

两种磺胺喹噁啉锌(II)配合物的合成、晶体结构和荧光性质

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摘要: 以磺胺喹噁啉为配体合成了 2 种锌的配合物 $[\text{Zn}(\text{L})_2(\text{phen})] \cdot \text{H}_2\text{O}$ (**1**) 和 $[\{\text{Zn}(\text{L})_2(\text{bpy})\} \cdot 2\text{EtOH}]_n$ (**2**) (L =磺胺喹噁啉, phen=菲咯啉, bpy=4,4'-联吡啶) 并对其进行了单晶 X-射线衍射, 粉末 X-射线衍射, 热重, 元素分析, 红外光谱, 紫外光谱和荧光光谱测定。单晶 X-射线分析表明化合物 **1** 是单核结构, 属单斜晶系, $P2_1/c$ 空间群。化合物 **2** 是一维结构, 属单斜晶系, $C2/c$ 空间群。热分析表明化合物 **1** 和 **2** 都有很高的热稳定性。

关键词: 磺胺喹噁啉; Zn(II)配合物; 晶体结构; 荧光性质

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Syntheses, Crystal Structures and Fluorescent Properties of Two Zn(II) Complexes Based on Sulfaquinoxalines

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Abstract: Two Zn(II) compounds, $[\text{Zn}(\text{L})_2(\text{phen})] \cdot \text{H}_2\text{O}$ (**1**) and $[\{\text{Zn}(\text{L})_2(\text{bpy})\} \cdot 2\text{EtOH}]_n$ (**2**) (L =sulfaquinoxaline, phen=phenanthroline, bpy=4,4'-bipyridine) have been synthesized and characterized by single crystal X-ray diffraction, thermal analysis, elemental analysis, IR, UV-Vis and fluorescence. Single crystal X-ray diffraction reveals that complex **1** is a mononuclear structure and complex **2** is one-dimensional structure. Thermal analyses show that complex **1** and **2** have high thermal stability. CCDC: 991934, **1**; 991935, **2**.

Key words: sulfaquinoxaline; Zn(II) compound; crystal structure; fluorescence

0 Introduction

In the field of supramolecular chemistry, great interest has recently been focused on the crystal engineering of coordination frameworks due to their new topologies, intriguing architectures, intertwining

phenomena, and potential applications in microelectronics, nonlinear optics, molecular selection, ion exchange, and catalysis^[1-4]. It has been documented that the geometries and properties of organic ligands exert great effect on structural frameworks of supramolecules^[5-6]. As we all know that sulfaquinoxaline

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is not only an excellently versatile ligand but also widely used in medicine due to their pharmaceutical properties such as antibacterial^[7] and antitumor^[8-13] activity. Sulfonamides belong to one class of synthetic antibiotics^[14]. They have been widely used for treatment of many human and animal diseases, such as infectious diseases of gastrointestinal and respiratory^[15-17]. The use of metal complexes as pharmaceutical has shown great promise in recent years as anticancer agents^[18]. For example, Ag(I) coordination compound^[19], Ce(III) coordination compound^[20], Ni(II) coordination compound^[21] and Cu(II) coordination compound^[22-24] have shown higher antimicrobial activity than free ligands. These findings have aroused considerable interests and much more effort has been devoted to design and synthesize new multifunctional coordination compounds. Currently, the complexes which are formed by sulfaquinoxaline and transition metals have not been storied. In this paper, we report the syntheses and crystal structures of two Zn(II) complexes, namely, $[\text{Zn}(\text{L})_2(\text{phen})] \cdot \text{H}_2\text{O}$ (**1**) and $\{[\text{Zn}(\text{L})_2(\text{bpy})] \cdot 2\text{EtOH}\}_n$ (**2**), which characterized by single crystal X-ray diffraction, powder X-ray diffraction, thermal analysis, elemental analysis, UV-Vis and fluorescence.

1 Experimental

1.1 Materials and measurements

All commercially available chemicals are of reagent grade and were used as received without further purification. Elemental analyses (C, H, and N) were performed using an EA1110CHNS-0 CE elemental analyzer. The FTIR spectra were recorded from KBr pellets in the range of 4 000~400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer. UV-visible spectra were recorded (190~400 nm region) on a TU-1901 UV-Vis spectrophotometer, Beijing pgeneral. Thermal analyses were carried out in air atmosphere with a heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$ on a S II TG/DTA 7300 integration thermal analyzer. The solid state fluorescence spectra were measured on F-4600 Fluorescence spectrophotometer. Powder X-ray diffraction(PXRD) data were collected on a Bruker D8 Focus X-ray diffractometer using Cu $K\alpha_1$ ($\lambda=0.154\ 06$

nm) radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program. Single crystal X-ray diffraction was performed on a Bruker SMART APEX-II CCD area detector.

