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两种基于硫醇配体的银(I)配合物的合成、表征和晶体结构

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摘要:通过 AgCl、PPh_3 和 MBT 以 1:2:1 的物质的量之比反应得到 2 种不同的配合物[$AgCl(PPh_3)_2$(BTZT)]·CH_3OH (**1**)和[$AgCl(PPh_3)_2$(BTZT)]$_2$ (**2**)(PPh_3=三苯基膦;MBT=2-巯基苯并噻唑;BTZT=苯并噻唑-2-硫酮)(其中 **2** 已报道)。配合物[$AgBr(PPh_3)_2$(BTZT)]·CH_3OH (**3**)和[$AgBr(PPh_3)_2$(BTZT)]$_2$ (**4**)改用 AgBr 以相似的反应获得(其中 **4** 已报道)。通过红外光谱、元素分析、核磁共振氢谱、X 射线单晶衍射、荧光光谱对配合物 **1** 和 **3** 进行了分析和表征。我们发现在不同的化学环境中,MBT 配体可以转化为 BTZT 配体,原因是其具有化学活性基团。荧光光谱表明 **1** 和 **3** 的发射峰均源于配体中的 π-π* 跃迁。

关键词:三苯基膦;2-巯基苯并噻唑;苯并噻唑-2-硫酮;配合物
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Syntheses, Characterizations and Crystal Structures of Two Kinds of Silver(I) Complexes Derived from Thiol Ligand

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Abstract: Two kinds of complexes [$AgCl(PPh_3)_2$(BTZT)]·CH_3OH (**1**) and [$AgCl(PPh_3)_2$(BTZT)]$_2$ (**2**) were obtained by the reaction of AgCl, PPh_3, and MBT in 1:2:1 molar ratio (PPh_3=triphenylphosphine; MBT=2-mercaptobenzothiazole BTZT=benzothiazoline-2-thione) (**2** has been reported). [$AgBr(PPh_3)_2$(BTZT)]·CH_3OH (**3**) and [$AgBr(PPh_3)_2$(BTZT)]$_2$ (**4**) were prepared in a manner similar to **1** and **2** using AgBr (**4** has been reported). Complexes **1** and **3** have been characterized by IR, elemental analysis, ^{1}H NMR spectroscopy, fluorescence spectrum and single-crystal X-ray diffraction. The MBT ligand can transform into the BTZT ligand in different chemical environment because of its chemically active groups. The luminescent spectra show that emission peaks of **1** and **3** are assigned to the ligand centered π-π* transition. CCDC: 1407305, **1**; 1407306, **3**.

Keywords: triphenylphosphine; 2-mercaptobenzothiazole; benzothiazoline-2-thione; complex

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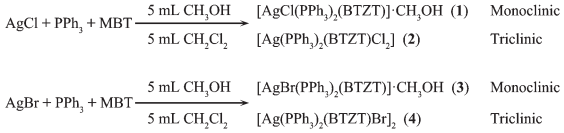
0 Introduction

Currently, quite a few novel coordination complexes are reported[1-2]. With the rapid development of coordination complexes, complexes with closed-shell d^{10} metals have attracted considerable attention due to important applications in catalysis[3-4] and biochemistry[5-6]. In particular, complexes bearing the Ag-S bond have raised continuously increasing interest, owing to their use in pharmacology[7] and thin films[8], as well as glass and ceramic technology[9]. In coordination chemistry, it is one of the most interesting phenomena that two or more stable products are synthesized by the same reactions. The success of designed synthesis and separation of materials still look upon as something of challenge[10-11].

Herein, we set out to design, prepare, and characterize silver(Ⅰ) complexes of silver halides AgX (X=Cl, Br), using same phosphine moieties and taking into account the coordination versatility of the thiol ligand (Scheme 1), namely [AgCl (PPh_3)$_2$ (BTZT)]·CH_3OH (**1**), [AgCl (PPh_3)$_2$ (BTZT)]$_2$ (**2**) [12], and [AgBr (PPh_3)$_2$(BTZT)]·CH_3OH (**3**), [AgBr(PPh_3)$_2$(BTZT)]$_2$ (**4**)[13] (PPh_3 =triphenylphosphine; BTZT =benzothiazoline-2-thione). The BTZT ligand was transformed from MBT ligand in different chemical environment because of chemically active groups of MBT (MBT=2-mercaptobenzothiazole)[14]. Complexes **1** and **3** have been synthesized and characterized by IR, elemental analysis, ^{1}H NMR spectroscopy and single-crystal X-ray diffraction.



