

## 含 $\text{Br}\cdots\pi$ 及 $\text{Br}\cdots\text{Br}$ 相互作用的 1-溴-3,5-二(1-咪唑基-亚甲基)苯-镉(II)配合物的合成和晶体结构

王 彦<sup>1,2</sup> 盛月激<sup>1</sup> 孙为银<sup>\*1</sup>

(<sup>1</sup> 南京大学化学化工学院, 配位化学研究所, 配位化学国家重点实验室, 南京 210093)

(<sup>2</sup> 安庆师范学院化学化工学院, 安徽省功能配合物重点实验室, 安庆 246011)

**摘要:** 利用双齿含氮有机配体 1-溴-3,5-二(1-咪唑基-亚甲基)苯(bib)与不同的镉盐反应合成了 2 个配合物  $[\text{Cd}(\text{bib})_2(\text{NO}_3)_2]$  (**1**) 和  $[\text{Cd}(\text{bib})\text{Br}_2]$  (**2**)。利用元素分析及 X-射线衍射单晶结构分析对其进行了表征。晶体结构表明标题化合物 **1** 晶体属于三斜晶系,  $P\bar{1}$  空间群。化合物 **2** 晶体属于单斜晶系,  $P2_1/c$  空间群。在化合物 **1** 中, 一维链状结构通过  $\text{Br}\cdots\pi$  相互作用连接成为二维网状结构; 而化合物 **2** 的二维结构通过卤素 $\cdots$ 卤素相互作用形成一个三维结构。

**关键词:** 晶体结构; 镉配合物;  $\text{Br}\cdots\pi$  相互作用;  $\text{Br}\cdots\text{Br}$  相互作用

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## Synthesis and Crystal Structure of 1-Bromo-3,5-bis(imidazol-1-ylmethyl)benzene-Cd(II) Complexes with $\text{Br}\cdots\pi$ and $\text{Br}\cdots\text{Br}$ Interactions

WANG Yan<sup>1,2</sup> SHENG Yue-Wei<sup>1</sup> SUN Wei-Yin<sup>\*1</sup>

(<sup>1</sup>State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute,  
School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093)

(<sup>2</sup>School of Chemistry and Chemical Engineering, Anhui Key Laboratory of  
Functional Coordination Compounds, Anqing Teachers College, Anqing, Anhui 246011)

**Abstract:** Two metal-organic frameworks,  $[\text{Cd}(\text{bib})_2(\text{NO}_3)_2]$  (**1**) and  $[\text{Cd}(\text{bib})\text{Br}_2]$  (**2**) were synthesized by reactions of ligand 1-bromo-3,5-bis (imidazol-1-ylmethyl)benzene (bib) with corresponding cadmium(II) salts, respectively. Their crystal structures were determined by X-ray crystal structure analyses. The results showed that **1** crystallizes in triclinic, space group  $P\bar{1}$  with  $a=0.836\ 18(14)$  nm,  $b=0.887\ 62(15)$  nm,  $c=1.165\ 9(2)$  nm,  $\alpha=84.211(3)^\circ$ ,  $\beta=74.321(3)^\circ$ ,  $\gamma=69.805(3)^\circ$ ,  $V=0.781\ 9(2)$  nm<sup>3</sup>,  $Z=1$ ,  $D_c=1.849$  g $\cdot$ cm<sup>-3</sup>,  $F(000)=430$ ,  $\mu=3.314$  cm<sup>-1</sup>,  $R=0.032\ 7$ ,  $wR=0.085\ 0$ ; while complex **2** crystallizes in monoclinic, space group  $P2_1/c$  with  $a=0.741\ 86(9)$  nm,  $b=1.423\ 77(18)$  nm,  $c=1.596\ 0(2)$  nm,  $\beta=94.729(2)^\circ$ ,  $V=1.680\ 0(4)$  nm<sup>3</sup>,  $Z=4$ ,  $D_c=2.330$  g $\cdot$ cm<sup>-3</sup>,  $F(000)=1\ 112$ ,  $\mu=8.435$  cm<sup>-1</sup>,  $R=0.030\ 1$ ,  $wR=0.066\ 7$ . Complex **1** has a 1D chain structure, which is further connected by  $\text{Br}\cdots\pi$  interactions to generate a 2D network. In the case of complex **2**, 2D sheet structure was further linked by  $\text{Br}\cdots\text{Br}$  interactions leading to the formation of a 3D framework. CCDC: 715302, **1**; 715303, **2**.

