

## 二维双层蜂窝状锌配合物的合成、晶体结构及性质研究

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**摘要:** 利用水热反应合成了一种新的二维双层蜂窝状锌配合物  $[\text{Zn}_2(\text{atz})_3(\text{N}_3)] \cdot \text{H}_2\text{O}$  (**1**) (atz=5-氨基四氮唑), 并用元素分析, 红外光谱和 X-射线单晶衍射对其结构进行了表征, 该配合物属单斜晶系,  $C2/m$  空间群, 晶胞参数为:  $a=1.039\ 7(2)\ \text{nm}$ ,  $b=1.792\ 7(4)\ \text{nm}$ ,  $c=1.109\ 2(2)\ \text{nm}$ ,  $V=1.887\ 0(7)\ \text{nm}^3$ ,  $Z=4$ 。该锌配合物是由  $\text{N}_3^-$  和原位合成的 5-氨基四氮唑阴离子构成, 拓扑分析表明该化合物显示出独特的 4-连接六边形的蜂窝双层结构。同时还测定了该化合物的热稳定性及荧光性质。

**关键词:** 锌配合物; 5-氨基四氮唑; 晶体结构; 热稳定性; 荧光性质

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## Synthesis, Crystal Structure and Properties of 2D Bilayer Honeycomb Network Zinc(II) Complex

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**Abstract:** A new 2D bilayer honeycomb zinc complex of  $[\text{Zn}_2(\text{atz})_3(\text{N}_3)] \cdot \text{H}_2\text{O}$  (**1**) (atz=5-amino-tetrazolate), has been synthesized under the hydrothermal condition and characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. The crystal structure of **1** is of monoclinic, space group  $C2/m$  with  $a=1.039\ 7(2)\ \text{nm}$ ,  $b=1.792\ 7(4)\ \text{nm}$ ,  $c=1.109\ 2(2)\ \text{nm}$ ,  $V=1.887\ 0(7)\ \text{nm}^3$ ,  $Z=4$ . Complex **1** is built from  $\text{N}_3^-$  anion and *in-situ* generated 5-amino-tetrazolate ligand. The topological net of **1** shows a unique four-connected hexagonal bilayer “hcb” topology (honeycomb network). Thermal stability and luminescent property of the complex have also been investigated. CCDC: 722571.

**Key words:** zinc complex; 5-amino-tetrazolate; crystal structure; thermal stability; luminescent property

Recently, supramolecular chemistry and crystal engineering of the metal-organic frameworks (MOFs) become hot topics in structural topology and material science, because the MOFs show great intriguing network topologies as well as their potential application in anion/guest exchange<sup>[1-3]</sup>, catalysis<sup>[4-5]</sup>, magnetism<sup>[6-7]</sup>, luminescence<sup>[8]</sup>, gas storage<sup>[9-10]</sup>, and so on. Since Wells

firstly used “node and spacer” approach in interpreting the inorganic crystal structures<sup>[11-12]</sup>, Robson<sup>[13-14]</sup> and others<sup>[15-16]</sup> applied this approach to generate numerous coordination polymers with topologies such as  $\alpha$ -polonium or NaCl, NbO, PtS, CdSO<sub>4</sub>, Pt<sub>3</sub>O<sub>4</sub>, Diamond, Rutile, Boracite, and so on, which are realistic topology of inorganic compounds or minerals in nature.

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Meanwhile, two-dimensional (2D) topologies compounds that contain three-, four-, five- or six-sided polygons has aroused particular attention because the 2D topologies always feature as (6,3) honeycomb, (4,4) square grid, bilayer, etc. However, it is rarely observed that the networks consist of mixed polygons or nodes in 2D arrangement. To the best of our knowledge, only one compound with a four-connected regular 2D bilayer honeycomb topological network has been reported by Wang' group<sup>[17]</sup>. Hereupon, we applied the mix-ligand synthetic approach to synthesize another four-connected 2D bilayer honeycomb topological network compounds. The crystalline phase purity was confirmed by the powder X-ray diffraction (PXRD) pattern of the bulk solids, and the composition was further defined from single crystal X-ray diffraction, elemental analysis and vibrational spectroscopy. Additionally, the thermal stability and photoluminescence behavior of this complex was also investigated.

