



Research Article

Synthesis, Structural Characterization, and Catalytic Property of A Zn(II) Complex with 5-Bromosalicylaldehyde Ligand

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Abstract

The study on catalytic activity of complex materials has been one of the hot spots in coordination chemistry. In order to extensively study the catalytic activity of complexes, a new six-coordination Zn(II) complex material, $[\text{ZnL}_2(\text{H}_2\text{O})_2]$ (C1) (HL = 5-bromosalicylaldehyde), has been prepared with 5-bromosalicylaldehyde, NaOH, and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ as raw materials. The structure of C1 was determined by elemental analysis, IR spectra, and single crystal X-ray diffraction. The Zn(II) complex shows a moderate catalytic activity for A^3 coupling reaction of benzaldehyde, piperidine, and phenylacetylene with the benzaldehyde conversion reached 54.6 %. Furthermore, the Zn(II) complex catalyst exhibited 54.8 %, 53.8 %, and 54.4 % conversions of benzaldehyde in the second, third, and fourth cycles, respectively. In addition, the Zn(II) complex features a selectivity of 100 % to the product of propargylamine for the A^3 coupling reaction. Copyright © 2017 BCREC Group. All rights reserved

Keywords: Zn(II) complex material; Synthesis; Structural characterization; Catalytic property; Ligand

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1. Introduction

Propargylamines are versatile synthetic intermediates in organic synthesis and are also important structural elements in natural products and therapeutic drug molecules, and are used for the synthesis of polyfunctional amino derivatives [1-3]. They were synthesized by three component coupling reaction (A^3 coupling) of aldehydes, alkynes and amines [4-6]. How-

ever, the traditionally catalysts used in the synthesis of propargylamines require very harsh reaction conditions, for example, they must be used in stoichiometric amounts, are highly moisture sensitive, and require strictly controlled reaction conditions [7].

In recent years, many chemists have been working on synthetic catalysts which could be used in mild condition. Therefore, different transition metals have been used as the catalysts for these reactions, such as: gold [4], silver [5], zinc [8], copper [9], and nickel [10]. Metal complex materials have also attracted attention

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due to their catalytic activity for many reactions [11-16]. Studies on the synthesis and catalytic activity of metal complexes have been the goal of our research group [17,18]. Herein, in this paper, a new six-coordination Zn(II) complex material was synthesized and characterized by elemental analysis, IR spectra and single crystal X-ray diffraction. The catalytic activity for A³ coupling reaction has also been investigated with Zn(II) complex as the catalysts.

2. Experimental

2.1 Materials and measurements

The analytical grade reagents used in this experimental works were: 5-bromosalicylaldehyde, Zn(CH₃COO)₂·2H₂O, NaOH, benzaldehyde, piperidine, phenylacetylene, and 1,4-dioxane. Elemental analyses (C, H, and N) were measured on an Elementar Vario III EL Elemental Analyzer. IR spectra were measured on a Nicolet AVATAR 360 infrared spectrometer in the 4000-400 cm⁻¹ region. The structural data of [ZnL₂(H₂O)₂] were collected by a Bruker Amart CCD diffractometer.

2.2 Synthesis of [ZnL₂(H₂O)₂] (C1)

Ten mL ethanol solution of 5-bromosalicylaldehyde (1.0 mmol, 0.2010 g) and NaOH (1.0 mmol, 0.040 g) was added to the solution of 5 mL ethanol/water (v:v = 1:1) containing Zn(CH₃COO)₂·2H₂O (0.5 mmol, 0.1097 g). The mixture turned light yellow transparent solution. Then, the mixture was heated to 60 °C and maintained at this temperature for 5 h while stirring. Light yellow crystals of [ZnL₂(H₂O)₂] was achieved by slowly evaporating the filtrate at room temperature (yield ca. 82 % based on Zn(CH₃COO)₂·2H₂O).

2.3 X-ray crystallography

The single crystal data of [ZnL₂(H₂O)₂] (C1) with dimensions of 0.22 mm × 0.19 mm × 0.18 mm was collected on a Bruker Smart CCD diffractometer at 293 K with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073$ Å). In the range of $3.03 < \theta < 25.01$, a total of 12283 reflections were collected and 5532 were independent with $R_{\text{int}} = 0.1099$, of which 2136 were observed with $I > 2\sigma(I)$. The structure was solved by direct methods with SHELXS-97 [19] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [20].