**Key words:** crystal structure; Cd(II) complex;  $\text{Br}\cdots\pi$  interaction;  $\text{Br}\cdots\text{Br}$  interaction

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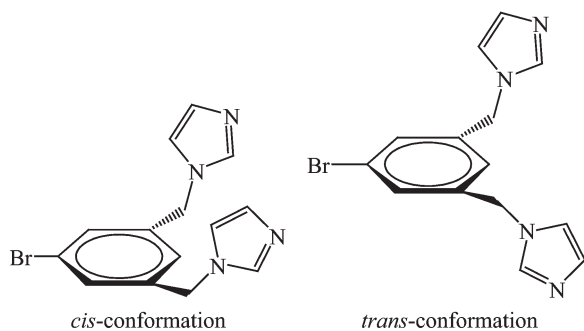
\*通讯联系人。E-mail: sunwy@nju.edu.cn; 会员登记号: S060015599P。

第一作者: 王 彦, 男, 28 岁, 博士, 讲师; 研究方向: 配位化学。

## 0 Introduction

In recent years, coordination polymers with novel structures and properties have been paid intense interests<sup>[1]</sup>. Self-assembled supramolecular complexes with interesting structures such as helices<sup>[2]</sup>, rotaxanes<sup>[3]</sup>, catenanes<sup>[4]</sup> and knots<sup>[5]</sup> as well as one-dimensional (1D) chains, two-dimensional (2D) networks and three-dimensional (3D) frameworks<sup>[6]</sup> have been widely reported. Meanwhile, due to their intriguing potential applications in catalysis, conductivity, sorption and guest exchange<sup>[7-10]</sup>, many efforts have been exerted on constructing coordination polymers with desirable properties on the basis of rational design, although it is difficult to predict the structure and property of the complexes at present due to the influence of unpredictable factors like flexibility of ligand, counterions, solvent system, temperature and so on<sup>[11]</sup>.

Flexible imidazole-containing ligands have been found to be good building blocks for preparation of coordination polymers with novel structures and properties, and various complexes were obtained through reactions of such kind of ligands with varied metal salts<sup>[6]</sup>. In the previous study, we designed a flexible bidentate imidazole-containing ligand 1-bromo-3,5-bis(imidazol-1-ylmethyl)benzene (bib), which can adopt *cis*- and *trans*-conformations (Scheme 1) as observed in 1D chain complex [Ag(bib)]ClO<sub>4</sub> and 2D network [Zn(bib)<sub>2</sub>



Scheme 1 *cis*- and *trans*- conformation of ligand bib

(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O, respectively<sup>[12]</sup>. In order to further investigate the influence of counter anions on the formation of coordination architectures, meanwhile to expand this system, the Cd(II) salts with different anions were used to react with ligand bib, and two new metal-organic frameworks [Cd(bib)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] (**1**) and [Cd(bib)Br<sub>2</sub>] (**2**) were prepared and characterized by X-ray crystal structure analyses.

## 1 Experimental

### 1.1 General

The ligand bib was prepared according to the reported procedures<sup>[12]</sup>. All commercially available chemicals are reagent grade and used as received without further purification. C, H, and N analyses were carried out on a Perkin-Elmer model 240C elemental analyzer at the analysis center of Nanjing University. Infrared (IR) spectra were recorded on a Bruker model Vector22 FTIR spectrophotometer by using KBr disks.

