

## 1, 3-双(2-(2,2-二氰乙烯基)苯氧基)-2-丙醇及其银(I) 配合物的合成、晶体结构及其荧光性质

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**摘要:** 用 1, 3-双(2-甲酰基苯氧基)-2-丙醇和丙二腈进行反应得到 1, 3-双(2-(2,2-二氰乙烯基)苯氧基)-2-丙醇配体 **L**, 然后将配体与  $\text{AgSbF}_6$  进行配位反应, 得到配合物  $[\text{AgLSbF}_6]_n \cdot n\text{CHCl}_3$  (**1**), 并用元素分析, FTIR 和 X-射线单晶衍射进行了表征。结果表明, 配体 **L** 属于单斜晶系, 空间群  $P2_1/n$ , 晶体学参数:  $a=0.990\ 2(11)\ \text{nm}$ ,  $b=2.181(2)\ \text{nm}$ ,  $c=1.012\ 2(11)\ \text{nm}$ ,  $\beta=109.374(10)^\circ$ ,  $V=2.062(4)\ \text{nm}^3$ ,  $Z=4$ ,  $D_c=1.277\ \text{g}\cdot\text{cm}^{-3}$ ,  $M_r=396.40$ ,  $\mu=0.087\ \text{mm}^{-1}$ ,  $F(000)=824$ ,  $R_1=0.064\ 2$ ,  $wR_2=0.117\ 4(I>2\sigma(I))$ 。配合物 **1** 属于单斜晶系, 空间群  $P2_1/n$ , 晶体学参数:  $a=1.270\ 57(11)\ \text{nm}$ ,  $b=1.456\ 44(13)\ \text{nm}$ ,  $c=1.669\ 85(14)\ \text{nm}$ ,  $\beta=105.643(3)^\circ$ ,  $V=2.975\ 6(4)\ \text{nm}^3$ ,  $Z=4$ ,  $D_c=1.918\ \text{g}\cdot\text{cm}^{-3}$ ,  $M_r=859.39$ ,  $\mu=1.907\ \text{mm}^{-1}$ ,  $F(000)=1\ 664$ ,  $R_1=0.0417$ ,  $wR_2=0.1\ 032(I>2\sigma(I))$ 。在配合物 **1** 中, 配体 **L** 表现为四齿配体分别与 4 个银(I)离子配位, 同时, 每一个银(I)离子与 4 个相邻配体配位形成 2D 层状结构。同时, 研究了配体和配合物的固体荧光性质。

**关键词:** 1, 3-双(2-(2,2-二氰乙烯基)苯氧基)-2-丙醇; 晶体结构; Ag(I)配合物; 荧光性质

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## Synthesis, Crystal Structures, and Fluorescent Properties of Ag(I) Complex Containing 1,3-Bis(2-(2,2-dicyanovinyl)phenoxy)-2-propanol Ligand

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**Abstract:** 1,3-bis (2-formylphenoxy)-2-propanol underwent an ammonium acetate-catalyzed condensation reaction with dicyanomethane to afford the ligand 1,3-bis(2-(2,2-dicyanovinyl)phenoxy)-2-propanol (**L**). Further, the ligand **L** was made to react with hexafluoroantimonate( $\text{AgSbF}_6$ ) which resulted in the formation of coordination polymer  $[\text{AgLSbF}_6]_n \cdot n\text{CHCl}_3$  (**1**). Complex **1** so-obtained was characterized by Fourier transform infrared spectroscopy, elemental analysis, and single crystal X-ray diffraction. The results of X-ray crystallographic analysis indicated that the ligand **L** crystallized in the monoclinic system, space group  $P2_1/n$ , with the following crystal cell parameters:  $a=0.990\ 2(11)\ \text{nm}$ ,  $b=2.181(2)\ \text{nm}$ ,  $c=1.012\ 2(11)\ \text{nm}$ ,  $\beta=109.374(10)^\circ$ ,  $V=2.062(4)\ \text{nm}^3$ ,  $Z=4$ ,  $D_c=1.277\ \text{g}\cdot\text{cm}^{-3}$ ,  $M_r=396.40$ ,  $\mu=0.087\ \text{mm}^{-1}$ ,  $F(000)=824$ ,  $R_1=0.064\ 2$ , and  $wR_2=0.1174$  (observed reflections with  $I>2\sigma(I)$ ). Complex **1** crystallized in the monoclinic system, space group  $P2_1/n$ , with the following crystallographic data:  $a=1.270\ 57(11)\ \text{nm}$ ,  $b=1.456\ 44(13)\ \text{nm}$ ,  $c=1.669\ 85(14)\ \text{nm}$ ,  $\beta=105.643(3)^\circ$ ,  $V=2.975\ 6(4)\ \text{nm}^3$ ,  $Z=4$ ,  $D_c=1.918\ \text{g}\cdot\text{cm}^{-3}$ ,  $M_r=859.39$ ,  $\mu=1.907\ \text{mm}^{-1}$ ,  $F(000)=1664$ ,  $R_1=0.041\ 7$ , and  $wR_2=0.103\ 2$  (observed reflections with  $I>2\sigma(I)$ ). In the crystal structure, each ligand **L** acted as a tetradentate ligand coordinating four Ag(I) centers, and each Ag

