

两个基于苯并噻唑-2-硫酮的银(I) 配合物的合成、晶体结构和光谱性质

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摘要: 合成了 2 个含有杂环硫酮的银(I)配合物, $[\text{AgCl}(\text{PPh}_3)_2(\text{BTZT})]_2$ (**1**), $[\text{Ag}(\text{PPh}_3)_2(\text{BTZT})_2](\text{NO}_3)\text{CH}_3\text{OH}$ (**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、荧光光谱和核磁共振氢谱进行表征和分析。杂环硫酮存在化学活性基团 $-\text{N}(\text{H})-\text{C}(=\text{S})-$, 在平衡中与其硫醇形式可以相互转化。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, AgCl 或 AgNO_3 与三苯基膦反应得到的。配合物 **1** 的每个不对称单元中包含 2 个相同的分子结构, 但是它们具有不同的键长和键角。配合物 **2** 是一个简单的单核杂配配合物, 它的主体结构通过氢键作用连接游离的 CH_3OH 和 NO_3^- 离子。配合物 **1** 和 **2** 发射峰的红移源于配体中的 $\pi-\pi^*$ 跃迁。

关键词: 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 Benzothiazoline-2-thione-Based Complexes for Silver(I)

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Abstract: Two silver(I) complexes with heterocyclic thione, $[\text{AgCl}(\text{PPh}_3)_2(\text{BTZT})]_2$ (**1**) and $[\text{Ag}(\text{PPh}_3)_2(\text{BTZT})_2](\text{NO}_3)\cdot\text{CH}_3\text{OH}$ (**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. Heterocyclic thiones possess chemically active groups $-\text{N}(\text{H})-\text{C}(=\text{S})-$ in equilibrium with its thiol form. **1** and **2** are obtained by the reactions of AgCl or AgNO_3 with PPh_3 in the presence of 2-mercaptobenzothiazole (MBT) in mixed solvent ($\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$). The complex **1** contains two same structures in each asymmetric unit, but there are different bond lengths and bond angles. Complex **2** is a simple mono-nuclear heteroleptic complex whose main structure links free CH_3OH and NO_3^- anion by hydrogen bonding interactions. The red-shift of emission peak of **1~2** is derived from ligand-centered $\pi-\pi^*$ transition. CCDC: 1059719, **1**; 1059720, **2**.

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

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0 Introduction

Current interest in the field of coordination chemistry stems from rapid developments in complexes' structural diversity^[1-2] and intriguing optical properties^[3-4]. Mono- and multinuclear complexes with closed-shell d^{10} metals have attracted considerable attention because of the potential applications in antibacterial agents^[5], nanomaterials^[6] and catalysis^[7].

Silver(I) complexes based on heterocyclic thione or thiolate are reported in the early 1990^[8]. Heterocyclic thiones have been drawn much attention due to possess chemically active groups -N(H)-C(=S)- in equilibrium with its thiol form^[9]. A kind of heterocyclic thiolate, 2-mercaptobenzothiazole (MBT), is bonded to metals in the unique fashion, such as $[\text{Ag}_6(\text{MBT})_6]$ ^[10], $[\text{Cu}_6(\text{MBT})_6]$ ^[11] and $[\text{Cd}_2(\text{MBT})_4]_n$ ^[12].

In previous literature, the similar complex $\{[\text{AgCl}(\text{TPP})_2(\text{MBZT})] \cdot (\text{MBZT}) \cdot 2(\text{toluene})\}$ is reported^[13]. Differently, we synthesize a complex whose each asymmetric unit contains two same structures in the mixed solution of CH_3OH and CH_2Cl_2 . The complex $[\text{Ag}(\text{PPh}_3)_2(\text{BTZT})_2](\text{NO}_3)$ is mentioned in 1998^[14], but the spectroscopic properties have not been researched. Maybe the single crystal of $[\text{Ag}(\text{PPh}_3)_2(\text{BTZT})_2](\text{NO}_3)$ is inexistent, so crystallographic data doesn't be acquired by single-crystal X-ray diffraction in previous literature.

