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Syntheses and Characterization of Two Coordination Polymers Constructed by the Ligand 3,5-Bis(pyridin-4-ylmethoxy)benzoic Acid

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Abstract. Two coordination polymers, namely [Zn(L1)(OAc)]·H_2O (**1**) and [Cd(L1)$_2$] (**2**), where L1 = 3,5-bis(pyridin-4-ylmethoxy)benzoic acid, have been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction analysis. Complex **1** has a 2D layer structure in which the hydrogen bonds between lattice water molecules and uncoordinated carboxylate oxygen atoms of the ligand L1 in the adjacent layers extend the 2D layer into a 3D supramolecular architecture. The structure of **2** is a 2D (3,5)-connected net with $(3{\cdot}5^2)(3^2{\cdot}5^3{\cdot}6^4{\cdot}7)$ topology. In addition, the luminescent properties of complexes **1** and **2** have been studied in the solid state at room temperature.

Introduction

The rational design and synthesis of coordination polymers have attracted intense attention in the field of supramolecular chemistry and crystal engineering because of their intriguing aesthetic structures and topological features as well as their potential applications as functional materials [1–4]. It is well known that the multiple coordination sites of ligands can form the structures of higher dimensions and the high symmetry of ligands may result in novel structures [5]. For example, pyridyl dicarboxylic acid ligands, such as pyridine-2,4-dicarboxylic acid, pyridine-2,5-dicarboxylic acid, pyridine-2,6-dicarboxylic acid, pyridine-3,4-dicarboxylic acid and pyridine-3,5-dicarboxylic acid have been widely used by *Kitagawa*, *Wang*, *Cao*, *Zhu* and their co-workers in the construction of high-dimensional structures with large pores or undulated layers [6–10]. However, relative to rigid ligands, flexible ones have more advantages because their flexibility and conformational freedom allow them to get conform to the coordination environment of the transition-metal ions [11]; based on this, we designed a new pyridyl carboxylic acid ligand, 3,5-bis(pyridin-4-ylmethoxy)benzoic acid (L1), which contains a rigid phenyl ring spacer and two freely rotating pyridyl arms. This new ligand may cause the planes of the pyridyl rings to rotate with respect to the plane of the central phenyl ring and therefore it is a good candidate to produce unique structural motifs with beautiful aesthetics.

On the other hand, d^{10} metal (Zn^{II} and Cd^{II}) complexes have attracted extensive interest in recent years because of their high transparency in the UV region and photoluminescent properties [12, 13]. However, to the best of our knowledge, there were no related reports of the polymers constructed by d^{10} metal and the ligand L1 so far. With the aim of understanding the coordination chemistry of L1 and preparing new materials with interesting structural topologies and excellent physical properties, we have recently been engaged in the research of polymer complexes with such ligands.

In this paper we report two new coordination polymers, [Zn(L1)(OAc)]·H_2O (**1**) and [Cd(L1)$_2$] (**2**) (L1 = 3,5-bis(pyridin-4-ylmethoxy)benzoic acid). Complex **1** has a 2D layer structure in which the hydrogen bonds between lattice water molecules and uncoordinated carboxylate oxygen atoms of L1 ligands in the adjacent layers extend the 2D layer into a 3D supramolecular architecture. The structure of **2** is a 2D (3,5)-connected net with $(3{\cdot}5^2)(3^2{\cdot}5^3{\cdot}6^4{\cdot}7)$ topology.

Experimental Section

Materials and Physical Measurements

All reagents and solvents employed were commercially available and used as received without further purification. The ligand L1 was synthesized readily by the procedure reported in the literature [14]. Elemental analyses (C, H and N) were performed with a Perkin–Elmer 240C elemental analyzer. The Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} with a Mattson Alpha-Centauri spectrometer. Solid-state luminescent spectra were measured with a Cary Eclipse spectrophotometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature. Thermogravimetric (TG) analysis was performed with a Perkin–Elmer TG-7 analyzer heated from 40 to 700 °C under nitrogen.

Syntheses

[Zn(L1)(OAc)]·H_2O (1): A mixture of Zn(OAc)$_2$·2H_2O (0.30mmol, 0.066g), L1 (0.20mmol, 0.036g) and NaOH (0.60mmol, 0.024g) in

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H_2O (14ml) was sealed in a 25 mL Teflon-lined stainless steel container, which was heated at 150 °C for 72 h and afterwards cooled down to room temperature at a rate of 5 $°C \cdot h^{-1}$. Colorless crystals of **1** were collected and washed with distilled water and dried in air to give the product; yield, 36.5 % (based on Zn^{II} salts). Elemental analyses calcd. (%) for $C_{21}H_{20}N_2O_7Zn$ (477.76): C, 52.73; H, 4.23; N, 5.86. Found C, 52.66; H, 4.28; N, 5.92. **IR** (KBr pellet): 3448 (s), 1592 (s), 1434 (s), 1374 (s), 1168 (m), 1064 (m), 815 (w), 778 (w) cm^{-1}.

