Research Article
Spectral, Structural, and Antibacterial Study of Copper(II) Complex with N$_2$O$_2$ Donor Schiff Base Ligand and Its Usage in Preparation of CuO Nanoparticles

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A new Schiff base complex, Cu(H$_2$L)$_2$ (H$_3$L: 6,6′-((1E,1′E)-((azanediylbis(ethane-2,1-diyl))bis(azanylylidene))bis(methanylylidene))bis(2-methoxyphenol)), through the reaction of ligand H$_3$L with Cu(NO$_3$)$_2$·3H$_2$O, in the ratio of 2 : 1 in methanol solvent was prepared. The obtained ligand (H$_3$L) was characterized by FT-IR, 13C NMR, 1H NMR and elemental analyses. Then its copper(II) complex was prepared and characterized by FT-IR spectroscopy, thermal studies, elemental analyses and single crystal X-ray diffraction. The X-ray crystallography revealed that the two H$_3$L ligands in bidentate fashion coordinated to one copper center for producing Cu(H$_2$L)$_2$ complex. We used copper(II) Schiff base complex, Cu(H$_2$L)$_2$, for the preparation of CuO nanoparticles via solid-state thermal decomposition. The crystalline structure of the product was studied by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). XRD indicated that the new product was copper oxide. SEM image showed that the size of CuO nanoparticles was between 46 and 53 nm, and they had uniform shape. The antibacterial properties of the complex and ligand were also investigated. The results revealed that Schiff base complex showed higher biological activity than Schiff base ligand.

1. Introduction

Schiff base complexes have attracted many attentions in coordination chemistry because of their interesting applications, structures, and properties [1–4]. These complexes have been highlighted in coordination chemistry where they are used as catalysts for organic reactions and they also have interesting magnetic properties [5–7]. Moreover, metal complexes of Schiff bases received great importance in biology for their widespread applications [8, 9]. In biological systems, the Schiff bases characterized by an imine group (N=CH) help to explain the process of Schiff transamination and racemization reaction [10]. Tetradentate Schiff base ligands with a N$_2$O$_2$ donor atom are popular for coordinating with different metal ions [11–13]. These Schiff base complexes have attracted more attentions since they can be used as antibacterial, antifungal, and antitumor agents [14–18]. Because of the applications of Schiff base complexes in the preparation of CuO nanoparticles, they have received considerable attention recently [19]. The synthesis and characterization of CuO nanoparticles through thermal decomposition of complexes have been widely studied because of their unique properties and applications. There are various methods for the preparation of CuO nanoparticles such as electrochemical, hydrothermal, and thermal decomposition and evaporation. Among them, thermal decomposition is a good choice because it can control process conditions and particle crystal structure, size, and purity [20–25]. Studies on thermal decomposition of metal complex for preparation of metal oxide nanoparticles indicated its superiority over other conventional methods since it is economical, rapid, and controllable [26, 27]. In the present study, we have synthesized 6,6′-((1E,1′E)-((azanediylbis(ethane-2,1-diyl))bis(azanylylidene))bis(methanylylidene))bis(2-methoxyphenol) (H$_3$L) Schiff base ligand and used it for the preparation of new Cu(H$_2$L)$_2$
complex (Scheme 1). We have also prepared a CuO nanoparticles by thermal decomposition of Cu(II) Schiff base complex, Cu(H$_2$L)$_2$. Antibacterial activities of Schiff base ligand and complex were tested against the *Escherichia coli*, *Acinetobacter baumannii*, *Klebsiella pneumoniae*, and *Pseudomonas aeruginosa*.

2. Experimental

2.1. Materials and Physical Measurements. In agreement with the published methods, the methanol was dried [28]. All materials and solvents for synthesis and analysis were commercially available. $^1$H NMR and $^{13}$C NMR spectra were collected using a Bruker Avance 400 spectrometer. The FT-IR spectra were recorded on Shimadzu (IR-60 model spectrometer) in KBr disk. Elemental analysis was carried out on a Perkin Heraeus CHN-ORAPID apparatus. Scanning electron microscopy (SEM) image was recorded on LEO 1430VP SEM.

