两个包含醚氧桥联三羧酸配体的锌(II) 配位聚合物的合成、晶体结构及荧光性质

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摘要:选用 2 种醚氧桥联三羧酸配体(H_3 cpta 和 H_3 dbba)和 4,4'-联吡啶(4,4'-bipy)或菲咯啉(phen)与 $ZnCl_2$ 进行水热合成反应,构筑了 2 个一维链状配位聚合物[$Zn(\mu$ -Hcpta)(4,4'-bipy)(H_2O)], (1)和{[$Zn_3(\mu_3$ -dbba)₂(phen)₃]·6 H_2O }, (2),并对其结构和荧光性质进行了研究。结构分析结果表明 2 个配合物分别属于单斜晶系 P_2 1 和 P_2 2 空间群。配合物 1 和 2 具有两种不同的一维链结构。

关键词:配位聚合物;三羧酸配体;荧光

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Syntheses, Crystal Structures and Luminescent Properties of Two Zinc(II) Coordination Polymers Constructed from Ether-Bridged Tricarboxylic Acid

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Abstract: Two 1D zinc(II) coordination polymers, namely $[Zn(\mu-Hcpta)(4,4'-bipy)(H_2O)]_n$ (1) and $\{[Zn_3(\mu_3-dbba)_2(phen)_3] \cdot 6H_2O\}_n$ (2), have been constructed hydrothermally using two ether-bridged tricarboxylic acids: 2-(4-carboxylphenoxy)terephthalic acid (H₃cpta) and 2-(3,5-dicarboxylatobenzyloxy)benzoic acid (H₃dbba), 4,4'-bipyridine (4,4'-bipy), 1,10-phenanthroline (phen) and zinc chloride. Single-crystal X-ray diffraction analyses revealed that two complexes crystallize in the monoclinic system, space groups $P2_1$ or I2. Complexes 1 and 2 show two different 1D chain structures. CCDC: 1866025, 1; 1866026, 2.

Keywords: coordination polymer; tricarboxylic acid; luminescent properties

0 Introduction

Over the past decades, there has been a deal of great interest in constructing zinc coordination polymers (CPs) due to their novel structural features and promising functional properties in the areas of photochemistry, selective sensing, catalysis, antibiosis, or gas adsorption^[1-8]. However, the construction of coordination polymers in a predictable and controlled manner still remains a challenging task, since their

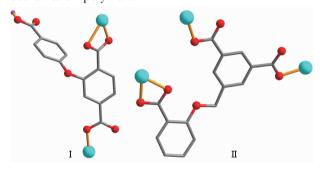
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structural and topological characteristics significantly depend on a lot of synthetic parameters^[9-12], such as the metal atoms, the type of the main building blocks, templates or auxiliary ligands^[13-16]. The preliminary work shows that different aromatic multicarboxylic acids have been extensively used as versatile building blocks toward the assembly of coordination polymers^[1,10,13,16-17].

In order to extend our research in this field, we have selected two semi-rigid ether-bridged tricarboxylate ligands (Scheme 1), namely 2-(4-carboxylphenoxy) terephthalic (H₃cpta) and 2-(3,5-dicarboxylatobenzyloxy)benzoic (H₃dbba) acids, and explored them for the construction of novel zinc (II) coordination polymers. Both H₃cpta and H₃dbba blocks show several interesting features: (1) they can rotate or twist to generate different angles between the two phenyl planes via the ether-oxygen functionality to furnish a subtle conformational adaptation; (2) both blocks possess seven potential coordination sites (six carboxylate O atoms and one O-ether functionality), thus leading to a variety of potential coordination modes; (3) two blocks still remain largely unexplored in the design of coordination polymers.



Scheme 1 Coordination modes of Hcpta²⁻ and dbba³⁻ ligands in complexes 1 and 2

Herein we report the syntheses, crystal structures, and luminescent properties of two Zinc(II) coordination polymers constructed from two ether-bridged tricarboxylic acids.

1 Experimental

1.1 Reagents and physical measurements

All chemicals and solvents were of AR grade and used without further purification. Carbon, hydrogen and nitrogen were determined using an Elementar Vario EL elemental analyzer. IR spectra were recorded using KBr pellets and a Bruker EQUINOX 55 spectrometer. Thermogravimetric analysis (TGA) data were collected on a LINSEIS STA PT1600 thermal analyzer with a heating rate of 10 ℃·min⁻¹. Excitation and emission spectra were recorded for the solid samples on an Edinburgh FLS920 fluorescence spectrometer at room temperature.

