Research Article

Synthesis, Characterization and Antibacterial Activity of Schiff Base, 4-Chloro-2-{(E)-[(4-Fluorophenyl)imino]methyl}phenol Metal (II) Complexes

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A new series of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes of the Schiff base ligand, 4-chloro-2-{(E)-[(4-fluorophenyl)imino]methyl}phenol (C13H9ClFNO), was synthesized in a methanolic medium. The Schiff base was derived from the condensation reaction of 5-chlorosalicylaldehyde and 4-fluoroaniline at room temperature. Elemental analysis, FT-IR, UV-Vis, and NMR spectral data, molar conductance measurements, and melting points were used to characterize the Schiff base and the metal complexes. From the elemental analysis data, the metal complexes formed had the general formulae \([M(L)2(H2O)2]\), where \(L\) = Schiff base ligand (C13H9ClFNO) and \(M\) = Mn, Co, Ni, Cu, and Zn. On the basis of FT-IR, electronic spectra, and NMR data, “O” and “N” donor atoms of the Schiff base ligand participated in coordination with the metal (II) ions, and thus, a six coordinated octahedral geometry for all these complexes was proposed. Molar conductance studies on the complexes indicated they were nonelectrolytic in nature. The Schiff base ligand and its metal (II) complexes were tested in vitro to evaluate their bactericidal activity against Gram-negative bacteria (Escherichia coli and Pseudomonas aeruginosa) and Gram-positive bacteria (Bacillus subtilis and Staphylococcus typhi) using the disc diffusion method. The antibacterial evaluation results revealed that the metal (II) complexes exhibited higher antibacterial activity than the free Schiff base ligand.

1. Introduction

The chemistry of metal complexes with Schiff base ligands containing oxygen and nitrogen as donor atoms has continued to attract the attention of researchers. These ligands are known to coordinate to metal atom in different ways under different reaction conditions. The ligands are derived from the condensation reaction of aldehydes and primary amines [1].

One of the major areas of research on the Schiff base metal complexes is their biological activity with the main aim being the discovery of safe and effective therapeutic agents for the treatment of bacterial infections and cancers. A number of Schiff base metal complexes have a diverse spectrum of biological and pharmaceutical activities. For instance, transition metal complexes of Schiff base ligands bearing “O” and “N” donor atoms are very important because of their biological properties such as antibacterial, antifungal, anti-inflammatory [2], analgesic [3, 4], anti-convulsant [5], antitubercular [6], antioxidant [7], and anthelmintic [8]. The Schiff base transition metal complexes have also been used as biological models to understand the structure of biomolecules and biological processes [9].

Manganese, cobalt, nickel, copper, and zinc are life-essential metallic elements and exhibit greater biological activity when associated with certain metal protein complexes, participating in oxygen transport, electronic transfer reactions, or the storage of ions [10]. This has created enormous interest in the study of systems containing these metals.
Mn (II), Co (II), Ni (II), Cu (II), and Zn (II) complexes of the Schiff base, 4-chloro-2-[(E)-[(4-fluorophenyl)imino]methyl]phenol (C\textsubscript{13}H\textsubscript{9}ClFNO) has been synthesized in our laboratories. The antibacterial activity of the new Mn (II), Co (II), Ni (II), Cu (II), and Zn (II) complexes of the Schiff base ligand, 4-chloro-2-[(E)-[(4-fluorophenyl)imino]methyl]phenol, which to the best of our knowledge has not been synthesized nor antibacterial activities carried out, was studied in our laboratories. The antibacterial activity of the new Mn (II), Co (II), Ni (II), Cu (II), and Zn (II) complexes of the Schiff base ligand, 4-chloro-2-[(E)-[(4-fluorophenyl)imino]methyl]phenol (C\textsubscript{13}H\textsubscript{9}ClFNO) has been investigated and is now reported in this article. The antibacterial evaluation results revealed that the metal complexes, with a proposed six coordinated octahedral geometry, exhibited higher antibacterial activity than the free Schiff base ligand against Gram-negative bacteria (E. coli and P. aeruginosa) and Gram-positive bacteria (B. subtilis and S. typhi).

