

N,N'-双(3-吡啶醛)-(1*R*,2*R*)-环己二胺席夫碱 Ag(I) 配合物的合成、结构和荧光性质研究

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摘要: 以 3-吡啶醛和(1*R*,2*R*)-环己二胺进行缩合得到 Schiff 碱配体 L¹, 然后, 用配体 L¹ 和 AgNO₃ 进行配位反应, 得到配合物[Ag(L¹)(NO₃)]_n (**1**), 并用元素分析、FT-IR、X-射线单晶衍射、热重分析、粉末衍射对其进行了表征。晶体结构表明: 配合物 **1** 属于单斜晶系, C₂ 空间群, Ag(I) 的配位环境均为扭曲四面体, 分别和硝酸根的氧原子, 配体中的 2 个吡啶氮原子以及 1 个亚胺氮原子配位, 配体 L¹ 有 2 种配位模式, 其中, 1 个配体用两臂的 2 个吡啶氮原子分别和 2 个 Ag(I) 离子配位, 另外 1 个配体用两臂的 2 个吡啶氮原子分别和 2 个 Ag(I) 离子配位, 同时 2 个亚胺氮原子也分别和 2 个 Ag(I) 离子配位, 这样配合物形成 3D 孔状结构。同时研究了配合物的固体荧光性质。

关键词: 席夫碱; Ag(I) 配合物; 晶体结构; 荧光性质

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Synthesis, Crystal Structure and Fluorescence Property of Ag(I) Complex with Schiff Base *N,N'*-Bis(3-pyridinecarboxaldehyde)-(1*R*,2*R*)-cyclohexanediimine Ligand

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Abstract: The Schiff base ligand L¹ (*N,N'*-bis(3-pyridinecarboxaldehyde)-(1*R*,2*R*)-cyclohexanediimine) was synthesized from the condensation reaction of (1*R*,2*R*)-1,2-cyclohexanediamine with 3-pyridinecarboxaldehyde. AgNO₃ reacted with L¹ to give the complex [Ag(L¹)(NO₃)]_n (**1**), which was characterized by elemental analysis, FT-IR, single crystal X-ray diffraction, thermogravimetric Analysis (TGA) and powder X-ray diffraction. In the complex, the coordination environment of Ag(I) adopted a distorted tetrahedral geometry, being bound to one oxygen donor from a monodentate nitrate anion as well as to nitrogen atoms and imine nitrogen atoms from three adjacent molecules of L¹. In compound **1**, the L¹ ligands coordinated to the Ag(I) ions in two different ways. The first involved L¹ bridging of Ag(I) centers in a bidentate fashion via the two terminal pyridyl *N*-donors only. The other binding mode involved L¹ coordination to Ag(I) ions in a tetradentate mode through both terminal pyridyl *N*-donors and both amine nitrogen atoms. In this mode, the complex 3D porous structure of **1** was formed. At the same time, the fluorescent properties of ligand and complex **1** are investigated in the solid state at room temperature. CCDC: 969699, L¹; 969700, **1**.

Key words: Schiff base; Ag(I) complex; crystal structure; fluorescent property

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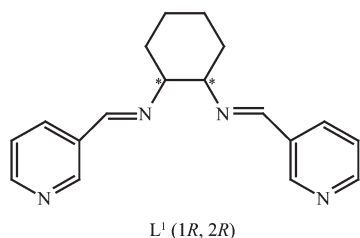
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0 Introduction

A great number of coordination polymers constructed by Schiff base ligands and transition-metal salts have been extensively studied due to the fact that Schiff base ligands have the great flexibility in the synthesis and good coordination ability^[1-6].

