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两个含有杂环硫酮的银(I)配合物的合成、晶体结构和光谱特性

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摘要:合成了 2 个含有杂环硫酮的银(I)配合物,$[AgBr(PPh_3)_2(BTZT)]_2$ (**1**),$[Ag_2Cl_2(PPh_3)_2(BTZT)_2]CH_3OH$ (**2**)(PPh_3=三苯基膦;BTZT=苯并噻唑-2-硫酮),并通过红外光谱、X 射线单晶衍射、荧光光谱和核磁氢谱进行表征。2 个配合物是在含有 2-巯基苯并噻唑(MBT)的甲醇与二氯甲烷混合溶液中,AgX(X=Cl,Br)与三苯基膦反应得到的。MBT 配体由于存在化学活性基团(-N(H)-C(=S)-),所以可以转化为 BTZT 配体。结构分析显示有 2 个相同的分子结构存在于配合物 **1** 中,但是它们具有不同的键长和键角。配合物 **2** 是一个含有菱形的$[Ag_2Cl_2]$单元在中心的反转对称二聚体,2 个相邻$[AgCl(PPh_3)(BTZT)]$单元由 2 个氯原子桥连。

关键词:荧光;银;三苯基膦;2-巯基苯并噻唑;苯并噻唑-2-硫酮
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Syntheses, Crystal Structures and Spectroscopic Properties of Two Silver(I) Complexes with Heterocyclic Thione

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Abstract: Two silver(I) complexes with heterocyclic thione, $[AgBr(PPh_3)_2(BTZT)]_2$ (**1**) and $[Ag_2Cl_2(PPh_3)_2(BTZT)_2]\cdot CH_3OH$ (**2**) (PPh_3=triphenylphosphine; BTZT=benzothiazoline-2-thione) have been synthesized and characterized by IR, single-crystal X-ray diffraction, fluorescence spectrum and ^1H NMR spectroscopy. **1** and **2** are obtained by the reactions of AgX (X=Cl, Br) with PPh_3 in the presence of 2-mercaptobenzothiazole (MBT) in mixed solvent (CH_3OH/CH_2Cl_2). The MBT ligand possesses chemically active groups (-N=C(-SH)), so MBT ligand can transform into BTZT ligand. Structure analysis shows that there exist two same molecular structures in complex **1**, but they have different bond lengths and bond angles. Complex **2** consists of inversion symmetric dimers with a diamond-shaped Ag_2Cl_2 group at the center, and two adjacent $[AgCl(PPh_3)(BTZT)]$ units are bridged by two Cl atoms. CCDC: 1035930, **1**; 1043199, **2**.

Key words: fluorescence; silver; triphenylphosphine; 2-mercaptobenzothiazole; benzothiazoline-2-thione

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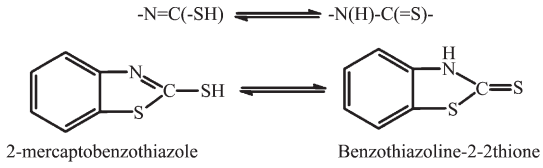
0 Introduction

In recent years, an increasing interest has been focused on the development of the silver(I) complexes because of their novel crystal structures[1-2] and potential applications as functional materials in catalysis[3-4], luminescence[5-6] and biochemistry[7]. Today, many efforts have been done to get a deeper research on the interrelationship between structures and photoluminescence properties of silver(I) complexes.

In previous literature, silver(I) complexes based on silver halides and organic P-donor ligands such as $[AgNO_2(PPh_3)_2]$[8] and $[Ag(PPh_3)_2(CH_3OH)]\cdot BF_4$[9] are reported. Many silver(I) complexes containing PPh_3 ligand have been drawn much attention, because they can act as functional materials[10-11]. 2-mercaptobenzothiazole (MBT) is a kind of heterocyclic NS ligand reported frequently because it possesses chemically active groups (-N=C (-SH)) (Scheme 1). It used not only as bridging ligand, for example, $[Ag_6(MBT)_6]$[12] and $[Cu_6(MBT)_6]$[13], but also as chelating ligand such as $[Cd_2(MBT)_4]_n$[14].



