

## Mononuclear Copper(I) Schiff Base Complex Cu((Cl-NO<sub>2</sub>-ba)<sub>2</sub>en)I(CH<sub>3</sub>CN): Synthesis and Crystal Structure

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**Summary:** New mononuclear copper(I) Schiff base complex Cu((Cl-NO<sub>2</sub>-ba)<sub>2</sub>en)I(CH<sub>3</sub>CN) (**1**) containing a bidentate Schiff base ligand (Cl-NO<sub>2</sub>-ba)<sub>2</sub>en = 2,4-dichloro-5-nitro-benzylidene-1,2-diaminopropane, was prepared in an acetonitrile solution and characterized by elemental analyses (CHN), FT-IR and UV-Vis spectroscopy. Suitable dark-orange single crystals were obtained by slow evaporation of solvent at 5 °C for several days. Crystal structure of the title compound **1** was determined by single-crystal X-ray diffraction. The complex **1** crystallizes in orthorhombic space group *Pna*2<sub>1</sub>, *a* = 16.8634 (5) Å, *b* = 8.4460 (5) Å, *c* = 17.4786 (2) Å, *V* = 2489.45 (17) Å<sup>3</sup> and *Z* = 4. In addition, the title compound **1** was used as new precursor for the synthesis of copper(II) oxide nanoparticles *via* solid state thermal decomposition. The as prepared CuO product was characterized by FT-IR, XRD and SEM.

**Keywords:** Copper(I) complex, Bidentate Schiff base, Crystal structure, X-ray diffraction, Copper(II) oxide, Nanoparticles.

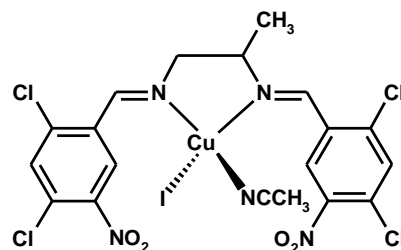
### Introduction

Schiff base compounds [1] and their transition metal complexes [2] have attracted interest of many researchers not only for structural diversity [3, 4] but also for various applications and properties [5, 6]. Symmetric bidentate NN Schiff base ligands are prepared from the reaction of 1 mol of diamine and 2 mols of aldehyde [7, 8] and often act as chelating ligands and coordinate to the various transition metal ions such as Zn(II) [9], Hg(II) [10], Ag(I) [11] and Cu(I) [12]. From d<sup>10</sup> electronic configuration ions, copper(I) is one of the best ions for the preparation of various structures such as mononuclear, dinuclear and polymeric complexes [12-14] and also for various applications and properties such as catalytic, redox and photochromism [15, 16].

Recently prepared and characterized of copper(II) oxide nanoparticles, a *p*-type semiconductor with a narrow band gap of 1.2 eV, have attracted attention of many researchers due to their various applications and properties such as removal of toxic pollutants [17], the anode material for Li-ion battery [18], optical [19, 20] and antibacterial properties [20, 21].

This study is a part of our ongoing effort to prepare of Schiff base complexes with bidentate NN Schiff base ligands [9-14] and also CuO nanoparticles [22]. Herein, we report synthesis, characterization and crystal structure of mononuclear

copper(I) Schiff base complex Cu((Cl-NO<sub>2</sub>-ba)<sub>2</sub>en)I(CH<sub>3</sub>CN) (**1**) (Scheme 1) as well as copper(II) oxide nanoparticles prepared by its calcination.



Scheme-1: Chemical structure of **1**.

### Experimental

#### Chemicals and apparatus

1,2-propanediamine, 2,4-dichlorobenzaldehyde, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, copper(I) iodide and acetonitrile were purchased commercially and used without further purification. Elemental analyses (CHN) were carried out using a Heraeus CHN-O-Rapid analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a KBr disk on an FT-IR Perkin-Elmer spectrophotometer. The <sup>1</sup>H-NMR spectrum was recorded on a BRUKER DRX-400 AVANCE spectrometer at 400 MHz for the

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Schiff base ligand. All chemical shifts are reported in  $\delta$  units downfield from TMS. X-ray powder diffraction (XRD) pattern of the complex was recorded on a Bruker AXS diffractometer D8 ADVANCE with Cu-K $\alpha$  radiation with nickel beta filter in the range  $2\theta = 10^\circ$ – $80^\circ$ . The scanning electron microscopy (SEM) images were obtained from a Philips XL-30ESEM.