1.2 Synthesis of $[\text{Zn}(\text{L})_2(\text{phen})] \cdot \text{H}_2\text{O}$ (**1**)

The sample of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mg, 4 μmol), sulfaquinoxaline sodium (26 μg , 4 μmol) and 1,10-phen (8 μg , 4 μmol) were placed in a small vial including ethanol(0.06 mL) and H_2O (0.5 mL). The vial was sealed and heated to 80 $^{\circ}\text{C}$ for two days and thereafter cooled slowly to room temperature, and yellow bulk crystal was gained (Yield: 27%). Anal. Calcd.(%) for **1** ($\text{C}_{40}\text{H}_{32}\text{N}_{10}\text{O}_5\text{S}_2\text{Zn}$): C 55.72, H 3.74, N 16.24; Found (%): C 54.21, H 3.86, N 17.16. IR (KBr, cm^{-1}): 3 442(m), 1 623(m), 1 596(m), 1 542(m), 1 518(w), 1 502(w), 1 490(w), 1 465(w), 1 418(s), 1 347(s), 1 328(w), 1 298(m), 1 277(m), 1 247(w), 1 183(w), 1 137(vs), 1 086(vs), 1 037(w), 1 014(w), 949(m), 764(m), 724(m), 685(vs), 609(s), 543(vs).

1.3 Synthesis of $\{[\text{Zn}(\text{L})_2(\text{bpy})] \cdot 2\text{EtOH}\}_n$ (**2**)

A aqueous solution (5.0 mL) of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.022 g, 0.10 mmol) was placed at the bottom of a glass tube. Ethanol (6.0 mL) were added slowly in middle part of glass tube, finally upon which a solution of sulfaquinoxaline 0.032 g (0.10 mmol) and 0.020 g (0.10 mmol) 4, 4-bpy in ethanol (5.0 mL) was carefully layered. The glass tube at room temperature was allowed to stand for 15 days, and the yellow crystal precipitated in the middle of tube (Yield: 59%). Anal. Calcd.(%) for **2** ($\text{C}_{42}\text{H}_{42}\text{N}_{10}\text{O}_6\text{S}_2\text{Zn}$): C 55.29; H 4.64; N 15.35; Found (%): C 56.02, H 4.77; N 15.47. IR(KBr, cm^{-1}): 3 525(m), 3 315(m), 3 195(m), 2 967(w), 1 642(m), 1 597(m), 1 543(m), 1 493(m), 1 426(m), 1 352(vs), 1 299(s), 1 287(s), 1 250(m), 1 217(s), 1 180(m), 1 134(m), 1 086(s), 951(m), 899(s), 853(s), 832(s), 817(s), 775(s), 761(s), 733(s), 719(s), 671(s), 635(w), 613(s), 556(m), 537(m), 510(w).

1.4 X-ray diffraction data collection and refinement

Crystallographic data for **1** (size: 0.48 mm×0.41 mm×0.34 mm) and **2** (size: 0.48 mm×0.45 mm×0.38 mm) were selected under a Bruker-AXS diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda =$

0.710 73nm) for cell determination and subsequent data collection at room temperature. All absorption corrections were applied using the ABSCOR (Higashi, 1995) program^[25]. The Lp factor and empirical absorption were performed to correct and store the data and correct the unit cell parameters by using SAINT and SMART software^[26-27]. The structure was solved by using direct method and followed by successive Fourier and difference Fourier syntheses. The metal atoms were located from the E-maps, and other non-hydrogen atoms were derived from the successive difference Fourier synthesis, All non-hydrogen atoms

were refined with anisotropic displacement parameters by full-matrix least-squares technique. All hydrogen atoms were placed geometrically and were refined in a riding-model approximation. The structure were refined on F^2 by full-matrix least-square using SHELX-97 programs package^[28]. The crystallographic data as well as details of the data collection and refinement for complexes **1** and **2** were listed in Table 1, the selected bond lengths and bond angles in Table 2 and hydrogen bond lengths and bond angles in Table 3.

CCDC: 991934, **1**; 991935, **2**.

Table 1 Crystal data and structure refinement for complexes **1** and **2**

Empirical formula	C ₃₀ H ₄₂ N ₃₀ O ₉ S ₄ Zn ₂ (1)	C ₄₂ H ₄₂ N ₁₀ O ₆ S ₂ Zn (2)
Formula weight	1 706.55	912.39
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a / nm	1.699 6(3)	2.681 7(9)
b / nm	1.066 83(18)	1.138 5(4)
c / nm	2.087 3(4)	1.697 2(6)
β / (°)	100.703(2)	126.553(3)
Volume / nm ³	3.718 8(11)	4.163(2)
Z	2	4
D_c / (g·cm ⁻³)	1.526	1.456
Absorption coefficient / mm ⁻¹	0.833	0.752
h, k, l range	-22~21, -13~13, -26~26	-34~33, -14~14, -22~22
$F(000)$	1 760	1 896
Reflections collected	31 771	17 742
Reflections unique	8 441	4 816
θ range for data collection / (°)	1.99 to 27.46	2.40 to 27.51
Completeness / %	99.3($\theta=27.46^\circ$)	99.7($\theta=27.57^\circ$)
R_{int}	0.050 5	0.050 9
Data / restraints / parameters	8441 / 22 / 402	4 805 / 0 / 279
Goodness of fit on F^2	1.099	1.023
Final R indices ($I > 2\sigma(I)$)	$R_1=0.100$ 8, $wR_2=0.281$ 0	$R_1=0.037$ 7, $wR_2=0.106$ 2
R indices (all data)	$R_1=0.161$ 7, $wR_2=0.327$ 2	$R_1=0.046$ 3, $wR_2=0.113$ 9
Largest diff. peak and hole / (e·nm ⁻³)	1 646 and -1 528	419 and -420

