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Research Article

Synthesis, Structural Characterization and Catalytic Activity of A Cu(II) Coordination Polymer Constructed from 1,4-Phenylenediacetic Acid and 2,2'-Bipyridine

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Abstract

In order to study the catalytic activity of Cu(II) coordination polymer material, a novel 1D chained Cu(II) coordination polymer material, [CuL(bipy)(H_2O)$_5$]n (**A1**) (H_2L = 1,4-phenylenediacetic acid, bipy = 2,2'-bipyridine), has been prepared by the reaction of 1,4-phenylenediacetic acid, 2,2'-bipyridine, $Cu(CH_3COO)_2 \cdot H_2O$ and NaOH. The composition of A1 was determined by elemental analysis, IR spectra and single crystal X-ray diffraction. The results of characterization show that each Cu(II) atom adopts six-coordination and forms a distorted octahedral configuration. The catalytic activity and reusability of **A1** catalyst for A^3 coupling reaction of benzaldehyde, piperidine, and phenylacetylene have been investigated. And the results show that the Cu(II) complex catalyst has good catalytic activity with a maximum yield of 54.3% and stability.

Keywords: Cu(II) coordination polymer; Preparation; Structural characterization; Catalytic activity

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1. Introduction

Metal coordination polymer materials have received more attention in recent years, because their novel structures and excellent properties such as catalysis, luminescence, magnetic and biological activity [1-5]. Cu(II) ion and podands containing carboxyl groups were used widely in the design of coordination polymer materials [6-8]. Propargylamines are versatile intermediates for organic synthesis and important structural elements of natural products and potential drug [9-12]. These compounds have traditionally been synthesized by nucleophilic attack of lithium acetylides or Grignard reagents on imines or their derivatives [13,14]. However, these reagents must be used in stoichiometric amounts, are highly moisture sensitive, and require strictly controlled reaction conditions [14]. Therefore, the synthesis of the catalyst used in mild condition is very meaningful. Propargylamines were synthesized by three component one-pot coupling (A^3) reaction of aldehydes, alkynes and amines and the high potential of this reaction motivates many research groups to design new highly active and stable catalysts, mostly based on gold, silver, and copper species [15-20]. In this paper, we report a novel Cu(II) coordination polymer,

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namely, $[CuL(bipy)(H_2O)_5]_n$ (**A1**), which displays a 1D chained structure. The catalytic activity and reusability of Cu(II) complex catalyst for A^3 coupling reaction of benzaldehyde, piperidine, and phenylacetylene have also been investigated.

2. Experimental

2.1. Materials and measurements

The chemical reagents used in this paper are as following: 1,4-phenylenediacetic acid (A.R., Alfa Aesar), 2,2'-bipyridine (A.R., Alfa Aesar), $Cu(CH_3COO)_2 \cdot H_2O$ (A.R., Alfa Aesar), NaOH, benzaldehyde (A.R., Alfa Aesar), piperidine (A.R., Alfa Aesar), phenylacetylene (A.R., Alfa Aesar), and 1,4-dioxane (A.R., Alfa Aesar).

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 crystal data of $[CuL(bipy)(H_2O)_5]_n$ were collected by a Bruker Amart CCD diffractometer.

2.2. Synthesis of $[CuL(bipy)(H_2O)_5]_n$ (A1)

The 0.5 mmol (0.9709 g) 1,4-phenylenediacetic acid was dissolved in 15 mL CH_3CH_2OH/H_2O (v:v = 2:1) containg 1.0 mmol (0.040 g) NaOH. 0.5 mmol (0.9933 g) $Cu(CH_3COO)_2 \cdot H_2O$ solid was added to the above solution, the mixture was refluxed for 1.5 h with stirring. Then 0.5 mmol (0.078 g) 2,2'-bipyridine was added, and the reaction mixture was continuously refluxed for 3.5 h with stirring. The light blue product was collected by filtration when the reaction mixture is cooled to the room temperature. The light blue crystals were obtained from evaporating the filtrate. From elemental analysis data, the calculated (%) for $C_{20}H_{26}CuN_2O_9$ are: C, 47.81; H, 5.18; N, 5.58. Found (%): C, 47.50; H, 5.49; N, 5.67. The selected IR bands (KBr) were: 3281 cm^{-1} (H_2O), 1638 cm^{-1} (–COO–), 1486 cm^{-1} (–C=N of bipy).