$[Cd(L1)_2]$ (2): Similar procedures were performed to obtain colorless crystals of complex **2**, except that $Cd(OAc)_2 \cdot 2H_2O$ (0.30mmol, 0.080g) was used instead of $Zn(OAc)_2 \cdot 2H_2O$. Yield, 42.5 % (based on Cd^{II} salts). Elemental analyses calcd. (%) for $C_{38}H_{30}N_4O_8Cd$ (783.06): C, 58.28; H, 3.87; N, 7.16. Found C, 58.32; H, 3.89; N, 7.13. **IR** (KBr pellet): 1571 (s), 1396 (s), 1222 (w), 1143 (s), 1049 (m), 803 (m), 774 (s), 663 (w) cm^{-1}.

X-ray Crystallographic Analysis

Data collection of complexes **1** and **2** were performed on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at room temperature. All absorption corrections were performed by using the SADABS program. The crystal structure was solved by direct methods and refined with full-matrix least-squares (SHELXTL-97) with atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of aromatic rings were included in the structure factor calculation at idealized positions by using a riding model. The detailed crystallographic data and structure refinement parameters for complexes **1** and **2** are summarized in Table 1. Selected bond lengths and angles are given in Table 2. CCDC-724696 and -724697 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinements for complexes **1** and **2**.

Complex	1	2
Formula	$C_{21}H_{20}N_2O_7Zn$	$C_{38}H_{30}N_4O_8Cd$
Formula weight	477.76	783.06
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a /Å	8.667(1)	13.098(3)
b /Å	10.414(2)	10.395(3)
c /Å	12.021(2)	24.441(4)
α /°	91.937(3)	90
β /°	108.644(2)	98.350(2)
γ /°	90.073(3)	90
V /Å^3	1027.4(5)	3292(2)
Z	2	4
$D_{calcd.}$ /$g \cdot cm^{-3}$	1.544	1.580
μ /mm^{-1}	1.242	0.726
F(000)	492	1592
Observed reflection/unique	5298/3612	18640/6942
R_{int}	0.0345	0.0368
Goodness-of-fit on F^2	1.037	1.006
R_1 $^{a)}$, wR_2 $^{b)}$ [$I > 2\sigma(I)$]	0.0580, 0.1058	0.0375, 0.0770
R_1, wR_2 (all data)	0.0986, 0.1238	0.0625, 0.0857

a) $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. b) $wR_2 = |\sum w(|F_o|^2-|F_c|^2)|/\sum|w(F_o^2)^2|^{1/2}$.

Table 2. Selected bond lengths /Å and angles /° for complexes **1** and **2**$^{a)}$.

Complex 1			
Zn(1)–O(2)	1.953(3)	Zn(1)–O(5)	1.955(5)
Zn(1)–N(2)#1	2.030(4)	Zn(1)–N(1)#2	2.047(4)
O(2)–Zn(1)–O(5)	101.81(2)	O(2)–Zn(1)–N(2)#1	122.17(2)
O(5)–Zn(1)–N(2)#1	106.72(2)	O(2)–Zn(1)–N(1)#2	97.68(2)
O(5)–Zn(1)–N(1)#2	121.92(2)	N(2)#1–Zn(1)–N(1)#2	107.58(2)
Complex 2			
Cd(1)–O(2)#1	2.209(2)	Cd(1)–O(6)#2	2.266(2)
Cd(1)–O(5)#2	2.581(2)	Cd(1)–N(3)#3	2.316(2)
Cd(1)–N(2)	2.379(3)	Cd(1)–N(4)	2.428(3)
O(2)#1–Cd(1)–O(6)#2	89.32(9)	O(6)#2–Cd(1)–O(5)#2	53.94(7)
O(2)#1–Cd(1)–O(5)#2	143.06(8)	N(3)#3–Cd(1)–O(5)#2	88.01(8)
N(2)–Cd(1)–O(5)#2	93.17(9)	N(4)–Cd(1)–O(5)#2	87.48(9)
O(2)#1–Cd(1)–N(3)#3	128.70(9)	O(6)#2–Cd(1)–N(3)#3	141.94(9)
O(2)#1–Cd(1)–N(2)	91.90(1)	O(6)#2–Cd(1)–N(2)	92.24(9)
N(3)#3–Cd(1)–N(2)	88.61(9)	O(2)#1–Cd(1)–N(4)	88.40(1)
O(6)#2–Cd(1)–N(4)	89.26(9)	N(3)#3–Cd(1)–N(4)	90.03(1)
N(2)–Cd(1)–N(4)	178.47(9)		