Table 2 Selected bond lengths (nm) and bond angles (°) for complexes **1** and **2**

Complex 1					
Zn(1)-N(10)	0.210 44(7)	Zn(1)-N(1)	0.211 41(8)	Zn(1)-N(9)	0.211 71(8)
Zn(1)-N(6)	0.215 10(8)	Zn(1)-N(5)	0.229 91(8)	Zn(1)-N(2)	0.234 67(7)
N(10)-Zn(1)-N(1)	105.72(3)	N(10)-Zn(1)-N(9)	79.06(2)	N(1)-Zn(1)-N(9)	101.35(3)

Continued Table 2

N(10)-Zn(1)-N(6)	99.29(3)	N(1)-Zn(1)-N(6)	103.89(3)	N(9)-Zn(1)-N(6)	154.13(4)
N(10)-Zn(1)-N(5)	97.37(3)	N(1)-Zn(1)-N(5)	153.91(3)	N(9)-Zn(1)-N(5)	94.73(3)
N(6)-Zn(1)-N(5)	59.672(18)	N(10)-Zn(1)-N(2)	162.11(4)	N(1)-Zn(1)-N(2)	59.950(17)
N(9)-Zn(1)-N(2)	92.79(3)	N(6)-Zn(1)-N(2)	94.93(3)	N(5)-Zn(1)-N(2)	99.18(3)
Complex 2					
Zn(1)-N(5)	0.214 7(2)	Zn(1)-N(6)	0.215 2(2)	Zn(1)-N(2)	0.2178 9(17)
Zn(1)-N(2) ⁱ	0.217 89(17)	Zn(1)-N(3)	0.227 87(17)	Zn(1)-N(3) ⁱ	0.227 87(18)
N(5)-Zn(1)-N(6)	180.0	N(5)-Zn(1)-N(2)	92.03(4)	N(6)-Zn(1)-N(2)	87.97(4)
N(5)-Zn(1)-N(2) ⁱ	92.03(4)	N(6)-Zn(1)-N(2) ⁱ	87.97(4)	N(2)-Zn(1)-N(2) ⁱ	175.94(8)
N(5)-Zn(1)-N(3)	86.01(4)	N(6)-Zn(1)-N(3)	93.99(4)	N(2)-Zn(1)-N(3)	60.38(7)
N(2)#-Zn(1)-N(3)	119.94(7)	N(5)-Zn(1)-N(3) ⁱ	86.01(4)	N(6)-Zn(1)-N(3) ⁱ	93.99(4)
N(2)-Zn(1)-N(3) ⁱ	119.94(7)	N(2)#1-Zn(1)-N(3) ⁱ	60.38(7)	N(3)-Zn(1)-N(3) ⁱ	172.01(7)

Symmetry codes: ⁱ 1-x, y, 1/2-z; ⁱⁱ x, y-1, z; ⁱⁱⁱ x, y+1, z for **2**

Table 3 Hydrogen bond lengths (nm) and bond angles (°) for complexes **1** and **2**

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠ DHA
Complex 1				
N4-H4A...N4 ^{iv}	0.085 98	0.237 93	0.276 2(17)	107.49
O5-H5A...O2 ^v	0.094 29	0.158 34	0.247 3(17)	155.71
C13-H13...S ^{vi}	0.093 09	0.251 28	0.328 3(13)	140.20
C37-H37...O4 ^{vii}	0.092 90	0.259 39	0.338 8(11)	143.75
Complex 2				
N1-H1B...N4 ^{viii}	0.086 04	0.218 44	0.303 6(5)	170.36
N1-H1C...O3 ^{ix}	0.085 97	0.231 33	0.308 8(6)	150.01
C13-H13...O2 ^x	0.092 96	0.253 06	0.343 1(4)	163.14

