

基于双咪唑基配体的两个镉(II)配位聚合物合成、晶体结构和表征

张卫国^{*1} 崔广华² 焦翠欢² 耿建琛²

(¹ 河北科技师范学院理学院, 秦皇岛 066004)

(² 河北联合大学化学工程学院, 唐山 063009)

摘要: 水热条件下, 合成了两个新的配位聚合物 $[\text{Cd}(\text{PhCOO})_2(\text{bmix})]_n$ (**1**) 和 $[\text{Cd}(\text{chdc})(\text{bmix})] \cdot \text{C}_2\text{H}_5\text{OH}$ (**2**) (bmix =1,4-双(2-甲基咪唑基-1-甲基)苯, H_2chdc =1,4-环己二酸)。单晶结构分析表明, 配合物 **1** 为一维锯齿状链结构平行于[001]平面; 配合物 **2** 为层状结构, 镉原子通过双配体桥连形成四连接的二维(4,4)网络。两个配合物中镉原子均具有 6 配位的畸变八面体几何构型, 另外, 测定了两个配合物的热稳定性。

关键词: 镉(II)配位聚合物; 晶体结构; 柔性双咪唑; (4,4)网络

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Synthesis, Crystal Structures and Characterization of Two Cadmium Coordination Polymers Based on a Bis(imidazole) Ligand

ZHANG Wei-Guo^{*1} CUI Guang-Hua² JIAO Cui-Huan² GENG Jian-Chen²

(¹Department of Chemistry, Hebei Normal University of Science and Technology, Qinhuangdao, Hebei 066004, China)

(²College of Chemical Engineering, Hebei United University, Tangshan, Hebei 063009, China)

Abstract: The two Cd(II) coordination polymers, $[\text{Cd}(\text{PhCOO})_2(\text{bmix})]_n$ (**1**) and $[\text{Cd}(\text{chdc})(\text{bmix})] \cdot \text{C}_2\text{H}_5\text{OH}$ (**2**) (bmix =1,4-bis (2-methylimidazole-1-ylmethyl)benzene, H_2chdc =1,4-cyclohexanedicarboxylic acid) were hydrothermally synthesized and characterized by elemental analysis, IR spectroscopy, TG and X-ray single crystal diffraction. **1** possesses a one-dimensional zigzag chain structure parallel to [001]; **2** displays a two-dimensional undulated (4,4) network constructed with bmix and chdc dianion bridge ligands. Each cadmium(II) ion in **1** and **2** has distorted octahedral coordination geometry. In addition, the thermal properties of two coordination polymers have been presented. CCDC: 842711, **1**; 842712, **2**.

Key words: coordination polymer; crystal structure; flexible di(imidazole); (4,4) network

0 Introduction

Metal-organic coordination polymers comprised of metal ions and bridging ligands have received much attention due to their potential applications as functional materials ranging from catalysis, gas adsorption, molecular recognition, optics, and so on^[1-5].

The structural motifs of coordination polymers rest on several factors, such as the central atoms, the performance of the ligands, the coordinated and/or non-coordinated counter ions, the solvent systems and the reaction conditions. The choice of appropriate ligands is no doubt the key factor because it has an obvious influence on the topologies of the coordination

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^{*}通讯联系人。E-mail: zhwgqhd@163.com

polymers and behavior of the molecules^[6-8]. Some flexible bis (imidazole) bidentate ligands, which can adopt various conformations to bend and rotate when coordinating to metal centers so as to conform to the coordination geometries of metal ions. We and other groups have focused on the synthesis and structural exploration of novel coordination polymers with mixed carboxylates and flexible di(imidazole) ligands^[9-14], with a view to making good progress in understanding how the nature of metal ions and the structures of the organic ligands affect the architectures assembled via coordination bonds properties.

In this paper, we report the synthesis, structures and thermal properties of two interesting coordination polymers: 1D zigzag chain $[\text{Cd}(\text{PhCOO})_2(\text{bmix})]_n$ (**1**) and 2D (4,4) sheet $\{[\text{Cd}(\text{chdc})(\text{bmix})] \cdot \text{C}_2\text{H}_5\text{OH}\}_n$ (**2**) (bmix = 1,4-bis (2-methylimidazole-1-ylmethyl)benzene, H_2chdc = 1,4-cyclohexanedicarboxylic acid). This work shows that different organic carboxylates used in self assembly process may play a crucial role in the topology diversity of the cadmium coordination polymers.

