

偶氮桥连羧酸配体与 Zn(II)构建的二维配位聚合物的合成、 晶体结构及荧光性质

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摘要: 合成了化合物 3-(5-叔丁基-2-甲氧羰基甲氧基苯基)偶氮苯甲酸甲酯(Me₂L), 并以此为配体与醋酸锌在水热条件下通过自组装获得了 1 个二维的配位聚合物 {[Zn(H₂O)L]·H₂O}_n(**1**), 通过红外、元素分析及 X-射线单晶衍射等检测手段对所合成的化合物进行了结构表征, 并测试了其荧光发射性质。相对于配位前驱体 H₂L 的荧光发射, 聚合物 **1** 的荧光发射略有红移。结构研究表明, 该化合物中配体采取了常见的反式构型, 形成了沿晶体学 *ab* 平面延伸的二维网状结构, 聚合物中的溶剂水分子通过氢键连接在二维结构的内部。该配位聚合物的合成对于研究偶氮类配合物的光化学反应奠定了基础。

关键词: 偶氮; 羧酸配体; Zn(II)配位聚合物; 晶体结构

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The Structure and Fluorescence Property of 2D Coordination Polymer Generated by Azo Dicarboxyl Ligand and Zn(II) Ion

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Abstract: A ligand, namely methyl 3-((5-*tert*-butyl-2-(2-methoxy-2-oxoethoxy) phenyl) diazenyl) benzoate (Me₂L), had been designed and synthesized. Under hydrothermal condition, one coordination polymer {[Zn(H₂O)L]·H₂O}_n (**1**) was obtained by using Me₂L and zinc acetate. The complex **1** was characterized by IR, elemental analysis and X-ray single crystal diffraction and the fluorescence property of the complex **1** was investigated. Compared to the emission spectrum of H₂L, the emission maximum of the complex **1** was red shift. The structural research revealed that the L²⁻ adopt the *trans*-configuration in the complex **1** which has a 2D network extends along crystallographic *ab* plane. The solvent water molecule was joined into the 2D network though four sets of H-bonds. The synthesis of the complex **1** could be the foundation of the photochemistry research of the coordinate complex based on Azo ligands. CCDC: 931724.

Key words: Azo; carboxylic acid; Zn(II) coordinate complex; crystal structure

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0 Introduction

Coordination polymers designed and constructed through crystal engineering have attracted considerable attention because of their fascinating structural topologies^[1] and functional applications in many research fields^[2]. Since the absorbing hydrogen of the Metal-Organic Frameworks (MOFs) was reported, more and more MOFs have been synthesized and applied to adsorption, gas storage, separation, photoluminescence, ion exchange, etc.^[3-7]. It is well known that the organic ligand is the primarily important for the construction of the coordination polymer while the environment factors such as the solvent, temperature, pH value and so on acted as a secondary role^[8]. According to the linear rigid ligands, the bend rigid ligand had taken more and more attention because they could adopt the different configuration to coordinate metal ions. Carboxylic acid ligands could be used to construct the high thermal stable coordinate complexes such as MOF-5 which was generated by terephthalic acid and Zn(II) ions^[9]. Compared to the linear single bonds, the double bond groups (C=C, C=N and N=N) have *cis*- and *trans*-configurations which can make the coordination complex more different. Moreover, the photodimerization of C=C group such as *trans*-bis(4-pyridyl)ethylene (4,4'-bpe) in the cage of the MOFs had been reported by many research groups. Among the double bond groups, the N=N group of the Azo compounds normally adopts the *trans*-configuration and could be changed to the *cis*-configuration under UV light which phenomenon can be applied as photo-switch^[10-12]. To our surprised, there have little reports about coordination complexes generated by Azo ligands and transition metals^[13-15]. We will report here the synthesis and coordination chemistry of an Azo ligand, 3-((5-*tert*-butyl-2-(carboxyoxo) phenyl) diazenyl) benzoic acid (H₂L) which was generated *in-situ* from the methyl esterized Me₂L. One coordination polymer {[Zn(H₂O)L]·H₂O}_n (**1**) was generated by Me₂L and zinc acetate under hydrothermal condition at 180 °C. In solid state, the ligand adopted the *trans*-

configuration and connected the neighboring Zn (II) centers to form a 2D structure. The fluorescence property of the complex **1** was also investigated and the red shift was found.

