

一个双核锌配合物 $[(\text{ZnCl}_2)(\text{PyBIm})]_2$ 的合成及结构

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摘要: 在水热条件下, 合成了 1 个新的双核锌配合物 $[(\text{ZnCl}_2)(\text{PyBIm})]_2$ (PyBIm=2-(4-pyridyl)benzimidazole)。该配合物为单斜晶系, $P2_1/n$ 空间群, 晶胞参数 $a=0.774\,51(4)$ nm, $b=1.252\,49(5)$ nm, $c=1.315\,96(7)$ nm, $\beta=100.294(3)^\circ$, $V=1.256\,0(1)$ nm³, $Z=2$ 。结构分析表明, Zn 被 2 个 Cl 原子和来自 PyBIm 配体的 2 个 N 原子配位, 形成了 1 个变形四面体结构。在该配合物中, Zn...Zn 距离为 $0.709\,4(5)$ nm, 结构中存在 $\pi\cdots\pi$ 堆积和氢键作用。

关键词: 锌; 2-(4-吡啶基)苯并咪唑; 晶体结构

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Synthesis and Structure of a Binuclear Zinc Complex $[(\text{ZnCl}_2)(\text{PyBIm})]_2$

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Abstract: A new binuclear zinc complex $[(\text{ZnCl}_2)(\text{PyBIm})]_2$ (PyBIm=2-(4-pyridyl)benzimidazole) has been synthesized by hydrothermal reaction. The complex crystallizes in triclinic $P2_1/n$ space group with crystal cell parameters of $a=0.774\,51(4)$ nm, $b=1.252\,49(5)$ nm, $c=1.315\,96(7)$ nm, $\beta=100.294(3)^\circ$, $V=1.256\,0(1)$ nm³ and $Z=2$. The crystal X-ray analysis shows that Zn atom is coordinated by two Cl atoms and two N atoms from two PyBIm ligands in a distorted tetrahedral geometry. The Zn...Zn separation is $0.709\,4(5)$ nm, and the hydrogen bonding and $\pi\cdots\pi$ interactions also exist in the structure. CCDC: 800921.

Key words: zinc; 2-(4-pyridyl)benzimidazole; crystal structure

Recently, much interest has been focused on the crystal engineering of supramolecular architectures, which are organized by coordinate covalent bonds or noncovalent interactions such as hydrogen bonding and $\pi\cdots\pi$ interactions^[1]. However, the influencing information on these architectures are not yet well understood, although some factors such as the functionality of ligands, the molar ratio of reagents and the pH value of solution, have been documented.

Therefore, the exploration of synthetic strategies and routines is a long-term challenge, and the work is required to extend the knowledge of relevant structural types and establish proper synthetic strategies leading to desirable supramolecular species.

Benzimidazole and its ramification with abundant non-coordinating N-H groups provide a good choice for studying hydrogen-bonding interactions^[2-5]. Among the benzimidazole deviates, the 2-(4-pyridyl)benzimi-

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dazole) (PyBIm) with three N-donors can be as a good candidate to construct metal-organic frameworks. When PyBIm is in neutral form, the ligand displays unidentate or bidentate coordination modes. In type of unidentate mode, imino nitrogen atom from pyridyl ring can directly coordinate with the metal ions while the N-H group and imino nitrogen atom from BIm ring behaves as hydrogen bonding donor (H-D) and acceptor (H-A), respectively. In type of bidentate mode, the ligand acts as bridge to link two metal ions with two imino nitrogen atoms from BIm and pyridyl rings, while the N-H group can be as H-D. Therefore, the PyBIm ligand in the two types of coordination modes can provide the weak interaction sites for the construction of supramolecular assemblies. In this work, we present the synthesis and structural characterization of a new supramolecular complex based on PyBIm ligand, $[(\text{ZnCl}_2)(\text{PyBIm})]_2$.

1 Experimental

1.1 Reagent and apparatus

All chemicals were of analytical reagent grade and were used directly without further purification. Elemental analysis (C, H, N) was performed with a Vario EL III CHNOS Elemental Analyzer. IR spectrum was recorded from KBr pellets in the range of 4 000~400 cm^{-1} on a FTS-40 spectrophotometer. The fluorescence spectrum in solid state was carried out on a FLS920 spectrometer.

