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# Synthesis, spectral, photolysis and electrochemical studies of mononuclear copper(II) complex with a new asymmetric tetradentate ligand: Application as copper nanoparticle precursor

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# HIGHLIGHTS

- ► A new asymmetric tetradentate Schiff base derived from 1,2diaminopropane is reported.
- Copper(II) complex was applied as copper nanoparticle precursor.
- The redox properties of complex exhibit pseudo-reversible Cu(II)/ Cu(I) reduction and Cu(I)/Cu(II) oxidation.

# G R A P H I C A L A B S T R A C T

Photochemical and electrochemical characterization of a copper(II) complex with a new Schiff base was studied. The copper(II) complex was applied as new precursor for synthesis of copper nanoparticle.



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# ABSTRACT

A copper(II) complex with asymmetric tetradentate Schiff base ligand, obtained by the single condensation of 1,2-diaminopropane with 2-hydroxy-5-methoxy benzaldehyde was prepared. The ligand and complex were characterized by their IR, UV–Vis, FT-IR, NMR spectra and CV. Crystal structures of the mononuclear copper complex have been obtained by X-ray diffraction studies which revealed to be distorted square planner coordination geometry. The spectral data confirm coordination of ligand to copper ion center. The redox properties of complex at different scan rates exhibit grossly similar features consisting of an electrochemically pseudo-reversible Cu(II)/Cu(I) reduction at ca. –0.97 V and pseudo-reversible Cu(I)/Cu(II) oxidation at ca. –0.81 V. The copper nanoparticles with average size of 73 nm were formed by thermal reduction of copper complex in the presence of triphenylphosphine.

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# Introduction

Multidentate Schiff base ligands have played an important role in the development of coordination chemistry due to their preparative accessibility and spectral properties. Schiff bases and their complexes embrace very wide and diversified subjects such as, catalysis [1,2], reversible oxygen transport [3,4] various aspects of bioinorganic chemistry [5–10], biological activities [11–14], clinical [15] and analytical fields [16–18]. Schiff base complexes of copper are amongst the most versatile catalysts known for oxygenation reactions. The copper ions with the active sites have stimulated efforts to design and characterize copper complexes as models for biological systems [19,20]. Synthesis and characterization of nano-structures are important for scientific and industrial applications [21]. Nanoparticles have attracted great interest in recent years because

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of their unique chemical and physical properties, which are different from those of either the bulk materials or single atoms. Nanostructure materials have potential applications in ceramics, optoelectronics and catalysis [22]. Copper nanoparticle has received enormous attention owing to its important properties and widespread applications [23]. Research on the synthesis of nanomaterials using metal complexes as precursors has been less reported. Application of copper complexes as precursors may be helpful to control the physical properties of copper oxide nanoparticles [24].

In continuation of our earlier work [25,26] and to widen the scope of investigation on the coordination behavior of Schiff base ligands, herein we report the synthesis and spectroscopic characterization of copper(II) complex of new Schiff base ligand (Scheme 1). The new copper complex is applied for the preparation of copper nanoparticles as a precursor. The results of our studies on the preparation of copper nanoparticles using a new copper complex as a precursor are also discussed.

#### Experimental

### Materials and methods

All solvents and chemicals were used as received, except for the amines which were distilled under reduced pressure prior to use. 2-Hydroxy-3 or 5-methoxy benzaldehyde, 1,2-propanediamine, copper acetate and other chemicals were purchased from Aldrich or Merck. UV–Vis spectra were recorded on a Varian Cary 500 Scan spectrophotometer. FT/IR spectra of compounds were recorded on JASCO-FT/IR6300 spectrophotometer in the range of the 4000–400 cm<sup>-1</sup> as KBr pellets. Electronic spectra were obtained in CH<sub>3</sub>CN solutions by use of a JASCO-V570 spectrophotometer. A Brucker H NMR spectrometer at 400 MHz was used for recording of <sup>1</sup>H spectra in CDCl<sub>3</sub>. Philips XL-30 scanning electron microscopy (SEM) was used to image the size and morphology of the copper nanoparticle. Cyclic voltammograms of compounds have been recorded on a BHP 2063 Potentiostat Galvanostat instrument.

# Synthesis of ligand (L), [N,N-bis(2-hydroxy-5methoxybenzylidene)propane-1,2-diamine], (1)

The title compound (1), was prepared by reaction of 2-hydroxy-5-methoxy benzaldehyde (0.4 mmol, 60 mg) and (1,2-diaminopropane) (0.2 mmol, 15 mg) which were dissolved in methanol (10 mL). The mixture was stirred for 30 min. The <sup>1</sup>H NMR data of ligand are as following: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 1.39–1.43 (d, 3H, CH<sub>3</sub>), 3.88 (s, 6H, OCH<sub>3</sub>), 6.74–6.90 (m, 6H, HAr), 8.28–8.32 (s, 2H, N=CH), 13.72 (s, 2H, OH), IR (KBr, cm<sup>-1</sup>): 1620 (C=N), 2872 (C-H sp<sup>3</sup>).

