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Preparation and Crystal Structure Determination of Zinc(II)bromide Complexes at the Presence of Various Ligands



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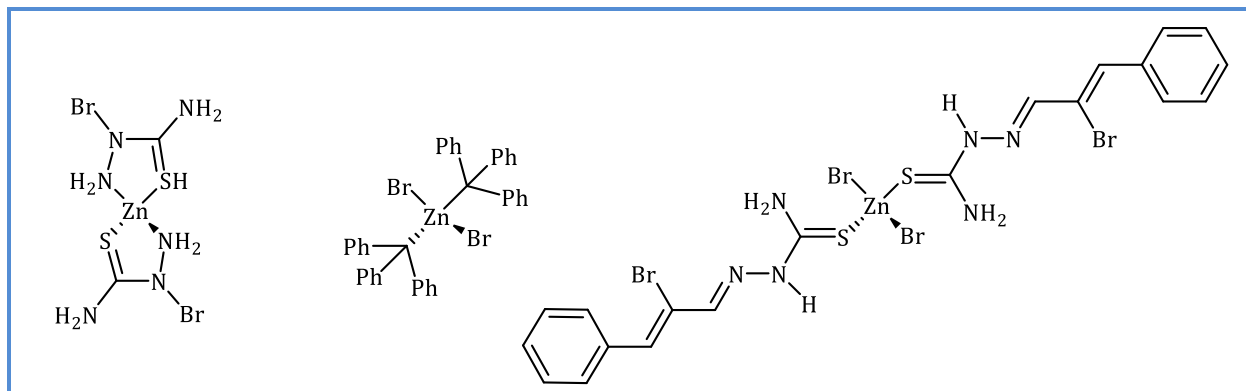
Distorted tetrahedral

ABSTRACT

In this paper, we report the syntheses and crystal structure determination of three mononuclear and four-coordinated zinc (II) bromide complexes with chemical formula of $[Zn(tsc)_2]Br_2$ (**1**), $Zn(PPh_3)_2Br_2$ (**2**) and $Zn(Brcatsc)Br_2$ (**3**). The synthesized complexes are characterized by elemental analysis (CHN) and their crystal structures are investigated by single crystal X-ray diffraction. In complex 1, the TSC coordinates to the zinc (II) ion as a bidentate ligand *via* N and S atoms. In complex 3, the thiosemicarbazone ligand Brcatsc coordinates to zinc (II) ion as a monodentate ligand *via* S atom. In these complexes, the zinc (II) ion coordinated in a distorted tetrahedral coordination geometry.

