Studii şi Cercetări Ştiinţifice 2018, **19** (3), pp. 337 – 344
Chimie şi Inginerie Chimică, Biotehnologii, Industrie Alimentară

Scientific Study & Research
Chemistry & Chemical Engineering, Biotechnology, Food Industry *ISSN 1582-540X*

ORIGINAL RESEARCH PAPER

SYNTHESIS AND CRYSTAL STRUCTURE OF A CU(II) COMPLEX AND ITS CATALYTIC ACTIVITY FOR THE OXIDATION OF BENZYL ALCOHOL

Jie Yin[1*], Xi-Shi Tai[2*], Qian-Qin Guo[3]

[1]*Xinyang Vocational and Technical College, College of Applied Chemistry and Environmental Engineering, Xinyang 464000, Xinyang, P. R. China*
[2]*Weifang University, College of Chemistry and Chemical Engineering, Weifang 261061, Weifang, P. R. China*
[3]*Weifang No. 1 Middle School, Weifang 261205, Weifang, P. R. China*

*Corresponding author: lively168@163.com and taixs@wfu.edu.cn

Received: January, 17, 2018
Accepted: September, 14, 2018

Abstract: A Cu(II) complex, [CuL_2(Phen)] (**1**) (HL = 2-benzoylbenzoic acid, Phen = 1,10-phenanthroline), has been synthesized and structurally characterized by elemental analysis and single-crystal X-ray diffraction. Structural analysis indicated that the Cu(II) complex (**1**) belongs to the monoclinic system with $P2_1/c$ space group, and a = 18.955(4) Å, b = 8.3618(17) Å, c = 27.890(8) Å, β = 131.635(18)°, V = 3303.8(15) Å^3, D_c = 1.396 g·cm^{-3}, the final R = 0.0505, wR_2 = 0.1154 with $I \geq 2\sigma$ (I). In Cu(II) complex, both the COO^- group of L ligand and Phen ligand adopt bidentate coordination mode. The Cu(II) center is six-coordinated by two N atoms of one Phen ligand and four O atoms of two different L ligands, forming a distorted octahedral coordination environment. The Cu(II) complex (**1**) molecules forms a 1D chain structure by π-π stacking effect of neighboring benzene rings, and the 1D chains further form a 3D network structure. The catalytic activity of [CuL_2(Phen)] (**1**) for the oxidation of benzyl alcohol has been tested with O_2 as the oxidant.

Keywords: *benzyl alcohol, 2-benzoylbenzoic acid, crystal structure, Cu(II) complex, oxidation, 1,10-phenanthroline, synthesis*

INTRODUCTION

The research on copper complex has been one of the hot topics in coordination chemistry, because they exhibit rich coordination mode [1, 2] and good properties in biological activities [3], fluorescence probes [4, 5], electrochemical properties [6], gas adsorption [7], catalytic activities [8, 9], and magnetic properties [10]. As an important chemical intermediate, benzaldehyde has wide applications in dyes, medicine, resins and other industries [11]. The benzaldehyde was prepared traditionally by oxidation of benzyl alcohol with toxic metal oxides, peroxides, and so on [12 – 14]. Our goal is the synthesis and application of environmental friendly catalyst [15 – 18]. So we present the synthesis, structure and catalytic activity of a Cu(II) complex, [CuL_2(Phen)] (1) (HL = 2-benzoylbenzoic acid, Phen = 1,10-phenanthroline) in this paper, which forms a 1D chain structure by π-π stacking effect of neighboring benzene rings, and the 1D chains further form a 3D network structure. The chemical diagram of the Cu(II) complex is shown in Figure 1.

