Facile Synthesis of CuO Nanoparticles from Cu(II) Schiff Base Complexes: Characterization, Antibacterial and Anticancer Activity

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ABSTRACT
In the anticancer activity studies, Cu(II) complexes have been considered as the best alternative to cis-platin due to their biocompatibility and significant functions in biological systems. Synthesis of nanoparticles from the Schiff base transition metal complexes was one of the most suitable methods, because the products obtained were of good purity and with perfect structure. Based on this, herein, we have reported the synthesis of two CuO Nps from two Copper Schiff base complexes by the thermal decomposition method. The Schiff base complexes were characterized by FTIR, UV-vis, 1H NMR, PXRD, EPR spectra, and TGA studies. The CuO Nps synthesized were characterized by FTIR, XRD, SEM, and EDX analyses. All the studies confirm the formation of the CuO nanoparticles. The Cu(II) complexes as well as the CuO Nps were analyzed for the antibacterial and anticancer studies. Studies indicate the high biological activity of the Cu(II) complexes than the CuO Nps. The decrease in activity of the CuO Nps may be due to the diminishing size of the particles in complexes.

1. Introduction
Metal complexes have been widely synthesized from the Schiff base ligands due to their huge applications in various fields [1–4]. Complexes synthesized from the metal ions like manganese, copper, and nickel were found to have high biological activities. In order to overcome the side effects caused by the anticancer drug cis-platin, metal complexes with similar activities but with fewer side effects have been reported by the researchers. Among the metal complexes, copper(II) complexes were found to be the best alternate to the cis-platin [5]. Recently synthesis of nanosized materials reached the researchers due their special properties like mechanical, physical, optical, and magnetic [6–8].
2. Materials and Methods

All chemicals were of analytical reagent grade and were used as received. The elemental analysis was performed on Carlo-Arabia 1106 instruments. The molar conductivity measurements were carried out by using Elico-CM Conductivity Bridge with \( 10^{-3} \) M DMSO as solvent. FTIR spectra were recorded as KBr pellet using a Thermo Nicolet, Avatar 370 model FT-IR spectrophotometer on arranging between 4000 and 400 cm\(^{-1}\). Electronic absorption spectra were recorded on Perkin Elmer Lambda 25 UV-vis spectrometer between 200–800 nm by using DMSO solvent. The magnetic properties of the complexes were studied by Gouy balance. \(^1\)HNMR spectra for the ligand were recorded on a Bruker Avance III, 400 MHz NMR spectrometer using DMSO-d\(_6\) solvent and TMS as internal standard. The EPR spectrum was recorded on a Bruker spectrometer operating in the X-band and using 100 kHz magnetic field modulation. The thermo gravimetric analysis of the complexes were recorded on Perkin Elmer STA 6000 thermal analysis system within the temperature range 40–740 °C. The SEM/EDS micrographs were recorded on JEOL Model JSM – 6390LV microscope.

\section{2.1. Synthesis}

\subsection{2.1.1. Synthesis of Ligand L1}

To a hot ethanolic solution (0.005 mol) of thiosemicarbazide, an ethanolic solution (0.0025 mol) of 5-aminoisophthalic acid was added with constant stirring and refluxed for 3 h and cooled at room temperature. The solid formed was filtered, washed with ethanol, and dried in a desiccator (Scheme 1).

Anal. Calcd. for \( \text{L1, } \text{C}_{10}\text{H}_{13}\text{N}_{7}\text{O}_{2}\text{S}_{2} \) (%): C, 36.62; H, 3.96; N, 29.96; O, 9.78; S, 19.57; Found: C, 36.69; H, 4.00; N, 29.95; O, 9.77; S, 19.59; Yield: 90%; Color: Sandal color; m.p: 190 °C. IR (KBr, cm\(^{-1}\)): 1612 (ν(C=N)); 863 (ν(C=S)); 3375 (ν(OH)); 1158 (ν(C-N)); UV-vis (\( \lambda_{\text{max}} \), nm): 247, 333.