1.2 Synthesis of $[Zn(\mu-Hcpta)(4,4'-bipy)(H_2O)]_n$ (1)

A mixture of ZnCl₂ (0.041 g, 0.30 mmol), H_3 cpta (0.091 g, 0.30 mmol), 4,4'-bipy (0.047 g, 0.3 mmol), NaOH (0.024 g, 0.60 mmol) and H_2 O (10 mL) was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C · h⁻¹. Colorless block-shaped crystals of **1** were isolated manually, and washed with distilled water. Yield: 55% (based on H_3 cpta). Anal. Calcd. for $C_{25}H_{18}ZnN_2O_8(\%)$: C 55.62, H 3.36, N 5.19; Found(%): C 55.74, H 3.37, N 5.16. IR (KBr, cm⁻¹): 3 658w, 3 060w, 1 702w, 1 576s, 1 540w, 1 492w, 1 413s, 1 366m, 1 234m, 1 167w, 1 130w, 1 071w, 1 040w, 1 008w, 957w, 909w, 857w, 820w, 783w, 763w, 720w, 694w, 641w.

1.3 Synthesis of $\{[\mathbf{Zn}_3(\mu_3\text{-dbba})_2(\mathbf{phen})_3]\cdot 6\mathbf{H}_2\mathbf{O}\}_n$ (2)

Complex **2** was prepared by $ZnCl_2$ (0.041 g, 0.30 mmol), H_3dbba (0.063 g, 0.2 mmol), phen (0.060 g, 0.3 mmol), NaOH (0.024 g, 0.60 mmol) and H_2O (10 mL) using the same procedure for complex **1**. Colorless block-shaped crystals of **2** were isolated manually, and washed with distilled water. Yield: 60% (based on H_3dbba). Anal. Calcd. for $C_{68}H_{54}Zn_3N_6O_{20}(\%)$: C 55.51, H 3.70, N 5.71; Found (%): C 55.37, H 3.68, N 5.74. IR (KBr, cm⁻¹): 3 440m, 1 608s, 1 586s, 1 564s, 1 520 w, 1 487w, 1 426m, 1 364s, 1 276w, 1 251w, 1 145w, 1 105w, 996w, 908w, 850m, 809w, 777m, 726m, 686w, 646w. The complexes are insoluble in water and common organic solvents, such as methanol, ethanol, acetone and DMF.

1.4 Structure determinations

Two single crystals with dimensions of 0.25 mm×

0.23 mm×0.22 mm (1) and 0.28 mm×0.25 mm×0.18 mm (2) were collected at 293(2) K on a Bruker SMART APEX II CCD diffractometer with Mo $K\alpha$ radiation (λ =0.071073 nm). The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-2014 program^[18]. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were positioned geometrically and refined using

a riding model. Details of the crystal parameters, data collection and refinements for 1 and 2 are summarized in Table 1. The selected bond lengths and angles for complexes 1 and 2 are listed in Table 2. Hydrogen bond parameters of complexes 1 and 2 are given in Table 3 and 4.

CCDC: 1866025, 1; 1866026, 2.