2.3. Crystal data and structure determination

A single crystal of $[CuL(bipy)(H_2O)_5]_n$ (**A1**) with dimensions of 0.22 mm × 0.19 mm × 0.18 mm was mounted on a Bruker Amart CCD diffractometer equipped with a graphite-monochromatic MoKα (λ = 0.71073 Å) for single crystal X-ray diffraction analysis. In the range of $3.01<\theta<25.01$, a total of 8019 reflections were collected and 3905 were independent with R_{int} = 0.0588, of which 3460 were observed with $I > 2\sigma(I)$. The structure was solved by direct methods with SHELXS-97 [21] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97 [22]. The most crystal data of **A1** are given in Table 1.

2.4. General procedure for the three component coupling reaction (A^3)

The benzaldehyde (0.25 mmol, 0.0265 g), piperidine (0.30 mmol, 0.0255 g), phenylacetylene (0.33 mmol, 0.0337 g) and 1,4-dioxane (1.50 g) were successively added to the Cu(II) complex (**A1**) catalyst (0.070 g), and then stirred at 120 ^oC. After the reaction, the catalyst was removed from the solution by centrifugation at 10000 rpm for 20 minutes. The yield of propargylamine is equal to the conversion of benzaldehyde, and was determined by using a by GC (GC1100, Capillary Column, SE-54) analysis. The recovered catalyst was thoroughly washed with 1,4-dioxane and used for the next run.

3. Results and Discussion

3.1. Structural Description of $[CuL(bipy)(H_2O)_5]_n$ (A1)

The coordination environment of Cu(II) in $[CuL(bipy)(H_2O)_5]_n$ (**A1**) is shown in Figure 1. There are one Cu(II) ion, one 1,4-phenylenediacetate ligand, one 2,2'-bipyridine ligand and five uncoordinated water molecules in the asymmetric unit. Each Cu(II) ion is six-coordinated by four carboxylate oxygen atoms (O1, O2, O3, O4) from two different 1,4-phenylenediacetate ligands and two nitrogen atoms (N1, N2) from one 2,2'-bipyridine ligand to form a distorted octahedral coordination architecture. The selected important bond parameters of complex A**1** are given in Table 2. The bond lengths of Cu-O and Cu-N in complex **A1** fall in the 1.942(2)-1.951(2) and 1.993(3)-2.001(3) Å regions, respectively, which are in accordance with ref. [23]. In complex **A1**, each 1,4-phenylenediacetate ligand adopts bidentate coordination mode with Cu(II). The 1,4-phenylenediacetate ligands bridge Cu(II) atoms into an infinite 1D chained structure (Figure 2).

3.2. Catalytic studies

The catalytic activity of Cu(II) complex was tested for A^3 coupling reaction of benzaldehyde, piperidine and phenylacetylene (Figure 3). Figure 4 shows the catalytic activity and reusabi-