#### X-ray structure determination

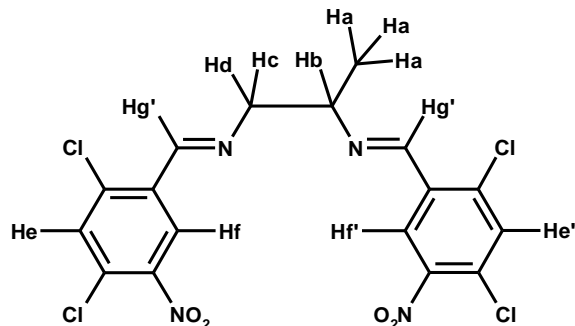
Suitable single crystal of the dimensions 0.25 mm  $\times$  0.10 mm  $\times$  0.07 mm was chosen for X-ray diffraction study. Crystallographic measurement was done at 120 K with a four circle CCD diffractometer Gemini ultra of Rigaku Oxford diffraction, using Cu-K $\alpha$  radiation from a sealed tube collimated by mirrors. As a detector we used the CCD detector Atlas S2. Crystal structures were solved by charge flipping with program SUPERFLIP [23] and refined with the Jana 2006 program package [24] by full-matrix least-squares technique on  $F^2$ . The molecular structure plots were prepared by Diamond 4.0 [25]. All hydrogen atoms were discernible in difference Fourier maps and could be refined to reasonable geometry, but according to common practice H atoms bonded to C were kept in ideal positions with C–H = 0.96 Å and U<sub>iso</sub>(H) set to 1.2U<sub>eq</sub>(C). All fully occupied non-hydrogen atoms were refined using harmonic refinement. The disordered carbon atoms were refined with restrained bond lengths using isotropic refinement since the harmonic refinement resulted in significant instability. All the atoms except the solvent, Cu1, I1 and disordered atoms were refined using the local mirror symmetry. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table-1.

#### Preparation of 2,4-dichloro-5-nitrobenzaldehyde

Into the mixture of sulfuric acid and nitric acid (2:1 v/v) kept at 0 °C, 2 g of 2,4-dichlorobenzaldehyde were slowly added and the mixture was stirred for about 0.5 h. After that the mixture was poured in ice-water. The precipitated bright yellow solid was filtered, washed with cold water and dried at room temperature for several days. Yield: 88%. Anal. Calcd. for C<sub>7</sub>H<sub>3</sub>NO<sub>2</sub>Cl<sub>2</sub>: C, 38.18%; H, 1.36%; N, 21.82%. Found; C, 38.22%; H, 1.32%; N, 21.85%. FT-IR (KBr, cm<sup>-1</sup>): 3087 (C–H aromatic), 2878 (C–H aldehyde), 1695 (C=O), 1410–1583 (C=C aromatic). <sup>1</sup>H-NMR (dms<sub>o</sub>-d<sub>6</sub>,  $\delta$ , ppm): 8.242 (s, 1 H), 8.470 (s, 1 H), 10.250 (s, 1 H).

