### Synthesis, Characterization, Crystal Structure and Catalytic Activity of An End-On

Azido-Bridged Polymeric Copper(II) Complex Derived From

#### 4-Methyl-2-[(3-methylaminopropylimino)methyl]phenol

### Li-Jun Liu<sup>\*</sup>

School of Chemistry and Chemical Engineering, Linyi University, Linyi Shandong 276005, P. R.

#### China

\*Corresponding author. Email: 18553903986@163.com

### Abstract

An end-on azido-bridged polymeric copper(II) complex,  $[CuL(\mu_{1,1}-N_3)]_n$  (HL = 4-methyl-2-[(3-methylaminopropylimino)methyl]phenol), was synthesized and characterized by elemental analysis, IR spectra and X-ray single crystal structure determination. X-ray structural analysis indicates that the complex crystallizes in the monoclinic with space group *Cc*, with *a* = 13.375(1) Å, *b* = 16.922(2) Å, *c* = 6.7666(6) Å,  $\beta$  = 117.967(2)°, *V* = 1352.6(2) Å<sup>3</sup>, *Z* = 4. The Cu atom is in square pyramidal coordination, with the phenolate oxygen, imino nitrogen and amino nitrogen of the Schiff base ligand and one azido nitrogen defining the basal plane, and with another azido nitrogen occupying the apical position. The complex show effective catalytic property on the oxidation of benzyl alcohol derivatives to carbonyl compounds by using hydrogen peroxide as the oxidant.

### Keywords

Polymeric structure, crystal structure, copper, Schiff base, catalytic property

## <sup>1</sup> ACCEPTED MANUSCRIPT

#### INTRODUCTION

Schiff bases are considered as a very important class of organic compounds which have wide applications in coordination chemistry and biological aspects [1-3]. Mono- and multinuclear complexes of cobalt in its varied oxidation states have become a central theme of current research because of their potentially applications in many fields [4-6]. In the last few years, copper complexes with multi-dentate Schiff base ligands are reported to possess interesting catalytic properties [7–9]. Among the N, O containing chelators, the tridentate mono-condensed Schiff base ligands have received much attention for the synthesis of mono- and polynuclear complexes. A literature search reveals that no complexes were reported with the Schiff base 4-methyl-2-[(3-methylaminopropylimino)methyl]phenol (HL; Scheme 1). In this paper, the author describes the synthesis and characterization of a new end-on azido-bridged polymeric copper(II) complex with the Schiff base HL as ligand. Crystal structure of the complex has been investigated by single crystal X-ray diffraction. The catalytic oxidation of benzyl alcohol derivatives to corresponding carbonyl compounds have been investigated for the complex by using hydrogen peroxide as the oxidant.

### **EXPERIMENTAL**

#### Materials and methods

All chemicals and solvents used for the synthesis and catalytic experiment were of analytical grade, and purchased from Aldrich Chemical Company. Other chemicals were obtained from commercial sources and used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C analytical instrument. The metal analysis was carried out by titration. IR spectra in the 4,000–400 cm<sup>-1</sup> range were measured with a Thermo Nicolet 320 FT-IR

## <sup>2</sup> ACCEPTED MANUSCRIPT

spectrometer using KBr discs. <sup>1</sup>H NMR spectra were recorded on a Bruker 300 MHz spectrometer.

#### Synthesis of the Schiff base HL

To a vigorously stirred methanol solution (30 ml) of 5-methylsalicylaldehyde (0.136 g, 1 mmol), a methanol solution (20 ml) of *N*-methylpropane-1,3-diamine (0.088 g, 1 mmol) was added. The mixture was stirred for about 30 min and then refluxed for 30 min. The resulting solution was evaporated under vacuum to remove the solvent to give a yellow gummy product. Anal. Calc. for  $C_{12}H_{18}N_2O$ : C, 69.87; H, 8.80; N, 13.58%. Found: C, 69.71; H, 8.92; N, 13.67%.

### Synthesis of $[CuL(\mu_{1,1}-N_3)]_n$

To a methanol solution (10 ml) of copper nitrate trihydrate (24.1 mg, 0.1 mmol), a methanol solution (10 ml) of HL (20.6 mg, 0.1 mmol) was added dropwise and the mixture was stirred for 10 min. Then to the mixture was added a minimum volume of aqueous solution of sodium azide (6.5 mg, 0.1 mmol) under stirring. The resulting mixture was further stirred for 1 h at ambient temperature to give a deep blue solution. The solution, on slow evaporation, gave blue single crystals of the complex. The crystals were filtered off and dried in air. Yield 18.7 mg (60% based on Cu). Anal. Calc. for  $C_{12}H_{17}CuN_5O$ : C, 46.37; H, 5.51; N, 22.53; Cu, 20.44%. Found: C, 46.15; H, 5.70; N, 22.31; Cu, 20.72%.

