

两个含 2,4-二氯苯氧乙酸及氮杂环配体的 Ag(I) 配合物的合成及晶体结构

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摘要: 以 2,4-二氯苯氧乙酸、2,2'-联吡啶、4,4'-联吡啶和硝酸银为原料, 采用自然挥发法制备了 2 个配合物 $[\text{Ag}_2(\text{ELBA})(4,4'\text{-bipy})_2(\text{NO}_3)] \cdot 2\text{H}_2\text{O}$ (**1**) 和 $[\text{Ag}_2(\text{ELBA})_2(2,2'\text{-bipy})]_n$ (**2**) (ELBA=2,4-二氯苯氧乙酸, 4,4'-bipy=4,4'-联吡啶, 2,2'-bipy=2,2'-联吡啶), 并对其进行了元素分析、红外光谱、热稳定性和 X-射线单晶衍射的表征, 研究了配合物 **2** 的荧光性质。结果表明, 配合物 **1** 和 **2** 均为一维结构, 其中, 配合物 **1** 是通过 4,4'-联吡啶和银离子间的作用形成梯状结构; 而配合物 **2** 是通过 $\text{Ag} \cdots \text{Ag}$ 作用构筑 S 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: 银配合物; 2,4-二氯苯氧乙酸; 晶体结构

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Syntheses and Crystal Structures of Two Ag(I) Complexes with 2,4-Dichlorophenoxyacetic Acid and Nitrogen Heterocyclic Ligands

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Abstract: Two coordination polymers $[\text{Ag}_2(\text{ELBA})(4,4'\text{-bipy})_2(\text{NO}_3)] \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Ag}_2(\text{ELBA})_2(2,2'\text{-bipy})]_n$ (**2**) were synthesized by evaporation methods using 2,4-dichlorophenoxyacetic acid (ELBA), 4,4'-dipyridyl (4,4'-bipy), 2,2'-dipyridyl (2,2'-bipy) and AgNO_3 . The complexes were characterized by elemental analysis, FT-IR, thermogravimetric analysis (TGA) and X-ray single-crystal structure analysis, and fluorescence properties of the complex **2** have been studied. As a result, complexes **1** and **2** are one-dimensional structure. Among others, in complex **1**, Ag(I) ion is surrounded by two nitrogen atoms from two bipy ligands form an infinite chain, and adjacent Ag-bipy chains produce “rungs” of a ladder by silver ions contacts. And in compound **2**, the similar S-shape one-dimensional infinite chain is obtained by $\text{Ag} \cdots \text{Ag}$ interactions. Hydrogen bonding and $\pi \cdots \pi$ interactions were observed in these complexes. CCDC: 997226, **1**; 997227, **2**.

Key words: silver complex; 2,4-dichlorophenoxyacetic acid; crystal structure

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0 Introduction

Designed syntheses of various open-frameworks have drawn wide attention in metal-organic coordination polymers because of their intriguing structures as well as potential application in various fields such as storage, fluorescence, magnetism, separation, catalysis, and so on^[1-3]. The structural diversity and topology of coordination polymers are attributed to the selection of metal centers, organic ligands and reaction pathways^[4]. Silver ion has a flexible coordination number and irregular coordination sphere which may lead to the discovery of fascinating structures, and the preparation of silver complexes have attracted much attention^[5-7]. A lot of effort has focused on the purposeful design and controllable synthesis of coordination polymers employing multidentate ligands such as carboxylate or N-heterocyclic ligands^[8-10]. It is well known that the flexible 2,4-dichlorophenoxyacetic acid (ELBA) is a preeminent candidate for constructing novel structures^[11-13]. Heterocyclic nitrogen donors, such as bipyridine (2,2'-bipy or 4,4'-bipy) have proved to be among the most important types of organic ligands for the design and construction of coordination polymers exhibiting remarkable properties for their excellent coordinating ability^[14-15]. In this study, we introduced ELBA with the nitrogen heterocyclic ligands in order to assemble two Ag(I) coordination polymer. In addition, thermal stability and luminescent property of the polymers were measured and discussed.