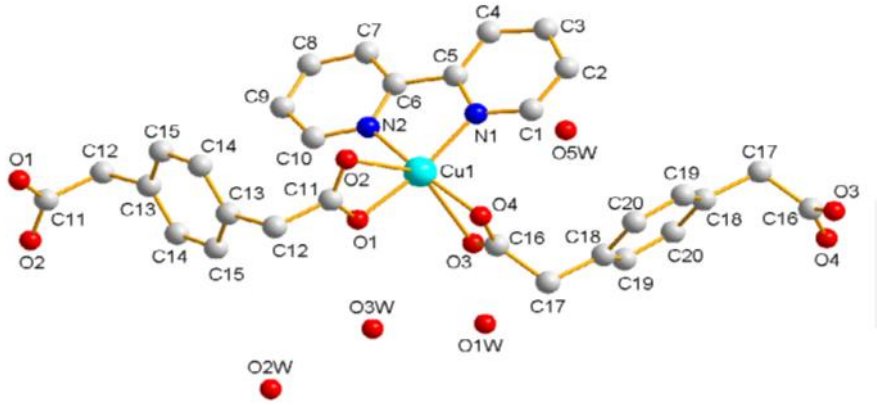

Figure 1. Coordination environment of Cu(II) center in **A1**

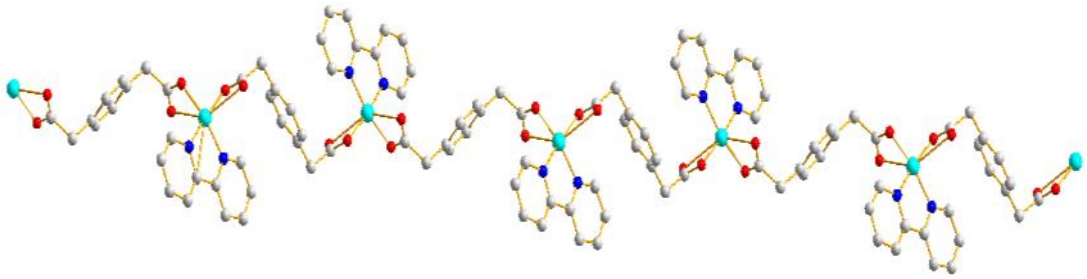

Figure 2. 1D chained structure of Cu(II) complex A**1**

Table 1. The most crystal data of **A1**

Empirical formula	$C_{20}H_{26}CuN_2O_9$
Formula weight	501.97
Temperature/K	293(2)
Crystal system	triclinic
Space group	*P*-1
a/Å	8.9701(18)
b/Å	9.883(2)
c/Å	13.418(3)
α/°	73.79(3)
β/°	78.99(3)
γ/°	86.36(3)
Volume/Å^3	1121.1(4)
Z	2
ρ_{calc}mg/mm^3	1.487
μ/mm^{-1}	1.027
S	1.082
F(000)	522
Index ranges	$-10 \le h \le 9$, $-11 \le k \le 11$, $-15 \le l \le 15$
Reflections collected	8109
Independent reflections	3905 [*R*(int) = 0.0588]
Data/restraints/parameters	3905/0/289
Goodness-of-fit on F^2	1.082
Final *R* indexes [$I \ge 2\sigma$ (*I*)]	R_1 = 0.0632, wR_2 = 0.1603
Final *R* indexes [all data]	R_1 = 0.0686, wR_2 = 0.1656

lity of Cu(II) complex for A^3 coupling reaction of benzaldehyde, piperidine, and phenylacetylene with 1,4-dioxane as solvent at 120 °C. It can be seen that Cu(II) complex exhibited a good catalytic activity for A^3 coupling reaction of benzaldehyde, piperidine, and phenylacetylene. At the initial stage of the A^3 coupling reaction, the yield of propargylamines increases with the increasing of reaction time. Maximum yield of 54.3% was obtained within 5 h over Cu(II) complex catalyst, and then remained constant. After two successive cycles of the Cu(II) complex catalyst being extensively washed with 1,4-dioxane each, the yield of propargylamines

Table 2. The selected important bond parameters of complex A**1**

Bond	Distance(Å)	Angle	(°)
Cu1-O1	1.951(2)	O4-Cu1-O1	93.06(11)
Cu1-O4	1.942(2)	O4-Cu1-N1	92.97(11)
Cu1-N1	1.993(3)	O1-Cu1-N1	170.27(10)
Cu1-N2	2.001(3)	O4-Cu1-N2	168.05(10)
C16-O3	1.241(4)	O1-Cu1-N2	94.22(10)
C11-O2	1.221(4)	N1-Cu1-N2	81.17(10)
		O2-C11-O1	122.9(3)
		O3-C16-O4	121.9(3)