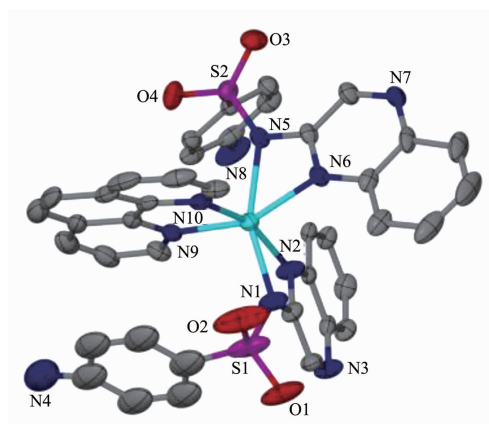
Symmetry codes: ^{iv} 1-x, 1-y, -z; ^v x, -1+y, z; ^{vi} 1-x, -y, -z; ^{vii} 1-x, 1/2+y, 1/2-z for **1**; ^{viii} 1/2-x, -1/2-y, 1/2-z; ^{ix} 1-x, -y, 1-z; ^x 1-x, y, 1/2-z for **2**

2 Results and discussion

2.1 Crystal and molecular structures

2.1.1 Structure description for complex **1**

Single-crystal X-ray diffraction analysis reveals that complex **1** is mononuclear structure crystallizes in the monoclinic with space group $P2_1/c$ and $Z=4$, the asymmetric unit of complex **1** contains one zinc ion, one 1,10-phen, two sulfaquinoxalinum ligands and one free water molecules. The local coordination environment of around Zn(II) ion is shown in Fig.1, in which Zn (II) exhibits six-coordinated octahedral distortion coordination geometry, of which four nitrogen atoms from two sulfaquinoxalinum ligands

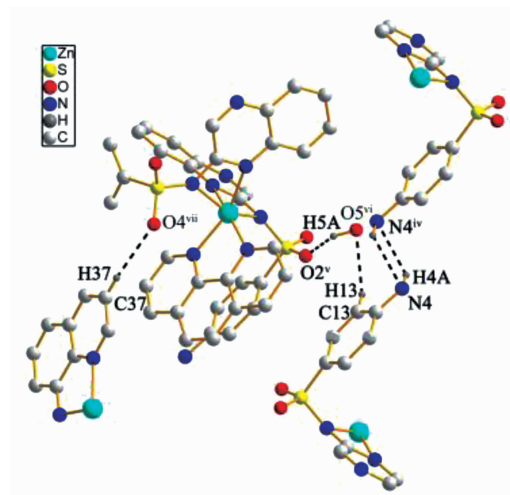


Hydrogen atoms are omitted for clarity

Fig.1 Coordination environment of metal ion in **1** with thermal ellipsoids at 30% probability

(N1, N2, N5, N6) and two nitrogen atoms from 1,10-phen ligand (N9, N10) with Zn-N distance from 0.210 44(7) to 0.234 67(7) nm^[29]. As showed in Fig.2, the N4 from sulfaquinoxalinum acts as hydrogen-bond donor, contributing an H atom to amine atom N4^{iv} of the other sulfaquinoxalinum forming N4-H4A \cdots N4^{iv}; the water molecule serves as hydrogen-bond donor to atom O2^v, forming O5-H5A \cdots O2^v; the benzene rings

acts as the donors, contributing the H atoms to the O atoms of water molecules forming C13-H13 \cdots O5^{vi}, and C37-H37 \cdots O4^{vii}. Through $\pi \cdots \pi$ stacking ($d=0.398$ 4 nm) and hydrogen bond interactions ($d(\text{N4} \cdots \text{N4}^{\text{iv}})=0.277$ 06 nm, $d(\text{O5} \cdots \text{O2}^{\text{v}})=0.250$ 70 nm, Symmetry code: ^{iv} 1-x, 1-y, -z; ^v x, -1+y, z; ^{vi} 1-x, -y, -z, ^{vii} 1-x, 1/2+y, 1/2-z)^[30], the complex **1** extends into a network structure(Fig.3).



Only H atoms involved in hydrogen bonding are shown; Symmetry code: ^{iv} 1-x, 1-y, -z; ^v x, -1+y, z; ^{vi} 1-x, -y, -z; ^{vii} 1-x, 1/2+y, 1/2-z

Fig.2 A view of the N-H \cdots N and C-H \cdots O interactions(dashed lines) in **1**

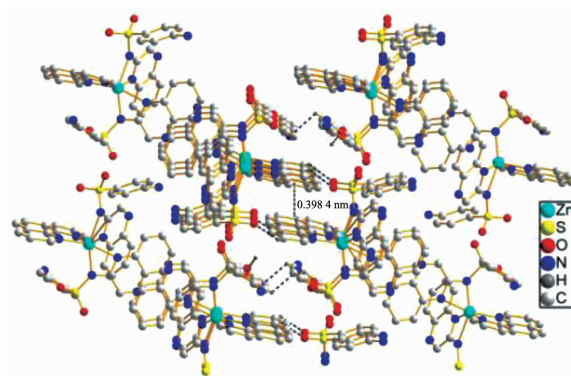


Fig.3 A view of packing framework in **1**

2.1.2 Structure description for complex **2**

Single crystal X-ray diffraction analysis reveals that complex **2** has a one-dimensional chain structure. It crystallizes in the monoclinic system with space group $C2/c$. The asymmetric unit consists of one Zn(II), one 4,4'-bpy, two sulfaquinoxalinum ligands and two free ethanol molecules. The local coordination environment of around zinc ion is shown in Fig.3, in