1 Experimental

1.1 Materials and general methods

All starting reagents are commercially available, analytical grade and used in the experiment without further purification. The ligand bmix was prepared according to the literature method^[15]. Elemental analyses were made on a Perkin-Elmer automatic analyzer. IR spectra were recorded on a FT-IR Avatar 360 (Nicolet) spectrophotometer in 4 000~400 cm^{-1} region by using KBr pellets method. The TG measurements were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800 °C under N_2 atmosphere with a heating rate of 10 °C·min⁻¹.

1.2 Synthesis of coordination polymers

1.2.1 Synthesis of $[\text{Cd}(\text{PhCOO})_2(\text{bmix})]_n$ (**1**)

A mixture of cadmium acetate dihydrate (1.0 mmol, 266.5 mg), bmix ligand (1.0 mmol, 266.3 mg), PhCOOH (1.0 mmol, 122.1 mg), NaOH (2.0 mmol, 80.0 mg), H_2O (4 mL) and ethanol (2 mL) was placed in a Teflon-lined stainless vessel and heated to 140 °C for 3 d under autogenous pressure, and then cooled to

room temperature at a rate of 5 °C·h⁻¹. The colorless crystal of **1** was obtained in 83% yield based on Cd. Element anal. calcd. for $\text{C}_{30}\text{H}_{28}\text{CdN}_4\text{O}_4$ (%): C 58.03, H 4.54, N 9.02; found (%): C 58.31, H 4.49, N 9.16. FT-IR (KBr pellet, cm^{-1}): 3 130 (m), 3 060 (m), 1 600 (vs), 1 550 (vs), 1 390 (vs), 1 280 (vs), 1 140 (s), 1 070 (m), 1 000 (m), 849 (s), 721 (vs), 496 (w).

1.2.2 Synthesis of $\{[\text{Cd}(\text{chdc})(\text{bmix})] \cdot \text{C}_2\text{H}_5\text{OH}\}_n$ (**2**)

2 was prepared using a similar method as for **1** with replacement of H_2chdc with PhCOOH . The colorless crystal of **2** was obtained in 78% yield based on Cd. Element anal. calcd. for $\text{C}_{24}\text{H}_{28}\text{CdN}_4\text{O}_4$ (%): C 52.51, H 5.14, N 10.21; found (%): C 52.25, H 5.52, N 9.65. FT-IR (KBr pellet, cm^{-1}): 3 440(m), 3 120(m), 2 940 (m), 1 550 (vs), 1 410 (vs), 1 340 (s), 1 280 (s), 1 140 (m), 1 040 (m), 935 (m), 849 (m), 725 (s), 588 (w).

Both complexes are stable in air and insoluble in common solvents such as water, ethanol, methanol, and acetone.

1.3 Crystallography data and crystal structure determination of **1** and **2**

The suitable single crystals of title coordination polymers were mounted on the top of a glass fiber with epoxy cement for the X-ray measurement. The crystallographic data collections for **1** and **2** were carried out on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated $\text{Mo } K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) and ω - 2θ scan mode at 296 K. The absorption corrections were applied using SADABS program^[16]. The structure was solved by direct methods and refined anisotropically by the full-matrix least-squares technique using the Bruker's SHELXTL program package^[17]. Anisotropic thermal parameters were applied to all nonhydrogen atoms. The organic hydrogen atoms were generated geometrically (C-H = 0.096 nm). In the structure of **2**, the one ethanol lattice molecule is disordered, thus this structure was refined by the SQUEEZE routine of PLATON program^[18]. A summary of crystallography data is given in Table 1. The selected bond lengths and angles are listed in Table 2.

CCDC: 842711, **1**; 842712, **2**.