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(I) was connected to four ligands **L**, forming two-dimensional layered structure. Moreover, the fluorescent properties of ligand **L** and complex **1** were investigated in the solid state at room temperature. CCDC: 1008802, **L**; 1008804, **1**.

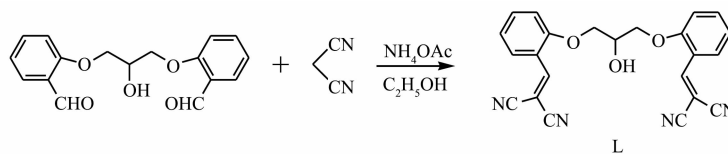
**Key words:** 3-bis(2-(2,2-dicyanovinyl)phenoxy)-2-propanol; crystal structure; Silver(I) Complex; Fluorescent property

## 0 Introduction

The assembly of coordination polymers (CPs), consisting of metal ions and organic polymers, with specific network topologies has attracted significant research interest in recent years owing to their tremendous potential applications as functional solid-state materials<sup>[1-4]</sup> in material science and engineering. However, the rational design and fabrication of CPs with specific structures and tunable physical properties is a challenging task. The diverse structures of such materials always depend on several factors, such as type of metal ion, template, metal-ligand ratio, pH value, counter anion, and number of coordination sites provided by organic ligands<sup>[5-6]</sup>. Silver(I)-based CPs (AgCPs) have attracted remarkable attention because of their distinct molecular structures. Moreover, they act as promising candidates for conductive, luminescent, and magnetic materials. Interestingly, Ag (I) exhibits strong preference toward coordination to nitrogen donor than to harder oxygen-containing ligands. Therefore, it is extremely important

to explore and rationalize the effect of different ligands on the topology of AgCPs.

An outstanding aspect of the AgCPs is that they possess unique luminescence features that have attracted significant interest of the researchers. Therefore, extensive research efforts have been devoted to the AgCPs. Great affinity of Ag ions leads to dynamic coordination range varying from two to six, even to seven and eight, showing strong tendency to display versatile coordination spheres, partly attributed to the  $d^{10}$  electronic configuration of Ag<sup>[7-10]</sup>. Moreover, there are numerous ligands with rational design and reasonable use to compose functional CPs with excellent structures and properties<sup>[11-12]</sup>. Based on the fact that flexible organic molecules adopt different conformations under different conditions<sup>[13-16]</sup>, in this study, interaction of the flexible ligand 1,3-bis(2-(2,2-dicyanovinyl)phenoxy)-2-propanol (**L**, Scheme 1) with Ag (I) was investigated. Herein, we describe the synthesis, crystal structure, and fluorescent properties of Ag(I) complex coordinated to flexible, ether-bridging, tetradentate ligand **L**.