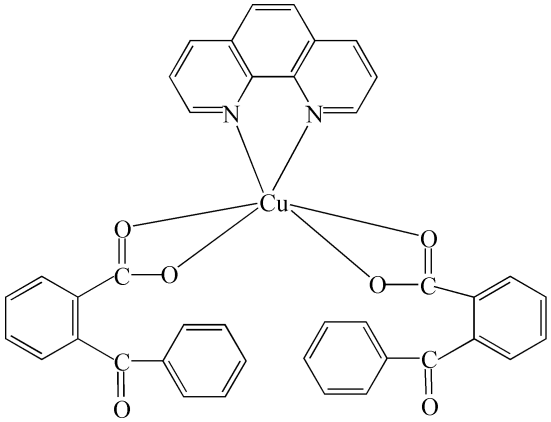

Figure 1. *Chemical diagram of Cu(II) complex*

EXPERIMENTAL

Materials and methods

2-Benzoylbenzoic acid, 1,10-phenanthroline and $Cu(CH_3COO)_2{\cdot}H_2O$ were commercially chemicals of analysis reagent and purchased from Shanghai Chemical Reagent Company. C, H and N were made on an Elementar Vario III EL elemental analyzer (Hanau, Germany). Crystal data of [CuL_2(Phen)] (**1**) were collected on a Bruker Smart CCD diffractometer (Bruker, Billerica, MA, USA).

Synthesis of [CuL_2(Phen)] (1)

The mixture of 2-benzoylbenzoic acid (1.0 mmol, 0.2262 g), NaOH (1.0 mmol, 0.040 g), 1,10-phenanthroline (0.5 mmol, 0.090 g), and $Cu(CH_3COO)_2{\cdot}H_2O$ (0.5 mmol, 0.100 g) were dissolved in 20 mL water-ethanol (v : v = 1 : 3) solution. The mixture solution was stirred and kept reacting at 70 °C for 3 h. Then the blue product was obtained by

filtration after the reaction mixture was cooled to room temperature. The blue crystals were yielded by slow evaporation of mother liquor for about 20 days. Yield: 62 %. Anal. calcd. (%) for [CuL_2(Phen)] (**1**): C, 69.15; H, 3.75; N, 4.03. Found (%): C, 69.36; H, 4.07; N, 3.78.

Crystal Data Collection and Handling

A single crystal of [CuL_2(Phen)] (**1**) (0.19 mm × 0.18 mm × 0.17 mm) was chose for X-ray diffraction analysis. The crystal data were collected in the range of 3.10 ° ≤ θ ≤ 25.10 ° at 293(2) K on a Brucker Smart Apex CCD diffractometer (Bruker, Karlsruhe, Germany) with graphite-monochromated Mo$K\alpha$radiation (λ = 0.71073 Å) using Olex2 program [19]. The structure was solved with the SHELXT [20] structure solution program using intrinsic phasing and refined with the SHELXL [21] refinement package using least squares minimisation. Crystal data and structural refinement for Cu(II) complex are given in Table 1.

Table 1. *Crystal data and structural refinement for Cu(II) complex*

Empirical formula	$C_{40}H_{26}CuN_2O_6$
Formula weight	694.18
Temperature [K]	293(2)
Crystal size [mm^3]	0.19 × 0.18 × 0.17
Crystal system	monoclinic
Space group	$P2_1/c$
A [Å]	18.955(4)
B [Å]	8.3618(17)
C [Å]	27.890(8)
β [°]	131.635(18)
Volume [$Å^3$]	3303.8(15)
Z	4
ρ_{calc} [$mg \cdot mm^{-3}$]	1.396
M [mm^{-1}]	0.713
S	1.098
F(000)	1428
Index ranges	$-22 \le h \le 22$, $-9 \le k \le 9$, $-33 \le l \le 33$
Reflections collected	24508
Independent reflections	5846 [*R*(int) = 0.0878]
Data/restraints/parameters	5846/0/442
Goodness-of-fit on F^2	1.059
Final *R* indexes [I >=2σ (*I*)]	R_1 = 0.0505, wR_2 = 0.1154
Final *R* indexes [all data]	R_1 = 0.1003, wR_2 = 0.1473
Largest diff. peak/hole [e $Å^{-3}$]	0.29/-0.47

Catalytic Test of Benzyl Alcohol Oxidation

Aerobic oxidation of benzyl alcohol catalyzed by Cu(II) complex was performed in a 10 mL stainless steel autoclave at 130-150 °C under 1 MPa. In a typical reaction, benzyl alcohol (21.6 mg, 0.2 mmol), solvent such as tetrahydrofuran, 1,4-dioxane, acetonitrile and toluene (1.5 g) and the requisite amount of Cu(II) complex (60 mg) were added into the autoclave, and then pure O_2 (99.999 %) was purged into the autoclave. The mixture was kept at 130-150 °C for 3 h at the stirring speed of 700 rpm. After the reaction, the mixture was centrifuged to remove the catalyst, and Na_2SO_4 was added into the mixture to remove a small amount of water. The conversion of benzyl alcohol and the selectivity of benzaldehyde were determined by gas chromatography spectrometer equipped with a SE-54 column. The external standard method was used for the qualitative analysis.