Table 1 Details of crystal data and structure refinement for **1** and **2**

Complex	1	2
Empirical formula	C ₃₀ H ₂₈ CdN ₄ O ₄	C ₂₄ H ₂₈ CdN ₄ O ₄
Formula weight	620.96	548.9
Wavelength / nm	0.071 073	0.071 073
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / nm	2.153 98(14)	1.051 74(6)
<i>b</i> / nm	1.492 59(9)	1.554 88(9)
<i>c</i> / nm	0.844 90(5)	1.702 14(10)
β / (°)	90	103.960 0(10)
<i>V</i> / nm ³	2.716 4(3)	2.701 4(3)
<i>Z</i>	4	4
<i>D_c</i> / (g·cm ⁻³)	1.518	1.463
<i>F</i> (000)	1 264	1 224
Crystal size /mm	0.35×0.32×0.28	0.25×0.22×0.20
θ range / (°)	2.33 to 27.41	2.08 to 27.22
Reflections collected	21 387	24 048
Independent reflections	6 125	6 037
<i>R</i> _{int}	0.029 6	0.027 9
Absorption coefficient / mm ⁻¹	0.847	0.85
<i>T</i> / K	296(2)	296(2)
Goodness of fit on <i>F</i>	1.025	1.073
Final <i>R</i> indices (<i>I</i> >2σ(<i>I</i>))	<i>R</i> ₁ =0.036 3, <i>wR</i> ₂ =0.083 7	<i>R</i> ₁ =0.027 1, <i>wR</i> ₂ =0.068 2
<i>R</i> (all data)	<i>R</i> ₁ =0.048 0, <i>wR</i> ₂ =0.090 4	<i>R</i> ₁ =0.035 3, <i>wR</i> ₂ =0.071 3
$\Delta\rho_{\max}$ / (e·nm ⁻³)	583	358
$\Delta\rho_{\min}$ / (e·nm ⁻³)	625	207

Table 2 Selected bond lengths (nm) and angles (°) for **1** and **2**

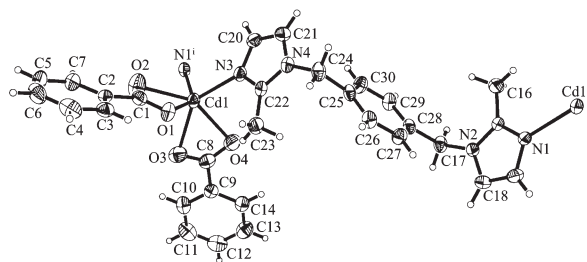
1					
Cd1-N3	0.225 7(3)	Cd1-O2	0.231 9(3)	Cd1-O4	0.246 5(4)
Cd1-N1 ⁱ	0.226 5(3)	Cd1-O3	0.234 0(4)	Cd1-O1	0.252 7(4)
N3-Cd1-N1 ⁱ	105.31(12)	N3-Cd1-O4	90.82(13)	O3-Cd1-O1	95.12(14)
N3-Cd1-O2	116.80(13)	N1 ⁱ -Cd1-O4	95.38(14)	O4-Cd1-O1	121.11(14)
N1 ⁱ -Cd1-O2	91.22(12)	O3-Cd1-O4	54.13(13)	N3-C22-N4	109.6(4)
N3-Cd1-O3	139.71(13)	N3-Cd1-O1	86.61(13)	O2-Cd1-O4	148.76(14)
N1 ⁱ -Cd1-O3	97.95(14)	N1 ⁱ -Cd1-O1	141.76(12)		
O2-Cd1-O3	94.73(14)	O2-Cd1-O1	51.87(12)		
2					
Cd1-O4	0.222 0(2)	Cd1-N3 ⁱ	0.227 50(2)	Cd1-O2 ⁱⁱ	0.251 7(2)
Cd1-O1 ⁱⁱ	0.225 6(2)	Cd1-O3	0.242 0(1)	Cd1-N1	0.227 70(2)
O4-Cd1-O1 ⁱⁱ	147.9(6)	O1 ⁱⁱ -Cd1-N1	111.91(7)	O4-Cd1-N1	87.9(4)
O4-Cd1-N3 ⁱ	107.1(6)	O1 ⁱⁱ -Cd1-N3 ⁱ	92.85(6)	N3 ⁱ -Cd1-N1	104.06(6)

Symmetry transformations used to generate equivalent atoms: **1**: ⁱ -0.5+*x*, 1.5-*y*, 1+*z*; **2**: ⁱ -1.5-*x*, *y*-0.5, -*z*-0.5;ⁱⁱ 0.5+*x*, -*y*+1.5, *z*+0.5.

