



新型吡啶双羧酸席夫碱配体锌配合物的合成、晶体结构及荧光性质

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Synthesis, Crystal Structure and Photoluminescent Property of a Zinc(II) Complex Based on Novel Pyridyl-dicarboxylate Schiff-Base Ligand

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Abstract: A novel pyridyl-dicarboxylate Schiff-base ligand (5-((pyridin-3-ylmethyl)amino)isophthalic acid, H₂L) and its Zinc(II) complex, namely, ZnL (**1**), were synthesized. The ligand was characterized by NMR analysis. The X-ray crystallographic analysis on complex **1** shows that **1** crystallizes in monoclinic, space group $P2_1/c$ with $a=0.753\ 83(10)$ nm, $b=1.040\ 52(14)$ nm, $c=1.734\ 67(19)$ nm, $\beta=112.123(5)^\circ$, $V=1.260\ 5(3)$ nm³, $Z=4$, $D_c=1.769$ g·cm⁻³, $F(000)=680$, $\mu=1.966$ mm⁻¹, the final $R=0.030\ 8$, $wR=0.085\ 6$. In complex **1**, the coordination environment of Zn(II) is distorted tetragonal-pyramid with N₁O₄ set. The 2D 4,4-topological sheets in **1** packed along a axis to form its 3D framework, which was stabilized by the $\pi\cdots\pi$ interactions between the adjacent aromatic rings on the neighbouring sheets. The photoluminescent property of **1** was also investigated. CCDC: 769437

Key words: crystal structure; Zn(II) complex; Schiff-base; $\pi\cdots\pi$ interaction; photoluminescent property

The crystal engineering of hybrid inorganic-organic materials based on transition metal are of continuous interests due to their structural diversities and relevance in a wide range of applications including superconductors, magnetic materials, catalysis, and luminescent probes^[1-3]. Up to now, many groups have focused their researches on metal-organic frameworks (MOFs) constructed by N- or O-donor ligands^[4-6]. Recent

years we have seen an upsurge in the joint-use of N- and O-donor ligands in the self-assembly process of MOFs. However, a literature survey shows that most research focused on the use of multiple ligands containing just N- or O-donor, while the multifunctional ligand containing both N and O are less documented^[7-10].

The ligands containing both N and O as coordina-

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tion atoms have been found to be good building blocks for the construction of hetero-metallic lanthanide-transition metal complexes^[11], which have attracted many attentions due to their special value in investigation on the nature of the magnetic exchange interactions between 3d and 4f metal ions in magnetic materials that contain rare earth metals^[12]. Meanwhile, Schiff-base ligands have also attracted many attentions of chemists during the past decades because of the convenience in synthesis, good coordination ability and wide applications of Schiff-base complexes including catalysis and biomimetic chemistry^[13]. In our previous work, we have reported one novel N,O-bifunctional Schiff-base ligand and its Cd(II) complex^[4]. In order to further investigate the self-assembly process of the N,O-bifunctional system, meanwhile to expand this system, Zn(II) salt was used to react with a novel pyridyl-dicarboxylate Schiff-base ligand H₂L (H₂L=5-((pyridin-3-ylmethyl) amino)isophthalic acid), and one new metal-organic frameworks ZnL (**1**) was prepared and characterized by X-ray crystallography. The photoluminescent property of **1** was also investigated.

1 Experimental

1.1 General

All commercially available chemicals are of reagent grade and used as received without further

purification. Solvents were purified according to the standard methods. C, H and N analyses were made on Elementar Vario EL-III elemental analyzer. Infrared (IR) spectra were recorded on Nicolet AVATAR 360 FTIR spectrophotometer by using KBr discs. ¹H NMR spectra were recorded on the Bruker DRX-500 spectrometer. Luminescent spectra were recorded on HITACHI F4500 fluorescence spectrophotometer.

1.2 Structure determinations

A suitable colorless single crystal of **1** with dimensions of 0.40 mm×0.20 mm×0.10 mm and 0.40 mm×0.10 mm×0.10 mm, respectively, were selected for data collection at 293 K, using a Bruker Smart Apex II CCD equipped with a Mo K α radiation (λ =0.071 073 nm). The structures were solved by direct methods with SHELXS-97 program^[14] and refined with SHELXL-97^[15] by full-matrix least-squares techniques on F^2 . All non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically. The hydrogen atoms except for those of water molecules were generated geometrically. The details of the crystal parameters, data collection and refinement for the compounds are summarized in Table 1, and selected bond lengths and angels with their estimated standard deviations of **1** are listed in Table 2

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Table 1 Crystallographic data for complex **1**