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Graphical Abstract



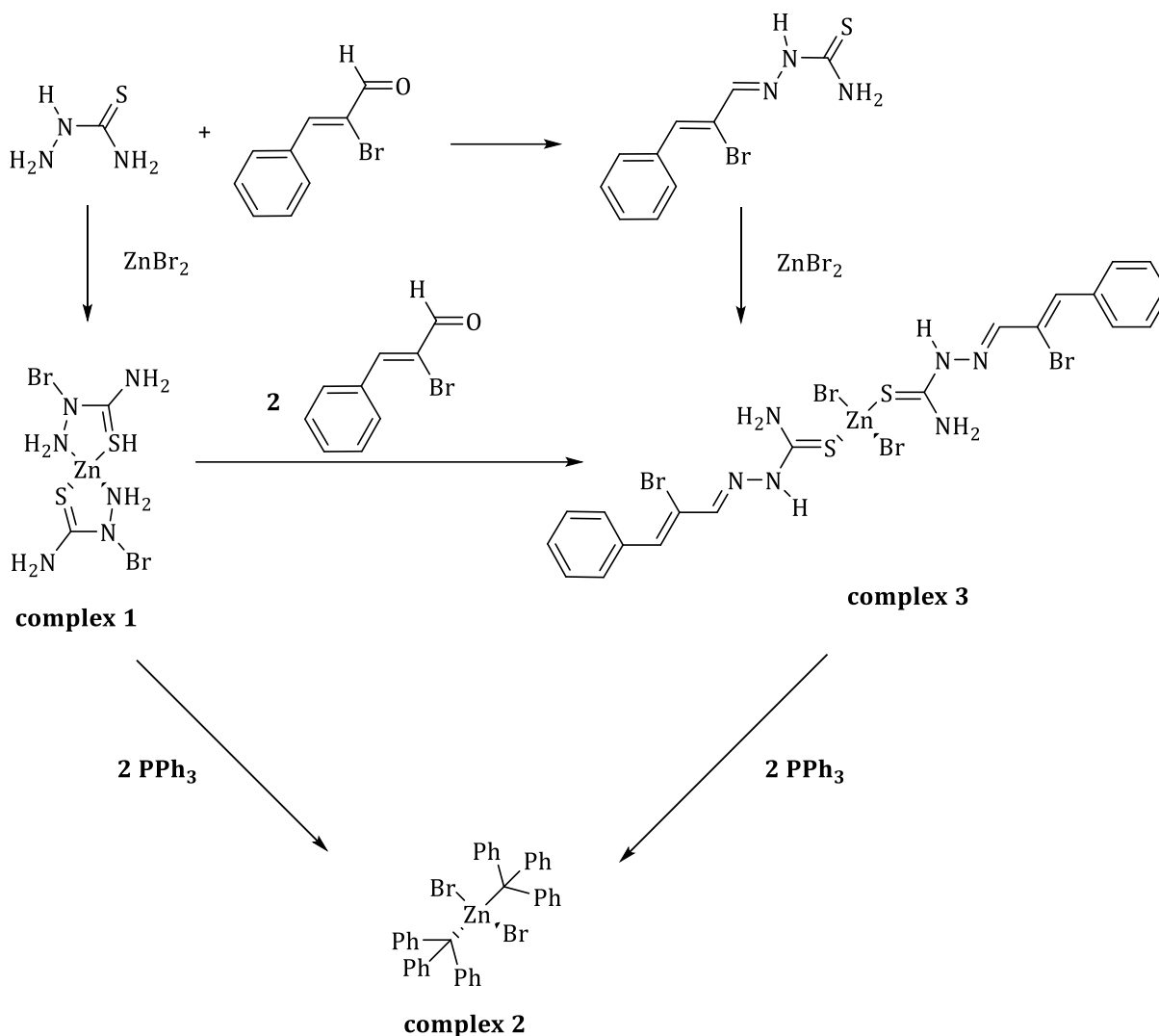
Introduction

The oxidation state of zinc in most complexes is +2 with zinc having an electronic configuration $[Ar] 3d^{10}$. Then, the zinc (II) complexes are generally colorless and adopt highly symmetrical structures [1-3]. Zinc (II) complexes with tetrahedral geometry are found in metallo-enzymes [4]. The complexes of zinc (II) are kinetically labile because the Zn-ligand bonds exchange with other ligands rapidly. The most common structure of zinc (II) complexes is tetrahedral [5-8]. The zinc (II) ion forms stronger complexes with oxygen or nitrogen donor atoms [5-8] than sulfur or phosphorus [9, 10]. Recently, preparation of zinc (II) complexes have received considerable attention because of their various applications and properties such as photoluminescence [11, 12], fluorescence studies [13], DNA binding [14], catalytic [15, 16] and biological activity [17, 18]. In continuation of our research on zinc (II) complexes [6-10], in this paper we report on the syntheses and crystal structures of three mononuclear zinc (II) complexes $[Zn(tsc)_2]Br_2$ (**1**), $Zn(PPh_3)_2Br_2$ (**2**) and $Zn(Brcatsc)Br_2$ (**3**) (Scheme 1).

Experimental

Materials and measurements

All chemicals such as $ZnBr_2$, PPh_3 , alpha-bromocinnamaldehyde, thiosemicarbazide, ethanol, methanol and acetonitrile were provided from the Merck and/or Aldrich chemical companies in high purity and used as received without purification. The thiosemicarbazone ligand Brcatsc was freshly prepared according to our previous report [19]. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer.



Scheme 1. Chemical structures and the procedure for the preparation of complexes 1-3

Synthesis of complex 1

The methanolic solution of thiosemicarbazid (2 mmol) was added to an acetonitrilic solution of ZnBr₂ (1 mmol) and stirred for 0.5 h until the color less clear solution was obtained. The solution was left at -4 °C for several days. The suitable crystals were filtered and washed twice with acetonitrile, and dried at room temperature. *Anal. calcd.* for C₂H₈Br₂N₆S₂Zn₁: C, 5.92; H, 1.97; N, 20.72; S, 15.79%. *Found:* C, 5.87; H, 2.01; N, 20.68; S, 15.85%.