## 1 Experimental

### 1.1 Materials and general methods

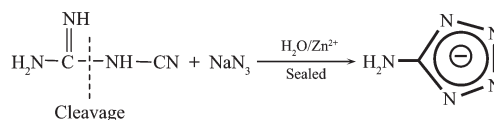
All reagents and solvents employed were commercially available and used without further purification. Infrared spectra were recorded in the range 4 000~400  $\text{cm}^{-1}$  on a Perkin-Elmer FTIR spectrum 2000 spectrometer using KBr pellets. Elemental analyses were performed with a Perkin-Elmer model 240C instrument. Thermal analyses were performed on a Delta Series TGA7 instrument in  $\text{N}_2$  atmosphere with heating rate of 10  $^{\circ}\text{C} \cdot \text{min}^{-1}$  from 30 to 750  $^{\circ}\text{C}$ . Powder X-ray diffraction (PXRD) data were obtained by using a Rigaku D/MAX 2500V/PC diffractometer with  $\text{Cu } K\alpha_1$  ( $\lambda=0.154\ 056\ \text{nm}$ ) radiation. A step size of 0.05 $^{\circ}$  and counting time of 1.2 s/step were applied in a 2 $\theta$  range of 8.0 $^{\circ}$ ~60.0 $^{\circ}$ .

### 1.2 Synthesis for complex 1

Synthesis of  $\{[\text{Zn}_2(\text{atz})_3(\text{N}_3)] \cdot \text{H}_2\text{O}\}_n$  (**1**): A mixture of

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.148 5 g, 0.5 mmol),  $\text{NaN}_3$  (0.065 g, 1.0 mmol), dicyandiamide (DCDA) (0.042 g, 0.5 mmol), ethanol (2 mL) and water (8 mL) was stirred for 30 min in air, then sealed in a 23 mL Teflon autoclave and heated at 130  $^{\circ}\text{C}$  for 3 d. After the sample was cooled to room temperature at a rate of 10  $^{\circ}\text{C} \cdot \text{h}^{-1}$ , colorless prism crystals were obtained in ca. 28% yield based on Zn. Anal. calcd. for  $\text{C}_3\text{H}_8\text{N}_{18}\text{OZn}_2$  ( $M_r=443.01$ , %): C, 8.13; H, 1.82; N, 56.92; Found(%): C, 8.22; H, 1.71; N, 56.03.

Herein, 5-amino-tetrazole was successfully *in situ* generated from the reactions of dicyandiamide (DCDA) and sodium azide under hydro(solvo)thermal conditions (Scheme 1). Here, the C-N cleavage occurring under these circumstances seems rather unusual but was observed in our past work<sup>[18-21]</sup>.



Scheme 1 Reaction mechanism for the *in situ* generated 5-amino-tetrazole

### 1.3 Single crystal structure determination

Suitable single crystal of complex was mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Rigaku Saturn 724 CCD diffractometer with graphite monochromatized  $\text{Mo } K\alpha$  radiation ( $\lambda=0.071\ 073\ \text{nm}$ ). Crystal structure was solved by the direct method and different Fourier syntheses. All calculations were performed using the SHELX-97 program<sup>[22]</sup>. All non-hydrogen atoms were refined by full-matrix least-squares techniques on  $F^2$  with anisotropic thermal parameters. The hydrogen atoms were fixed at calculated positions and refined by using a riding mode. Crystal data and details of the data collection and the structure refinement are given in Table 1. Selected bond lengths and bond angles of the compounds are listed in Table 2.