# Synthesis of copper complex, [N,N-bis(2-hydroxy-5methoxybenzylidene)propane-1,2-diamine] copper(II), (**2**)

N,N-bis(2-Hydroxy-5-methoxybenzylidene)propane-1,2-diamine (1.0 mmol, 342 mg) was dissolved in methanol (5 mL) with stirring for 30 min at room temperature. A methanol solution



**Fig. 1.** Cyclic voltammogram of [(N,N-bis(2-hydroxy-5-methoxybenzylidene)propane-1,2-diamine]copper(II) in acetonitrile at 298 K in different scan rates (from 100 mV s<sup>-1</sup> to 600 mV s<sup>-1</sup>),  $c = 4 \times 10^{-3}$  M.

(5 mL) of Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (1.0 mmol, 199 mg) was then added. The mixture was stirred for further 30 min and then filtered. After keeping the filtrate in air for 3 days, green crystals were formed at the bottom of the vessel on slow evaporation of the solvent. Yield: 82%, mp: 183 °C, IR (KBr, cm<sup>-1</sup>): 1605 (C=N), 2868 (C-H sp<sup>3</sup>).

# Cyclic voltammetry

All cyclic voltammograms were recorded in a cell containing three electrodes: glassy carbon as working, platinum disk as supporting and silver wire as reference electrodes at room temperature. The potentials were scanned between 0.7 and -2.05 V at a scan rate of 100 mV s<sup>-1</sup>. For recording of cyclic voltammograms,  $10^{-3}$  M of ligand and its copper complex in dry acetonitrile as well as tetrabutylammonium hexafluorophosphate (TBAHFP) as supporting electrolyte were used. All solutions were deoxygenated by passing a stream of pre-purified N2 into the solution for at least 10 min prior to recording the voltammograms. All chemical potentials were modified using ferrocene/ferrocenium as internal standard electrode.

#### Preparation of copper nanoparticle

[N,N-bis(2-Hydroxy-5-methoxybenzylidene)propane-1,2-diamine] copper(II) was added to Triton X-100 as surfactant in the presence of triphenylphosphine to create a homogenous solution, then refluxed for 1 h at 140 °C. The supernatant was removed, and the nanoparticle sediment was washed, dried (62% yield). Triton X-100 plays a dual role, i.e. of an extractant and of a surface-capping agent that protects the outer surface of the newly formed particles thus avoiding the possibility of further growth.

### **Results and discussion**

#### Electrochemical studies

The cyclic voltammogram of [N,N-bis(2-hydroxy-5-methoxybenzylidene)propane-1,2-diamine]copper(II) was conducted at



Scheme 1. Synthesis of copper(II) complex of new Schiff base ligand.



**Fig. 2.** Spectral changes during the photolysis of  $0.3 \times 10^{-4}$  M N,N-bis(3-methoxy-benzylidene)-1,2-diaminopropane in CHCl<sub>3</sub> at room temperature at 5 min (a), 78 min (b), 130 min (c) and 170 min (d).



**Fig. 3.** Spectra changes during the photolysis of  $0.5 \times 10^{-4}$  M of copper(II) complex in CHCl<sub>3</sub> at 0, 10, 20, 30, 40 and 50 min irradiation times.

25 °C under an argon atmosphere using acetonitrile solutions containing 0.05 mol dm<sup>-3</sup> TBAHFP as supporting electrolyte and complex concentrations of about  $3 \times 10^{-3}$  M. The ligand is electroinactive over a range of +0.7 to -2.0 V. The redox properties of complex at different scan rates exhibit grossly similar features consisting of an electrochemically pseudo-reversible Cu(II)/Cu(I) reduction at ca. -0.97 V and pseudo-reversible Cu(I)/Cu(II) oxidation at ca. -0.81 V (Fig. 1). Copper(II) complex exist as five or six coordinate species (tetragonal) in solution while Cu(I) complex favors four (tetrahedral) coordination numbers. Reduction leads to loss of coordinated solvent from copper.