Synthesis of complexes 2 and 3

For the synthesis of the zinc complexes 2 and 3, the fresh ligand solution (2 mmol), PPh₃ for 2 and Brcatsc for 3, was gradually added to complex 1 (1 mmol) in acetonitrile and the mixture was

stirred about 0.5 h at room temperature until the color less clear solution was obtained. The solution was left at -4 °C for several days. The suitable crystals were filtered and washed twice with acetonitrile, and dried at room temperature.

Anal. calcd. for $C_{72}H_{60}Br_4P_4Zn_2$ (**2**): C, 57.62; H, 4.00%. Found: C, 57.68; H, 4.02%.

Anal. calcd. for $C_{20}H_{20}Br_4N_6S_2Zn_1$ (**3**): C, 30.25; H, 2.52; N, 10.59; S, 8.07%. Found: C, 30.28; H, 2.55; N, 10.67; S, 7.99%.

X-ray crystallography

Single crystals of **1**, **2** and **3** were chosen for X-ray diffraction study. Crystallographic measurements were done with four circle CCD diffractometer gemini of oxford diffraction, Ltd., with mirrors-collimated Cu-K α radiation. Crystal structure were solved by charge flipping with program superflip [20] and refined with the Jana 2006 program package [21], by full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by diamond 4.0 [22]. All hydrogen atoms were discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice H atoms bonded to C were kept in ideal positions with C-H = 0.96 Å, $U_{iso}(H)$ was set to 1.2 $U_{eq}(C)$. All non-hydrogen atoms were refined using harmonic refinement. For disordered lattice water molecules hydrogen atoms could not be determined. Crystallographic data, details of the data collection, structure solution and refinements are listed in Table 1.

Table 1. Crystallographic data and structural refinement details

	1	2	3
Chemical formula	$C_2H_8Br_2N_6S_2Zn_1$	$C_{72}H_{60}Br_4P_4Zn_2^*$	$C_{20}H_{20}Br_4N_6S_2Zn_1$
Formula weight	405.4	1499.5	793.5
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$C2/c$	$Pca2_1$	$P2_1/c$
$a, \text{Å}$	11.3735 (7)	17.6227 (5)	15.3619 (6)
$b, \text{Å}$	8.2622 (6)	10.1159 (4)	12.1504 (3)
$c, \text{Å}$	12.3667 (6)	36.1386 (13)	14.7313 (6)
β, deg	97.227 (4)	90**	106.638 (3)
$V, \text{Å}^3$	1152.87 (12)	6442.4 (4)	2634.53 (17)
μ, mm^{-1}	14.24	5.08	10.08
Z	4	4	4
S	1.04	1.05	1.63
R_{int}	0.046	0.091	0.027
Measured reflections	2920	44432	7915
Measured independent	1007	11088	4465
Reflections with $I > 3\sigma(I)$	852	8287	3723
Parameters	72	739	316
$R(F^2 > 2\sigma(F^2))$	0.026	0.041	0.038
$wR(F^2)$	0.032	0.089	0.047
$\Delta\rho_{max}$	0.59	0.53	2.05
$\Delta\rho_{min}$	-0.55	-0.42	-0.77

Results and Discussion

An elemental analysis is shown in the experimental section. There is a good agreement between experimental and theoretical results. Colorless crystals of the complexes were very stable at the solid state. From the reaction of TSC and ZnBr_2 results in monomeric complex $[\text{Zn}(\text{tsc})_2]\text{Br}_2$ (**1**). Single crystals of complexes **2** and **3** were prepared by the reaction of ligand (PPh_3 or Brcatsc) with complex **1**. The formation of complexes is shown in Scheme 1.