2.2. Preparation of 6,6’-((1E,1’E)-((Azanediylbis(ethane-2,1diyl))bis(azanylylidene)) bis(methanylylidene))bis(2-metho

**Scheme 1**: Preparation of H$_3$L ligand and Cu(H$_2$L)$_2$ complex.
xyphenol) \((H_2L)\). N-(2-Amino-ethyl)-ethane-1,2-diamine (0.207 g, 2 mmol) in 80 mL dry methanol was added slowly to the solution of 2-hydroxy-3-methoxy-benzaldehyde (0.608 g, 4 mmol) in 80 mL dry methanol. The mixture was refluxed for 5 h under Argon. Then, the mixture was cooled to room temperature, and methanol was evaporated under reduced pressure. The yellow precipitation was collected and then recrystallized with methanol (Yield 0.66g, 82%). M.p.:
95°C. Anal. Calc. for C20H25N3O4: C, 64.67; H, 6.78; N, 11.31. Found: C, 64.87; H, 6.92; N, 11.33%. IR (KBr pellet cm⁻¹): 3480 (O-H), 3086 (N-H), 2935, 2835 (w, C-H aliphatic), 1631 (s, C=N), 1502, 1554 (m, C=C aromatic), 1455, 1413, 1272 (m, C-O). ¹H NMR (CDCl₃, δ (ppm)): 2.95 (s, 2H) 3.67 (s, 2H) 3.85 (s, 3H) 6.88 (dd, 1H, J =8) 6.82 (dd, 1H, J =7.2) 6.74 (t, 2H, J =8) 8.29 (s, 1H). ¹³C NMR (CDCl₃, δ (ppm)): 30.57 (CH₂-NH), 55 (CH₂-N), 75.5 (OCH₃), 112.9 (Ar), 116.9 (Ar), 117.7 (Ar), 121.6 (Ar), 147.4 (Ar), 150.8 (Ar), 164.5 (CH=N).

2.3. Preparation of Cu(H₂L)₂ Complex. 1 mmol (0.24 g) of Cu(NO₃)₂ 3H₂O was dissolved in methanol (50 mL) and added slowly to the solution of 2 mmol (0.74 g) of H₃L ligand in 50 mL methanol. The mixture was refluxed and stirred for 3 h. The solvent was evaporated and dark green precipitate was formed. After the recrystallization in acetonitrile, dark green crystals were formed (Yield 0.7gr, 61.5%). M.p. >260°C (dec). Anal. Calc. for Cu(NO₃)₂ 3H₂O: C, 59.73; H, 6.01; N, 10.45. Found: C, 59.48; H, 5.91; N, 10.45%. IR (KBr pellet cm⁻¹): 3446w, 3252, 2997, 2835, 1616 (s, C=O), 1522 (m, C=O), 1546 (s, C=O), 1272 (m, C=O).

2.4. Preparation of CuO Nanoparticles. Crucible containing Cu(H₂L)₂ complex was put in an oven and heated at rate of 10°C/min in air. After 3 h, CuO nanoparticles were formed at 500°C. The product was washed with methanol and dried. FT-IR and SEM techniques were used for characterization of CuO nanoparticles.

2.5. Antibacterial Activity Determination. The antibacterial activity of ligand and complex was performed for four bacteria: Escherichia coli, Acinetobacter baumannii, Klebsiella pneumoniae, and Pseudomonas aeruginosa by using disc method [29]. The bacterial culture (10⁴-10⁶ CFU/mL) was swabbed onto Muller Hinton agar plates. From each compound, 1 mg/mL in DMSO was loaded in to each disc (6 mm diameter) and then was put on the Muller Hinton agar plates. The plates were incubated at 37°C for 24 h, for determination of antibacterial activity of ligand and complex, the inhibition zone (in mm) was measured, and the results were compared with the standard drug tetracycline. Also, the MIC (minimal inhibitory concentration) and MBC (minimum bactericidal concentration) of the ligand and complex were determined [30]. MIC and MBC concentrations were recorded 24 h of incubation at 35°C.