Scheme 1　Equilibrium between 2-mercaptobenzothiazole and benzothiazoline-2-thione

It is reported that different solvents can affect the structures of the products. The solvent CH_3OH is the simplest amphiphile which consists of hydrophobic ($-CH_3$) group and hydrophilic (-OH) group. This solvent can not only adjust the weak solubility of the reactant Ag(I) salts effectively but also form hydrogen bonds with the silver(I) halide.

We are interested in silver(I) complexes with phosphorus and heterocyclic NS ligand. Recently, we prepared two new complexes $[AgBr(PPh_3)_2(BTZT)]_2$ (**1**) (PPh_3=triphenylphosphine; BTZT=benzothiazoline-2-thione) and $[Ag_2Cl_2(PPh_3)_2(BTZT)_2]\cdot CH_3OH$ (**2**) which have not been reported before. The complexes **1** and **2** have been characterized by IR, single-crystal X-ray diffraction, fluorescence spectrum and ^{1}H NMR spectroscopy.

1 Experimental

1.1 Materials and measurements

All chemical reagents are commercially available and used without furthermore treatment. FT-IR spectra (KBr pellets) were measured on a Perkin-Elmer Infrared spectrometer. C, H and N elemental analysis were carried out on an Elementar Vario MICRO CUBE (Germany) elemental analyzer. Room-temperature fluorescence spectra were measured on F-4500 FL Spectrophotometer. ^{1}H NMR was recorded at room temperature with a Bruker DPX 600 spectrometer.

1.2 Synthesis of $[AgBr(PPh_3)_2(BTZT)]_2$

Complex **1** was prepared by reaction of 2-mercaptobenzothiazole (0.033 3 g, 0.2 mmol), triphenylphosphine (0.104 7 g, 0.4 mmol) and AgBr (0.037 2 g, 0.2 mmol) in a mixture of CH_3OH and CH_2Cl_2 (10 mL, 1∶1, *V*/*V*). The solution was stirred for 6 h at room temperature. After slow evaporation of the filtrate at ambient temperature for 6 days, colorless and transparent crystals of the title complex were obtained. Yield: 69%. Element analysis Calcd.(%) for $C_{43}H_{35}AgBrNP_2S_2$: C, 58.67; H, 3.98; N, 1.59. Found (%): C, 58.57; H, 4.16; N, 1.33. IR data (cm^{-1}, KBr pellets): 3 431w, 3 053w, 2 933w, 2 735w, 1 596w, 1 492m, 1 478m, 1 459w, 1 431s, 1 323m, 1 251w, 1 180w, 1 093 m, 1 031m, 743s, 694s, 664m, 606w, 513m, 422w. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ=13.76 (s, NH), 7.52~7.43(m, $CH_{benzene}$).

1.3 Synthesis of $[Ag_2Cl_2(PPh_3)_2(BTZT)_2]\cdot CH_3OH$

Complex **2** was prepared in a manner similar to that described for **1**, using 2-mercaptobenzothiazole (0.033 5 g, 0.2 mmol), triphenylphosphine (0.051 1 g, 0.2 mmol) and AgCl(0.029 3 g, 0.2 mmol). Yield: 48%. Element analysis Calcd.(%) for $C_{51}H_{44}Ag_2Cl_2N_2OP_2S_4$: C, 51.97; H, 3.74; N, 2.38; Found(%): C, 51.81; H, 3.71; N, 2.38. IR data (cm^{-1}, KBr pellets): 3 425w, 3 050w, 3 000w, 2 737w, 1 598w, 1 584w, 1 496m, 1 478 m, 1 458w, 1 433s, 1 328m, 1 253w, 1 093m, 1 029m, 744s, 694s, 605w, 512s, 422w. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ=7.52~7.42(m, $CH_{benzene}$), 3.47(s, CH_3),

1.24(s, OH).