1.2 Synthesis

The ligand 2-(4-pyridyl)benzimidazole (PyBIm) was synthesized according to the procedure reported

by Alcade^[6]. A solution of ZnCl_2 (1.8 mmol), PyBIm (1.22 mmol) and 15 mL H_2O was stirred under ambient condition. The mixture was then sealed in a Teflon-lined steel vessel and heated at 170 $^\circ\text{C}$ for 3 d. After slow cooling to room temperature, the resulting single crystals were obtained. Anal. Calcd. for $\text{C}_{24}\text{H}_{18}\text{Cl}_4\text{N}_6\text{Zn}_2$ (%): C, 43.48; H, 2.74; N, 12.68. Found (%): C, 43.37; H, 2.89; N, 12.51. IR (KBr): 3 061 (s), 1 635 (s), 1 597 (s), 1 489 (m), 1 433 (m), 1 383 (s), 1 223 (s), 815 (s), 783 (s), 729 (s) cm^{-1} .

1.3 X-ray crystallography

A yellow single crystal with dimensions of 1.0 mm \times 0.50 mm \times 0.40 mm was mounted on a computer-controlled Siemens SMART CCD diffractometer equipped with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071\,073\,\text{nm}$) at room temperature. Cell parameters were determined by the Smart program with θ angles ranging from 2.85 $^\circ$ to 27.48 $^\circ$. An empirical absorption correction was applied using SADABS^[7]. A total of 9 042 independent reflections were collected and 2 839 reflections were independent ($R_{\text{int}}=0.020\,6$), of which 2 703 were observed with $I>2\sigma(I)$. The structure was solved by direct method and refined on F^2 by full-matrix least-square using the SHELXL-97 program package^[8] giving a final $R_1=0.026\,1$, $wR_2=0.06\,9$. The largest peak and hole on the final difference-Fourier map were 378 and $-648\,\text{e}\cdot\text{nm}^{-3}$, respectively. Crystal data and structure refinement parameters are listed in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC: 800921.

Table 1 Crystal data and structure refinement for title complex

Molecule formula	$\text{C}_{24}\text{H}_{18}\text{Cl}_4\text{N}_6\text{Zn}_2$	V / nm^3	1.256 0(1)
Molecule weight	662.98	Z	2
Crystal size / mm	1.0 \times 0.5 \times 0.4	$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.753
Crystal color	Yellow	$F(000)$	664
Crystal system	Monoclinic	Goodness of fit on F^2	1.095
Space group	$P2_1/n$	Data / restraints / parameters	2 839 / 0 / 163
a / nm	0.774 51(4)	Absorption coefficient / mm^{-1}	2.363
b / nm	1.252 49(5)	Largest diff. Peak and hole / ($\text{e}\cdot\text{nm}^{-3}$)	378 / -648
c / nm	1.315 96(7)	$R_1, wR_2 (I>2\sigma(I))$	0.0261, 0.0679
$\beta / (^\circ)$	100.294(3)	R_1, wR_2 (all data)	0.027 9, 0.069 0

Table 2 Selected bond lengths (nm) and angles ($^\circ$) for title complex

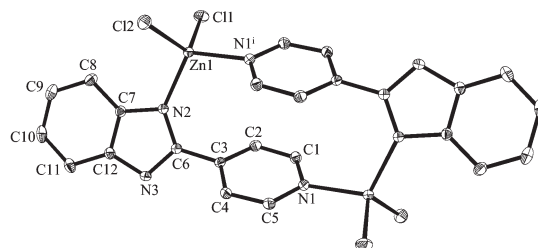
Zn(1)-N(2) ⁱ	0.202 7(1)	Zn(1)-Cl(2)	0.222 70(5)	Zn(1)-Cl(1)	0.225 79(5)
Zn(1)-N(1)	0.205 9(1)				
N(2) ⁱ -Zn(1)-N(1)	112.06(6)	N(1)-Zn(1)-Cl(2)	104.58(4)	N(1)-Zn(1)-Cl(1)	104.28(4)
N(2) ⁱ -Zn(1)-Cl(2)	107.76(4)	N(2) ⁱ -Zn(1)-Cl(1)	108.40(4)	Cl(2)-Zn(1)-Cl(1)	119.72(2)

Symmetry transformations used to generate equivalent atoms: ⁱ $-x, -y+1, -z+1$.