The structural diversity of these materials derives from many factors, such as the metal ion, the template, the metal-to-ligand ratio, the pH value, the counter anion, and the number of coordination sites provided by the organic ligands^[7-10]. Anions, being a permanent part of the final product, can influence the structure directly by coordinating to the metal ions or by acting as templates to induce self-assembly^[11-13]. Therefore, fully incorporating different counter anions may cause significant structural changes in the resultant polymers. Silver (I) ions play a central role in the formulation of such organic-inorganic hybrid assemblies; as soft acids, they favor stable coordination to soft bases, such as ligands that contain sulfur and unsaturated nitrogen atoms^[14]. Among of these MOF materials, bidentate *N*-containing heterocyclic ligands for the construction of some unique porous assemblies have been designed and synthesized, and their potential applications are now well documented^[15]. However, the use of chiral diamines, such as *trans*-(1*R*,2*R*)-1,2-cyclohexanedia-mine for the synthesis of chiral Schiff base ligands derived from pyridine carboxaldehydes, has not received much attention^[16-18].

In a recent study, we investigated the interaction of L^1 (Scheme 1) with $AgCF_3SO_3$ and found that the product complex, $[Ag(L^1)_2](CF_3SO_3) \cdot 4H_2O$, existed as a (4,4)-connected two-dimensional (2D) sheet with a corrugated surface^[19]. In this article, we report the synthesis, structural characterization, and thermal



Scheme 1 Schematic drawing of ligand L^1

behavior of the complex resulting from the interaction of the (1*R*,2*R*)-*N,N'*-bis(4-pyridyl)idene diaminocyclohexane ligand (L^1) with $AgNO_3$.

1 Experimental

1.1 Materials and measurements

All chemicals from commercial sources were of reagent grade and used without purification. Elemental (C, H, N) analysis data were obtained with a Vario EL III elemental analyzer. IR spectra were recorded by KBr pellets on Bio-Rad FTIR spectrophotometer (in the 400~4 000 cm^{-1} range). 1H NMR spectra were recorded on a JEOLCX 500 MHz spectrometer using $CDCl_3$ solution at room temperature. Thermogravimetric measurements were carried out in a nitrogen stream using a Netzsch STA449C apparatus with a heating rate of 10 $^{\circ}C \cdot min^{-1}$. X-Ray powder diffraction (XRPD) was carried out on a RIGAKU DMAX2500 apparatus.

1.2 Synthesis of the ligand L^1

1*R*,2*R*-diaminocyclohexane (1.14 g, 10 mmol) and 3-formyl pyridine (2.14 g, 20 mmol) in a 1:2 molar ratio were dissolved in 100 mL of anhydrous methanol. The reaction mixture was refluxed for 6~8 h, whilst maintaining dry conditions. The resulting solution was then evaporated under reduced pressure to obtain a light yellow semisolid, which on recrystallization from diethyl ether gave a white solid. Yield: 2.05 g, 70%. 1H NMR ($CDCl_3$, TMS): δ 8.73 (s, 2H, pyridyl), 8.56 (s, 2H, pyridyl), 8.22 (s, 2H, -CH=N), 7.94 (s, 2H, pyridyl), 7.25 (m, 2H, pyridyl), 3.44 (s, 2H, chiral-H), 1.50~1.90 (m, 8H, CH_2). Anal. Calcd. for $C_{18}H_{20}N_4$ (%): C, 73.94; H, 6.89; N, 19.16; Found(%): C, 74.08; H, 6.77; N, 19.20. FTIR (KBr pellet, cm^{-1}): 3 432(w), 3 129(s), 2 934(m), 1 642(m), 1 401(m), 1 326(w), 1 191(w), 1 026(w), 819(w), 706(w).