We are interested in silver(I) complexes with phosphorus and heterocyclic NS ligand. We report our successful syntheses of two novel complexes, $[\text{AgCl}(\text{PPh}_3)_2(\text{BTZT})_2]$ (**1**) (PPh_3 =triphenylphosphine; BTZT=benzothiazoline-2-thione) and $[\text{Ag}(\text{PPh}_3)_2(\text{BTZT})_2](\text{NO}_3) \cdot \text{CH}_3\text{OH}$ (**2**). The complexes **1~2** have been characterized by IR, single-crystal X-ray diffraction, fluoresc-

ence spectrum and ^1H NMR spectroscopy. Last year, we prepared two new complexes $[\text{AgBr}(\text{PPh}_3)_2(\text{BTZT})_2]$ (**3**) and $[\text{Ag}_2\text{Cl}_2(\text{PPh}_3)_2(\text{BTZT})_2] \cdot \text{CH}_3\text{OH}$ (**4**). Different structures of **1~4** are formed due to different proportion of martials and different anions (Scheme 1).

1 Experimental

1.1 Materials and measurements

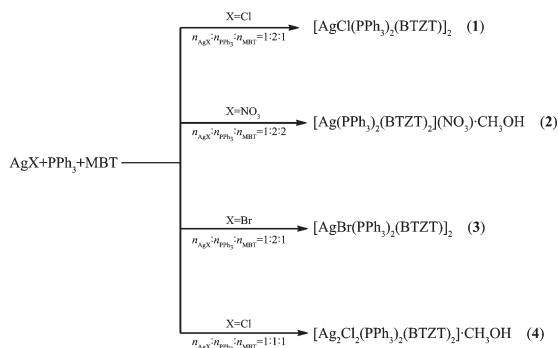
All chemical reagents are commercially available and used without furthermore treatment. FT-IR spectra (KBr pellets) were measured on a Perkin-Elmer Infrared spectrometer. C, H and N elemental analysis were carried out on an Elementar Vario MICRO CUBE (Germany) elemental analyzer. Room-temperature fluorescence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

1.2 Synthesis of $[\text{AgCl}(\text{PPh}_3)_2(\text{BTZT})_2]$ (**1**)

2-mercaptobenzothiazole (MBT, 0.2 mmol, 0.033 0 g) was added to a stirred solution of triphenylphosphine (0.4 mmol, 0.105 1 g) and AgCl (0.2 mmol, 0.028 9 g) in CH_3OH (5 mL) and CH_2Cl_2 (5 mL). After stirred for 6 h, the solution was filtered 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: 64%. Element analysis Calcd.(%) for $\text{C}_{43}\text{H}_{35}\text{AgClNP}_2\text{S}_2$: C, 61.79; H, 4.19; N, 1.68. Found (%): C, 62.26; H, 4.59; N, 1.47. IR data (KBr pellets, cm^{-1}): 3 429w, 3 054w, 3 000w, 2 936w, 1 596w, 1 497s, 1 478s, 1 460m, 1 432s, 1 324s, 1 292w, 1 254m, 1 093m, 1 077 m, 1 031s, 1 021m, 997m, 744s, 695s, 664m, 606w, 513s, 503s, 492s, 439w. ^1H NMR (600 MHz, CDCl_3 , 298 K): δ 7.51~7.23(m, $\text{CH}_{\text{benzene}}$), 7.26(s, $\text{CH}_{\text{CDCl}_3}$).

