

SYNTHESIS, CRYSTAL STRUCTURE AND CATALYTIC ACTIVITY OF A CU(II) COMPLEX WITH N-NICOTINOYLGLYCINE

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Abstract: A new Cu(II) complex, $[\text{CuL}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (HL = N-nicotinoylglycine), has been obtained using N-nicotinoylglycine, copper(II) acetate monohydrate and NaOH as raw materials. The structure of the Cu(II) complex was characterized by elemental analysis and single crystal X-ray diffraction analysis. The Cu(II) ion is six-coordinated with two N atoms from two pyridine groups of L ligand and four O atoms of four coordinated H_2O molecules. The Cu(II) complex forms a 2D layered structure and 3D network structure by the interaction of $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds. The catalytic activities of the Cu(II) complex catalyst for benzyl alcohol oxidation were determined with molecular oxygen as oxidant.

Keywords: catalytic activity, Cu(II) complex, crystal structure, N-nicotinoylglycine, synthesis

INTRODUCTION

For many years, functional metal complexes based on *N*-heterocyclic and carboxylic ligands have been one of the hot topics studied and concerned by inorganic chemists [1 – 5]. During the past decades, many Cu(II) complexes with *N*-heterocyclic or carboxylic ligands have been reported [6 – 10]. And many Cu(II) complexes have known to possess diverse intriguing structures and significant properties such as antibacterial activity [11], catalytic activity [12 – 14], magnetic property [15], cytotoxicity [16 – 18], electrochemical property [19], and photoluminescent property [20]. Recently, some transition complexes with bifunctional ligand, *N*-nicotinoylglycine, have been reported [21 – 23]. However, the structure and property of Cu(II) complex with *N*-nicotinoylglycine has not been studied. Our group has been working on the synthesis and properties characterization of metal complexes with polypodand [24 – 30]. In this paper, we reported a Cu(II) complex, $[\text{CuL}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, and the catalytic activities of the Cu(II) complex catalyst for benzyl alcohol oxidation were determined with molecular oxygen as oxidant.

MATERIALS AND METHODS

Experimental

All chemicals (*N*-nicotinoylglycine, copper (II) acetate monohydrate, NaOH and ethanol solvent) used in this work were analytical reagent and used as received. Element analyses (C, H, and N) were performed using an Elementar Vario III EL elemental analyzer (Elementar, Hanau, Germany). Single-crystal data of the Cu(II) complex were collected on a Bruker Smart CCD diffractometer (Bruker, Billerica, MA, USA).

Synthesis of $[\text{CuL}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$

N-nicotinoylglycine (0.1802 g, 1.0 mmol), NaOH (0.040 g, 1.0 mmol), ethanol (10.0 mL) and H_2O (5.0 mL) were added into a 50 mL round flask. Then the mixture solution was stirred at room temperature for 1 h, and copper(II) acetate monohydrate (0.1000 g, 0.5 mmol) was added. The reactant mixture was kept at 65 °C for 6 h with stirring. The blue precipitation was collected by filtration. Yield: 62 %. Anal. Calcd. for $\text{C}_{16}\text{H}_{26}\text{N}_4\text{CuO}_{12}$: C, 36.23; H, 4.91; N, 10.57 %. Found: C, 36.62; H, 4.67; N, 10.37 %. The blue block crystals of the Cu(II) complex were obtained by slow evaporation of the filtrate after 15 days.

Crystal Data and Structure Determination

A single crystal of the Cu(II) complex (0.13 mm × 0.12 mm × 0.10 mm) was placed on a Bruker Smart CCD diffractometer equipped with a graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. 5402 ($R_{\text{int}} = 0.0469$) was independent for the Cu(II) complex. The structure was solved by direct method using *SHELXL*-2014/7 program [31]. The *OLEX2* [32] program was used to refine the structure. Crystal data for complex: triclinic system, space group $P\bar{1}$ with $a = 7.8201(16) \text{ \AA}$, $b = 8.8852(18) \text{ \AA}$, $c =$

