



Research Article

Preparation, Characterization, and Catalytic Property of a Cu(II) Complex with 2-Carboxybenzaldehyde-*p*-Toluenesulfonyl Hydrazone Ligand

Xi-Shi Tai¹, Peng-Fei Li², Li-Li Liu^{1*}

¹College of Chemistry and Chemical Engineering, Weifang University, Weifang 261061, P.R. China

²College of Chemical Engineering, Qingdao University of Science and Technology, Qingdao 266061, P.R. China

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Abstract

Metal-organic complex hybrid materials constructed from carboxylate ligands and hydrazone ligands have exhibited potential application in many fields. In order to enrich the applications of the metal-organic complex materials, a new hydrazone ligand contains carboxylate group, 2-carboxybenzaldehyde-*p*-toluenesulfonyl hydrazone (L1), and its Cu(II) complex (C2), have been prepared. The structure of L1 was determined by elemental analysis, IR spectra and single crystal X-ray diffraction, and the composition of Cu(II) complex (C2) has also been determined by elemental analysis, IR and UV spectra. The catalytic activity for A³ coupling reaction of benzaldehyde, piperidine, and phenylacetylene has been investigated. The results show that Cu(II) complex displays a 100 % selectivity to the product of propargylamine during A³ coupling reaction and benzaldehyde conversions were 95.3, 94.2, and 93.4 % at 120 °C for 12 h in the first, second, and third reaction cycles, respectively. Copyright © 2018 BCREC Group. All rights reserved

Keywords: Hydrazone ligand; Cu(II) complex material; Catalyst preparation and characterization; Catalytic property

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1. Introduction

Metal-organic complex hybrid materials constructed from carboxylate ligands, and hydrazone ligands have exhibited potential application in many fields. For example, they have been widely exploited for luminescence [1-4], antitumor [5-8], antibacterial [9-12], gas storage [13], as well as magnetic [14-17]. Meanwhile, metal complex materials have also been

attracted interests due to their excellent catalytic activities for many organic reactions [18-22].

However, to the best of our knowledge, the studies on the three component coupling reaction (A³ coupling) of aldehydes, alkynes and amines with Cu(II) complexes as catalysts are relatively few. Therefore, the investigation on catalytic activity for three component coupling reaction (A³ coupling) of aldehydes, alkynes and amines with metal complexes as catalysts has been the goal of our research group [23-25].

* Corresponding Author.

E-mail: taixs@wfu.edu.cn (Tai, X.S.)

Telp.: +86-536-8785363; Fax.: +86-536-8785363

Herein, in this paper, we have synthesized a new hydrazone ligand named 2-carboxybenzaldehyde-*p*-toluenesulfonyl hydrazone (**L1**), and its Cu(II) complex (**C2**). Cu(II) complex (**C2**) catalyst shows better catalytic activity for three component coupling reaction (A^3 coupling) of benzaldehyde, piperidine, and phenylacetylene with the benzaldehyde conversion reached 95.3 %. Interestingly, Cu(II) complex catalyst (**C2**) is very stable because the catalytic efficiency remained above 93.4 % after four cycles. This study was significant for the further study of Cu(II) complex catalyst. The simple flow charts for synthesis procedure of **L1** and **C2** are shown in Figure 1.

2. Materials and Method

2.1 Materials and measurements

All chemical reagents were analytical grade. 2-Carboxybenzaldehyde, *p*-toluenesulfonyl hydrazine, $Cu(CH_3COO)_2 \cdot H_2O$, and NaOH were ordered from Xiya reagent, while phenylacetylene, piperidine, benzaldehyde, and 1,4-dioxane were ordered from Alfa Aesar. Elemental analyses (C, H, and N) were analyzed on an Elementar Vario III EL Elemental Analyzer. IR spectra in the 4000-400 cm^{-1} region were carried out on a Nicolet AVATAR 360 infrared spectrometer. The crystal data of 2-carboxybenzaldehyde-*p*-toluenesulfonyl hydrazone (**L1**) were collected by a Bruker Smart CCD diffractometer.