#### Preparation of Schiff base ligand (Cl-NO<sub>2</sub>-ba)<sub>2</sub>en

A methanolic solution (10 mL) of 1,2-propanediamine (0.1 mmol, 0.06 g) is added drop-wise to a methanolic solution (10 mL) of 2,4-dichloro-5-nitrobenzaldehyde (0.2 mmol, 0.44 g) under stirring condition. The reaction mixture is refluxed for 1.5 h and the yellow-orange precipitates were filtered, washed with cold methanol and dried at room temperature for several days. Yield: 83%. Anal. Calcd. for C<sub>17</sub>H<sub>12</sub>N<sub>4</sub>Cl<sub>4</sub>O<sub>4</sub>: C, 42.68%; H, 2.51%; N, 11.71%. Found; C, 42.71%; H, 2.52%; N, 11.70%. FT-IR (KBr, cm<sup>-1</sup>): 2985–3060 (C–H aliphatic and aromatic), 1603 (C=N), 1410–1575 (C=C aromatic). <sup>1</sup>H-NMR (dms<sub>o</sub>-d<sub>6</sub>,  $\delta$ , ppm): 1.31 (d, 3 Ha), 3.65–3.70 (dd, 1 Hc), 3.77–3.84 (m, 1 Hb), 3.92–3.95 (dd, 1 Hd), 7.46, 7.48 (2 He,e'), 7.67, 7.68 (2 Hf,f'), 8.52, 8.55 (2 Hg,g'). The type of hydrogen atoms in Schiff base ligand (Cl-NO<sub>2</sub>-ba)<sub>2</sub>en are demonstrated in Scheme-2.



Scheme-2: The type of hydrogen atoms in Schiff base ligand L

#### Preparation of copper(I) Schiff base complex Cu((Cl-NO<sub>2</sub>-ba)<sub>2</sub>en)I(CH<sub>3</sub>CN)

A solution of (Cl-NO<sub>2</sub>-ba)<sub>2</sub>en (0.1 mmol, 0.464 g) in 10 mL acetonitrile is added drop-wise to a solution of CuI (0.1 mmol, 0.190 g) in 20 mL acetonitrile, and then was stirred for 1 h. Dark-orange crystals were prepared by slow evaporation of solvent, filtered, washed with cold methanol and dried at room temperature. Yield: 74%. Anal. Calcd. for C<sub>19</sub>H<sub>15</sub>N<sub>5</sub>Cl<sub>4</sub>O<sub>4</sub>CuI: C, 32.13%; H, 2.11%; N, 9.86%. Found; C, 32.09%; H, 2.12%; N, 9.89%. FT-IR (KBr, cm<sup>-1</sup>): 2990–3075 (C–H aliphatic and aromatic), 1594 (C=N), 1405–1565 (C=C aromatic).

#### Preparation of copper(II) Oxide nanoparticles

For preparation of CuO nanoparticles, 0.5 gr of copper(I) complex (1) was loaded into a crucible and grinded for 5 min. Then the crucible was placed in the electrical furnace and heated, at a rate of 10 °C/min in air, followed by a calcination at 500 °C for

2.5 h. The resulting CuO nanoparticles, were washed with ethanol, dried at room temperature and characterized by XRD and SEM.

## Results and discussion

The bidentate Schiff base ligand (Cl-NO<sub>2</sub>-ba)<sub>2</sub>en and its copper(I) complex are stable in air as solid and in solution. However, the solubility of ligand is good in common solvents such as methanol, ethanol, chloroform and dichloromethane, but the solubility of copper(I) complex is very low. Therefore, we report the <sup>1</sup>H-NMR spectrum of Schiff base ligand (Cl-NO<sub>2</sub>-ba)<sub>2</sub>en. By reaction of Schiff base ligand (Cl-NO<sub>2</sub>-ba)<sub>2</sub>en and copper(I) iodide in acetonitrile as solvent, we prepared suitable dark-orange single crystals of copper(I) complex. The ligand and its complex were characterized by elemental analysis (CHN) and FT-IR spectroscopy. In addition, crystal structure of copper(I) complex was determined by single-crystal X-ray diffraction. In the FT-IR of free ligand, there is a sharp band at 1603 cm<sup>-1</sup> confirming the presence of imine group

(C=N). This band is shifted to the lower frequency, 1594 cm<sup>-1</sup>, in the FT-IR spectrum of complex, which confirms the coordination of the imine nitrogen to the copper(I) ion [12-14]. The <sup>1</sup>H-NMR spectral data and peak assignments are presented in the experimental section for 5-nitro-2,4-dichlorobenzaldehyde and its bidentate Schiff base ligand (Cl-NO<sub>2</sub>-ba)<sub>2</sub>en. There are several groups of protons in the Schiff base ligand (Cl-NO<sub>2</sub>-ba)<sub>2</sub>en (Scheme 2). In Schiff base ligand, two types of iminic protons (H<sub>g</sub> and H<sub>g'</sub>) were observed at 8.52 and 8.55 ppm.