9.0104(18) Å, $\alpha = 83.11(3)^\circ$, $\beta = 65.25(3)^\circ$, $\gamma = 81.72(3)^\circ$, $V = 561.4(2)\text{Å}^3$, $Z = 1$, $\text{C}_{16}\text{H}_{26}\text{N}_4\text{CuO}_{12}$, $Mr = 529.95$, $D_c = 1.568\text{ Mg/m}^3$, $F(000) = 275$ and $\mu(\text{Mo } K\alpha) = 1.042\text{ mm}^{-1}$. The final $R = 0.0875$, $wR = 0.2523$ ($w = 1/[\sigma^2(F_o^2) + (0.1555P)^2 + 1.4168P]$, where $P = (F_o + 2F_c^2)/3$), $S = 1.115$. The maximum and minimum peaks are 1.259 and -0.795 e/Å³, respectively.

Selective Oxidation of Benzyl Alcohol

Selective oxidation of benzyl alcohol with molecular oxygen was conducted in a 10 mL stainless-steel high-pressure reactor. In a typical reaction, benzyl alcohol (0.2 mmol, 21.6 mg), 1,4-dioxane (1.5 g) and Cu(II) complex catalyst (0.01 g) were mixed in a 10 mL stainless steel autoclave. After the reactor was sealed, the system was pumped six times with pure O₂ (99.999 %) to remove air prior to reaction. Subsequently, the reactor was kept in an oil bath at 100-120 °C for 4 h under 3 bar of O₂ with stirring at 550 rpm. After the reaction, the Cu(II) complex catalyst was removed from the solution by centrifugation at 14000 rpm for 20 minutes. The conversion of benzyl alcohol and the selectivity of benzaldehyde were determined by a gas chromatography analysis (GC-6890, Purkinje General instrument Co., Ltd., Beijing, China) equipped with a SE-54 column (0.25 mm×0.25 mm×30 m). The products were identified by comparison with known standards samples, and an external standard method was used for the qualitative analysis of the conversion and selectivity. In the recycling experiment, the recovered Cu(II) complex catalyst was thoroughly washed with ethanol and then dried at 60 °C for 6 h for the next reaction.

RESULTS AND DISCUSSION

Structural Description of [CuL₂(H₂O)₂]·H₂O

The molecular structure of [CuL₂(H₂O)₂]·H₂O is illustrated in Figure 1. The 2D layered structure and 3D network structure of [CuL₂(H₂O)₂]·H₂O are shown in Figure 2 and Figure 3, respectively. And the selected bond distances and bond angles are given in Table 1. As shown in Figure 1, there is one Cu(II) ion, two L ligands, four coordinated H₂O molecules and one uncoordinated H₂O molecule in the fundamental unit of [CuL₂(H₂O)₂]·H₂O, where the COO⁻ group of L ligand do not coordinate to Cu(II) ion. The Cu(II) ion is six-coordinated with a distorted octahedron coordination geometry by four oxygen atoms from four coordinated H₂O molecules and two nitrogen atoms from two pyridine groups of L ligand. The Cu-O bond distances are 2.136(3) Å (Cu(1)-O(4) and Cu(1)-O(4A)) and 2.149(3) Å (Cu(1)-O(5) and Cu(1)-O(5A)), and the Cu-N bond distance is 2.349(4) Å (Cu(1)-N(2) and Cu(1)-N(2A)) (Table 1). The sum of bond angles around Cu1 are 360.9° (O(4)-Cu(1)-O(5) 90.05(13)°, O(4A)-Cu(1)-O(5A) 90.05(13)°, O(4A)-Cu(1)-O(5) 89.95(13)°, O(4)-Cu(1)-O(5A) 89.95(13)°), showing that O(4), O(5), O(5A) and O(4A) locate at the equatorial plane. The Cu(II) complex forms a 2D layered structure and 3D network structure by the interaction of O-H···O hydrogen bonds (Figures 2 and 3).