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

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 ElementarVario MICRO CUBE (Germany) elemental analyzer. ^{1}H NMR was recorded at room temperature with a Bruker DPX 600 spectrometer.

1.2 Synthesis of [AgCl(PPh_3)$_2$(BTZT)]·CH_3OH (1)

A mixture of AgCl (0.2 mmol, 0.0291g), PPh_3 (0.4 mmol, 0.104 9 g) and MBT (0.2 mmol, 0.033 3 g) were dissolved in a mixture of CH_3OH (5 mL) and CH_2Cl_2 (5 mL), stirred for 6 h and filtered. Colorless crystal 1 was obtained from the filtrate after standing at the room temperature for several days. Yield: 56%. Element analysis Calcd. for $C_{44}H_{39}AgClNOP_2S_2$ (%): C, 60.89; H, 4.50; N, 1.61; Found(%): C, 61.08; H, 4.39; N, 1.52. IR data (KBr pellets, cm^{-1}): 3 418w, 3 049w, 2 937w, 2 815w, 1 598w, 1 583w, 1 495m, 1 478m, 1 432 s, 1 328m, 1 092m, 1 077w, 1 028m, 1 012w, 743s, 693s, 604w, 512m. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ 7.51~7.23(m, $CH_{benzene}$).

1.3 Synthesis of [AgBr(PPh_3)$_2$(BTZT)]CH_3OH (3)

Complex **3** was prepared in a manner similar to that described for **1**, using AgBr (0.2 mmol, 0.037 0 g), PPh_3 (0.4 mmol, 0.104 8 g) and MBT (0.2 mmol, 0.033 2 g) as starting materials. Yield: 51%. Element analysis Calcd. for $C_{44}H_{39}AgBrNOP_2S_2$(%): C, 57.92; H, 4.27; N, 1.53. Found (%): C, 57.81; H, 4.02; N, 1.46. IR data (KBr pellets, cm^{-1}): 3 434w, 3 052w, 3 001w, 2 935w, 2 875w, 2 825w, 1 596w, 1 492m, 1 478m, 1 432s, 1 323m, 1 093m, 1 076w, 1 030m, 1 012w, 996w, 743s, 694s, 606w, 513m. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): δ 7.51~7.23(m, $CH_{benzene}$).

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 at 298 K. Semi-empirical absorption corrections were applied using SADABS program[15a]. All the structures were solved by direct methods using SHELXS program of the SHELXTL-97 package and refined with SHELXL-97[15b]. 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** and **3** are summarized in Table 2. The bond lengths and angles of hydrogen bonds of complexes **1** and **3** are listed in Table 3.

CCDC: 1407305, **1**; 1407306, **3**.

Table 1　Crystallographic data for complexes 1 and 3

	1	**3**
Formula	$C_{44}H_{39}AgClNOP_2S_2$	$C_{44}H_{39}AgBrNOP_2S_2$
Formula weight	867.14	911.60
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Crystal size / mm	0.25×0.14×0.12	0.43×0.37×0.26
a / nm	1.299 63(8)	1.305 57(14)
b / nm	2.483 83(16)	2.490 5(3)
c / nm	1.341 65(8)	1.339 05(14)
β / (°)	107.873(4)	107.041(2)
V / nm^3	4.121 9(4)	4.162 8(8)
Reflections collected, unique	56 151, 9 914	20 912, 7 325
Data, restraints, parameters	9 914, 0, 471	7 325, 0, 470
Reflections with $I>2\sigma(I)$	6 704	5 213
Z	4	4
μ / mm^{-1}	0.767	1.655
F(000)	1 776	1 848
Goodness-of-fit on F^2	1.056	1.065
R_{int}	0.062 4	0.041 4
R_1 [$I>2\sigma(I)$][a]	0.047 0	0.050 9
wR_2 [$I>2\sigma(I)$][b]	0.096 9	0.124 3
R_1 (all data)[a]	0.079 2	0.131 7
wR_2 (all data)[b]	0.111 0	0.156 8

