Preparation, Structural Characterization and Luminescent Property of Binuclear Silver(I) Complex Formed by Benzotriazole and 1-Hydroxymethyl Benzotriazole

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Dinuclear silver(I) six-membered ring complex $[Ag_2(bta)_2(hmbta)_2](ClO_4)_2$ (3) has been synthesized by the reaction of benzotriazole (bta) (1) and 1-hydroxymethyl benzotriazole (hmbta) (2) with $Ag(CH_3CN)_4ClO_4$. The structures of compound 2 and Complex 3 have been studied by single crystal X-ray diffraction analysis. The change of luminescent intensity of 1, 2 and 3 was reported. Compound 2 crystallizes in the monoclinic system with space group $P2(1)/c$, $a = 0.7655(10)$ nm, $b = 1.0126(14)$ nm, $c = 0.9502(13)$ nm, $\beta = 95.07(2)°$, $V = 0.7337(17)$ nm^3 and $Z = 4$. Complex 3 crystallizes in the triclinic system with space group $P\bar{1}$, $a = 0.73611(18)$ nm, $b = 0.9152(2)$ nm, $c = 1.2277(3)$ nm, $\beta = 87.170(5)°$, $V = 0.8221(3)$ nm^3 and $Z = 1$. The main structural feature of complex 3 is a symmetric dinuclear six-membered ring formed by two silver(I) atoms and four N-atoms from two benzotriazoles. The second structural feature of complex 3 is the π-π stacking interaction between two adjacent molecular planes, which forms the two-dimentional layer structure. Besides, compared with 2, the luminescent intensity of complex 3 shows a remarkable enhancement.

Keywords benzotriazole, 1-hydroxymethylbenzotriazole, binuclear silver(I) complex

Introduction

Dinuclear complexes of silver(I) have been extensively studied,[1] owing to their importance as catalysts and transfer reagents.[2] Aromatic N-heterocycles have been proved to be suitable ligands in coordination chemistry.[3] The triazole derivatives, for instance, have been widely investigated in some metallic chemistry of discrete compounds or supermolecules.[4] In particular, benzotriazole is a N-heterocyclic species exhibiting three vicinal coordinating N-atoms for the formation of mono- and dinuclear complexes with transition metal ions. In addition, benzotriazole has been employed as an efficient corrosion inhibitor for copper and its alloys,[5] and provides an interesting model species in bioinorganic chemistry.[6] Nevertheless, the coordination chemistry of benzotriazole with first- or second-row transition metals has scarely been explored up to the present time.[7] Herein we wish to report the synthesis, structural characterization and luminescent property of $[Ag_2(bta)_2(hmbta)_2](ClO_4)_2$[bta = benzotriazole, hmbta = 1-hydroxymethyl benzotriazole].

Experimental

Materials and general methods

All manipulations were performed using Schlenk techniques, and solvents were purified by standard procedures. All the reagents for syntheses and analyses were of analytical grade and used without further purification. Melting points were determined with a Boetius Block apparatus. ^{1}H NMR spectra were recorded on a Bruker AC-P200 spectrometer at 200 MHz. ^{1}H chemical shifts are reported in ppm (δ) relative to $SiMe_4$($\delta = 0$). IR spectra (KBr) were taken on an EQUINOX55 spectrometer.

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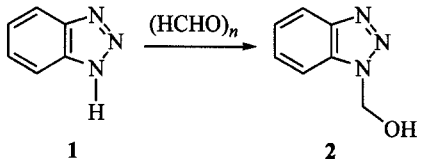
Elemental analyses were measured using a Perkin-Elmer 2400C Elemental Analyzer. $Ag(CH_3CN)_4ClO_4$ was synthesized as reported previously.[8] The luminescent intensities of benzotriazole (**1**), 1-hydroxymethyl benzotriazole (**2**) and $[Ag_2(bta)_2(hmbta)_2](ClO_4)_2$ (**3**) were measured using a Cary Eclipse Fluorescence spectrophotometer.