### **X-Ray Crystallography**

Diffraction intensities for the complex were collected on a Bruker SMART 1000 CCD area diffractometer equipped with graphite monochromated Mo K $\alpha$  radiation with a radiation wavelength of 0.71073 Å using the  $\omega$ -scan technique at 298(2) K. Absorption corrections were performed using the SADABS program [10]. The structure was solved by direct method and

### <sup>3</sup> ACCEPTED MANUSCRIPT

refined by full-matrix least-squares against  $F^2$  using SHELXTL [11]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atom isotropic displacement parameters were all treated as riding on the parent atoms (1.2 or  $1.5U_{eq}$  for the carbon H atoms). All hydrogen atoms were generated geometrically and were included in the refinement in the riding model approximation. Selected crystallographic data are summarized in the Table 1. Coordinate bond lengths and angles are listed in Table 2.

#### **Catalytic Oxidation Procedure**

To an acetonitrile solution (10 mL) of benzyl alcohol derivative, the copper complex as the catalyst (0.002 mmol) and  $H_2O_2$  (V:V = 50%, 5 mL) were added and the mixture was refluxed at 80 °C for 2 h. The mixture was then poured into water and the product was extracted with dichloromethane and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed and the product was purified by column chromatography. The product was characterized by IR and <sup>1</sup>H NMR spectra.

### **RESULTS AND DISCUSSION**

A 1:1 molar ratio of 5-methylsalicylaldehyde and *N*-methylpropane-1,3-diamine in methanol was reacted to prepare the tridentate Schiff base HL. The complex was prepared by the reaction of 1:1:1 molar ratio of HL, copper nitrate trihydrate and sodium azide in methanol. The air-stable, moisture-insensitive complex was obtained as deep blue crystals, which are soluble in a range of common organic solvents such as methanol, ethanol, dichloromethane, acetonitrile, dimethylformamide and dimethylsulphoxide, but insoluble in water. The molar conductance value of the complex measured in methanol at the concentration of  $10^{-3}$  M is 27  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>, indicating the non-electrolytic nature [12]. Microanalytical analyses of the complex are in agreement with the formula proposed by the single crystal X-ray determination.

## **ACCEPTED MANUSCRIPT**

### **Infrared and Electronic Spectra**

Comparison of the IR spectra of the complex with that of the free Schiff base gives information regarding bonding sites of the ligand. The weak and sharp bands indicative of the N–H vibrations of HL and the complex are located at 3217 and 3241 cm<sup>-1</sup>, respectively. The complex displays intense peak at 1627 cm<sup>-1</sup> due to the azomethine (C=N) stretching [13,14], which are shifted by 13 cm<sup>-1</sup> to lower frequency compared to the free Schiff base. The shift of the band towards lower frequency compared to that of the free Schiff base indicates the coordination of the imino nitrogen to the metal center. For the complex, the strong stretching related to the azide group is observed at 2047 cm<sup>-1</sup> [15,16]. The presence of new bands in the spectrum of the complex in low wavenumbers can be attributed to the Cu–O and Cu–N stretching vibrations [17].

The electronic spectrum (Figure 1) of the complex in methanol exhibits obvious bands at 273, 300, and 380 nm owing to  $\pi$ - $\pi$ \* and n- $\pi$ \* transitions. The complex shows relatively a weak absorption band centered at 640 nm due to ligand field transition.

#### **Crystal Structure Description of the Complex**

The single-crystal X-ray diffraction shows that the complex is an end-on azido-bridged polymeric copper(II) complex (Figure 2). The Cu…Cu distance is 3.614(1) Å. Each Cu is in a square-pyramidal coordination, with the phenolate oxygen, imino nitrogen and amino nitrogen of the Schiff base ligand, and the terminal nitrogen of a bridging azide ligand defining the basal plane, and with another terminal azido nitrogen occupying the apical position. The deviation of the Cu atom from the least-squares plane defined by the basal donor atoms is 0.169(2) Å. The azide ligands coordinate to two different but symmetry-related Cu atoms through the end-on