1.4 Structure determination

Single crystals of the title complexes were mounted on a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromated Mo $K\alpha$ (λ= 0.071 073 nm) radiation. Semi-empirical absorption corrections were applied using SABABS program. All the structures were solved by direct methods using SHELXS program of the SHELXTL-97 package and refined with SHELXL-97[15]. Metal atom centers were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinements were performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were generated geometrically and refined with displacement parameters riding on the concerned atoms.

Crystallographic data and experimental details for structural analysis are summarized in Table 1, and selected bond lengths and angles of complexes **1**~**2** are summarized in Table 2. The hydrogen bonds of complexes **1**~**2** are observed in Table 3.

CCDC: 1035930, **1**; 1043199, **2**.

Table 1 Crystallographic data for complexes 1 and 2

	1	**2**
Formula	$C_{43}H_{35}AgBrNP_2S_2$	$C_{51}H_{44}Ag_2Cl_2N_2OP_2S_4$
Formula weight	879.56	1 177.70
T / K	293(2)	298(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Crystal size / mm	0.35×0.33×0.32	0.15×0.11×0.10
a / nm	1.478 37(16)	1.048 54(8)
b / nm	1.742 78(12)	1.439 28(9)
c / nm	1.821 88(14)	1.707 21(15)
α / (°)	103.396 0(10)	90.00
β / (°)	113.015(2)	98.685(2)
γ / (°)	102.798 0(10)	90.00
V / nm^3	3.939 3(6)	2.546 9(3)
Reflections collected / unique	28 893 / 13 888	12 648 / 4 506
Data / restraints / parameters	13 888 / 2 / 901	4 506 / 0 / 295
Reflections with $I>2\sigma(I)$	9 472	2 793
Z	4	2
μ / mm^{-1}	1.744	1.139
F(000)	1 776	1 188
Goodness-of-fit on F^2	1.067	1.076
R_{int}	0.034 5	0.043 3
R_1 ($I>2\sigma(I)$)[a]	0.041 2	0.034 4
wR_2 ($I>2\sigma(I)$)[b]	0.079 0	0.060 3
R_1 (all data)[a]	0.075 4	0.068 5
wR_2 (all data)[b]	0.095 7	0.065 4

[a] $R=\sum(||F_o|-|F_c||)/\sum|F_o|$; [b] $wR=[\sum w(|F_o|^2-|F_c|^2)^2/\sum w(F_o^2)]^{1/2}$

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

1					
Ag(1)-P(1)	0.247 84(11)	Ag(1)-S(1)	0.278 82(12)	Ag(2)-Br(2)	0.270 84(6)
Ag(1)-P(2)	0.249 52(11)	Ag(2)-P(3)	0.247 54(11)	Ag(2)-S(3)	0.273 33(12)
Ag(1)-Br(1)	0.269 87(6)	Ag(2)-P(4)	0.250 78(11)		

Continued Table 2

P(1)-Ag(1)-P(2)	121.49(3)	P(2)-Ag(1)-S(1)	97.82(4)	P(4)-Ag(2)-Br(2)	104.84(3)
P(1)-Ag(1)-Br(1)	114.56(3)	Br(1)-Ag(1)-S(1)	103.61(3)	P(3)-Ag(2)-S(3)	108.99(4)
P(2)-Ag(1)-Br(1)	109.30(3)	P(3)-Ag(2)-P(4)	120.39(3)	P(4)-Ag(2)-S(3)	99.23(4)
P(1)-Ag(1)-S(1)	107.09(4)	P(3)-Ag(2)-Br(2)	117.48(3)	Br(2)-Ag(2)-S(3)	103.15(3)
			2		
Ag(1)-P(1)	0.243 24(10)	Ag(1)-S(2)	0.251 87(11)	Cl(1)-Ag(1)	0.274 42(10)
Ag(1)-Cl(1)	0.264 82(10)				
P(1)-Ag(1)-S(2)	120.61(4)	S(2)-Ag(1)-Cl(1)	111.03(4)	P(1)-Ag(1)-Cl(1)	104.77(3)
S(2)-Ag(1)-Cl(1)	107.66(4)	P(1)-Ag(1)-Cl(1)	118.56(3)	Cl(1)-Ag(1)-Cl(1)	89.54(3)