Empirical formula	C ₁₄ H ₁₀ N ₂ O ₄ Zn	D_c / (g·cm ⁻³)	1.769
Formula weight	335.61	Absorption coefficient / mm ⁻¹	1.966
Temperature / K	293	$F(000)$	680
Crystal system	Monoclinic	θ range / (°)	2.33~27.50
Space group	$P2_1/c$	Reflections collected	7 382
a / nm	0.753 83(10)	Independent reflections	2 870
b / nm	1.040 52(14)	R_{int}	0.032 7
c / nm	1.734 67(19)	Goodness-of-fit on F^2	1.065
β / (°)	112.123(5)	R [$I > 2\sigma(I)$]	0.030 8
V / nm ³	1.260 5(3)	wR [$I > 2\sigma(I)$]	0.085 6 ^a
Z	4		

$$^a w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.5099P] \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

Table 2 Selected Bond lengths (nm) and bond angles (°) for complex **2**

Zn1-O1	0.201 08(18)	Zn1-O2#1	0.197 12(18)	Zn1-O3#2	0.222 0(2)
Zn1-O4#2	0.209 9(2)	Zn1-N1#3	0.205 3(2)		

Continued Table 2

O1-Zn1-O2#1	101.68(7)	O1-Zn1-O3#2	92.24(8)	O1-Zn1-O4#2	126.55(10)
O1-Zn1-N1#3	110.75(8)	O2#1-Zn1-O3#2	154.92(8)	O2#1-Zn1-O4#2	96.01(8)
O2#1-Zn1-N1#3	103.03(8)	O3#2-Zn1-O4#2	59.11(8)	O3#2-Zn1-N1#3	91.12(9)
O4#2-Zn1-N1#3	113.58(11)				

Symmetry codes: #1: $1-x, 5/2+y, 3/2-z$; #2: $1-x, -1-y, 1-z$; #3: $x, 3/2-y, -1/2+z$.

1.3 Synthesis of 5-((pyridin-3-ylmethyl)amino)isophthalic acid (H_2L)

The ligand was synthesized according to the previously reported literatures^[16]. To a dry CH_3OH solution (30 mL) of 5-aminoisophthalic acid (50 mmol, 9.05 g) was slowly added 3-picolinaldehyde (50 mmol, 5.36 g) in 25 mL CH_3OH . The resulting yellow solution was stirred over night and then refluxed for 8 h. After been cooled to room temperature, excess $NaBH_4$ was added. The pH value of the solution was adjusted to 5.5 with HCl and the pale yellow precipitate was collected, washed with water and recrystallized in ethanol/ H_2O solution. The ligand was obtained in 75% yield. FTIR (KBr pellet, cm^{-1}): 1 677s, 1 602s, 1 566m, 1 525s, 1 469s, 1 437m, 1 421m, 1 315s, 1 288s, 1 174s, 835m, 777m, 763m. 1H NMR (500 MHz, DMSO): δ 8.52(s, 1H); δ 8.44(d, 1H); δ 7.90(t, 2H); δ 7.58(s, 2H); δ 7.38(t, 1H); δ 4.39(s, 2H).

1.4 Synthesis of ZnL (1)

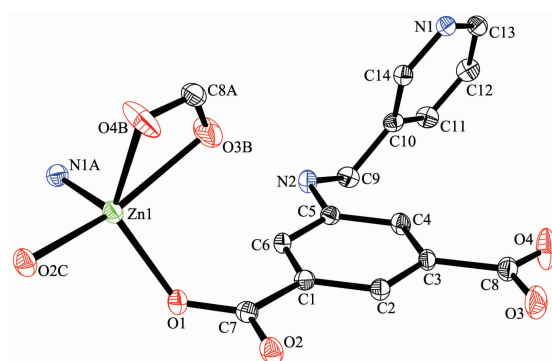
Complex **1** was synthesized by hydrothermal method. To a suspension of H_2L (0.027 2 g, 0.1 mmol) in 10 mL water was added NaOH (0.008 g, 0.2 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.029 7 g, 0.1 mmol), and 2 mL C_2H_5OH . After being stirred for 30 min, the resulting solution was sealed into a bomb equipped with a Teflon liner and heated at 120 °C for 72 h. After slow cooling of the reaction mixture to room temperature, colorless crystals of **1** suitable for X-ray analysis were obtained in 60% yield. Anal. Calcd for compound **1**, $C_{14}H_{10}N_2O_4Zn$: C 50.10, H 3.01, N 8.35; found: C 50.02, H 3.06, N 8.33.