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Table 1 Crystal data and structure refinement for complex 1

Empirical formula	$\text{C}_3\text{H}_8\text{N}_{18}\text{OZn}_2$	$\mu(\text{Mo } K\alpha) / \text{mm}^{-1}$	2.574
Formula weight	443.01	$F(000)$	880
Crystal system	Monoclinic	$2\theta / ^{\circ}$	3.04~5.99
Space group	$C2/m$	Reflections collected / unique ( $R_{\text{in}}$ )	6 854 / 1 921 (0.057 2)

Continued Table 1

$a / \text{nm}$	1.039 7(2)	Observed reflections [ $I > 2\sigma(I)$ ]	1 472
$b / \text{nm}$	1.792 7(4)	Data completeness	0.996
$c / \text{nm}$	1.109 2(2)	Data / restraints / parameters	1 985 / 0 / 123
$\beta / (^{\circ})$	114.12(3)	GOF on $F^2$	1.034
$V / \text{nm}^3$	1.887 0(7)	$R_1, wR_2$ [ $I > 2\sigma(I)$ ]	0.0444, 0.0986
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.559	$R_1, wR_2$ [all data]	0.061 1, 0.104 2
$Z$	4	Max peak, hole / ( $\text{e} \cdot \text{nm}^{-3}$ )	467, -449

Table 2 Selected bond lengths (nm) and angles ( $^{\circ}$ ) for 1

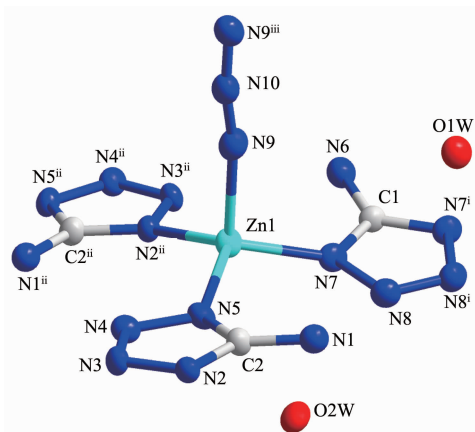
N5-Zn1	0.197 7(3)	N2 <sup>ii</sup> -Zn1	0.199 2(3)	N7-Zn1	0.198 5(4)
N9-Zn1	0.196 5(4)	N9-N10	0.113 9(4)		
N9-Zn1-N5	103.90(14)	N9-Zn1-N7	104.62(14)	N5-Zn1-N7	113.76(13)
N9-Zn1-N2 <sup>iv</sup>	104.68(14)	N5-Zn1-N2 <sup>iv</sup>	114.34(13)	N7-Zn1-N2 <sup>iv</sup>	113.99(13)
N9-N10-N9 <sup>iii</sup>	169.2(6)				

Symmetry codes: <sup>ii</sup>  $0.5+x, 1.5-y, z$ ; <sup>iii</sup>  $-x, y, -z$ ; <sup>iv</sup>  $x-1/2, -y+3/2$ .

## 2 Results and discussion

### 2.1 Description of the structure

Single crystal X-ray analysis shows that complex **1** is a 2D bilayer structure, which contains one  $\text{Zn}^{2+}$  cation, one and half of one crystallographically independent anionic  $\text{atz}^-$  ligands, half of one crystallographically azide anion, and half of one free water molecule disordered and sited on two positions with the occupancy factor ratio of 0.3:0.2 in the asymmetric unit (Fig.1). The  $\text{Zn}(\text{II})$  ion is coordinated with four nitrogen atoms from three bridging  $\mu_2\text{-atz}^-$  ligands and one bridging  $\mu_{1,3}$ -azide ligand to form a  $\text{ZnN}_3\text{O}$  tetrahedron