[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 3

		1			
Ag(1)-P(1)	0.245 03(8)	Ag(1)-Cl(1)	0.264 28(10)	Ag(1)-P(2)	0.248 30(9)
Ag(1)-S(1)	0.265 75(10)				
P(1)-Ag(1)-P(2)	129.27(3)	P(1)-Ag(1)-S(1)	106.98(3)	P(1)-Ag(1)-Cl(1)	112.30(3)
P(2)-Ag(1)-S(1)	102.89(3)	P(2)-Ag(1)-Cl(1)	100.50(3)	Cl(1)-Ag(1)-S(1)	101.42(3)
		3			
Ag(1)-P(1)	0.248 38(13)	Ag(1)-P(2)	0.245 78(12)	Ag(1)-S(2)	0.267 57(14)
Ag(1)-Br(1)	0.274 68(7)				
P(2)-Ag(1)-P(1)	129.04(5)	P(2)-Ag(1)-Br(1)	110.53(4)	P(2)-Ag(1)-S(2)	106.21(4)
P(1)-Ag(1)-Br(1)	101.13(4)	P(1)-Ag(1)-S(2)	103.21(5)	S(2)-Ag(1)-Br(1)	104.24(4)

Table 3 Hydrogen bonds of complexes 1 and 3

D–H···A	*d*(D-H)/ nm	*d*(H···A) / nm	*d*(D···A) / nm	∠DHA / (°)
		1		
N1–H1A···Cl1	0.086	0.227	0.311 6(3)	170.0
		3		
N1–H1···Br1	0.086	0.242	0.326 9(5)	169.2
O1–H1A···Br1	0.082	0.252	0.332 9(7)	171.2

2 Results and discussion

2.1 Synthesis of complexes

As is known to all, many factors can influence the structures of the compounds, such as temperature, solvent and molar ratio of the starting materials. We obtain two kinds of complexes **1** and **2** by the reactions of AgCl, PPh_3, and BTZT in 1∶2∶1 molar ratio in mixed solvent (CH_3OH/CH_2Cl_2). Complex **1** crystallizes in the monoclinic system with space group $P2_1/n$, while **2**[12] crystallizes in the triclinic system with space group $P\bar{1}$.

3 and **4** were obtained by the reactions of AgBr with PPh_3 in the presence of 2-mercaptobenzothiazole (MBT) in 1∶2∶1 molar ratio in mixed solvent (CH_3OH/CH_2Cl_2). **3** crystallizes in the monoclinic system with space group $P2_1/n$, while **4**[13] crystallizes in the triclinic system with space group $P\bar{1}$.

Complexes **2** and **4** were synthesized in winter, but **1** and **3** were obtained in summer. So we think that the temperature of volatilization may influence the structures of the compounds.

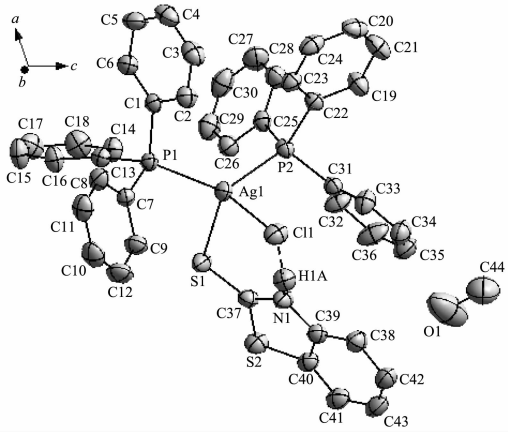
2.2 Infrared spectroscopy

The infrared spectra of complexes **1** and **3** show the absorption around 1 459~1 495 cm^{-1} due to C-C stretch vibration of the phenyl rings and the middle absorption around 3 049 or 3 052 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 743 and 694 cm^{-1}. The absorption of the N-H stretch vibration is in the range of 3 418~3 434 cm^{-1}. The C=N bond vibration is found in 1 432 cm^{-1}.