Scheme 1 Schematic representation of the formation of ligand **L**

## 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  $\text{cm}^{-1}$  range).  $^1\text{H}$  NMR spectra were recorded on a JEOLCX 500MHz spectrometer using DMSO solution at room temperature. Thermogravimetric measurements were carried out in a nitrogen stream using a Netzsch STA449C apparatus with a heating rate of  $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . X-Ray powder diffraction (XRPD) was carried out on a RIGAKU DMAX2500 apparatus.

### 1.2 Synthesis of the ligand **L**

1,3-bis(2-formylphenoxy)-2-propanol<sup>[17]</sup> (0.3 g, 1.0 mmol), excess of malononitrile ( $\text{CH}_2(\text{CN})_2$ ), and ammonium acetate ( $\text{NH}_4\text{OAc}$ ) were mixed thoroughly in a mortar. The product so obtained was purified by column chromatography on silica gel using dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) as an eluent to afford yellow crystalline solid (0.26 g, 65 %).  $^1\text{H}$  NMR (500MHz,  $\text{DMSO}-d_6$ ): 8.623 (s, 2H,  $\text{C}=\text{CH}$ ), 8.029~7.133 (m, 8H,  $\text{C}_6\text{H}_4$ ), 5.732 (s, 1H,  $\text{CHOH}$ ), 4.337 (s, 1H, OH), 4.284~4.153 (m, 4H,  $\text{OCH}_2\text{CH}_2\text{O}$ ). Anal. Calcd. (%) for  $\text{C}_{23}\text{H}_{16}\text{N}_4\text{O}_3$ : C, 69.69; H, 4.07; N, 14.13; Found(%): C, 69.62; H, 4.00; N, 14.17. IR (KBr,  $\text{cm}^{-1}$ ): 3 524 (m), 3 046 (w), 2 924(w), 2 226(m), 1 581(s), 1 482(m), 1 453(m), 1 363(w), 1 307 (w), 1 257(s), 1 163(w), 1 116(w), 1 045(w), 1 006(w), 947 (w), 812(w), 759(w), 616(w), 490(w).

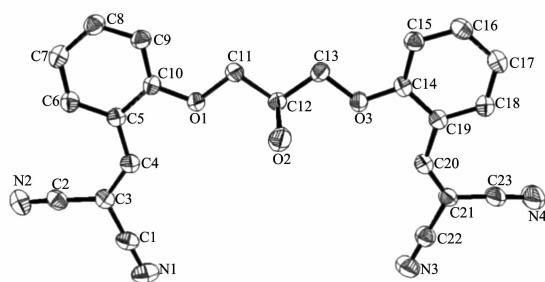
### 1.3 Synthesis of $[\text{AgLSbF}_6]_n \cdot n\text{CHCl}_3$ (**1**)

Hexafluoroantimonate (V) ( $\text{AgSbF}_6$ , 0.17 g, 0.1 mmol) in chloroform ( $\text{CHCl}_3$ , 20 mL) was added dropwise with stirring to ligand **L** (0.2 g, 0.5 mmol) in ethanol (20 mL) and stirring was continued at room temperature for several days. Slow evaporation of this solution yielded yellow block crystals suitable for X-ray analysis. The precipitate so formed was collected by filtration, and

dried at room temperature to give **1** (0.26 g, 60%). Anal. Calcd. (%) for  $\text{AgC}_{24}\text{H}_{17}\text{Cl}_3\text{N}_4\text{O}_3\text{SbF}_6$ : C, 33.54; H, 1.99; N, 6.52. Found(%): C, 33.60; H, 1.92; N, 6.60. IR (KBr,  $\text{cm}^{-1}$ ): 3 444(s), 2 928(w), 2 228(m), 1 726(w), 1 587(s), 1 483(m), 1 454(m), 1 362(w), 1 310(w), 1 253(s), 1 166 (w), 1115(w), 1 005(w), 809(w), 757(s), 615(s).

