

含硫柔性二苯甲酸及氮杂环配体的 Zn(II)和 Mn(II) 配合物的合成及晶体结构

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摘要: 以 2,2'-二硫代二苯甲酸、2,2'-联吡啶、咪唑、硝酸锌和硝酸锰为原料,使用水热方法合成了配合物[Zn(EBLA)(2,2'-bipy)(H₂O)](EBLA=2,2'-二苯甲酸硫醚)(2,2'-bipy=2,2'-联吡啶)(**1**),自然挥发法制备了配合物[Mn(EBSA)(im)₂(H₂O)]_n(EBSA=2,2'-二硫代二苯甲酸)(im=咪唑)(**2**)。利用元素分析、红外和热重分析对其进行了表征。利用 X-射线单晶衍射对结构进行了测定,并研究了配合物 **1** 的荧光性质。配合物 **1** 中,2,2'-二苯甲酸硫醚是通过水热方法由 2,2'-二硫代二苯甲酸发生原位反应制备,Zn²⁺离子是五配位的四角锥双核结构;配合物 **2** 中,Mn²⁺离子是六配位的变形八面体一维链状结构。配合物中存在氢键和 π - π 堆积等弱的分子间作用力。

关键词: 2,2'-二硫代二苯甲酸; 2,2'-二苯甲酸硫醚; 原位反应; 晶体结构

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Syntheses, Crystal Structures of Zn(II) and Mn(II) Complexes with Flexible Sulfur Containing Aromatic Acid and Nitrogen Heterocyclic Ligands

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Abstract: Two coordination polymers [Zn(EBLA)(2,2'-bipy)(H₂O)] (**1**) and [Mn(EBSA)(im)₂(H₂O)]_n (**2**) were synthesized by hydrothermal and evaporation methods using 2,2'-dithiosalicylic acid (EBSA), 2,2'-dipyridyl, imidazole, Zn(NO₃)₂·6H₂O and Mn(NO₃)₂·4H₂O. And the complexes were characterized by elemental analysis, FT-IR and thermogravimetric analysis (TGA), meanwhile the crystal structures and fluorescence properties of the complex **1** have been studied. In complex **1**, 2,2'-dicarboxydiphenylthioether (EBLA) was prepared with 2,2'-dithiosalicylic acid (EBSA) *in situ* reaction by hydrothermal method. The complex **1** is a dinuclear structure and Zn²⁺ ion is five-coordination in a distorted square pyramidal geometry; The complex **2** is a one-dimensional infinite linear chain and Mn²⁺ ion is six-coordination in a distorted octahedral geometry. Hydrogen bonding and π - π interactions are observed in these complexes. CCDC: 998513, **1**; 1000616, **2**.

Key words: 2,2'-dithiosalicylic acid; 2,2'-dicarboxydiphenylthioether; *in situ* reaction; crystal structure

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0 Introduction

During the past decade, metal-organic frameworks (MOFs) attract considerable interest of chemists because of the realization of interesting architectures and potential properties such as gas storage, nonlinear optics, magnetism, luminescence, catalysis^[1-5] and so on. Currently, appropriate selection of multifunctional organic ligands and controlling reaction condition are key factors for achieving expected metal-organic frameworks (MOFs)^[6-7]. Aromatic-carboxylic ligands can provide various coordination modes (monodentate, bis-monodentate and so on) and widely used for building various structural and topological coordination polymers with metal ions. It is well known that the flexible 2,2'-dithiosalicylic acid (EBSA) is a preeminent candidate for constructing novel structures^[8-10]. Moreover, disulfides have proven to be desirable objects for the in situ reaction because of versatile S-S transformations through the facile cleavage of S-S which can occur both reductively and oxidatively^[11-14]. In this study, we introduced 2,2'-dithiosalicylic acid (EBSA) with the nitrogen heterocyclic ligands in order to assemble Zn(II) and Mn(II) coordination polymer. Unexpectedly, in situ reaction of 2,2'-dithiosalicylic acid provided 2,2'-dicarboxydiphenylthioether (EBLA) ligand in the presence of Zn(II) ions. In addition, thermal stability of complexes **1** and **2** and luminescent property of complex **1** were measured and discussed.

1 Experimental

1.1 Materials and measurements

All chemicals purchased were of reagent grade and used without further purification. Elemental analysis were performed on a CARLO ERBA 1106 analyzer, it shows the percentage of carbon, hydrogen and nitrogen of the complexes. The FT-IR spectra were recorded on a BRUKER EQUINOX 55 FT-IR spectrometer using KBr pellet at a resolution of 0.5 cm⁻¹ (400~4 000 cm⁻¹). Luminescence spectra for crystal solid samples were recorded at room temperature on a PERKIN ELMER LS 55 luminance meter. Thermogravimetry analyses were performed on

an automatic simultaneous thermal analyzer (PE TG/DTA 6300) under a flow of N₂ at a heating rate of 10 °C·min⁻¹ between ambient temperature and 800 °C.

