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Syntheses, structures, and properties of coordination polymers based on acrylpimaric acid

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ABSTRACT

Using acrylpimaric acid (H_2L) as the ligands, two coordination polymers $\{[Cd_2L_2(DMF)(H_2O)_{0.5}] \cdot 0.5H_2O\}_n$ (**1**) and $[Zn_3L_2(\mu_3-OH)_2]_n$ (**2**) were successfully prepared under solvothermal condition, and characterized by elemental analysis, IR, and single crystal X-ray diffraction. In **1**, there is a tetranuclear Cd(II) unit consisting of 5-, 6-, and 7-coordinated Cd(II) ions. The unit forms a 1D chain structure along *a* axis, which is interconnected through the weak intermolecular C–H...O hydrogen bondings. In **2**, there is a tetranuclear Zn(II) unit consisting of 4-, and 6-coordinated Zn(II) ions. The tetranuclear unit produces a 1D infinite nanosized ribbon along the *a* axis, which is connected through the L ligands to form a 2D layer. The framework of **1** and **2** began to decompose at ca. 370 °C, and displayed medium fluorescence emission peaks at ca. 430 nm.

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1. Introduction

Coordination polymers built from transition metal ions and organic bridging ligands have attracted considerable interest not only due to their fascinating structural beauty and diversity but also their promising applications in gas storage, selective gas adsorption and separation, optics, electrics, magnetism, molecular recognition and catalysis [1]. Over the past decades, a large number of coordination polymers have been successfully constructed. Furthermore, some coordination polymers with specific topologies can be designed by the wise selection of metal ions and organic ligands [2]. However, precise control of the coordination polymers structure through a self-assembly process is still exceedingly difficult because subtle factors may affect the assembly results. The nature of the ligand, metal ion, the metal–ligand ratio, pH value, and other factors can impact the final topology of the coordination polymers, leading to unexpected structural diversity. Among all the factors, the choice of the ligands is very important because it determines the macrostructures of the final coordination polymers, as does the choice of the metal ions. So far, numerous rigid aromatic multicarboxylic acids such as 1,4-benzenedicarboxylic acid (H_2BDC) [3], 1,3,5-benzenetricarboxylic acid (H_3BTC) [4], and 4,4'-biphenyldicarboxylic acid (H_2BPDC) [5], have been adopted

as organic linkers. Flexible aliphatic carboxylic acid ligand such as mesoxalic acid [6,7], glutaric acid [8–11], and fumaric acid [12,13], have been reported. However, far less effort has been expended on rigid and flexible acyl carboxylic acids [14]. In this work, a pine rosin derivative, acrylpimaric acid (Scheme 1), has been used as organic linker in order to synthesize novel coordination polymers. Notably, rosin is an abundant and renewable material composed of a series of diterpenic resin acids. Its derivatives have been widely used in production and daily life [15]. This work may expand rosin's application.

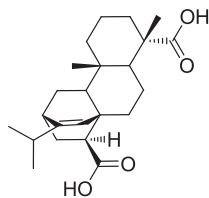
2. Experimental

2.1. Materials and measurements

All chemicals purchased were of analytical grade and used as received. Elemental analyses (C, H, N) were carried out with a Thermo Finnigan Flash 1112A elemental analyzer. IR spectra were recorded in the range 4000–400 cm^{-1} using KBr pellets on a Bruker Vector 22 FT-IR spectrophotometer. Thermogravimetric analyses (TGA) were performed on a NETZSCH STA 449C thermal analyzer under nitrogen atmosphere at a heating rate of 10 °C min^{-1} . Powder X-ray diffraction (XRD) data were collected on a Bruker D8 Advance diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Fluorescence spectroscopy was recorded on a Perkin-Elmer LS-55 spectrophotometer.

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Scheme 1. Acrylpimaric acid (H_2L).

2.2. Synthesis

2.2.1. Synthesis of the ligand H_2L

H_2L was obtained via Diels–Alder reaction of levopimaric acids and acrylic acid, which was synthesized by a modified method according to literature [16] as shown in Scheme 2.

2.2.2. Preparation of $[Cd_2L_2(DMF)(H_2O)_{0.5}] \cdot 0.5H_2O$ (**1**)

$[Cd_2L_2(DMF)(H_2O)_{0.5}] \cdot 0.5H_2O$ (**1**) was synthesized as follows: a mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.1542 g, 0.5 mmol), H_2L (0.1873 g, 0.5 mmol), DMF (10 mL), and H_2O (1.5 mL) was heated in a 25 mL stainless-steel reactor lined with Teflon at 85 °C for 3 days and after cooled to room temperature, colorless needle crystals of **1** suitable for X-ray diffraction were obtained. Yield, 60.1% (0.1595 g) based on ligand. IR (cm^{-1}): 3430(w), 2925(s), 1656(s), 1547(s), 1399(s). Anal. Calc. for $C_{49}H_{73}Cd_2NO_{10}$: C, 55.47; H, 6.94; N, 1.32. Found: C, 55.65; H, 6.83; N, 1.16%.