### Crystal structure description of Cu((Cl-NO<sub>2</sub>-ba)<sub>2</sub>en)I(CH<sub>3</sub>CN)

Single-crystal X-ray analysis shown that the copper(I) complex is monomer, four coordinate, neutral and crystallizes in orthorhombic space group *Pna*2<sub>1</sub>. An ORTEP view of this complex is shown in Fig 1. The selected bond distances and angles are presented in Tables-2 and 3, respectively.

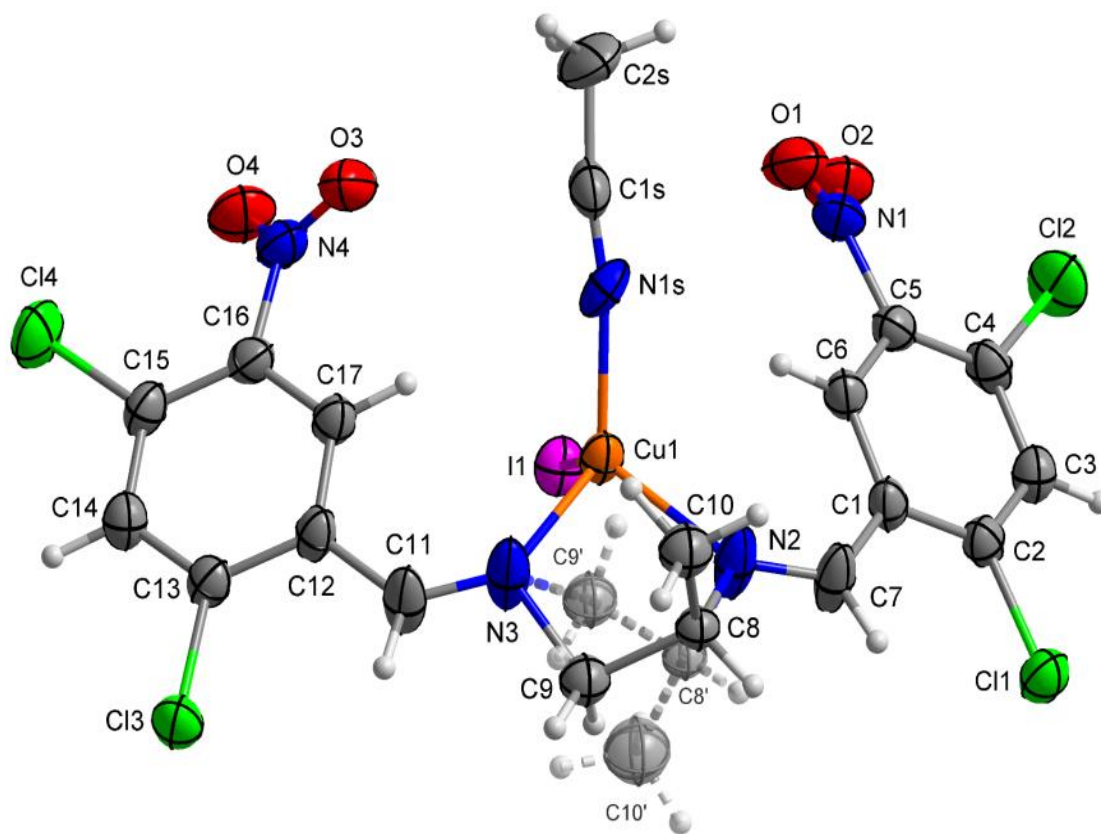


Fig -1: An ORTEP view of **1**. ADPs drawn at 50 % probability level.