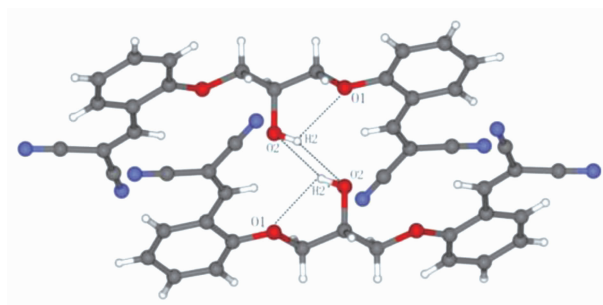
### 1.4 X-ray crystallographic study

X-ray diffraction data were collected at room temperature with graphite monochromated  $\text{Mo K}\alpha$  radiation on Bruker Smart Apex single crystal diffractometer by using a  $\varphi$ - $\omega$  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<sup>[18]</sup>. 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  $U_{\text{iso}}(\text{H})=(1.2\sim1.5) U_{\text{eq}}(\text{C})$ . The ORTEP-3<sup>[19]</sup> drawing of the molecules is shown in Fig.1 and Fig.3. 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 and Table 4.



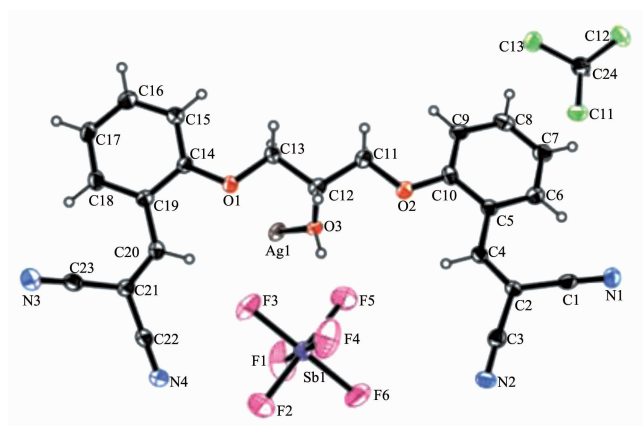
Probability of ellipsoid is 30%

Fig.1 Molecular structure of ligand **L**



Symmetry code: 1-x, y, 1-z

Fig.2 Dimers formed by the ligand through  $\text{O2-H2}\cdots\text{H2-O2}$  hydrogen bonds

Fig.3 Thermal ellipsoid plot at 25% level of the asymmetric units of the complex **1****Table 1** Crystallographic data for ligand **L** and **1**

Compound	<b>L</b>	<b>1</b>
Empirical formula	C <sub>23</sub> H <sub>16</sub> N <sub>4</sub> O <sub>3</sub>	C <sub>34</sub> H <sub>17</sub> AgCl <sub>3</sub> F <sub>6</sub> N <sub>4</sub> O <sub>3</sub> Sb
Formula weight	396.40	859.39
Temperature / K	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> / nm	0.990 2(11)	1.270 57(11)
<i>b</i> / nm	2.181(2)	1.456 44(13)
<i>c</i> / nm	1.012 2(11)	1.669 85(14)
$\beta$ / (°)	109.374(10)	105.643(3)
Volume / nm <sup>3</sup>	2.062(4)	2.975 6(4)
<i>Z</i>	4	4
<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	1.277	1.918
$\theta$ range / (°)	2.33~25.00	1.80~26.00
Absorption coefficient / mm <sup>-1</sup>	0.087	1.907
<i>F</i> (000)	824	1 664
Crystal size / mm	0.23×0.21×0.21	0.25×0.22×0.21
Reflections collected	12 702	26 362
Independent reflections	3 562	5 730
Observed reflections [ <i>I</i> >2σ( <i>I</i> )]	1 963	4 238
Refinement method	Full-matrix least squares on <i>F</i> <sup>2</sup>	Full-matrix least squares on <i>F</i> <sup>2</sup>
Number of parameters	272	380
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.918	1.090
Final <i>R</i> indices [ <i>I</i> >2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> <sup>a</sup> =0.064 2, <i>wR</i> <sub>2</sub> =0.169 8	<i>R</i> <sub>1</sub> <sup>b</sup> =0.041 7, <i>wR</i> <sub>2</sub> =0.096 4
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.117 4, <i>wR</i> <sub>2</sub> =0.198 2	<i>R</i> <sub>1</sub> =0.063 4, <i>wR</i> <sub>2</sub> =0.103 2
(Δρ) <sub>max</sub> , (Δρ) <sub>min</sub> / (e·nm <sup>-3</sup> )	489, -488	712, -730