1.2 Synthesis of [Zn(EBLA)(2,2'-bipy)(H₂O)] (**1**)

2,2'-dithiosalicylic acid (0.304 3 g, 1.0 mmol), 2,2'-bipy (0.156 2 g, 1.0 mmol) and Zn(NO₃)₂·6H₂O (0.297 5 g, 1.0 mmol) were added in a mixed solution of DMF (*N,N*-dimethylformamide), water and methanol (1:6:1, *V/V*, 16 mL). The vial was sealed and heated at 180 °C for four days. After being cooled to room temperature, dark yellow crystals were obtained in 35% yields (based on Zn). Analysis calculated for C₄₈H₃₆N₄O₁₀S₂Zn₂(%): C 55.32, H 3.54, N 5.47; Found (%): C 55.09, H 3.49, N 5.39. IR (KBr pellet, cm⁻¹): 3 337(s), 1 629(s), 1 595(s), 1 579(s), 1 493(s), 1 474(m), 1 445(s), 1 376(s), 1 279(m), 1 255(m), 1 060(m), 1 026(m), 829(m), 757(s), 462(m).

1.3 Synthesis of [Mn(EBSA)(im)₂(H₂O)]_n (**2**)

Mn(NO₃)₂·4H₂O (0.251 0 g, 1.0 mmol), 2,2'-dithiosalicylic acid (0.304 3 g, 1.0 mmol) and imidazole (0.136 1 g, 2.0 mmol) were dissolved in methanol and water (1:10, *V/V*, 30 mL) solution and the pH value was adjusted to 7 with 0.1 mol·L⁻¹ potassium hydroxide solution. After the mixture was stirred for 45 min. Colorless crystals of complex were obtained by evaporation of the solution for 8 days at room temperature in 41% yields (based on Mn). Analysis calculated for C₂₀H₁₈N₄O₅S₂Mn (%): C 46.78, H 3.54, N 10.92; Found (%): C 48.09, H 3.49, N 10.67. IR (KBr pellet, cm⁻¹): 3 691 (s), 3 504 (w), 3 445 (w), 3 321 (s), 3 139(w), 1 622 (s), 1 591 (m), 1 574 (m), 1 517 (m), 1 391(s), 1 374(w), 1 282(w), 1 162(w), 1 133(w), 1 064(m), 944(w), 740(m), 654(m), 509(w).

1.4 Crystal structure determination

Single-crystal X-ray diffraction measurements were carried out on a Bruker SMART APEX II CCD diffractometer. The diffraction data were collected with Mo *K*α radiation (λ=0.071 073 nm). Empirical absorption corrections were carried out by using the SADABS program^[15]. The structures were solved by direct methods, and all of the non-hydrogen atoms were refined anisotropically on *F*² by the full-matrix least-squares technique using the SHELXL crystallographic

software package^[16]. The hydrogen atoms were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. The crystal structure data of complexes **1** and **2** were listed in

Table 1. The selected bond lengths and bond angles were listed in Table 2 and hydrogen bond lengths and bond angles were listed in Table 3.

CCDC: 998513, **1**; 1000616, **2**.

Table 1 Crystal data and structure refinements of complexes **1** and **2**

Complex	1	2
Empirical formula	C ₄₈ H ₃₆ N ₄ O ₁₀ S ₂ Zn ₂	C ₂₀ H ₁₈ N ₄ O ₅ S ₂ Mn
Formula weight	1 023.67	513.44
Temperature / K	296(2)	296(2)
Size / mm	0.24×0.20×0.17	0.36×0.28×0.20
θ range for data collection / (°)	2.30 to 28.29	1.79 to 25.00
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2₁/c</i>
<i>a</i> / nm	1.815 85(11)	1.257 2(5)
<i>b</i> / nm	1.282 06(8)	2.279 7(9)
<i>c</i> / nm	1.885 61(12)	0.821 3(3)
β / (°)	96.731 0(10)	106.310(4)
<i>V</i> / nm ³	4.359 5(5)	2.259 1(15)
<i>Z</i>	4	4
μ / mm ⁻¹	1.263	0.808
<i>D_c</i> / (g·cm ⁻³)	1.560	1.510
<i>F</i> (000)	2 096	1 052
Reflections collected	17 173	12 572
Independent reflections (<i>R_{int}</i>)	5 383 (0.023 3)	3 972 (0.023 4)
Observed reflections (<i>I</i> >2 σ (<i>I</i>))	4 282	3 432
Goodness of fit on <i>F</i> ²	1.077	1.037
<i>R₁</i> , <i>wR₂</i> (<i>I</i> >2 σ (<i>I</i>))	0.031 7, 0.081 9	0.038 3, 0.087 4
<i>R₁</i> , <i>wR₂</i> (all data)	0.045 0, 0.088 2	0.045 7, 0.090 4
($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} / (e·nm ⁻³)	428, -279	546, -535