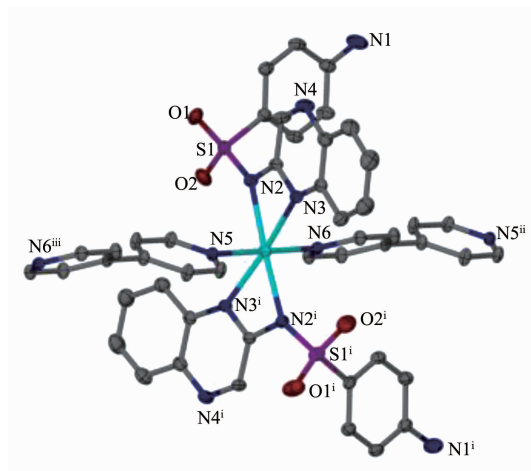
which Zn(II) exhibits six-coordinated octahedral distortion coordination geometry with four nitrogen atoms from two sulfaquinoxalinum ligands (N2, N3, N2ⁱ, N3ⁱ) and two nitrogen atoms from two different 4,4'-bpy ligand (N5, N6). The Zn-N distance ranges from 0.214 7(2) to 0.227 87(18) nm. The structure extends into one-dimensional chain by bridging of 4,4'-bpy ligand with the adjacent Zn(II) distance of

1.138 5 nm (Fig.4). Different kinds of hydrogen bonds can be observed in the structure of **2** (Fig.5). The benzene ring of sulfaquinoxalinum acts as a hydrogen-bond donor, contributing an H atom to O2 of the other sulfaquinoxalinum forming C13-H13 \cdots O2^x hydrogen-bonding interaction. The N1-H1 from sulfaquinoxalinum and N4 from the neighboring sulfaquinoxalinum ligand form the N1-H1 \cdots N4^{viii} hydrogen-bonding interaction.

The ethanol molecule serves as the hydrogen-bond receptor, accepting H atoms from amine atom N1 forming N1-H1C \cdots O3^{ix} hydrogen-bonding interaction (Table 3). The structural units further extend into a two-dimensional hydrogen-bonding network (Fig.6).

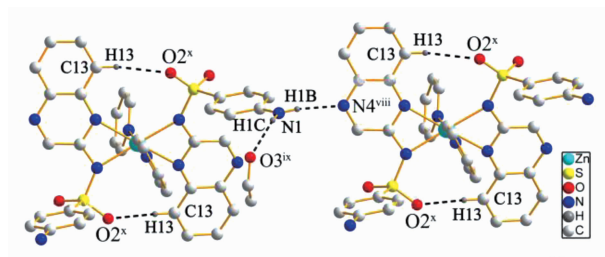
2.2 Powder X-ray diffraction analysis

In an attempt to confirm the homogeneity of the synthesized material, we have analyzed the PXRD



Hydrogen atoms were omitted for clarity, Symmetry code: ⁱ 1-x, y, 1/2-z; ⁱⁱ x, y-1, z; ⁱⁱⁱ x, y+1, z

Fig.4 Coordination environment of metal ion in **2** with thermal ellipsoids at 30% probability



Only H atoms involved in hydrogen bonding are shown; Symmetry code: ^{viii} 1/2-x, -1/2-y, 1/2-z; ^{ix} 1-x, -y, 1-z; ^x 1-x, y, 1/2-z

Fig.5 A view of the N-H \cdots N, N-H \cdots O and C-H \cdots O interactions(dashed lines) in **2**