a) Symmetry transformations used to generate equivalent atoms: for **1**: #1 $x-1, y, z-1$; #2 $x-1, y-1, z$; for **2**: #1 $x, y-1, z$; #2 $x, y+1, z$; #3 $x+1/2, -y-1/2, z+1/2$.

Results and Discussion

Crystal Structures

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the triclinic space group $P\bar{1}$ and there are one crystallographically independent Zn^{II} ion, one L1 ligand, one OAc^- ligand and one lattice water molecule in the asymmetric unit. As shown in Figure 1a, the Zn^{II} ion is in a tetrahedral arrangement with one carboxylate oxygen atom [Zn–O 1.953(3) Å] of one L1 ligand, one carboxylate oxygen atom [Zn–O 1.955(5) Å] of one OAc^- ligand and two nitrogen atoms [Zn–N 2.030(4)–2.047(4) Å] of two L1 ligand molecules. The Zn–O and Zn–N bond lengths are all in the normal ranges [15].

The coordination modes of L1 ligand in this work are summarized in Scheme 1. In complex **1**, each L1 ligand molecule acts as a tri-connector linking three Zn^{II} ions (Scheme 1a), the carboxylate group connects one Zn^{II} atom through a monodentate oxygen atom, two pyridyl nitrogen atoms bind to two Zn^{II} atoms. Figure 1b shows that in the *ac* plane all zinc atoms are connected with each other by carboxyl groups and pyridyl nitrogen atoms of L1 ligand molecules, thus forming novel $\{Zn_3O_6C_{27}N_4\}$ 40-membered rings. All the rings are further linked to form a 2D Zn–O–C–N layer. By trying the Zn^{II} atom as a single node and connecting the nodes according to the connectivity defined by the geometrical centers of the L1 ligand, a distorted 2D (6^3) network sustained by 3-connected nodes is then yielded, as illustrated in Figure 1c. Moreover, the hydrogen bonds between lattice water molecules and uncoordinated carboxylate oxygen atoms of L1 ligand molecules in the adjacent layers extend the 2D layer into a 3D supramolecular architecture.

The crystal structure of **2** contains one Cd^{II} atom and two L1 ligands in the asymmetric unit. As shown in Figure 2a, each Cd^{II} atom is coordinated by three carboxylate oxygen atoms [Cd–O 2.209(2)–2.581(2) Å] of two L1 ligand molecules and three nitrogen atoms [Cd–N 2.316(2)–2.428(3) Å] of two L1 ligands to furnish a distorted octahedral arrangement. The Cd–O and Cd–N bond lengths are all in the normal ranges [16]. In complex **2**, the L1 ligand molecules adopt two coordination modes: one L1 (L1b) ligand bridges two Cd^{II} atoms through one carboxylate

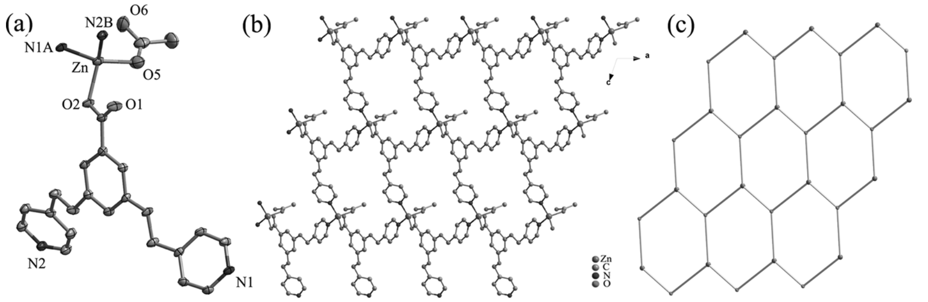
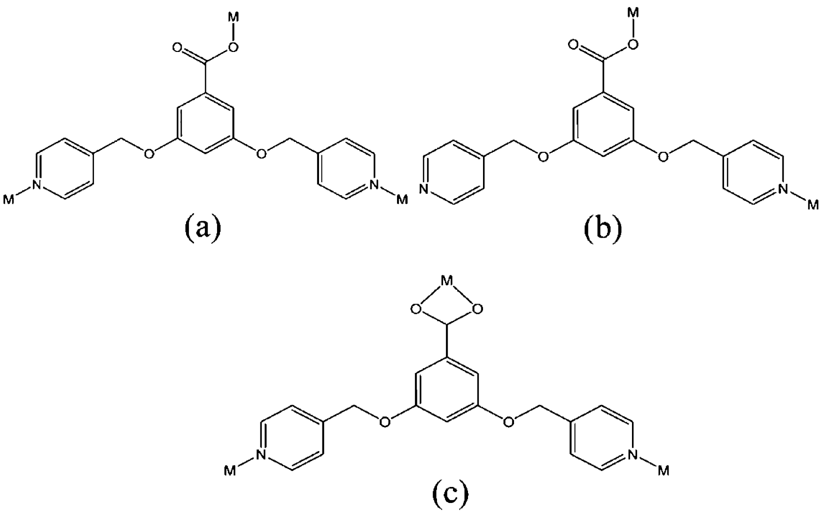