2.4 General procedure for the three-component coupling reaction (A³)

Typical procedure for the three-component (A³) coupling reaction: a mixture of benzaldehyde (0.125 mmol, 0.014 g), phenylacetylene (0.165 mmol, 0.017 g), piperidine (0.150 mmol, 0.013 g), and Zn(II) complex catalyst (0.070 g) were added into 1,4-dioxane (1.500 g). The reaction mixtures were put into a closed glass reactor (8 mL) and were extensively stirred at 120 °C for 12 h. At the end of each catalytic A³ coupling reaction, the catalysts were isolated by centrifugation from the reaction solution, dried at 50 °C under vacuum for 5 h, and then reused in the next run of each reaction. The products were analyzed using a gas chromatograph (GC-1100) equipped with a SE-54 capillary column and a hydrogen flame detector.

3. Results and Discussion

3.1 EA and IR spectra of [ZnL₂(H₂O)₂] (C1)

The IR spectra of [ZnL₂(H₂O)₂] (C1) is given in Figure 1. The IR spectrum of 5-bromosalicylaldehyde showing strong absorption band at 1672 cm⁻¹ may be assigned to the characteristic band of -C(O)- of 5-bromosalicylaldehyde. In [ZnL₂(H₂O)₂] (C1), the characteristic band of -C(O)- appears at 1631 cm⁻¹, which indicating that the O atom of -C(O)- coordinates to the Zn(II) ion. Besides, the band at 3443 cm⁻¹ shows that the Zn(II) complex containing water molecules [21]. The IR results show that [ZnL₂(H₂O)₂] (C1) is formed, which is consistent with element and X-ray single crystal analysis. Elemental analysis calculated for C₁₄H₁₂Br₂O₆Zn (%) is C, 33.50; and H, 2.39. Meanwhile, found elemental analysis (%) is: C, 33.26; and H, 2.49.

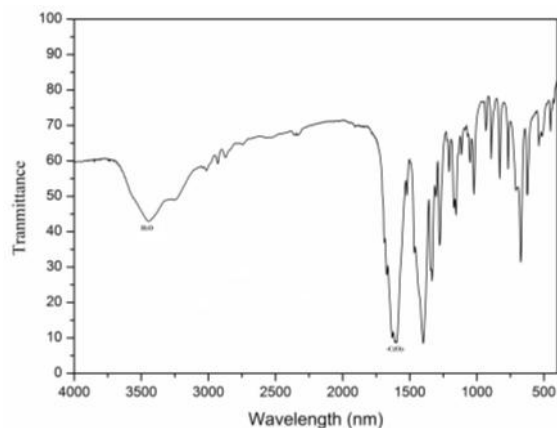


Figure 1. IR spectra of 5-bromosalicylaldehyde and [ZnL₂(H₂O)₂] (C1)

The selected IR bands (KBr) were: 3443 cm⁻¹ (H₂O), 1631 cm⁻¹ (–C(O)–).

3.2 Structural description of [ZnL₂(H₂O)₂] (C1)

Structural analysis suggests that the Zn(II) complex (C1) crystallizes in triclinic *P*-1 space group. The coordination environment of Zn(II) center in C1 is shown in Figure 2. The selected bond distances and angles of complex C1 are listed in Table 2. The Zn(II) complex (C1) consists of a Zn(II) ions, two 5-bromosalicylaldehyde ligands with losing of

proton, and two coordinated water molecules. The Zn(II) ion in C1 is surrounded by four O atoms from two 5-bromosalicylaldehyde ligands and O atoms from two coordinated water molecules, which resulting in a distorted octahedral coordination environment (Figure 3). The four coordinated O atoms of O1, O2, O3 and O4 from 5-bromosalicylaldehyde ligands are in the equatorial plane and the two coordinated O atoms of O1W and O2W from coordinated water molecules are situated axial place. The Zn–O bond distances range from 2.011(8) Å to 2.190(7) Å, which are closed to those of

