

两个基于 β -二酮席夫碱配体构筑的银配合物的合成、晶体结构和荧光性质

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摘要: 在常温的条件下, 分别将 2 个双 β -二酮席夫碱配体与银盐进行配位反应得到 2 个银配合物, $\{[\text{Ag}(\text{L}_1)](\text{SbF}_6)\}_n$ (**1**) 和 $[\text{Ag}_2(\text{L}_2)_2](\text{BF}_4)_2$ (**2**) ($\text{L}_1=1,3\text{-bis(4-methylamino-pentan-2-one)phenyl}$, $\text{L}_2=1,3\text{-bis(3-methylamino-1-phenyl-butan-1-one)phenyl}$), 并通过元素分析、红外光谱、粉末 X 射线衍射分析、单晶 X 射线衍射等对其结构进行了表征。结构分析表明, 在配合物 **1** 中, 银离子与配体 L_1 中的 2 个碳原子和 2 个氧原子配位, 形成一维链状结构, 而配合物 **2** 中银离子与 L_2 配体中的 2 个氧原子和 2 个碳原子配位, 最终得到双核二聚体结构。化合物 **1** 和 **2** 都通过阴离子与结构单元之间的 $\text{C-H}\cdots\text{F}$ 作用, 最终形成三维超分子结构。此外, 我们还研究了化合物 **1**, **2** 以及配体的荧光性质。

关键词: 银配合物; 晶体结构; 荧光性质; 氢键作用

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Syntheses, Structures and Luminescent Properties of Two Silver Coordination Complexes Based on Bis(β -diketone) Schiff Bases

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Abstract: Two silver complexes, namely $\{[\text{Ag}(\text{L}_1)](\text{SbF}_6)\}_n$ (**1**) and $[\text{Ag}_2(\text{L}_2)_2](\text{BF}_4)_2$ (**2**), have been obtained by the reaction of silver salts with two different bis(β -diketone) Schiff bases ($\text{L}_1=1,3\text{-bis(4-methylamino-pentan-2-one)phenyl}$, and $\text{L}_2=1,3\text{-bis(3-methylamino-1-phenyl-butan-1-one)phenyl}$) in the ethanol solution. In complex **1**, the center Ag(I) ions connected with two C atoms and two O atoms to form a one-dimensional chain, while the complex **2** is a binuclear silver complex. Expanded by the weak $\text{C-H}\cdots\text{F}$ interactions between the units and anions and $\text{C-H}\cdots\text{O}$ hydrogen bonds between the adjacent units, three-dimensional supramolecular structures of two complexes formed finally. Moreover, the luminescent properties of two silver complexes and their based organic ligands have been investigated. CCDC: 1469231, **1**; 1469232, **2**.

Keywords: silver complex; crystal structure; fluorescent property; hydrogen bonds

0 Introduction

As an outstanding representative of inorganic-organic hybrid materials, the coordination complexes have drawn much attention in last two decades for

their diverse structures as well as tunable applications^[1-5]. The acetylacetone Schiff bases, which holding semi-enclosed structure, generally contain carbonyl groups and secondary nitramine groups together, can act as the hydrogen bonds donors and acceptors in the

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assembly of coordination complexes^[6-8]. Owing to their strong coordination ability and multiple coordination modes, the acetylacetonate Schiff bases have been widely used in the assembly of coordination complexes, which show potential applications in the field of gas storage and separation, heterogeneous catalysis, magnetism, luminescence, and so on^[9-10].

Inspired by the above-mentioned points, we were interested in the syntheses and properties of bis(β -diketone) Schiff bases coordination complexes and reported two novel silver coordination complexes, $\{[\text{Ag}(\text{L}_1)](\text{SbF}_6)\}_n$ (**1**) and $[\text{Ag}_2(\text{L}_2)_2](\text{BF}_4)_2$ (**2**) (L_1 =1,3-bis(4-methylamino-pentan-2-one)phenyl, L_2 =1,3-bis(3-methylamino-1-phenyl-butan-1-one)phenyl). In complex **1**, the center Ag(I) ions connected with two C atoms and two O atoms to form a one-dimensional chain, while the complex **2** is a binuclear silver complex. Moreover, the luminescence investigation shows that complexes **1** and **2** emitted green and blue fluorescence, respectively.