RESULTS AND DISCUSSION

Structural Description of [CuL_2(Phen)] (1)

The molecular structure of [CuL_2(Phen)] (**1**) is shown in Figure 2. In the molecule of [CuL_2(Phen)] (**1**), there are one Cu(II) ion, one bidentate Phen ligand and two bidentate 2-benzoylbenzoate. The important bond lengths and bond angles are shown in Table 2. The center Cu(II) ion is six-coordinated to two N atoms (N1 and N2) from one bidentate Phen ligand, four O atoms (O2, O3, O5 and O6) from two different bidentate 2-benzoylbenzoate ligands. The coordination geometry around Cu(II) ion is a distorted octahedral configuration. In the complex, two bidentate 2-benzoylbenzoate ligands are not coplanar because the dihedral angles of benzene ring 1 (C1-C2-C3-C4-C5-C6) and benzene ring 2 (C8-C9-C10-C11-C12-C13), benzene ring 3 (C15-C16-C17-C18-C19-C20) and benzene ring 4 (C22-C23-C24-C25-C26-C27) are 99.1 and 96.9°, respectively.

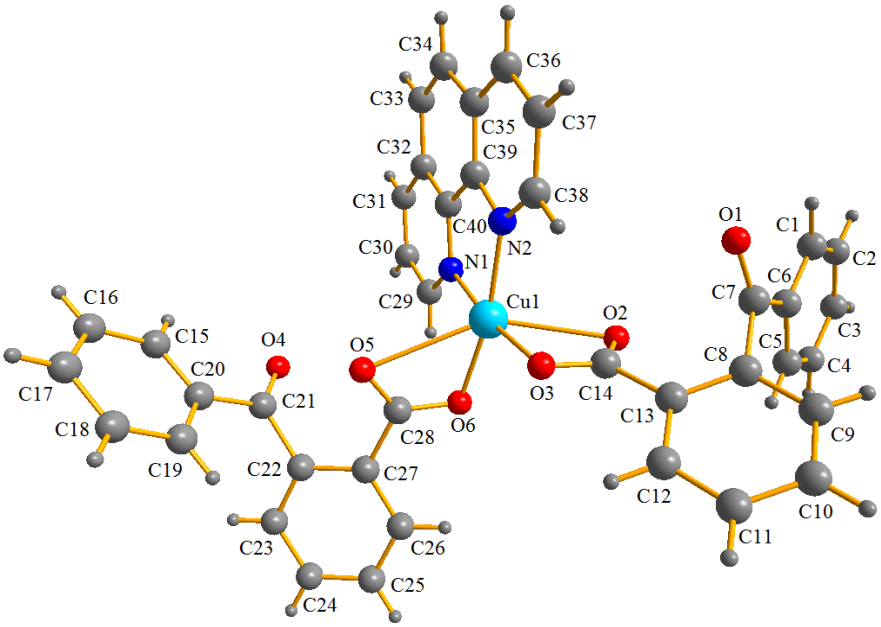

Figure 2. *Molecular structure of [CuL_2(Phen)]* ***(1)***

Table 2. *Important bond lengths [Å] and bond angles [°] for Cu(II) complex*

Bond	***d***	**Bond**	***d***
Cu1-O2	2.526(3)	Cu1-O3	1.952(3)
Cu1-O5	2.629(3)	Cu1-O6	1.939(3)
Cu1-N1	2.013(3)	Cu1-N2	2.006(3)
C7-O1	1.225(4)	C14-O2	1.242(4)
C14-O3	1.269(5)	C21-O4	1.210(5)
C28-O5	1.236(4)	C28-O6	1.272(4)
Angle	**ω**	**Angle**	**ω**
O2-Cu1-O5	149.13(9)	O3-Cu1-O2	57.38(10)
O3-Cu1-O5	102.34(10)	O3-Cu1-N1	172.30(11)
O3-Cu1-N2	93.44(12)	O6-Cu1-O2	99.55(10)
O6-Cu1-O3	93.02(11)	O6-Cu1-O5	55.36(9)
N1-Cu1-O6	93.24(12)	N2-Cu1-O6	169.82(10)
N1-Cu1-O2	117.02(11)	N1-Cu1-O5	84.93(10)
N2-Cu1-O2	90.56(11)	N2-Cu1-O5	115.42(10)
N2-Cu1-N1	81.01(13)		