2 Results and discussions

As shown in Fig.1, the title complex displays discrete structure. Two same $[(\text{ZnCl}_2)(\text{PyBIIm})]$ units are centrosymmetric via the special position $(0, 0.5, 0.5)$. The Zn atom is coordinated by two Cl atoms and two N atoms from two PyBIIm ligands in a distorted tetrahedral geometry. In the metal coordination center, Zn-Cl1, Zn-Cl2 distances are 0.225 79(5) and 0.222 70(5) nm with Cl1-Zn-Cl2 bond angle of $119.72(2)^\circ$, and Zn-N1ⁱ, Zn-N2 distances are 0.2059(1) and 0.2027(1) nm with N1ⁱ-Zn-N2 bond angle of $112.06(6)^\circ$ (Table 2). Two metal atoms, Zn1 and Zn1ⁱ (Zn \cdots Zn 0.709 4(5) nm), are connected by two PyBIIm ligands to form a Zn1-PyBIIm-Zn1ⁱ ring (-Zn1-N2-C6-C3-N1-Zn1ⁱ-N2ⁱ-C6ⁱ-C3ⁱ-N1ⁱ), of which all the atoms are coplanar with mean deviation of 0.004 83 nm. The dihedral angle between pyridyl ring (C1-C2-C3-C4-C5-N1) and Zn1-PyBIIm-Zn1ⁱ ring is 62.8° (symmetry code: ⁱ $-x, 1-y, 1-z$).

The PyBIIm ligand adopts bidentate coordination mode^[9-10], acting as bridge to link two metal atoms with two nitrogen atoms (N2 and N1) from benzimidazole and pyridyl rings, respectively. In the previously reported



Symmetry code: ⁱ $-x, 1-y, 1-z$

Fig.1 Structure of title complex

complexes, when the benzimidazole and pyridyl rings of PyBIIm are coplanar, the PyBIIm ligand generally displays unidentate coordination mode^[11-13], whereas in the title complex, the two rings are not coplanar with dihedral angle of 54.6° . The difference results from the different coordination surroundings, which spurs the ligand in the complex to make the change required to build the additional connection. Therefore, the bidentate PyBIIm complexes^[9-10,13] generally contain non-coplanar benzimidazole and pyridyl rings.

It is notable that there exists hydrogen bonding and $\pi \cdots \pi$ interactions in the title complex. As shown in Fig.2a, one type of hydrogen bonding, N-H \cdots Cl, occurs in the molecular packing. The N3 \cdots Cl1 bond

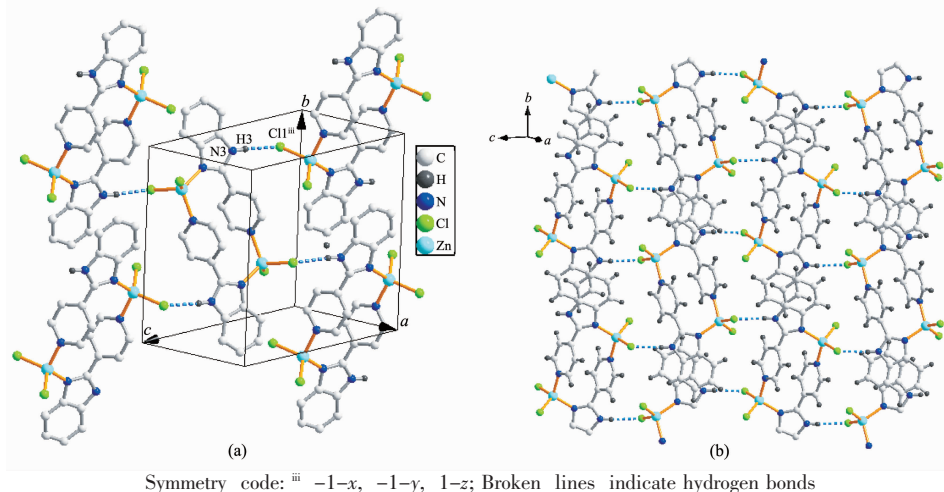


Fig.2 (a) Hydrogen binding interactions in the molecule structures; (b) Two dimensional layer formed by hydrogen bonds