Figure 1 shows a molecular structure of **1** with the numbering scheme. The zinc (II) ion in **1** is four coordinated by two nitrogen and two sulfur atoms from two thiosemicarbazide molecules and geometry around it is distorted tetrahedral. Bond distances and angle of **1** are presented in Table 2. The bond distance $\text{Zn1-S1} = 2.2799(11) \text{ \AA}$ is larger than the bond distance $\text{Zn1-N2} = 2.063(4) \text{ \AA}$, confirming the distortion from a regular tetrahedron. The bond distance $\text{S1-C1} = 1.718 \text{ \AA}$ is larger than the similar bond in the free thiosemicarbazone ligand Brcatsc [19], indicating the coordination of the S atom to the zinc (II) ion in **1**. Also, the deviation from 109.5° by the chelate bond angle $\text{S1-Zn1-N2} = 113.42(11)^\circ$ and other bond angles (see Table 1) confirmed the distorted from tetrahedral geometry in **1**.

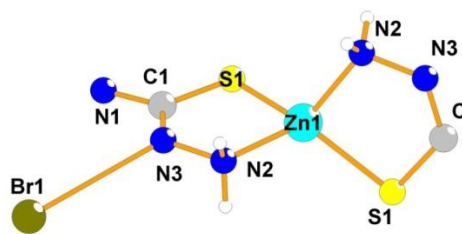


Figure 1. An ORTEP view of **1**

Table 2. Bond distances (in \AA) and angles (in deg) of **1**

Br1 N3	3.266(4)	Zn1 N2	2.063(4)
Zn1 S1	2.2799(11)	S1 C1	1.718(4)
N1 C1	1.319(5)	N3 C1	1.335(6)
N2 N3	1.413(5)		
S1 Zn1 S1	136.87(5)	S1 Zn1 N2	88.79(11)
S1 Zn1 N2	113.42(11)	N2 Zn1 N2	118.42(17)
Zn1 S1 C1	94.42(14)	Zn1 N2 N3	111.1(3)
Br1 N3 N2	116.9(3)	Br1 N3 C1	119.4(3)
N2 N3 C1	121.4(4)	S1 C1 N1	119.0(3)
S1 C1 N3	124.1(3)	N1 C1 N3	116.8(4)

Figure 2 shows a molecular structure of **2** with the numbering Scheme. Selected bond distances and angles of **2** are presented in Table 3. Figure 2 shows that the zinc (II) ion in **2** is four coordinated by two P atoms from two triphenylphosphine (PPh_3) molecules and two Br atoms. The unit cell of **2**

contains two crystallographic independent moieties. The coordination number of the zinc (II) ion in **2** is four with a distorted tetrahedral ZnBr₂P₂ coordination environment. The average bond distances of Zn1-P = 2.45 and Zn2-P = 2.46 Å is larger than the average bond distance Zn-Br = 2.39 Å. The deviation from 109.5° by bond angles Br-Zn-Br, Br-Zn-P and P-Zn-P (see Table 3) confirmed the distortion from tetrahedral geometry in **2**.

Table 3. Bond distances (in Å) and angles (in deg) of **2**

Br1 Zn1	2.3871(11)	Br4 Zn2	2.3796(12)
Br3 Zn1	2.3893(10)	Br2 Zn2	2.3958(10)
Zn1 P3	2.4442(19)	Zn2 P1	2.4665(19)
Zn1 P4	2.4420(17)	Zn2 P2	2.4376(17)
Br1 Zn1 Br3	114.65(4)	Br2 Zn2 Br4	113.73(4)
Br1 Zn1 P3	109.76(6)	Br2 Zn2 P1	111.67(5)
Br1 Zn1 P4	105.93(5)	Br2 Zn2 P2	103.21(5)
Br3 Zn1 P3	112.71(5)	Br4 Zn2 P1	113.09(6)
Br3 Zn1 P4	104.10(5)	Br4 Zn2 P2	105.06(5)
P3 Zn1 P4	109.19(6)	P1 Zn2 P2	109.29(6)

An ORTEP view of **3** is shown in Figure 3. Selected bond distances and angles of **3** are collected in Table 4. The coordination sphere around the zinc (II) ion in **3** is well described as four coordinated distorted tetrahedral with two sulfur atoms from two Brcatsc ligands and two Br atoms bonded to zinc. In this complex, each ligand remains in the same form as the free ligand [19] and are in Z position. The bond distances of Zn1-S1 = 2.3583(16) and Zn1-S2 = 2.3419(17) Å are smaller than the bond Zn1-Br3 = 2.3756 (9) and Zn1-Br4 = 2.4118(10) Å. The deviation from 109.5° by bond angles Br-Zn-Br, Br-Zn-P and P-Zn-P (see Table 4) confirmed the distortion from tetrahedral geometry in **2**.