# <sup>5</sup> ACCEPTED MANUSCRIPT

bridging mode. Significant distortion of the square pyramid is revealed by bond lengths and angles between the apical and basal donor atoms. The apical Cu–N bond length is much longer than usual; the other bond lengths are within normal ranges and comparable to the corresponding values observed in Schiff base copper(II) complexes [18,19]. The bridging azide groups are nearly linear and show bent coordination with Cu atoms [N3–N4–N5 = 178.6(3)°, Cu1–N3–N4 = 120.0(2)°, Cu1A–N3–N4 = 118.3(2)°]. The chelate ring formed by the atoms Cu1, N1, C8-C10, and N2 in the complex has chair conformation. The diagonally positioned atoms, Cu1 and C9, are shifted from the least-squares plane defined by the atoms N1, N2, C8 and C10 by 0.439(2) and -0.712(2) Å, respectively.

In the crystal structure of the complex, the [CuL(N<sub>3</sub>)] units are linked through end-on azido bridging groups, forming polymeric chains running along the *c* axis. The chains are further linked through intermolecular C–H···N hydrogen bonds [C4–H4···N5<sup>i</sup>: C4–H4 = 0.93 Å, H4···N5<sup>i</sup> = 2.61 Å, C4···N5<sup>i</sup> = 3.4053(3) Å, C4–H4···N5<sup>i</sup> = 144(3)°; C11–H11B···N3: C11–H11B = 0.96 Å, H11B···N3 = 2.34 Å, C11···N3 = 2.9539(3) Å, C11–H11B···N3 = 121(3)°; symmetry code for i: x, -y, -1/2 + z], to form a three dimensional network (Figure 3). In addition, there are  $\pi \cdot \cdot \pi$  stacking interactions among the adjacent benzene rings ( $Cg1 \cdot \cdot \cdot Cg5^{ii} = 4.4865(4)$ Å,  $Cg2 \cdot \cdot \cdot Cg5 = 4.4865(4)$  Å,  $Cg5 \cdot \cdot \cdot Cg5^{iii} = 4.1074(4)$  Å,  $Cg5 \cdot \cdot \cdot Cg5^{ii} = 4.10745(4)$  Å; symmetry codes: ii: x, -y, 1/2 + z; ii: x, -y, -1/2 + z).

#### **Oxidation of Benzyl Alcohols**

The results of the oxidation reactions are listed in Table 3. The results are in consistent with the literature that Schiff base copper complexes can oxidize benzyl alcohol and its derivatives into corresponding aldehydes [9,20,21]. The oxidation reactions were carried out at normal

### <sup>6</sup> ACCEPTED MANUSCRIPT

pressure with 50%  $H_2O_2$  and copper complex with catalytic amount in acetonitrile. Benzyl alcohol oxidation was studied in different reactions to find out the optimized condition for the oxidation process. In the presence of 4 mol% catalyst,  $H_2O_2$  as oxidant and 10 mL acetonitrile at 80 °C for 2 h the best yield of benzaldehyde (90%) was obtained after the oxidation of benzylalcohol. As comparison, the yield of the reaction was very low (< 10%) at room temperature. A blank reaction was also performed in absence of catalyst which gave very low yield of oxidation product. From Table 3, it can be seen that the presence of *para*-substituent groups can decrease the yield of the oxidation reactions.

#### CONCLUSION

A new end-on azido bridged polymeric copper(II) complex with 4-methyl-2-[(3-methylaminopropylimino)methyl]phenol as ligand has been synthesized and characterized by various physicochemical studies. Crystallographic study shows that the Cu coordination sphere is square pyramidal. The complex can catalyze the oxidation of benzyl alcohol derivatives to corresponding benzaldehydes in presence of  $H_2O_2$  as oxidant under atmospheric condition with high yields.

#### ACKNOWLEDGEMENTS

The author acknowledges the Experimental Center of Linyi Normal University for supporting this work.

## <sup>7</sup> ACCEPTED MANUSCRIPT

#### REFERENCES

1. Constable, E. C., Zhang, G., Housecroft, C. E., and Zampese, J. A., Mix and match: Templating chiral Schiff base ligands to suit the needs of the metal ion. *Dalton Trans.*, **2010**, 39, 5332-5340.

2. Sönmez, M., Çelebi, M., and Berber, İ., Synthesis, spectroscopic and biological studies on the new symmetric Schiff base derived from 2,6-diformyl-4-methylphenol with *N*-aminopyrimidine. *Eur. J. Med. Chem.*, **2010**, 45, 1935-1940.