1 Experimental

1.1 Materials and measurements

All chemicals purchased were of reagent grade and used without further purification. Elemental analyses were performed on a CARLO ERBA 1106 analyzer. The FT-IR spectra were recorded on a PerkinElmer Spectrum 100 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 {[Ag₂(ELBA)(4,4'-bipy)₂(NO₃)]·2H₂O}_n (1)

Silver nitrate (0.169 9 g, 1 mmol), 2,4-dichlorophenoxyacetic acid (0.221 0 g, 1 mmol) and 4,4'-bipy (0.312 4 g, 2 mmol) were dissolved in 30ml methanol/water solution (1:1, V/V) and the pH was adjusted to 7 with 0.1 mol·L⁻¹ potassium hydroxide solution. After the mixture was stirred for 30 min, the precipitate was dissolved in the aqueous solution of NH₃ (14 mol·L⁻¹) which was added drop by drop. Colorless crystals of compound were obtained by evaporation of the solution for 14 days at room temperature in 47% yields (based on Ag). Analysis calculated for C₂₈H₂₅Cl₂N₅O₈Ag₂(%): C 39.74, H 2.98, N 8.28; Found(%): C 39.12, H 3.01, N 8.31. IR (KBr pellet, cm⁻¹): 3 473(w), 3 066(w), 2 917(w), 2 371(w), 1 968(w), 1 605(s), 1 531(w), 1 529(w), 1 482(m), 1 415(w), 1 373(s), 1 257(w), 1 071(w), 913(w), 870(w), 807(m), 721(w), 628(m), 572(w), 494(m).

1.3 Synthesis of [Ag₂(ELBA)₂(2,2'-bipy)]_n (2)

The synthesis of complex **2** was carried out in the same procedure as that of complex **1**, except 4,4'-bipy was replaced by 2,2'-bipy. After reaction, colorless crystals were obtained in 41% yields (based on Ag). Analysis calculated for C₂₆H₁₈Cl₄N₂O₆Ag₂(%): C 38.46, H 2.23, N 3.45; Found: C 38.58, H 2.34, N 3.41. IR (KBr pellet, cm⁻¹): 3 421(w), 3 094(w), 2 917(w), 2 371(w), 1 616(s), 1 483(s), 1 423(s), 1 417(W), 1 349(m), 1 266(s), 1 153(w), 1 103(w), 1 068(m), 940(w), 855(w), 800(m), 764(s), 686(w), 601(w), 558(w), 467(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^[16]. 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^[17]. 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: 997226, **1**; 997227, **2**.

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

Complex	1	2
Empirical formula	C ₂₈ H ₂₅ Cl ₂ N ₅ O ₈ Ag ₂	C ₂₆ H ₁₈ Cl ₄ N ₂ O ₆ Ag ₂
Formula weight	846.17	811.96
Temperature / K	295(2)	296(2)
Size / mm	0.30×0.20×0.18	0.30×0.15×0.10
θ range for data collection / (°)	2.32~25.00	1.94~24.99
Crystal system	Monoclinic	Orthorhombic
Space group	<i>Cc</i>	<i>Pna</i> 2 ₁
<i>a</i> / nm	1.048 2(3)	0.732 87(15)
<i>b</i> / nm	1.805 6(5)	1.106 9(2)
<i>c</i> / nm	1.667 4(4)	3.335 5(7)
β / (°)	106.768(4)	90
<i>V</i> / nm ³	3.021 6(14)	2.705 9(10)
<i>Z</i>	4	4
μ / mm ⁻¹	1.532	1.889
<i>D_c</i> / (g·cm ⁻³)	1.860	1.993
<i>F</i> (000)	1 680	1 592
Reflections collected	7 617	14 032
Independent reflections (<i>R</i> _{int})	4 007 (0.026 1)	3 946 (0.018 0)
Observed reflections (<i>I</i> >2 σ (<i>I</i>))	3 882	3 870
Goodness of fit on <i>F</i> ²	1.047	1.047
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> >2 σ (<i>I</i>))	0.022 0, 0.056 0	0.020 0, 0.044 4
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.023 3, 0.056 9	0.020 7, 0.044 6
($\Delta\rho$) _{max} , ($\Delta\rho$) _{min} / (e·nm ⁻³)	313, -451	225, -537