2.6. Single-Crystal X-Ray Diffraction. Suitable Cu(H₂L)₂ single crystals of sizes 0.50 × 0.40 × 0.20 mm were chosen for X-ray. At temperature 293 K, diffraction data were gathered by the ω-scans technique, with graphite-monochromatized MoKα radiation (λ = 0.71073 Å) on an Xcalibur sapphire3.

### Table 2: Selected bond lengths and bond angles for Cu(H₂L)₂.

| Bond lengths (Å) | Bond angles (°) | Dihedral angles (°) |
|------------------|----------------|---------------------|
| Cu1-O3           | 1.913 (13)     | 150.6 (13)          | Cu1-O3-C2-C1          |
| Cu1-O4           | 1.918 (13)     | 87.2 (8)            | Cu1-O3-C2-C3          |
| Cu1-N6           | 2.02 (3)       | 166.2 (13)          | C6-C1-C2-O3           |
| Cu1-N1           | 2.04 (2)       | 95.5 (7)            | C7-C1-C2-O3           |
| O1-C3            | 1.28 (3)       | 83.9 (7)            | O1-C3-C4-C5           |
| O1-C18           | 1.45 (2)       | 137.5 (12)          | C8-N1-C7-C1           |
| O2-C33           | 1.40 (4)       | 120.4 (18)          | Cu1-N1-C8-C9          |
| O2-C38           | 1.45 (3)       | 122 (2)             | N1-C8-C9-N2           |
| O3-C2            | 1.26 (3)       | 125 (2)             | N5-C29-C30-N6         |
| O4-C32           | 1.28 (3)       | 111.3 (19)          | Cu1-C4-O3-C2-C3       |
| N1-C7            | 1.25 (3)       | 122 (2)             | C11-N3-C40-C12        |
| N6-C30           | 1.56 (3)       | 117.8               | C39-C31-C32-O4        |

![Figure 2: Molecular structure and atom numbering scheme for Cu(H₂L)₂.](image-url)
Figure 3: Illustration of S(20), S(6), and S(17) graph sets in the Cu(H₂L)₂.

Figure 4: π-π interaction between phenyl rings in Cu(H₂L)₂, Cg1:C12-C17, Cg2:C31-C36, Cg3:C20-C25, and Cg4:C1-C6. Cg stands for the center of gravity.
differometer. For Lorentz and polarization effects, data were improved but not for absorption. By a least-squares fit of 719 reflections of the highest intensity, the exact unit-cell parameters were investigated. After solving the structure with SHELXT [31], it was refined with the full-matrix least-squares method on $F^2$ by SHELXL97 [32]. By using ORTEX, the operations of SHELX were automated [33]. The incorporated scattering factors in SHELXL97 were employed. Anisotropically, the nonhydrogen atoms were purified. After putting the hydrogen atoms in idealized positions, they were refined as rigid groups with their Uiso’s as 1.2 times Ueq of the proper carrier atom. The function $\Sigma w(|F_0|^2 - |F_C|^2)^2$ was minimized, with $W^{-1} = [\sigma^2(F_0)^2 + (0.2000.P)^2](P = [\max (F_0^2) + 2F_C^2]/3)$.

3. Results and Discussion

3.1. Synthesis of Compounds. In the present study, the Schiff base ligand H$_3$L was made in one-pot synthesis by the condensation of 1 equivalent of N-(2-amino-ethyl)-ethane-1,2-diamine with 2 equivalent of 2-hydroxy-3-methoxybenzaldehyde. In Scheme 1 synthesis of the H$_3$L, Cu(H$_2$L)$_2$ and CuO nanoparticles are demonstrated. The mononuclear complex Cu(H$_2$L)$_2$ was formed in the reaction, in which the Cu(NO$_3$)$_2$ 3H$_2$O : H$_3$L molar ratio was 1 : 2, and it was used for the preparation of nanosized CuO particles.