distance is 0.325 0(2) nm ($\angle \text{DHA}=174.9^\circ$). The molecules of the complex are joined together by such hydrogen bonding interactions and further extend the structure into a two-dimensional layer (Fig.2b). In the binuclear metal structure the two pyridyl rings are parallel each other and cause $\pi \cdots \pi$ stacking (Fig.3a) with centroid-to-centroid distance of 0.349 7 nm ($\text{Cg} \cdots \text{Cg}^i$, symmetry code: $^i -x, 1-y, 1-z$) and interplanar spacing of 0.320 3 nm. On the other hand, there also exists inter-molecular $\pi \cdots \pi$ interactions in the two-dimensional layer. The adjacent aromatic rings of the PyBIIm molecules occur weak $\pi \cdots \pi$ stacking (Fig.3b) with centroid-to-centroid distance of 0.374 5 nm ($\text{Cg} \cdots \text{Cg}^{ii}$, symmetry code: $^{ii} -1+x, 1+y, z$) and interplanar spacing of 0.341 6 nm, respectively. Obviously, these noncovalent interactions further consolidate the structural architecture.

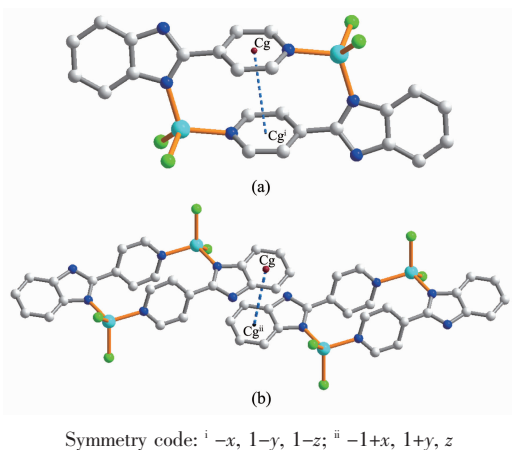


Fig.3 (a) Intra-molecular $\pi \cdots \pi$ interaction; (b) Inter-molecular $\pi \cdots \pi$ interaction

It is well-known that d^{10} transition metal complexes possess varied luminescent properties. Organic ligands and their coordinate modes obviously affect their emission wavelengths and luminescent mechanisms^[14]. To study the luminescence of the title complex, the fluorescent analysis was performed at room temperature in solid state. The result shows that the complex exhibits an intense luminescence with a maximum peak at 570 nm ($\lambda_{\text{ex}}=450$ nm) (Fig.4). It is known that the free ligand has a weak luminescence at ca. 490 nm in the solid state at room temperature. So, the luminescence of the complex may be assigned to be ligand-to-metal charge transfer (LMCT) emission.

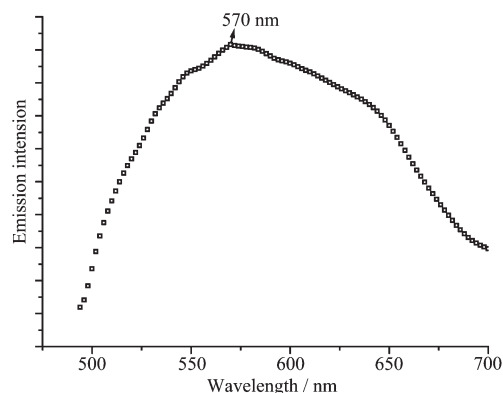


Fig.4 Fluorescent spectrum of the title complex

The TGA result shows that the complex exhibits high thermal stability. From 35 to 430 $^\circ\text{C}$, the complex is stable. In the temperature range of 430~900 $^\circ\text{C}$, the weight loss is ca. 45.0%, corresponding to the release of PyBIIm ligands. However, the observed weight loss is lower than the predicted value (58.8%). This may be due to the retention of some carbonaceous residue in the final solid phase (black in color).

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