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氢键和 π-π 诱导的二维双层 Zn(Ⅱ)配位聚合物的晶体结构和荧光性能

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摘要: 本文以间苯二吡啶(1,3-dpb)和 4,4′-二苯醚二甲酸(H_2oba)为配体,溶剂热合成了一个二维锌配位聚合物{[Zn(oba)(dpb)]·H_2O}$_n$ (**1**),对其进行了红外,热重,粉末单晶衍射等表征,配合物属于三斜晶系,空间群 *C*2/*c*。相邻的 Zn(Ⅱ)离子通过连接 oba^{2-}和 dpb 形成二维波浪形面,两个相邻的面相互互锁形成 2D→2D 的结构,并且面与面之间存在氢键。两组 2D→2D 的结构通过 π-π 作用进一步形成双层的二维超分子网络。此外,本文也研究了配合物的荧光性能。

关键词: 配位聚合物; 氢键; π-π 作用; 荧光
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Structure and Fluorescence Property of 2D Bilayer Zn(Ⅱ) Coordination Polymer Induced by H-Bonding and π-π Interaction

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Abstract: Solvothermal reaction of 1,3-dipyridyl benzene (1,3-dpb) with 4,4′-oxybis(benzoic acid) (H_2oba) produced a two dimensional (2D) zinc(Ⅱ) coordination polymer {[Zn(oba)(dpb)]·H_2O}$_n$ (**1**). The complex was characterized by elemental analysis, IR spectroscopy, and X-ray single-crystal diffraction. It crystallizes in the monoclinic system, space group *C*2/*c*. The neighboring Zn(Ⅱ) ions are linked by oba^{2-} anions and 1,3-dpb to form infinitely 2D sheet, two 2D sheets are interlocked each other to form 2D→2D structure, and these two 2D sheets were linked each other by H-bonding. Two groups of interlocked structures further linked to form bilayer 2D supermolecule network by π-π interaction. In addition, the fluorescence property of **1** was also studied. CCDC: 917714.

Key word: coordination polymer; H-bonding; π-π interaction; fluorescence

0 Introduction

The designed construction of coordination polymers from various molecular building blocks connected by coordination bond, supramolecular contacts, has been of great interest due to their intriguing aesthetic structures and topological features[1-2], as well as their potential applications in photochemistry areas[3-4], molecular magnetism[5-6], heterogeneous catalysis[7-8], and molecular sorption[9-10]. Recently, a number of N-containing ligands have been widely employed to construct coordination polymers with fascinating architectures and interesting properties[11-12]. 1,3-dipyridyl benzene (1,3-dpb), which can be regarded as a V-shaped rigid ligand. To test the ability to obtain new architectures and topologies, we selected this ligand,

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1,3-dipyridyl benzene (1,3-dpb), and Zn(Ⅱ) salt to solvothermally synthesize a new coordination polymers [Zn(oba)(dpb)]·H_2O (**1**). The compound was characterized by elemental analysis, IR spectra and X-ray crystallography. In addition, the fluorescence of complex **1** was studied.

1 Experimental

1.1 Materials and methods

The reagents and solvents employed were commercially available and used as received. IR absorption spectrum of **1** was recorded in the range of 400~4 000 cm^{-1} on a Nicolet (Impact 410) spectrometer with KBr pellet. C, H, and N analyses were carried out with a Perkin-Elmer 240C elemental analyzer. Luminescent spectra were recorded with a SHIMAZU VF-320 X-ray fluorescence spectrophotometer at room temperature. The as-synthesized sample was characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 1023 K using heating rate of 10 K·min^{-1} under N_2 atmosphere.

1.2 Synthesis of the compound

{[Zn(oba)(dpb)]·H_2O}$_n$ (**1**): A mixture of $Zn(NO_3)_2$·$6H_2O$ (15 mg), H_2oba (13 mg) and 1,3-dpb (12 mg) was dissolved in 9 mL of DMF/H_2O (2∶1, *V*/*V*). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 110 °C for 3 d. A large number of colorless crystals were obtained, which were washed with mother liquid, and dried under ambient conditions (Yield: 63% based on H_2oba). Anal. Calcd. for $C_{30}H_{22}N_2O_6Zn$ (%): C, 63.00, H, 3.88, N, 4.90; found (%): C, 62.77, H, 4.16, N, 4.76. IR (KBr, cm^{-1}): 3 444 (w), 3 062(w), 1 595(s), 1 540(m), 1 381(s), 1 227(s), 1 145(m), 882(w), 767(m), 675(m), 552(w).