2 Results and discussion

2.1 Structure description

Complex **1** was offered by treatment of $Zn(NO_3)_2 \cdot 6H_2O$ with the sodium salt of H_2L ligand in C_2H_5OH/H_2O system and crystallized in monoclinic system, space group $P2_1/c$. As shown in Fig.1, there are one

$Zn(II)$ ion and one ligand in the asymmetric unit of **1**. Four of the five sites of $Zn(II)$ ion are coordinated by four carboxylic O atoms from three different ligand with Zn-O bond lengths varying from 0.197 12(18) to 0.222 0(2) nm, and the remaining one site is occupied by one pyridyl N atom of another ligand with Zn-N distances of 0.205 3(2) nm (Table 2). The N-Zn-O and O-Zn-O bond angles around $Zn(II)$ ions are in the range of 59.11 (8)° to 154.92 (8)°. Thus, the coordination geometry of the five-coordinated $Zn(II)$ center can be regarded as a distorted tetragonal-pyramid in N_1O_4 set with τ value of 0.47^[17]. In complex **1**, each ligand coordinates to four $Zn(II)$ ions, and each $Zn(II)$ links four different ligands. With this connection mode spreading along the bc plane, the 2D (4,4)-topological sheet structure of **1** come into being (Fig.2). As shown in Fig. 2, there are three kinds of M_2L_2 cycles in the 2D sheet of **1** and the Zn-Zn distances are 3.980 3(6), 7.253 9(10) and 8.851 6(10), respectively. In **1**, the ligands all adopt identical coordination pattern, in which the two carboxylate groups are in $\mu_1-\eta^1:\eta^1$ and $\mu_2-\eta^1:\eta^1$ coordination modes, respectively (Fig.2a). It is also noteworthy that,



Symmetric code: A: $x, 1.5-y, -0.5+z$; B: $1-x, -0.5+y, 1.5-z$; C: $1-x, 2-y, 1-z$

Fig.1 ORTEP plot of the coordination environment around the $Zn(II)$ atoms in complex, where the thermal ellipsoids were draw at 30% possibility and the hydrogen atoms were omitted for clarity

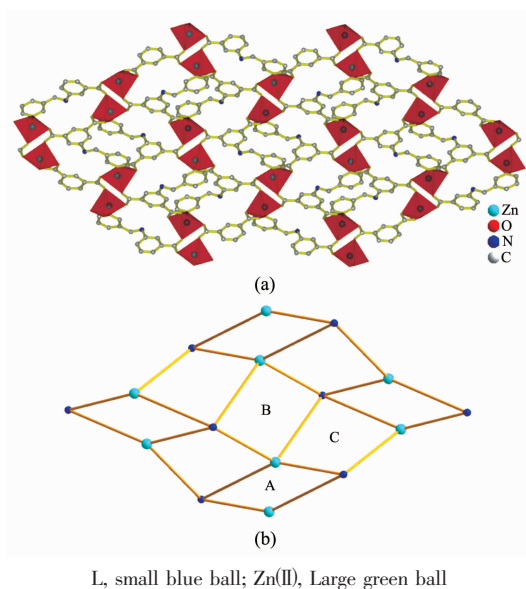


Fig.2 (a) 2D network of complex viewing along the a axis where the hydrogen atoms were omitted for clarity; (b) Schematic drawing of the (4,4)-topological structure of **1**

although the pyridyl N atoms coordinate to Zn(II) center, the amino N atoms do not participate in the coordination environment of Zn(II) in the title complex, and the dihedral angle of the pyridine ring and central benzene ring is 72.2° .

The packing arrangement of the 2D sheets is shown in Fig.3. The layers repeat along the a axis. In complex **1**, the distance between the central benzene rings and the corresponding centroids of adjacent pyridine rings on the neighboring 2D sheets is 0.3576 nm with dihedral angles of 2.690° indicating strong π

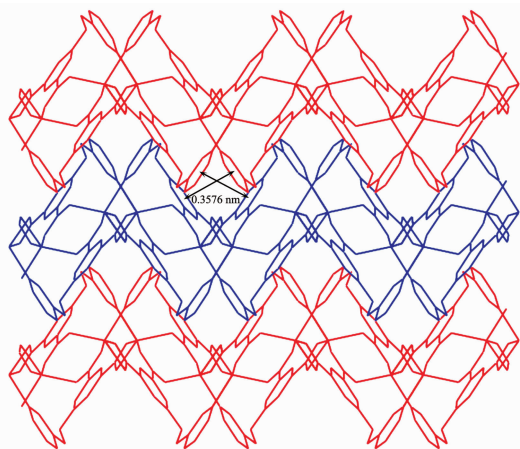


Fig.3 Stacking mode of the 2D sheets in complex **1** viewing along c axis, where the hydrogen atoms were omitted for clarity

$\cdots \pi$ interactions between these two adjacent aromatic rings, which stabilize the packing pattern of the 2D sheets into its 3D framework^[18-19]. The results reveal that the $\pi \cdots \pi$ interactions play distinguished role in stabilizing the whole structure of complex **1**.