1 Experimental

1.1 Materials and methods

All chemicals were commercially obtained without further purification. IR spectra were measured on a Nicolet 740 FTIR Spectrometer at the range of 400~4 000 cm^{-1} . Elemental analyses were carried out on a CE instruments EA 1110 elemental analyzer. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Powder X-ray diffraction (PXRD) analyses were performed on an X-ray diffractometer (D/max 2500 PC, Rigaku) with Cu $K\alpha$ radiation ($\lambda=0.154\ 06\ \text{nm}$).

1.2 Synthesis

1.2.1 Synthesis of $\{[\text{Ag}(\text{L}_1)](\text{SbF}_6)\}_n$ (**1**)

AgSbF_6 (34.4 mg, 0.1 mmol) in ethanol (20 mL) was added dropwise with stirring to L_1 (30.4 mg, 0.1 mmol) in ethanol (20 mL) and the mixture was stirred at room temperature for several days. Slow evaporation of this solution yielded colorless block crystals that proved suitable for X-ray analysis. The precipitate that formed was collected by filtration, and dried at room temperature to give **1** in 48% yield based on Ag.

Anal. Calcd. for $\text{C}_{18}\text{H}_{24}\text{AgF}_6\text{N}_2\text{O}_2\text{Sb}$ (%): C, 33.57; H, 3.76; N, 4.35. Found (%): C, 33.31; H, 3.58; N, 4.41. IR (KBr pellet, cm^{-1}): 3 438 (s), 3 149(m), 1 617(vs), 1 519(s), 1 401(s), 1 303(m), 1 169(w), 1 074(s), 808 (m), 592(m), 472(m).

1.2.2 Synthesis of $[\text{Ag}_2(\text{L}_2)_2](\text{BF}_4)_2$ (**2**)

The synthesis of **2** is similar to **1** using AgBF_4 (19.4 mg, 0.1 mmol) and L_2 (42.8 mg, 0.1 mmol) instead of AgSbF_6 and L_1 . Colorless block. Yield: 54% yield based on Ag. Anal. Calcd. for $\text{C}_{56}\text{H}_{56}\text{Ag}_2\text{B}_2\text{F}_8\text{N}_4\text{O}_4$ (%): C, 54.31; H, 4.56; N, 4.52. Found (%): C, 54.37; H, 4.61; N, 4.56. IR (KBr pellet, cm^{-1}): 3 440 (s), 3 129 (m), 1 587(vs), 1 544(m), 1 436(m), 1 393(s), 1 319 (m), 1 223(w), 1 061(vs), 1 008(m), 857(w), 782(m), 707(m), 569(w), 523(w).

1.3 X-ray crystallography

The single-crystal X-ray diffraction was performed on a Bruker Smart Apex II CCD diffractometer. Intensities of reflections were measured using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 296 (2) K with the data collection θ ranging from 1.67° to 26° for **1**, and at 293(2) K with the data collection θ ranging from 1.73° to 25.01° for **2**, respectively. The structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL^[11]. Anisotropic thermal factors were assigned to all the non-hydrogen atoms. H atoms attached to C were placed geometrically and allowed to ride during subsequent refinement with an isotropic displacement parameter fixed at 1.2 times U_{eq} of the parent atoms. H atoms bonded to O or N atoms were first located in difference Fourier maps and then placed in the calculated sites and included in the refinement. Crystallographic data parameters for structural analyses are summarized in Table 1. Selected bond lengths and angles for complex **1** and **2** are listed in Table 2 and Table 3, respectively.

CCDC: 1469231, **1**; 1469232, **2**.