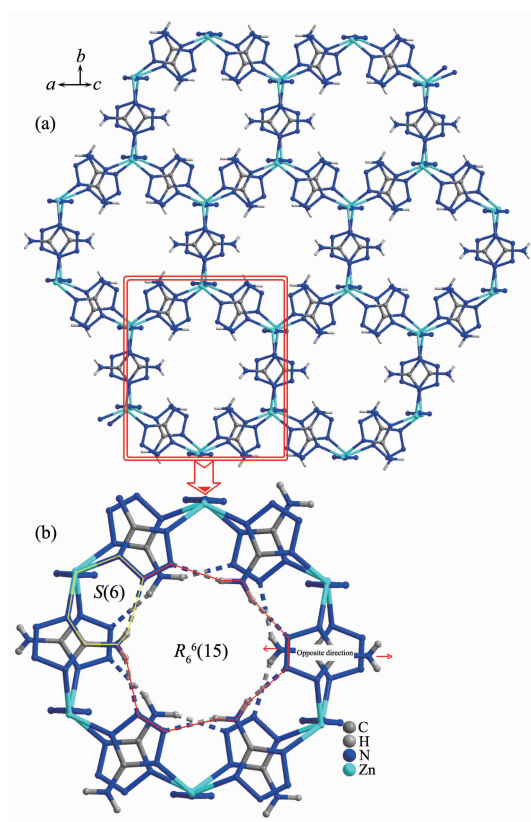
Hydrogen atoms are omitted for clarity; Symmetry codes: <sup>i</sup>  $x, 1-y, z$ ; <sup>ii</sup>  $0.5+x, 1.5-y, z$ ; <sup>iii</sup>  $-x, y, -z$

Fig.1 View of the coordination environment of  $\text{Zn}^{2+}$  in **1** at 30%

with the *cis*-bond angles ranging from  $103.9(3)^{\circ}$ ~ $114.3(2)^{\circ}$ . The bond lengths of Zn-N range from  $0.196\ 5(4)$ ~ $0.199\ 2(3)$  nm. All the Zn-N bond lengths are comparable to those of the  $\text{Zn}(\text{II})$ -tetrazole [17,20,23] and the  $\text{Zn}(\text{II})$ -azide[24] complexes.

In this complex, the tetrahedrally coordinated Zn atoms are bridged by the  $\mu_2\text{-atz}^-$  ligands into (6,3) topological networks paralleling the *ab* plane, which are further interlinked by  $\mu_{1,3}$ -azide group along the [001] direction to form a bilayer honeycomb feature with the six-sided polygon length range about  $0.590\ 9(2)$ ~ $0.602\ 9(1)$  nm (Fig.2a).

Remarkable, the topological net of **1** shows unique four-connected hexagonal bilayer “hcb” topology (honeycomb network)[25-26], with the Schlfl symbol[27] of  $4^3 \cdot 6^3$  and the vertex symbol or long symbol[28] of  $4 \cdot 6_2 \cdot 4 \cdot 6_2 \cdot 4 \cdot 6_2$  (Fig.3). According to the classification of the double-net sphere packing graphs for layer group, this network is of the type (6,3)Ia. To the best of our knowledge, there are still few reported complexes exhibiting highly regular 2D bilayer topology that possess four-connected nodes and a mix of squares and hexagons[29-31]. Furthermore, only one similar 2D four-connected  $4^3 \cdot 6^3$  network compound containing a mix of four- and six-sided polygons has been reported[17]. Complex **1** is another complex with this topology net. Compared carefully with the similar compound reported



Disorder water molecules are omitted; Red arrow indicated the amino groups with the opposite orientation in (b)

Fig.2 (a) View of the 2D honeycomb bilayer of **1**; (b) Hexagonal bilayer “hcb” topology SBU showing the N–H···N hydrogen bonds and the formation  $S(6)$  and  $R_6^6(15)$  motifs