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

Complex 1					
N(1)-Zn(1)	0.212 74(16)	N(2)-Zn(1)	0.209 32(16)	O(2)-Zn(1)	0.202 47(13)
O(4)-Zn(1) ⁱ	0.197 46(13)	OW-Zn(1)	0.212 32(14)	C(1)-O(1)	0.124 4(2)
C(1)-O(2)	0.126 6(2)				
O(2)-Zn(1)-N(1)	87.70(6)	N(2)-Zn(1)-N(1)	77.19(6)	O(2)-Zn(1)-N(2)	111.24(6)
O(2)-Zn(1)-OW	92.57(6)	N(2)-Zn(1)-OW	89.94(6)	OW-Zn(1)-N(1)	166.25(6)
O(4) ⁱ -Zn(1)-O(2)	105.74(6)	O(4) ⁱ -Zn(1)-N(2)	142.94(7)	O(4) ⁱ -Zn(1)-OW	90.76(6)
O(4) ⁱ -Zn(1)-N(1)	102.41(6)	C(7)-S(1)-C(8)	101.57(9)		
Complex 2					
Mn(1)-O(4) ⁱ	0.211 3(2)	Mn(1)-N(3)	0.219 1(3)	Mn(1)-N(1)	0.221 2(2)
Mn(1)-O(1W)	0.223 06(19)	Mn(1)-O(1)	0.229 11(19)	Mn(1)-O(2)	0.232 39(18)
O(1)-C(1)	0.127 0(3)	O(2)-C(1)	0.125 4(3)	O(3)-C(14)	0.123 8(3)
O(4)-C(14)	0.125 9(3)				

Continued Table 2

O(4) ⁱ -Mn(1)-N(3)	105.46(9)	O(4) ⁱ -Mn(1)-N(1)	91.56(9)	N(3)-Mn(1)-N(1)	92.35(10)
O(4) ⁱ -Mn(1)-O(1W)	91.98(8)	N(3)-Mn(1)-O(1W)	90.33(8)	N(1)-Mn(1)-O(1W)	174.83(8)
O(4) ⁱ -Mn(1)-O(1)	94.10(8)	N(3)-Mn(1)-O(1)	160.01(8)	N(1)-Mn(1)-O(1)	91.15(8)
O(1W)-Mn(1)-O(1)	84.84(6)	O(4) ⁱ -Mn(1)-O(2)	150.47(8)	N(3)-Mn(1)-O(2)	103.99(8)
N(1)-Mn(1)-O(2)	85.14(8)	O(1W)-Mn(1)-O(2)	89.92(7)	O(1)-Mn(1)-O(2)	56.73(6)

Symmetry codes: **1**: ⁱ $-x+1, -y+1, -z+2$; **2**: ⁱ $x-1, y, z$ Table 3 Hydrogen bonds for complexes **1** and **2**

D-H \cdots A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^\circ)$
Complex 1				
OW-H(1W) \cdots O(1)	0.085	0.181	0.260 0(2)	153.9
C(3)-H(3) \cdots O(1)	0.093	0.240	0.273 7(3)	101.0
C(24)-H(24) \cdots OW	0.093	0.253	0.306 9(3)	117.2
OW-H(2W) \cdots O(4) ⁱⁱ	0.088	0.198	0.285 51(19)	175.1
C(5)-H(5) \cdots O(3) ⁱⁱⁱ	0.093	0.255	0.331 3(3)	139.1
Complex 2				
C(3)-H(3) \cdots O(1)	0.093	0.246	0.278 1(3)	100.4
C(6)-H(6) \cdots S(2)	0.093	0.268	0.321 4(3)	117.6
C(9)-H(9) \cdots S(1)	0.093	0.262	0.316 2(3)	117.5
C(12)-H(12) \cdots O(4)	0.093	0.246	0.278 1(4)	100.0
O(1W)-H(1W1) \cdots O(3) ⁱ	0.086(3)	0.182(3)	0.262 0(3)	154(3)
O(1W)-H(2W1) \cdots O(2) ⁱⁱⁱ	0.097(3)	0.184(3)	0.279 4(3)	168(3)
O(1W)-H(2W1) \cdots S(1) ⁱⁱⁱ	0.097(3)	0.286(3)	0.347 3(2)	122(2)
N(2)-H(2N) \cdots O(1) ^{iv}	0.086	0.198	0.280 1(3)	159.5
N(4)-H(4N) \cdots O(1) ^v	0.086	0.237	0.304 9(4)	136.4
C(4)-H(4) \cdots S(1) ^{vi}	0.093	0.277	0.368 0(3)	165.6