Table 1 Crystal data for complexes 1 and 2

Complex	1	2
Chemical formula	$C_{25}H_{18}ZnN_2O_8$	$C_{68}H_{54}Zn_3N_6O_{20}$
Molecular weight	539.78	1 471.28
Crystal system	Monoclinic	Monoclinie
Space group	$P2_1$	<i>I</i> 2
a / nm	0.593 97(3)	2.039 9(2)
<i>b</i> / nm	1.559 08(8)	0.968 52(7)
c / nm	1.231 11(6)	1.765 05(19)
β / (°)	91.014(4)	109.568(12)
V / nm^3	1.139 90(10)	1.650 95(17)
Z	2	2
F(000)	552	1 508
Crystal size / mm	0.25×0.23×0.22	0.28×0.25×0.18
θ range for data collection / (°)	3.307~25.049	3.463~25.049
Limiting indices	$-5 \le h \le 7, -18 \le k \le 16, -14 \le l \le 11$	$-24 \leq h \leq 13, -10 \leq k \leq 11, -16 \leq l \leq 21$
Reflection collected, unique $(R_{\rm int})$	4 211, 3 507 (0.043 5)	6 003, 4 757 (0.035 0)
$D_{\rm c}$ / (g · cm ⁻³)	1.573	1.487
μ / mm $^{ ext{-l}}$	1.133	1.166
Data, restraint, parameter	3 507, 1, 327	4 757, 1, 438
Goodness-of-fit on \mathbb{F}^2	1.073	1.080
Final R indices $[I \ge 2\sigma(I)] R_1, wR_2$	0.049 6, 0.110 6	0.051 2, 0.106 4
R indices (all data) R_1 , wR_2	0.062 9, 0.123 8	0.065 9, 0.120 2
Largest diff. peak and hole / $(e \cdot nm^{-3})$	366 and -334	492 and -333

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

		1			
Zn(1)-O(1)	0.195 2(7)	Zn(1)-O(3)A	0.231 5(6)	Zn(1)-O(4)A	0.208 4(7)
Zn(1)-O(8)	0.199 8(6)	Zn(1)-N(1)	0.202 8(7)		
O(1)-Zn(1)-O(8)	98.3(3)	O(1)-Zn(1)-N(1)	128.6(3)	O(8)-Zn(1)-N(1)	96.7(3)
O(1)-Zn(1)-O(4)A	105.7(3)	O(8)- $Zn(1)$ - $O(4)A$	95.8(3)	N(1)- $Zn(1)$ - $O(4)A$	121.2(3)
O(1)-Zn(1)-O(3)A	91.6(3)	O(8)- $Zn(1)$ - $O(3)A$	154.9(2)	N(1)- $Zn(1)$ - $O(3)A$	94.9(3)
O(3)A-Zn(1)-O(4)A	59.2(2)				
		2			
Zn(1)-O(2)	0.199 9(5)	Zn(1)-O(6)A	0.214 6(6)	Zn(1)-O(7)A	0.215 9(7)
Zn(1)- $N(1)$	0.210 3(7)	$\operatorname{Zn}(1)\text{-}\operatorname{N}(2)$	0.209 2(7)	Zn(2)-O(4)	0.198 7(5)
Zn(2)-O(4)B	0.198 7(5)	Zn(2)-N(3)	0.209 7(7)	Zn(2)- $N(3)B$	0.209 7(7)

Continued Table 2					
O(2)-Zn(1)-N(2)	112.1(2)	O(2)-Zn(1)-N(1)	107.7(3)	N(1)-Zn(1)-N(2)	79.7(3)
O(2)- $Zn(1)$ - $O(6)A$	98.6(2)	O(6)A-Zn(1)-N(2)	94.6(3)	N(1)- $Zn(1)$ - $O(6)A$	153.5(2)
O(2)- $Zn(1)$ - $O(7)A$	136.1(3)	N(2)- $Zn(1)$ - $O(7)A$	107.6(3)	N(1)- $Zn(1)$ - $O(7)A$	96.9(2)
O(6)A-Zn(1)-O(7)A	59.8(2)	O(4)- $Zn(2)$ - $O(4)B$	124.6(3)	O(4)- $Zn(2)$ - $N(3)B$	122.0(2)
O(4)- $Zn(2)$ - $N(3)$	100.7(2)	N(3)- $Zn(2)$ - $N(3)B$	79.5(4)		

Symmetry codes: A: -x+2, y-1/2, -z+1 for 1; A: -x+1, y, -z; B: -x+1, y, -z+1 for 2

Table 3 Hydrogen bond parameters for complex 1

D–H···A	d(D-H) / nm	$d(\mathbf{H}\cdots\mathbf{A})$ / nm	$d(\mathrm{D}\cdots\mathrm{A})$ / nm	∠ DHA / (°)
O(6)-H(1)···O(2)A	0.082	0.188	0.266 7	162.0
O(8)- $H(1W)$ ··· $N(2)B$	0.086	0.191	0.273 9	163.0
O(8)- $H(2W)$ ··· $O(6)$ C	0.086	0.188	0.271 0	163.3