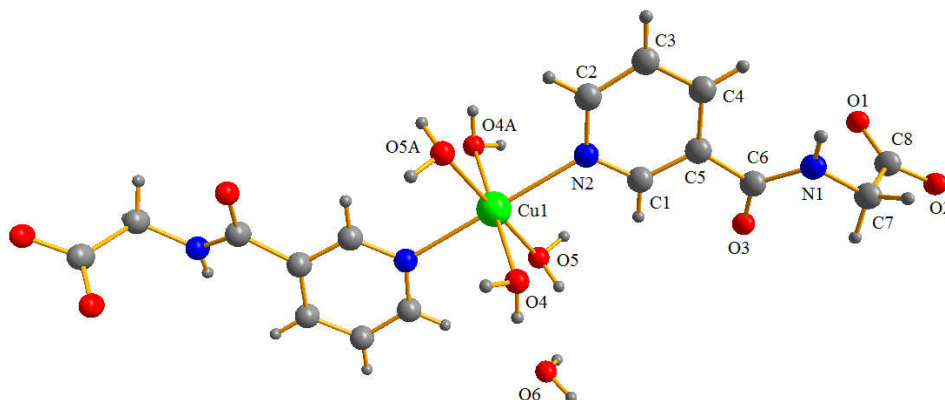


Figure 1. The coordination environment of Cu(II) ion in $[\text{CuL}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, symmetry transformation: $-x, -y, -z$

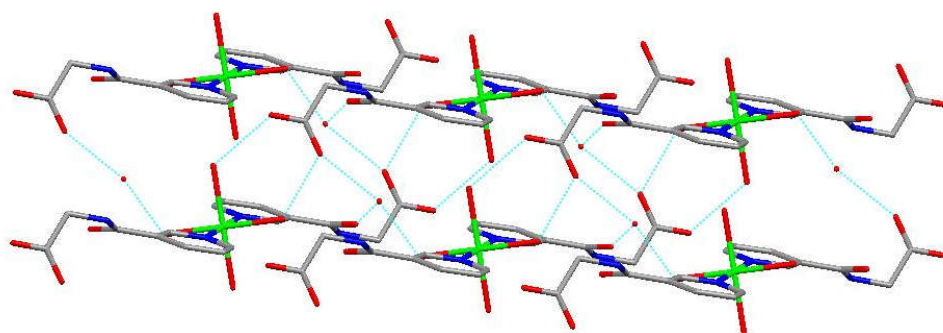


Figure 2. 2D layered structure of $[\text{CuL}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$

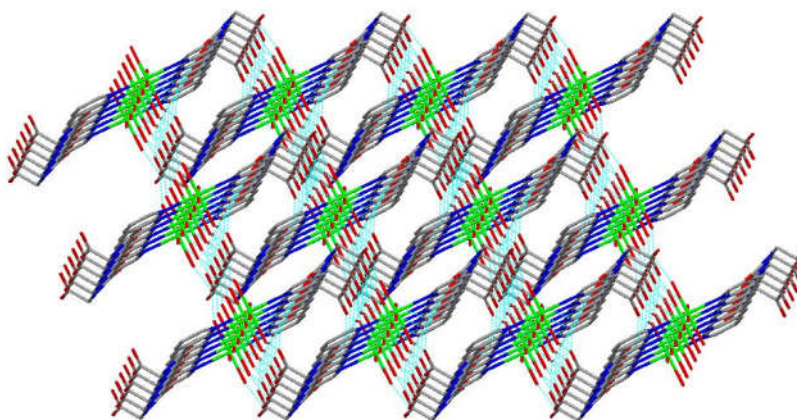


Figure 3. 3D network structure of $[\text{CuL}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$

Table 1. Selected bond lengths (\AA) and bond angles ($^\circ$)

Bond	<i>D</i>	Bond	<i>d</i>
Cu(1)-O(4)	2.136(3)	Cu(1)-O(5A)	2.149(3)
Cu(1)-O(5)	2.149(3)	Cu(1)-O(4A)	2.136(3)
Cu(1)-N(2)	2.349(4)	Cu(1)-N(2A)	2.349(4)
C(8)-O(1)	1.238(5)	C(8)-O(2)	1.262(5)
C(6)-O(3)	1.229(5)	C(6)-N(1)	1.335(5)
C(7)-N(1)	1.444(5)		
Angle	ω	Angle	ω
O(4)-Cu(1)-O(5)	90.05(13)	O(5A)-Cu(1)-N(2)	89.51(13)
O(4A)-Cu(1)-O(5)	89.95(13)	O(5)-Cu(1)-N(2)	90.49(13)
N(2)-Cu(1)-N(2A)	180.0	O(4A)-Cu(1)-N(2A)	89.54(14)
O(4A)-Cu(1)-O(5A)	90.05(13)	O(4)-Cu(1)-N(2)	89.54(14)
O(4)-Cu(1)-O(5A)	89.95(13)	O(4)-Cu(1)-N(2A)	90.46(14)
O(5A)-Cu(1)-O(5)	180.0	C(6)-N(1)-C(7)	121.4(4)
O(1)-C(8)-O(2)	123.9(4)	O(3)-C(6)-N(1)	121.5(4)
O(3)-C(6)-C(5)	121.2(4)		