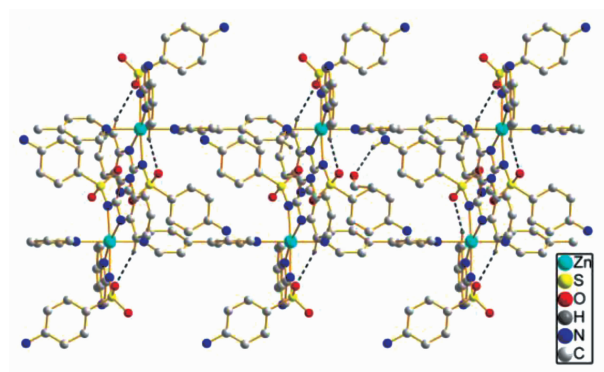


Fig.6 A view of 2D chain structure of complex **2**

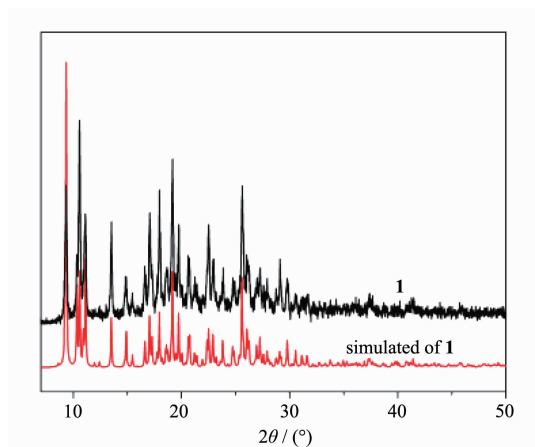


Fig.7 Experimental and simulated powder XRD patterns of **1**

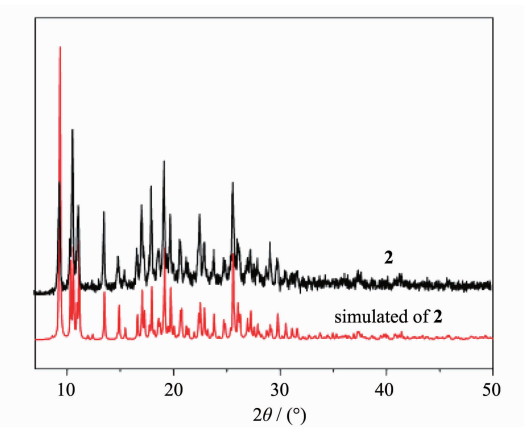


Fig.8 Experimental and simulated powder XRD patterns of **2**

pattern of the complex and correlated the results with the simulated powder pattern obtained from the single crystal data of complex **1** and **2**. As depicted in Fig.5 and Fig.6, the basic feature peaks of the PXRD patterns resemble the simulated from single crystal data for the complex, indicating that the bulk products obtained are homogenous for complex **1** and **2**, respectively.

2.3 UV-Vis absorption and fluorescent spectra

The UV-Vis absorption spectra of compound **1** and **2** are shown in Fig.9 and Fig.10 and, respectively. The UV-Vis absorption of phen is at 230, 264 and 347 nm, and the UV-Vis absorption of sulfaquinoxalinum is at 230 and 260 nm. Therefore, the high-energy peaks of 227 and 266 nm in **1** could come from fluorescent emissions of the phen, and

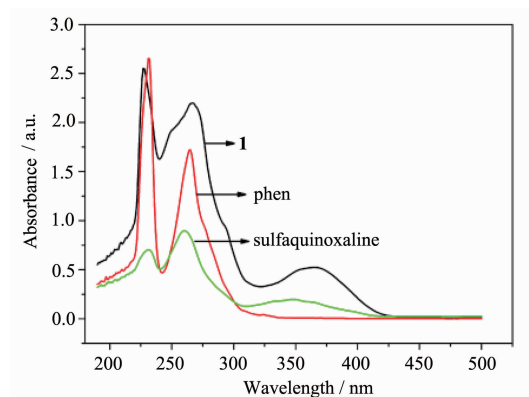


Fig.9 UV-Vis absorption spectra of compound **1**, phen and sulfaquinoxaline in the dichloromethane at room temperature

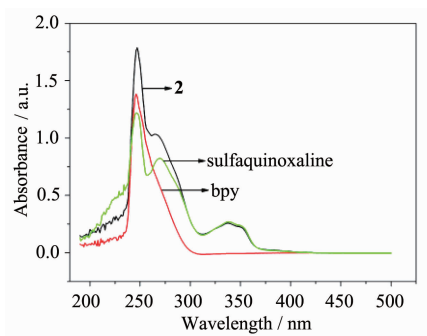


Fig.10 UV-Vis absorption spectra of compound **2**, bpy and sulfaquinoxaline in the tetrahydrofuran solution at room temperature

peak of 366 nm from the fluorescent emissions of sulfaquinoxalinum ligand (Fig.9). The UV-Vis absorption of the compounds **2** is an overlay enhancement from the UV-Vis absorption of the bpy and the sulfaquinoxalinum ligands because these ligands have similar absorption bond (Fig.10).

2.4 Fluorescent emission

Previous studies have shown that compounds containing zinc could exhibit fine photoluminescent properties^[31]. The solid-state fluorescent spectra of **1** and **2** at room temperature are displayed in Fig.11 and Fig.12, respectively. The phen shows the strong emission peaks at 361 and 379 nm upon the excitation at 400 nm and the free sulfaquinoxaline shows the strong emission peak at 448 nm upon the excitation at 419 nm. Compound **1** displays the strong

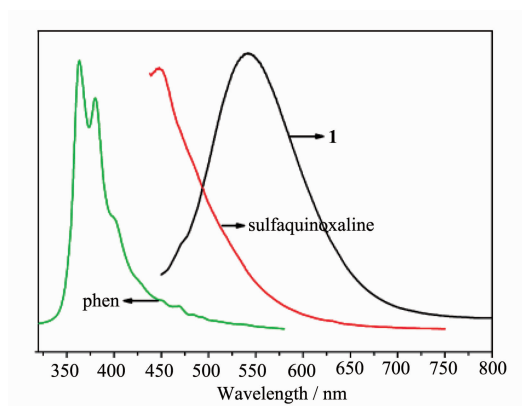


Fig.11 Fluorescent spectra of **1** ($\lambda_{\text{ex}}=423$ nm), phen ($\lambda_{\text{ex}}=400$ nm) and sulfaquinoxaline ($\lambda_{\text{ex}}=419$ nm)

