room temperature. CCDC: 708656.

Key words: cadmium(II) coordination polymer; crystal structure; luminescent property

0 Introduction

The design and synthesis of metal-organic frameworks based on the selection of ligands and metal ions has become a very attractive research field. The motive comes not only from the intriguing structural diversity but also from the demand for applications of functional materials in the fields of catalysis, porosity, magnetism, luminescence, conductivity, sensing, nonlinear optics and chirality^[1-3]. It is well acknowledged that the effective strategy to construct such architectures is based on relatively simple subunits, in which the nature of metal ions, coordination geometry, and number of coordina-

tion donors provided by organic ligands are all important parameters for directing the self-assembly process. Aromatic carboxylate ligands constitute an important family of organic building blocks and have been extensively selected to construct a variety of coordination architectures because of their robust and rich binding tendency^[4-8]. On the other hand, recently significant work has been carried out by using metal ions assembly with bis (imidazole) ligands interconnected by flexible spacers, a series of outstanding examples of which are $(N\text{-im})_2(\text{CH}_2)_n$ ($n=1 \sim 4, 6$)^[9-13]. From careful inspection of the reported cases, we found that:

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the ligand exhibits a special ability to formulate the compounds, and different organic anions play an important role in directing the final structures and topologies. Inspired by the aftermentioned considerations, 1,2-bis(imidazol-1-ylmethyl)benzene (obix) was chosen as neutral ligand and 1,4-benzenedicarboxylic acid (H₂BDC) was chosen as co-ligand. This paper describes the synthesis, structure and luminescent property of a novel coordination polymers [Cd₂(BDC)₂(obix)₂]·H₂O (**1**).

1 Experimental

1.1 Materials and general methods

All reagents for syntheses and analyses were purchased from commercial sources and used as received without further purification. Elemental analyses (C, H and N) were determined using a Vario EL III elemental analyzer. The IR spectrum as a KBr disk was recorded on a Nicolet Avatar 360 FTIR spectrometer. The emission/excitation spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. Thermal gravimetric analyses (TGA) were performed on a Perkin-Elmer TGA7 instrument in flowing N₂ with a heating rate of 20 °C·min⁻¹.

1.2 Synthesis of obix

Ligand obix was prepared as follows^[14]: imidazole (1.36 g, 20 mmol) and sodium hydroxide (1.6 g, 40 mmol) were dissolved in dimethylsulfoxide (DMSO) (25 mL) and the solution was stirred for 2 h at room temperature, then 1,2-bis(bromomethyl)benzene (2.64 g, 10 mmol) was added. After stirring for another 24 h at room temperature, an equivalent volume of water was added to the mixture. The aqueous solution was extracted with chloroform (3×25 mL) and the chloroform solution was dried over anhydrous sodium sulfate and filtered. Solvent was removed on a rotary evaporator and excess diethyl ether was added to the residue. After standing overnight at -15 °C, the white powder was

filtered, washed with diethyl ether and dried in a vacuum desiccator. Yield: 1.78 g (75%). Anal. Calcd for C₁₄H₁₄N₄(%): C, 70.57; H, 5.92; N, 23.51. Found(%): C, 70.53; H, 5.97; N, 23.48.

1.3 Syntheses of [Cd₂(BDC)₂(obix)₂]·H₂O (**1**)

The single crystals of **1** were prepared by hydrothermal reaction. A mixture of Cd(NO₃)₂·4H₂O (61.6 mg, 0.2 mmol), 1,4-benzenedicarboxylic acid (16.6 mg, 0.1 mmol), obix (23.8 mg, 0.1 mmol), NaOH (8 mg, 0.2 mmol) and H₂O (5 mL) was added in a Teflon-lined stainless steel vessel. The vessel was sealed and heated for 3 d at 180 °C. After the mixture was slowly cooled to room temperature, colorless platelet crystals of **1** were obtained. Yield: 54%. IR spectrum: 3 389, 3 059, 2 965, 1 625, 1 567, 1 521, 1 468, 1 410, 1 361, 1 224, 1 100, 1 084, 1 024, 947, 823, 782, 755, 664 and 582 cm⁻¹.