Synthesis of 1-*hydroxmethyl benzotriazole* (hmbta) (**2**)

Polyformaldehyde (2.25 g, 75 mmol) was added to a solution of benzotriazole (5.096 g, 50 mmol) in toluene (150 mL) and several drops of hydrochloric acid were added to the solution. The suspension was refluxed for 8 h under Ar. Then, the volume of solution was reduced to 50 mL, and the solution was cooled to 4 ℃. 1-Hydroxmethyl benzotriazole was deposited as a white crystalline solid, which was isolated by filtration and dried under reduced pressure (6.95 g, 93.2% yield) (Scheme 1). The crystal suitable for X-ray analysis was grown by diffusing Et_2O to CH_2Cl_2 at room temperature. M.p. 148—151 ℃ (lit.[9] m.p. 148—151 ℃); ^1H NMR ($CDCl_3$) δ: 8.03 (d, J = 8.4 Hz, 1H, ArH), 7.91 (d, J = 8.4 Hz, 1H, ArH), 7.61 (t, J = 8.4 Hz, 1H, ArH), 7.42 (t, J = 8.4 Hz, 1H, ArH), 6.01 (s, 2H, CH_2), 3.49 (s, 1H, OH); IR (KBr) ν: 3196 (s), 2969 (w), 2875 (w), 1495 (m), 1306 (m), 1222 (m), 1234 (m), 1159 (m), 1076 (vs), 986 (m), 755 (s), 618 (m) cm^{-1}.

Scheme 1

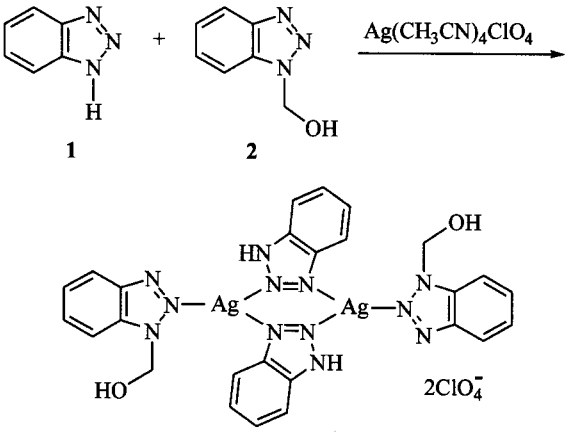


1 2

Synthesis of $[Ag_2(bta)_2(hmbta)_2](ClO_4)_2$(**3**)

A dichloromethane solution of $Ag(CH_3CN)_4ClO_4$ (0.318 g, 0.839 mmol) was added to an acetone solution of bta (0.1 g, 0.839 mmol) and hmbta (0.125 g, 0.839 mmol). The solution was stirred for 4 h at room temperature. After this period, the mixture was filtered and the solvent is removed from the filtrate with a rotary evaporator. The residue was washed with diethyl ether, giving $[Ag_2(bta)_2(hmbta)_2](ClO_4)_2$ as a grey powder (0.267 g, 67% yield) (Scheme 2). The crystal suitable for X-ray analysis was grown by the slow evaporation from a solution of acetone at room temperature. M.p. 242—244 ℃; ^1H NMR ($CDCl_3$) δ: 8.30 (d, J = 8.0 Hz, 2H, ArH), 8.21 (d, J = 8.0 Hz, 2H, ArH), 8.01 (d, J = 8.0 Hz, 2H, ArH), 7.69 (t, J = 8.0 Hz, 2H, ArH), 7.65 (d, J = 8.0 Hz, 2H, ArH), 7.60 (t, J = 8.0 Hz, 2H, ArH), 7.51 (t, J = 8.0 Hz, 2H, ArH), 7.28 (t, J = 8.0 Hz, 2H, ArH), 6.12 (s, 4H, CH_2), 3.13 (s, 2H, OH), (the peak of NH was not observed); IR (KBr) ν: 3189 (s), 2953 (w), 2860 (w), 1453 (m), 1387 (m), 1306 (m), 1222 (m), 1234 (m), 1159 (m), 1102 (vs), 1076 (vs), 986 (m), 783 (m), 755 (s), 618 (m) cm^{-1}. Anal. calcd for $C_{26}H_{24}Ag_2Cl_2N_{12}O_{10}$: C 32.83, H 2.54, N 17.67; found C 32.53, H 2.62, N 17.50.

