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Zinc(II) and Cadmium(II) coordination polymers constructed from phenylenediacetate ligands

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ABSTRACT

A series of new coordination polymers $\{[Zn(\mu\text{-opda})(\mu\text{-bpa})]\cdot 2H_2O\}_n$ (**1**), $[Zn(\mu_3\text{-ppda})(\mu\text{-bpa})]_n$ (**2**), $[Cd(\mu_3\text{-ppda})(\mu\text{-bpa})]_n$ (**3**), $[Cd(\mu_3\text{-mpda})(\mu\text{-bpa})]_n$ (**4**) and $[Cd(\mu_3\text{-mpda})(\mu\text{-bipy})]_n$ (5), (o/m/ppda = 1,2/1,3/1,4-phenylenediacetate, bpa = 1,2-bi(4-pyridyl)ethane, bipy = 4,4′-bipyridine) were synthesized. Their structures were characterized by elemental analysis, IR spectroscopy, single-crystal and powder X-ray diffraction. Furthermore, the effect of metal sources (zinc acetate and zinc oxide) and acidity of the solution on the structure of the coordination polymers was discussed for complexes **1** and **5**, respectively. The single-crystal X-ray crystallographic studies revealed that complexes **1**, **3**, **4** and **5** are uninodal (4)-connected 2D frameworks and display sql topology with the point symbol of $(4^4.6^2)$. Complex **2** is 3D coordination polymer and exhibits pcu topology with the point symbol of $(4^{12}.6^3)$. In addition, the luminescent properties and thermal behavior of all complexes were also investigated.

1. Introduction

In the last two decades, the design and construction of coordination polymers (CPs) have attracted considerable attention, not only due to their fascinating structures and topologies, but also due to their limitless potential applications in many fields such as storage, separation, purification, catalysis, sensing, etc [1–7]. It is well known that organic ligands are the most important building blocks to construct desirable CPs [8]. In addition, the coordination geometry of the central atom, the pH value of the reaction solution, the reaction temperature and time play an important role in the rational construction of CPs [8]. Rigid aromatic di-, tri-, and tetra-carboxylic acids which have more important advantages than other organic ligands are extensively used [9–11]. In contrast, the flexible carboxylic acids that have both rigid aromatic and flexible aliphatic character, such as phenylenediacetic acid, which possesses ortho-, meta-, and para position isomers have been rarely used for the construction of CPs [12,13]. In fact, they are good candidates for the enrichment of the structural and functional diversities of CPs. Rigid phenyl ring can provide the necessary structural scaffolding [14]. Aliphatic groups, which provide flexibility and conformational freedom, can easily adjust their conformations to meet the coordination requirement of the metal ions. When the carboxylic acid groups completely deprotonated, which results in variable carboxylate binding modes and higher dimensional frameworks [15]. Moreover, they can act not only as a hydrogen-bond acceptor but also as a hydrogen-bond donor, depending upon the number of deprotonated carboxyl groups [16]. Some coordination polymers containing phenylenediacetic acid, d^{10} metal centers and N-containing bidentate ligands, such as 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethane or 1,2-bis(4-pyridyl)ethylene have been studied to build higher dimensional frameworks and novel topology [17–19]. According to the reported studies, the selection of a suitable ligand and the combination of dicarboxylate and dipyridyl ligands with d^{10} metal centers which have large radii, high coordination numbers, and photoluminescent properties are crucial to construct various coordination frameworks with different structures and functions [3,10–12,14–35].

Due to the reasons mentioned above, systematic studies were carried out with the reaction of Cd(II) or Zn(II) sources, the H_2pda isomers, and a series of N-containing auxiliary ligand to investigate the influence of flexible carboxylic acids which possess aromatic and aliphatic groups and N-containing auxiliary ligands on the properties and construction of coordination polymers. In this work, five new coordination polymers, $\{[Zn(\mu\text{-opda})(\mu\text{-bpa})]\cdot 2H_2O\}_n$ (**1**), $[Zn(\mu_3\text{-ppda})(\mu\text{-bpa})]_n$ (**2**), $[Cd(\mu_3\text{-ppda})(\mu\text{-bpa})]_n$ (**3**), $[Cd(\mu_3\text{-mpda})(\mu\text{-bpa})]_n$ (**4**) and $[Cd(\mu_3\text{-mpda})(\mu\text{-bipy})]_n$ (**5**) were successfully synthesized and characterized.

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Table 1
Crystal data and structure refinement parameters for complexes **1**–**5**.