Table 1. Crystal data and refinement details for C1

Empirical formula	C ₁₄ H ₁₂ ZnBr ₂ O ₆
Formula weight	501.43
Temperature/K	293(2)
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	9.5560(19)
<i>b</i> /Å	12.588(3)
<i>c</i> /Å	14.945(3)
<i>α</i> /°	98.53(3)
<i>β</i> /°	99.11(3)
<i>γ</i> /°	112.29(3)
Volume/Å ³	1599.1(6)
<i>Z</i>	4
ρ_{calc} /mg/mm ³	2.083
μ /mm ⁻¹	6.559
<i>S</i>	1.049
<i>F</i> (000)	976
Index ranges	-11 ≤ <i>h</i> ≤ 11, -14 ≤ <i>k</i> ≤ 14, -17 ≤ <i>l</i> ≤ 17
Reflections collected	12283
Independent reflections	5532 [<i>R</i> (int) = 0.1099]
Data/restraints/parameters	5532/0/418
Goodness-of-fit on <i>F</i> ²	1.049
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.2382, <i>wR</i> ₂ = 0.1992
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1236, <i>wR</i> ₂ = 0.0818

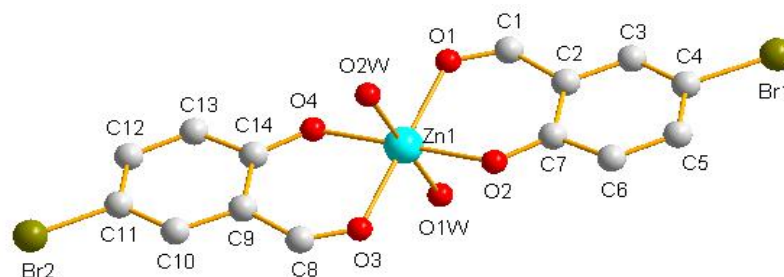


Figure 2. Coordination environment of Zn(II) center in C1

Zn(II) complexes [22]. The distances of C1-O1 and C14-O4 are longer than those of C7-O2 and C8-O3, which suggest that C1-O1 and C14-O4 are double bonds. In the complex **C1**, two six-member rings were formed by the coordinated effect of Zn(II) ion with O1, O2, O3 and O4 atoms, and the dihedral angle between the ring 1 (C8-C9-C14-O4-Zn1-O3) and ring 2 (C1-C2-C7-O2-Zn1-O1) is 0.6 (3)°. The 1D chained structure was formed through the effect of O–H···O hydrogen bonds between the adjacent **C1** molecules (Figure 4). The perspective view of stacking is shown in Figure 5. Main crystal data and refinement details of **C1** are listed in Table 1.

3.3 Catalytic studies

The catalytic activity of Zn(II) complex catalyst was tested for A³ coupling reaction of benzaldehyde, piperidine, and phenylacetylene with 1,4-dioxane as a solvent. The results are summarized in Table 3. The Zn(II) complex catalyst shows a moderate catalytic activity, and the benzaldehyde conversion reached 54.6 % for 12 h at 120 °C. Furthermore, the Zn(II) complex catalyst exhibited 54.8 %, 53.8 %, and 54.4 % conversions of benzaldehyde at 120 °C for 12 h in the second, third, and fourth cycles, respectively. The Zn(II) complex catalyst could be recovered easily by centrifugation and re-

Table 2. The selected important bond parameters of complex **C1**

Bond	Distance(Å)	Angle	(°)
Zn1-O1	2.118(8)	O4-Zn1-O2	179.4(4)
zn1-O4	2.011(8)	O4-Zn1-O3	87.4(3)
Zn1-O2	2.023(8)	O2-Zn1-O3	92.1(3)
Zn1-O3	2.104(8)	O4-zn1-O1	92.8(3)
Zn1-O1W	2.179(6)	O1-Zn1-O2	87.7(3)
Zn1-O2W	2.190(7)	O1-Zn1-O3	179.7(4)
		O4-Zn1-O1W	89.7(3)
		O2-Zn1-O1W	90.6(3)
		O3-Zn1-O1W	93.2(3)
		O1-Zn1-O1W	87.0(3)
		O4-Zn1-O2W	90.8(3)
		O2-Zn1-O2W	88.9(3)
		O3-Zn1-O2W	87.2(3)
		O1-Zn1-O2W	92.6(3)
		O2-Zn1-O2W	179.4(4)