1.3 Synthesis of $[\text{Ag}(\text{PPh}_3)_2(\text{BTZT})_2](\text{NO}_3) \cdot \text{CH}_3\text{OH}$ (**2**)

2-mercaptobenzothiazole (MBT, 0.4 mmol, 0.066 9 g) was added to a stirred solution of triphenylphosphine (0.4 mmol, 0.104 9 g) and AgNO_3 (0.2 mmol, 0.034 0 g) in CH_3OH (5 mL) and CH_2Cl_2 (5 mL). After stirred for 6 h, the solution was filtered at room temperature. After slow evaporation of the filtrate at ambient temperature for 6 days, colorless and



Scheme 1 Routine of synthesis for complexes **1~4**

transparent crystals of the title complex were obtained. Yield: 47%. Element analysis Calcd.(%) for $C_{51}H_{44}AgN_3O_4P_2S_4$: C, 57.68; H, 4.15; N, 3.96. Found (%): C, 57.75; H, 4.16; N, 3.94. IR data (KBr pellets, cm^{-1}): 3 449m, 3 068m, 2 959w, 2 821w, 1 637w, 1 597m, 1 583 w, 1 494s, 1 478m, 1 433s, 1 384s, 1 326s, 1 293s, 1 093 m, 1 077m, 1 029s, 1 012s, 849w, 744s, 721w, 692s, 670m, 514s, 497s, 425w. 1H NMR (600 MHz, $CDCl_3$, 298 K): δ 7.56~7.22(m, $CH_{benzene}$), 7.26(s, CH_{CDCl_3}), 3.49 (s, CH_3).

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 $K\alpha$ ($\lambda = 0.071\ 073$ nm) radiation at 298 K. Semi-empirical absorption corrections were applied using SABABS program^[15]. All the structures were solved by direct

methods using SHELXS program of the SHELXTL-97 package and refined with SHELXL-97^[16]. 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: 1059719, **1**; 1059720, **2**.

Table 1 Crystallographic data for complexes **1~2**

Complex	1	2
Formula	$C_{43}H_{35}AgClNP_2S_2$	$C_{51}H_{44}AgN_3O_4P_2S_4$
Formula weight	835.10	1 060.94
T / K	298(2)	298(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Crystal size / mm	0.43×0.38×0.31	0.44×0.39×0.38
a / nm	1.465 00(12)	1.356 88(11)
b / nm	1.748 27(15)	1.475 53(12)
c / nm	1.799 53(16)	2.561 9(2)
$\alpha / (^\circ)$	103.080(2)	90.00
$\beta / (^\circ)$	112.664(3)	105.286(2)
$\gamma / (^\circ)$	103.219 0(10)	90.00
V / nm^3	3.878 5(6)	4.947 7(7)
Reflections collected / unique	19 649 / 13 416	24 919 / 8 714
Data / restraints / parameters	13 416 / 0 / 901	8 714 / 0 / 587
Reflections with $I > 2\sigma(I)$	7 820	4 666
Z	4	4
μ / mm^{-1}	0.810	0.688
$F(000)$	1 704	2 176
Goodness-of-fit on F^2	1.046	1.046
R_{int}	0.025 9	0.058 7
$R_1 (I > 2\sigma(I))^a$	0.040 8	0.046 2
$wR_2 (I > 2\sigma(I))^b$	0.071 8	0.086 7
R_1 (all data) ^a	0.095 6	0.098 4
wR_2 (all data) ^b	0.086 7	0.097 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**~**2**