3. Abdel-Aal, W. S., Hassan, H. Y., Aboul-Fadl, T., and Youssef, A. F., Pharmacophoric model building for antitubercular activity of the individual Schiff bases of small combinatorial library. *Eur. J. Med. Chem.*, **2010**, 45, 1098-1106.

4. Saghatforoush, L. A., Chalabian, F., Aminkhani, A., Karimnezhad, G., and Ershad, S., Synthesis, spectroscopic characterization and antibacterial activity of new cobalt(II) complexes of unsymmetrical tetradentate (OSN<sub>2</sub>) Schiff base ligands. *Eur. J. Med. Chem.*, **2009**, 44, 4490-4495.

5. Pui, A., Policar, C., and Mahy, J. P., Electronic and steric effects in cobalt Schiff bases complexes: Synthesis, characterization and catalytic activity of some cobalt(II) tetra-halogens-dimethyl salen complexes. *Inorg. Chim. Acta*, **2007**, 360, 2139-2144.

6. Zhang, J., Pan, F., Cheng, H., and Du, W. Synthesis, crystal structures, and antibacterial activity of cobalt(III) complexes with bidentate Schiff base ligands. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **2010**, 40, 211-215.

7. Heshmatpour, F., Rayati, S., Hajiabbas, M. A., Abdolalian, P., Neumuller, B. Copper(II)

### <sup>a</sup> ACCEPTED MANUSCRIPT

Schiff base complexes derived from 2,2'-dimethyl-propandiamine: Synthesis, characterization and catalytic performance in the oxidation of styrene and cyclooctene. *Polyhedron*, **2012**, 31, 443-450.

8. Ramadan, A. El-M. M., Ibrahim, M. M., Shaban, S. Y. Synthesis, characterization, and *tyrosinase* biomimetic catalytic activity of copper(II) complexes with schiff base ligands derived from  $\alpha$ -diketones with 2-methyl-3-amino-(3*H*)-quinazolin-4-one. *J. Mol. Struct.*, **2011**, 1006, 348-355.

9. Pattanayak, P., Pratihar, J. L., Patra, D., Brandao, P., Felix, V. Synthesis, crystal structure, spectral properties and catalytic activity of binuclear copper(II), mononuclear nickel(II) and cobalt(III) complexes containing Schiff base ligand. *Inorg. Chim. Acta*, **2014**, 418, 171-179.

10. Sheldrick, G. M., Program SADABS: Area-detector absorption correction, University of Göttingen, Germany, 1996.

11. Sheldrick, G. M., A short history of SHELX. Acta Crystallogr., 2008, A64, 112-122.

12. Geary, W. J., The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coord. Chem. Rev.*, **1971**, 7, 81-122.

13. Hothi, H. S., Makkar, A., Sharma, J. R., Manrao, M. R. Synthesis and antifungal potential of Co(II) complexes of 1-(2'-hydroxyphenyl)ethylideneanilines. *Eur. J. Med. Chem.*, **2006**, 41, 253-255.

14. Saghatforoush, L. A., Chalabian, F., Aminkhani, A., Karimnezhad, G., Ershad, S. Synthesis, spectroscopic characterization and antibacterial activity of new cobalt(II) complexes of unsymmetrical tetradentate (OSN<sub>2</sub>) Schiff base ligands. *Eur. J. Med. Chem.*, **2009**, 44, 4490-4495.

## <sup>9</sup> ACCEPTED MANUSCRIPT

15. Zhang, M., Xian, D.-M., Zhang, N., Li, H.-H., You, Z.-L. The construction of versatile azido-bridged Schiff base copper(II) complexes with xanthine oxidase inhibitory activity. *Struct. Chem.*, **2012**, 23, 1489-1496.

16. Zhou, X.-S., You, Z.-L., Xian, D.-M., Dong, D.-P. Synthesis, crystal structure, thermal stability, and magnetic property of an end-to-end azido-bridged dinuclear Schiff base copper(II) complex. *Chinese J. Inorg. Chem.*, **2013**, 29, 850-854.

17. Yaul, A. R., Pethe, G. B., Aswar, A. S. Synthesis, spectral, catalytic, and thermal studies of vanadium complexes with quadridentate Schiff bases. *Russ. J. Coord. Chem.*, 2010, 36, 254-258.
18. Niu, F., Yan, K.-X., Pang, L., Qu, D., Zhao, X., You, Z. Synthesis and structural characterization of Schiff base copper(II) complexes with Helicobacter pylori urease inhibitory

activities. Inorg. Chim. Acta, 2015, 435, 299-304.

