

# Cadmium coordination polymers based on flexible bis(imidazole) ligands: A rare example for doublet of doublet cadmium polyhedron arrangements



Chatla Naga Babu<sup>a</sup>, Paladugu Suresh<sup>a</sup>, Natarajan Sampath<sup>b</sup>, Ganesan Prabusankar<sup>a,\*</sup>

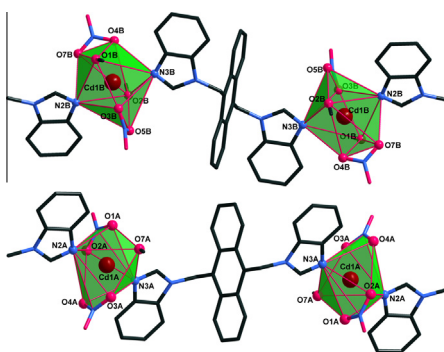
<sup>a</sup> Department of Chemistry, Indian Institute of Technology Hyderabad, ODF Campus, Yeddumailaram, Andhra Pradesh 502 205, India

<sup>b</sup> School of Chemical and Biotechnology, Sastra University, Tirumalaisamudram, Thanjavur, Tamil Nadu 613 401, India

## HIGHLIGHTS

- Cd coordination polymers based on flexible bis(imidazole) ligands.
- Doublet of doublet Cd polyhedron arrangements.
- Coordination polymer with hepta- and octa-coordinated Cd centers.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Two one-dimensional (1D) coordination polymers,  $[\{LCd(O_2NO)_2(DMF)_2\}_2\{LCd(O_2NO)_2(DMF)(DMF)\}_2]_n$  (**1**) and  $[L'Cd(O_2NO)(ONO_2)(DMF)_2]_n$  (**2**), having an aryl chromophoric unit and a flexible bis(imidazole) tail, 9,10-bis((benzimidazol)methyl)anthracene (**L**) and 1,4-bis((imidazol)methyl)benzene (**L'**), with various coordination modes have been obtained. Molecule **1** represents the first structurally characterized one dimensional coordination polymer consisting of both hepta- and octa-coordinated cadmium centers. In **1**, two distorted pentagonal bipyramidal Cd(II) centers and two distorted triangular dodecahedral Cd(II) centers are alternately arranged *via* bridging bidentate *N,N*-chelating ligand, **L**. Whereas, a distorted pentagonal bipyramidal Cd(II) center is formed in **2** where the sterically less crowded **L'** serves as a bridging bidentate *N,N*-chelating ligand. Furthermore, **1** and **2** have been characterized by elemental analysis, FT-IR, <sup>1</sup>H NMR, UV-vis and fluorescent techniques.

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## Introduction

The functional coordination polymers (CPs) with transition-metal cores have stimulated great interests for not only the diverse structures but also their potential technological applications in

fields such as drug delivery [1], gas storage [2], luminescence [3], catalysis [4], separations [5,6]. The CPs with versatile topologies derived by multifunctional organic building blocks often exhibit structural diversities and tunable functionalities, especially those bearing multidentate bridging ligands because of their tunable coordination fashions under different experimental conditions [7]. However, the structural uncertainty of CPs is an inherent characteristic of a self-assembled system [8], which can be mainly

\* Corresponding author. Tel.: +91 40 2301 6089; fax: +91 40 2301 6032.

E-mail address: [prabu@iith.ac.in](mailto:prabu@iith.ac.in) (G. Prabusankar).

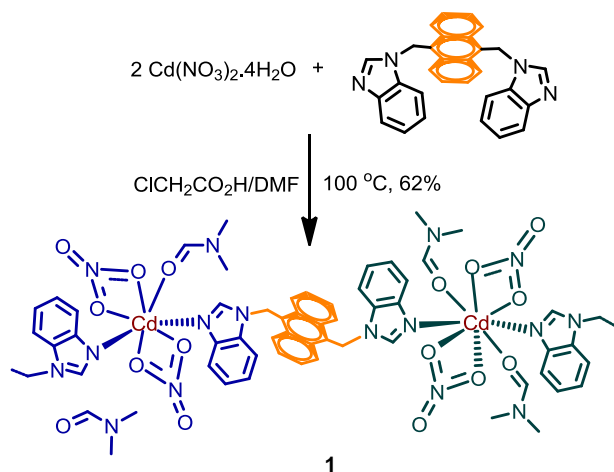
attributed to the steric factors and crystallization conditions. Thus, a detailed study of supramolecular isomerism is essential to understand the self-assembled system of CPs.