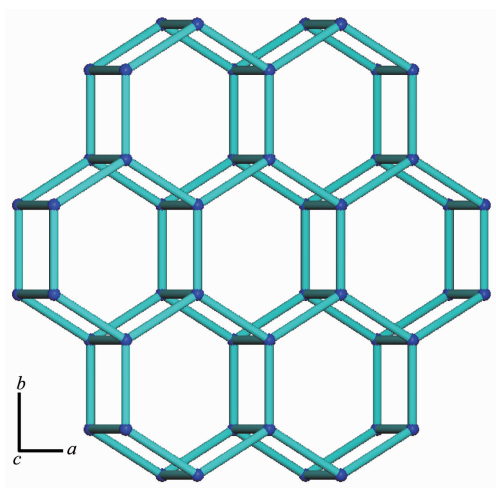


Fig.3 View of the unique 4-connected topology suggesting the highly regular 2D bilayer “hcb” topological network

by Wang, there are two distinct features between them: one is the bridging ligand ( $\mu_2$ -atz<sup>−</sup> for Wang's complex,

$\mu_{1,3}$ -azide<sup>−</sup> for **1**) between the bilayer. The other is orientation of the amino group ligands between the over against honeycomb in the bilayer (oriented the opposite direction for **1**, shown as Fig.2b; oriented the same direction for Wang's complex). Within the crystal structure of **1**, the terminal amino groups of each atz<sup>−</sup> donate H atoms to the adjacent noncoordinated tetrazole ring N atoms to generate intra-molecular N–H···N hydrogen bonding interactions with  $S(6)$  and  $R_6^6(15)$  motifs<sup>[32]</sup> (Fig.2b). These specific hydrogen-bonding interactions play a critical role in stabilizing the hexagonal honeycomb framework. The 2D bilayers further pack along [001] direction into 3D porous supramolecular structure via  $\pi \cdots \pi$  stacking interactions between the neighboring layers. The distance between the centroids of the tetrazole rings is 0.340 3(1) nm. Complex **1** has large open channels, a total potential solvent accessible volume of 36.3% calculated using PLATON<sup>[33]</sup>. These voids are filled with disorder free water molecules in this structure.

## 2.2 Powder X-ray diffraction

PXRD experiment was carried out on this complex in order to establish its crystalline phase purity. As shown in the PXRD patterns (Fig.4), the major peak positions of the PXRD patterns of the bulk solid of **1** matched well with that of the simulated patterns obtained from respective single-crystal data, indicating the presence of mainly one crystalline phase in complex **1**.

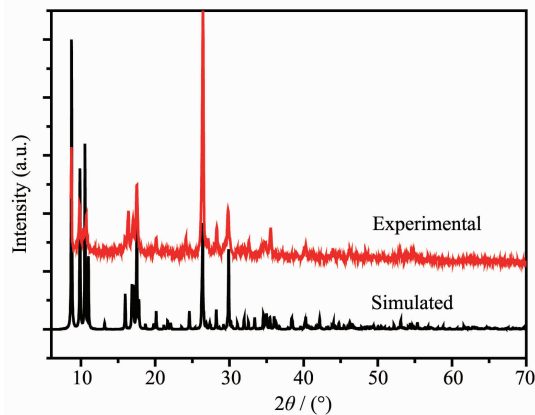


Fig.4 Powder XRD pattern of the product obtained from the experiment associated with the XRD pattern simulated from the single crystal X-ray data for complex **1**

### 2.3 Vibrational spectroscopy

Vibrational spectroscopy, such as IR and Raman spectroscopy, is adequate to identify the existence of azide group and tetrazole ring in complex **1**<sup>[34]</sup>. Fig.5 illustrates the IR as well as the Raman spectrum of **1**. The most intensive vibration in the IR spectrum is the  $\nu_{\text{sym}}$  vibration of the azide group ( $\text{N}_3^-$ ) at  $2\,179\text{ cm}^{-1}$ , which can also be seen in the Raman spectrum. The broad signal at  $1\,611\text{ cm}^{-1}$  can be assigned to the stretch vibration between the atoms C and N. In the range of  $1\,000\sim1\,165\text{ cm}^{-1}$  many deformation vibrations and combinations of the tetrazole ring can be found in complex **1**.