Figure 1. (a) The coordination environment of Zn^{II} atoms in complex **1**. All of the hydrogen atoms and lattice water molecules were omitted for clarity. (b) View of the 2D layer structure of **1** along the *ac* plane. (c) Schematic view of the 2D 3-connected net of **1** with (6^3) topology. (Symmetry transformations used to generate equivalent atoms: A, 1+*x*, 1+*y*, *z*; B, *x*, *y*, −1+*z*.).



Scheme 1. Coordination modes of the L1 ligand in complexes **1** and **2**.

group and one pyridyl nitrogen atom, containing an uncoordinated pyridyl nitrogen atom; and the other molecule (L1c) connects three Cd^{II} atoms through one carboxylate group and two pyridyl nitrogen atoms (Scheme 1b and Scheme 1c). The Cd^{II} atoms are first connected by L1b to generate 1D zigzag chains with the separation between two Cd^{II} atoms of 10.395 Å. The 1D zigzag chains are further connected by L1c from the positions of the metal atoms to generate a 2D layer structure (Figure 2b).

Topologically, each Cd^{II} atom is attached to five L1 ligand molecules, which can be considered as a 5-connected node; each L1b ligand connects to two Cd^{II} atoms and each L1c molecule connects three Cd^{II} atoms, thus, L1b can be considered as a linear

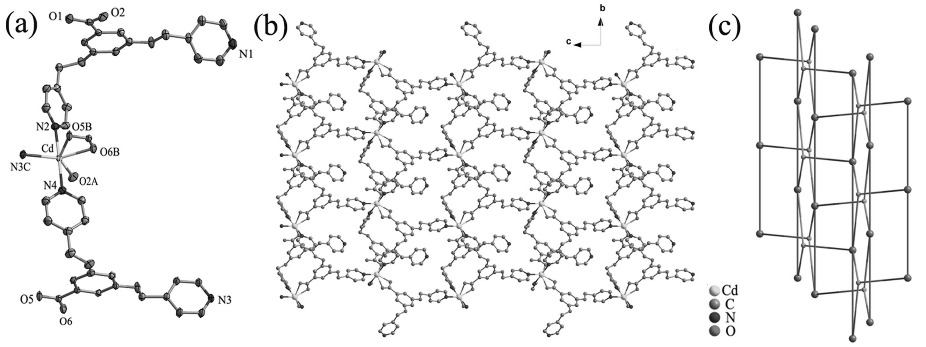


Figure 2. (a) The coordination environment of Cd^{II} atoms in complex **2**. All of the hydrogen atoms were omitted for clarity. (b) View of the 2D layer structure of **2** along the *bc* plane. (c) Schematic view of the 2D (3,5)-connected net of **2** with $(3.5^2)(3^2{\cdot}5^3{\cdot}6^4{\cdot}7)$ topology. (Symmetry transformations used to generate equivalent atoms: A, 1+*x*, 1+*y*, *z*; B, *x*, *y*, −1+*z*.).

linker between two Cd^{II} atoms, whereas L1c can be considered as a 3-connected node. On the basis of this simplification, complex **2** possesses a 2D (3,5)-connected net, as shown in Figure 2c. The Schläfli symbol of the network is $(3{\cdot}5^2)(3^2{\cdot}5^3{\cdot}6^4{\cdot}7)$. In the literature, the (3,5)-connected frameworks are often encountered [17], but we are not aware of a precedent characterized by such topology like that found in **2**.