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

Complex 1					
Ag(1)-O(3)	0.276 8(3)	Ag(1)-N(3)	0.217 0(5)	Ag(2)-N(2)	0.215 7(6)
Ag(1)-O(5)	0.279 2(4)	Ag(2)-O(2)	0.262 6(2)	Ag(1)-Ag(2)	0.336 98(8)
Ag(1)-O(6)	0.288 2(4)	Ag(2)-O(3)	0.268 8(3)		
Ag(1)-N(4) ⁱ	0.216 8(5)	Ag(2)-N(1) ⁱⁱ	0.215 0(5)		
N(4) ⁱ -Ag(1)-N(3)	168.61(2)	N(1) ⁱⁱ -Ag(2)-N(2)	171.20(2)	N(2)-Ag(2)-Ag(1)	94.99(2)
N(4) ⁱ -Ag(1)-Ag(2)	91.05(2)	O(2)-Ag(2)-O(3)	49.26(2)	O(3)-Ag(1)-O(6)	165.14(2)
N(3)-Ag(1)-Ag(2)	96.42(2)	N(1) ⁱⁱ -Ag(2)-Ag(1)	91.83(2)	O(5)-Ag(1)-O(6)	43.93(3)
Complex 2					
Ag(1)-O(3)	0.231 4(3)	Ag(1)-N(2)	0.241 7(4)	Ag(1)-Ag(2)	0.301 24(7)
Ag(1)-O(1)	0.235 2(3)	Ag(2)-O(4)	0.213 8(3)	Ag(1)-Ag(2) ⁱ	0.308 79(7)
Ag(1)-N(1)	0.239 2(3)	Ag(2)-O(2)	0.214 1(3)	Ag(2)-Ag(1) ⁱⁱ	0.308 79(7)

Continued Table 2

O(1)-Ag(1)-N(1)	121.88(2)	N(1)-Ag(1)-N(2)	68.56(2)	O(4)-Ag(2)-Ag(1) ⁱⁱ	110.91(9)
O(1)-Ag(1)-Ag(2) ⁱ	127.75(8)	Ag(1)-Ag(2)-Ag(1) ⁱⁱ	123.560(2)	O(4)-Ag(2)-Ag(1)	92.01(8)
O(1)-Ag(1)-N(2)	91.14(2)	Ag(2)-Ag(1)-Ag(2) ⁱ	84.913(2)	N(1)-Ag(1)-Ag(2) ⁱ	102.79(9)
O(3)-Ag(1)-Ag(2) ⁱ	71.20(9)	C(11)-O(6)-C(10)	118.20(3)	N(2)-Ag(1)-Ag(2) ⁱ	80.57(9)
O(3)-Ag(1)-N(2)	139.87(2)	O(1)-Ag(1)-Ag(2)	68.48(7)	N(1)-Ag(1)-Ag(2)	152.19(9)
O(3)-Ag(1)-O(1)	128.67(2)	O(2)-Ag(2)-Ag(1) ⁱⁱ	71.67(8)	N(2)-Ag(1)-Ag(2)	139.22(8)
O(3)-Ag(1)-N(1)	90.18(2)	O(2)-Ag(2)-Ag(1)	89.37(7)	C(6)-O(5)-C(7)	115.50(3)
O(4)-Ag(2)-O(2)	175.55(2)	O(3)-Ag(1)-Ag(2)	66.75(7)		

Symmetry atoms: for **1**: ⁱ $x+1, -y+1, z+1/2$; ⁱⁱ $x-1, -y+1, z-1/2$; for **2**: ⁱ $x+1/2, -y+3/2, z$; ⁱⁱ $x-1/2, -y+3/2, z$