2.2 Synthesis of 2-Carboxybenzaldehyde-*p*-toluenesulfonyl hydrazone (**L1**)

The 2-Carboxybenzaldehyde (0.1501 g, 1.0 mmol) in ethanol solution (10 mL) was added to the ethanol solution (10 mL) containing *p*-toluenesulfonyl hydrazine (0.1862 g, 1.0 mmol). The mixture was refluxed for 6 h with stirring, and then cooled to room temperature. The crystals of 2-carboxybenzaldehyde-*p*-

toluenesulfonyl hydrazone (**L1**) were obtained by slowly evaporating the filtrate at room temperature. Elemental analysis calculated for $C_{15}H_{14}N_2O_4S$ (%) were C, 56.54; H, 4.40; N, 8.80. Found (%): C, 56.36; H, 4.69; N, 8.91. The selected IR bands (KBr) were: 3439 cm^{-1} ($-NH-$), 1762 cm^{-1} ($-COO-$), 1589 cm^{-1} ($-C=N-$), UV-vis: 278 nm.

2.3 Synthesis of Cu(II) complex (**C2**)

The 2-carboxybenzaldehyde-*p*-toluenesulfonyl hydrazone (**L1**) ligand (1.0 mmol, 0.3183 g) and NaOH (1.0 mmol, 0.040 g) were dissolved in 10 mL ethanol/water (v:v = 2:1) solution. The $Cu(CH_3COO)_2 \cdot H_2O$ (0.5 mmol, 0.0985 g) was added to the above solution. Then the mixture was stirred at 60 °C for 7 h. The blue precipitation of Cu(II) complex was collected by filtration, purified by washing three times with ethanol and dried for 12 h at 80 °C.

The elemental analyses of C, H, and N were 48.29, 4.40, 7.04 (Calc.), and 48.59, 4.19, 6.91 (Found). The selected IR bands (KBr) were: 3444 cm^{-1} ($H_2O + -NH-$), 1776 cm^{-1} ($-COO-$), 1594 cm^{-1} ($-C=N-$), 1394 cm^{-1} (CH_3COO-), UV-vis: 315 nm.

2.4 X-ray crystallography

The single crystal of 2-carboxybenzaldehyde-*p*-toluenesulfonyl hydrazone (**L1**) (0.22 mm × 0.19 mm × 0.18 mm) was measured on a Bruker Smart CCD diffractometer with graphite-monochromatic Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. The structure was solved by direct methods with SHELXS-97 [26] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [27]. Absorption correction was carried out using semi-empirical methods from equivalents. Crystallographic data and refinement details of **L1** are listed in Table 1.

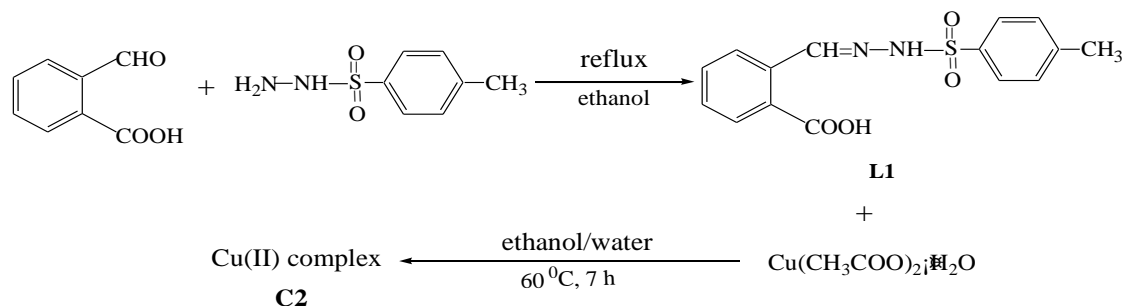


Figure 1. The flow charts for synthesis procedure of **L1** and **C2**

2.5 General procedure for the three component coupling reaction (A³)

The catalytic performance of Cu(II) complex was assessed in the three component coupling reactions (A³) of benzaldehyde, phenylacetylene, and piperidine (Figure 2). In typical, the benzaldehyde (0.13 mmol), phenylacetylene (0.17 mmol), piperidine (0.15 mmol), Cu(II) complex catalyst (40 mg) and 1,4-dioxane (1.5 g) were put in a 8 mL a closed glass reactor (8 mL, Synthware) and the mixture was extensively stirred (ca. 400 rpm) at 120 °C for 12 h. After completion of the reaction, the solid cata-

lyst was removed from the solution by centrifugation at 14000 rpm for 6 minutes. The product was analysed by GC ((GC-1100, capillary column SE-54) using *n*-nonane as the external standard. The conversion and selectivity were calculated by Equations (1) and (2), respectively.