2.3 Description of the crystal structure

Single-crystal X-ray diffraction analysis of **1** reveals the Ag(I) metal adopts four-coordinated mode, which is bonded to two P atoms from two PPh_3 ligands, one chlorine atom and one S atom from the C=S fragment of the BTZT ligand peripherally establishing a distorted tetrahedral geometry about the metal. In particular, the complex **2** contains two same moieties in each asymmetric unit[12].

In complex **1** (Fig.1), the Ag-P bond distance is similar to that in previous literature. The Ag-Cl bond distance is comparable with those observed in related complexes [AgCl (κ^1-S-C_3H_5NS (NeMe)) (PPh_3)$_2$] (0.257 0 (1) nm)[16] and [AgCl (κ^1-S-C_3H_5NS (NePrn) (PPh_3)$_2$)] (0.257 51(5) nm)[16]. The Ag-S bond distance is longer than that found in [Ag (imdt)Cl]$_n$[17] (0.248 66 (14) nm), but it is shorter than that of complex **2**[12]. The angles around the Ag atom are in the range of 100.50(3)°~129.27(3)°. The Cl-Ag-S bond angle is smaller than that of [AgCl (TPP)$_2$ (MTZD)] (102.68 (3)°) and {[AgCl (TPP)$_2$(MBZT)]·(MBZT)·2(toluene)} (104.91(4)°)[18].

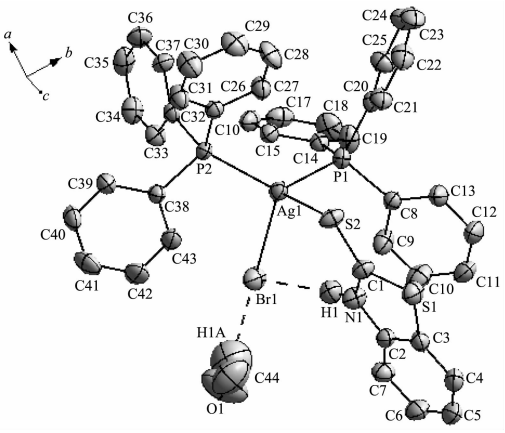


A part of hydrogen atoms are omitted for clarity

Fig.1 Perspective view of complex **1** with thermal ellipsoids drawn at the 30% probability level

Moreover, intramolecular N–H ··· Cl hydrogen bonds are observed (N···Cl 0.311 6(3) nm, N–H···Cl 170.0°) in the complex **1**. The main structure of **1** links free CH_3OH by hydrogen bonding interactions.

In complex **3** (Fig.2), the angles around the Ag atom are in the range of 101.13(4)°~129.04(5)°.The coordination geometry around each Ag atom indicates a distorted tetrahedron. The Ag-P bond length is typical Ag-P distance[19]. The Ag-Br distance is found in good agreement with the reported values[16,20], but is longer than those of complex **4**. The Ag-S bond length is longer than that observed in $[Ag_2(\mu\text{-S-pySH})_2(PPh_3)_2Br_2]$ (0.260 8(1) nm)[14]. The P-Ag-P bond angle is all longer than those in another similar complex[21]. Moreover, intramolecular N–H⋯Br hydrogen bonds are observed (N⋯Br 0.326 9(5) nm, N–H⋯Br 169.2°) in the complex **3**. The main structure of **3** links free CH_3OH by hydrogen bonding interactions. The O–H⋯Br hydrogen bond to link free CH_3OH and NO_3^- anion is observed (O⋯Br 0.332 9(7) nm, O–H⋯Br 171.2°) in the complex **3**.



A part of hydrogen atoms are omitted for clarity

Fig.2　Perspective view of complex **3** with thermal ellipsoids drawn at the 30% probability level

Compared to complex **3**, the complex **4** contains two same structures in each asymmetric unit. 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).