Complex 1					
Ag(1)-P(1)	0.246 98(10)	Ag(1)-S(2)	0.273 94(14)	Ag(2)-Cl(2)	0.258 27(12)
Ag(1)-P(2)	0.250 01(11)	Ag(2)-P(3)	0.246 99(10)	Ag(2)-S(4)	0.278 13(13)
Ag(1)-Cl(1)	0.259 37(12)	Ag(2)-P(4)	0.249 49(11)		
P(1)-Ag(1)-P(2)	120.76(4)	P(2)-Ag(1)-S(2)	99.05(5)	P(4)-Ag(2)-Cl(2)	110.75(4)
P(1)-Ag(1)-Cl(1)	117.67(4)	Cl(1)-Ag(1)-S(2)	100.47(4)	P(3)-Ag(2)-S(4)	106.88(4)
P(2)-Ag(1)-Cl(1)	106.97(4)	P(3)-Ag(2)-P(4)	121.27(4)	P(4)-Ag(2)-S(4)	98.26(4)
P(1)-Ag(1)-S(2)	108.35(4)	P(3)-Ag(2)-Cl(2)	114.95(4)	Cl(2)-Ag(2)-S(4)	101.03(4)
Complex 2					
Ag(1)-P(1)	0.246 31(11)	Ag(1)-P(2)	0.244 59(12)	Ag(1)-S(2)	0.257 75(13)
Ag(1)-S(4)	0.275 36(14)				
P(2)-Ag(1)-P(1)	126.89(4)	P(2)-Ag(1)-S(4)	96.47(4)	P(2)-Ag(1)-S(2)	117.89(4)
P(1)-Ag(1)-S(4)	105.98(4)	P(1)-Ag(1)-S(2)	106.77(4)	S(2)-Ag(1)-S(4)	96.41(5)

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

D-H...A	<i>d</i> (D-H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠DHA
Complex 1				
N1-H1...Cl1	0.086 0	0.225 4	0.310 3	169.18
N2-H2...Cl2	0.086 0	0.225 4	0.308 5	162.59
Complex 2				
N1-H1...O1	0.086 0	0.194 3	0.278 3	165.17
N1-H1...O2	0.086 0	0.262 1	0.333 4	141.07
N1-H1...N3	0.086 0	0.264 6	0.348 9	166.88
N2-H2...O1	0.086 0	0.218 3	0.300 2	158.97
N2-H2...S2	0.086 0	0.298 8	0.340 0	111.59
O4-H4...O2	0.082 0	0.220 1	0.301 9	175.75