\subsection{2.1.2. Synthesis of Ligand L2}

To an ethanolic solution (0.005 mol) of benzamide, an ethanolic solution (0.0025 mol) of 5-aminoisophthalic acid was added with constant stirring and refluxed for 3 h and cooled at room temperature. The solid formed was filtered, washed with ethanol, and dried in a desiccator (Scheme 2).

Anal. Calcd. for \( \text{L2, } \text{C}_{22}\text{H}_{17}\text{N}_{7}\text{O}_{4} \) (%): C, 68.21; H, 4.42; N, 10.85; O, 16.53; Found: C, 68.14; H, 4.39; N, 10.85; O, 16.53; Yield: 90%; Color: White color; m.p: 250 °C. IR (KBr, cm\(^{-1}\)): 1624 (ν(C=N)); 1552 (ν(C=O)); 1417 (ν(M-O)); 619 (ν(M-O)); UV-vis (\( \lambda_{\text{max}} \), nm): 223, 342.

\subsection{2.1.3. Synthesis of Cu(II) Complexes 1 and 2}

To an ethanolic solution of the ligands L1 and L2 (0.001 mol) an ethanolic solution of Cu(OAc)\(_2\) (0.001 mol) was added, respectively, with constant stirring and refluxed for 3 h. The Copper complexes thus synthesized was filtered and dried in a desiccator [17].

Anal. Calcd. for \( \text{1, } [\text{CuO}_{2}\text{N}_{7}\text{S}_{2}\text{C}_{10}\text{H}_{13}]\text{(OAc)_{2}} \) (%): C, 33.03; H, 3.73; N, 19.27; O, 18.87; S, 12.49; Cu, 12.49; Found: C, 33.00; H, 3.76; N, 19.26; O, 18.86; S, 12.60; Cu, 12.43; Yield: 85%; Color: Black; m.p: 250 °C. IR (KBr, cm\(^{-1}\)): 1612 (ν(C=N)); 828 (ν(C=S)); 3173 (ν(OH)); 1294 (ν(C-N)); 442 (ν(M-N)); UV-vis (\( \lambda_{\text{max}} \), nm): 223, 321, 449, 641.

Anal. Calcd. for \( \text{2, } [\text{C}_{22}\text{H}_{17}\text{N}_{7}\text{O}_{4}\text{Cu}]\text{(OAc)_{2}} \) (%): C, 54.87; H, 4.04; N, 7.38; O, 22.51; Cu, 11.17; Found: C, 54.75; H, 3.96; N, 7.31; O, 22.45; Cu, 11.01; Yield: 85%; color: Green; m.p: >250 °C. IR (KBr, cm\(^{-1}\)): 1632 (ν(C=N)); 1524 (ν(C=O)); 3303 (ν(OH)); 1101 (ν(C-N)); 468 (ν(M-N)); 619 (ν(M-O)); UV-vis (\( \lambda_{\text{max}} \), nm): 227, 314, 423, 654.

\subsection{2.1.4. Preparation of CuO Nanoparticles}

The CuO nanoparticles were prepared from Precursors 1 and 2 by Calcination method [18].

The Copper Schiff base complexes were prepared from Precursors and 2 by Calcination method [18]. The Copper Schiff base complexes were taken in a porcelain crucible and heated to 500 °C in an electric furnace for 2 h. The decomposition product generated from the complexes was cooled to room temperature and kept in a desiccator. The pure CuO Nps thus obtained was characterized by spectroscopic studies.

\subsection{2.1.5. In-vitro Antibacterial Assay}

In order to know the antibacterial activity of the synthesized compounds, the compounds were tested against the gram-positive bacteria \( S.aureus \) E.coli by the disk diffusion method using Streptomycin as control and DMSO as the solvent or media [19,20].
2.1.6. In-vitro Cytotoxic Activity
The In-vitro cytotoxic activities of the synthesized Schiff bases, its complexes, and CuO nanoparticles were studied on MCF-7 cell line (human breast cancer cells) by applying the MTT colorimetric assay [21]. The protocol for this MTT assay was discussed in our already-published article [18].