1.3 Crystal structure determination

X-ray crystallographic data of **1** was collected at room temperature using epoxy-coated crystal mounted on glass fiber. All measurements were made on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo *Kα* radiation (λ=0.071 073 nm). The structure of complex **1** was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure based on F^2 values[13]. The hydrogen atoms positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The crystallographic data are summarized in Table 1, while the selected bond lengths and angles are given in Table 2.

CCDC: 917714.

2 Results and discussion

2.1 Crystal structure

X-ray analysis reveals that compound **1** is solved in monoclinic space group *C*2/*c*. The asymmetric unit contains half an independent Zn(Ⅱ) cation, half a oba^{2-} anion, half a 1,3-dpb ligand, and half a lattice water.

Table 1　Crystal data and structure refinement for complex 1

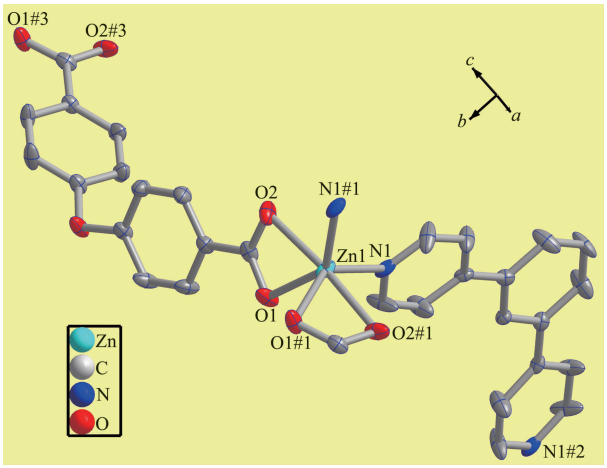
Formula	$C_{30}H_{22}N_2O_6Zn$	*F*(000)	1 176
Formula weight	571.89	Crystal size / mm	0.09×0.11×0.13
Crystal system	Monoclinic	Temperature / K	296
Space group	*C*2/*c*	Tot., Uniq. Data	10 037, 2 932
a / nm	1.328 96(17)	R_{int}	0.042
b / nm	2.630 2(4)	Observed data ($I>\sigma(I)$)	2 075
c / nm	0.873 98(13)	N_{ref}, N_{par}	2 32, 179
β / (°)	125.261(2)	*R*, wR_2 (all data)	0.054 1, 0.133 9
V / nm^3	2.494 5(6)	*S* (all data)	1.04
Z	4	Max. and Av. Shift / Error	0.000, 0.000
D_c / (g·cm^{-3})	1.523	Min. and max resd dens / (e·nm^{-3})	−920, 660
μ / mm^{-1}	1.035		

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

Zn1-O1	0.215 2(3)	Zn1-O2	0.226 9(3)	Zn1-N1	0.208 8(3)
O1-Zn1-O2	57.80(12)	O1-Zn1-O1#1	90.98(11)	O2-Zn1-O2#1	174.63(12)
O1-Zn1-N1	91.70(12)	O1-Zn1-N1#1	139.49(12)	O2-Zn1-N1#1	85.67(13)
O1-Zn1-O2#1	117.85(12)	O2-Zn1-N1	97.37(13)	N1-Zn1-N1#1	111.42(14)

Symmetry codes: #1: $-x$, y, $0.5-z$.

The cation displays a distorted ZnN_2O_4 coordination sphere that can be best described as distorted octahedral geometry. In **1**, the two carboxyl groups of H_2oba displays bidentate chelating coordination mode. As shown in Fig.1, the Zn(Ⅱ) center is six coordinated by four carboxylic O atoms from two H_2oba, two N atoms from 1,3-dpb ligand. The Zn-N length is 0.208 8 nm, and the Zn-O lengths are in the range of 0.215 2(3) ~0.226 9 (3) nm. The dihedral angle between the two phenyl rings in the anion is 82.303(2)°, and two pyridine rings in the 1,3-dpb is 9.761(2)°.