1.3 Synthesis of $[Ag(C_{18}H_{20}N_4)NO_3]_n$

$AgNO_3$ 0.17 g (1 mmol) in ethanol (20 mL) was added dropwise with stirring to L^1 (0.292 g, 1 mmol) in ethanol (10 mL) and stirring was continued at room temperature for 2 h. Then the reaction mixture was kept in a refrigerator over-night. A white amorphous solid separated out. The solid was collected by filtration, washed with a few drops of methanol, and

dried at room temperature to give **1** as a white solid in 43% yield. The solid was dissolved in excess ethanol at room temperature, and slow evaporation of this solution yielded colorless block-shaped single crystals that proved suitable for X-ray analysis. FTIR (KBr pellet, cm^{-1}): 3 459(m), 2 928(w), 2 856(w), 1 635(m), 1 382(s), 1 298(w), 1 1189(w), 1 110(w), 1 130(w), 934(w), 703(w), 631(w). Anal. Calcd. for $\text{C}_{18}\text{H}_{20}\text{AgN}_5\text{O}_3$ (%): C, 46.77; H, 4.36; N, 15.15; Found(%): C, 46.71; H, 4.45; N, 15.22.

1.4 X-ray crystallographic study

X-ray diffraction data were collected at room temperature with graphite monochromated Mo $K\alpha$ radiation on Bruker Smart Apex single crystal diffractometer by using a φ - ω scan method. Unit cell dimensions were obtained with least-squares refinements and multi-scan absorption corrections were applied by

using SADABS program. The structures were solved by direct methods using the program SHELXL-97 in the winGX package^[20]. H atoms were placed in calculated positions, with C-H distances of 0.093~0.096 nm and N-H 0.086 nm, and refined using a riding model with $U_{\text{iso}}(\text{H})=1.2\sim1.5U_{\text{eq}}(\text{C})$. The ORTEP-3^[21] drawing of the molecules is shown in Fig.1 and Fig.2. Crystal and experimental data are listed in Table 1, selected bond lengths and angles are given in Table 2. Hydrogen bonding geometry is given in Table 3.

CCDC: 969699, **L**¹; 969700, **1**.

2 Results and discussion

2.1 Crystal structure of ligand and $[\text{Ag}(\text{C}_{18}\text{H}_{20}\text{N}_4)\text{NO}_3]_n$ (**1**)

The crystal structure of the ligand is shown in Fig.1. The ligand crystallized in the orthorhombic

Table 1 Crystallographic data for ligand **L**¹ and **1**

Compound	L ¹	1
Empirical formula	$\text{C}_{18}\text{H}_{20}\text{N}_4$	$\text{C}_{18}\text{H}_{20}\text{AgN}_5\text{O}_3$
Formula weight	292.38	462.26
Temperature / K	293(2)	293(2)
Crystal system	Orthorhombic	Monoclinic
Space group	$Pbcn$	$C2$
a / nm	1.910 2(5)	1.376 08(9)
b / nm	0.927 4(2)	0.899 38(5)
c / nm	0.950 8(3)	1.648 34(10)
β / (°)	90.00	107.169(3)
Volume / nm^3	1.684 4(8)	1.949 1(2)
Z	4	4
D_c / ($\text{g}\cdot\text{cm}^{-3}$)	1.153	1.575
θ range / (°)	$2.13 \leq \theta \leq 24.99$	$1.29 \leq \theta \leq 26.00$
Absorption coefficient / mm^{-1}	0.071	1.062
$F(000)$	624	936
Crystal size / mm	0.24×0.21×0.19	0.23×0.21×0.19
Reflections collected	13 438	8 301
Independent reflections	1 482	3 291
Observed reflections ($I>2\sigma(I)$)	1 076	3 096
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Number of parameters	100	244
Goodness-of-fit on F^2	1.061	1.162
Final R^a indices ($I>2\sigma(I)$)	$R_1=0.043$ 7, $wR_2=0.114$ 7	$R_1=0.024$ 9, $wR_2=0.062$ 1
R^a indices (all data)	$R_1=0.065$ 1, $wR_2=0.124$ 4	$R_1=0.028$ 6, $wR_2=0.078$ 2
$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}}$ / ($\text{e}\cdot\text{nm}^{-3}$)	101, -124	101, -124