Table 3　Hydrogen bond distances (nm) and bond angles (°) for complexes 1 and 2

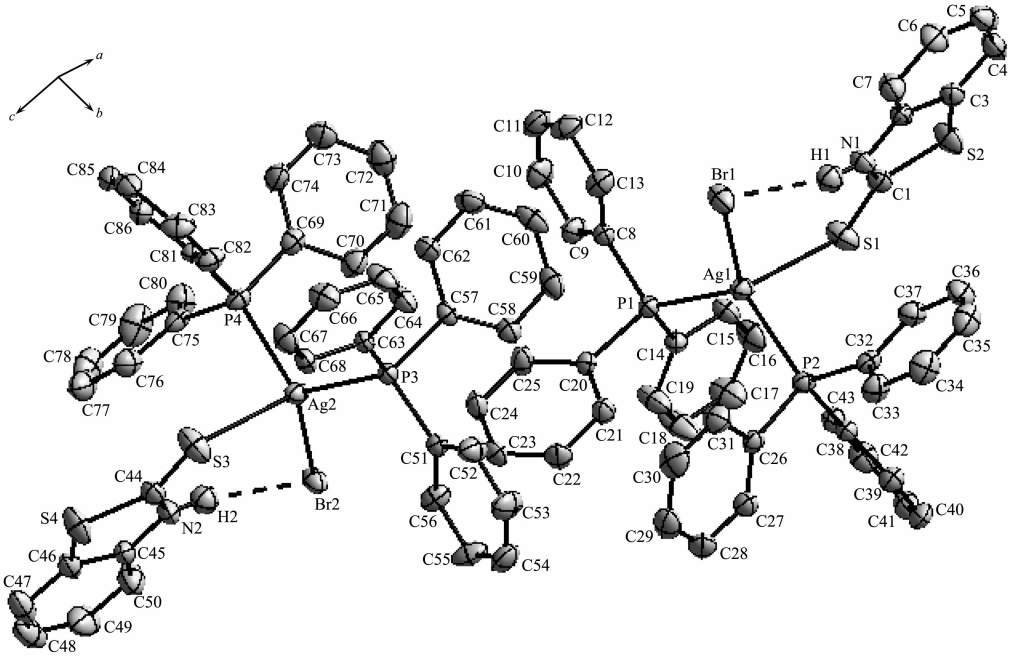
D–H···A	*d*(D-H)	*d*(H···A)	*d*(D···A)	∠DHA
1				
N1–H1···Br1	0.086 0	0.242 0	0.325 6	163.95
N2–H2···Br2	0.086 0	0.243 3	0.328 1	168.81
2				
N1–H1···Cl1	0.086 0	0.230 8	0.316 1	171.11
O1–H1Ai···Cl1	0.082 0	0.281 5	0.361 4	165.55

Symmetry code: ^{i} $-x-1/2, -y+3/2, z-1/2$

2　Results and discussion

2.1　Description of the crystal structure

The crystal structure of complex **1** contains two mononuclear [$AgBr(PPh_3)_2(BTZT)$] units, but they have different bond lengths and bond angles. Each Ag atom adopts four-coordinated mode, which is coordinated with two P atoms from two PPh_3, one Br atom and one S atom from benzothiazoline-2-thione ligand (BTZT) (Fig.1).