Table-1: Crystal data and structure refinement details.

Formula weight	C <sub>19</sub> H <sub>15</sub> Cl <sub>4</sub> Cu <sub>1</sub> I <sub>1</sub> N <sub>5</sub> O <sub>4</sub>
Formula weight	709.6
Crystal system	Orthorhombic
Space group	<i>Pna</i> 2 <sub>1</sub>
<i>T</i> (K)	120.0
<i>a</i> (Å)	16.8634(5)
<i>b</i> (Å)	8.4460(5)
<i>c</i> (Å)	17.4786(2)
<i>V</i> (Å <sup>3</sup> )	2489.45(17)
<i>Z</i> , <i>S</i>	4, 1.29
$\mu$ , mm <sup>-1</sup>	15.25
<i>R</i> <sub>int</sub>	0.035
Measured reflections	15759
Independent reflections	3536
Parameters parameter	188
Flack parameter	0.47 (2)
Reflections with <i>I</i> > 3 $\sigma$ ( <i>I</i> )	3127
<i>R</i> ( <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )), <i>wR</i> ( <i>F</i> <sup>2</sup> )	0.032, 0.083
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.087, 0.458
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.43, -0.47

Table-2: The selected bond distances of copper(I) Schiff base complex **1**

II-Cu1	2.5541(6)	Cu1-N2	2.063(3)	N3-C11	1.271(4)
Cu1-N3	2.056(3)	Cu1-N1s	1.964(4)	N1s-C1s	1.135(7)
O1-N1	1.223(4)	O2-N1	1.220(3)	N3-C9	1.526(9)
O3-N4	1.223(4)	O4-N4	1.220(3)	N4-C16	1.470(4)
N1-C5	1.470(4)	N2-C7	1.271(4)	N3-C9'	1.505(15)
N2-C8	1.500(7)	N2-C8'	1.496(14)		

The copper(I) cation is coordinated by two imine nitrogen atoms from bidentate Schiff base ligand, one nitrogen atom from acetonitrile and one iodide anion. The resulting coordination can be described as distorted tetrahedral with bond angles ranging from 84.63(10)° for N-Cu-N in a chelate ring [26] to 114.03(12)° for I-Cu-N. The discrepancies were also observed in bond distances (Table 2) with the Cu1-I1 being the longest with 2.5541(6) Å followed by Cu1-N2 with 2.063(3) Å, Cu1-N3 with 2.056(3) Å and Cu1-N1s with 1.964(4) Å, due to the bulky iodide anion. The bond distances N2-C7, N3-C11 and N1s-C1s are 1.271(4) Å, 1.271(4) Å and 1.135(7) Å, respectively and confirmed the double bond for N2-C7 and N3-C11 and triple bond for N1s-C1s. The bond angle for C2s-C1s-N1s of the coordinated acetonitrile is 171(2)° and shown the coordination of acetonitrile molecule is almost linear and confirms the sp hybridization for C1s. The bond angles of C8-N2-C7 and C9-N3-C11 are 118.1(3)° and 112.7(4)°, respectively and confirm the sp<sup>2</sup> hybridization for N2 and N3 atoms.

Table -3: The selected bond angles of copper(I) Schiff base complex **1**

II-Cu1-N2	114.03(12)	II-Cu1-N3	113.99(12)	II-Cu1-N1s	104.98(11)
N2-Cu1-N3	84.63(10)	N2-Cu1-N1s	118.5(4)	N3-Cu1-N1s	120.3(4)
O1-N1-O2	124.4(3)	C7-N2-C8	118.1(3)	C9-N3-C11	112.7(4)
O3-N4-O4	124.4(3)	N1s-C1s-C2s	171(2)		

The bond angle O-N-O for nitro group is 124.4(3)°, confirmed the sp<sup>2</sup> hybridization for N atoms. In this complex, the bidentate Schiff base ligand is not planar and the dihedral angles between the plane A, contains C1-C2-C3-C4-C5-C6-C7-N2 atoms, and plane B, contains N3-C11-C12-C13-C14-C15-C16-C17 atoms, is 45.01(10)°. There is a disorder in the aliphatic carbons of the ligands (Fig 1). In the unit cell of this complex, there are four molecules and there are two different non-classic hydrogen bonds of C-H...O and C-H...I (Fig. 2).