2.4　Fluorescence spectra

The luminescent excitation and emission spectra of complexes **1**, **3** and MBT ligand in the solid state at room temperature are obtained. The emission peak of PPh_3 is at 402 nm (λ_{ex}=372 nm)[19]. In the fluorescence emission spectrum of MBT ligand, the emission peak is found at 419 nm (λ_{ex}=342 nm). When excited at 365 nm, a fluorescence emission peak of complex **1** is found at 431 nm. The complex **3** exhibits fluorescence

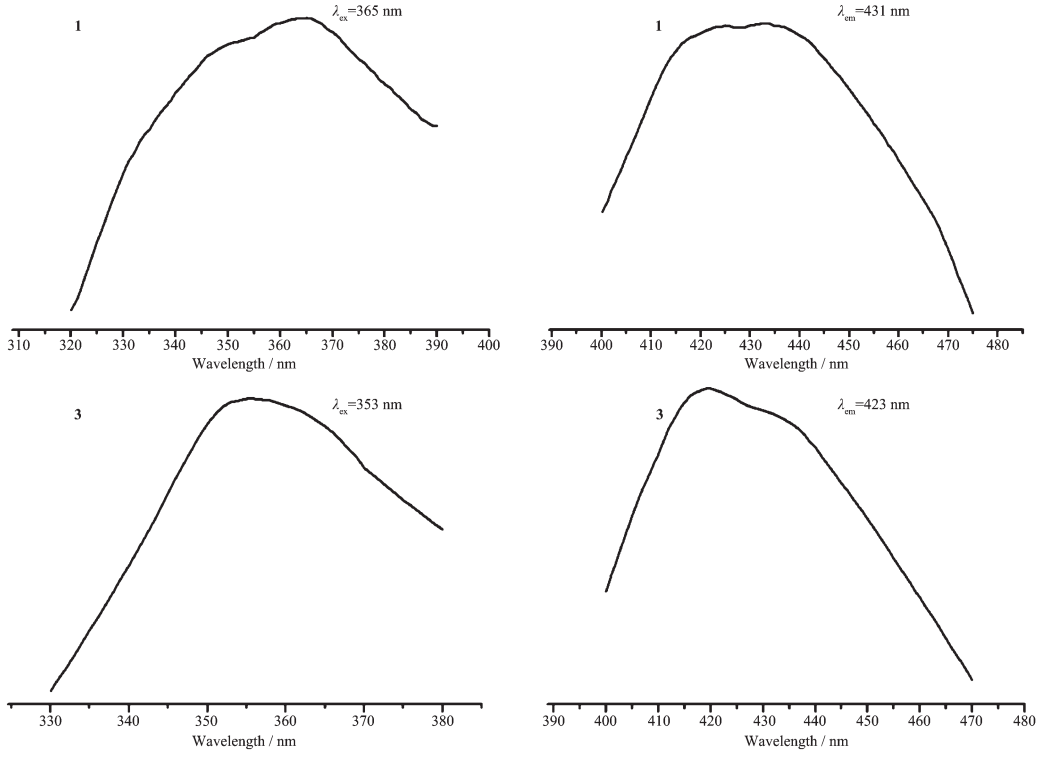


Fig.3　Solid-state excitation and emission spectra of **1** and **3** at 298 K

signal centered at 423 nm with an excitation maximum at 353 nm. The red-shift of emission peaks of **1** and **3** are derived from ligand-centered π-π* transition.

3 Conclusions

In summary, two kinds of silver(I) halide complexes based on triphenylphosphine and benzothiazoline-2-thione, $[AgCl(PPh_3)_2(BTZT)]\cdot CH_3OH$ (**1**), and $[AgBr(PPh_3)_2(BTZT)]\cdot CH_3OH$ (**3**), were synthesized and characterized by IR, elemental analysis, ^1H NMR spectroscopy, luminescent spectra and single-crystal X-ray diffraction. However, by the same reactions two different products **2** (The reaction condition was same as **1**) and **4** (The reaction condition was same as **3**) were synthesized. Single-crystal X-ray diffraction analysis reveals that **1** and **3** crystallize in the monoclinic system with space group $P2_1/n$, while **2** and **4** crystallize in the triclinic system with space group $P\bar{1}$. The luminescent spectra show that **1** and **3** emission peaks were assigned to the ligand centered π-π* transition.

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