2.2.3. Preparation of $[Zn_3L_2(\mu_3-OH)_2]_n$ (**2**)

$[Zn_3L_2(\mu_3-OH)_2]_n$ (**2**) was synthesized as follows: a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.0119 g, 0.04 mmol), H_2L (0.0150 g, 0.04 mmol), *m*-hydroxybenzoic acid (0.0059 g, 0.04 mmol), CH_3CN (4 mL), CH_3OH (2 mL), H_2O (2 mL) and three drops of acetic acid (2 M) was heated in a 25 mL capacity stainless-steel reactor lined with Teflon at 120 °C for 3 days and after cooled to room temperature, colorless needle crystals of **2** suitable for X-ray diffraction were obtained. Yield, 76.1% (0.0099 g) based on $Zn(NO_3)_2 \cdot 6H_2O$. IR (cm^{-1}): 3612(s), 3432(w), 2924(s), 1578(s), 1403(s). Anal. Calc. for $C_{46}H_{66}O_{10}Zn_3$: C, 56.65; H, 6.82. Found: C, 56.76; H, 6.65%.

2.3. X-ray crystallography

Diffraction data for **1** and **2** were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Empirical absorption corrections were applied by using the *SADABS* program. The structures were

Table 1
Crystal data and structure refinement details for **1** and **2**.

Complexes	1	2
Empirical formula	$C_{49}H_{73}Cd_2NO_{10}$	$C_{46}H_{66}O_{10}Zn_3$
Formula weight	1060.88	975.10
Crystal system	orthorhombic	orthorhombic
Space group	$P222_1$	$C222_1$
<i>a</i> (Å)	11.3112(18)	6.5049 (6)
<i>b</i> (Å)	15.137(2)	22.0211(19)
<i>c</i> (Å)	29.387(5)	29.430(3)
<i>V</i> (Å ³)	5031.6(14)	4215.8(6)
<i>Z</i>	4	4
<i>D_c</i> (g cm ⁻³)	1.400	1.536
μ (mm ⁻¹)	0.899	1.753
Flack parameter	0.00(7)	0.00(2)
<i>F</i> (000)	2200	2048
<i>T</i> (K)	173(2)	173(2)
Crystal size (mm)	0.14 × 0.12 × 0.10	0.15 × 0.13 × 0.12
θ Range (°)	1.35–25.02	1.38–25.49
Reflections collected	26395	15450
Independent reflections	8789	3902
Reflections observed [<i>I</i> > 2 σ (<i>I</i>)]	6612 (<i>R</i> _{int} = 0.0529)	3217 (<i>R</i> _{int} = 0.0549)
Data/restraints/parameters	8789/313/562	3902/60/277
Goodness-of-fit on (GOF) <i>F</i> ²	1.051	1.056
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0880/0.2335	0.0436/0.1044
<i>R</i> indices (all data)	0.1120/0.2489	0.0566/0.1101
Largest difference peak and hole (e Å ⁻³)	4.031, –1.558	1.074, –0.606

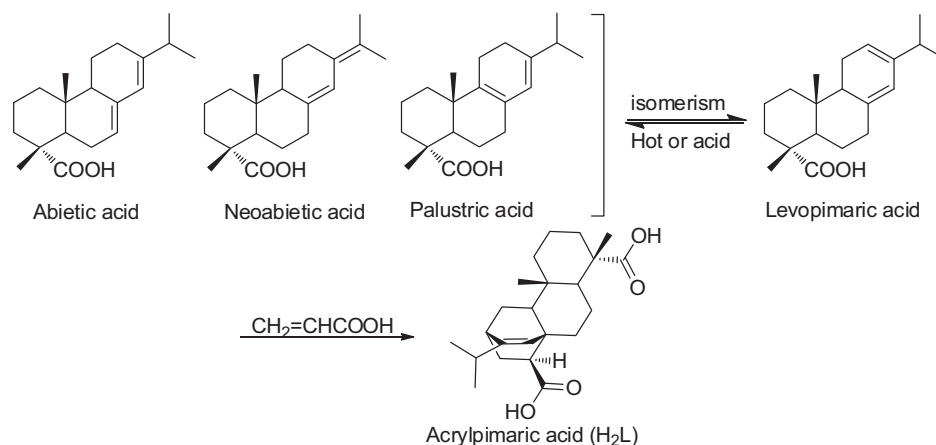
solved by direct methods and refined by the full-matrix least-squares based on F^2 using *SHELXL-97* program. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, except for those of the water molecules, were placed on calculated positions (C–H 0.93–0.98 Å) and assigned isotropic thermal parameters riding on their parent atoms, while the H atoms of water molecules were located from the different map. C21 in **2** is disordered over two sites and fixed at 0.5. The crystal data and structure refinement of **1** and **2** are summarized in Table 1. Selected bond lengths and angles of **1** and **2** are listed in Table S1 and Table S2, respectively. The hydrogen-bonding geometry parameters of **1** are listed in Table S3.

3. Results and discussion

3.1. Description of the crystal structures of **1** and **2**

3.1.1. $[Cd_2L_2(DMF)(H_2O)_{0.5}] \cdot 0.5H_2O$ (**1**)

X-ray crystallographic analysis reveals that **1** crystallizes in a chiral space group $P222_1$ with a Flack parameter of 0.00(7) [17].

Scheme 2. The preparing process of the ligand H_2L .

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