3.2. Spectroscopic Characterization. The H$_3$L ligand has been determined by FT-IR, $^1$H NMR, and $^{13}$C NMR. Strong absorption band about 1632 cm$^{-1}$ in the IR of H$_3$L is related
to C=N stretching vibration. Besides, stretching vibrations of the ν(Cu-N) and ν(Cu-O) were observed at 563 and 480 cm⁻¹, respectively [34]. Furthermore, a singlet peak at 8.29 ppm in the ¹H NMR spectrum of H₃L was observed which was related to the HC=N protons. From the reaction of copper(II) nitrate salt with H₃L ligand, Cu(H₂L)₂ complex was produced. The ratio of the metal to ligand in complex was 1:2. Considering X-ray and elemental analysis, copper complex was formulated as Cu(H₂L)₂. The comparison of the FT-IR spectra of H₃L and Cu(H₂L)₂ showed distinct changes in the place of C=N and C–O stretching frequencies, which demonstrated that the ligand was coordinated to the metal ion [35]. In metal complex FT-IR, C=N vibrational frequency blue shifts by 16 cm⁻¹ showing that imine nitrogen was coordinated.

3.3. Thermal Studies. Under N₂ atmosphere, thermogravimetric analysis (TGA) of the Cu(H₂L)₂ was studied with slowly increasing of the temperature (20°C per min) until 600°C (Figure 1). In the first stage, the curve showed the thermogram for Cu(H₂L)₂ complex demonstrating that little loss of water in the lattice takes place in a range of 85°C-125°C with a mass change of 2.71%. In the next stage, the complex indicated much loss of 81.39% in the range from 125 to 568°C, and it is in agreement with the ligand decomposition and copper (II) oxide formation with a residual mass of 15.9% at 600°C.

3.4. Crystal Structure of Cu(H₂L)₂. Complex Cu(H₂L)₂ crystallizes in the triclinic space group Pī. Table 1 indicates the details of the X-ray analysis and crystal data for Cu(H₂L)₂. Table 2 also shows selected angles and bond lengths, and the crystal structure of Cu(H₂L)₂ is illustrated in Figure 2. In the crystal structure of Cu(H₂L)₂, two ligand H₃L acts as a bis(bidentate) ligands which are connected to one Cu(II) atom. From the two different ligands, nitrogen atoms N(1) and N(6) and also oxygen atoms O(3) and O(4) are coordinated to Cu(II) atom. In the coordination environment in which metal center has a seesaw (CuN₂O₂), the geometrical parameter τ₄ is defined as [360 – (α + β)]/141, where α and β are the two largest coordination angles [36]. For the tetrahedral and square planar, geometry values of τ₄ are one and zero, respectively. The value of the τ₄ (0.29) for Cu corresponds with distorted square planar structure. The angle between the Phenoxy–Cu–O_S and N_imine–Cu–N_imine mean planes is 85.80. The Cu–N_imine bond distances 2.047
and 2.066 Å and the Cu–O phenoxide bond distances 1.885 and 1.894 Å are similar to the reported distances in related complexes [36–42]. A geometrical analysis has been done on pi–pi stacking in Cu(H₂L)₂ complex. In the crystal structure of complex, there are two types of pi–pi interactions between phenyl rings (Cg1…Cg2 and Cg3…Cg4). In the crystal lattice of Cu(H₂L)₂ complex, linking of N3H1…O5 (2.482 Å), N3H3…O7 (2.307 Å), and C29H29…O8 (2.510 Å) hydrogen bonds led to forming S(20), S(6), and S(17) motifs (Figure 3) [43]. The centroid-centroid distances are 3.792 and 3.958 Å for Cg1…Cg2 and Cg3…Cg4, respectively (Figure 4). The interaction of phenyl rings in this structure is in a parallel displaced mode, and the noncovalent pi–pi interaction has an important effect on the orientation of the ligand during the crystallization process.