Table 3 Hydrogen bonds for complexes **1** and **2**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{D-H}\cdots\text{A} / (^\circ)$
Complex 1				
OW1-H(1W1)···O(4)	0.083 4(2)	0.259(4)	0.329 4(6)	143(6)
OW1-H(1W1)···O(6)	0.083 4(2)	0.224(2)	0.305 1(5)	166(6)
OW2-H(1W2)···O(2)	0.083 6(2)	0.184 5(2)	0.268 0(4)	176(6)
C(11)-H(11)···O(6) ⁱⁱ	0.093	0.247	0.323 2(5)	139.4
C(17)-H(17)···O(3)	0.093	0.257	0.324 3(5)	129.8
C(21)-H(21)···O(2)	0.093	0.247	0.323 3(5)	138.8
C(26)-H(26)···O(2) ⁱ	0.093	0.250	0.321 6(4)	134.3
OW2-H(2W2)···O(4) ⁱⁱⁱ	0.083 3(2)	0.251(4)	0.313 5(5)	133(4)
OW2-H(2W2)···O(5) ⁱⁱⁱ	0.083 3(2)	0.226(2)	0.305 7(5)	161(6)
C(5)-H(5)···OW1 ⁱⁱⁱ	0.093	0.253	0.338 5(5)	152.1
C(28)-H(28)···OW1 ⁱⁱⁱ	0.093	0.257	0.346 8(5)	162.8
C(7)-H(7)···OW2 ^{iv}	0.093	0.237	0.329 5(5)	171.3
C(9)-H(9)···OW1 ^v	0.093	0.246	0.337 0(5)	166.9
Complex 2				
C(26)-H(26A)···O(2) ⁱ	0.093	0.245	0.316 3(5)	133.6
C(23)-H(23A)···O(1) ⁱⁱⁱ	0.093	0.258	0.340 8(5)	148.7

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

2 Results and discussion

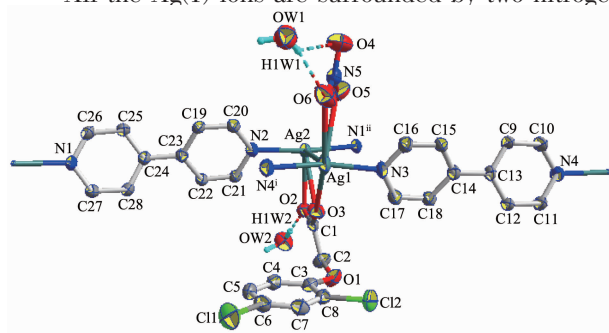
2.1 Structure description of {[Ag₂(ELBA)(4,4'-bipy)₂(NO₃)]·2H₂O}_n (**1**)

The molecular structure of the complex **1** is shown in Fig.1. Single-crystal X-ray diffraction analysis reveals that the asymmetric unit of **1** contains two Ag(I) cations, three coordinated ELBA anions, two coordinated nitrate anions, two 4,4'-bipy ligands, and two free water molecule (Fig.1). The Ag1 ion is five-coordinated with two different N atoms of bipy, two O atoms of nitrate and O atoms carboxylate from ELBA ligands, and the local coordination sphere around the

Ag1 ion can be described as a distorted square pyramidal with a AgO₃N₂ chromophore. Atoms O3, O6, N3 and N4ⁱ define the equatorial plane, while nitrate O5 atoms occupies the apical site (N4ⁱ-Ag1-N3 168.61(2)[°]; O3-Ag1-O6 165.14(2)[°]). The Ag1-O and Ag1-N distances were in the range of 0.216 8(5)~0.288 2(4) nm. Moreover, the Ag2 ion coordinates to two oxygen atoms from ELBA ligands and two nitrogen atoms from different bipy ligands, and the local coordination sphere around the Ag2 ion can be described as a similar “wedge” shaped with a AgO₂N₂ chromophore (O2-Ag2-O3 49.26(2)[°]; N1ⁱⁱ-Ag2-N2 171.20(2)[°]). The Ag2-O and Ag2-N distances are in the range of