Symmetry codes: **1**: ⁱⁱ $x, -y+1, z-1/2$; ⁱⁱⁱ $-x+1, -y, -z+2$; **2**: ⁱ $x-1, y, z$; ⁱⁱⁱ $-x+1, -y+1, -z+1$; ^{iv} $x, -y+3/2, z-1/2$; ^v $x, y, z-1$; ^{vi} $x, y, z+1$

2 Results and discussion

2.1 Structure description of [Zn(EBLA)(2,2'-bipy)(H₂O)] (**1**)

The molecular structure of the complex **1** is shown in Fig.1 and the selected bond distances and angles are listed in Table 2. The X-ray diffraction analysis shows that this complex has a dinuclear structure. Each EBLA²⁻ ligand has one coordination types of monodentate modes. The Zn(II) ion is five-coordinated by two carboxylate O atoms from two different EBLA²⁻ groups, and two N atoms from one 2,2'-dipyridyl co-ligands as well as one water molecule, and the local coordination sphere around the Zn(II) ion can be described as a distorted square pyramidal with a ZnO₃N₂ chromophore. Atoms OW,

O4ⁱ, N1 and N2 define the equatorial plane, while carboxylate O2 atoms occupies the apical site (Fig.1 (a)). Two Zn(II) atoms are double-bridged by two EBLA²⁻ ligands, generating a macrocyclic ring with the Zn \cdots Zn separation distance of 0.677 3 nm (Fig.1 (b)). The dihedral angle between two benzene ring plane of EBLA²⁻ ligand is 84.74(7)°, and the bond angle(C7-S1-C8) is 101.57(9)°. The coordinated water molecule OW form intramolecular hydrogen bond with the coordinated EBLA²⁻ ligand O1, with the O \cdots O bond length of 0.260 0(2) nm and the OW-H1W \cdots O1 bond angle of 153.9° (Table 3).

There is π - π stacking interactions between nitrogen heterocyclic rings of 2,2'-dipyridyl. The centroids Cg1 (coordinate: 0.155 32, 0.086 00, 0.052 28) and Cg4 (coordinate: 0.344 68, 0.414 00, -0.052 28) is

made up of atoms of N1, C15, C16, C17, C18 and C19, moreover, the centroids Cg2 (coordinate: 0.211 08, 0.360 55, 0.110 05) and Cg3 (coordinate: 0.288 92, 0.139 45, -0.110 05) is made up of atoms of N2, C20, C21, C22, C23 and C24. The centroid-centroid distance (Cg1-Cg2 and Cg3-Cg4) and the dihedral angle between two pyridyl ring plane (Cg1-Cg2 and Cg3-Cg4) is 0.378 71 nm and 10.028°, respectively. In

complex **1**, π - π stacking interactions and intermolecular hydrogen bonding (C5-H5 \cdots O3ⁱⁱⁱ, $d(\text{H}\cdots\text{O})=0.255\ 37(18)$ nm) formed the two-dimensional layer structure. With the help of hydrogen-bonded interactions between adjacent 2D sheet (OW-H2W \cdots O4ⁱⁱ, $d(\text{H}\cdots\text{O})=0.197\ 77(13)$ nm), the polymeric sheet are assembled to form a supramolecular 3D network structure (Fig.2).