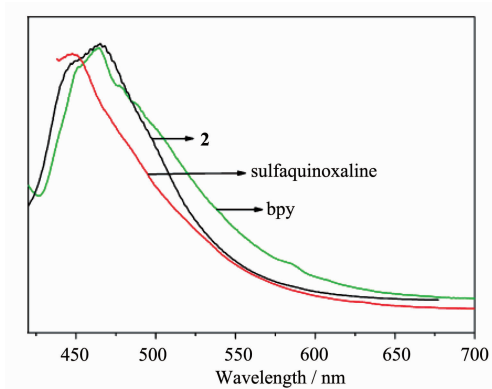


Fig.12 Fluorescent spectra of **2** ($\lambda_{\text{ex}}=400$ nm), bpy ($\lambda_{\text{ex}}=342$ nm) and sulfaquinoxaline ($\lambda_{\text{ex}}=419$ nm)

emission peak at 542 nm, which may originate from the radiative transition of ligand-to-metal or metal-to-ligand charge transfer emission.

The bpy shows the strong peak at 468 nm upon the excitation at 400 nm. In comparison, compound **2** displays the similarly fluorescent emission peak 469 nm, which is attributed to that the sulfaquinoxaline has no effect on the interaction between the metal and the ligand^[32].

2.5 Thermal analysis

Thermal analyses are conducted to determine the thermal stability of the title complexes, which is an important aspect for coordination compounds^[33-34]. As shown in Fig.13, The DTA curve of **1** shows two weak endothermic peaks and one strong exothermic peak centered at 233, 510 and 677 °C, respectively, corresponding to the physical or chemical reactions^[35]. The first weight loss of 1.9% (Calcd. 2%) corresponds

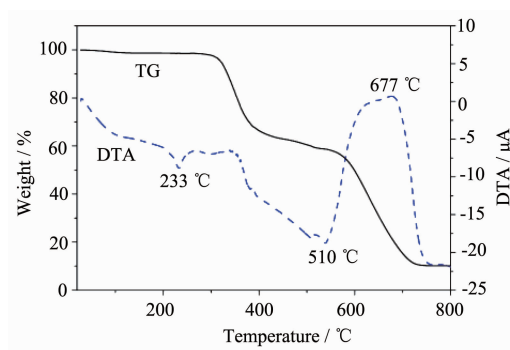


Fig.13 TG-DTA curve of compound **1**

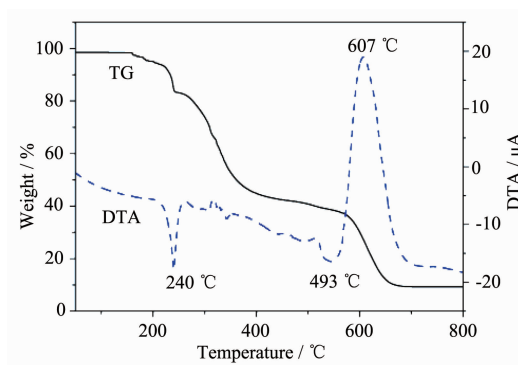


Fig.14 TG-DTA curve of compound **2**

to removal of one water molecule from room temperature to 289 °C. The second sharp weight loss of 33.5% (Calcd. 34.83%) corresponds to removal of one sulfaquinoxaline molecule per formula unit from 289 °C to 418 °C, which exhibits that the framework stability of **1** is up to 289 °C, the third sharp weight loss of 55.5% (Calcd. 55.73%) corresponds to removal of one sulfaquinoxaline and one phen molecule per formula unit from 418 °C to 774 °C. The final decomposed product presumably is ZnO (Obsd. 10.14%, Calcd. 8.9%, based on the remaining mass) upon 774 °C.

Similarly, the DTA curve of **2** shows two weak endothermic peaks and one strong exothermic peak centered at 240, 493 and 607 °C, respectively (Fig. 14). The first drop of weight is observed from 153 to 231 °C, with a weight loss of 9.3% (Calcd. 10.1%) corresponding to elimination of two EtOH molecule. The second sharp drop of weight is observed from 231 to 485 °C, with a weight loss of 49.4% (Calcd. 50%) corresponding to elimination of one bpy molecule and one sulfaquinoxaline per formula unit, which indicates

the stability of the framework of **2** up to 231 °C. The third sharp weight decrease of 31.6% (Calcd. 32.9%) upon 485 °C can be attributed to loss of the other sulfaquinoxaline ligand per formula unit in **2**. The final decomposed product presumably is ZnO (Obsd. 9.7%, Calcd. 8.9 %, based on the remaining mass) upon 683 °C.

3 Conclusions

In this paper, two Zn(II) complexes derived from sulfaquinoxaline have been synthesized and characterized. TGA show high thermal stabilities of the frameworks for **1** and **2**. The fluorescence shows that the complexes **1** and **2** have photoluminescent properties. This work may provide useful information to assemble new luminescent materials.