Scheme 2



1 2 3

X-Ray structure determination

X-Ray data collection and refinement parameters for **2** and **3** are summerized in Table 1. X-Ray diffraction data were collected on a Bruker Smart 1000 CCD diffractometer equipped with a graphic crystal monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo Kα radiation (λ = 0.071073 nm). The unit cell dimensions were obtained with least-squares refinements and the structure was solved by direct methods using SHELXTL-97 program.[10]

Table 1 Crystallgraphic data for compound **2** and complex **3**

	Compound **2**	Complex **3**
Formula	$C_7H_7N_3O$	$C_{26}H_{24}Ag_2Cl_2N_{12}O_{10}$
Formular weight	149.16	951.21
Crystal system	Monoclinic	Triclinic
Space group	$P2(1)/c$	$P\bar{1}$
a (nm)	0.7655(10)	0.73611(18)
b (nm)	1.0126(14)	0.9152(2)
c (nm)	0.9502(13)	1.2277(3)
β (°)	95.07(2)	87.170(5)
V (nm^3)	0.07337(17)	0.8221(3)
D_c(g/cm^3)	1.350	1.921
Z	4	1
μ (cm^{-1})	0.96	14.29
T (K)	293(2)	293(2)
θ range (°)	2.67—25.02	1.67—25.03
Ind reflections	1201 [R(int) = 0.0299]	2907 [R(int) = 0.0424]
R_1	0.0413	0.0639
wR_2	0.0806	0.1366

Results and discussion

The synthetic method of compound **2** has been reported,[9] but no crystallographic data were afforded. Herein the previous synthetic method is modified (Scheme 1) and the crystallographic data (Table 1) and molecular structure are given (Fig. 1). The π-π stacking interaction exists between two adjacent benzotriazole molecular planes in compound **2**, and all of these interaction distances are 0.3529 nm.[11]

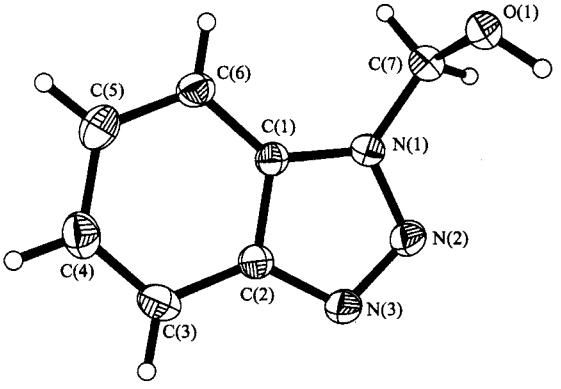
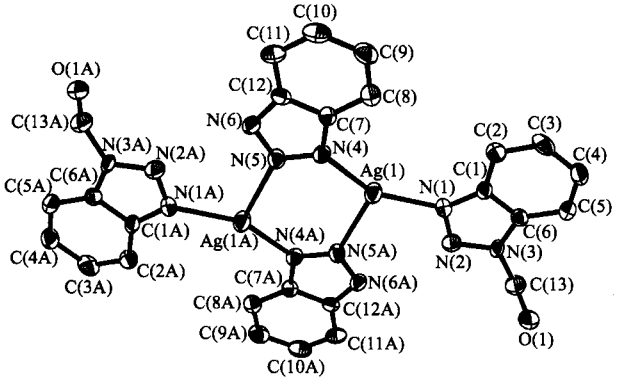
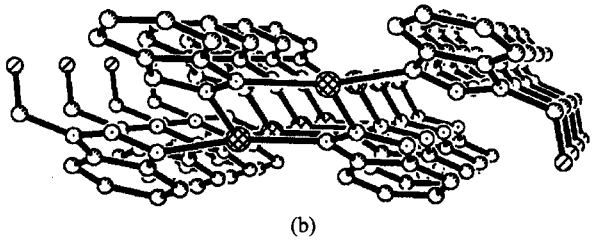


Fig. 1 Molecular structure of **2**.