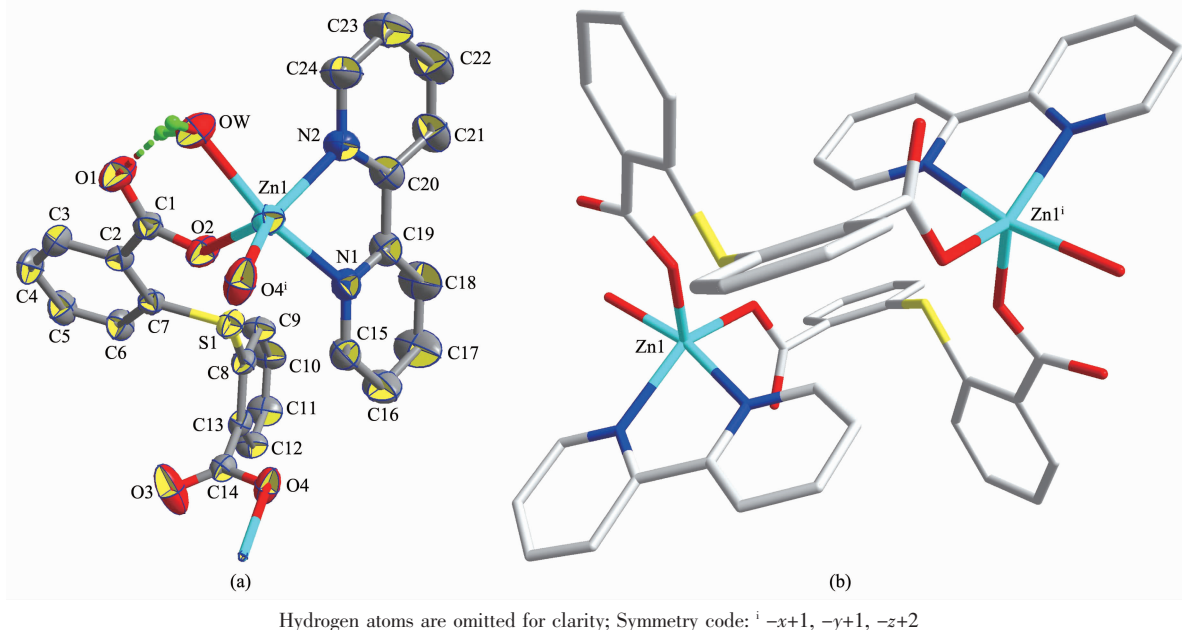


Fig.1 (a) Coordination environment of Zn(II) in **1** with the ellipsoids drawn at the 30% probability level;
(b) Dual-molecular structure of complex **1**

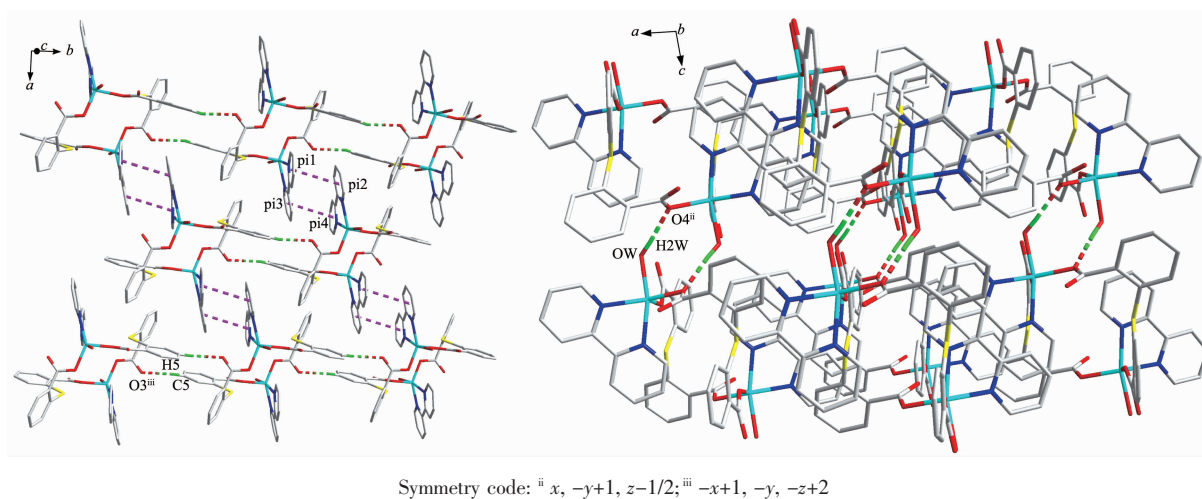


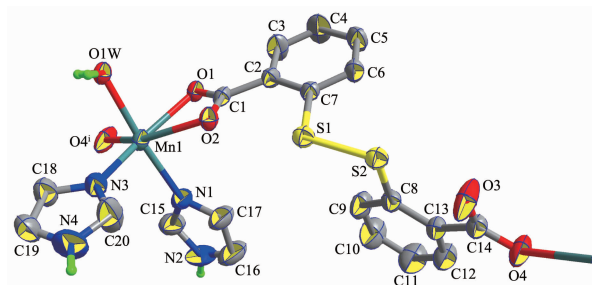
Fig.2 2D and 3D structure of complex **1**