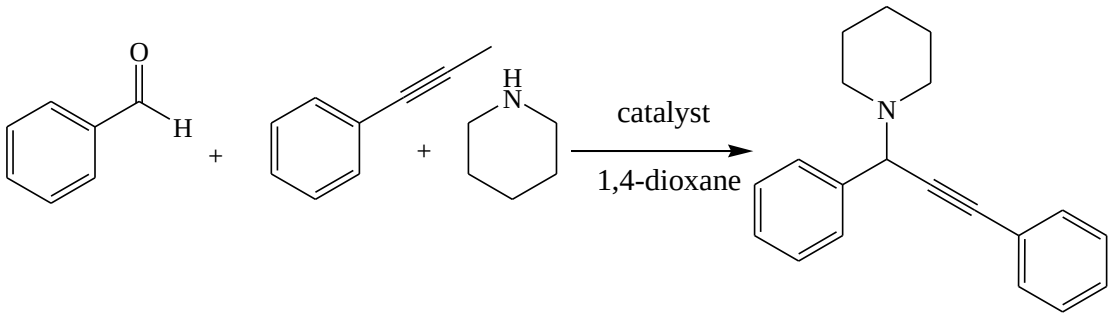

Figure 3. A^3 coupling reaction of benzaldehyde, piperidine and phenylacetylene using Cu(II) complex as catalyst

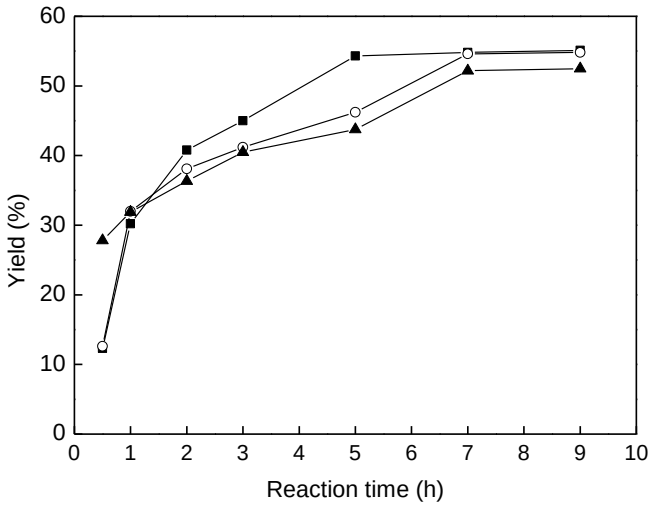

Figure 4. The catalytic activity and reusability over Cu(II) complex for A^3 coupling reaction of benzaldehyde, piperidine, and phenylacetylene with 1,4-dioxane as solvent at 120 °C. **(■)** Fresh; **(○)** run1; **(▲)** run2

were 54.6% and 52.2% at reaction time of 7 h, respectively. There is very slight drop in catalytic activity was found over Cu(II) complex for successive three uses in A^3 coupling reaction of benzaldehyde, piperidine and phenylacetylene, so the Cu(II) complex catalyst has good stability. These features render the catalysts particularly attractive in the practice of propargylamines synthesis in an environmentally friendly manner.

4. Conclusions

In summary, a novel 1D chained Cu(II) coordination polymer has been synthesized. And its structure has been characterized by elemental analysis, IR spectra and single crystal X-ray diffraction. The catalytic activity and reusability of Cu(II) complex catalyst for A^3 coupling reaction of benzaldehyde, piperidine, and phenylacetylene show that the Cu(II) coordination polymer catalyst has good catalytic activity and stability.

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