1.4 X-ray crystal structure determination

A colorless platelet single crystal of **1** with dimensions of 0.26 mm × 0.22 mm × 0.20 mm was carefully selected under a polarizing microscope. The data collection was performed on a Bruker Smart Apex II CCD diffractometer equipped with a normal focus, 3 kW sealed tube X-ray source (Mo Kα radiation, λ = 0.071 073 nm) operating at 50 kV and 30 mA. A total of 11 946 reflections were collected in the range of 1.79° ≤ θ ≤ 26.00° (-12 ≤ h ≤ 12, -16 ≤ k ≤ 17, -19 ≤ l ≤ 19), of which 8 395 are unique (R_{int} = 0.024 3) and 8 395 with I > 2σ(I) were used in the refinement of the structure of **1**. The structure was solved by the direct method using the SHELXS-97 and refined by full-matrix least squares on F² using the SHELXL-97 software^[15,16]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added according to the theoretical model. The crystal data and refinement results for complex **1** are shown in Table 1. The selected bond distances and angles are listed in Table 2.

CCDC: 708656.

Table 1 Crystal data and structure refinement for complex **1**

Formula	C ₄₄ H ₃₈ N ₈ O ₉ Cd ₂	D _c / (g·cm ⁻³)	1.597
Formula weight	1 047.62	Absorption coefficient / mm	1.041
Temperature / K	296(2)	F(000)	1 052
Crystal system	Triclinic	θ range / (°)	1.79~26.00
Space group	P $\bar{1}$	Limiting indices	-12 ≤ h ≤ 12, -16 ≤ k ≤ 17, -19 ≤ l ≤ 19

Continued Table 1

a / nm	1.027 55(9)	Reflections collected	11 946
b / nm	1.432 55(12)	Independent reflections (R_{int})	8 395 (0.024 3)
c / nm	1.585 54(14)	Reflections observed [$I > 2\sigma(I)$]	5 868
α / ($^\circ$)	100.651(1)	Data / restraints / parameters	8 395 / 0 / 586
β / ($^\circ$)	92.172(1)	Goodness-of-fit on F^2	1.031
γ / ($^\circ$)	107.300(1)	R_1, wR_2 [$I > 2\sigma(I)$]	0.052 8, 0.110 1
V / nm ³	2.179 2(3)	Largest difference peak and hole / (e \cdot nm ⁻³)	713, -1 076
Z	2		

Table 2 Selected bond lengths (nm) and angles ($^\circ$)

Cd1-N1	0.226 8(4)	Cd1-O8 ⁱ	0.247 8(3)	Cd2-O3 ⁱⁱ	0.238 3(3)
Cd1-N5	0.227 0(4)	Cd1-O1	0.250 4(3)	Cd2-O4 ⁱⁱ	0.247 2(3)
Cd1-O5	0.238 0(3)	Cd2-N7	0.225 2(4)	Cd2-O8 ⁱ	0.249 4(3)
Cd1-O2	0.237 8(3)	Cd2-N3	0.227 9(4)	Cd2-O5	0.252 1(3)
Cd1-O7 ⁱ	0.246 3(3)	Cd2-O6	0.238 2(3)		
N1-Cd1-N5	177.11(15)	O7i-Cd1-O8 ⁱ	52.77(10)	N3-Cd2-O4 ⁱⁱ	92.17(13)
N1-Cd1-O2	94.44(14)	N1-Cd1-O1	87.25(13)	O6-Cd2-O4 ⁱⁱ	87.71(11)
N5-Cd1-O2	86.10(12)	N5-Cd1-O1	90.81(12)	O3 ⁱⁱ -Cd2-O4 ⁱⁱ	53.94(11)
N1-Cd1-O5	88.65(13)	O2-Cd1-O1	53.16(11)	N7-Cd2-O8 ⁱ	83.69(12)
N5-Cd1-O5	94.17(13)	O5-Cd1-O1	144.50(11)	N3-Cd2-O8 ⁱ	81.71(13)
O2-Cd1-O5	92.12(11)	O7i-Cd1-O1	86.15(11)	O6-Cd2-O8 ⁱ	125.45(11)
N1-Cd1-O7 ⁱ	90.92(13)	O8i-Cd1-O1	138.92(11)	O3 ⁱⁱ -Cd2-O8 ⁱ	91.85(11)
N5-Cd1-O7 ⁱ	86.81(13)	N7-Cd2-N3	165.11(15)	O4 ⁱⁱ -Cd2-O8 ⁱ	145.41(11)
O2-Cd1-O7 ⁱ	138.50(10)	N7-Cd2-O6	104.72(13)	N7-Cd2-O5	90.01(12)
O5-Cd1-O7 ⁱ	129.18(11)	N3-Cd2-O6	86.24(13)	N3-Cd2-O5	88.70(13)
N1-Cd1-O8 ⁱ	93.02(14)	N7-Cd2-O3 ⁱⁱ	87.65(12)	O6-Cd2-O5	52.91(11)
N5-Cd1-O8 ⁱ	87.03(13)	N3-Cd2-O3 ⁱⁱ	89.91(13)	O3 ⁱⁱ -Cd2-O5	165.56(11)
O2-Cd1-O8 ⁱ	166.24(11)	O6-Cd2-O3 ⁱⁱ	141.30(11)	O4 ⁱⁱ -Cd2-O5	140.48(11)
O5-Cd1-O8 ⁱ	76.50(10)	N7-Cd2-O4 ⁱⁱ	98.22(12)	O8 ⁱ -Cd2-O5	73.72(11)