0.215 0(5)~0.268 8(3) nm. The ELBA ligands is connected to two Ag(I) atoms through deprotonated carboxylate groups with $\eta_3;\mu_2$ coordination modes(chelating/bridging bidentate fashion). The dihedral angle between two pyridine ring plane of bipy ligands is $34.21(3)^\circ$ (N1 atoms and N2 atoms of pyridine rings) and $32.46(3)^\circ$ (N3 atoms and N4 atoms of pyridine rings). The torsion angles of $69.0(5)^\circ$ (C3-O1-C2-C1) distinction may be attributed to the remarkable conformational flexibility of ELBA ligands. The two free water molecules (OW1 and OW2) form intramolecular hydrogen bond with the coordinated ELBA ligands O2 atom and nitrate ligands O4, O6 atoms, with the $\text{OW}\cdots\text{O}$ bond length of 0.184 5(2)~0.259(4) nm and the $\text{OW}-\text{H}\cdots\text{O}$ bond angle of $143(6)^\circ$ ~ $176(6)^\circ$ (Table 3).

All the Ag(I) ions are surrounded by two nitrogen



Hydrogen atoms are omitted for clarity; symmetry code: ⁱ $x+1, -y+1, z+1/2$; ⁱⁱ $x-1, -y+1, z-1/2$

Fig.1 Molecular structure of complex **1** with the ellipsoids drawn at the 30% probability level

atoms from two bipy ligands to form an infinite $[\text{Ag}(\text{bipy})]_n$, and adjacent Ag-bipy chains produce “rungs” of a ladder by weak ligand-supported $\text{Ag1}\cdots\text{Ag2}$ (0.336 9(3) nm) contacts. The adjacent $\text{Ag}\cdots\text{Ag}$ distances of a ladder are 1.137 9 nm ($\text{Ag1}\cdots\text{Ag1}^{\text{ii}}$) or 1.135 7 nm ($\text{Ag2}\cdots\text{Ag2}^{\text{i}}$) (Fig.2). The two-dimensional layer structure of compound is formed by intermolecular interactions including intermolecular hydrogen bonds, $\pi\cdots\pi$ and $\text{C}-\text{H}\cdots\pi$ interactions. There are one kind of intermolecular hydrogen bond ($\text{OW2}-\text{H2W2}\cdots\text{O4}^{\text{iii}}$ 0.250 8 nm, Symmetry codes: ⁱⁱⁱ $x+1/2, y+1/2, z$). In addition, the 2D layer structure in complex **1** are further linked by $\pi\cdots\pi$ interactions ($\text{Cg1}\cdots\text{Cg2}$ 0.365 6 nm) and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond ($\text{C7}-\text{H7}\cdots\text{OW2}^{\text{iv}}$ 0.237 3 nm, Symmetry codes: ^{iv} $x-1/2, -y+3/2,$

$z+1/2$). The centroids Cg1 is made up of atoms of N2, C19, C20, C21, C22 and C23, and the centroids Cg2 is made up of atoms of N3, C14, C15, C16, C17 and C18. With the help of hydrogen-bonded interactions ($\text{OW1}-\text{H1W1}\cdots\text{O6}$) and $\text{C}-\text{H}\cdots\text{O}$ between adjacent 2D sheet ($\text{C9}-\text{H9}\cdots\text{OW1}^{\text{v}}$ 0.245 9 nm, $\text{C28}-\text{H28}\cdots\text{OW1}^{\text{iii}}$ 0.256 9 nm; Symmetry codes: ⁱⁱⁱ $x+1/2, y+1/2, z$; ^v $x-1/2, -y+1/2, z-1/2$), the polymeric sheet is assembled to form a supramolecular 3D network structure (Fig.3).