2. Experimental Section

2.1. Materials and Methods. The chemicals and solvents used in this research work were of analytical grade sourced from Sigma Chemicals Company. Synthesis of Schiff base ligand was carried out in pure solvent using standard literature methods [11]. Melting points were recorded on a Gallenkamp apparatus and are uncorrected. FT-IR spectra of synthesized compounds (in a KBr matrix) were recorded in the 4000–400 cm\(^{-1}\) region on a SHIMADZU FTIR-8400 spectrophotometer. The \(^1\)H NMR and \(^{13}\)C NMR spectra of the Schiff base ligand and its diamagnetic metal (II) complexes were recorded in deuterated DMSO on a Bruker Avance III HD Nanobay 400MHz NMR spectrometer equipped with a 5mm BBO probe at room temperature. Tetramethylsilane was used as an internal standard, and chemical shift is given in \(\delta\). Elemental analysis (C, H, and N) was recorded on a LECO CNHS-932 microanalyzer. The electronic spectra of the synthesized compounds were recorded on a AOE Instruments UV-1800 PC spectrophotometer in the 200–800 nm range, with a quartz cuvette (path length, 1 cm) and studies performed in HPLC grade acetonitrile. Conductivity measurements of the Schiff base ligand and its metal (II) complexes were carried out on a SIBATA Conductivity meter Model SC–17A, at room temperature. A mass spectrum was recorded on a Shimadzu GCMS QP 2010SE spectrometer.

The synthesized compounds were screened in vitro for their antibacterial activities against E. coli, P. aeruginosa, B. subtilis, and S. typhi using the disc diffusion method [12].

2.2. Synthesis of Schiff Base Ligand, L. The Schiff base ligand (L) (Scheme 1) was prepared according to literature methods with a few modifications [11].

4-fluoroaniline (0.3549 g; 3.19 mmol) was added to a 30 mL magnetically stirred ethanolic solution of 5-chlorosalicylaldehyde (0.5000 g; 3.19 mmol) in a 50 mL round-bottomed flask at room temperature. Two drops (0.2 mL) of glacial acetic acid was added to the mixture, to adjust its pH to \(\approx 6\), upon which a thick yellow orange precipitate formed instantly. The precipitate was separated by filtration and purified by recrystallization from ethanol. Shiny, needle-like yellow-orange crystals were formed. The crystals were washed with cold ethanol and diethyl ether to remove unreacted amine and aldehyde. The crystals were dried in air. Yield: 70.99%, 0.4210 g, colour: yellow orange, m.p = 133–135°C, and molar conductance (\(\Lambda\)) = 5 Ohm\(^{-1}\)·cm\(^2\)·mol\(^{-1}\). Elemental analysis data for C\textsubscript{26}H\textsubscript{20}Cl\textsubscript{2}F\textsubscript{2}NiN\textsubscript{2}O\textsubscript{4} (FW = 588.28) found: C, 53.08%; H, 3.43%; N, 4.72% calculated: C, 53.04%; H, 3.40%; N, 4.76%.

FT-IR (KBr, disc cm\(^{-1}\)) 3243.0 v (O-H), 1596.2 v (HC=O), 1213.7 v (C-O), 697.0 v (H\textsubscript{2}O), 526.6 v (Mn-O), 489.1 v (Mn–O). UV-Vis (acetonitrile) \(\lambda_{\text{max}}\) (nm) 221.4, 251.8, and 342.1.

2.3. Synthesis of the Schiff Base Metal (II) Complexes, C. The Schiff base metal (II) complexes (C) (Scheme 1) were prepared by reacting the Schiff base with the metal (II) ions as per the literature methods [11]. A solution of hydrated metal (II) chloride (0.1 mmol) in 10 mL hot methanol at 50°C was added dropwise to a solution of the Schiff base ligand (L) (0.2 mmol) in 20 mL of hot methanol at 50°C in a 50 mL round-bottomed flask. The resulting mixture was magnetically stirred and refluxed for 3 hours on an oil bath at 65°C whereupon a precipitated product formed. The precipitate was separated by filtration and washed with methanol, hot ethanol, and diethyl ether to remove unreacted Schiff base and metal (II) salt chloride.

2.3.1. Manganese (II) Complex, C1. Yield: 65.03%, 0.0383 g, colour: grey, m.p > 350°C, and molar conductance (\(\Lambda\)) = 21 Ohm\(^{-1}\)·cm\(^2\)·mol\(^{-1}\). Elemental analysis data for C\textsubscript{26}H\textsubscript{20}Cl\textsubscript{2}F\textsubscript{2}MnN\textsubscript{2}O\textsubscript{4} (FW = 588.28) found: C, 53.08%; H, 3.43%; N, 4.72% calculated: C, 53.04%; H, 3.40%; N, 4.76%.