### 1.2 Structure Determinations

Suitable colorless single crystals of **1** and **2** with dimensions of 0.40 mm×0.20 mm×0.05 mm and 0.15 mm×0.05 mm×0.05 mm, respectively, were selected for data collection at 298 K, using a Bruker Smart Apex II CCD diffractometer equipped with a Mo *K*α radiation (λ=0.071 073 nm). The structures were solved by direct methods and refined by full-matrix least-squares methods anisotropically for non-hydrogen atoms. The hydrogen atoms were generated geometrically and refined isotropically using the riding model. Calculations were performed on a personal computer with the Siemens SHELXTL program package<sup>[13]</sup>. Details of the crystal parameters, data collection, and refinements of complexes **1** and **2** are summarized in Table 1. Selected bond lengths and angles with their estimated standard deviations are listed in Table 2.

CCDC: 715302, **1**; 715303, **2**.

Table 1 Crystallographic data for complexes **1** and **2**

Complex	<b>1</b>	<b>2</b>
Empirical formula	C <sub>28</sub> H <sub>26</sub> Br <sub>2</sub> N <sub>10</sub> O <sub>6</sub> Cd	C <sub>14</sub> H <sub>13</sub> Br <sub>3</sub> N <sub>4</sub> Cd
Formula weight	870.81	589.41
Temperature / K	298(2)	298(2)
Crystal system	Triclinic	Monoclinic

Continued Table 1

Space group	$P\bar{1}$	$P2_1/c$
$a$ / nm	0.836 18(14)	0.741 86(9)
$b$ / nm	0.887 62(15)	1.423 77(18)
$c$ / nm	1.165 9(2)	1.596 0(2)
$\alpha$ / (°)	84.211(3)	90.00
$\beta$ / (°)	74.321(3)	94.729(2)
$\gamma$ / (°)	69.805(3)	90.00
$V$ / nm <sup>3</sup>	0.781 9(2)	1.680 0(4)
$Z$	1	4
$D_c$ / (g·cm <sup>-3</sup> )	1.849	2.330
$\theta$ range / (°)	1.81~25.00	1.92~25.99
Reflns. collected	3 889	8 862
Independent reflns.	2 690	3 285
Observed reflns.	2 400	2 696
$R_{int}$	0.023 9	0.027 1
$R$ [ $I > 2\sigma(I)$ ]	0.032 7	0.030 1
$wR_2$ [ $I > 2\sigma(I)$ ]	0.085 0 <sup>a</sup>	0.066 7 <sup>b</sup>
Goodness of fit	1.071	1.016

<sup>a</sup>  $w = 1/[\sigma^2(F_o^2) + (0.046 \ 9P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$ ; <sup>b</sup>  $w = 1/[\sigma^2(F_o^2) + (0.035 \ 2P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$ .

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

<b>1</b>					
Cd1-N1	0.229 8(3)	Cd1-N3	0.230 1(3)	Cd1-O1	0.238 7(3)
N1-Cd1-N1A	180.0	N1-Cd1-N3A	87.88(9)	N1-Cd1-N3	92.12(9)
N3A-Cd1-N3	180.0	N1-Cd1-O1	100.18(9)	N1-Cd1-O1A	79.82(9)
N3-Cd1-O1	94.26(10)	N3-Cd1-O1A	85.74(10)	O1-Cd1-O1A	180.0
<b>2</b>					
Cd1-N1	0.233 3(3)	Cd1-N3	0.234 7(3)	Cd1-Br1	0.283 97(5)
Cd1-Br1A	0.275 81(5)	Cd1-Br2	0.278 26(5)	Cd1-Br2B	0.276 12(5)
N1-Cd1-N3	81.81(11)	N1-Cd1-Br1A	89.12(8)	N3-Cd1-Br1A	166.23(9)
N1-Cd1-Br2B	172.26(8)	N3-Cd1-Br2B	92.72(9)	Br1A-Cd1-Br2B	97.218(17)
N1-Cd1-Br2	90.13(8)	N3-Cd1-Br2	93.19(8)	Br1A-Cd1-Br2	97.195(16)
Br2B-Cd1-Br2	84.691(16)	N1-Cd1-Br1	90.51(8)	N3-Cd1-Br1	85.91(8)
Br1A-Cd1-Br1	83.816(15)	Br2B-Cd1-Br1	94.577(16)	Br2-Cd1-Br1	178.815(15)