19. You, Z.-L., Xian, D.-M., Zhang, M. Two lattern-like 1D polymeric Schiff base copper(I/II) complexes derived from copper(II) salts containing rarely seen [Cu<sup>I</sup>(NCS)<sub>4</sub>] bridges. *CrystEngComm*, **2012**, 14, 7133-7136.

20. Punniyamurthy, T., Velusamy, S., Iqbal, J. Recent advances in transition metal catalyzed oxidation of organic substrates with molecular oxygen. *Chem. Rev.*, **2005**, 105, 2329-2363.

Goberna-Ferrón, S., Lillo, V., Galán-Mascarós, J. R. [Cu(L-prolinate)<sub>2</sub>]: A catalyst for environmentally friendly oxidation of alkanes and alkenes with H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>. *Catal. Commun.*, 2012, 23, 30-33.

### <sup>10</sup> ACCEPTED MANUSCRIPT

Parameters	Values
Empirical formula	C <sub>12</sub> H <sub>17</sub> CuN <sub>5</sub> O
Formula weight	310.85
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	Cc
Unit cell dimensions	
<i>a</i> (Å)	13.375(1)
b (Å)	16.922(2)
<i>c</i> (Å)	6.7666(6)
β (°)	117.967(2)
V (Å <sup>3</sup> )	1352.6(2)
Ζ	4
$\rho_{\rm calc} ({\rm g \ cm}^{-3})$	1.526
$\mu (\mathrm{mm}^{-1})$	1.614
<i>F</i> (000)	644
Crystal size (mm)	0.29  imes 0.27  imes 0.27
$\theta$ Range for data collection (°)	3.24-25.49
Max. and min. transmission	0.6518, 0.6697
Reflections collected	6017
Unique ( <i>R</i> <sub>int</sub> )	2271
Observed reflections $[I > 2\sigma(I)]$	2209
Restraints	3
Parameters	175
Goodness-of-fit on $F^2$	1.064
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0201, wR_2 = 0.0515$
<i>R</i> indices (all data)	$R_1 = 0.0210, wR_2 = 0.0519$
Largest diffraction peak and hole $(e \text{\AA}^{-3})$	0.275 and -0.184

 Table 1. Crystallographic parameters of the complex

Bond lengths			
Cu1-O1	1.923(2)	Cu1-N1	1.987(2)
Cu1-N2	2.057(2)	Cu1-N3	2.034(2)
Cu1-N3A	2.464(3)		
Bond angles			
O1-Cu1-N1	91.20(9)	O1-Cu1-N3	88.51(10)
N1-Cu1-N3	158.08(9)	O1-Cu1-N2	173.66(10)
N1-Cu1-N2	94.98(8)	N3-Cu1-N2	86.27(11)
O1-Cu1-N3A	85.69(8)	N1-Cu1-N3A	95.50(9)
N3-Cu1-N3A	106.32(10)	N2-Cu1-N3A	92.33(9)

Table 2. Selected bond distances (A)	Å) and bond angles (°) for the complex

# <sup>12</sup> ACCEPTED MANUSCRIPT

Substrate	Product	Yield (%)
СН2ОН	СНО	93
F-CH <sub>2</sub> OH	FСНО	89
СІСН2ОН	СІ-СНО	88
Br — CH <sub>2</sub> OH	Вг-СНО	85
O2N CH2OH		90
— СН <sub>2</sub> ОН	— Сно	81

**Table 3.** Details of the catalytic oxidation reactions catalyzed by the complex

<sup>13</sup> ACCEPTED MANUSCRIPT



Figure 1. The electronic spectrum of the complex.

# <sup>14</sup> ACCEPTED MANUSCRIPT



Figure 2. Molecular structure of the complex drawn with 30% probability ellipsoids for non-hydrogen atoms. Atoms with suffix A are related to the symmetry operation x, -y, 1/2 + z.

# <sup>15</sup> ACCEPTED MANUSCRIPT



Figure 3. The end-on azido bridged polymeric structure of the complex, viewed down the c axis. Hydrogen bonds are shown as dashed lines.

# <sup>16</sup> ACCEPTED MANUSCRIPT



Scheme 1. HL

# <sup>17</sup> ACCEPTED MANUSCRIPT