2 Results and discussion

2.1 Description of the crystal structures of complexes **1** and **2**

[Cd(PhCOO)₂(bmix)]_n (**1**): X-ray diffraction analysis indicates that the structure of complex **1** is a 1D zigzag chain and the asymmetric unit contains one Cd²⁺ cation, one bmix ligand and two PhCOO⁻ ligands. The Cd1 center locates in a distorted octahedral geometry defined by three O (O1, O2 and O4) atoms from two PhCOO⁻ ligands and one N (N1ⁱ, ⁱ -0.5+x, 1.5-y, 1+z) atom from one bmix ligand locate in the equatorial positions, while two apical sites are occupied by one O(O3) atom from one PhCOO⁻ ligand and one N (N3) atom from another bmix ligand. The coordination environment of Cd atom in complex **1** is shown in Fig.1, and selected bond lengths and angles are listed in Table 2. The Cd-O bond lengths range from 0.231 9(3) to 0.252 7(4) nm, and the two Cd-N bond lengths amount 0.2257(3) and 0.2265(3) nm, respectively. The coordination angles range from 51.87 (12)° to 141.76 (12)°, showing the distortion of octahedral geometry in **1**.



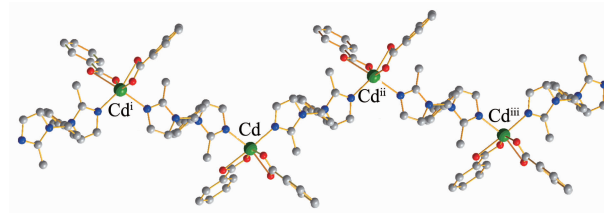
Symmetry transformations used to generate equivalent atoms:

$$^i -0.5+x, 1.5-y, 1+z$$

Fig.1 Coordination environment around Cd(II) center in **1**

In **1**, each Cd(PhCOO)₂ unit is linked to adjacent Cd(II) center through the bridging bmix, forming a 1D zigzag chain structure (Fig.2), where the Cd1-Cd1ⁱ (Cd1-Cd1ⁱⁱ) distance and the Cd1ⁱ-Cd1-Cd1ⁱⁱ angle (Symmetry transformations code ⁱ -0.5+x, -y+1.5, z+1; ⁱⁱ 0.5+x, -y+1.5, z-1), defined by the orientation of the bmix ligands in the chain, are 1.436 19(7) nm and 144.771(2)°, respectively. The carboxylate group of PhCOO⁻ ligand shows a chelating coordination mode to cadmium ion. The dihedral angles between the

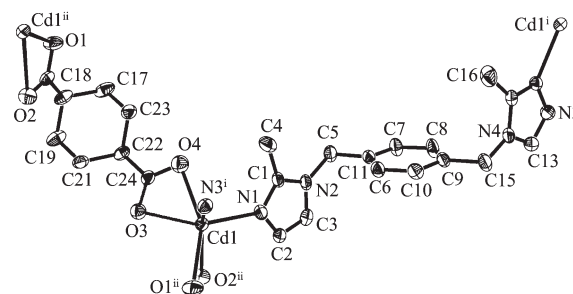
mean-planes of the benzene ring and the imidazole rings are 77.110° and 88.899° in the same bmix ligand, respectively.



Symmetry code: ⁱ -0.5+x, 1.5-y, 1+z; ⁱⁱ x+0.5, 1.5-y, -1+z; ⁱⁱⁱ 1+x, y, -2+z

Fig.2 1D zigzag chain connected by bmix in **1**

[Cd(chdc)(bmix)]_n (**2**): Single-crystal X-ray analysis shows that the structure of **2** is a 2D layer framework possessing a (4,4) network and the asymmetric unit consists of one cadmium ion, one chdc ligand, one bmix ligand. As displayed in Fig.3, each Cd(II) ion with a distorted octahedral coordination geometry is coordinated by four oxygen atoms (O1ⁱⁱ, O2ⁱⁱ, O3, O4, ⁱ -1.5-x, y-0.5, -z-0.5; ⁱⁱ 0.5+x, -y+1.5, z+0.5) from two chdc ligands and two N atoms (N1, N3ⁱ) from two different bmix ligands. The N3ⁱ, O1ⁱⁱ, O2ⁱⁱ, and O4 atoms comprise the equatorial plane, and the axial positions are occupied by N1 and O3. The Cd-O distances range from 0.222 0(2) to 0.225 6(2) nm, and the Cd-N distances are 0.227 5 (2) and 0.227 7(2) nm, respectively (Table 2).