It is well-known that the plenty of cadmium coordination polymers exhibiting fascinating structures and various properties, such as luminescence, have been synthesized [9]. Although d–d transitions are not expected for Cd(II) due to a  $d^{10}$  closed shell electronic configuration, ligand-to-ligand charge transfer (LLCT) and ligand-to-metal charge transfer (LMCT) have been reported [10]. To achieve this goal, one effective way is the selection of suitable organic ligands as antenna chromophores, which can improve the emission efficiency of cadmium cations. As of now, a lot of aromatic oxygen/nitrogen donor ligands have been demonstrated to be chromophoric antenna ligands, which are good sensitizers to stimulate cadmium ion luminescence. Among the various luminescent multidentate ligands, flexible multidentate ligands with imidazole groups have the ability to form various types of topological architectures with photoluminescent properties [11]. The flexible multidentate ligands with imidazole groups can be derived using aryl spacers or alkyl spacers. The study for coordination polymers containing the aryl or alkyl substituted bis(imidazole) and tris(imidazole) have already been widely reported with fascinating architectures and interesting properties, whereas only a few coordination polymers based on the anthracene substituted bis(imidazole) have been observed [12–16]. To the best of our knowledge, the anthracene bis(imidazole) ligand coordination chemistry of cadmium is not explored much [15]. Thus in this work, 9,10-bis((benzimidazol)methyl)anthracene (**L**), a ligand having an anthracene chromophoric unit and a flexible bis(imidazole) tail, has been selected to react with  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  to isolate the first one dimensional coordination polymer,  $[\{\text{LCd}(\text{O}_2\text{NO})_2(\text{DMF})_2\}_2\{\text{LCd}(\text{O}_2\text{NO})_2(\text{DMF})(\text{DMF})_2\}]_n$  (**1**) consists of both hexa- and hepta-coordinated cadmium(II) centers. Furthermore, one dimensional coordination polymer,  $[\text{L}'\text{Cd}(\text{O}_2\text{NO})(\text{ONO}_2)(\text{DMF})_2]_n$  (**2**) comprises of hepta-coordinated cadmium(II) center has been isolated for comparison. For which, the sterically less crowded [1,4-bis((imidazol)methyl)benzene] (**L'**) has been selected to react with  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  under similar conditions to yield **2**. Molecules **1** and **2** have been structurally and spectrally characterized.

## Results and discussion

### Synthesis of Cd(II) coordination polymer **1**

The pale yellow crystals of **1** are obtained from the reaction between 9,10-bis((benzimidazol)methyl)anthracene,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$



Scheme 1. Synthesis of **1**.

$4\text{H}_2\text{O}$  and chloro acetic acid in DMF at  $100\text{ }^\circ\text{C}$  for 12 h (Scheme 1). **1** is soluble only in DMSO and insoluble in most of the common solvents. The molecule **1** is characterized by CHN analysis, FT-IR, multinuclear ( $^1\text{H}$  and  $^{13}\text{C}$ ) NMR, UV–vis and fluorescent spectroscopy. The FT-IR spectrum of **1** shows a characteristic stretching frequency for  $\text{C}=\text{O}$  of DMF at  $1651$  and  $1511\text{ cm}^{-1}$ ; in addition to the presence of bridging and free  $\text{NO}_3^-$  ions ( $1440$ ,  $1293$ ,  $1247$  and  $1202\text{ cm}^{-1}$ ).

### Single crystal X-ray structure of Cd(II) coordination polymer **1**

The solid state structure of **1** has been further confirmed by single crystal X-ray diffraction (Figs. 1 and 2). **1** crystallizes in the triclinic space group, *Pt* (Table 1) [17–19]. Asymmetric unit of **1** consists of two cadmium atoms, two 9,10-bis((benzimidazol)methyl)anthracene ligands, four coordinated  $\text{NO}_3^-$  anions, three coordinated DMF molecules and two uncoordinated DMF molecules. Molecule **1** is one dimensional zig-zag coordination polymer, where each cadmium center is bridged by fluorescent active 9,10-bis((benzimidazol)methyl)anthracene ligand (Fig. 2(iii)). Two different coordination modes of cadmium centers are observed in **1**, which is very rare in cadmium chemistry [20]. Interestingly, two octacoordinated and two heptacoordinated cadmium centers are alternatively arranged in one dimensional chain fashion (Fig. 2). The differences in the coordination environment of octacoordinated and heptacoordinated cadmium centers are compared in Fig. 1. The bond distances and angles of octacoordinated and heptacoordinated cadmium centers are compared in Table 2.