3. Results and Discussions
Schiff base ligands and its Cu(II) complexes were characterized by FTIR, UV-vis, $^1$H NMR, TGA, EPR, and PXRD methods. Cu(II) complexes were used as the precursors for the synthesis of CuO nanoparticles and the nanoparticles were characterized by XRD, SEM & EDX analysis methods. Molar conductance values of the complexes fall in the range of 76–89 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ in Ethanol solution, which indicates 1:2 electrolytic nature of the complexes [22].

3.1. FTIR Spectra
The very strong and sharp band located at 1612 and 1624 cm$^{-1}$ due to the azomethine group of the ligands L1
and L2, respectively, were shifted to 1621 and 1632 cm\(^{-1}\) in the complexes 1 and 2, respectively, after complexation [23]. The bands observed at 863 and at 1552 cm\(^{-1}\) in the ligands L1 and L2, respectively, were due to the C=S and C=O stretching vibrations, which was shifted in the complex 1 and complex 2, respectively, indicates the coordination of sulfur atom to the metal ion in complex 1 and oxygen to the metal ion in complex 2. The sharp band found at 3375 and 3367 cm\(^{-1}\) in the spectra of L1 and L2, respectively, was assigned to the -OH stretching frequency of the 5-aminoisophthalic acid. These bands were shifted to 3173 and 3303 cm\(^{-1}\) in the complexes 1 and 2, respectively, after complexation [24]. The bands corresponding to C-N stretching frequency obtained at

3.2. UV-vis Spectra

The ligands L1 and L2 show band in the region 247 and 223 nm, respectively, which can be attributed to \(\pi-\pi^*\) transition for the aromatic system. The \(\pi-\pi^*\) transition was shifted to a corresponding wavelength 223 & 227 nm upon formation of the complex 1 and complex 2, respectively.

Scheme 2. Synthetic route for the synthesis of Ligand 2 and its metal complex 2.
The wavelength observed at 333 and 342 nm in the UV – Vis spectra of the ligands L1 and L2 corresponding to the n-π* transition was shifted to 321 and 314 nm in the complexes 1 and 2, respectively, upon complexation. In the electronic spectrum of the Cu(II) complexes 1 and 2, the new absorption bands observed at 449 and 423 nm, respectively were attributed to the LMCT transition, and also the band observed at 641 nm for complex 1 and 654 nm for complex 2, respectively was attributed to the d-d transition, which was assigned to the two spin-allowed \( ^2A_g \leftarrow ^2B_{1g} \) and \( ^2E_g \leftarrow ^2B_{1g} \) transitions. All these assignments were incompatible with the square planar geometry of the Cu(II) complexes. The square planar geometry of the Cu(II) complexes was further confirmed from its magnetic moment values 1.78 and 1.76 B.M. [26].

3.3. \(^1\)H NMR Spectra

The \(^1\)H NMR spectra of the ligands L1 and L2 (Figures 1 and 2) shows multiplets at 7.2–7.6 and 7.3–7.9 ppm, respectively, was attributed to the aromatic protons [27]. The signal appeared at 5.63 ppm in the ligands was assigned to the aromatic NH\(_2\) (Ar-NH\(_2\)) groups [28]. The sharp signal observed at 9.9 and 13.05 in the ligands L1 and L2, respectively, were due to the carboxylic –OH group of 5-aminoisophthalic acid [29]. The signal obtained at 2.5 ppm in the \(^1\)H-NMR spectra of L1 was due to the alkyl -NH proton [30].

3.4. PXRD Studies

Crystals that are suitable for single-crystal studies were not obtained for the Cu(II) complexes. In order to know the crystalline nature of the complexes powder XRD patterns of the complexes were studied. PXRD (Figure 3) of the complex 2 shows sharp peaks indicating its crystalline nature, whereas the complex 1 (Figure 4) shows only less intense crystalline peaks, which indicates its non-crystalline nature. The 2θ values for the important peaks have been listed in Table 1. The d-spacing values calculated for the complex 2 were found to be in good agreement with that of the observed one. Absence of the forbidden number 7 shows that the complex 2 may have cubic symmetry. The crystallite size was estimated according to the

Figure 1. NMR spectra of the ligand L1.
Figure 2. NMR spectra of the ligand L2.