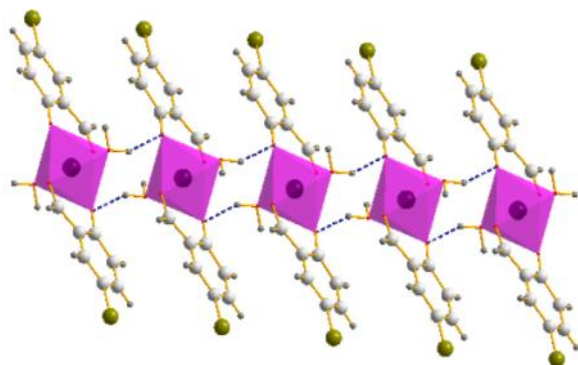


Figure 3. Coordination polyhedra of Zn(II) complex **C1**

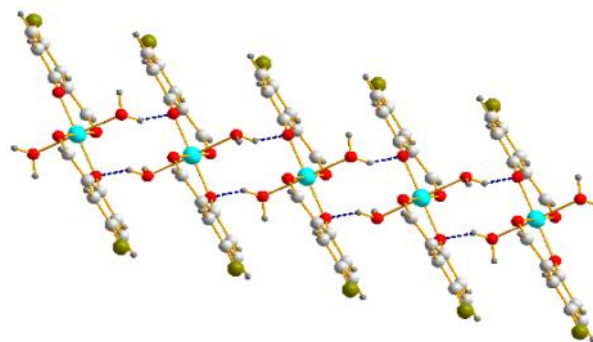


Figure 4. The H-Bonds interaction in Zn(II) complex **C1**

used up to four times without any decrease in catalytic activity. It means that an active site is a part of the Zn(II) complex catalyst and is not reduced. Moreover, the Zn(II) complex catalyst features a selectivity of 100% to the product of propargylamine for the A³ coupling reaction. These features render the catalysts of Zn(II) complex particularly attractive in the practice of propargylamines synthesis in an environmentally friendly manner.

4. Conclusions

In summary, a new Zn(II) complex material has been prepared, and its structure was determined by elemental analysis, IR spectra, and single crystal X-ray diffraction. It was shown that this Zn(II) complex can catalyze the A³ coupling reaction of benzaldehyde, piperidine, and phenylacetylene with a moderate catalytic activity.

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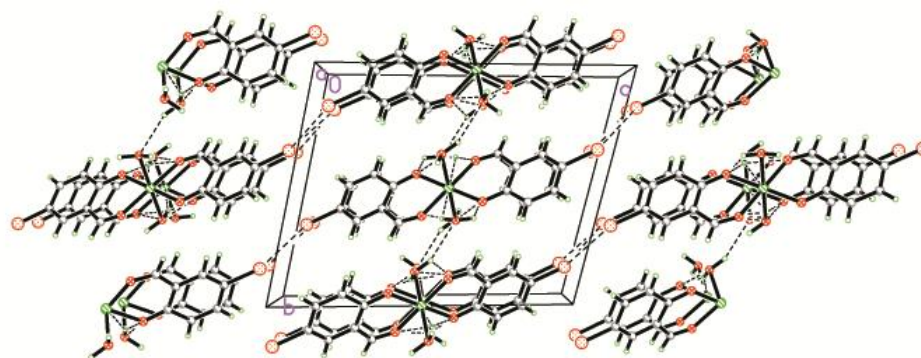


Figure 5. The perspective view of stacking of Zn(II) complex C1

Table 3. Coupling of benzaldehyde, piperidine, and phenylacetylene catalyzed by Zn(II) complex catalyst in dioxane^[a]

Run	Catalyst	Solvent	Temperature (°C)	Time (h)	Conv. (%)
1	Zn(II) complex	1,4-dioxane	120	12	54.6
2	Zn(II) complex	1,4-dioxane	120	12	54.8
3	Zn(II) complex	1,4-dioxane	120	12	53.8
4	Zn(II) complex	1,4-dioxane	120	12	54.4

^[a] Reaction conditions: aldehyde (0.125 mmol), amine (0.17 mmol), alkyne (0.15 mmol), catalyst (70 mg), dioxane (1.500 g)

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