1 Experimental

1.1 Materials and instruments

All reagents and solvents were obtained from commercial sources and used without further purification. 3-[(5-*tert*-butyl-2-hydroxyphenyl)azo] benzoic acid (PL) was prepared according to the literature^[16]. Infrared (IR) samples were prepared as KBr pellets, and the spectra were obtained in the 400~4000 cm⁻¹ range using Thermo Nicolet 380 FTIR spectrometer. Elemental analysis was performed on a Perkin-Elmer model 2400 analyzer. ¹H NMR data were collected using Bruker Avance-300 spectrometer. Chemical shifts were reported in δ relative to TMS. Fluorescence measurements were carried out on a Cary Eclipse Spectrofluorimeter (Varian, Australia) equipped with a xenon lamp and quartz carrier at solid state under room temperature.

1.2 Syntheses of the Me₂L

Under ice bath, SOCl₂ (2.36 g, 20 mmol) was added slowly to a stirred mixture of the 3-[(5-*tert*-butyl-2-hydroxyphenyl)azo] benzoic acid (5.94 g, 20 mmol) and methanol (50 mL). After the reaction mixture was stirred under reflux for 6 h, the solvent was removed and 100 mL water was added and filtered, washed by 10% Na₂CO₃ solution. The residue was dissolved in acetone(60 mL), anhydrous potassium carbonate (8.3 g, 60 mmol) and methyl bromoacetate (3.3 g, 22 mmol) were added and the mixture was stirred under reflux for about 8 h. After removal of the solvent under reduced pressure, the residue was purified on a silica gel column using CH₂Cl₂ as the eluent to afford Me₂L as a red solid (4.46 g, Yield: 58%). IR (KBr pellet, ν /cm⁻¹): 2 957 (m), 2 868(m), 1 762(m), 1 725(vs), 1 601(w), 1 499(m), 1 437(m), 1 365(m), 1 293(vs), 1 204(vs), 1 102(m), 1 070(s), 983(w), 815(m), 760(s), 686(w). ¹H NMR: δ 8.61(1H, s), 8.15(4H, m), 8.08(1H, s), 7.63(1H, m), 5.3(2H, s), 4.0(6H, s), 1.46(9H, s).

1.3 Syntheses of **1**

A mixture of Me₂L (8 mg), Zn(OAc)₂ (14 mg) and water (2 mL) was sealed within a 5 mL glass tube. The mixture was heated at 180 °C for 3 d under autogenous pressure. After the mixture was allowed to cool to room temperature, deep red cubic crystals were isolated from the tube in 58% yield. IR (KBr pellet, ν / cm⁻¹): 3 400(s), 2 959(m), 1 604(s), 1 563(s), 1 486(m), 1 394(s), 1 302 (m), 1 224(m), 829(m), 772(s). Elemental analysis(%): Calcd. for C₁₉H₂₂N₂O₇Zn: C 50.07, H 4.87, N 6.15; Found: C 49.91, H 4.93, N 6.09.

1.4 Crystal structure determination

X-ray intensity data were measured at 293(2) K on a Bruker SMART APEX CCD-based diffractometer (Mo K α radiation, λ =0.071 073 nm). The data collection

and reduction were performed using the SMART and SAINT software^[17]. Multi-scan absorption corrections were applied for all the data sets using the SADABS^[17]. The structure was solved by direct methods and refined by full matrix least squares on F^2 using the SHELXTL program package^[18]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and refined using a riding model.

Details of the crystal parameters and data collection, refinements for coordinate complex **1** are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2 and Hydrogen bond lengths and bond angles are listed in Table 3.

CCDC: 931724.

Table 1 Crystallographic data of the **1**

Empirical formula	ZnC ₁₉ H ₂₂ O ₇ N ₂	D_c / (g·cm ⁻³)	1.501
Formula weight	455.76	Size / mm	0.16×0.15×0.12
Crystal system	Orthorhombic	$F(000)$	1 888
Space group	<i>Pbca</i>	Absorption coefficient / mm ⁻¹	1.262
a / nm	1.156 89(14)	Reflections collected/used	20 536 / 3 967
b / nm	0.913 38(11)	Independent reflections (R_{int})	2 914(0.086 1)
c / nm	3.816 3(5)	Goodness-of-fit on F^2	1. 088
V / nm ³	4.032 6(8)	θ range for data collection / (°)	1.07 to 25.99
Z	8	$R_1, wR_2(I>2\sigma(I))$	0.058 0, 0.152 3