Figure 3. PXRD of the Cu(II) Complex 1.
bond nature. If the $g_{‖}$ value is <2.3, metal to ligand bond will have covalent character and if $g_{‖}$ value is >2.3, metal to ligand bond will have ionic character [33]. The $g_{‖}$ value of the complexes indicates that the M-L bond in these complexes were in Covalent nature.

The value of the exchange interaction term $G$ is estimated from the expression,

$$G = \frac{g_{‖} - 2}{g_{┴} - 2}$$

[34], and if $G > 4$, then the exchange interaction is negligible between the copper centres. On the other hand, if $G < 4$ indicates the presence of exchange interaction in the solid complex. The observed value for the exchange interaction parameter for both the copper complexes ($G > 4.0$) indicates that there is no considerable interaction between the copper centres.

### 3.6. TGA

In the present investigation, thermal stability of the complexes was studied at temperature range of 50–720 °C in highest value of intensity compared with the other peaks using Deby–Scherrer Equation (1) [31]

$$D = \frac{K\lambda}{\beta \cos \theta}$$

(1)

where, $D$ is the crystallite size, $K$ is a constant (0.94 for Cu grid), $\lambda$ is the X-ray wavelength ($\lambda = 1.5406\AA$), $\theta$ is the Bragg diffraction angle and $\beta$ is the integral peak width. The crystallite size of the complex 2 was found to be 15.05 nm.

### Table 1. Powder XRD data of Cu(II) complex 2.

| Peak | $2\theta$ | $\Theta$ | $\sin \theta$ | $\sin^2 \theta$ | $h^2+k^2+l^2$ | Hkl | $d_{\text{obs}}$ | $d_{\text{calc}}$ |
|------|-----------|----------|---------------|-----------------|----------------|-----|----------------|-----------------|
| 1    | 8.950     | 4.475    | 0.0780        | 0.0060          | 2              | 110 | 9.8723         | 9.8725          |
| 2    | 11.361    | 5.680    | 0.0968        | 0.0097          | 3              | 111 | 7.7203         | 7.7822          |
| 3    | 13.464    | 6.732    | 0.1172        | 0.0137          | 4              | 200 | 6.5708         | 6.5711          |
| 4    | 15.865    | 7.933    | 0.1380        | 0.0190          | 5              | 210 | 5.5817         | 5.5812          |
| 5    | 16.804    | 8.402    | 0.1461        | 0.0213          | 6              | 211 | 5.2719         | 5.2717          |
| 6    | 18.051    | 9.0255   | 0.1568        | 0.0245          | 6              | 211 | 4.9103         | 4.9103          |
| 7    | 20.450    | 10.225   | 0.1775        | 0.0315          | 8              | 220 | 4.3392         | 4.3393          |
| 8    | 22.194    | 11.095   | 0.1924        | 0.0370          | 10             | 310 | 4.0021         | 4.0021          |
| 9    | 24.056    | 12.028   | 0.2083        | 0.0433          | 11             | 311 | 3.6964         | 3.6944          |
| 10   | 25.573    | 12.628   | 0.2186        | 0.0477          | 13             | 320 | 3.4804         | 3.4804          |
| 11   | 26.697    | 13.348   | 0.2308        | 0.0532          | 14             | 321 | 3.3364         | 3.3365          |
| 12   | 28.431    | 14.2155  | 0.2455        | 0.0603          | 16             | 400 | 3.1368         | 3.1367          |

Figure 4. PXRD of the Cu(II) Complex 2.