FT-IR (KBr, disc cm\(^{-1}\)) 3427.1 v (O-H), 1597.4 v (HC=O), 1217.2 v (C-O), 697.0 v (H\textsubscript{2}O), 526.6 v (Mn-N), 489.1 v (Mn–O). UV-Vis (acetonitrile) \(\lambda_{\text{max}}\) (nm) 221.4, 251.8, and 342.1.

2.3.2. Cobalt (II) Complex, C2. Yield: 70.99%, 0.4210 g, colour: dark brown, m.p > 350°C, and molar conductance (\(\Lambda\)) = 19 Ohm\(^{-1}\)·cm\(^2\)·mol\(^{-1}\). Elemental analysis data for C\textsubscript{26}H\textsubscript{20}Cl\textsubscript{2}F\textsubscript{2}CoN\textsubscript{2}O\textsubscript{4} (FW = 592.27) found: C, 52.69%; H, 3.35%; N, 4.88% calculated: C, 52.68%; H, 3.38%; N, 4.73%.

FT-IR (KBr, disc cm\(^{-1}\)) 3427.1 v (O-H), 1597.4 v (HC=O), 1213.3 v (C-O), 692.6 v (H\textsubscript{2}O), 530.6 v (Co-N), 488.3 v (Co–O). UV-Vis (acetonitrile) \(\lambda_{\text{max}}\) (nm) 249.1 and 401.9.

2.3.3. Nickel (II) Complex, C3. Yield: 61.05%, 0.0362 g, colour: red brown, m.p > 350°C, and molar conductance (\(\Lambda\)) = 20 Ohm\(^{-1}\)·cm\(^2\)·mol\(^{-1}\). Elemental analysis data for C\textsubscript{26}H\textsubscript{20}Cl\textsubscript{2}F\textsubscript{2}NiN\textsubscript{2}O\textsubscript{4} (FW = 592.03) found: C, 52.68%; H, 3.36%; N, 4.70% calculated: C, 52.70%; H, 3.38%; N, 4.73%.

FT-IR (KBr, disc cm\(^{-1}\)) 3415.7 v (O-H), 1595.7 v (HC=O), 1210.8 v (C-O), 697.9 v (H\textsubscript{2}O), 526.4 v (Ni-N), 489.2 v (Ni–O). UV-Vis (acetonitrile) \(\lambda_{\text{max}}\) (nm) 245.2, 325.1 and 421.9. \(^1\)H NMR (ppm \(d_6\)-DMSO, 400 MHz): \(\delta\) 8.87 (s, 1H, CH=N),
2.4. Biological Assay. The synthesized ligand and its transition metal (II) complexes were screened in vitro for their antibacterial activities against *E. coli*, *P. aeruginosa*, *B. subtilis*, and *S. typhi* bacterial strains using the disc diffusion method [11, 13]. The disc diffusion method was used because of its convenience, efficiency, and low cost. The stock solutions (1 mgmL⁻¹) of the ligand and its metal complexes were prepared by dissolving 20 mg of the test compound in 20 mL of dimethyl sulfoxide (DMSO) solvent. From this stock solution, concentrations of 10, 20, 30, and 40 μg·mL⁻¹ were prepared by dilution with DMSO. The solvent (DMSO) was used as control for each dilution. The bacteria were subcultured in an agar nutrient medium. Standard antibacterial drugs (Amoxyclycl, Nalidixic acid, and Gentamicin) were used as positive controls for comparison with the ligand and the synthesized metal complexes. Whatman filter paper (no. 1) discs of 7 mm diameter were sterilized in an autoclave and then soaked in the desired concentration of the synthesized compounds. The paper discs were placed aseptically in the petri dishes containing nutrient agar media seeded with *E. coli*, *P. aeruginosa*, *B. subtilis*, and *S. typhi* separately and then incubated for 24 hours at 37°C. The diameters of the zones of inhibition were measured after 24 hours of incubation. The antibacterial activities were calculated as mean ± SD of three replicates (Table 1). The zones of inhibition (Figures 1 and 2) were measured using a Vernier caliper in millimeters (mm), and the following criteria were applied [12]; low activity (1–7 mm), moderate activity (7–10 mm), high activity (11–15 mm), very high activity (≥16), and no activity (0).

### 3. Results and Discussion

The Schiff base ligand in this study was first synthesized by Feng [14] using the reflux method. In this research, however, the ligand was prepared using the room temperature method which afforded a higher yield. The metal (II) complexes of the ligand are new and thus reported for the first time. The Schiff base ligand is soluble in hot ethanol and solvents such as DMF and DMSO. The imine and its metal (II) complexes are coloured solids which are stable in air. The complexes were insoluble in common organic solvents such as methanol, dichloromethane, ethanol, and acetone but soluble in DMSO and DMF.