Symmetry code: ⁱ $x-1, y, z$; ⁱⁱ $x-1, y-1, z$.

2 Results and discussion

In the IR spectrum of complex **1**, the absence of bands in the range of 1 760~1 680 cm⁻¹ indicates the complete deprotonation of the H₂BDC ligand, which agrees well with the single-crystal structure. Strong absorption bands between 1 361 and 1 625 cm⁻¹ in the IR spectra of complex **1** can be assigned to the coordinated carboxylate groups. The C=N stretching vibration of imidazolyl group in the infrared spectrum at 1 521 cm⁻¹[17].

Complex **1** crystallizes in the triclinic with space group $P\bar{1}$, and the asymmetric unit consists of two kinds

of unique Cd atoms, two kinds of unique BDC anions, two kinds of unique obix ligand and one lattice water molecules. As depicted in Fig.1, each Cd atom is coordinated by five carboxylate oxygen atoms from three different BDC anions and two nitrogen atoms from two obix ligands. The Cd-O and Cd-N distances are in the range of 0.237 8(3)~0.252 1(3) nm and 0.225 2(4)~0.227 9(4) nm, respectively, which are similar to the reported Cd-O and Cd-N distances in other Cd (II) coordination polymers^[18-20]. Each BDC ligand coordinates to three Cd atoms, in which one carboxylate group adopts a $\mu_2\text{-}\eta^2\text{:}\eta^1$ -bridging coordination mode connecting two Cd atoms, while the other adopts a $\mu_1\text{-}\eta^1\text{:}\eta^1$ -

chelating mode coordinating to one Cd atom, respectively. Two Cd atoms are bridged by two carboxylate groups to give a binuclear molecular building block with shorter separation of $\text{Cd}\cdots\text{Cd}$ (0.391 0 nm). The adjacent binuclear building blocks connect to each other through BDC ligands resulting in the formation of 2D grid layer framework (Fig.2) with 4^4 topology. While *cis*-obix, acts as a bis-monodentate bridging ligand, link two Cd atoms from the same binuclear unit.⁴ The 2D grid layers are closely stacked in an offset way. Two neighboring offset planes have $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding and $\pi-\pi$ weak interactions, in which link the 2D layers into the 3D supramolecular structure (Fig.3).

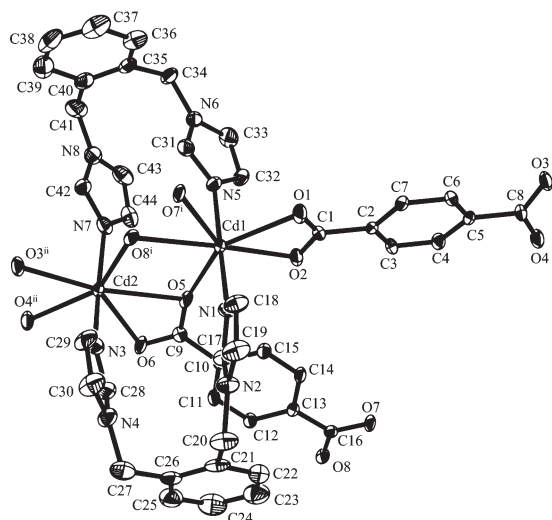


Fig.1 ORTEP drawing of **1** showing the labeling of atoms with thermal ellipsoids at 30% probability