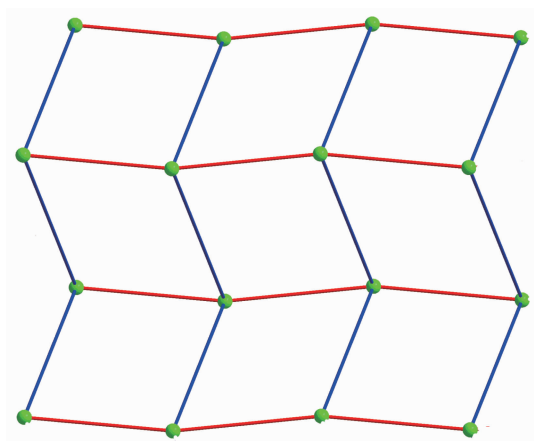


All hydrogen atoms were omitted for clarity; Symmetry transformations used to generate equivalent atoms: ⁱ -1.5-x, y-0.5, -z-0.5; ⁱⁱ 0.5+x, -y+1.5, z+0.5

Fig.3 Coordination environment around Cd(II) center in **2**

In **2**, the bmix ligand adopt bis-monodentate bridging mode to connect the cadmium ion. Thus, the cadmium ions are infinitely connected by bmix ligands to generate a 2₁ helical chain with the nearest Cd-Cd distance in the chain being 1.466 88(7) nm

Fig.7 44-membered metallo-macrocycles with the two imidazole rings of the two bmix ligands adopting tail-to-tail arrangement of **2**

Fig.8 2D undulated (4,4) network of **2**

2.2 IR spectral characterization of complex **1** and **2**

The IR spectra of the title complexes show broad bands at $3\,440\text{ cm}^{-1}$ for **2** can be attributed to the stretching vibrations of O-H. The two absorption bands of $1\,280$ and $1\,070\text{ cm}^{-1}$ in complex **1** ($1\,280$ and $1\,040\text{ cm}^{-1}$ in complex **2**) can be assigned to the vibrations of imidazole rings of bmix ligand. In complex **1**, the absorption band for stretching carboxylate vibrations appear at $1\,550\text{ cm}^{-1}$ for asymmetry (ν_{as}), at $1\,390\text{ cm}^{-1}$ for symmetry (ν_{s}). For complex **2**, the absorption for antisymmetric stretching carboxylate vibration ν_{as} appears at $1\,550\text{ cm}^{-1}$. The corresponding symmetric stretching vibration ν_{s} appears at $1\,410\text{ cm}^{-1}$. The separation of ν_{as} and ν_{s} ($\Delta\nu=160\text{ cm}^{-1}$ for **1** and 140 cm^{-1} for **2**) imply the presence of chelating coordination mode of the carboxylic groups.

2.3 Thermal properties of complex **1** and **2**

The TG analyses for the two complexes have been investigated under N_2 . **1** has two weight-loss processes. Firstly, **1** is stable up to about $289.5\text{ }^\circ\text{C}$ and with further heating to $379\text{ }^\circ\text{C}$, a gradual weight loss occurs, which is due to the departure of PhCOO^- ligand (Obsd. 38.33% ; Calcd. 39.01%). Secondly, the mass loss of 41.11% was observed in the temperature range of $393.9\sim 459.8\text{ }^\circ\text{C}$, which is attributed to the release of bmix ligand (Calcd. 42.88%). The remaining weight corresponds to the formation of CdO (Obsd. 20.56% ; Calcd. 20.68%). **2** can be divided into three steps from the TG curve. The first mass loss of 7.62% between 99.3 and $127.2\text{ }^\circ\text{C}$ corresponds to the release

of the uncoordination ethanol molecule (Calcd. 7.74%). The second weight loss of 28.09% is observed from 316.6 to $394.2\text{ }^\circ\text{C}$, assigned to the decomposition of chdc ligand (Calcd. 28.6%). The third mass loss of 42.79% from 401.4 to $496.6\text{ }^\circ\text{C}$ is ascribed to the loss of bmix ligand (Calcd. 44.75%) leading to the decomposition of the complex to CdO with a residual mass of 21.50% (Calcd. 21.58%).

3 Conclusions

Two new cadmium coordination polymers with di(imidazole) and organic carboxylate ligand, $[\text{Cd}(\text{PhCOO})_2(\text{bmix})]_n$ (**1**) and $[\text{Cd}(\text{chdc})(\text{bmix})] \cdot \text{C}_2\text{H}_5\text{OH}]_n$ (**2**), were obtained by hydrothermal reaction under similar conditions. The complex **1** exhibits a 1D zigzag chain united by bmix ligand while the **2** displays a 2D (4,4)-connected net. The different complexity in the structures of coordination architectures is due to variation of organic carboxylate part.

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