2 Results and discussion

2.1 Crystal structure of $\{[\text{Ag}(\text{L}_1)](\text{SbF}_6)\}_n$ (**1**)

Complex **1** crystallizes in the triclinic space group $P\bar{1}$, and its asymmetric unit contains one

Table 1 Crystal structure parameters of complexes **1** and **2**

Complex	1	2
Empirical formula	C ₁₈ H ₂₄ AgF ₆ N ₂ O ₂ Sb	C ₃₆ H ₅₆ Ag ₂ B ₂ F ₈ N ₄ O ₄
Formula weight	644.01	1 238.41
Crystal size / mm	0.23×0.21×0.20	0.27×0.25×0.23
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
<i>a</i> / nm	0.907 81(5)	1.228 89(13)
<i>b</i> / nm	0.999 69(6)	1.761 53(18)
<i>c</i> / nm	1.326 46(7)	1.254 88(13)
α / (°)	102.553(2)	90
β / (°)	108.236(2)	107.073(4)
γ / (°)	92.496(2)	90
<i>V</i> / nm ³	1.107 90(11)	2.596 8(5)
<i>Z</i>	2	2
<i>D_c</i> / (g·cm ⁻³)	1.931	1.584
<i>F</i> (000)	628	1 256
μ (Mo <i>K</i> α) / mm ⁻¹	2.169	0.834
Index ranges (<i>h</i> , <i>k</i> , <i>l</i>)	-11~10, -12~12, -15~16	-14~14, -20~20, -14~14
θ range for data collection / (°)	1.67~26	1.73~25.01
Reflections collected, unique	12 476, 4 217	27 501, 4 577
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Goodness-of-fit on <i>F</i> ²	1.148	1.024
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2 σ (<i>I</i>)]	0.048 9, 0.141 9	0.029 6, 0.076 3
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.058 9, 0.161 0	0.037 1, 0.081 3
<i>R</i> _{int}	0.038 7	0.038 5

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

C(10)-Ag(1)	0.234 1(6)	C(15)-Ag(1)	0.236 7(1)	Ag(1)-O(1) ⁱ	0.237 1(4)
Ag(1)-O(2) ⁱⁱ	0.274 4(9)				
C(10)-Ag(1)-C(15)	149.2(2)	C(10)-Ag(1)-O(1) ⁱ	112.0(2)	C(15)-Ag(1)-O(1) ⁱ	98.4(2)
C(10)-Ag(1)-O(2) ⁱⁱ	95.02(4)	C(15)-Ag(1)-O(2) ⁱⁱ	79.36(8)	O(1) ⁱ -Ag(1)-O(2) ⁱⁱ	109.37(6)

Symmetry codes: ⁱ -*x*, -*y*+1, -*z*+2; ⁱⁱ -*x*, -*y*+2, -*z*+2.**Table 3** Selected bond lengths (nm) and bond angles (°) for **2**

Ag(1)-C(21)	0.228 4(3)	Ag(1)-C(8) ⁱ	0.230 2(2)	Ag(1)-O(1)	0.236 70(18)
C(21)-Ag(1)-O(1)	114.65(8)	C(21)-Ag(1)-C(8) ⁱ	142.28(9)	C(8) ⁱ -Ag(1)-O(1)	101.97(7)

Symmetry codes: ⁱ -*x*+1, -*y*+2, -*z*+1.

crystallographically independent Ag(I) ion, one L₁ ligand, and one SbF₆⁻ anion. As shown in Fig.1, the Ag(I) ion is four-coordinated by two oxygen atoms (O1ⁱⁱ and O2ⁱ), and two carbon atoms (C10 and C15) from three different L₁ ligands. The central Ag(I) ion located in a distorted AgC₂O₂ tetrahedral coordination