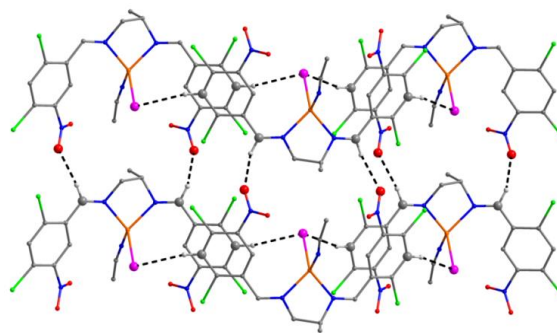


Fig. 2: The weak hydrogen bonds in structure of **1**. The hydrogen bonds shown as dashed lines. The weakly occupied atoms and hydrogen atoms not involved in hydrogen bonds were omitted for clarity.

#### Characterization of copper(II) oxide nanoparticles

The XRD pattern of the as-prepared CuO nanoparticles is shown in Fig 3. The characteristic peaks appear at distinct 2 $\theta$  values, 32.6 (110), 35.6 (-111), 38.7 (111), 48.9 (-202), 53.4 (020), 58.3 (202), 61.5 (-113), 66.8 (-311), 68.1 (220), 72.3 (311) and 75.1 (004), that can be assigned to the standard monoclinic pattern of CuO [20, 21].

Scanning electron microscopy (SEM) was used to study morphology of the as-prepared CuO nanoparticles. Fig 4 presents the SEM images of as-prepared CuO nanoparticles and show that the average size of the particles is about 100 nm with spherical shape.

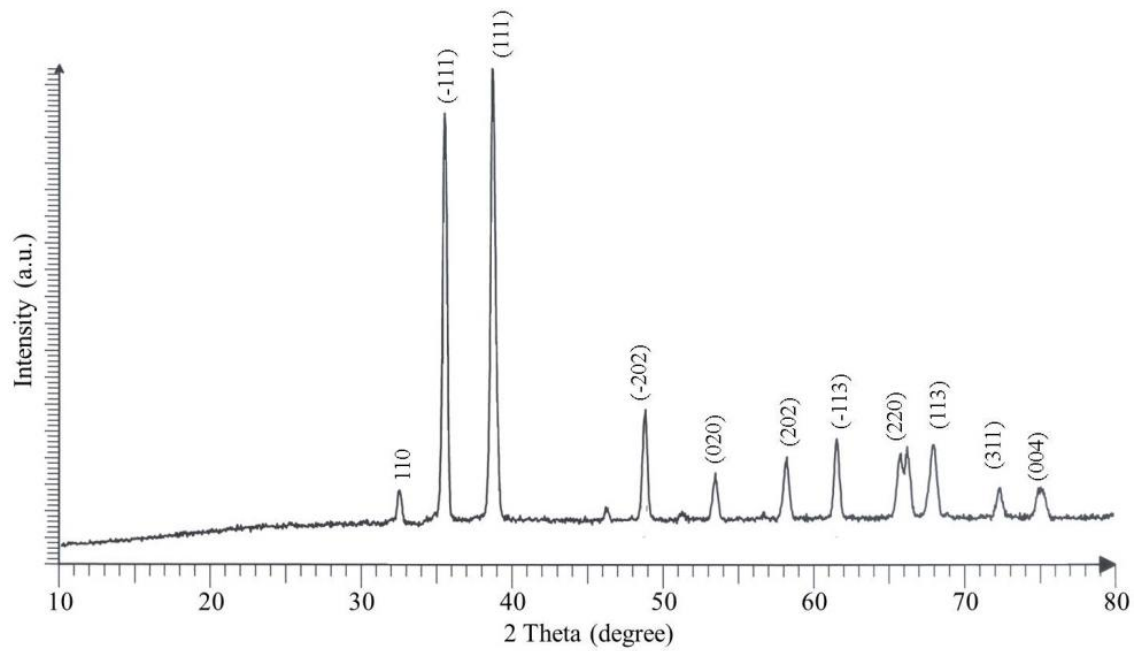


Fig -3: XRD pattern of the as-prepared copper(II) oxide nanoparticles.