Symmetry transformation used to generate equivalent atoms: **1**: A: 1-x, 2-y, -z; **2**: A: 1-x, 1-y, 1-z; B: -x, 1-y, 1-z.

### 1.3 Synthesis of complex [Cd(bib)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>] (**1**)

The compound **1** was prepared by a layering method. A buffer layer of a solution (10 mL) of ethanol and water (3:1) was carefully layered over an aqueous solution (2 mL) of Cd (NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (15.4 mg, 0.05 mmol). Then a solution of bib (15.9 mg, 0.05 mmol) in ethanol (2 mL) was layered over the buffer layer. Colorless needle crystals were obtained in 48% yield

after a week. Elemental analysis calcd. for complex **1**, C<sub>28</sub>H<sub>26</sub>Br<sub>2</sub>N<sub>10</sub>O<sub>6</sub>Cd (%): C, 38.62; H, 3.01; N, 16.08. Found (%): C, 38.23; H, 3.42; N, 16.15. FTIR (KBr pellet, cm<sup>-1</sup>): 1 576 (s), 1 516 (s), 1 384 (m), 1 315(m), 1 235(s), 1 112(s), 845(s), 742(s), 658(s).

### 1.4 Synthesis of complex [Cd(bib)Br<sub>2</sub>] (**2**)

The complex **2** was synthesized by similar procedures to complex **1** except that CdBr<sub>2</sub> (13.6 mg, 0.05

mmol) was used, instead of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , to react with bib (15.9 mg, 0.05 mmol) by the layering method (Yield: 54%). Elemental analysis calcd. for complex **2**,  $\text{C}_{14}\text{H}_{13}\text{Br}_3\text{N}_4\text{Cd}$ (%): C, 28.53; H, 2.22; N, 9.51. Found (%): C, 28.96; H, 2.01; N, 9.35. FTIR (KBr pellet,  $\text{cm}^{-1}$ ): 1 578(m), 1 510(s), 1 432(s), 1 289(m), 1 237(s), 1 109(s), 1 093(s), 1 082(s), 931(m), 839(m), 761(s), 745(s), 657(s).

## 2 Results and discussion

### 2.1 Crystal structure description

The coordination environment around the Cd(II) in compound **1** is shown in Fig.1a. The Cd(II) locates in an inversion center and is six-coordinated with  $\text{N}_4\text{O}_2$  binding set in a distorted octahedral geometry. The equatorial plane is completed by four nitrogen atoms from four different bib ligands with the Cd-N bond lengths of 0.229 8(3) and 0.230 1(3) nm, and the N1-Cd-N3 bond angle of  $92.12(9)^\circ$  (Table 2). The apical positions are occupied by two oxygen atoms from two nitrate anions with Cd-O distance of 0.238 7(3) nm, and N-Cd-O angle of  $79.82(9)^\circ$ . The Cd-N and Cd-O bond lengths are similar to those in the reported complexes<sup>[14]</sup>. The bib ligand in **1** adopts cis-conformation (L-shape) and coordinates with two Cd(II) atoms using its two flexible arms to generate an infinite 1D chain with the metal $\cdots$ metal separation (Cd $\cdots$ Cd) of 1.238 6(2) nm (Fig.1b). The two imidazole groups are inclined to the central benzene ring at angles of  $74.0^\circ$  and  $72.6^\circ$ , respectively.