2 Results and discussion

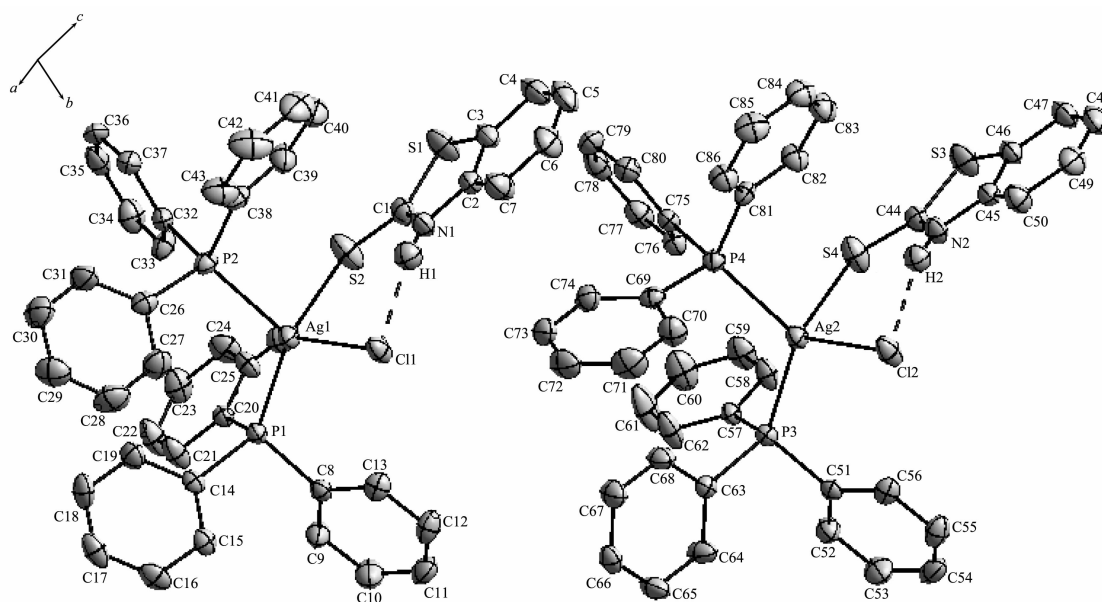
2.1 Synthesis of the single crystals

Different proportions of the metal and ligand influence the structures of the compounds. The complex **1** is synthesized by AgCl, PPh₃, and BTZT in 1:2:1 molar ratio generating a complex whose each asymmetric unit contains two same structures. Also the complex **3** is similar with **1**, because of the same proportion. While, the complex **4** is synthesized by AgCl, PPh₃ and BTZT in 1:1:1 molar ratio generating inversion symmetric dimers with a diamond-shaped Ag₂Cl₂ group at the center. And two adjacent [AgCl (PPh₃) (BTZT)] units are bridged by two Cl atoms. Different anions also influence the structures of the compounds. As is well-known, NO₃⁻ is an uncoordinated

anion in the most of cases and halide atoms usually have the ability to connect Ag cations. Complex **2** is a mononuclear compound.

2.2 Description of the crystal structure

The complex **1** contains two same structures in each asymmetric unit, but there are different bond lengths and bond angles. Each asymmetric unit is comprised of AgCl, PPh₃, and BTZT in 1:2:1 molar ratio. The Ag(I) metal adopts four-coordinated mode, which is bonded to two P atoms from two PPh₃ ligands, a chlorine atom and a S atom from the C=S fragment of the BTZT ligand peripherally establishing a distorted tetrahedral geometry about the metal (Fig. 1). The geometry around each metal center is distorted tetrahedral as is evident from the angles in the range of 98.26(4)°~121.27(4)°. The angles around one Ag



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

Fig.1 Molecular structure of complex 1

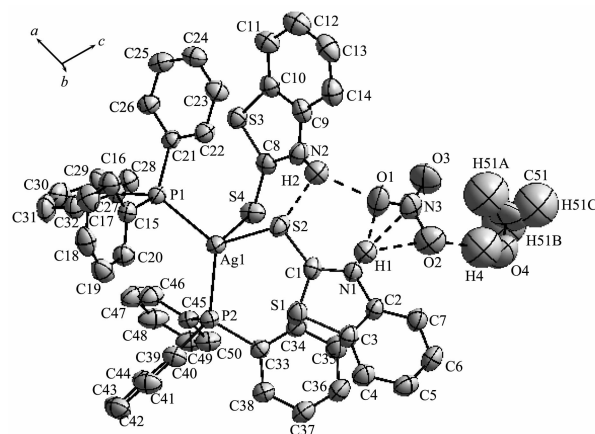
atom are in the range of $99.05(5)^\circ \sim 120.76(4)^\circ$. The angles around the other Ag atom are in the range of $98.26(4)^\circ \sim 121.27(4)^\circ$. Geometrical distortion from ideal angles can be derived from the need to accommodate the bulky PPh_3 ligand and BTZT ligand.

The Ag-Cl bond distances (0.259 37(12) nm and 0.258 27(12) nm) are shorter than that observed in $[\text{AgCl}(\eta^1\text{-S-H}_2\text{stsc-NHEt})(\text{PPh}_3)_2]$ (0.265 91(12) nm)^[17]. But the Ag-Cl bond distances are close to those found in: $[\text{AgCl}(\kappa^1\text{-S-C}_3\text{H}_5\text{NS}(\text{NeMe}))(\text{PPh}_3)_2]$ (0.257 0(1) nm)^[18] and $[\text{AgCl}(\kappa^1\text{-S-C}_3\text{H}_5\text{NS}(\text{NePrn}))(\text{PPh}_3)_2]$ (0.257 51(5) nm)^[18]. The Ag-P bond distance is similar with that in previous literature. The Ag-S bond distances (0.273 94(14) nm and 0.278 13(13) nm) in the complex 1 is longer than that observed in $[\text{AgCl}(\text{TPP})_2(\text{MTZD})]$ (0.268 61(10) nm) and $\{[\text{AgCl}(\text{TPP})_2(\text{MBZT})] \cdot (\text{MBZT}) \cdot 2(\text{toluene})\}$ (0.270 37(13) nm)^[13].