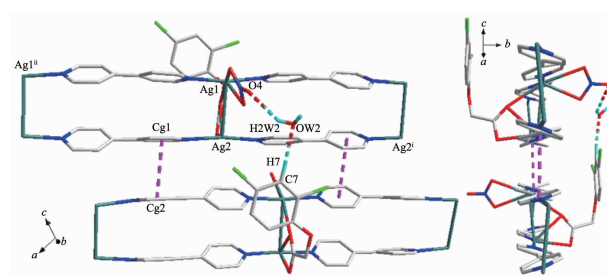


Fig.2 2D structure of complex **1**

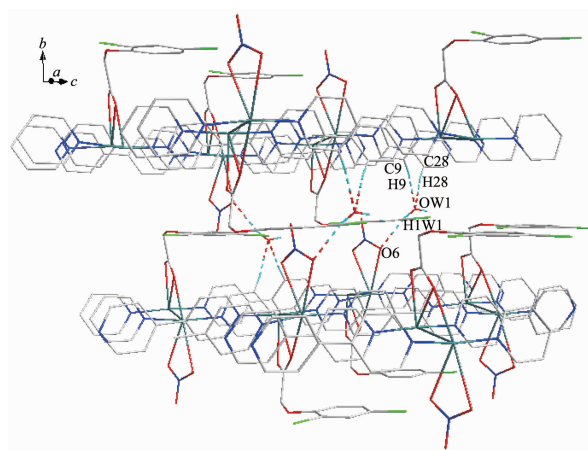
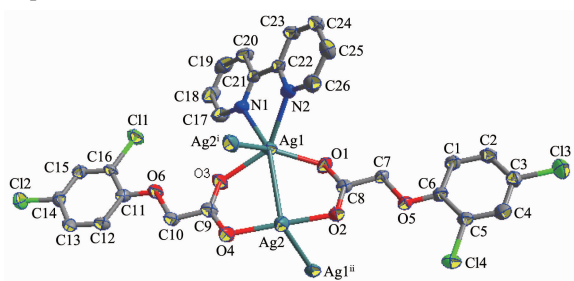


Fig.3 3D structure of complex **1**

2.2 Structure description of $[\text{Ag}_2(\text{ELBA})_2(2,2'\text{-bipy})]_n$ (**2**)

The molecular structure of the complex **2** is shown in Fig.4 and the selected bond distances and angles were listed in Table 2. Single-crystal X-ray diffraction analysis reveals that the asymmetric unit of **2** contains two Ag(I) cations, two ELBA anions, and one 2,2'-bipy ligands (Fig.4). Ag1 ion is four-coordinated ones, consisted of two N atoms from one 2,2'-dipyridyl co-ligand and two carboxylate O atoms from two different ELBA ligands, and the local coordination sphere around the Ag1 ion can be described as a

distorted triangular pyramidal with a AgO_2N_2 chromophore. Its equatorial plane is defined by the atoms O1, O3 and N2, and N1 atoms of nitrate occupies the apical site (the deviation of Ag1 from the mean plane is 0.005 37(4) nm). The Ag1-O and Ag1-N distances were within the range of 0.231 4(3)~0.241 7(4) nm. Moreover, the Ag2 ion coordinates to two oxygen atoms from different ELBA ligands, and the local coordination sphere around the Ag2 ion can be described as linear pattern with a AgO_2 chromophore (O4-Ag2-O2 175.55(2) $^\circ$). The Ag2-O2 and Ag2-O4 distances are 0.214 1(3) and 0.213 8(3) nm, respectively. The dihedral angle between two benzene ring planes of two different ELBA ligands is 3.477(3) $^\circ$. The distinction of torsion angles between $\angle \text{C6-O5-C7-C8}$ (−171.9(3) $^\circ$) and $\angle \text{C11-O6-C10-C9}$ (176.4(3) $^\circ$) may be attributed to the outstanding conformational flexibility of ELBA groups.



Hydrogen atoms are omitted for clarity; Symmetry code: ⁱ $x+1/2$, $-y+3/2$, z ; ⁱⁱ $x-1/2$, $-y+3/2$, z

Fig.4 Molecular structure of complex **2** with the ellipsoids drawn at the 30% probability level

The similar S-shape one-dimensional infinite chain are formed by $\text{Ag}\cdots\text{Ag}$ interactions. In the chain, the adjacent $\text{Ag}\cdots\text{Ag}$ distance is 0.301 2 (Ag1 \cdots Ag2) and

0.308 8 nm (Ag2 \cdots Ag1ⁱⁱⁱ or Ag1 \cdots Ag2ⁱ), much shorter than van der Waals radii of two silver ions (0.344 0 nm)^[18]. The two-dimensional layer structure of compound are formed by intermolecular interactions including $\pi\cdots\pi$ interaction (Cg1 \cdots Cg2 0.372 1 nm) and C-H \cdots O hydrogen bond (C23-H23A \cdots O1ⁱⁱⁱ 0.257 9 nm, Symmetry codes: ⁱⁱⁱ $x+1/2$, $-y+1/2$, z). The centroids Cg1 and Cg2 are made up of atoms of N1, C17, C18, C19, C20 and C21. With the help of C-H $\cdots\pi$ (C15-H15A $\cdots\pi$ 0.367 5 nm, Cg: C1, C2, C3, C4, C5, C6) between adjacent 2D sheet, the polymeric sheet assembled to form a supramolecular 3D network structure (Fig.5).