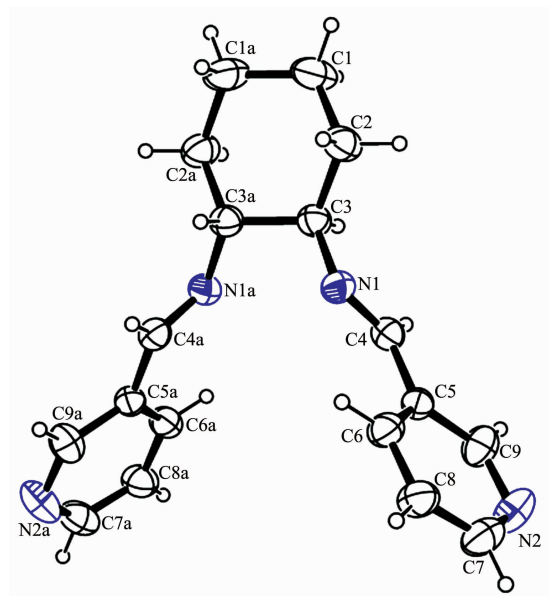
^a for **L**¹: $\omega=1/[\sigma^2(F_o^2)+(0.060\ 9P)^2+0.161\ 6P]$, $P=(F_o^2+2F_c^2)/3$; for **1**: $\omega=1/[\sigma^2(F_o^2)+(0.041\ 9P)^2+0.000\ 0P]$, $P=[F_o^2+2F_c^2]/3$

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

Ligands					
C1-C1	0.151 7(4)	C4-N1	0.125 9(2)	C6-C8	0.137 3(2)
C1-C2	0.152 5(3)	C4-C5	0.146 8(2)	C7-N2	0.132 1(3)
C2-C3	0.152 3(2)	C5-C6	0.137 8(2)	C7-C8	0.136 2(3)
C3-N1	0.146 4(2)	C5-C9	0.138 1(2)	N2-C9	0.133 7(2)
C3-C3	0.152 7(3)				
C1-C1-C2	110.25(15)	N1-C4-C5	122.18(15)	N2-C7-C8	123.98(18)
C3-C2-C1	111.96(15)	C6-C5-C9	116.70(16)	C7-N2-C9	116.20(16)
N1-C3-C2	109.18(13)	C6-C5-C4	122.19(15)	C4-N1-C3	118.57(14)
N1-C3-C3	108.95(12)	C9-C5-C4	121.08(16)	C7-C8-C6	118.89(18)
C2-C3-C3	110.71(12)	C8-C6-C5	119.44(16)	N2-C9-C5	124.78(18)
Complex 1					
N1-Ag1	0.231 0(3)	N2-Ag1 ⁱ	0.228 9(3)	N4-Ag1	0.249 6(4)
O1-Ag1	0.252 0(4)				
N2-Ag1-N1 ⁱ	140.92(13)	N2-Ag1-N4 ⁱ	92.84(12)	N1-Ag-O1	90.32(12)
N1-Ag1-N4	92.42(13)	N2-Ag1-O1	126.04(13)	N4-Ag1-O1	102.40(12)

Symmetry relations: ⁱ -1/2+x, -1/2+y, z.Table 3 C-H... π interactions in complex 1

X-H...Cg	Cg	d(H...Cg) / nm	d(X...Cg) / nm	\angle X...Cg / (°)
C9-H9B...Cg1 ⁱⁱ	Cg1 (N1/C1/C2/C3/C4/C5)	0.279 23	0.359 2	140.22
C14-H14...Cg1	Cg1 (N1/C1/C2/C3/C4/C5)	0.321 40	0.401 6	145.52
C18-H18A...Cg2 ⁱⁱⁱ	Cg2 (N4/C10/C11/C12/C12/C14)	0.254 56	0.342 4	150.64

Symmetry relations: ⁱⁱ -1/2+x, 1/2+y, z; ⁱⁱⁱ x, 1+y, z.system, space group *Pbcn*.