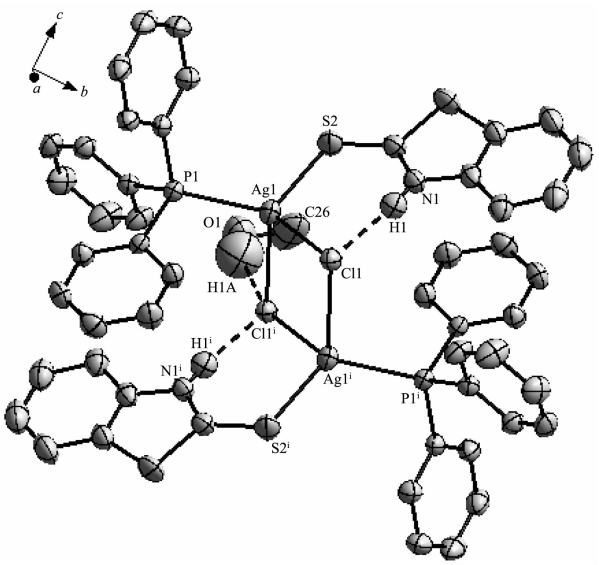
A part of hydrogen atoms are omitted for clarity; Thermal ellipsoids were drawn at the 30% probability level

Fig.1　Perspective view of complex **1**

The coordination pattern of complex **1** is consistent with that of the compound [AgI(PPh$_3$)$_2$(BTZT)][7]. The angles around one Ag atom are in the range of 97.82(4)°~121.49(3)°. The angles around the other Ag atom are in the range of 99.23(4)°~120.39(3)°. The coordination geometry around each Ag atom indicates a distorted tetrahedron. Geometrical distortion from ideal angles can be derived from the need to accommodate the bulky PPh$_3$ ligand and BTZT ligand. The Ag-Br bond distances (0.269 87(6) nm and 0.270 84(6) nm) are close to those found in: [AgBr(η^1-S-H$_2$stsc-NHEt)(PPh$_3$)$_2$][16] (0.272 06(3) nm) and [Ag$_2$(μ-Br)$_2$(κ^1-S-C$_3$H$_5$NS(N-Et))$_2$(PPh$_3$)$_2$] (0.272 47(6) nm)[17]. But the Ag-Br bond distances are shorter than that observed in [Ag$_2$(μ-Br)$_2$(κ^1-S-C$_3$H$_5$NS(N-Me))$_2$(PPh$_3$)$_2$] (0.279 70(5) nm)[17]. The Ag-P bond distance is similar with that in previous literature. The Ag-S bond distance in the complex **1** is longer than that observed in [Ag$_2$(μ-S-py-SH)$_2$(PPh$_3$)$_2$Br$_2$] (0.260 8(1) nm)[18].

Moreover, intramolecular N–H···Br hydrogen bonds are observed (N···Br 0.325 6 nm and 0.328 1 nm, N–H···Br 163.95° and 168.81°) in the complex **1**. The Br-Ag-S bond angles (103.61(3)°, 103.15(3)°) are smaller than the P-Ag-P bond angles (121.49(3)°, 120.39(3)°). The P-Ag-P bond angles (121.49(3)°, 120.39(3)°) in the complex **1** are smaller than that in [Ag(κ^1-S-L^{IV}-NH)$_2$(PPh$_3$)$_2$](OAc)·H$_2$O (123.846(19)°) (L^{IV}-NH=benz-imidazoline-2-thione)[19].

Single-crystal X-ray diffraction analysis reveals that complex **2** consists of inversion symmetric dimers with a diamond-shaped Ag$_2$Cl$_2$ group at the center. Each Ag is four-coordinated, surrounded by two Cl atoms, one P atom from one PPh$_3$ ligand and one S atom from one BTZT ligand (Fig.2). Two adjacent [AgCl(PPh$_3$)(BTZT)] units are bridged by two Cl atoms to form a dimer. The angles around Ag(I) ranging from 89.54(3)° to 120.61(4)° indicate that the geometry around Ag atom is distortedly tetrahedral. In the plane, the Ag···Ag distance of 0.382 88(5) nm is longer than the sum of van der Waals radii of two silver atoms (0.344 nm), indicating that there is no metal-metal bonding interaction in the complex **2**. The Ag-Cl bond distances (0.264 82(10) nm and 0.274 42(10) nm) are slightly longer than that in the complex [AgCl(η^1-S-H$_2$stsc-NHEt)(PPh$_3$)$_2$][16] (0.265 91(12) nm). The Ag-S bond distance (0.251 87(11) nm) is close to that found in [Ag(imdt)Cl]$_n$[20] (0.248 66(14) nm). The Ag-Cl-Ag bond angle (90.46(3)°) is greater than that in the complex [Ag$_2$(μ-Cl)$_2$(η^1-S-Haptsc)$_2$(PPh$_3$)$_2$][21] (78.01(2)°). The sum of the internal angles of the four-member ring [-Ag-Cl-Ag-Cl-] in the Ag$_2$Cl$_2$ core are 360°, demonstrating that the ring is a parallelogram.