<sup>a</sup> *w*=1/[σ<sup>2</sup>*F*<sub>o</sub><sup>2</sup>+(0.124 5*P*)<sup>2</sup>+0.000 0*P*], where *P*=(*F*<sub>o</sub><sup>2</sup>+2*F*<sub>c</sub><sup>2</sup>)/3; <sup>b</sup> *w*=1/[σ<sup>2</sup>*F*<sub>o</sub><sup>2</sup>+ (0.043 7*P*)<sup>2</sup>+1.776 7*P*], where *P*=(*F*<sub>o</sub><sup>2</sup>+2*F*<sub>c</sub><sup>2</sup>)/3

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

L					
C1-N1	0.115 2(4)	C4-C5	0.146 1(4)	C8-C9	0.138 6(4)
C1-C3	0.146 0(5)	C5-C6	0.140 8(4)	C9-C10	0.138 5(4)
C2-N2	0.115 1(4)	C5-C10	0.143 4(4)	C10-O1	0.137 9(3)
C2-C3	0.145 2(5)	C6-C7	0.138 3(4)	C11-O1	0.144 7(4)
C3-C4	0.136 5(4)	C7-C8	0.139 8(5)	C11-C12	0.151 8(4)
C12-O2	0.141 8(4)	C14-C15	0.140 3(4)	C17-C18	0.138 0(4)
C12-C13	0.151 4(4)	C14-C19	0.143 0(4)	C18-C19	0.140 7(4)
C13-O3	0.145 6(4)	C15-C16	0.138 9(4)	C19-C20	0.145 9(4)
C14-O3	0.137 5(3)	C16-C17	0.140 1(4)	C20-C21	0.136 0(4)
C21-C23	0.143 2(5)	C21-C22	0.145 6(5)	C22-N3	0.115 1(4)
C23-N4	0.115 3(5)				
N1-C1-C3	179.2(4)	N2-C2-C3	175.7(4)	C4-C3-C2	128.2(3)
C4-C3-C1	119.0(3)	C2-C3-C1	112.8(3)	C10-C5-C4	117.9(3)
C3-C4-C5	130.6(3)	C6-C5-C10	117.7(3)	C6-C5-C4	124.4(3)
C7-C6-C5	120.9(3)	C6-C7-C8	120.2(3)	C9-C8-C7	120.5(3)
C10-C9-C8	119.9(3)	O1-C10-C9	123.9(3)	O1-C10-C5	115.3(2)
C9-C10-C5	120.7(3)	O1-C11-C12	106.3(2)	O2-C12-C13	108.0(2)
O2-C12-C1	111.0(2)	C13-C12-C11	109.8(2)	O3-C13-C12	106.8(2)
O3-C14-C15	123.8(3)	O3-C14-C19	115.3(3)	C15-C14-C19	120.8(3)
C16-C15-C14	119.1(3)	C15-C16-C17	121.4(3)	C18-C17-C16	119.2(3)
C17-C18-C19	122.1(3)	C18-C19-C14	117.4(3)	C18-C19-C20	124.7(3)
C14-C19-C20	117.8(3)	C21-C20-C19	130.5(3)	C20-C21-C23	126.4(3)
C20-C21-C22	119.3(3)	C23-C21-C22	114.3(3)	N3-C22-C21	179.8(5)
N4-C23-C21	178.1(4)	C10-O1-C11	118.7(2)	C14-O3-C13	118.9(2)
Complex 1					
Ag1-N1 <sup>i</sup>	0.240 5(4)	N2-Ag1-N4 <sup>iii</sup>	138.57(15)	N2-Ag1-O3	109.46(12)
Ag1-N2 <sup>ii</sup>	0.217 0(4)	N2-Ag1-N1 <sup>i</sup>	124.40(14)	N4-Ag1-O3 <sup>iii</sup>	94.13(15)
Ag1-N4 <sup>iii</sup>	0.223 1(5)	N4-Ag1-N1 <sup>iii</sup>	87.14(15)	N1-Ag1-O3 <sup>i</sup>	91.32(12)
Ag1-O3	0.246 7(3)				