Symmetry codes: A: x+1, y, z-1; B: x, y, z-1; C: -x+1, y-1/2, -z+1

Table 4 Hydrogen bond parameters for complex 2

D–H···A	d(D-H) / nm	$d(\mathbf{H}\cdots\mathbf{A})$ / nm	$d(\mathrm{D}\cdots\mathrm{A})$ / nm	∠DHA / (°)
O(8)-H(1W)···O(3)	0.085	0.207	0.291 6	179.7
O(8)- $H(2W)$ ··· $O(9)A$	0.085	0.187	0.271 8	179.4
O(9)- $H(3W)$ ··· $O(4)$	0.085	0.207	0.292 3	179.7
O(9)- $H(4W)$ ··· $O(7)B$	0.085	0.196	0.281 0	179.2
O(10)- $H(5W)$ ··· $O(1)$	0.085	0.191	0.276 4	179.0
O(10)- $H(6W)$ ··· $O(8)$	0.085	0.199	0.283 9	178.9

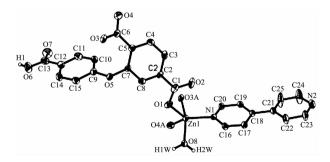
Symmetry codes: A: -x+1, γ , -z+1; B: -x+3/2, $\gamma-1/2$, -z+1/2

2 **Results and discussion**

Description of the structures of complexes

2.1.1 $[Zn(\mu-Hcpta)(4,4'-bipy)(H_2O)]_n$ (1)

Complex 1 is a 1D coordination polymer and its asymmetric unit consists of a Zn1 atom, a μ-Hcpta²⁻ block, one 4,4'-bipy ligand and one coordinated water molecule. As shown in Fig.1, penta-coordinate Zn1 atom adopts a distorted trigonal bipyramid {ZnNO₄}



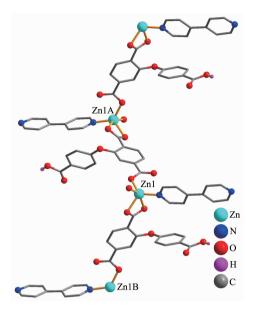
H atoms and lattice water molecules are omitted for clarity except H of COOH group; Symmetry codes: A: -x+2, y-1/2, -z+1

Fig.1 Drawing of the asymmetric unit of complex 1 with 30% probability thermal ellipsoids

geometry, which is taken by three carboxylate O atoms from two different μ-Hcpta²⁻ linkers, one O atom from the coordinated water molecule and one N atom from the 4,4'-bipy moiety. Distances of the Zn-O bonds vary from 0.195 2(7) to 0.231 5(6) nm, while the Zn-N ones are 0.202 8(7) nm; all of them are in good agreement with those in related Zn(II) complexes^[2,13-14]. The Hcpta²⁻ moiety acts as a μ-linker (Scheme 1, mode I) with two COO groups showing monodentate or bidentate modes; the COOH functionality remains uncoordinated. The 4,4'-bipy moiety adopts a terminal coordination fashion. In Hcpta²⁻, a dihedral angle (between two benzene rings) and a C-O_{ether}-C angle are 67.27° and 118.46° , respectively. The μ -Hcpta²⁻ blocks connect the Zn1 centers to form a 1D chain structure with the Zn1···Zn1 separation of 1.087 5(6) nm (Fig.2).

2.1.2 $\{[Zn_3(\mu_3-dbba)_2(phen)_3]\cdot 6H_2O\}_n$ (2)

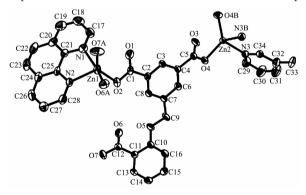
Polymer 2 also discloses a 1D chain structure and its asymmetric unit comprises two individual Zn (II) atoms (Zn1 with full occupancy; Zn2 with half