Thermal ellipsoid at 30% level

Fig.1 Molecular structure of ligand with atom numbering

The crystal structure of the complex is shown in Fig.2. Single-crystal X-ray diffraction analysis revealed that compound **1** crystallized in the monoclinic space group *C2*. The asymmetric unit of the title complex, $[\text{Ag}(\text{C}_{18}\text{H}_{20}\text{N}_4)\text{NO}_3]_n$ (**1**), was composed of two Ag(I) centers, two unique L¹ ligands, and two coordinated nitrate anions (Fig.3). Each silver ion had a distorted tetrahedral coordination environment, being bound to three nitrogen donors from the three adjacent molecules of L¹ and one oxygen atom from nitrate anion; the nitrate ligands were monodentate. The Ag1-N1, Ag1-N2, and Ag1-N4 bond lengths were 0.231 0(3), 0.228 9(3), and 0.249 6(4) nm, and the Ag1-O1 bond length was 0.252 0(4) nm. The N-Ag-N angles were in the range 84(12)°~140.92(13)°, and the O-Ag-N angles ranged from 90.32(12)° to 126.04(13)°. In compound **1**, the L¹ ligands coordinated to the Ag(I) ions in two different ways. First, L¹ was bound to Ag(I) centers in

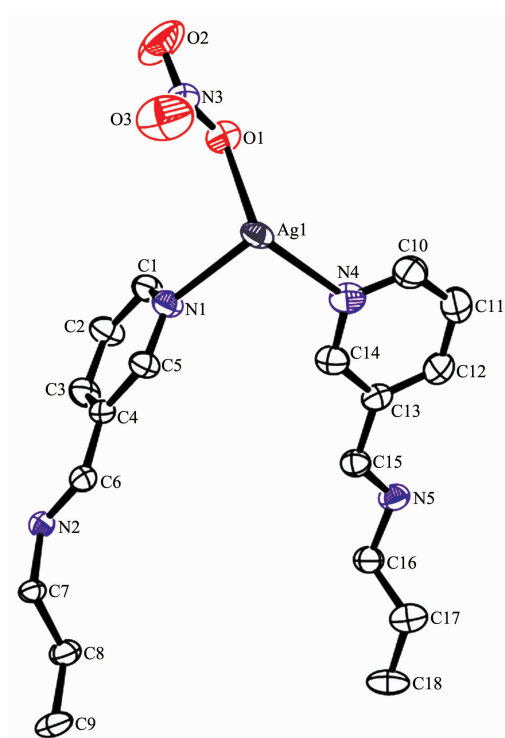


Fig.2 Thermal ellipsoid plot at 30% level of the asymmetric units of the complex **1**

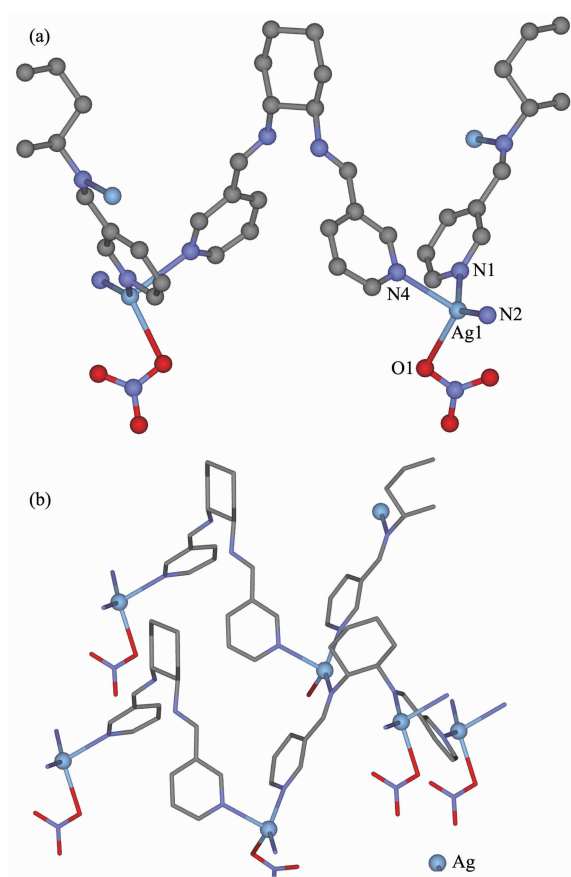


Fig.3 (a) Complex of Ag(I) ion coordination modes;
(b) Ligands with different coordination patterns