A part of hydrogen atoms are omitted for clarity; Thermal ellipsoids drawn at the 30% probability level; Symmetry code: ^{i} $-x-1/2, -y+3/2, z-1/2$

Fig.2 Perspective view of complex **2**

Moreover, intramolecular N–H ··· Cl hydrogen bonds are observed (N···Cl 0.316 1 nm, N–H···Cl 171.11°) in the complex **2**, and the hydrogen bond type is consistent with that of complex **1**. In addition, the hydrogen bond O1–H1A···Cl1 is formed between O1-H1A group of the free methanol molecule and Cl1 atom of the [AgCl(PPh$_3$)(BTZT)] units. (O···Cl 0.2815 nm, O–H···Cl 165.55°).

2.2 Infrared spectroscopy and ^{1}H NMR spectroscopy

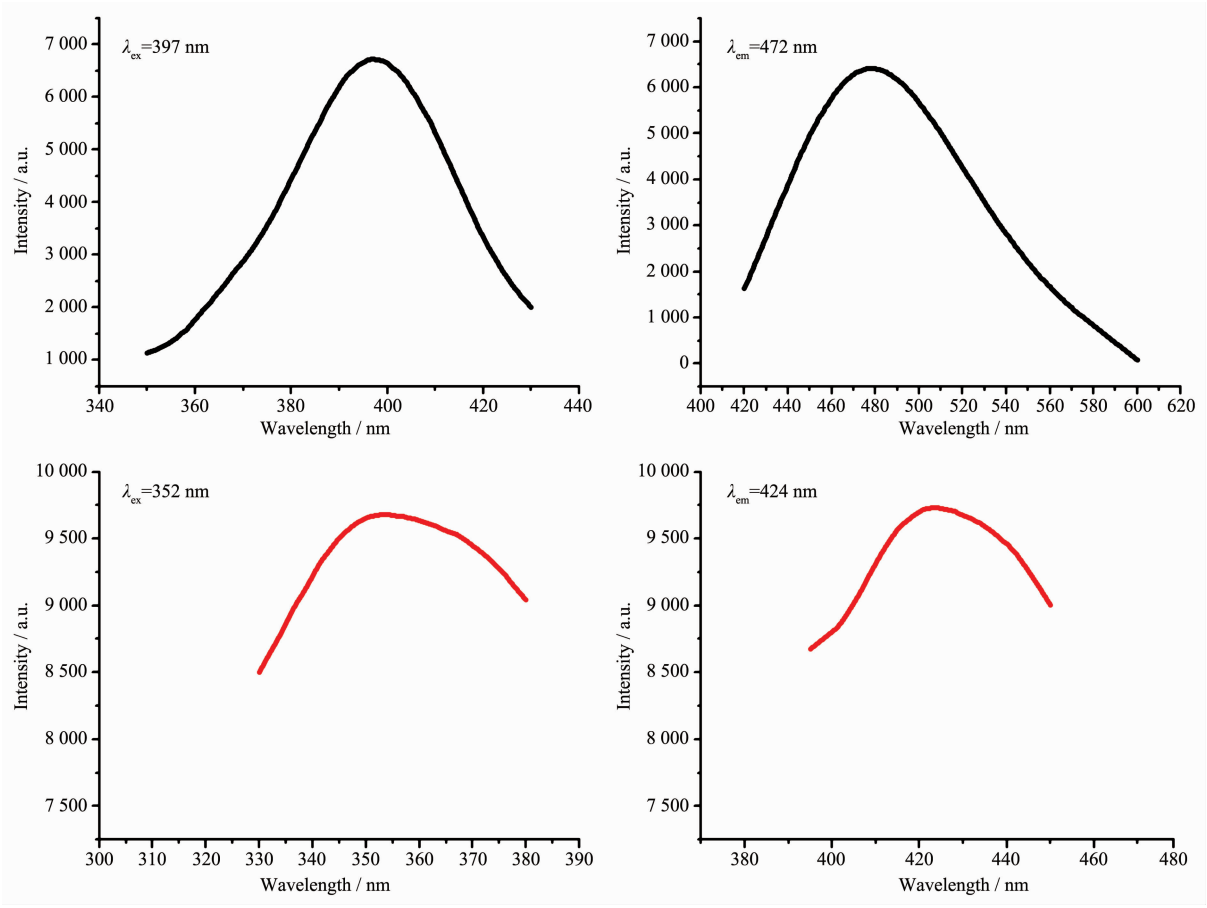
The infrared spectra of complexes **1** and **2** show the absorption around 1 459~1 492 cm^{-1} due to C-C stretch vibration of the phenyl rings, and the middle absorption around 3 053 cm^{-1} is caused by C-H vibration of the phenyl rings. The C-H out-of-plane bending vibrations of the phenyl rings are found around 744 and