Hydrogen atoms are omitted for clarity; Symmetry codes: #1: $-x$, y, $0.5-z$; #2: $1-x$, y, $0.5-z$; #3: $1-x$, y, $2.5-z$

Fig.1 Coordination environment of complex **1**

The neighboring Zn(Ⅱ) are linked by oba^{2-} and 1,3-dpb to form infinitely 2D wavelike sheet. In the sheet, two oba^{2-}, two dpb and four Zn cations afford a square grid with the size of ~1.463 nm×1.329 nm (Fig.2). Because of the spacious nature of a single sheet, it allows another identical sheet to interlock, leading to a 2-fold interlocked structure (Fig.3). These interlocked double sheets (red and green) are packed in an offset fashion. There are strong (O1W–H···O2) hydrogen bonds (O1W···O2 distance is 0.282 1 nm, d (O1W-H) =0.096 nm, d (H ··· O2) =0.188 nm, ∠O1WHO2=168.3°) between the interlocked sheets by lattice water. Further inspection shows that the adjacent two groups of sheets are actually contacting each other by π-π interactions. These hydrogen bonds and π-π interactions change the framework from 2D sheet to 2D bilayer network (Fig.4). Obviously, these H-bonded and π-π interactions increase the stability of whole crystal structure. This suggests that latticed water play an important role in changing the structure and sustaining the stabilizing the whole structure.

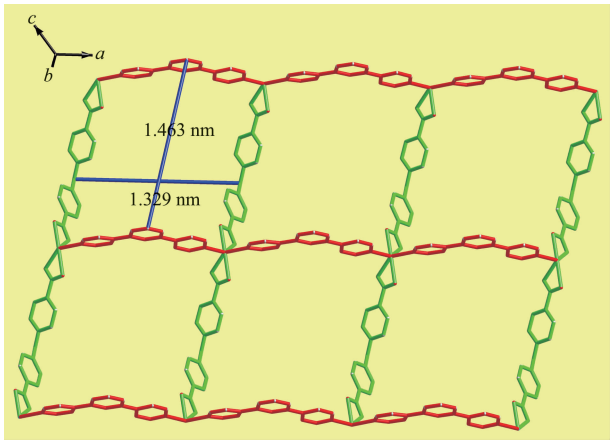


Fig.2 View of the 2D wavelike sheet

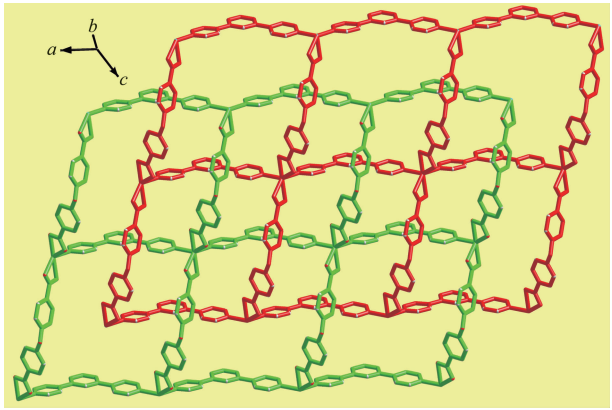


Fig.3 View of interlocked sheets

2.2 Thermal analysis and XRD results

To characterize the complex more fully in terms

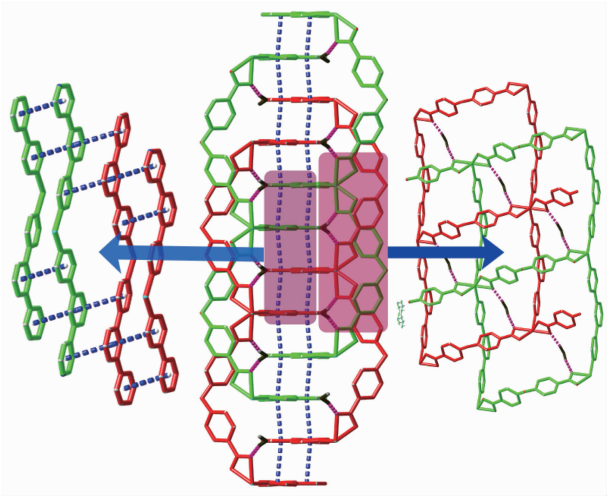


Fig.4　Views of bilayer network by H-bondings and π-π bonds

of thermal stability, the thermal behavior of **1** was studied by TGA. A weight loss of 2.74% (Calcd. 2.91%) is observed from 40 to 220 ℃ which is attributed to the loss of the lattice water, and the structure was decomposes starting at 360 ℃ (Fig.5). The PXRD experimental and computer-simulated pattern demonstrates that the experimental PXRD patterns perfectly match the simulated patterns based on the single-crystal X-ray data (Fig.6).