Catalytic Studies

The catalytic activities of the as-prepared Cu(II) complex catalyst for benzyl alcohol oxidation were determined with molecular oxygen as oxidant. The conversions of benzyl alcohol were 18.8, 33.2, and 55.5 % within 4 h under 3 bar of O₂ at 100, 110, and 120 °C, respectively (Table 2, entries 1-3). The selectivities of benzaldehyde were 99.0, 99.0 and 87.7 % at 100, 110 and 120 °C, respectively (Table 2, entries 1-3). The benzyl alcohol conversion continuously increased with increasing reaction temperature from 100 to 120 °C. However, the selectivity of benzaldehyde decreased when the reaction temperature increasing to 120 °C. The highest catalytic activity (yield of 48.7 %) was achieved at 120 °C under 3 bar of O₂ within 4 h using 1,4-dioxane as solvent for the catalyst of Cu(II) complex in the selective oxidation of benzyl alcohol to benzaldehyde.

The reusability of Cu(II) complex catalyst in the selective oxidation of benzyl alcohol was tested at 120 °C under 3 bar of O₂ within 4 h. The results are summarized in Table 3. The benzyl alcohol conversion, benzaldehyde selectivity, and yield for fresh Cu(II) complex catalyst were 55.5, 87.7, and 48.7 % at 120 °C within 4 h under 3 bar of O₂, respectively (Table 3, entry 1). The conversions of benzyl alcohol were 53.9, 53.3, and 52.3 % in the second, third, and fourth reaction cycles, respectively. The selectivities and yields were 88.0 and 87.4, 87.9 % and 46.9, 47.4 and 46.3 % in the second, third, and fourth reaction cycles, respectively (Table 3, entries 2-4). It has a slight decrease of the benzyl alcohol conversion in the second, third, and fourth reaction cycles for Cu(II) complex, and no loss of benzaldehyde selectivity was detected during four consecutive cycles for the selective oxidation of benzyl alcohol. This result indicated that the Cu(II) complex has good stability in the selective oxidation of benzyl alcohol to benzaldehyde.

Table 2. Catalytic performance of the Cu(II) complex in the oxidation of benzyl alcohol^a

Entry	Solvent	Temperature [°C]	Conversion [%]	Selectivity [%]	Yield [%]
1	1,4-dioxane	100	18.8	99.0	18.61
2	1,4-dioxane	110	33.2	99.0	32.9
3	1,4-dioxane	120	55.5	87.7	48.7

^aReaction conditions: benzyl alcohol (0.2 mmol), 1,4-dioxane (1.5 mL), and Cu(II) complex (0.01 g), 3 bar, 4 h**Table 3.** Recyclability of Cu(II) complex in the oxidation of benzyl alcohol^a

Entry	Solvent	Conversion [%]	Selectivity [%]	Yield [%]
fresh	1,4-dioxane	55.5	87.7	48.7
run 1	1,4-dioxane	53.9	88.0	46.9
run 2	1,4-dioxane	53.3	87.4	47.4
run 3	1,4-dioxane	52.3	87.9	46.3

^aReaction conditions: benzyl alcohol (0.2 mmol), 1,4-dioxane (1.5 mL), and Cu-complex (0.01 g), 3 bar, 120 °C, 4 h

CONCLUSIONS

A new Cu(II) complex, $[\text{CuL}_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$, was successfully synthesized and structural characterized. The catalytic activities of the Cu(II) complex catalyst for benzyl alcohol oxidation were tested with molecular oxygen as oxidant.

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SUPPLEMENTARY MATERIALS

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 1946980. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

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