References:

- [1] Noro S, Kitagawa S, Kondo M, et al. *Angew. Chem. Int. Ed.*, **2000**,**39**:2082-2085
- [2] Zaworotko M J. *Chem. Soc. Rev.*, **1994**,**23**:283-288
- [3] Yaghi O M, Li H, Davis C, et al. *Acc. Chem. Res.*, **1998**,**31**:474-484
- [4] JIANG Jing (江晶), WANG Dong-Jie (王冬杰), LIU Zhi-Peng (刘志鹏), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2013**,**29**(9):1952-1956
- [5] Li X, Wei D Y, Huang S J, et al. *J. Solid State Chem.*, **2009**,**182**:95-101
- [6] LIU Xian-Chun (刘羨春), XU Qing (徐清), WANG Li (王丽), et al. *J. Ningbo Univ.* (宁波大学学报), **2009**,**22**(2):251-254
- [7] Kremer E, Facchin G, Estévez E, et al. *J. Inorg. Biochem.*, **2006**,**100**:1167-1175
- [8] Supuran C T, Casini A, Scozzafava A, et al. *Curr. Cancer Drug Targets*, **2002**,**2**:55-75
- [9] Owa T, Nagasu T. *Expert Opin. Ther. Patents*, **2000**,**10**:1725-1740
- [10] Supuran C T, Scozzafava A. *Expert Opin. Ther. Patents*, **2000**,**10**:575-600
- [11] Saleh N, Khowdiary M, Badawi A F. *Tenside Surfactants Deterg.*, **2001**,**1**:61-97
- [12] Lobb K L, Hippskind P A, Aikins J A, et al. *Eur. J. Med. Chem.*, **2004**,**47**:5367-5380
- [13] Medina J C, Roche D, Shan B, et al. *Bioorg. Med. Chem. Lett.*, **1999**,**9**:1843-1846
- [14] Shao B, Dong D, Wu Y, et al. *Anal. Chim. Acta*, **2005**,**546**:173-181
- [15] Harun A L P. *J. Anim. Vet. Adv.*, **2008**,**7**:1174-1178
- [16] Nebot C, Regal P, Mirtinez B, et al. *J. Food Drug Anal.*, **2010**,**18**:191-201
- [17] Fang G Z, He J X, Wang S. *J. Chromatogr. A*, **2006**,**1127**:12-17
- [18] Wong E, Giandomenico C M. *Chem. Rev.*, **1999**,**99**:2451-2466
- [19] Milliam M. *Martindale: The Extra Pharmacopoeia*. London: Pharmaceutical Press, **1996**:31-35
- [20] Sigel A, Sigel H. *Metal Ions in Biological Systems*, New York: CRC, **1983**:261-278
- [21] Kocer S, Urus S, Cakir A, et al. *Dalton Trans.*, **2014**,**43**:6148-6164
- [22] Cabaleiro S, Castro J, Romero J, et al. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.*, **2000**,**56**:293-295
- [23] Beloso I, Castro J, Garcia-Vazquez J A, et al. *Polyhedron*, **2006**,**25**:2673-2682
- [24] ZHAO Xiu-hua (赵秀华), ZHAO Ya-yun (赵亚云), ZHANG Jie (张洁), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2014**,**30**(3):633-639
- [25] Higashi T. *ABSCOR*, Rigaku Corporation, Tokyo, Japan, **1995**.
- [26] Sheldrick G M. *SADABS 2.05*, University of Göttingen, Germany, **2002**.
- [27] RAN Fan-Min (冉繁敏), ZHAO Ya-Yun (赵亚云), ZHAO Xiu-Hua (赵秀华), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2014**,**30**(4):913-920
- [28] Sheldrick G M. *SHELXL97, Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, **1997**.
- [29] Blasco F, Ortiz R, Perelló L, et al. *J. Inorg. Biochem.*, **1994**,**53**:117-126
- [30] JIANG Jing (江晶), WANG Dong-Jie (王冬杰), LI Xing (李星), et al. *J. Ningbo Univ.* (宁波大学学报), **2013**,**26**(1):74-76
- [31] Xue X, Wang X S, Wang L Z, et al. *Inorg. Chem.*, **2002**,**41**:6544-6546
- [32] WANG Qing-Qi (王清琪), XU Qing (徐清). *J. Ningbo Univ.* (宁波大学学报), **2012**,**25**(2):112-115
- [33] HUANG You-Gui (黄有桂), ZHOU You-Fu (周有福), WU Ben-Lai (吴本来), et al. *Chinese J. Struct. Chem.* (结构化学), **2005**,**24**:1123-1128
- [34] Guo H D, Guo X M, Batten S R, et al. *Cryst. Growth Des.*, **2009**,**9**:1394-1401
- [35] Qi J L, Xu W, Zheng Y Q. *Z. Naturforsch.*, **2012**,**67b**:1185-1190