The melting points of the complexes were higher than that of the Schiff base ligand indicating that the complexes are more stable than the ligand. The chemical equations showing the preparation of the Schiff base ligand and its metal (II) complexes are represented in Scheme 1.

### 3.1. Conductivity Measurements

The molar conductance values of the synthesized compounds in 10⁻³ M DMSO were measured at room temperature. The conductance values of the synthesized compounds were below 50 Ohm⁻¹·cm²·mol⁻¹, indicating their nonelectrolytic nature [15, 16]. This suggested that there were no anions present outside the coordination sphere of the complexes.

### 3.2. Electronic Spectral Analysis

The electronic spectral data of the Schiff base ligand and its metal (II) complexes are given in the experimental section. The Schiff base ligand...
showed three bands at 225.3 nm (44385.26 cm$^{-1}$), 269.1 nm (37160.91 cm$^{-1}$), and 345.1 nm (28977.11 cm$^{-1}$). The band at 225.3 nm is due to the $\pi$–$\pi^*$ transition in benzene. The band appearing at 269.1 nm is assignable to $n$–$\pi^*$ transition of nonbonding electrons present on the nitrogen of the azomethine group (-HC=N). The band at 345.1 nm is due to $n$–$\pi^*$ transition of the phenolic group [17, 18].

The UV-Vis spectra of the Schiff base metal (II) complexes (Figure 3) displayed similar absorption spectra as the ligand but have either undergone a blue shift or red shift. The bands in the electronic spectrum of the Mn (II) complex shifted towards shorter wavelength and gave three bands at 221.4 nm (45167.12 cm$^{-1}$), 251.8 nm (39714.06 cm$^{-1}$), and 342.1 nm (29231.22 cm$^{-1}$). The band at 221.4 nm and 251.8 nm was due to intraligand transition, and the band at

Table 1: Antibacterial screening data for the Schiff base ligand and its metal (II) complexes at concentrations of 10, 20, 30, and 40 $\mu$g/mL.

| Sample     | Conc. ($\mu$g/mL) | Gram-positive | Gram-negative |
|------------|-------------------|---------------|---------------|
|            |                   | E. coli       | P. aeruginosa | B. subtilis   | S. typhi     |
| L          | 10                | 7.3 ± 0.5     | 8.4 ± 0.5     | 7.7 ± 0.9     | 8.4 ± 0.5    |
|            | 20                | 7.5 ± 0.5     | 8.7 ± 0.5     | 7.9 ± 0.9     | 8.6 ± 0.5    |
|            | 30                | 7.7 ± 0.5     | 8.9 ± 0.8     | 8.3 ± 0.8     | 8.8 ± 0.5    |
|            | 40                | 8.0 ± 0.5     | 10.0 ± 0.8    | 9.0 ± 0.8     | 8.9 ± 0.5    |
| [Mn(L)$_2$(H$_2$O)$_2$] | 10         | 8.1 ± 0.5     | 10.7 ± 0.8    | 9.7 ± 0.5     | 9.3 ± 0.5    |
|            | 20                | 8.6 ± 0.5     | 11.0 ± 0.8    | 10.3 ± 0.8    | 9.6 ± 0.5    |
|            | 30                | 8.9 ± 0.5     | 12.0 ± 0.5    | 10.9 ± 0.5    | 9.8 ± 0.5    |
|            | 40                | 9.7 ± 0.5     | 14.7 ± 0.8    | 11.7 ± 0.5    | 10.2 ± 0.5   |
| [Co(L)$_2$(H$_2$O)$_2$] | 10         | 9.0 ± 0.9     | 9.7 ± 1.2     | 8.3 ± 0.5     | 9.4 ± 1.2    |
|            | 20                | 9.2 ± 0.8     | 10.7 ± 1.4    | 8.9 ± 0.9     | 9.7 ± 0.5    |
|            | 30                | 9.8 ± 0.5     | 11.3 ± 1.2    | 9.3 ± 0.5     | 11.0 ± 0.8   |
|            | 40                | 10.0 ± 0.8    | 12.0 ± 0.8    | 10.2 ± 0.5    | 11.7 ± 0.5   |
| [Ni(L)$_2$(H$_2$O)$_2$] | 10         | 9.5 ± 0.8     | 11.3 ± 0.5    | 9.7 ± 0.5     | 8.6 ± 0.5    |
|            | 20                | 10.0 ± 0.8    | 11.8 ± 0.5    | 9.9 ± 0.5     | 8.8 ± 0.5    |
|            | 30                | 10.4 ± 0.8    | 12.4 ± 0.5    | 10.8 ± 0.5    | 9.0 ± 0.8    |
|            | 40                | 11.3 ± 0.9    | 12.7 ± 1.2    | 11.0 ± 0.8    | 9.3 ± 0.8    |
| [Cu(L)$_2$(H$_2$O)$_2$] | 10         | 8.1 ± 0.8     | 10.3 ± 1.2    | 8.6 ± 0.5     | 8.7 ± 0.5    |
|            | 20                | 8.3 ± 0.5     | 10.6 ± 1.2    | 9.3 ± 0.5     | 8.9 ± 0.5    |
|            | 30                | 8.6 ± 0.5     | 10.9 ± 1.2    | 10.0 ± 0.8    | 9.3 ± 0.5    |
|            | 40                | 8.9 ± 0.9     | 11.7 ± 1.2    | 10.7 ± 0.5    | 9.6 ± 0.5    |
| [Zn(L)$_2$(H$_2$O)$_2$] | 10         | 7.6 ± 0.9     | 10.0 ± 0.5    | 8.4 ± 0.9     | 10.1 ± 0.9   |
|            | 20                | 7.8 ± 0.5     | 10.4 ± 1.4    | 8.9 ± 0.9     | 10.3 ± 0.9   |
|            | 30                | 8.1 ± 0.5     | 10.9 ± 1.2    | 9.7 ± 0.5     | 11.0 ± 1.2   |
|            | 40                | 8.3 ± 0.5     | 11.4 ± 0.8    | 9.9 ± 0.9     | 11.6 ± 1.4   |
| Amoxyclav (AMC) |         | 8.0 ± 0.0     | —             | —             | —            |
| Nalidixic acid (NA) |         | 12.0 ± 1.0    | 20.0 ± 2.0    | 13.0 ± 1.0    | 30.5 ± 0.5   |
| Gentamicin (GEN)  |         | 9.0 ± 0.0     | 14.0 ± 0.0    | 9.5 ± 0.5     | 10.5 ± 1.5   |