Symmetry code: <sup>i</sup> 1-x, 1+y, 2-z; <sup>ii</sup> 0.5+x, 0.5-y, 0.5+z; <sup>iii</sup> 1-x, -y, 1-z

**Table 3** Hydrogen Bond Lengths (nm) and Bond Angles (°) for ligand L

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠ DHA
O(2)-H(2)···O(1)	0.082 00	0.255 71	0.283 7(4)	101.52
O(2)-H(2)···O(2) <sup>iv</sup>	0.082 00	0.231 12	0.291 6(5)	131.08

Symmetry code: <sup>iv</sup> 1-x, y, 1-z

**Table 4** C-H... $\pi$  interactions in complex 1

X-H...Cg	Cg	d(H...Cg) / nm	d(X...Cg) / nm	∠ X-H...Cg / (°)
C4-H4...Cg1 <sup>v</sup>	Cg1(C5/C6/C7/C8/C9/C10)	0.315 45	0.334 0	93.33

Symmetry code: <sup>v</sup> 2-x, y, 1-z

CCDC:1008802, **L**; 1008804, **1**.

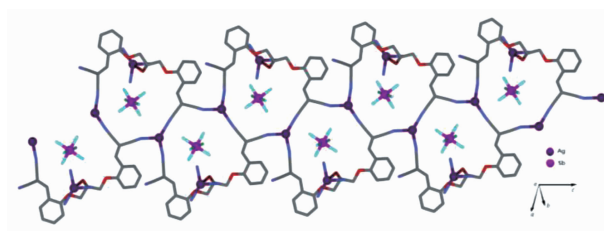
## 2 Results and discussion

### 2.1 Crystal structures of ligand **L** and complex **1**

The bond lengths and bond angles of ligand **L** are listed in Table 2, and its crystal structure is shown in Fig.1. The hydroxyl groups present in the flexible ligand are connected by the ether chain bridge. Fig.1 and values listed in Table 2 show that the two pairs of  $\text{C}(\text{CN})_2$  are located toward the end of the base in the same direction. However, the two benzene rings are not in a plane, and the dihedral angle between them is  $168.37^\circ$ . The ligand forms dimers through  $\text{O2-H2} \cdots \text{H2-O2}$  hydrogen bonds (Fig.2 and Table 3).

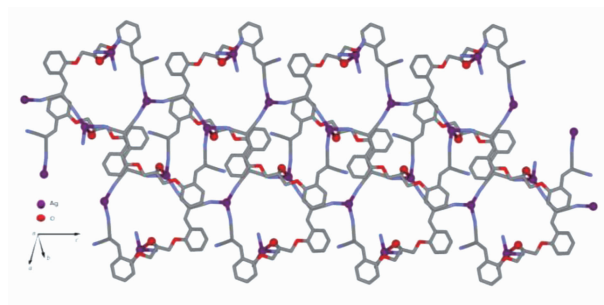
The crystal structure of the complex **1** is shown in Fig.3. Single-crystal XRD analysis reveals that compound **1** crystallizes in the monoclinic space group  $P2_1/n$ . The asymmetric unit is composed of a  $\text{Ag}(\text{I})$  center, a unique ligand **L**, an  $\text{SbF}_6^-$  anion, and  $\text{CHCl}_3$  solvent molecules (Fig.3). Each  $\text{Ag}(\text{I})$  ion is tetracoordinated in a distorted tetrahedron coordination environment to three N atoms and one O atom from four different ligands. The  $\text{Ag1-N1}$ ,  $\text{Ag1-N2}$ , and  $\text{Ag1-N4}$  bond lengths are 0.240 5(4), 0.217 0(4), and