Treatment of the tetraacetonitrile silver(I) perchlorate $Ag(CH_3CN)_4ClO_4$ with bta (**1**) and hmbta (**2**) results in formation of a light-sensitive binuclear six-membered ring complex $[Ag_2(bta)_2(hmbta)_2](ClO_4)_2$ (**3**) (Scheme 2). The molecular structure of **3** has been determined by X-ray diffraction analysis, as illustrated in Fig. 2. A symmetric six-membered ring structure formed



(a)



(b)

Fig. 2 Molecular structure of **3** (a) and two-dimentional layer structure of **3** (b).

Table 2 Atomic coordinates ($\times 10^4$) and thermal parameters ($nm^2 \times 10$) of non-hydrogen atom for complex **3**

Atom	x	y	z	U_{eq}
Ag(1)	1909(1)	9957(1)	8833(1)	61(1)
N(1)	2910(11)	9108(9)	7266(6)	47(2)
N(2)	2094(12)	8054(9)	6852(7)	57(2)
N(3)	3258(11)	7534(8)	6085(6)	48(2)
N(4)	2224(11)	11244(8)	10239(6)	47(2)
N(5)	826(11)	11470(9)	10918(7)	49(2)
N(6)	1280(11)	12478(8)	11564(7)	49(2)
O(1)	3599(13)	5021(9)	5949(7)	97(3)
C(1)	4599(13)	9280(10)	6782(7)	43(2)
C(2)	6003(14)	10201(11)	6931(8)	53(3)
C(3)	7582(15)	10036(12)	6326(9)	67(3)
C(4)	7819(15)	8975(12)	5556(9)	62(3)
C(5)	6478(15)	8070(11)	5388(9)	57(3)
C(6)	4829(14)	8250(10)	6012(8)	45(3)
C(7)	3576(13)	12127(10)	10448(8)	41(2)
C(8)	5350(14)	12295(11)	9957(8)	53(3)
C(9)	6417(15)	13270(12)	10356(10)	63(3)
C(10)	5781(17)	14057(12)	11239(10)	67(3)
C(11)	4080(15)	13925(11)	11740(9)	55(3)
C(12)	2990(13)	12920(10)	11325(8)	44(2)
C(13)	2782(17)	6291(13)	5516(10)	72(3)

Table 3 Selected bond lengths and bond angles of **2** and **3**

Bond lengths (10^{-1} nm)

Compound **2**		Complex **3**			
C(1)—N(1)	1.383(3)	Ag(1)—N(4)	2.205(7)	C(1)—C(6)	1.395(12)
C(1)—C(2)	1.414(3)	Ag(1)—N(1)	2.221(7)	N(4)—N(5)	1.314(9)
C(2)—N(3)	1.406(3)	Ag(1)—N(5A)	2.434(8)	N(4)—C(7)	1.355(11)
N(1)—N(2)	1.371(3)	N(1)—N(2)	1.310(11)	N(5)—N(6)	1.333(10)
N(2)—N(3)	1.328(3)	N(1)—C(1)	1.360(11)	N(6)—C(12)	1.348(11)
O(1)—C(7)	1.408(3)	N(2)—N(3)	1.349(10)	O(1)—C(13)	1.364(14)
N(1)—C(7)	1.483(3)	N(3)—C(6)	1.347(11)	N(3)—C(13)	1.451(12)

Bond angles (°)