Table 2 Selected bond lengths (nm) and bond angles (°) of the complex **1**

1					
Zn(1)-O(1) ⁱ	0.191 3(3)	Zn(1)-O(4) ⁱⁱ	0.195 9(3)	Zn(1)-O(6)	0.196 6(3)
Zn(1)-O(5)	0.197 2(3)	N(1)-N(2)	0.125 1(5)		
O(1) ⁱ -Zn(1)-O(4) ⁱⁱ	108.74(14)	O(1) ⁱ -Zn(1)-O(6)	124.48(17)	O(4) ⁱⁱ -Zn(1)-O(6)	102.27(14)
O(1) ⁱ -Zn(1)-O(5)	115.50(15)	O(4) ⁱⁱ -Zn(1)-O(5)	109.00(14)	O(6)-Zn(1)-O(5)	95.26(15)
N(2)-N(1)-C(8)	114.4(4)	N(1)-N(2)-C(5)	114.0(4)		

Symmetry code: ⁱ -x+1, y-1/2, -z+1/2; ⁱⁱ -x+3/2, y+1/2, z

Table 3 Hydrogen bond lengths and bond angles of **1**

D-H···A	$d(D-H)$ / nm	$d(H-A)$ / nm	$d(D\cdots A)$ / nm	$\angle DHA$ / (°)
O(7)-H(7A)···O(1) ^v	0.085	0.254	0.320 9(6)	136.3
O(6)-H(6A)···O(7)	0.085	0.182	0.266 3(6)	174.5
O(6)-H(6B)···O(2)	0.085	0.184	0.268 4(5)	171.9
O(7)-H(7B)···N(1)	0.086	0.241	0.317 7(6)	148.2
O(7)-H(7B)···O(3)	0.086	0.247	0.317 4(6)	139.5

Symmetry code: ^v -x+1/2, y-1/2, z

2 Results and discussion

2.1 Crystal structure of the complex 1

Under hydrothermal conditions, the coordinate complex **1** was obtained using Me_2L and $\text{Zn}(\text{OAc})_2$ ($\text{OAc} = \text{CH}_3\text{CO}_2^-$). The complex **1** crystallizes in orthorhombic space group pbca , $a = 1.156\ 89\ (14)\ \text{nm}$, $b = 0.913\ 38\ (11)\ \text{nm}$, $c = 3.816\ 3\ (5)\ \text{nm}$. In the asymmetric unit of the complex, there exist only one $\text{Zn}(\text{II})$ centre, one L^{2-} ligand, one coordinated water and one solvent water molecules, as shown in Fig.1. The $\text{Zn}(\text{II})$ ion was situated in the center of the tetrahedral $\{\text{ZnO}_4\}$, three O-donors came from three different L^{2-} ligands (O(1), O(4) and O(5)) and the rest

came from coordinated water molecule(O(6)). The Zn-O distances range from $0.191\ 3\ \text{nm}$ to $0.197\ 2\ \text{nm}$ and were consistent with the corresponding bond lengths in similarly to the reported Zn coordinate complexes generated from carboxyl ligands such as MOF-5 ($0.194\ 33$ to $0.194\ 75\ \text{nm}$). The Zn-O(2) distance was $0.275\ 5\ \text{nm}$ which was considered as a weak coordination interaction. Its worth to point out that the ligand adopted the trans-configuration which was the lowest energy state.

In the solid state, the ligand L^{2-} connected the neighboring $\text{Zn}(\text{II})$ centers with two carboxyl groups to form a 2D structure extending along the crystallographic ab plane, and the *tert*-butyl groups of