The solid state emission spectra of title complex and free ligand at room temperature are depicted in Fig. 4. Complex **1** exhibits intense blue emissions maximum at 424 nm, when excited at 352 nm. Comparably, the free ligand shows similar emission at 420 nm with excitation at 352 nm. The luminescence of **1** is tentatively assigned to the intraligand fluorescent emission and the slightly red-shift in **1** is probably due to the coordination of the ligand to the Zn(II) centers^[20-21]. The investigations on the reactions of 5-((pyridin-3-ylmethyl)amino)isophthalic acid with other metal salts are still in progress.

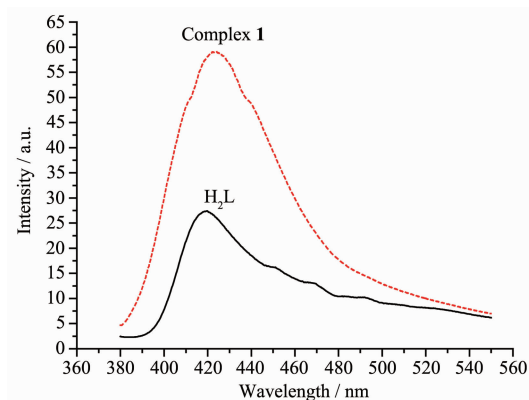


Fig.4 Photoluminescent emission spectra of the free ligand ($\lambda_{\text{em, max}}$ at 420 nm, $\lambda_{\text{ex, max}}$ at 352 nm) and complex **1** ($\lambda_{\text{em, max}}$ at 424 nm, $\lambda_{\text{ex, max}}$ at 352 nm) in the solid state at room temperature

References:

- [1] Desiraju G R. *Angew. Chem. Int. Ed.*, **2007**, *46*:8342-8356
- [2] Barnett S A, Blake A J, Champness N R, et al. *Dalton Trans.*, **2005**, *24*:3852-3861
- [3] Kitagawa S, Uemura K. *Chem. Soc. Rev.*, **2005**, *34*:109-119
- [4] WANG Yan(王彦), SHENG Yue-Wei(盛玥微), SUN Wei-Yin(孙为银). *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2009**, *25*(7):1182-1186
- [5] Gu X J, Xue D F. *Cryst. Growth Des.*, **2007**, *7*:1726-1732
- [6] Lin Z Z, Jiang F L, Chen L, et al. *Inorg. Chem.*, **2005**, *44*:73-76
- [7] Su Z, Fan J, Okumura T, et al. *Cryst. Growth Des.*, **2010**, *10*:1911-1922

- [8] Su Z, Xu J, Fan J, et al. *Cryst. Growth Des.*, **2009**,**9**:2801-2811
- [9] BAI Zheng-Shuai (白正帅), CHEN Man-Sheng (陈满生), CHEN Shui-Sheng (陈水生), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2009**,**25**(3):402-406
- [10] Su Z, Bai Z S, Xu J, et al. *CrystEngComm.*, **2009**,**11**:873-880
- [11] Gu X J, Xue D F. *Cryst. Growth Des.*, **2007**,**7**:1726-1732
- [12] Liang Y C, Cao R, Su W P, et al. *Angew. Chem. Int. Ed.*, **2000**,**39**:3304-3307
- [13] Bazzicalupi C, Bencini A, Bianchi A, et al. *Coord. Chem. Rev.*, **2008**,**252**:1052-1068
- [14] Sheldrick G M. *SHELXS-97, Program for Crystal Structure Determination*, University of Göttingen, Germany, **1997**.
- [15] Sheldrick G M. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.
- [16] Ganguly R, Sreenivasulu B, Vittal J J. *Coord. Chem. Rev.*, **2008**,**252**:1027-1050
- [17] Addison A W, Rao T N, Reedijk J, et al. *J. Chem. Soc. Dalton Trans.*, **1984**:1349-1356
- [18] KONG Xue-Jun (孔学军), ZHU Kun (朱 坤), KAI Tian-Han (开天瀚), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2009**,**25**(12):2193-2196
- [19] LIU Guo-Cheng (刘国成), ZHANG Jin-Xia (张金霞), WANG Xiu-Li (王秀丽), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **2010**,**26**(5):913-916
- [20] Chen S S, Fan J, Okamura T, et al. *Cryst. Growth Des.*, **2010**,**10**:812-822
- [21] Bai Z S, Chen S S, Zhang Z H, et al. *Sci. China Ser. B: Chem.*, **2009**,**52**:459-464