a bridging, bidentate mode through the terminal pyridyl N-donors only. Here, the inner imino N-atoms were oriented in different directions, with nearly gauche N-C-C-N torsion angles equal to 64.84° . The distance between the two Ag(I) centers was 1.106 4 nm. The second binding mode for **L**¹ was coordination to Ag(I) ions in a tetradentate fashion through both terminal pyridyl N-donors and both inner imino N-atoms. The latter were oriented in different directions, with the nearly gauche N-C-C-N torsion angles equal to 59.69° . The distance that the two nitrogen atoms on the pyridine ring coordinated Ag(I) ions was 1.197 9 nm. The chiral ligands resulted in a coordination configuration in which a bidentate pyridyl nitrogen atom was coordinated to Ag(I), which in turn was coordinated to a tetradentate pyridyl nitrogen. Alternation of this sequence ultimately generated the 1D chain structure helix (Fig.4) observed crystallographically. Furthermore, imino nitrogen atoms in the tetradentate ligands, which were located on the opposite sides of the ligand-bridged helix, coordinated different Ag(I) ions in other helices, such that the supramolecular assembly of complex **1** with bonds connected through a 3D porous network structure was

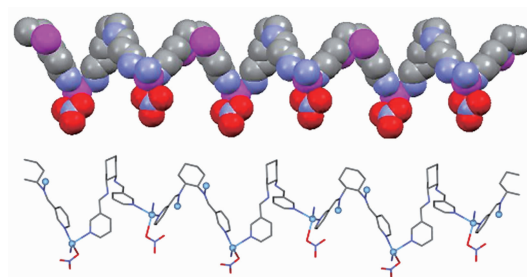


Fig.4 1D right-handed helical chain in the complex **1**

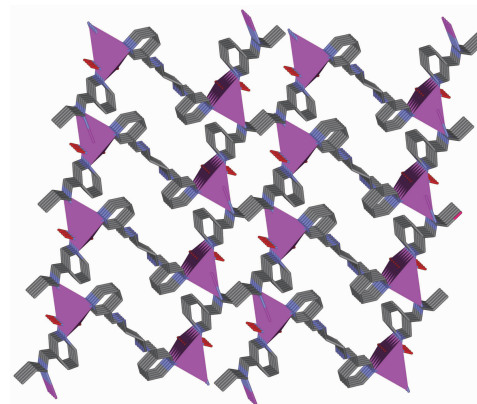


Fig.5 Part of the 3D network structure of the complex **1**

obtained (Fig.5). In complex **1**, C9–H9B...Cg(1), C14–H14...Cg(1), and C18–H18A...Cg(2) existed. In a recent study, we investigated the interaction of L¹ with AgCF₃SO₃ and found that the product complex, {[Ag(L¹)₂](CF₃SO₃)·4H₂O}_n, every silver ion has a distorted tetrahedral coordination environment, being bound to four nitrogen donors from the four adjacent molecules of L¹, the Ag(I) centers are extended by L¹ ligands along two directions, resulting in a (4,4)-connected two-dimensional layer with a corrugated surface^[19]. In the complex, imine nitrogen atoms not involved in the coordination. This shows that different counter anions on the structure of the complexes have a great impact.

2.2 PXRD results

To examine the phase purity of the complexes, the PXRD patterns of title complex was obtained at room temperature. As shown in Fig.6, the peak positions of the simulated and experimental PXRD patterns were in agreement, demonstrating good phase purity for the complex. The dissimilarities in intensities may be due to the preferred orientation of the crystalline powder samples.