2.2 Structure description of [Mn(EBSA)(im)₂(H₂O)]_n (**2**)

As shown in Fig.3, each Mn(II) atom is in a distorted octahedral coordination environment, defined

by three carboxyl O atoms from two different EBSA²⁻ groups and two N atoms from the two imidazole ligands in complex **2**. Its equatorial plane is defined by the atoms of O1, O2, O4ⁱ and N3 (Rms deviation of

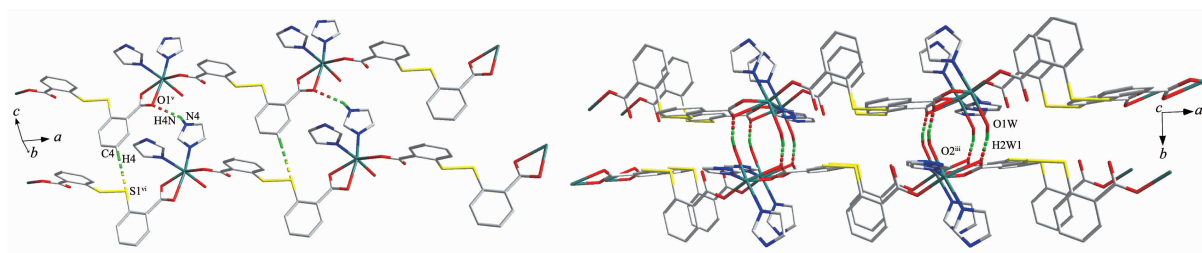
fitted atoms=0.007 52 nm; deviation of Mn atom from this plane is 0.001 49 nm). The axial positions are occupied by the atoms of O1W and N1, with an angle of 174.83(8)°. The imidazole molecules act as typical monodentate ligands terminally coordinated to the metal center. The Mn-O(carboxyl) distances (Table 2) are in the range of the corresponding bond distances of Mn-terephthalate complexes (0.211 3(2)~0.232 39(18) nm). It should be noted that the O4-C14 distance (0.125 9(3) nm) is longer than the O3-C14 distance (0.123 8(3) nm), agreeing with the greater double-bond character of the latter bond. In contrast, the O1-C1 (0.127 0(3) nm) and O2-C1 (0.125 4(3) nm) distances are nearly identical, suggesting delocalization of electrons throughout. This can be explained by the influence of the different coordination modes of the carboxyl groups. In the former (O3-C14-O4), the carboxyl group is in a monodentate mode through the O4 atom, and the other carboxyl group (O1-C1-O2) is in a bidentate chelating mode through atoms O1 and O2. The dihedral angles between two imidazole and between two benzene ring plane of EBSA are 87.01(15)° and 84.25(12)°, respectively. The torsion angles of -82.87(12)° [C7-S1-S2-C8] distinction may be attributed to the remarkable conformational flexibility of EBSA²⁻ ligand.



Hydrogen atoms are omitted for clarity; Symmetry code: ⁱ $x-1, y, z$

Fig.3 Coordination environment of Mn(II) in **2** with the ellipsoids drawn at the 30% probability level

Each EBSA group adopts a tridentate coordinated mode to link two Mn(II) atoms into a one-dimensional infinite linear chain. In the chain, the adjacent Mn...Mn distance is 1.257 2(5) nm. The N4 and C4 atoms and the O1 and S1 of EBSA ligand form intramolecular hydrogen bonds (N4-H4N...O1ⁱ and C4-H4...S1^{vi}), with bond distances of 0.236 84(19) (H...O) and 0.277 24(12) (H...S) nm, and the bond angles of 136.4° and 165.6°, respectively, leading into a two-dimensional layer structure. Furthermore, such layer are connected through intermolecular hydrogen bonds (O1W-H2W...O2ⁱⁱⁱ) involving the coordination water molecules and oxygen atoms of EBSA²⁻ groups, yielding a three-dimensional hydrogen-bonding supramolecular network (Fig.4).