As to the synthesis of complexes **1** and **2**, all the reaction conditions are the same except for the difference of the metal ions. From the structural difference of **1** and **2**, we can see that the increase in coordination number (from 4 to 6) of metal ions induces the progressive increase in complexity of the ultimate net [from uninodal 3 to binodal (3,5)]; in other words, the coordination number of metal ions plays a significant role in tuning the connectivity of a specific network. On the other hand, the flexible ligand L1 has the advantage that its flexibility and conformational freedom allows it to get conform to the coordination environment of the transition metal ions. This is further evidence that the selection of suitable metal ions and organic ligands is a major strategy to synthesize functional materials with useful properties.

Luminescent Properties

The photoluminescent behaviors of polymers **1**, **2** and the free ligand L1 were studied in the solid state at room temperature. As shown in Figure 3, the main emission peak of L1 is at 391 nm (λ_{ex} = 246 nm), which can be assigned to $\pi^* \rightarrow n$ and $\pi^* \rightarrow \pi$ transitions of the intraligands. Complex **1** shows the emission maxima at 423 nm (λ_{ex} = 374 nm), complex **2** shows the emission maxima at 405 nm (λ_{ex} = 365 nm). The emission of complexes **1** and **2** may be attributed to intraligand fluorescence emission [5b,18].

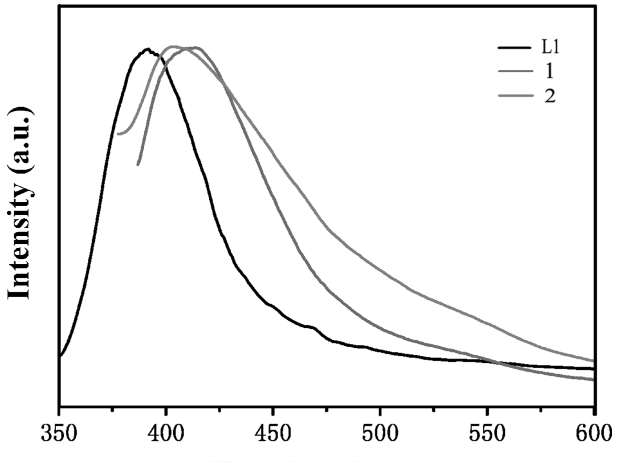


Figure 3. Solid-state luminescent spectra of L1, **1** and **2** at room temperature.

Thermal Properties

To study the thermal stability of the complexes thermogravimetric (TG) analyses were performed on polycrystalline samples under nitrogen with a heating rate of 10 °C·min^{-1} (Figure 4). The TG curve of **1** shows that the first weight loss of 3.64 % between 50 and 140 °C corresponding to the loss of the lattice water molecules (calcd. 3.77 %), afterwards it is stable up to 240 °C. The framework collapsed in the temperature range of 240–560 °C before the final formation of ZnO (obsd. 17.26 %, calcd. 17.03 %). The TG curve of **2** shows one main weight loss. No weight losses were observed for the complex up to 300 °C; above 300 °C, significant weight losses occurred and ended at 540 °C, indicating the removal of the corresponding organic components. The remaining weight may correspond to the final products of CdO (obsd. 16.58 %, calcd. 16.40 %).

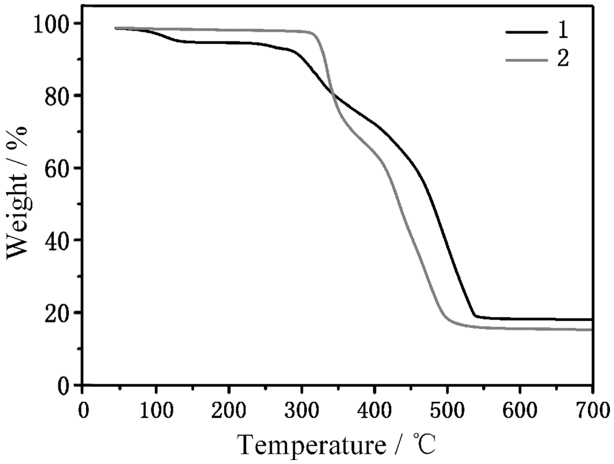


Figure 4. TG curves of **1** and **2**.

Conclusion

In summary, we synthesized two novel coordination polymers, namely $[Zn(L1)(OAc)]{\cdot}H_2O$ (**1**) and $[Cd(L1)_2]$ (**2**), constructed from 3,5-bis(pyridin-4-ylmethoxy)benzoic acid ligand under hydrothermal conditions. The successful syntheses of the two complexes indicate that it is promising to build up unusual architectures by combining transition metals and L1 ligands, thus opening a new field in the preparation of metal coordination polymers with potential luminescent properties.

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