It is noticeable that the 1D chains of **1** are further connected by  $\text{Br}\cdots\pi$  interactions to generate a 2D network as shown in Fig.1c, evidenced by the distance of 0.380 62(7) and 0.362 85(7) nm between the Br atoms and centroids of benzene and imidazole rings of the neighboring chains, respectively<sup>[15]</sup>.

In complex **2**, the coordination geometry around the Cd(II) center can be described as distorted octahedral. Each Cd(II) atom is coordinated by four Br atoms with Cd-Br bond distances varying from 0.275 81(5) to 0.283 97(5) nm, slightly longer than the reported Cd-Br distances<sup>[14]</sup>, and Br-Cd-Br coordination angles in the range from  $83.816(15)^\circ$  to  $178.815(15)^\circ$ . The additional positions are completed by two nitrogen atoms of the imidazole groups from two bib ligands with the N-Cd-N angle of  $81.81(11)^\circ$ . The Cd-N bond lengths are

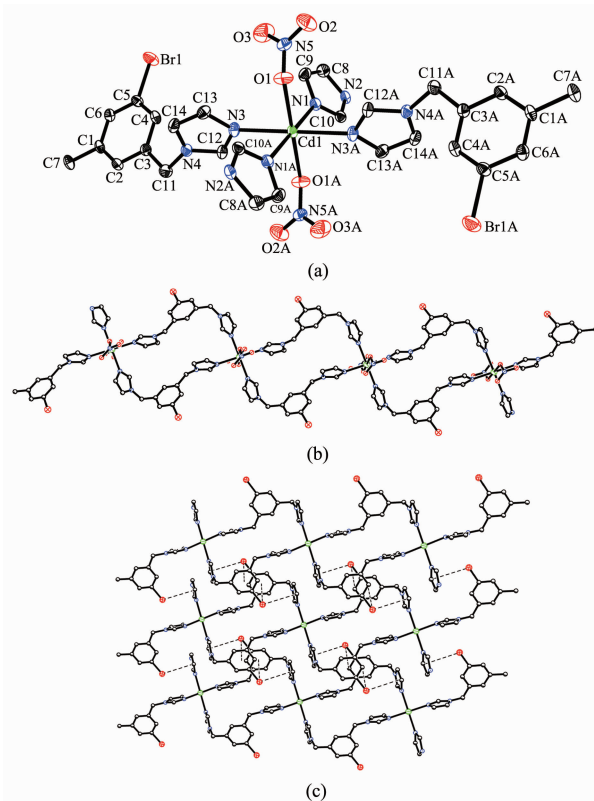


Fig.1 (a) Coordination environment around the Cd(II) in compound **1** (the hydrogen atoms were omitted for the sake of clarity), the thermal ellipsoids are drawn at 30% probability, symmetry code: A:  $1-x$ ,  $2-y$ ,  $-z$ ; (b) 1D chain structure of compound **1**; (c) 2D network of complex **1** connected by  $\text{Br}\cdots\pi$  interactions viewing along the  $a$  axis, the  $\text{Br}\cdots\pi$  interactions are indicated by dashed lines

0.233 3(3) and 0.234 7(3) nm, respectively, which are similar to those observed in complex **1** and other related complexes<sup>[14]</sup>. However, the ligand bib adopts *trans*-conformation in complex **2**, which is different from that in complex **1**, and the two imidazole rings are inclined to the central benzene ring at angles of  $92.2^\circ$  and  $76.8^\circ$ .