3.5. Hirshfeld Surface Analysis. One of the significant and complementary procedures for crystal development pattern by visualization and comparing ratio of the intermolecular interactions is Hirshfeld surface analysis (HS) [44, 45]. For the complex, HS and fingerprint plots (FPs) were prepared by using Crystal Explorer 3.1 according to Crystallographic Information Files [46]. By applying a standard surface resolution with a fixed color scale of -0.172 to 2.698 Å, the HS is mapped over d_{norm}. The 3D d_{norm} surface of the complex is indicated in Figure 5(a). The prominent red areas on the d_{norm} Hirshfeld surfaces of complex around the metal ion are due to the significant intermolecular N–H…C interactions. The shape index of the HS is a means for visualizing the pi–pi stacking by the presence of adjacent red and blue triangles. As illustrated in Figure 5(b), pi–pi interactions are observed between adjacent molecules in the complex. The curvedness plan (Figure 5(c)) of the complex also indicates the big green area and blue region. The first shows a relatively planar surface area, while the last represents areas of curvature. The planar regions around the rings on the HS mapped over curvedness indicate the presence of pi–pi stacking interactions. Figure 6 demonstrates the contribution percentage of the different interactions to the HS area. Figure 6 shows that all contribution contacts of H atoms with N and O atoms are 1.6 and 1.4, respectively. In the complex, the molecules are held together mainly through C•••H and H•••H contacts (Figure 7). Figure 8 illustrates fingerprint plots (2D representation) of HS for Cu(H₂L)₂ complex. According to the fingerprint plots, percentage contributions of intermolecular interactions are remarkably noticeable in H•••H and C•••H contacts. All in all, the interactions of these two groups form nearly 92% of the HS.
Figure 9: FTIR spectra of (a) H$_2$L, (b) Cu(H$_2$L)$_2$, and (c) CuO nanoparticles.
Because of the large atomic radii of carbon C⋯H contacts, the distance between C⋯H contacts is more than H⋯H contacts; therefore, $d_i$ and $d_e$ distances are increased.

3.6. CuO Nanoparticles. The SEM and FT-IR techniques were used for the characterization of CuO nanoparticles. In the FT-IR spectra, the strong absorption band at 580 and 495 cm$^{-1}$ is related to the stretching vibrations of Cu-O (Figure 9) [47]. The presence of this band and the loss of stretching vibrations of C=N, C-H, and other ligand groups in the FT-IR spectra confirm the preparation of CuO nanoparticles.

Figure 10 represents the XRD pattern of the obtained CuO products calcined at 500°C. The entire diffraction peaks of copper oxide can be indexed to the monoclinic structure (JCPDS database No. 05-0661) [47]. The peaks at about $2\theta$ values of 34°, 35°, 38°, 48°, 53°, 58°, 62°, 66°, and 68° are assignable to (110), (002), (111), (202), (020), (202), (113), (310), and (220).

Figure 11 demonstrates SEM image for CuO nanoparticles. The sizes of the CuO nanoparticles are approximately 46–53 nm with spherical shape. The CuO nanoparticles do not decompose into other compounds in the air. The average size of CuO nanoparticles is also estimated via
Debye-Scherer equation $D = 0.9\lambda/\beta \cos \theta$ ($D$ is the average size, $\lambda$ is the X-ray source wavelength (1.54 Å), $\beta$ is the full width at half maximum (FWHM) of the diffraction peak, and $\theta$ is the Bragg’s angle) to be approximately 52 nm.