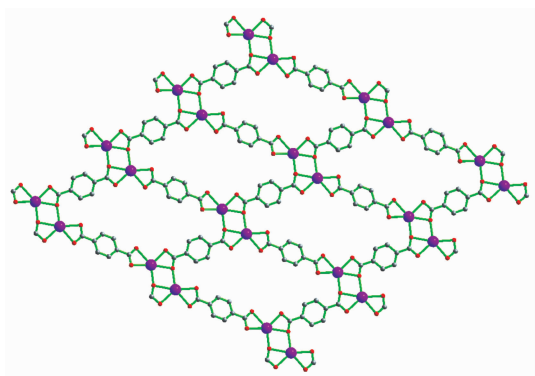
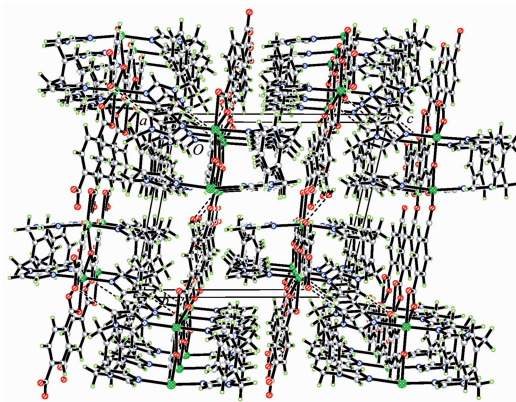


Fig.2 2D grid layer representation for complex **1**

Thermal gravimetric analyses (TGA) were carried out to examine the thermal stability of **1**. The results show that complex **1** is stable in air at ambient



Dotted lines represent hydrogen bonding

Fig.3 A packing diagram for **1** along *a*-axis

temperature. The samples were heated up in flowing N_2 with a heating rate of $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$, as shown in Fig.4. For **1**, the weight loss corresponding to the release of one lattice water molecule is observed from 70 to $140\text{ }^\circ\text{C}$. The anhydrous complex begins to decompose at $320\text{ }^\circ\text{C}$. The framework collapsed in the temperature range $310\sim 800\text{ }^\circ\text{C}$ before the final formation of a metal oxide.

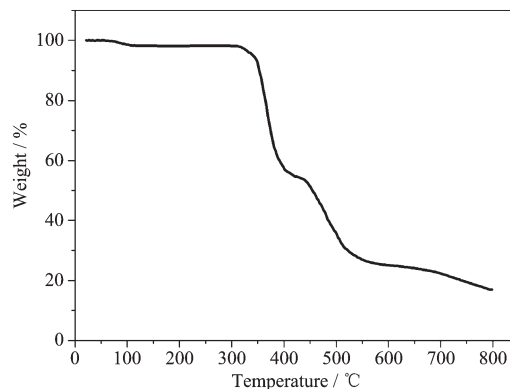


Fig.4 TG curve of **1**

The solid-state photoluminescent properties of **1** and the neutral ligand obix are depicted in Fig.5. Complex **1** exhibits two intense emission maxima at 440 and 461 nm. The main emission peak of ligand obix is at 465 nm. The peak at 461 nm of **1** is probably due to $\pi^*\rightarrow\pi$ transitions of neutral ligand because similar peak also appear for the free obix ligand^[21]. The peak at 440 nm for **1** exhibits a red-shift with respect to the free H_2BDC (393 nm, $\lambda_{\text{ex}}=357\text{ nm}$), which may be assigned to the intraligand fluorescent emission of BDC^[22]. The N-donors ligand and O-donors ligand show contribution to the fluorescent emission of the title complex simultaneously.

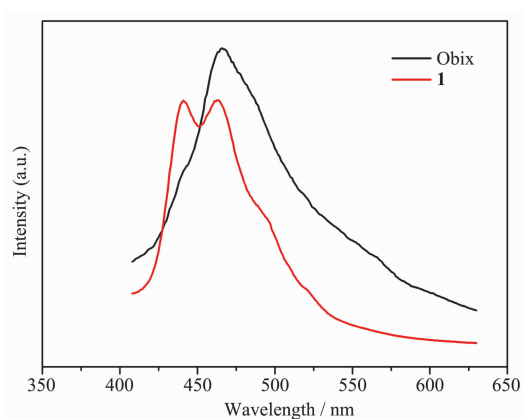


Fig.5 Photoluminescent spectra of **1** and obix in the solid state at room temperature

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