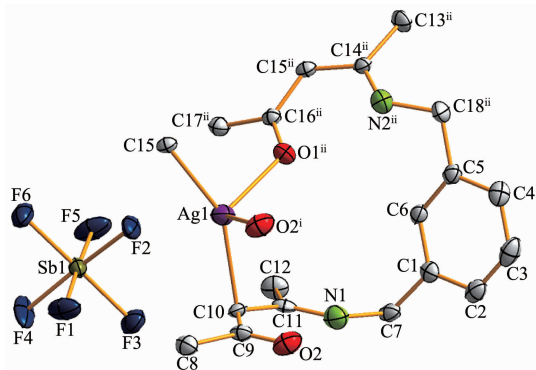
geometry, with the $\tau_4=0.70(\tau_4=[360^\circ-(\alpha+\beta)]/141^\circ)$, in which α and β are the two largest bond angles in the four-coordinate complex^[12]. Besides, the Ag-C bond lengths are 0.234 0(9) and 0.236 7(1) nm, while the Ag-O distances are 0.237 1(4) and 0.274 4(9) nm (Table 2). Except the weak Ag1-O2ⁱⁱ interactions,

Table 4 Hydrogen bond geometry of complex **1**

D-H...A	$d(\text{D}\cdots\text{H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle \text{D-H}\cdots\text{A} / (^\circ)$
C(13)-H(13B)-F(4) ⁱⁱⁱ	0.096	0.247	0.330 1(13)	145
C(17)-H(17A)-F(2) ^{iv}	0.096	0.235	0.328 3(11)	163
C(18)-H(18B)-F(6)	0.097	0.244	0.322 0(11)	137

Symmetry codes: ⁱⁱⁱ $x+1, y, z$; ^{iv} $-x+2, -y+1, -z$.

other bond lengths are in the normal ranges of Ag-O bonds in silver complexes^[13]. In the complex **1**, two



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

Fig.1 Asymmetric unit of complex **1** with 30% probability level

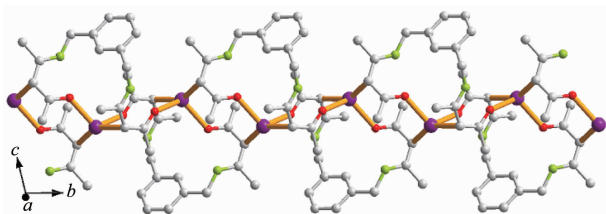
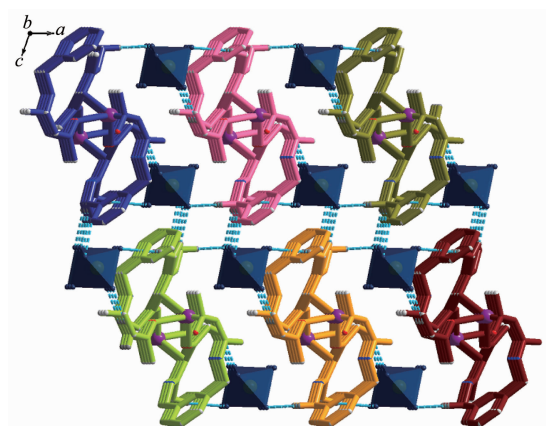


Fig.2 One-dimensional polymeric chain structure of complex **1**



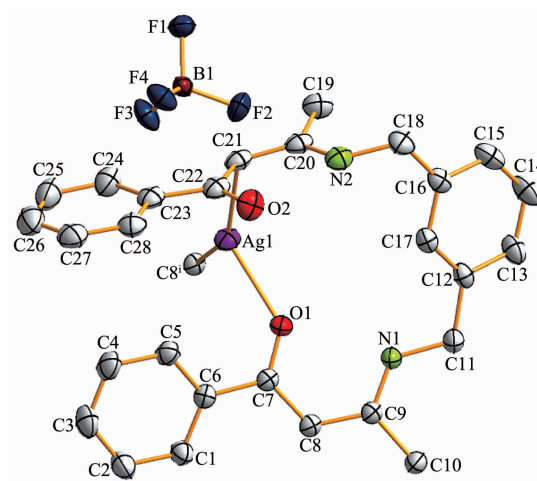
Hydrogen atoms not involved in hydrogen bonds are omitted for clarity