Moreover, intramolecular N-H...Cl hydrogen bonds are observed (N...Cl 0.310 3 nm and 0.308 5 nm, $\angle \text{N-H} \cdots \text{Cl}$ 169.18° , 162.59°) in the complex 1. The Cl-Ag-S bond angles ($100.47(4)^\circ$ and $101.03(4)^\circ$) are smaller than $[\text{AgCl}(\text{TPP})_2(\text{MTZD})]$ ($102.68(3)^\circ$) and $\{[\text{AgCl}(\text{TPP})_2(\text{MBZT})] \cdot (\text{MBZT}) \cdot 2(\text{toluene})\}$ ($104.91(4)^\circ$)^[13]. The P-Ag-P bond angles ($120.76(4)^\circ$ and $121.27(4)^\circ$) are smaller than that in $(\text{Ph}_3\text{P})_2\text{AgO}_3\text{SCH}_3$ ($132.4(4)^\circ$)^[19].

Complex 2 is a simple mono-nuclear heteroleptic

complex formed with distinctly soft Ag(I) and PPh_3 , BTZT and NO_3^- anion. Each Ag is four-coordinated, surrounded by two P atoms from two PPh_3 ligands and two S atoms from two BTZT ligands (Fig.2). The angles around Ag(I) ranging from $96.41(5)^\circ$ to $126.89(4)^\circ$ indicate that the geometry around Ag atom is distortedly tetrahedral. The Ag-P bond distances (0.244 59(12) nm and 0.246 31(11) nm) are longer than those in the complex $[(\text{Ph}_3\text{P})_2\text{Ag}(\text{thione})]\text{NO}_3$ (0.240 29(10) nm and 0.241 57(10) nm)^[20]. The Ag-S bond distances (0.257 75(13) nm and 0.275 36(14) nm) are longer than those in the complex $[\text{Ag}(\text{DPEphos})(\text{py}_2\text{SH})_2]\text{NO}_3$



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

Fig.2 Molecular structure of complex 2

(0.254 37(6) nm and 0.259 49(6) nm)^[21].

The main structure of **2** links free CH₃OH and NO₃⁻ anion by hydrogen bonding interactions. The O—H···O hydrogen bond linking free CH₃OH and NO₃⁻ anion is observed (O···O 0.301 9 nm, O—H···O 175.75°) in the complex **2**. The main structure and NO₃⁻ anion are sustained by hydrogen bonding interactions (N1—H1···O1, N1—H1···O2, N1—H1···N3, N2—H2···O1). The N2—H2···S2 hydrogen bonding interaction can be ignored, because the N2—H2···S2 angle (111.59°) deviates from 180° so much. The S—Ag—S angle (96.41(5)°) is smaller than those in the complex [(Ph₃P)₂Ag(thione)]NO₃ (112.18(5)° and 113.64(3)°)^[20]. The P—Ag—P angle (126.89(4)°) is larger than that in the [Ag(DPEphos)(py₂SH)₂](NO₃) (112.20(2)°)^[21].

2.3 Infrared spectroscopy

The infrared spectra of complexes **1**~**2** shows the absorption around 1 460~1 497 cm⁻¹ due to C—C stretch vibration of the phenyl rings. The middle absorption

around 3 054 cm⁻¹ for **1** and 3 068 cm⁻¹ for **2** 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 695 cm⁻¹ for **1**, while 744 and 692 cm⁻¹ for **2**. The absorption of the N—H stretch vibration is in 3 429 cm⁻¹ for **1** and 3 449 cm⁻¹ for **2**. The C=S bond vibration is found in 1 077 cm⁻¹.