The [CuL_2(Phen)] (**1**) molecules form 1D chained structure by the π-π stacking effect between the neighboring benzene rings of 2-benzoylbenzoate ligands. And the 1D chains further form a 3D network structure by the π-π stacking effect of the neighboring benzene rings and Phen rings (Figure 3).

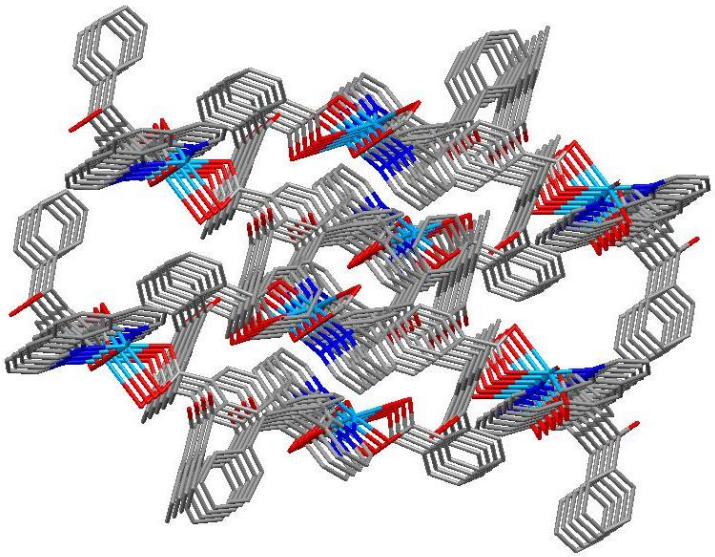

Figure 3. *3D supramolecular network structure of Cu(II) complex*

Catalytic Activities of [CuL_2(Phen)] (1)

The catalytic oxidation was carried out in a stainless steel autoclave placed in an oil bath and equipped with a magnetic stirrer. The mixture was stirred at defined reaction temperatures and pure O_2 inside the reactor was used as the oxidant. The oxidation of

benzyl alcohol to benzaldehyde was selected as the model reaction to examine the performance of Cu(II) complex. Along with the oxidation to benzaldehyde, disproportionation and dehydration reactions of benzyl alcohol may also accompany depending on the catalyst and reaction conditions yielding toluene and dibenzylether. For optimization of reaction conditions, a series of experiments was conducted to investigate the factors like solvent and temperature on the reaction. The results are shown in Table 3. Four different solvents were selected to preliminary test the oxidation of benzyl alcohol without Cu(II) complex catalyst. The benzyl alcohol conversions and benzyldehyde selectivities were 11.2, 10.3, 1.5, 1.0 % and 79.1, 89.7, 99.0, 99.0 % (Table 3, entry 1-4), respectively. Keeping reactant and catalyst amounts unchanged, catalytic conversion of benzyl alcohol and the selectivity of benzaldehyde were studied in various solvents at 130 °C. The highest conversion and selectivity were achieved in 1,4-dioxane (Table 3, entry 5). The conversions of benzyl alcohol in tetrahydrofuran, acetonitrile and toluene were 27.7, 5.2, and 4.4 % at 130 °C within 3 h, respectively (Table 3, entries 6-8). The selectivities of benzaldehyde were 99, 74.7, and 94.5 % in 1.4-dioxane, tetrahydrofuran, acetonitrile and toluene, respectively (Table 3, entries 6-8). The results of the reactions conducted in 1,4-dioxane at various temperatures in the range 130-150 °C, keeping reactant and catalyst amounts unchanged (Table 3, entries 5, 9, 10). The benzyl alcohol conversion increase when increasing the reaction temperature. The conversions and selectivities were 74.9 and 84.9 %, 35.2 and 24.7 % in 1,4-dioxane for 3 h at 140 and 150 °C, respectively (Table 3, entries 9 and 10). The good conversion of benzyl alcohol (53.3 %) and excellent selectivity of benzaldehyde (99 %) was achieved when the reaction was carried out at 130 °C in 1,4-dioxane over Cu(II) complex.