Symmetry code: ⁱⁱⁱ $-x+1, -y+1, -z+1$; ^v $x, y, z-1$; ^{vi} $x, y, z+1$

Fig.4 2D and 3D structure of complex **2**

2.3 IR Spectrum and thermal analysis

In the complex **1**, the characteristic band at 3 337 cm⁻¹ reveals existence of H₂O molecule. While the absorption band at 3 321, 3 139 cm⁻¹ in complex **2** were attributed to the O-H and -N-H characteristic stretching vibrations of H₂O and imidazole, respectively, corresponding to the known structure. The IR spectra of the complex **1** exhibit the typical

antisymmetric 1 629, 1 595 cm⁻¹ and symmetric 1 376 cm⁻¹ stretching bands of two carboxy groups, and the values $\Delta\nu(\nu_{as}(\text{COO}^-)-\nu_s(\text{COO}^-))$ of 253 and 219 cm⁻¹, respectively, indicate that EBSA²⁻ (2,2'-dicarboxydi-phenylthioether) is monodentate. In the compound **2**, the absorptions at 1 622, 1 517 cm⁻¹ and 1 391, 1 374 cm⁻¹ correspond to asymmetric $\nu_{as}(\text{COO}^-)$ and symmetrical $\nu_s(\text{COO}^-)$ stretching vibrations of the coordinated

carboxylate groups. The $\Delta\nu(\nu_{\text{as}}(\text{COO}^-)-\nu_{\text{s}}(\text{COO}^-))$ value is 231 and 143 cm^{-1} , respectively. We can infer that the two carboxylate groups show monodentate and bidentate-chelating coordination mode. Meanwhile, characteristic bands 1 579, 1 445 cm^{-1} in **1** and 1574 cm^{-1} in **2** belong to the stretching vibration of $-\text{N}=\text{C}-$ of 2,2'-dipyridyl^[17] and imidazole^[18] ligands, respectively. The characteristic bands 1 376, 829 cm^{-1} in **1** belong to the stretching vibration of $-\text{S}-\nu(\text{aromatic})$ of EBLA ligand^[19]. In addition the weak absorptions at 1 162, 1 133 and 509 cm^{-1} in **2** belong to the stretching vibration of $-\text{S}-\text{S}-\nu(\text{aromatic})$ of EBSA ligand^[20]. The results of the IR spectra analyses of the complexes are in consistent with that of single-crystal X-ray analyses.

The thermal stability and thermal decomposition behavior of complexes **1** and **2** were studied by thermal analysis in a static N_2 atmosphere in the temperature range of 30~800 $^{\circ}\text{C}$, as shown in Fig.5. In complex **1**, the first weight loss corresponding to the escape of one coordinated water molecule is observed from 30 to 166 $^{\circ}\text{C}$ (Obsd. 3.90%, Calcd. 3.52%). The second weight loss corresponding to the escape of EBLA^{2+} ligand is observed from 279 to 516 $^{\circ}\text{C}$ (Obsd. 53.15%, Calcd. 56.72%). In complex **2**, the weight-loss step occurs from 99 to 487 $^{\circ}\text{C}$ (Obsd. 62.71%, Calcd. 62.87%), which corresponds to the decomposition of framework structure by losing one coordinated water molecule and EBSA^{2+} ligand. Complexes **1** and **2** slowly start to decompose after 517 and 488 $^{\circ}\text{C}$, respectively, which is similar with $[\text{Co}(\text{bpp})(\text{H}_2\text{O})(\text{nip})]_n$ ^[21].

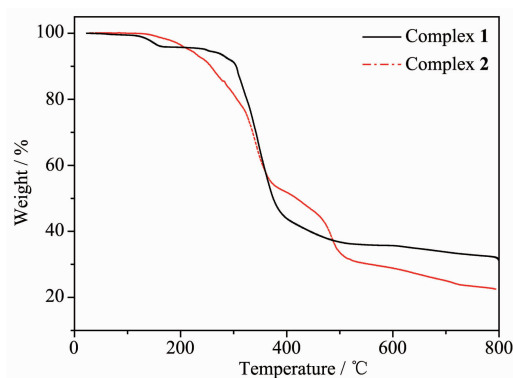


Fig.5 Thermogravimetric curves (TG) for **1** and **2**

2.4 Photoluminescence properties

Coordination polymers based on d^{10} metal centers

and organic ligands are promising candidates for photoactive materials with potential applications. For complex **1**, fluorescent property of compound has been investigated in the solid state. 2,2'-bpy shows strong emission peak centered at 530 nm upon excitation at 342 nm and the emission peaks were not observed for free EBLA (2,2'-dicarboxydiphenylthioether) ligand because the EBLA ligand was obtained by hydrothermal in situ ligand syntheses. When these ligands complexed with $\text{Zn}(\text{II})$ atoms, strong fluorescence with emission broad peak centered at 460 nm ($\lambda_{\text{ex}}=387$ nm) for complex **1** was observed at room temperature (Fig. 6), which may originate from the $\pi-\pi^*$ transition emission of ligand-to-ligand charge transfer (LLCT) in aromatic rings of the two ligands^[22].