### Spectroscopic properties

FT-IR spectral data of the copper complex was compared with the ligand. The ligand, N,N-bis(2-hydroxy-3-methoxybenzylidene)propane-1,2-diamine shows a broad band characteristic of the OH group in the 3395–3585  $\text{cm}^{-1}$  region (SI. 1). The disappearance of this band in the FT-IR spectra of the complexes is indicative of the fact that the tetradentate N<sub>2</sub>O<sub>2</sub> ligands are coordinated as dianions. Deporotonation of OH group in free ligand forms a corresponding negative phenolate ion during complex formation. The (C=N) band appearing at 1620 cm<sup>-1</sup> in the ligands is shifted to lower frequencies by 15 cm<sup>-1</sup> in the copper complex, indicating that the ligands are coordinated to the metal ions through the  $N_2O_2$ groups (SI. 2). The UV-Vis spectrum of the free ligand showed major peaks at 270, 340 ( $\pi \rightarrow \pi^*$ ) and 300, 380 nm ( $n \rightarrow \pi^*$ ), identified as characteristic  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  absorption bands (Fig. 2). The UV-Vis spectrum of the complex showed major peak at 280 related to a ligand centered transition of the ligand and another at 400 nm which is identified as MLCT (Figs. 3 and 4). The <sup>1</sup>H NMR spectra of Schiff base shows one singlet at 13.72 ppm corresponding to phenolic-OH proton and one singlet at 8.27 ppm corresponding to azomethine proton (HC=N). Also, the <sup>1</sup>H NMR spectra of Schiff base ligand revealed a multiplet at 6.74-6.90 ppm corresponding to aromatic protons [27–30]. Crystal structures of the monouclear copper com-



Fig. 4. Photolysis set up: (a) oxygen cylinder; (b) power supply; (c) High pressure mercury lamps; (d) photoreactor with aluminum foil as reflector for a full irradiate of catalyst; (e) fan; (f) magnetic stirrer; (g) 2 l Pyrex beaker; (h) photolysis cell; (i) water thermostat Haake model F-122.



Fig. 5. ORTEP of copper(II) complex.

Table 1							
Selected	bond	lengths	[Å]	and	angles	[°]	for complex.

N(1) = Cu(1)	1 938(6)	O(1) = Cu(1) = O(2)	892(2)
N(2)-Cu(1)	1.926(6)	O(1) - Cu(1) - N(2)	176.7(2)
O(1) - Cu(1)	1.906(5)	O(2)-Cu(1)-N(2)	92.6(2)
O(2) - Cu(1)	1.910(5)	O(2)-Cu(1)-N(1)	176.3(2)

plex have been obtained by X-ray diffraction studies which revealed to be distorted square planner coordination geometry (Fig. 5). Table 1 shows selected bond lengths and angles for complex.

### Photochemical properties

Irradiating the chloroform solution of ligand with a high pressure mercury lamp, the absorption maximum at 270 and 340 nm decreased while 300 and 380 nm increased with isobestic points at 280, 320 and 350 nm (Fig. 2). The isobestic points indicates the keto-enol phototutomerization of the C=N bond of the coordinated ligand in solution (Scheme 2). The absorption maximum of complex at 295 nm decreased and 379 nm increased with an isobestic point at 280 and 370 nm (Fig. 3). The shift indicates the transformation from *syn* to *anti* configuration of the C=N bond of the coordinated ligand (Scheme 2). It is suggested that the photoisomerization is initiated through the rotation around the C=N bond in both singlet and triplet states.

#### Characterization of copper nanoparticle

The reaction of copper complex with Triton X-100 as surfactant in the presence of triphenylphosphine afforded brown copper



Fig. 6. Scanning electron microscope (SEM) image of the copper nanoparticles synthesized by thermal reduction.

nanoparticle. Triton X-100 plays a dual role, i.e. of an extractant and of a surface-capping agent that protects the outer surface of the newly formed particles thus avoiding the possibility of further growth. The SEM images of the copper nanoparticle prepared using [N,N-bis(2-hydroxy-5-methoxybenzylidene)propane-1,2-diamine] copper(II) as precursor and Triton X-100 showed that the average size 73 nm for copper nanoparticle (Fig. 6). This is attributed to the homogeneous nucleation process produced by the reduction of Cu<sup>2+</sup> to Cu.



Imine form

**Enamine form** 

Scheme 2. Imine-Enamine phototutomerization of the ligand in methanol solution.

# Conclusion

The present paper reports on the synthesis and electronic absorption spectra of new unsymmetrical tetradentate ligands Schiff base ligands and its Cu(II) complex. The synthetic procedure in this work resulted in the formation of complex in the molar ratio (1:1) (M:L). The newly synthesized Schiff base acts as dibasic tetradentate ligand. The copper ion is coordinated through the azomethine nitrogens and phenolic oxygen atoms via deprotonation forming stable. The present study revealed square planar geometry for Cu(II) complexes. Based on IR, electronic and <sup>1</sup>H NMR and single crystal X-ray structural studies a square planar geometry has been proposed for the for Cu(II) complex. Photolysis of the ligand shows isobestic points indicate that the ligand is presumably undergoing keto-enol tautomerization. The new copper complex was applied as a new precursor in preparation of copper nanoparticles using thermal reduction method. The present study illustrates simple and significant methods for the synthesis of copper complex and its application for copper nanoparticle.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.05.081.

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