Table 3. *Catalytic performance of the Cu(II) complex in the oxidation of benzyl alcohol*

Entry	Solvent	Catalyst	Temperature [°C]	Time [h]	Conversion [%]	Selectivity [%]
1	1,4-dioxane	-	130	3	11.2	79.1
2	tetrahydrofuran	-	130	3	10.3	89.7
3	acetonitrile	-	130	3	1.5	99.0
4	toluene	-	130	3	1.0	99.0
5	1,4-dioxane	Cu(II) complex	130	3	53.3	99.0
6	tetrahydrofuran	Cu(II) complex	130	3	27.7	99.0
7	acetonitrile	Cu(II) complex	130	3	5.2	74.7
8	toluene	Cu(II) complex	130	3	4.4	94.5
9	1,4-dioxane	Cu(II) complex	140	3	74.9	35.2
10	1,4-dioxane	Cu(II) complex	150	3	84.9	24.7

CONCLUSIONS

A Cu(II) complex with 2-benzoylbenzoic acid and 1,10-phenanthroline was synthesized and structurally characterized in this paper. The Cu(II) complex catalyst shows good catalytic activity for benzyl alcohol oxidation with conversion of benzyl alcohol (53.3 %) and selectivity of benzaldehyde (99 %) at 130 °C in 1,4-dioxane.

ACKNOWLEDGMENTS

This project was supported by the National Natural Science Foundation of China (No. 21171132), the Natural Science Foundation of Shandong (ZR2017LB025 and ZR2014BL003), the project of Shandong Province Higher Educational Science and Technology Program (J14LC01) and Science Foundation of Weifang.

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 1812622. 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).

REFERENCES

1. Golbedaghi, R., Azimi, S., Molaei, A., Hatami, M., Notash, B.: X-ray crystal structure and theoretical study of a new dinuclear Cu(II) complex with two different geometry centers bridged with an oxo group, *Journal of Molecular Structure*, **2017**, **1146**, 309-313;
2. Jaramillo-García, J., Téllez-López, A., Martínez-Domínguez, R., Morales-Luckie, R.A., Martínez-Otero, D., Sánchez-Mendieta, V., Escudero, R.: 1D and 3D supramolecular structures exhibiting weak ferromagnetism in three Cu(II) complexes based on malonato and di-alkyl-2,2'-bipyridines, *Journal of Coordination Chemistry*, **2016**, **69**, 1525-1540;
3. Gou, Y., Li, J., Fan, B., Xu, B., Zhou, M., Yang, F.: Structure and biological properties of mixed-ligand Cu(II) Schiff base complexes as potential anticancer agents, *European Journal of Medicinal Chemistry*, **2017**, **134**, 207-217;
4. Ravotto, L., Ceroni, P.: Aggregation induced phosphorescence of metal complexes: from principles to applications, *Coordination Chemistry Reviews*, **2017**, **346**, 62-76;
5. Sarıoğlu, A.O., Ceylan, Ü., Yalçın, Ş.P., Sönmez, M., Ceyhan, G., Aygün, M.: Synthesis of a new ONNO donor tetradentate schiff base ligand and binuclear Cu(II) complex: quantum chemical, spectroscopic and photoluminescence investigations, *Journal of Luminescence*, **2016**, **176**, 193-201;
6. Tai, X.S., Liu, L., Yin, J.: Synthesis, spectral characterization, and electrochemical property of Cu(II) complex with 1,2-phenylenedioxydiacetic acid and 1,10-phenanthroline, *Research on Chemical Intermediates*, **2015**, **41**, 8279-8287;
7. Takahashi, K., Hoshino, N., Noro, S.I., Nakamura, T., Akutagawa, T.: Crystal structures, dielectric, and CO_2 adsorption properties of one-dimensional $[Cu(II)_2(adamantane\text{-}1\text{-}carboxylate)_4(pyrazine)]_\infty$ coordination polymers with polar ligands, *Science of Advanced Materials*, **2014**, **6**, 1417-1424;
8. Renuka, M.K., Gayathri, V.: A polymer supported Cu(II) catalyst for oxidative amidation of benzyl alcohol and substituted amines in TBHP/H_2O, *Catalysis Communications*, **2018**, **104**, 71-77;
9. Godhani, D.R., Nakum, H.D., Parmar, D.K., Mehta, J.P., Desai, N.C.: Zeolite-Y immobilized Metallo-ligand complexes: a novel heterogenous catalysts for selective oxidation, *Inorganic Chemistry Communication*, **2016**, **72**, 105-116;
10. Lin, C.J., Xu, J.Q., Zheng, Y.Q., Zhu, H.L., Xu, W.: Synthesis, crystal structures, and properties of two new Cu(II) complexes with *p*-hydroxybenzoic acid, *Journal of Cluster Science*, **2015**, **26**, 1253-1265;
11. Liu, M.M., Du, M.M., Qin, L., Zhang, G.L., Li, G.Q.: Research on the preparation benzaldehyde by benzyl alcohol oxidation, *Zhejing Chemical Industry*, **2016**, **47**, 26-29;