694 cm^{-1}. The absorption of the N-H stretch vibration is at 3 431 cm^{-1}. C=N bond vibration is found in 1 431 cm^{-1} and C=S bond vibration is found at 1 251 cm^{-1}.

The ^1H NMR spectra of complexes **1** and **2** and benzothiazoline-2-thione (BTZT) ligand have been measured at room temperature in $CDCl_3$. The ^1H NMR spectra of **1** and **2** exist a broad multiple signal between 7.52 and 7.43, which should be the signal of aromatic protons (PPh_3 or BTZT). Meanwhile in the complex **1**, there exists a signal at 13.76, which is attributed to the N-H signal of benzothiazoline-2-thione. In ^1H NMR spectra of benzothiazoline-2-thione ligand, N-H signal of benzothiazoline-2-thione is found at 11.44.

2.3 Fluorescence spectrum

The solid-state fluorescence emission spectra of the MBT ligand and complexes **1** and **2** are measured at room temperature. The emission and excitation spectra of complexes **1** and **2** is displayed in Fig.3. When excited at 397 nm, complex **1** displays a fluorescence emission peak at 472 nm. When excited at 352 nm, a fluorescence emission peak of complex **2** is found at 424 nm. The emission peak of PPh_3 is at 402 nm (λ_{ex}=372 nm)[22]. In the fluorescence emission spectra of MBT ligand, the emission peaks are found at 419 nm (λ_{ex}=342 nm). The red shift of emission peak of **1** and **2** is derived from ligand-centered π-π* transition.



Top: complex **1**; Bottom: complex **2**

Fig.3　Solid-state excitation and emission spectra of **1** and **2** at 298 K

3 Conclusions

In summary, two novel silver(I) halide complexes based on triphenylphosphine and benzothiazoline-2-thione were synthesized and characterized by IR, single-crystal X-ray diffraction, fluorescence spectrum and ^1H NMR spectroscopy. **1** is a mononuclear compound and **2** is a binuclear compound which is bridged by two Cl atoms. From the ^1H NMR spectra of complex **1**, we find that the complex can activate N-H

in benzothiazoline-2-thione ligand. The luminescent spectra show that these emissions all involve emissive state derived from ligand centered π-π^* transition. The research plays a role in designing and synthesizing new Ag(I) complexes of heterocyclic NS ligands.

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