Fig.3 Three-dimensional supramolecular framework of complex **1**

acetylacetonate units of the L₁ ligand bridge three Ag(I) centres through O_{acetylacetonate} and C_{acetylacetonate}, extending in the direction of a axis, leaving a one-dimensional polymeric chain finally, with the nearest Ag...Ag distances being 0.527 7(6) and 0.565 3(2) nm (Fig.2). The one-dimensional polymeric chains interacted with the SbF₆⁻ anions through C-H...F hydrogen bonds (Table 4), finally gave a three-dimensional supramolecular network (Fig.3).

2.2 Crystal structure of [Ag₂(L₂)₂](BF₄)₂ (**2**)

In complex **2**, the steric effects of phenyl group in L₂ ligand make it impossible to form a similar 1D polymeric chain structure like **1**. Complex **2** crystallizes in the monoclinic space group *P*2₁/*c*. There are one crystallographically independent silver ion, one L₂ ligand, and one BF₄⁻ anion in the asymmetric unit of **2** (Fig.4). The central Ag(I) ion is three-coordinated by one oxygen atom (O1), and two carbon atoms (C21 and C8') from two different L₂ ligands. And the Ag-C bond lengths are 0.228 3(7) and 0.230 1(6) nm, the Ag-O distance is 0.236 7(0) nm, respectively (Table 3).



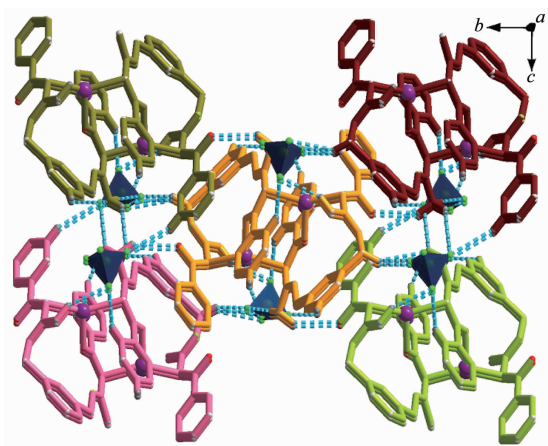
Hydrogen atoms are omitted for clarity; Symmetry codes: ⁱ $-x+1, -y+2, -z+1$

Fig.4 Molecular structure of complex **2** with 30% probability level

Table 5 Hydrogen-bond geometry of complex **2**

D-H \cdots A	$d(\text{D}\cdots\text{H})$ / nm	$d(\text{H}\cdots\text{A})$ / nm	$d(\text{D}\cdots\text{A})$ / nm	$\angle \text{D-H}\cdots\text{A}$ / ($^\circ$)
C(10)-H(10B)-F(3) ⁱ	0.096	0.254	0.329 9(4)	137
C(10)-H(10B)-F(4) ⁱ	0.096	0.243	0.337 8(4)	170
C(3)-H(3)-F(1) ⁱⁱ	0.093	0.254	0.343 0(4)	161
C(10)-H(10C)-O(2) ⁱⁱⁱ	0.096	0.257	0.337 9(4)	141
C(18)-H(18A)-F(4) ⁱⁱⁱ	0.097	0.251	0.331 3(4)	140
C(19)-H(19B)-F(2)	0.096	0.250	0.338 6(4)	153

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



Hydrogen atoms not involved in hydrogen bonds are omitted for clarity

Fig.5 Three-dimensional supramolecular framework of complex **2**

The units interacted with the adjacent ones and the BF_4^- anions through the C-H \cdots F and C-H \cdots O hydrogen bond interactions (Table 5), and finally give a stable three-dimensional supramolecular architecture (Fig.5).