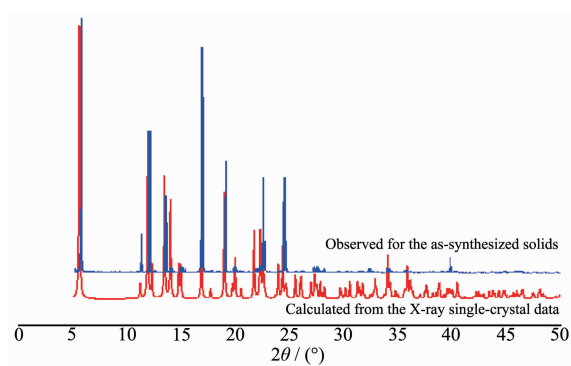


Fig.6 PXRD patterns of complex **1**

2.3 TG analysis

The thermal behaviors of **1** were studied by thermogravimetric analysis (TGA). The experiments were performed on samples consisting of numerous single crystals under N₂ atmosphere with a heating rate of 10 °C·min⁻¹, as shown in Fig.7. Complex **1** was stable to 210 °C, whereupon the framework of complex **1** began to collapse with a mass loss of 50.58% (Calcd. 49.87%).

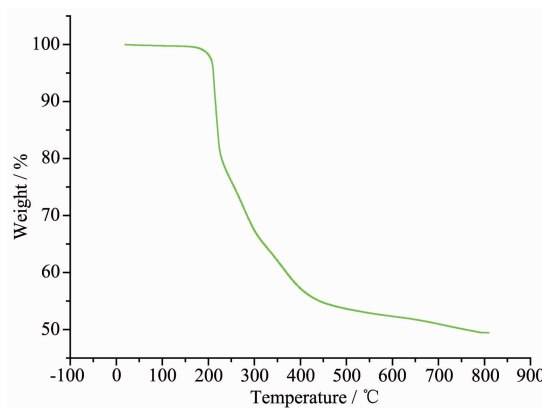


Fig.7 TGA curve for complex **1**

2.4 Photoluminescent properties of ligand and complex

The photoluminescencespectra of the ligand L¹ and complex **1** are shown in Fig.8. The ligand L¹ display photoluminescence with emission maxima at 504 nm (λ_{ex} =370 nm), respectively. It can be presumed that the peak originate from the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions^[22]. It can be observed that intense emissions occur at 579 nm (λ_{ex} =400 nm) for complex **1**, The emissions of complex **1** is probably attribute to the intraligand (IL) $\pi \rightarrow \pi^*$ transitions modified by metal coordination^[23]. The enhancement and slight red-shift of complex **1** compared to that of the ligand probably result from the fact that the coordination of Ag(I) ions increases the ligand conformational rigidity and thus reduces the loss of energy by thermal vibrational decay^[24-25].

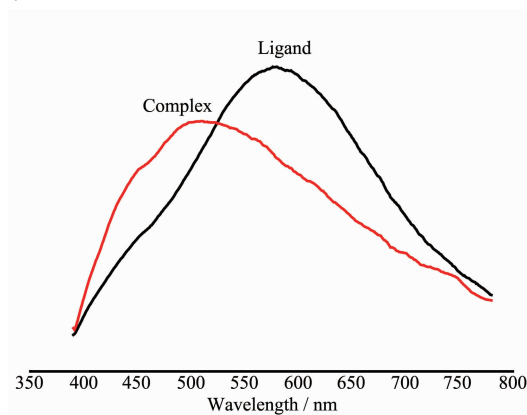


Fig.8 Photoluminescences of ligand and complex

3 Conclusions

This study demonstrates that the pyridyl-containing Schiff base ligands (L¹) is capable of

coordinating metal centers with both Npyridyl donors、both inner imino N-atoms and generate novel coordination polymers. At the same time, this study revealed that different counter anions in the structure of the complexes have a great impact.

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