2.4 Fluorescence spectrum

The luminescent excitation and emission spectra of complexes **1**~**2** and MBT ligand in the solid state at room temperature are obtained. The emission peak of PPh₃ 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). When excited at 361 nm, a fluorescence emission peak of complex **1** is found at 432 nm. The complex **2** exhibits fluorescence signal centered at 435 nm with an excitation maximum at 353 nm. The red-shift of emission peak of **1**~**2** is derived from ligand-centered π-π* transition.

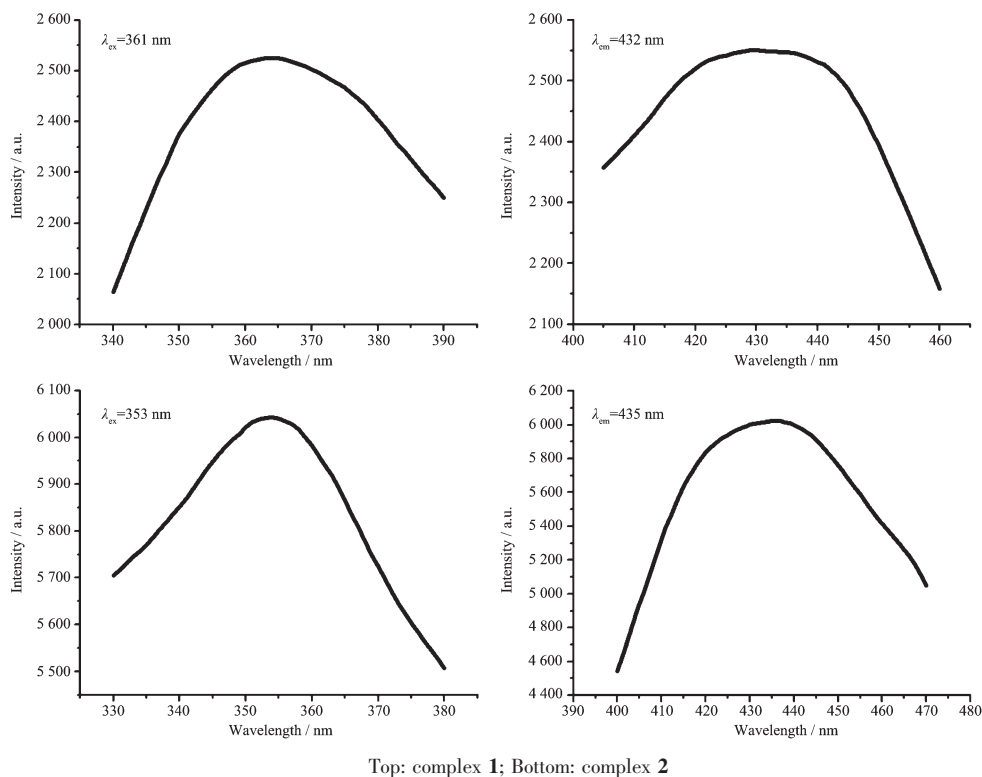


Fig.3 Solid-state excitation and emission spectra of **1**~**2** at 298 K

3 Conclusions

In summary, we have successfully synthesized

and characterized two novel thione complexes, [AgCl(PPh₃)₂(BTZT)]₂ and [Ag(PPh₃)₂(BTZT)₂](NO₃)·CH₃OH, using IR, single-crystal X-ray diffraction, fluorescence

spectrum and ^1H NMR spectroscopy. The complex **1** contains two same structures in each asymmetric unit, but there are different bond lengths and bond angles. Complex **2** is a simple mono-nuclear heteroleptic complex whose main structure links free CH_3OH and NO_3^- anion by hydrogen bonding interactions. The red-shift of emission peak of **1~2** is derived from ligand-centered $\pi-\pi^*$ transition. The research plays an important role in designing and synthesizing sulfur/phosphine ligand-based Ag(I) complexes.

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