$$C_{\text{benzaldehyde}} = \frac{n_{\text{initial}} - n_{\text{after reaction}}}{n_{\text{initial}}} \times 100\% \quad (1)$$

$$S = \frac{n_{\text{propargylamine}}}{n_{\text{initial}} - n_{\text{after reaction}}} \times 100\% \quad (2)$$

Table 1. Crystallographic data and refinement details for L1

Empirical formula	C ₁₅ H ₁₄ N ₂ O ₄ S
Formula weight	318.35
Temperature/K	293(2)
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	5.7518(12)
<i>b</i> /Å	10.677(2)
<i>c</i> /Å	11.975(2)
<i>α</i> /°	95.80(3)
<i>β</i> /°	93.60(3)
<i>γ</i> /°	95.02(3)
Volume/Å ³	726.9(2)
<i>Z</i>	2
ρ_{calc} /mg/mm ³	1.454
μ /mm ⁻¹	0.243
<i>S</i>	1.09
<i>F</i> (000)	332
Index ranges	-6 ≤ <i>h</i> ≤ 5 ; -12 ≤ <i>k</i> ≤ 12 ; -14 ≤ <i>l</i> ≤ 14
Reflections collected	5648
Independent reflections	2552 [<i>R</i> (int) = 0.0321]
Data/restraints/parameters	2552/0/201
Goodness-of-fit on <i>F</i> ²	1.085
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0489, <i>wR</i> ₂ = 0.1208
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0563, <i>wR</i> ₂ = 0.1269
Largest diff. peak and hole	0.474 and -0.320 e ⁻³ Å ⁻³

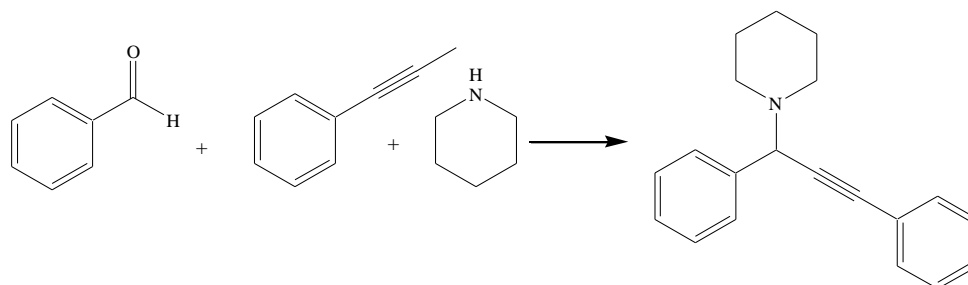


Figure 2. The coupling of benzaldehyde, piperidine and phenylacetylene with 1,4-dioxane as solvent using Cu(II) complex as a catalyst

The recovered catalyst was washed with 1,4-dioxane (3×10 mL), dried under vacuum at 50°C for 6 h, and stored for another consecutive reaction run.

3. Results and Discussion

3.1 FTIR Spectra of Cu(II) complex (C2)

The IR spectrum of Cu(II) complex (C2) is given in Figure 3. The strong absorption band at 3444 cm^{-1} in the IR spectrum of Cu(II) complex (C2) can be assigned to the vibration peaks of $-\text{NH}-$ and $-\text{OH}$, which show that the Cu(II) complex (C2) containing H_2O . The weak vibration peak of $-\text{COO}-$ at 1776 cm^{-1} shows that the oxygen atom of $-\text{COO}-$ coordinates to Cu(II). The characteristic band of $-\text{C}=\text{N}-$ appears at 1594 cm^{-1} , which indicates that the N atom of $-\text{C}=\text{N}-$ does not coordinate to the Cu(II) ion. The strong vibration peak at 1394 cm^{-1} shows that the Cu(II) complex (C2) containing $\text{CH}_3\text{COO}-$, which is consistent with the results of elemental analysis [28].