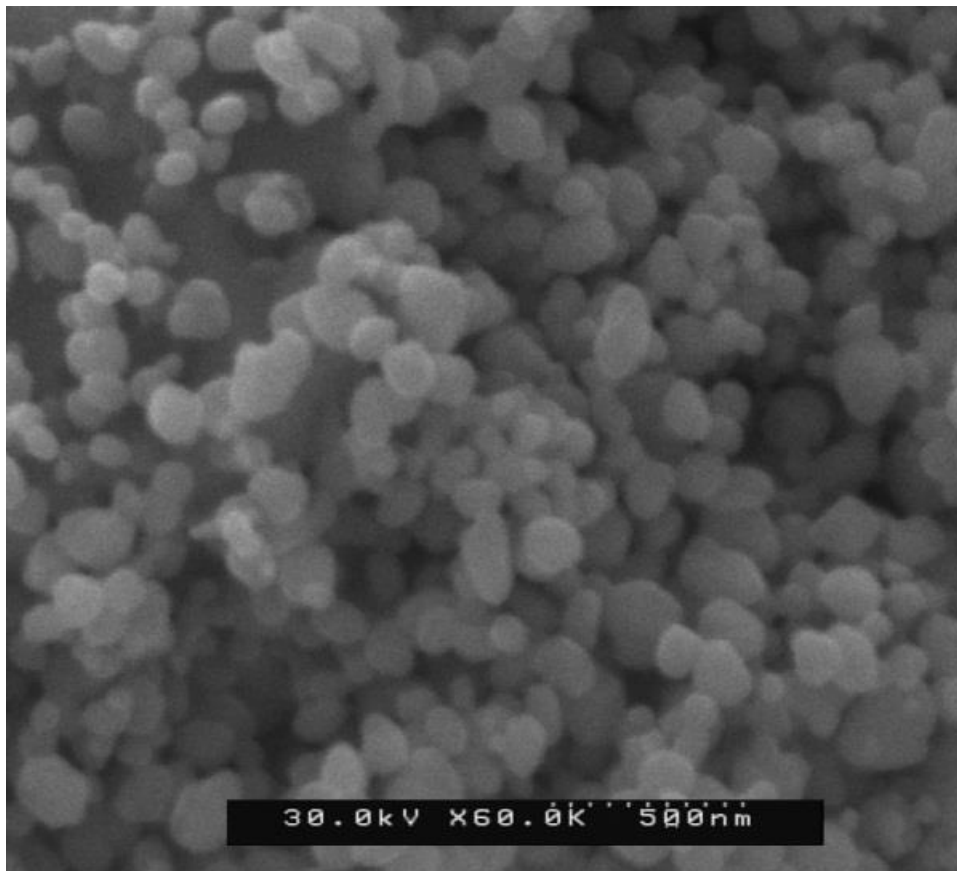


Fig -4: SEM image of the as-prepared copper(II) oxide nanoparticles.

## Conclusions

In this study, new mononuclear four coordinated copper(I) Schiff base complex **1** has been reported. In this complex one acetonitrile as solvent has been coordinated to copper(I) ion, and complete the tetrahedral geometry around it. The Schiff base ligand acts as chelating ligand with bite angle  $84.63(10)^\circ$  that is smaller than the ideal angle ( $109.5^\circ$ ) for tetrahedral. In addition, spherical shape of CuO nanoparticles were prepared by thermal decomposition of copper(I) Schiff base complex **1** at  $500^\circ\text{C}$ .

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