3.5. EPR Spectra

The EPR spectra of the complexes 1 and 2 appear with $g_{∥}$ values at 2.17 & 2.26 and $g_{┴}$ value at 2.03 & 2.06, respectively. (Figures 5 and 6) For both the complexes $g_{∥} > g_{┴} > 2$, which indicate that the unpaired electrons lie in the $d_{x^2−y^2}$ orbital, suggesting a square planar geometry for the complexes [32]. The $g_{∥}$ value indicates the M-L bond nature. If the $g_{∥}$ value is <2.3, metal to ligand bond will have covalent character and if $g_{∥}$ value is >2.3, metal to ligand bond will have ionic character [33]. The $g_{∥}$ value of the complexes indicates that the M-L bond in these complexes were in Covalent nature.

The value of the exchange interaction term $G$ is estimated from the expression, $G = (g_{∥} - 2)/(g_{┴} - 2)$ [34], and if $G > 4$, then the exchange interaction is negligible between the copper centres. On the other hand, if $G < 4$ indicates the presence of exchange interaction in the solid complex. The observed value for the exchange interaction parameter for both the copper complexes ($G > 4.0$) indicates that there is no considerable interaction between the copper centres.

3.6. TGA

In the present investigation, thermal stability of the complexes was studied at temperature range of 50–720 °C in
between 120 and 350 °C, a mass loss of 23(23.2)% occurs, which indicates the loss of acetate present in the complex. The remaining decomposition steps between 350 and air (Figures 7 and 8). The decomposition at a temperature range between 40 and 120 °C indicates the presence of lattice water in complex 1. At the temperature ranges between 120 and 350 °C, a mass loss of 23(23.2)% occurs, which indicates the loss of acetate present in the complex. The remaining decomposition steps between 350 and
450 °C and above 450 °C indicate the loss of ligand moiety with a mass loss of 29(29.3)% leaving the CuO residue at the end of the decomposition.

The loss of lattice water in the complex 2 occurs between the temperature ranges of 90–120 °C. At the temperature range of 280–400 °C the complex decomposes with a total mass loss of 88%, which was assigned for the loss of the ligand moiety leaving the CuO residue above 700 °C [35]. The thermal analysis data are listed in Table 2.

Table 2. Thermal analysis data of complexes.

| Complex                  | Temp. range (°C) | Mass loss found (calcd) (%) | Assignment            |
|--------------------------|------------------|-----------------------------|-----------------------|
| [C_{10}H_{13}N_{7}O_{2}S_{2}Cu]_{(OAc)}_{2} | 40–120           | –                           | Loss of lattice water |
|                          | 120–350          | 23 (23.2)                   | Loss of 2CH_{3}COO    |
|                          | 350–450          | 29 (29.3)                   | Loss of Cu_{n}O_{n}N_{n} |
|                          | 450–710          | –                           | CuS                   |
| [C_{22}H_{17}N_{3}O_{4}Cu]_{(OAc)}_{2}   | 90–120           | –                           | Loss of lattice water |
|                          | 280–400          | 88 (88.8)                   | Loss of Cu_{n}O_{n}N_{n} |
|                          | 400–700          | –                           | CuO                   |
the CuO Nps synthesized from the complexes 1 and 2 was found to be 28 and 42 nm, respectively. Thus, the XRD spectrum confirms the formation of CuO Nps.

### 3.7.2. SEM & EDX

Figures 11 and 12 show the SEM images of CuO Np’s synthesized from complexes 1 and 2. The SEM images of the CuO Np’s show uniform distribution of the particles. The particle size calculated for the CuO Np’s synthesized from
complexes 1 and 2 were found to be 24–32 and 36–48 nm, which is in good agreement with that the particle size calculated by Debye–Scherrer equation using the XRD spectra.

EDX spectra of the CuO Np’s show peaks corresponding to Cu and O, which confirms the purity and formation of CuO Np’s. (Figures 13 and 14)

3.7.3. FTIR Spectra
The FTIR spectra (Figures 15 and 16) of the CuO Np’s synthesized from the complexes 1 and 2, shows CuO vibrations at 538, 516, and 464 cm$^{-1}$.