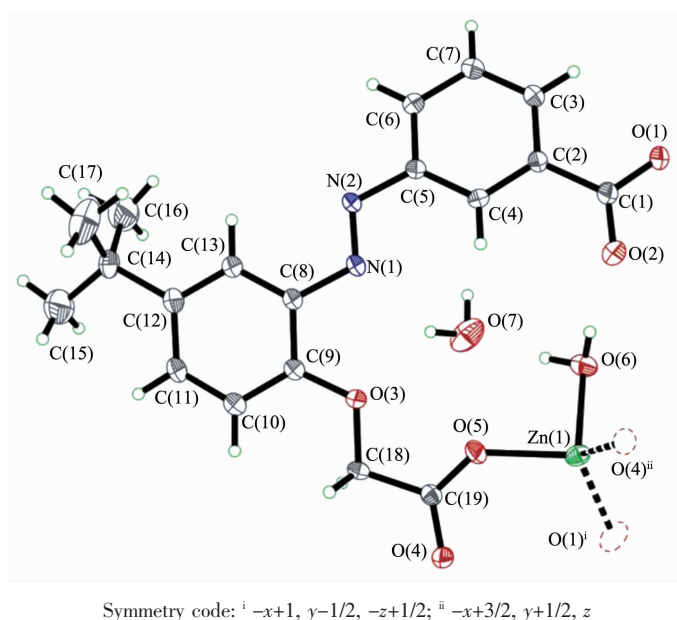
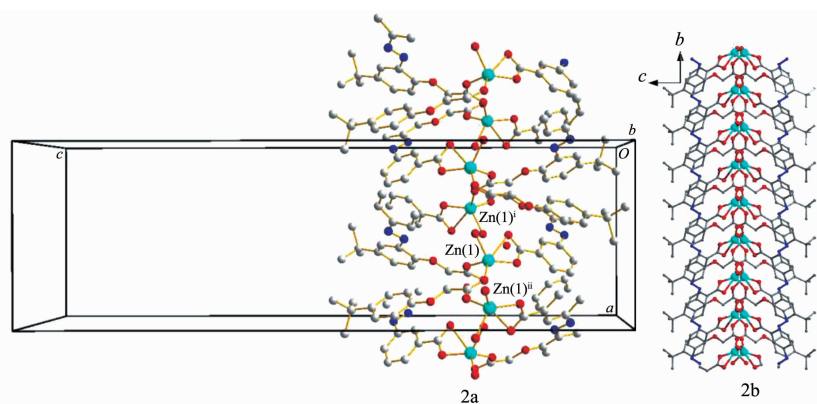
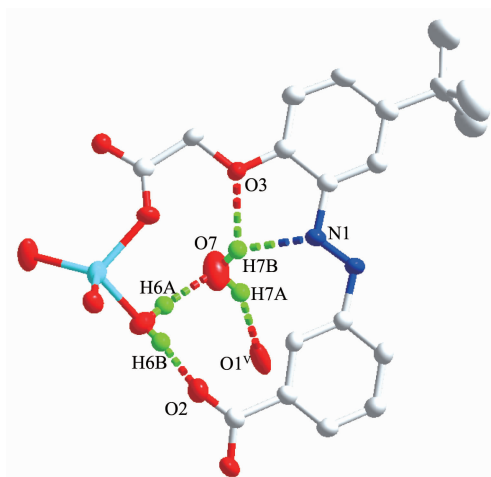


Fig.1 An ORTEP view of the asymmetric unit of complex **1** with ellipsoids of 50% probability



(a) viewed down from b axis, (b) viewed down from a axis; Symmetry code: $i -x+1, y-1/2, -z+1/2$; $ii -x+3/2, y+1/2, z$

Fig.2 2D structure of the complex **1**



Symmetry code: $v-x+1/2, y-1/2, z$

Fig.3 Five sets of H-bonds in complex **1** with ellipsoids of 50% probability

the ligands on the plane were pointed to the outside of the 2D networks, as shown in Fig.2. The solvent water molecule was fixed in the centre of the coordination structure through three sets of intramolecular H-bonds (O(6)-H(6A)···O(7), O(7)-H(7B)···N(1) and O(7)-H(7B)···O(3)) and one set of intermolecular H-bond (O(7)-H(7A)···O(1)^v, symmetry code: $-x+1/2, y-1/2, z$) just as shown in Fig.3. The coordinated water has one set of intramolecular H-bond to the O-donor of carboxyl group (O(6)-H(6B)···O(2)) which enhances the rigidity of the coordination structure. The detail of the H-bonds was listed in Table 3. The 2D networks stacked along crystallographic *c* axis into a 3D structure by an ABAB fashion.

2.2 The fluorescence emission of the complex **1**

In the solid state, the fluorescence emission

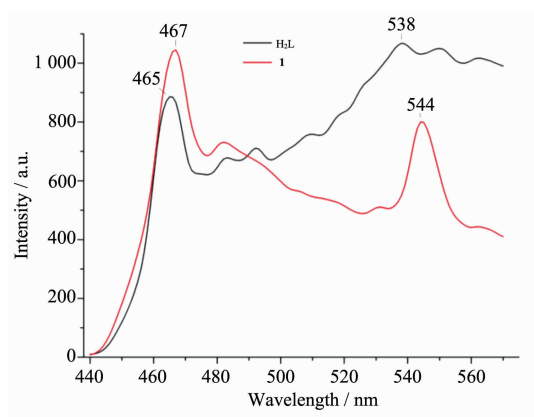


Fig.4 Emission spectrum of H₂L and complex **1** in solid state (λ_{ex} =312 nm)

spectrum of complex **1** and H₂L were measured as shown in Fig.4. As shown in Fig.4, the emission spectrum of H₂L has two maximum at 465 and 538 nm, and the spectrum of complex **1** has emission maximum at 467 and 544 nm. The red shift may be assigned to the ligand-to-metal charge transfer (LMCT) transition.

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