3.2 Structural description of 2-carboxybenzaldehyde-*p*-toluenesulfonyl hydrazone (L1)

The molecular structure of L1 ligand is

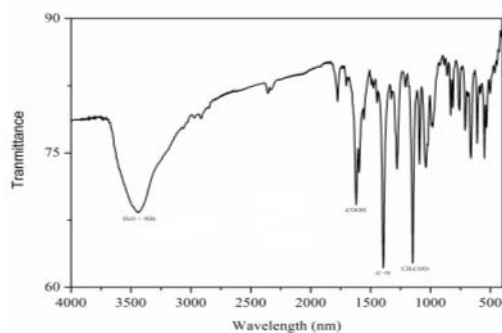


Figure 3. The IR spectra of Cu(II) complex (C2)

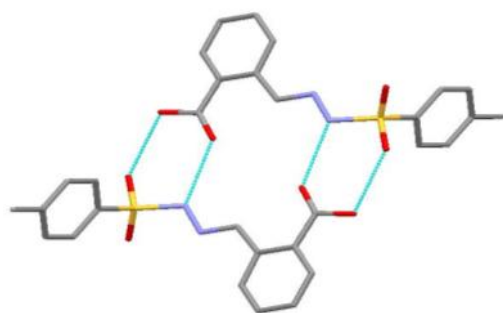


Figure 5. The H-Bonds interaction in L1 ligand

given in Figure 4. The selected bond lengths and bond angles were listed in Table 2. Single crystal analysis reveals that the L1 ligand crystallizes in triclinic $P-1$ space group. The dihedral angle is 81.8° between the plane 1 (C1-C2-C3-C4-C5-C6) and the plane 2 (C9-C10-C11-C12-C13-C14), which showing that the L1 ligand is not coplanar. The bond length of C8-N2 is $1.274(3)\text{ \AA}$, which is consistent with those hydrazone compounds reported in the other Ref. [29], and indicating that C8-N2 bond is double bond. Two L1 molecules form dimeric through $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds (Figure 5). Furthermore, the dimeric forms a one-dimensional chain structure by the interaction of π - π stacking (Figure 6).

3.3 Catalytic studies

The catalytic performance of C2 was assessed in the A^3 coupling reaction of benzaldehyde, phenylacetylene, and piperidine in a 1:1.2:1.3 mole ratio with 1,4-dioxane as a solvent at 120°C . The results of catalytic activity are summarized in Table 3. The C2 exhibited good catalytic activity in the A^3 reaction of benzaldehyde, phenylacetylene, and piperidine at 120°C with 1,4-dioxane as solvent. The conversion of benzaldehyde is 95.2 % at 120°C for 12 h over C2. The C2 could be recycled at least

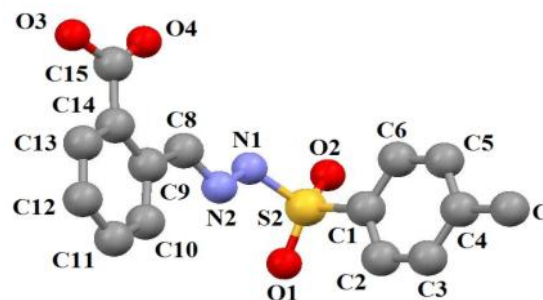


Figure 4. The molecular structure of L1 ligand

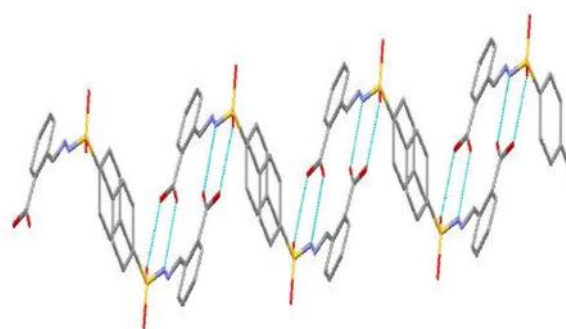


Figure 6. 1D chained structure by the interaction of H-Bonds and π - π stacking

three times, and the catalytic activity decreased slightly. The benzaldehyde conversions were 95.3, 94.2, and 93.4 % at 120 °C within 12 h in the first, second, and third reaction cycles, respectively.