0.223 1(5) nm, respectively. The  $\text{Ag1-O3}$  bond length is 0.246 7(3) nm, N-Ag-N bond angles are in the range of  $87.14(15)^\circ \sim 138.57(15)^\circ$ , and N-Ag-O bond angles are in the range of  $91.32(12)^\circ \sim 109.46(12)^\circ$ . The ligands act as a  $\mu_4$ -bridge connecting four  $\text{Ag}(\text{I})$  ions, with three nitrogen atoms of the three cyano groups, respectively and one oxygen atom of hydroxyl group. The two cyano nitrogen atoms at one end of ligand **L** coordinate with two  $\text{Ag}(\text{I})$  ions independently. In contrast, only one of the two cyano nitrogen atoms at the other end coordinates with a  $\text{Ag}(\text{I})$  ion; the uncoordinated nitrogen atom undergoes weak interaction with the molecules of solvent  $\text{CHCl}_3$ . The two adjacent cyano nitrogen atoms at the two ends of ligand **L** and the two cyano nitrogen atoms at one end of another ligand **L** coordinate with two  $\text{Ag}(\text{I})$  ions simultaneously and thus, form a 24-member macrocycle. Such 24-member macrocycles alternately extend to either side and form a one-dimensional (1D) ribbon structure (Fig.4), in which the hydroxyl oxygen atoms of ligand **L** coordinate individually to  $\text{Ag}(\text{I})$  ion, bridging the 1D ribbon structures into the CPs consisting of two-dimensional (2D) mesh structure. In this 2D mesh structure (Fig.5),  $\text{C-H} \cdots \pi$  interactions



$\text{CHCl}_3$  molecules have been omitted for clarity

Fig.4 1D ribbon structure in the complex **1**



Hydrogen atoms,  $\text{SbF}_6^-$  anions, and  $\text{CHCl}_3$  molecules have been omitted for clarity

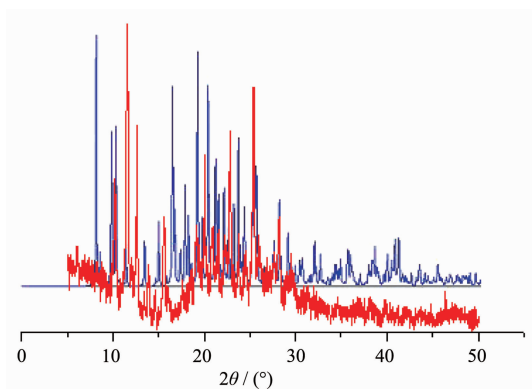
Fig.5 View of 2D coordination layer structure in the complex **1**



exist between the hydrogen on C4 (H4) and ring Cg1, with an C4-H4...Cg (1) angle of 93.33°, a H4...Cg(1) distance of 0.315 45 nm, where Cg (1) is the centroid of the phenyl ring formed by atoms C5, C6, C7, C8, C9, and C10 (Table 4). The ligands act as four-connecting nodes; the Ag atoms act as four-connecting links.

## 2.2 PXRD analysis

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.



Upside: calculated from the X-ray single-crystal data; Underside: observed for the as-synthesized solids

Fig.6 PXRD patterns of complex 1

## 2.3 Photoluminescent properties of Ligand L and Complex 1

The photoluminescence spectra of the ligand **L** and complex **1** are shown in Fig.7. The ligand **L** exhibited photoluminescence with emission maxima at 474 nm ( $\lambda_{\text{ex}}=337$  nm). Presumably, the peak originated from the  $\pi^* \rightarrow n$  or  $\pi^* \rightarrow \pi$  transitions<sup>[20]</sup>. Intense emissions occurred at 525 nm ( $\lambda_{\text{ex}}=338$  nm) for complex **1**, which was attributed to the intraligand  $\pi \rightarrow \pi^*$  transitions modified by metal coordination<sup>[21]</sup>. The enhancement and slight red-shift of complex **1** compared to that of the ligand **L** probably resulted from the fact that the coordination of Ag(I) ions increased the conformational rigidity of the ligand and; thus, reduced the loss of energy by thermal vibrational decay<sup>[22-23]</sup>.