3.7. Antibacterial Activity. The antibacterial activity of ligand ($\text{H}_3\text{L}$) and Cu(II) complex were tested against $E. \text{coli}$, $A. \text{baumannii}$, $K. \text{pneumoniae}$, and $P. \text{aeruginosa}$ by making disc diffusion method (Figure 12). Findings of antibacterial activity studies are reported in Table 3. The obtained results show that antibacterial activity of Cu(II) complex against the microorganism is more than ligand ($\text{H}_3\text{L}$). Nazirkar et al. prepared metal complexes including Schiff base ligand and examined the antibacterial activity of them against $E. \text{coli}$, $S. \text{Aureus}$, and $B. \text{subtilis}$. Joseph et al. also prepared copper complexes with Schiff base ligand and studied their antibacterial activity against the $E. \text{coli}$, $B. \text{subtilis}$, $S. \text{aureus}$, and $P. \text{aeruginosa}$. The results revealed that metal complexes have more antibacterial activity properties than free ligand [48, 49]. The increasing of the antibacterial activity of the complex comparing to ligand can be justified by Tweedy’s theory and Overtone’s concept [50]. Cell permeability concept of Overtone claims that liposolubility is a significant factor that governs the activity of antibacterial agents. By chelation, the polarity of the metal ions is decreased because of the overlap of the ligand orbitals and partial sharing of positive charge of metal atom with donor groups. Furthermore, it enhances the delocalization of pi-electrons over the whole chelate ring and increases the lipophilicity of the complexes, and this leads to the increasing of the penetration of the complexes into the lipid membrane and increases their antibacterial activities. Remarkably, $\text{Cu(H}_2\text{L})_2$ complex exposes higher antibacterial activity on $A. \text{baumannii}$. Also, the MIC and MBC of the ligand and complex are measured, and the results are presented in Table 4.

4. Conclusion

The compounds were synthesized in good yields. The calculated $\tau_4$ index showed that the copper complex is distorted square planar. In the crystal lattice of $\text{Cu(H}_2\text{L})_2$ complex, linking of N3H1…O5 (2.482 Å), N3H3…O7 (2.307 Å), and C29H29…O8 (2.510 Å) hydrogen bonds led to forming S (20), S(6), and S(17) motifs. In the crystal structure, the pi-pi interactions between phenyl rings at adjacent molecules were remarkable. By thermal decomposition of Cu(II)

Table 3: Antibacterial activity of synthesized compounds.

| Compound | Antimicrobial activity (zone of inhibition in mm) |
|----------|-----------------------------------------------|
|          | $E. \text{coli}$ | $A. \text{baumannii}$ | $K. \text{pneumoniae}$ | $P. \text{aeruginosa}$ |
| $\text{H}_3\text{L}$ | 15 ± 1.2 | 18 ± 1.42 | 12 ± 0.91 | 14 ± 1.71 |
| $\text{Cu(H}_2\text{L})_2$ | 16 ± 0.76 | 20 ± 0.43 | 11 ± 56 | 13 ± 0.45 |
| Std* | 23 ± 0.9 | 15 ± 0.85 | 10 ± 0.45 | 9 ± 0.65 |

*Tetracycline was used as standard. The inhibition zones were reported as mean ± SE.

Table 4: Antimicrobial activity (MIC/MBC) ($\mu$g/$\mu$L) of compounds.

| Compound | $E. \text{coli}$ | $A. \text{baumannii}$ | $K. \text{pneumoniae}$ | $P. \text{aeruginosa}$ |
|----------|----------------|---------------------|---------------------|---------------------|
|          | MIC | MBC | MIC | MBC | MIC | MBC | MIC | MBC |
| $\text{H}_3\text{L}$ | 145 | 220 | 75 | 110 | 170 | 250 | 90 | 135 |
| $\text{Cu(H}_2\text{L})_2$ | 95 | 150 | 70 | 100 | 145 | 230 | 80 | 125 |

MIC: minimum inhibitory concentration; MBC: minimum bactericidal concentration.
Schiff base complex, CuO nanoparticles with the size of 46–53 nm were synthesized. The Schiff base ligand and complex were screened for their antibacterial activity against Gram-negative bacteria. The zones of inhibition were determined. Schiff base complex showed potent antibacterial activity than Schiff base ligand.

Data Availability
The [DATA TYPE] data used to support the findings of this study are included within the article.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

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