The coordinative unsaturated metal site of Cu(II) of C2 has high stability in the processing of A³ coupling reaction. This could be the reason for the catalyst C2 can be reused at least three times with slight decreased in conversion of benzaldehyde. The C2 displays 100 % selectivity to the product of propargylamines during A³ coupling reaction. Borah *et al.* [30] reported that the yield of propargylamines was 94 % over Cu⁰ nanoparticles catalyst with toluene as solvent at 110 °C for 3 h [30], however, the activity of the catalysts decreased in the successive reuse, the yields were 90 % and 88 % in the second and third cycles. Liu *et al.* [31] reported that the yield of propargylamine reached 97.9 % for 5 h over Au/MIL-53(Al) [31], however, the leaching of gold was unavoidable for the first reuse. The NH₂-MIL-53(Al) supported Au³⁺/Au⁰ gave 58.6 % yield of

propargylamine at 120 °C for 4 h [32]. Copper nanoparticles supported on starch micro particles (CuNPs@MS) gave a yield of 30 % within 20 h at 60 °C for the A³ coupling reaction of benzaldehyde, phenylacetylene, and piperidine in 1,4-dioxane [33]. Although the C2 shows the similar yields/conversions with the catalysts of Cu⁰ nanoparticles catalyst and Au/MIL-53(Al), the C2 catalyst shows higher catalytic activity than Au³⁺/Au⁰ supported on NH₂-MIL-53(Al) and copper nanoparticles supported on starch micro particles.

4. Conclusions

In summary, a new hydrazone ligand, 2-carboxybenzaldehyde-*p*-toluenesulfonyl hydrazone (**L1**), and its Cu(II) complex (**C2**), have been prepared and characterized. The Cu(II) complex (**C2**) catalyst shows better catalytic activity for three component coupling reaction (A³ coupling) of benzaldehyde, piperidine, and phenylacetylene with the benzaldehyde conversion reached 95.3 %. Furthermore, the catalytic

Table 2. The selected t bond parameters of **L1**

Bond	Distance(Å)	Angle	(°)
S2-O1	1.4215(17)	O1-S2-O2	119.43(11)
S2-O2	1.4400(17)	O1-S2-N1	109.84(11)
S2-N1	1.6175(19)	O2-S2-N1	102.82(10)
S2-C1	1.762(2)	O1-S2-C1	108.06(11)
N2-C8	1.274(3)	C1-S2-O2	108.36(11)
N1-N2	1.386(2)	N1-S2-C1	107.77(11)
C15-O4	1.196(3)	N1-N2-C8	114.38(18)
C15-O3	1.324(3)	N2-N1-S2	117.12(14)
		O3-C15-O3	121.0(2)
		O4-C15-C14	125.8(2)
		O3-C15-C14	113.26(19)

Table 3. Coupling of benzaldehyde, phenylacetylene, and piperidine catalyzed by Cu(II) complex in 1,4-dioxane^a

Entry	Solvent	Temperature (°C)	Time (h)	Conversion (%) ^b
Fresh	1,4-dioxane	120	12	95.2%
Run 1	1,4-dioxane	120	12	95.3%
Run 2	1,4-dioxane	120	12	94.2%
Run 3	1,4-dioxane	120	12	93.4%

^aReaction conditions: aldehyde (0.13 mmol), amine (0.17 mmol), alkyne (0.15 mmol), Cu(II) complex (40 mg), dioxane (1.500 g).

^bThe products was determined by GC analysis of the samples (GC-1100, capillary column SE-54) using nonane as the external standard.

activity imply Cu(II) complex catalyst (C2) may be a good candidate for catalytic material.

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