Crystal data	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{22}H_{24}N_2O_6Zn$	$C_{22}H_{20}N_2O_4Zn$	$C_{22}H_{20}CdN_2O_4$	$C_{22}H_{20}CdN_2O_4$	$C_{20}H_{16}CdN_2O_4$
Formula weight	477.80	441.77	488.80	488.80	460.75
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	$P2_1/n$	P-1	P-1	P-1
***a* (Å)**	7.7740 (1)	10.0931 (6)	9.919 (5)	10.0728 (5)	9.1652 (1)
***b* (Å)**	8.8560 (2)	14.2804 (8)	10.556 (5)	10.2300 (5)	9.6897 (1)
***c* (Å)**	16.4130 (2)	13.4732 (8)	10.562 (5)	11.6668 (5)	11.3093 (1)
α (deg.)	86.079 (1)	90.00	82.088 (5)	102.891 (3)	93.087 (1)
***β* (deg.)**	87.8520 (11)	103.016 (1)	64.752 (6)	100.905 (2)	111.0030 (11)
***γ* (deg.)**	81.940 (1)	90.00	71.410 (5)	118.203 (2)	110.136 (1)
V ($Å^3$)	1115.75 (3)	1892.05 (19)	948.1 (8)	970.14 (8)	862.13 (2)
Z	2	4	2	2	2
D_c ($g\ cm^{-3}$)	1.422	1.551	1.712	1.673	1.775
μ (mm^{-1})	1.14	1.33	1.18	1.16	1.30
θ range (deg.)	3.5–26.0	2.3–27.5	2.4–27.4	2.3–23.0	2.5–32.9
Measured refls.	7172	13394	8827	4921	17972
Independent refls.	4332	4334	4319	3353	6213
R_{int}	0.046	0.077	0.044	0.205	0.014
S	0.97	1.00	1.01	1.06	1.14
$R1/wR2$	0.035/0.079	0.035/0.092	0.036/0.079	0.075/0.149	0.035/0.083
$\Delta\rho_{max}/\Delta\rho_{min}$ ($eÅ^{-3}$)	0.37/−0.29	0.68/−0.72	0.76/−1.13	1.70/−2.45	0.66/−0.54

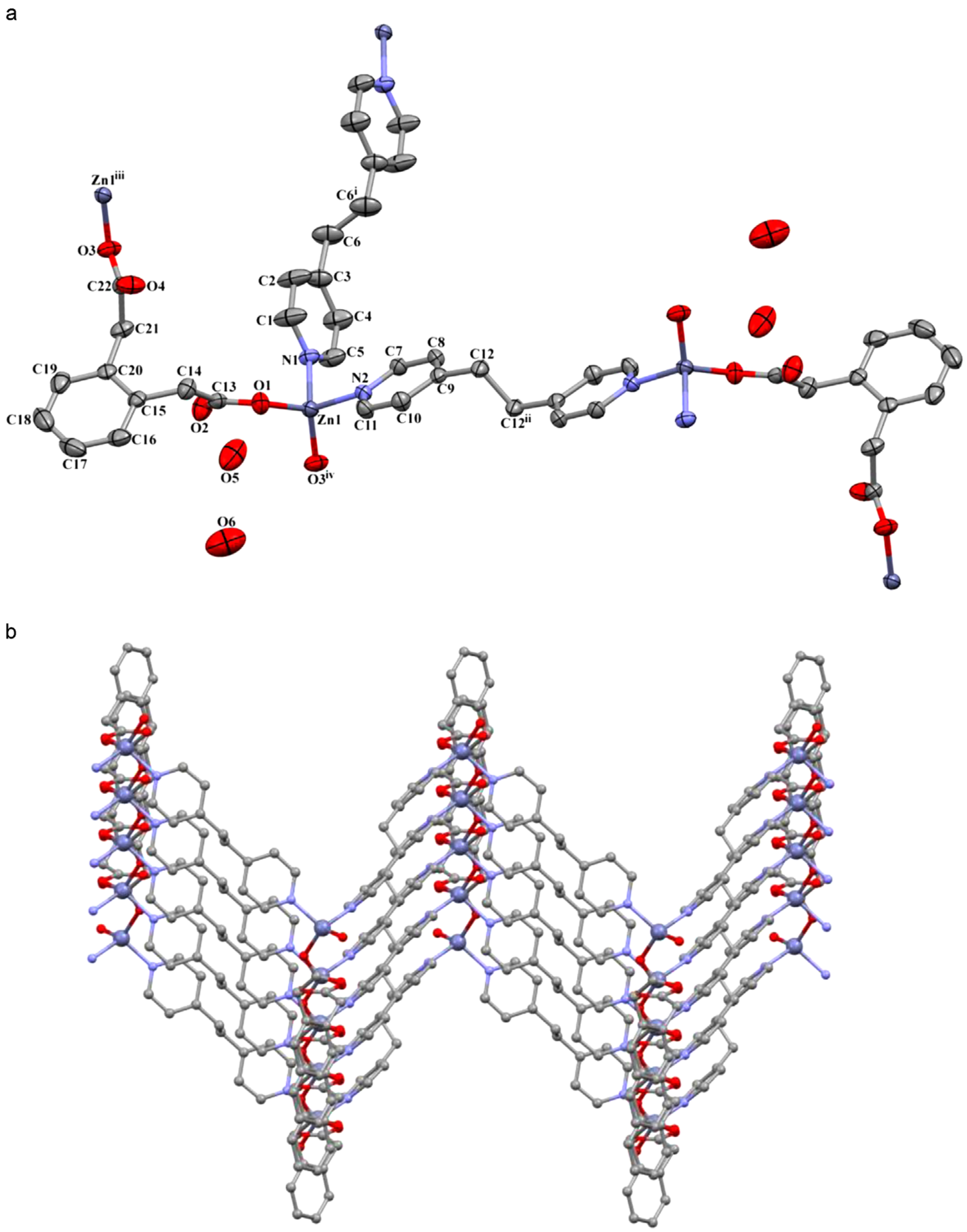

Fig. 1. (a) The molecular structure of **1** showing the atom numbering scheme (b) 2D layer of **1**.