Compound **2**		Complex **3**			
N(1)-C(1)-C(6)	133.56(19)	N(4)-Ag(1)-N(1)	152.1(3)	N(5)-N(4)-C(7)	108.8(7)
N(1)-C(1)-C(2)	104.4(2)	N(4)-Ag(1)-N(5A)	111.0(3)	N(5)-N(4)-Ag(1)	119.9(6)
N(3)-C(2)-C(1)	108.1(2)	N(1)-Ag(1)-N(5A)	96.6(3)	C(7)-N(4)-Ag(1)	130.1(6)
N(2)-N(1)-C(1)	110.48(18)	N(2)-N(1)-C(1)	110.2(8)	N(4)-N(5)-N(6)	107.7(7)
N(3)-N(2)-N(1)	108.79(16)	N(1)-N(2)-N(3)	106.9(8)	N(4)-N(5)-Ag(1A)	126.5(6)
N(2)-N(3)-C(2)	108.22(17)	C(6)-N(3)-N(2)	111.1(7)	N(6)-N(5)-Ag(1A)	125.1(6)
		N(1)-C(1)-C(6)	107.0(9)	N(5)-N(6)-C(12)	111.6(8)
		N(3)-C(6)-C(1)	104.8(8)	N(4)-C(7)-C(12)	108.3(8)
				N(6)-C(12)-C(7)	103.6(8)

by two silver(I) atoms and four N-atoms from two benzotriazoles is the most notable feature of complex **3**. Six atoms of the six-membered ring are at the same plane (deviation 0.00618 nm).

Each silver(I) atom is coordinated with three N-atoms (two N-atoms from **1** and one N-atom from **2**) and possesses a planar triangle configuration. Only one N-atom in compound **2** coordinates with silver(I). This can be attributed to the electron withdrawing effect of hydroxyl group, which leads to weak coordinating capacity of N(2)-atom. There is no interaction between Ag—Ag (distance is 0.3919 nm).[12] The six-membered ring, two molecules **1** and two molecules **2** form a big plane. Two molecules **2** lie on both sides of the big plane, respectively. The dihedral angle of benzotriazole plane of **2** and the big plane is zero. Bond lengths of all of five-membered heterocycles in complex **3** are slightly shorter than those in **1** and **2**, and bond angles also have some changes. The second noteworthy structural feature of complex **3** is the π-π stacking interaction between two adjacent big planes, which forms the two-dimentional layer structure, and all of these interaction distance are 0.26536 nm (Table 2).[11]

In addition, compound **1** has a very weak luminescence, while luminescent intensity of compound **2** shows an obvious enhancement. The reason is that π-electron system containing N-atoms in compound **2** has different dipole moments in its ground and lowest energy single excited states from compound **1** due to the effect of hydroxyl group. The luminescent intensity of complex **3** is larger than that of **2** (*ca.* 1.1-fold) (Fig. 3). The emission enhancement can be attributed to the electron withdrawing

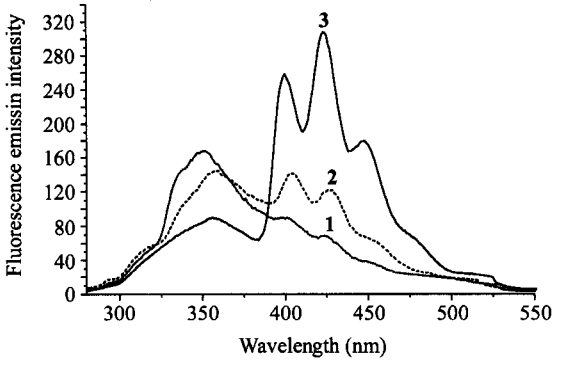


Fig. 3 Emission spectra of compounds **1**, **2** and complex **3** at 298 K upon excitation at 256 nm in CH_2Cl_2(**1**: 5.0×10^{-6} mol/L, **2**: 5.0×10^{-6} mol/L, **3**: 1.25×10^{-6} mol/L).

effect of silver ions to ligands leading to the charge density of π-electron systems lowing.[13]

In contrast with **1** and **2**, in ^{1}H NMR spectra the resonances of **3** slightly shift to the downfield (*ca.* δ 0.2) due to the electron withdrawing effect of silver(I). For compound **1**, ^{1}H NMR ($CDCl_3$) δ: 11.50 (s, 1H, NH), 7.91 (dd, J = 6.2, 2.8 Hz, 2H, ArH), 7.43 (dd, J = 6.2, 6.0 Hz, 2H, ArH).

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