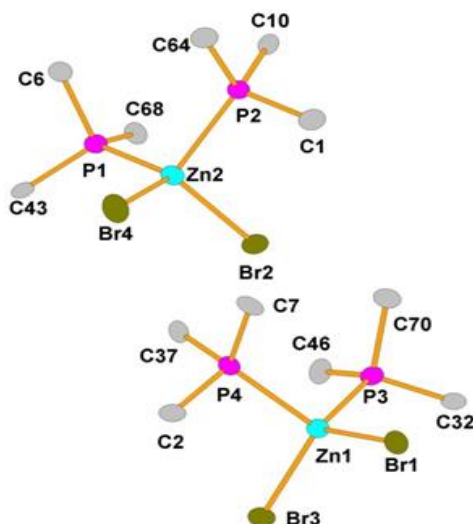
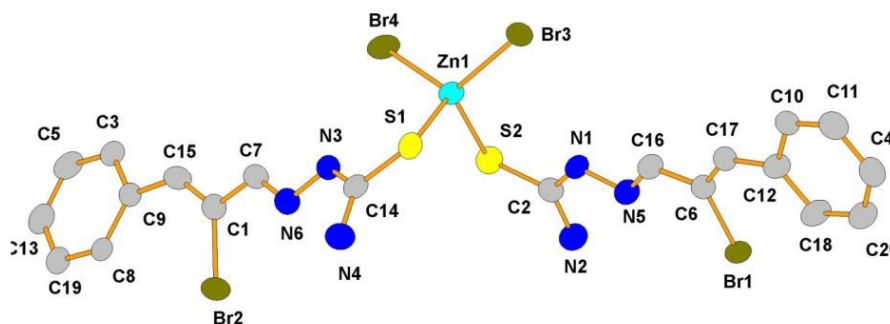


Figure 2. An ORTEP view of two independent molecules of **2**. For clarity other carbon atoms of aromatic rings are omitted

Table 4. Selected bond distances (in Å) and angles (in deg) of **3**

Br3 Zn1	2.3756(9)	Br4 Zn1	2.4118(10)
Zn1 S1	2.3583(16)	Zn1 S2	2.3419(17)
S1 C14	1.720(6)	S2 C2	1.714(6)
N1 N5	1.373(6)	N1 C2	1.330(8)
N2 C2	1.312(8)	N3 N6	1.374(6)
N3 C14	1.324(8)	N4 C14	1.310(8)
N5 C16	1.268(8)	N6 C7	1.276(8)
Br3 Zn1 Br4	118.88(3)	Br3 Zn1 S1	100.72(5)
Br3 Zn1 S2	116.41(4)	Br4 Zn1 S1	115.82(4)
Br4 Zn1 S2	97.18(5)	S1 Zn1 S2	108.20(6)
Zn1 S1 C14	105.1(2)	Zn1 S2 C2	108.4(2)
N5 N1 C2	118.6(5)	N6 N3 C14	119.8(5)
N1 N5 C16	115.1(5)	S2 C2 N1	121.6(4)
S2 C2 N2	119.8(5)	N1 C2 N2	118.7(5)
N6 C7 C1	122.8(5)	S1 C14 N3	120.0(4)
S1 C14 N4	121.2(5)	N3 C14 N4	118.8(5)
N5 C16 C6	123.0(5)		

**Figure 3.** An ORTEP view of **3**. For clarity other carbon atoms of aromatic rings are omitted

In the crystal packing of **3**, there are two intermolecular interactions of N2 H1n2...N5 (Table 5). These N-H...N hydrogen bonding interactions are contributing to the additional stability of **3**.

Table 5. Intermolecular interaction of **3**

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N2 H1n2...N5	0.85(5)	2.20(6)	2.617(8)	110(6)
N4 H1n4...N6	0.85(5)	2.23(7)	2.641(8)	110(6)

Conclusions

Three new mononuclear zinc (II) complexes have been synthesized and characterized by elemental analysis and X-ray crystal structure analysis. Single crystal structure determination shows that the

central zinc (II) ion coordinates only with two atoms (S/N), (P/Br), (S/Br) and the zinc (II) ion adopts a distorted tetrahedral geometry.

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