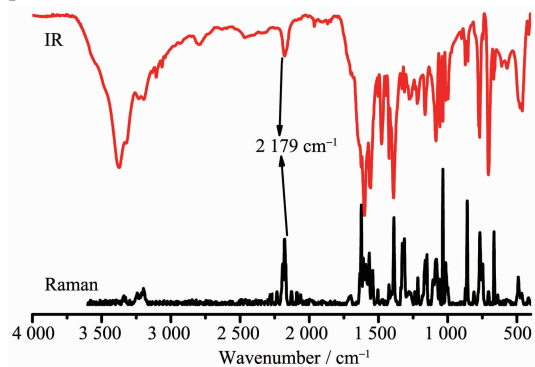


Fig.5 Vibrational spectra of **1**

### 2.4 Fluorescent property

The solid-state fluorescent property of **1** was investigated at room temperature. As illustrated in Fig. 6, upon excitation of this solid sample at 370 nm, the intensely broad blue-fluorescent emission bands are observed about 430 and 475 nm. For excitation wavelengths between 280 and 480 nm, the free Hatz ligand presents photoluminescence emissions at 325 nm according to the reported literature<sup>[17]</sup>. Taking

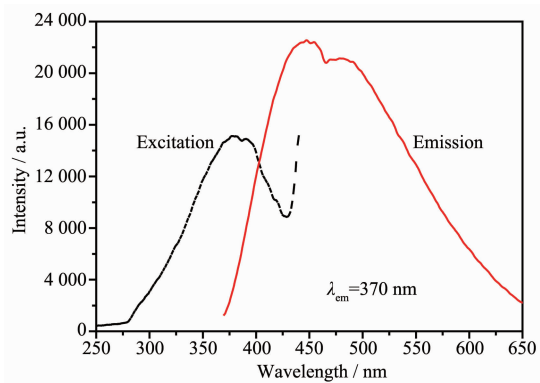


Fig.6 Solid-state fluorescence spectra of **1** at room temperature

the emission bands of these free organic ligands into consideration, the fluorescence emission and red-shift of **1** may be attributed to the cooperative effects of intraligand emission and/or ligand-to-metal charge transition (LMCT), which has been observed in other tetrazole-based Zn(II) coordination polymer<sup>[17,21,35-36]</sup>. Along with the high thermal stability and insolubility in common inorganic or organic solvents, the emission in the blue region makes this compound potential blue-light emitting material.

### 2.5 Thermal stability analyses

The thermal stability of this complex in  $\text{N}_2$  was examined by the TG techniques in the temperature range of  $30\sim800\text{ }^\circ\text{C}$ . The TG curve for complex **1** is at a heating rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  under  $\text{N}_2$  atmosphere. As shown in Fig.7, there is no significant weight loss within the temperature range of  $30\sim300\text{ }^\circ\text{C}$ . Beyond  $300\text{ }^\circ\text{C}$ , complex **1** undergoes two weight loss processes, corresponding to the removal of the azide groups and atz ligands and resulting in the collapse of the framework of this complex.

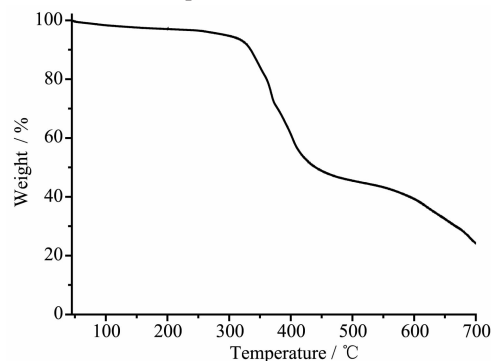


Fig.7 TG curve for complex **1**

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