3.7.4. Antibacterial Activity
The antibacterial activity of the Copper Schiff base complexes 1 & 2 and its CuO Np’s were tested against the gram-positive bacteria S.aureus and gram-negative bacteria E.coli by the disk diffusion method using Streptomycin as control and DMSO as the solvent or media. The activity of the compounds is represented by size of the diameter in mm. The concentrations used to study the antibacterial activities were 30 and 60 μg mL$^{-1}$ [36]. The antibacterial activity of the Schiff base ligand and their metal complexes arises due to the presence of azomethine groups. The activity of the ligands, their complexes and CuO Np’s increases as the concentration increases (Figure 17). The results indicate that the complexes are found to be more active than that of the free ligands, due to the chelation [37] of the ligands with metal ions. Such increased activity of the metal chelates can be explained on the basis of overtone’s concept of cell permeability, the lipid membrane
that surrounds the cell favors the passage of only lipid solvable materials, due to which liposolubility is an important factor that controls antimicrobial activity. On chelation, the polarity of the metal ion is reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor group. Further, it increases the delocalization of electron over the whole chelate ring and enhances the lipophilicity of the complex. This increased lipophilicity enhances the penetration of the complexes into lipid membranes and blocking of metal binding sites on the enzymes of the microorganism [36]. The result shows that among the

Figure 14. EDX spectra of CuO Np 2.

Figure 15. FTIR spectra of CuO Np 1.
3.7.5. In-vitro Cytotoxic Activity of the Precursors and its Nanoparticles

In-vitro Cytotoxic activity of the Cu(II) Schiff base complexes 1, 2 and CuO NPs were evaluated against the MCF-7 cell line using 5-fluorouracil (IC$_{50}$ = 11.24 μM) as control by the MTT assay. The anticancer activity of the Cu(II) complexes synthesized, the complex 2 was found to be more active than the complex 1. Both the CuO NPs were found to have similar antibacterial activity. The decrease in activity of the nanoparticles may be due to diminishing the size of the particles in the metal complexes [38] (Figure 18).

Figure 16. FTIR spectra of CuO Np 2.

Figure 17. Antibacterial activity of Ligands, metal complexes and CuO Np’s synthesized from corresponding complexes against gram ‘+’ve and gram ‘−’ve bacterial strains.
complex 2 with IC_{50} value 18.34 was found to have high activity than the Cu(II) complex 1 (12.82). From the Figure 19, it was inferred that as the concentration of the complexes increases, the cell viability decreases. Whereas in the case of CuO Nps as the concentration increases, the cell viability also increases, this indicates its low anticancer activity [18]. The decrease in activity of the nanoparticles may be due to the diminishing size of the particles in complexes.

4. Conclusion

The main goal of the present work is to synthesize Copper Oxide nanoparticles from the Schiff base complexes and their utilization as antibacterial and anticancer agents. The Schiff base ligands were synthesized from the starting compounds in 1:1 M ratio. Cu(II) Schiff base complexes 1 and 2 were synthesized from the corresponding ligands and were used as precursors for the synthesis of CuO Nps. FTIR spectra of the compounds reveal that the ligand L1 coordinates through the azomethine nitrogen atoms and sulfur atoms, whereas the ligand L2 coordinates through the azomethine nitrogens and oxygens atoms. Magnetic susceptibility values, Electronic and EPR spectra suggest square planar geometry for both the complexes. PXRD of the complexes 2 shows its crystalline nature. Thermal stability of the complexes was obtained by TGA studies. Formation of the CuO nanoparticles synthesized from the Cu(II) complexes were obtained by FTIR, XRD, SEM, and EDAX spectra. These are also helpful to further study the anti-micro bacterial activity of synthesis ligands and metal complexes. Antibacterial and anticancer activities of the complex 2 was found to be more than the complex 1 and ligands, due to the aromatic nature of the ligand 2. Both

Figure 18. Bar diagram representation of the antibacterial activity for the synthesized compounds.

Figure 19. Cytotoxic activities of compounds against MCF-7 cell line at different concentrations, where, a- Cu(II) complex 1, b- Cu(II) complex 2, c- CuO Np synthesized from complex 1 and CuO Np synthesized from complex 2.
the CuO NPs were found to have similar antibacterial and anticancer activities.

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Disclosure statement
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