The combination of the *trans*-conformation of the bib ligand and the Br atoms serving as bridging ligands results in formation of a ladder-like 2D network as illustrated in Fig.2b. A remarkable feature of the complex **2** is that  $\text{Br}\cdots\text{Br}$  interactions play an important role in controlling the molecular packing. Due to the non-sphericity of atomic charge distribution, the halogen atom can interact with a nucleophile “head-on” and an electrophile “side-on”, which include halogen $\cdots$ halogen and halogen $\cdots$ hydrogen interactions<sup>[16]</sup>. The

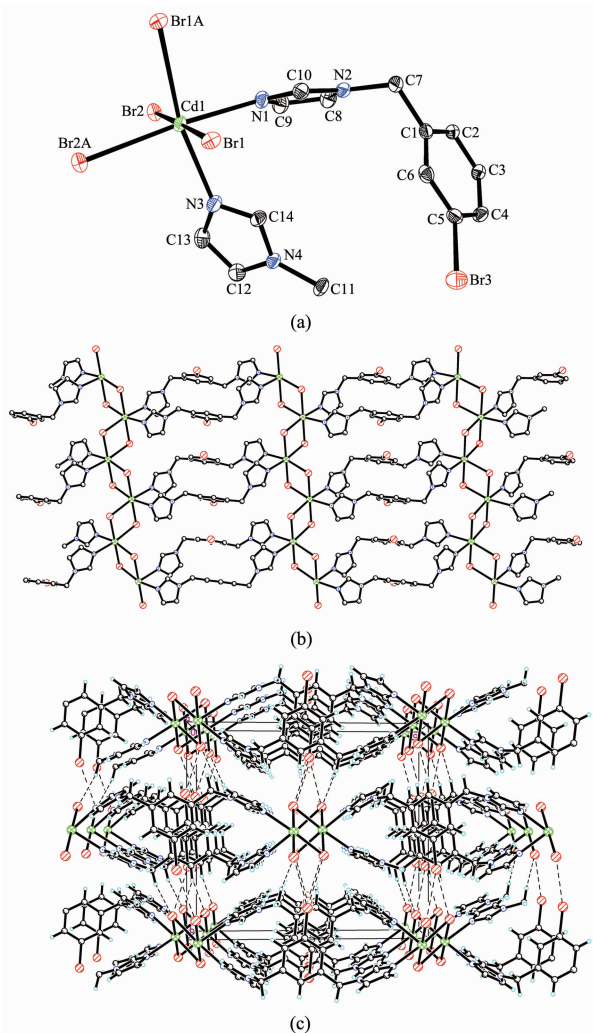


Fig.2 (a) ORTEP representation of compound **2** (the hydrogen atoms were omitted for the sake of clarity), the thermal ellipsoids are drawn at 30% probability, symmetry code: A:  $1-x, 1-y, 1-z$ ; (b) 2D sheet structure of compound **2** along  $b$ -axis; (c) View of 3D coordination framework of complex **2** constructed by  $\text{Br}\cdots\text{Br}$  interactions along  $a$ -axis

$\text{Br}\cdots\text{Br}$  distance within the range of 0.32~0.40 nm is considered to have  $\text{Br}\cdots\text{Br}$  contacts<sup>[15,16]</sup> and in complex **2**, the distances between two nearest intermolecular Br atoms are 0.375 40(4) and 0.385 57(4) nm, indicating that there are  $\text{Br}\cdots\text{Br}$  interactions between Br atoms of two adjacent 2D sheets. The  $\text{C}-\text{Br}\cdots\text{Br}$  angles are  $144.803(3)^\circ$  and  $148.469(3)^\circ$ , comparable to those in polymers formed by substituted benzoic acids<sup>[17]</sup>. Fig.2c illustrates the 3D framework of complex **2** linked by  $\text{Br}\cdots\text{Br}$  contacts.

In summary, complexes **1** and **2** were obtained by

reactions of an imidazole-containing ligand with corresponding cadmium salts containing different counter anions. Compound **1** has 1D chainlike structure that is further linked by  $\text{Br}\cdots\pi$  interactions to give 2D sheet. The complex **2** has 2D ladder-like network that are stabilized by  $\text{Br}\cdots\text{Br}$  interactions to form its 3D framework. The difference between the structures of **1** and **2** is caused by the different counter anions and different conformation of the ligand bib. Further investigations of the bib system are still in progress.

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