2.3 Powder X-ray diffraction

In order to check the phase purity of the complexes, the PXRD patterns of title complexes were determined at room temperature. As shown in Fig.6, the peak positions of the simulated and experimental PXRD patterns are in agreement with each other, demonstrating the good phase purity of the complexes. The dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples.

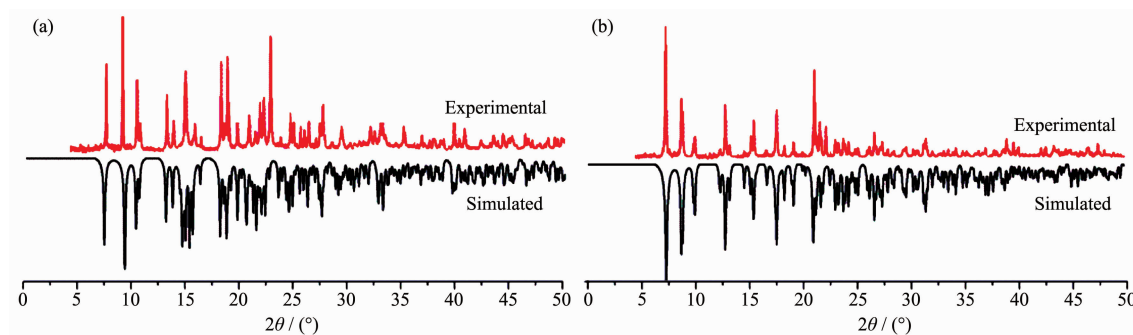


Fig.6 PXRD patterns of **1** (a) and **2** (b)

2.4 Photoluminescent properties

Many coordination complexes have been extensively studied due to their potential applications as luminescent materials^[14-16]. The solid-state luminescent properties of the complexes and the ligands were investigated at room temperature. The photoluminescence spectra of two organic ligands and complex **1** and **2** are shown in Fig.7. The L_1 and L_2 display photoluminescence with max emission peak at 518 nm

(λ_{ex} =488 nm), and 483 nm (λ_{ex} =398 nm), respectively. It can be presumed that the peak originate from the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions^[17-18]. It can be observed that intense emissions occur at 514 nm (λ_{ex} =486 nm) for **1**, and 481 nm (λ_{ex} =396 nm) for **2**, respectively. The resemblance of the emissions between the organic ligands and their based coordination complexes indicates that the emissions of the two complexes are probably attributed to the $\pi \rightarrow \pi^*$ transitions^[19].

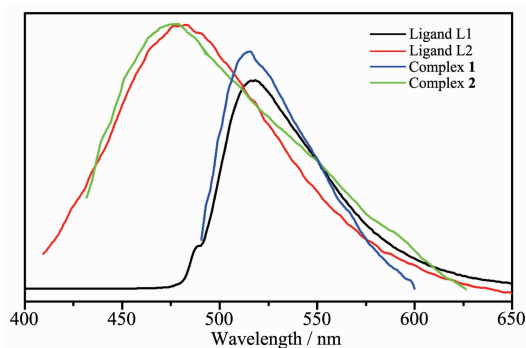


Fig.7 Solid-state emission spectra of **1** and **2**, and two free ligands at room temperature

3 Conclusions

In summary, two bis(β -diketone) Schiff bases silver coordination complexes, $\{[Ag(L_1)](SbF_6)\}_n$ (**1**), and $[Ag_2(L_2)_2](BF_4)_2$ (**2**) have been reported. In complex **1**, the center Ag(I) ions connected with two C atoms and two O atoms to form a one-dimensional chain, while the complex **2** is a binuclear silver complex. Expanded by the weak C-H \cdots F interactions between the units and anions and C-H \cdots O hydrogen bonds between the adjacent units, two complexes formed three-dimensional supramolecular framework finally. Moreover, the luminescence investigation shows that complexes **1** and **2** emitted green and blue fluorescence, respectively.

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