2.3 IR spectrum

In the complex **1**, the absence of the absorption at 1 730 cm^{-1} for the free ELBA indicates the complete deprotonation of the ligands in the reaction with Ag(I) ion. The asymmetric $\nu_{\text{as}}(\text{COO}^-)$ and symmetrical $\nu_{\text{s}}(\text{COO}^-)$ appear in 1 605, 1 482 and 1 373 cm^{-1} , respectively. The two values of $\Delta\nu(\text{COO}^-)$ suggest the presences of two different coordinated modes of the carboxylate groups^[19]. In complex **2**, the very strong band at 1 616 cm^{-1} is assigned to the asymmetrical stretching mode of the COO^- groups, while the shoulder at 1349 cm^{-1} corresponds to the symmetrical COO^- stretching modes. The separation ($\Delta\nu$) between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ is 267 cm^{-1} , indicating bidentate-chelating mode for the coordinated carboxylate groups^[20]. Meanwhile, the bands at 1 531, 1 415 cm^{-1} and 1 483, 1 417 cm^{-1} are assigned to the stretching vibration of $-\text{N}=\text{C}-$ of pyridine in **1** and **2**, respectively^[21]. In addition the absorptions at 1 257,

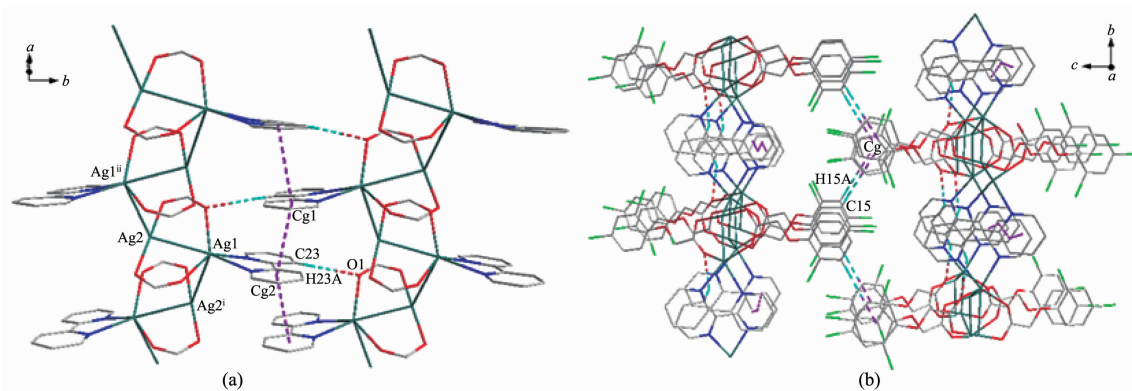


Fig.5 2D (a) and 3D (b) structure of complex **2**

1 071, 807 and 721 cm^{-1} in complex **1** belong to the absorption band of NO_3^- groups^[22].

2.4 Thermal analysis

The thermal stability 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.6. In complex **1**, the first weight loss corresponding to the escape of two free water molecules is observed in a temperature range of 30~148 $^{\circ}\text{C}$ (Obsd. 4.01%, Calcd. 4.28%). The second weight loss corresponding to the escape of nitrate anion, ELBA and 4,4'-bipy ligands is observed from 149 to 306 $^{\circ}\text{C}$ (Obsd. 69.01%, Calcd. 70.27%). In complex **2**, the weight-loss step occurred in the temperature range of 173~368 $^{\circ}\text{C}$ (Obsd. 72.22%, Calcd. 73.40%), which corresponds to the decomposition of framework structure of ELBA and 2,2'-bipy ligands. For further heating in complexes **1** and **2**, the final decomposition product is metallic silver, with a residue of 26.89% and 27.88% (Calcd. 25.45% and 26.60%), respectively^[23].