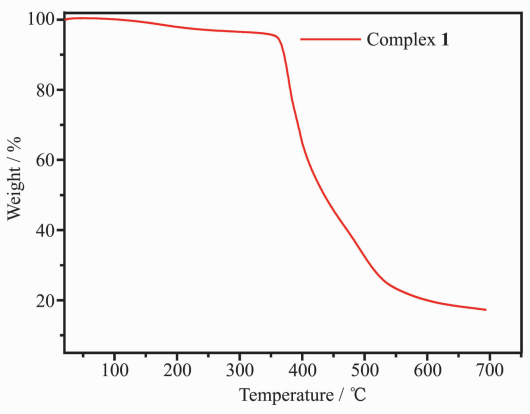


Fig.5　TGA pattern of complex **1**

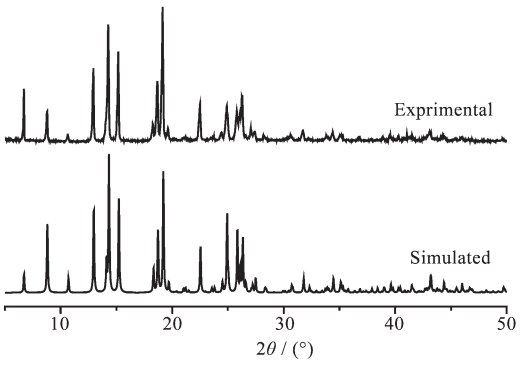


Fig.6　Powder X-ray diffraction pattern of complex **1**

2.3　Fluorescence properties

The fluorescence properties of free ligands 1,3-dpb, H_2oba, and complex **1** in the solid state at room temperature are investigated. Intense emissions of the 1,3-dpb was observed with wavelength from 300 to 500 nm (λ_{max}=420 nm), which could be attributed to the $\pi^* \rightarrow n$ transitions. However, no obvious emission band is observed for the free H_2oba under the same experimental condition. Complexe **1** exhibits mission characteristics similar to 1,3-dpb, the emission peaks at 425 nm (λ_{ex}=370 nm) shows a slightly red shift compared with that of 1,3-dpb, The emission peaks for **1** in nature are probably assigned to ligand-to-metal charge-transfer (LMCT) transitions. The enhancement of luminescence may be attributed to the chelating of the ligand to the central metals and weak bond interactions, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay (Fig.7)[14-16].

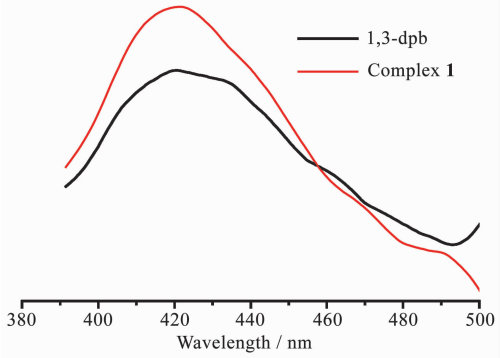


Fig.7　Solid-state photoluminescent spectra of **1** and 1,3-dpb at room temperature

3　Conclusions

In summary, a new complex $\{[Zn(oba)(dpb)]\cdot H_2O\}_n$ has been synthesized under solvothermal conditions. Complex **1** is an interlocked infinitely 2D sheet, which further to generate bilayer 2D framework by H-bonded and π-π interactions. The results demonstrate that the free water can be well used as the structure-directing tool and can produce various H-bonding in the synthesis of unusual coordination frameworks. Subsequent works will be focused on the structures and properties of a series of coordination polymers

constructed by 1,3-dpb with more auxiliary ligands and metal ions.

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