12. Cai, J., Lu, J.Y., Chen, Q.Y., Qu, L.L., Lu, Y.Q., Gao, G.F.: Eu-Based MOF/graphene oxide composite:a novel photocatalyst for the oxidation of benzyl alcohol using water as oxygen source, *New Journal of Chemistry*, **2017**, **41**, 3882-3886;
13. Tan, T.H., Scott, J., Ng, Y.H., Taylor, R.A., Aguey-zinsou, K.F., Amal, R.: C–C cleavage by Au/TiO_2 during ethanol oxidation: understanding bandgap photoexcitation and plasmonically mediated charge transfer via quantitative in situ drifts, *ACS Catalysis*, **2016**, **6**, 8021-8029;
14. Zhou, H., Xiao, L.P., Liu, X.N., Li, S., Kobayashi, H., Zheng, X.M., Fan, J.: Defect-less, layered organo-titanosilicate with superhydrophobicity and its catalytic activity in room-temperature olefin epoxidation, *Chemical Communications*, **2012**, **55**, 6954-6956;
15. Tai, X.S., Liu, L.L., Yin, J.: Synthesis, crystal structure of tetra-nuclear macrocyclic Cu(II) complex material and its application as catalysts for A^3 coupling reaction, *Journal of Inorganic and Organometallic Polymers and Materials*, **2014**, **24**, 1014-1020;
16. Wang, L.H., Wang, X., Tai, X.S.: Synthesis, Crystal structure and catalytic activity of a 1D chained Ca(II) coordination polymer with 3,5-bis(4-pyridylmethoxy)benzoate ligand, *Crystals*, **2017**, **7**, 72;
17. Tai, X.S., Li, P.F., Wang, X., Liu, L.L.: Synthesis, structural characterization, and catalytic property of a Zn(II) complex with 5-bromosalicylaldehyde ligand, *Bulletin of Chemical Reaction Engineering & Catalysis*, **2017**, **12**, 364-369;
18. Wang, L.H., Tai, X.S., Liu, L.L., Li, P.F.: Synthesis, crystal structure and catalytic activity of a novel Ba(II) complex with pyridine-2-carboxaldehyde-2-phenylacetic acid hydrazone ligand, *Crystals*, **2017**, **7**, 305;
19. Dolomanov, O.V., Bourhis, L.J., Gildea, R. J., Howard, J.A.K., Puschmann, H.: *OLEX2*: a complete structure solution, refinement and analysis program, *Journal of Applied Crystallography*, **2009**, **42**, 339-341;
20. Sheldrick, G.M.: *SHELXT*-Integrated space-group and crystal-structure determination, *Acta Crystallographica*, **2015**, **A71**, 3-8;
21. Sheldrick, G. M.: Crystal structure refinement with SHELXL, *Acta Crystallographica*, **2015**, **C71**, 3-8.