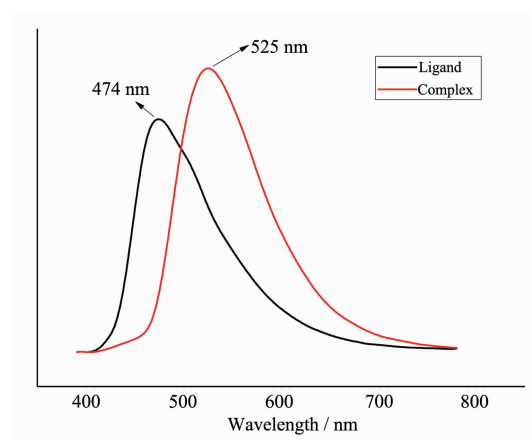


Fig.7 Fluorescence spectra of the ligand and complex

## References:

- [1] CHENG Xiao-Ning(程小宁), ZHANG Wei-Xiong(张伟雄), XUE Wei(薛玮), et al. *Chinese. J. Inorg. Chem.* (无机化学学报), **2014**,**30**(1):142-148
- [2] Chen X Y , Huang R B, Zheng L S, et al. *Inorg. Chem.*, **2014**,**53**:5246-5252
- [3] Manus L M, Holbrook R J, Atesin T A, et al. *Inorg. Chem.*, **2013**,**52**:1069-1076
- [4] ZHANG Chun-Li(张春丽), QIN Ling(覃玲), ZHENG He-Gen(郑和根). *Chinese J. Inorg. Chem.* (无机化学学报), **2014**,**30** (4):800-804
- [5] Halper S R, Do L, Stork J R, et al. *J. Am. Chem. Soc.*, **2006**,**128**:15255-15268
- [6] Fan L M, Zhang X T, Sun Z, et al. *Cryst. Growth Des.*, **2013**,**13**,2462-2475
- [7] Zhou X, Lu Y, Zhai L L, et al. *RSC Adv.*, **2013**,**3**:1732-1734
- [8] ZHANG Qi-Long(张奇龙), ZHANG Yun-Qian(张云黔), ZHU Bi-Xue(朱必学). *Chinese J. Inorg. Chem.* (无机化学学报), **2011**,**27**(11):2191-2194
- [9] Omary M A, Elbjeirami O, Gamage C S, et al. *Inorg. Chem.*, **2009**,**48**:1784-1786
- [10] Hu X H, Liang Y, Li C, et al. *Dalton Trans.*, **2014**,**43**:2458-2464
- [11] Zhang Q L, Zhu B X, Zhang Y Q, et al. *Cryst. Growth Des.*, **2011**,**11**:5688-5695
- [12] Liu S J, Huang Y B, Lin Z J, et al. *RSC Adv.*, **2013**,**3**:9279-9287
- [13] Ma L F, Wang L Y, Du M, et al. *Inorg. Chem.*, **2010**,**49**: 365-367
- [14] Yang Y, Yang J, Du P, et al. *CrystEngComm*, **2014**,**16**: 6380-6390
- [15] Wang X L, Sui F F, Lin H Y, et al. *CrystEngComm*, **2013**,**15**:7274-7284

- [16]Dong Y B, Jiang Y Y, Li J, et al. *J. Am. Chem. Soc.*, **2007**,**129**:4520-4521
- [17]ZHAO Bin(赵斌), XIA Min(夏闽), WANG Xue-Zhi(王学之), et al. *Chinese J. Chemical Reagents* (化学试剂), **2000**,**22**: 224-227
- [18]Sheldrick G M. *Acta Crystallogr.*, **1990**,A46,467
- [19]Sheldrick G M. *SHELX-97*, University of Göttingen, Germany, **1997**.
- [20]Zhang X T, Fan L M, Sun Z, et al. *CrystEngComm*, **2013**,**15**:4910-4916
- [21]Liu F J, Sun D, Hao H J, et al. *Cryst. Growth Des.*, **2012**,**12**:354-361
- [22]Zheng S L, Zhang J P, Chen X M, et al. *J. Solid State Chem.*, **2003**,**172**:45-52
- [23]Yi L, Zhu L N, Ding B, et al. *Inorg. Chem. Commun.*, **2003**,**6**:1209-1212