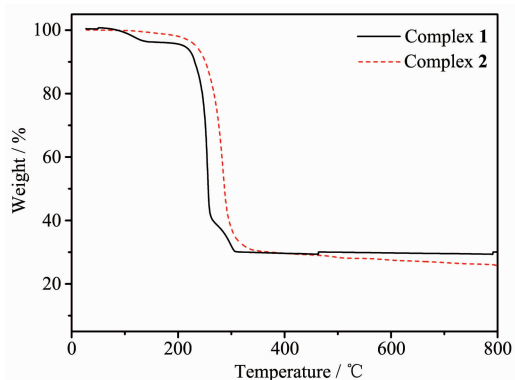


Fig.6 Thermogravimetric (TG) curves for **1** and **2**

2.5 Photoluminescence properties

Coordination polymers based on d^{10} metal centers and organic ligands are promising candidates for photoactive materials with potential applications. For complex **2**, fluorescent property of compound has been investigated in the solid state. The emission peaks at about 530 nm ($\lambda_{\text{ex}}=342$ nm) and 490 nm ($\lambda_{\text{ex}}=280$ nm) were observed for free 2,2'-bipy^[24] and ELBA^[25] ligands, respectively. For compound **2**, strong fluorescence with emission broad peak centered at 475 nm ($\lambda_{\text{ex}}=349$ nm) was observed at room temperature (Fig.7), which

may originate from the $\pi_{\text{L}}-\pi_{\text{L}}^*$ transition emission of ligand-to-ligand charge transfer (LLCT) in aromatic rings of the two ligands^[26]. Fluorescence was hardly ever observed for complex **1**, which may be due to heavy atom effects^[27].

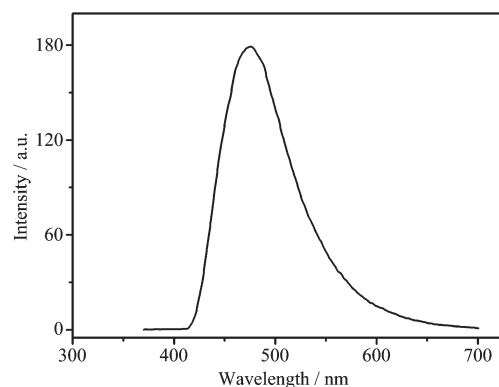


Fig.7 Solid-state photoluminescent spectrum for **2**

3 Conclusions

The complexes of $[\text{Ag}_2(\text{ELBA})(4,4'\text{-bipy})_2(\text{NO}_3)] \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Ag}_2(\text{ELBA})_2(2,2'\text{-bipy})]_n$ (**2**) were synthesized and characterized. The complexes **1** and **2** were the chains of trapezoid and S-shape one-dimensional infinite chain structures formed by $\text{Ag} \cdots \text{Ag}$ interactions, respectively. Complex **2** emits intensely luminescence with emission broad peak of 475 nm in a solid state at room temperature.

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中国化学会第九届全国无机化学学术会议第二轮通知

由中国化学会和国家自然科学基金委主办、南昌大学承办的“中国化学会第九届全国无机化学学术会议”定于2015年7月25—29日在江西省南昌市南昌大学前湖校区召开。本次会议以学术交流为平台,充分展示近四年来我国无机化学领域各研究团队和个人的研究新成果,讨论无机化学未来发展的新思路、新领域和新趋势,促进各方面的合作与自主创新。会议将邀请两院院士、长江学者、国家杰出青年基金获得者、“千人计划”入选者在内的多位国内知名学者及部分海外学者参加会议并作特邀报告。热忱欢迎广大化学工作者积极参加,踊跃投稿。同时,欢迎相关企业、高校、科研院所积极参与会展。会议已经开放注册、报告申请及住房预订。详见网址:<http://www.chemsoc.org.cn/meeting/wjhxhy2015/>

第九届全国无机化学学术会议组委会

2015-4-20