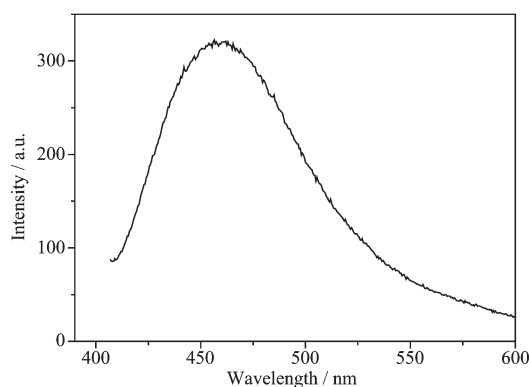


Fig.6 Solid-state photoluminescent spectrum for **1**

3 Conclusions

In conclusion, two new $\text{Zn}(\text{II})$ and $\text{Mn}(\text{II})$ complexes, $[\text{Zn}(\text{EBLA})(2,2'\text{-bpy})(\text{H}_2\text{O})]$ and $[\text{Mn}(\text{EBSA})(\text{im})_2(\text{H}_2\text{O})]_n$, has synthesized and structurally characterized. The complex **1**, **2** is a dinuclear and a one-dimensional infinite linear chain structure, respectively. The 2,2'-dithiosalicylic acid in situ reaction provided 2,2'-dicarboxydiphenylthioether(EBLA) ligand at 180 $^{\circ}\text{C}$ by hydrothermal method. Complex **1** emits intensely luminescence with the fluorescence of 460 nm in solid state at room temperature.

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References:

- [1] Jiang J, Yu J, Corma A. *Angew. Chem. Int. Ed.*, **2010**, **49**: 3120-3145
- [2] Lee L W, Vittal J J. *Chem. Rev.*, **2011**, **111**: 688-764
- [3] Deng Z P, Huo L H, Li M S, et al. *Cryst. Growth Des.*, **2011**, **11**: 3090-3100
- [4] Zhang Z Y, Deng Z P, Huo L H, et al. *Inorg. Chem.*, **2013**, **52**: 5914-5923
- [5] MA Zhi-Feng(马志峰), ZHANG Ying-Hui(章应辉), HU Tong-Liang(胡同亮), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2014**, **30**(1): 204-212
- [6] Li J R, Ma Y G, Mearthy M C, et al. *Coord. Chem. Rev.*, **2011**, **255**: 1791-1823
- [7] ZHAO Yue(赵越), ZHAI Ling-Ling(翟玲玲), SUN Wei-Yin(孙为银). *Chinese J. Inorg. Chem.*(无机化学学报), **2014**, **30**(1): 99-105
- [8] Feng R, Jiang F L, Chen L, et al. *Chem. Commun.*, **2009**: 5296-5298
- [9] Murugavel R, Baheti K, Anantharaman G. *Inorg. Chem.*, **2001**, **40**: 6870-6878
- [10] Yu J H, Yao R, Yuan L M, et al. *Inorg. Chim. Acta*, **2011**, **376**: 222-229
- [11] Bu Y, Jiang F L, Zhang S Q, et al. *CrystEngComm*, **2011**, **13**: 6323-6326
- [12] Wang J, Zheng S L, Hu S, et al. *Inorg. Chem.*, **2007**, **46**: 795-800
- [13] Han L, Bu X H, Zhang Q C, et al. *Inorg. Chem.*, **2006**, **45**: 5736-5738
- [14] Humphrey S M, Mole R A, Rawson J M, et al. *Dalton Trans.*, **2004**: 1670-1678
- [15] Sheldrick G M. *SADABS, Siemens Area Detector Absorption Corrected Software*, University of Göttingen, Germany, **1996**.
- [16] Sheldrick G M. *SHELXL-97, Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, **1997**.
- [17] ZHAO Yong-Liang(赵永亮), ZHAO Feng-Ying(赵凤英). *Spectrosc. Spect. Anal.*(光谱学与光谱分析), **2000**, **20**(6): 822-824
- [18] YANG Hui(杨卉), DING Yi-Gang(丁一刚), YANG Chang-Yan(杨昌炎), et al. *J. Wuhan Inst. Tech.*(武汉工程大学学报), **2011**, **11**: 19-22
- [19] Bhubon S R K, Abdul M K M, Ozra G M S, et al. *Inorg. Chem. Commun.*, **2001**, **4**: 315-318
- [20] Grant A B, Ryan P A B, Edward R T. *CrystEngComm*, **2008**, **10**: 879-887
- [21] XIANG Lei(向磊), GUO Xiao-Fang(郭小芳), LI Xin-Xiong(李新雄), et al. *Chinese J. Struct. Chem.*(结构化学), **2013**, **32**(11): 1680-1686
- [22] 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