Symmetry codes: A: -x+2, y+1/2, -z+1; B: -x+2, y-1/2, -z+1

Fig.2 Perspective of 1D chain parallel to the bc plane in 1

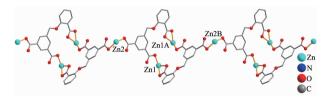
occupancy), a μ_3 -dbba³⁻ block, one and a half phen ligand and three lattice water molecules. As illustrated in Fig.3, the five-coordinate Zn1 atom is surrounded by three O atoms from two different μ_3 -dbba³⁻ blocks and two N atoms of phen, resulting in a distorted square pyramid $\{ZnN_2O_3\}$ geometry. The Zn2 center is tetra-coordinate and reveals a distorted tetrahedral $\{ZnN_2O_2\}$ environment, which is completed by two O atoms from two different μ_3 -dbba³⁻ blocks and two N atoms from phen. The lengths of the Zn-O and Zn-N bonds span in the 0.198 7(5)~0.215 9(7) nm and 0.209 2(7)~0.210 3(7) nm range; these are comparable to those observed in other zinc comp-



H atoms were omitted for clarity, symmetry codes: A: -x+1, y, -z; B: -x+1, y, -z+1

Fig.3 Drawing of the asymmetric unit of complex ${\bf 2}$ with 30% probability thermal ellipsoids

lexes^[17,19-20]. In **2**, the dbba³⁻ block adopts a μ_3 -coordination mode (Scheme 1, mode II), wherein three COO ⁻ groups adopt a monodentate or a bidentate mode. The μ_3 -dbba³⁻ block shows a C-O_{ether}-C angle of 118.54°, while a dihedral angle involving two aromatic rings attains 14.55°. The μ_3 -dbba³⁻ linkers alternately connect the neighboring Zn(II) atoms to form a 1D metal-organic chain (Fig.4). The structural differences of two polymers may be attributed to the different ether-bridged tricarboxylate ligands and auxiliary ligands.



All phen ligands were omitted for clarity; Symmetry codes: A: -x+1, -y, z; B: x, y, z-1

Fig. 4 One dimensional metal-organic chain viewed along the b axis in complex ${\bf 2}$

2.2 TGA analysis

To determine the thermal stability of polymers 1 and 2, their thermal behaviors were investigated under nitrogen atmosphere by thermogravimetric analysis (TGA). As shown in Fig.5, complex 1 lost its one coordinated water molecule in the range of $120 \sim 159$ °C (Obsd. 3.4%; Calcd. 3.3%), followed by the decomposition at 222 °C. The TGA curve of 2 shows that six lattice water molecules were released between 30 and 129 °C (Obsd. 7.0%; Calcd. 7.3%), and the dehydrated solid begins to decompose at 251 °C.

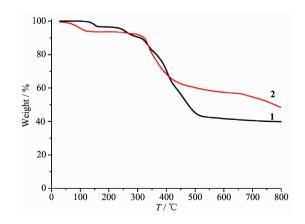


Fig.5 TGA curves of complexes 1 and 2

2.3 Luminescence properties

The emission spectra of H₃cpta, H₃dbba and complexes 1 and 2 were measured in the solid state at room temperature, as shown in Fig.6. The free H₃cpta and H₃dbba ligands showed two weak photoluminescence with emission maximum at 463 nm (λ_{ex} =378 nm) and 456 nm (λ_{ex} =325 nm), respectively. For polymers 1 and 2, the more intense emission bands were observed with maximum at 467 nm for 1 and 395 nm for 2 (λ_{ex} =320 nm in both cases). All bands can be assigned to an intraligand $(\pi^* \rightarrow n \text{ or } \pi^* \rightarrow \pi)$ emission [2,7,13] The enhancement of luminescence of complexes 1 and 2 can be attributed to the binding of ligands to the metal atoms, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay[1,14,16].

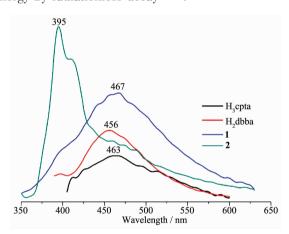


Fig.6 Solid state emission spectra of H₃cpta, H₃dbba and complexes 1 and 2

3 Conclusions

In summary, we have successfully synthesized and characterized two new zinc coordination polymers by using two ether-bridged tricarboxylic acids as bridging ligands under hydrothermal conditions. Two polymers feature two different 1D chain structures. Both the complexes also show promising luminescent properties. The obtained herein results should motivate further research aiming at the exploration of 2-(4-carboxylphenoxy)terephthalic acid and 2-(3,5-dicarboxylatobenzyloxy)benzoic acid as versatile semi-

rigid tricarboxylate building blocks for the assembly of functional coordination polymers.

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