The coordination environment around octacoordinated cadmium(II) is satisfied by two 9,10-bis((benzimidazol)methyl)anthracene ligands, two *ansobidentate* nitrate ions and two DMF molecules (Fig. 1(i)). As shown in Fig. 1(i), the coordination geometry around Cd(1B) in  $\text{CdN}_2\text{O}_6$  core resembles distorted triangular dodecahedral geometry, which is comparable to cadmium di-2-pyridyl ketone complex  $[\text{Cd}_2(\text{NO}_3)_4(\text{py})_2\text{CO}]_2$  [21]. Whereas the polyhedron of known octacoordinated Cd(II) complexes are tetragonal antiprism [22], dodecahedron [23], irregular polyhedron with the double pseudo-tetrahedral geometry [24], highly distorted square prism [25] and transition between dodecahedron and tetragonal antiprism [26]. Two adjacent distorted triangular dodecahedral  $\text{CdN}_2\text{O}_6$  cores are linked through 9,10-bis((benzimidazol)methyl)anthracene ligands (Fig. 2(i)).

The  $\text{Cd}-\text{O}_2\text{NO}$  bond lengths around Cd(1B) are not comparable. The  $\text{Cd}(1\text{B})-\text{O}(4\text{B})$  bond distance ( $2.397(6)\text{ \AA}$ ) is considerably shorter than  $\text{Cd}(1\text{B})-\text{O}(7\text{B})$  ( $2.760(8)\text{ \AA}$ ) ( $\Delta d = 0.363\text{ \AA}$ ). Similar trend also observed between  $\text{Cd}(1\text{B})-\text{O}(3\text{B})$  ( $2.488(5)\text{ \AA}$ ) and  $\text{Cd}(1\text{B})-\text{O}(7\text{B})$  ( $2.764(7)\text{ \AA}$ ) ( $\Delta d = 0.276\text{ \AA}$ ), which indicates the existence of *ansobidentate* mode of coordination between cadmium(II) and  $\text{NO}_3^-$  moiety [27]. The  $\text{Cd}-\text{O}(\text{DMF})$  bond lengths are nearly comparable ( $\text{Cd}(1\text{B})-\text{O}(1\text{B})$ ,  $2.390(4)\text{ \AA}$  and  $\text{Cd}(1\text{B})-\text{O}(2\text{B})$ ,  $2.325(5)\text{ \AA}$ ) and  $\text{O}(2\text{B})-\text{Cd}(1\text{B})-\text{O}(1\text{B})$  angle is  $166.3(18)^\circ$ . The  $\text{ONO}_2-\text{Cd}-\text{O}_2\text{NO}$  angles are comparable ( $\text{O}(7\text{B})-\text{Cd}(1\text{B})-\text{O}(5\text{B})$ ,  $142.35(2)^\circ$  and  $\text{O}(3\text{B})-\text{Cd}(1\text{B})-\text{O}(4\text{B})$ ,  $146.02(2)^\circ$ ). The  $\text{Cd}(1\text{B})-\text{N}(2\text{B})$  bond length ( $2.250(6)\text{ \AA}$ ) is considerably shorter than that of  $\text{Cd}(1\text{B})-\text{N}(3\text{B})$  ( $2.311(6)\text{ \AA}$ ). The  $\text{N}(2\text{B})-\text{Cd}(1\text{B})-\text{N}(3\text{B})$  bond angle is  $161.1(2)^\circ$ .

The coordination environment around heptacoordinated cadmium is fulfilled by two 9,10-bis((benzimidazol)methyl)anthracene ligands, two bidentate nitrate ions and one DMF molecules (Fig. 1(ii)). The geometry of heptacoordinated cadmium(II) is in distorted pentagonal bipyramidal geometry. The  $\text{Cd}-\text{O}_2\text{NO}$  bond lengths around heptacoordinated cadmium(II) are comparable ( $\text{Cd}(1\text{A})-\text{O}(1\text{A})$ ,  $2.453(5)$ ;  $\text{Cd}(1\text{A})-\text{O}(2\text{A})$ ,  $2.471(5)$ ;  $\text{Cd}(1\text{A})-\text{O}(3\text{A})$ ,  $2.436(5)$ ;  $\text{Cd}(1\text{A})-\text{O}(4\text{A})$ ,  $2.422(5)\text{ \AA}$ ), which indicates the bidentate nitrate coordination at cadmium center. The  $\text{O}(1\text{A})-\text{Cd}(1\text{A})-\text{O}(4\text{A})$  ( $147.02(17)^\circ$ ) and  $\text{O}(2\text{A})-\text{Cd}(1\text{A})-\text{O}(3\text{A})$  ( $148.21(17)^\circ$ ) bond angles

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