$L$ = Schiff base ligand, 4-chloro-2-[(E)-[(4-fluorophenyl)imino][methyl]phenol (C$_{13}$H$_9$ClFNO) * = average of three replicates ± SD.
342.1 nm was a result of d-d low-spin transition for $^6A_{1g} \rightarrow ^2E_g$ which suggestive of octahedral geometry around Mn (II) ion [19, 20]. In the Co (II) complex, two bands were observed at 249.1 nm (40144.52 cm$^{-1}$) and 401.9 nm (24881.81 cm$^{-1}$). This was a shift towards longer wavelength with respect to the spectrum of the Schiff base ligand. The band at 249.1 nm was due to intraligand transition, and the band at 401.9 nm was as a result of d-d transition for $^3T_{2g}$ (F) $\rightarrow ^3T_{2g}$ which is within the range for octahedral configuration as reported in many octahedral cobalt (II) complexes [20–22].

The electronic spectrum of Ni (II) complex showed three bands at 245.2 nm (40783.03 cm$^{-1}$), 325.1 nm (30759.77 cm$^{-1}$), and 421.9 nm (23702.30 cm$^{-1}$). The band at 245.2 nm was probably due to intraligand transition, while the band at 325.1 nm was due to charge transfer. The observed band at 421.9 nm was as a result of d-d transition for $^3A_{2g}$ $\rightarrow ^3T_{2g}$ which favours an octahedral geometry for the Ni (II) complex [19].

The copper (II) complex spectrum showed three bands at 229.1 nm (43649.06 cm$^{-1}$), 266.1 nm (37579.86 cm$^{-1}$), and 349.7 nm (28595.94 cm$^{-1}$), which were all shifted to longer wavelength. The band at 229.1 nm and 266.1 nm was due to intraligand transition, and the one at 349.7 nm was as a result of d-d spin allowed transition for $^3T_{1g} \rightarrow ^3T_{2g}$. This transition is suggestive of octahedral geometry around Cu (II) ion [23].

Zn (II) complex displayed absorption bands at 223.4 nm (44762.76 cm$^{-1}$), 303.2 nm (32981.53 cm$^{-1}$), and 343.9 nm (29078.22 cm$^{-1}$). The band at 223.4 nm and 303.2 nm was due to intraligand transition, and the band at 343.9 nm was assignable to the metal to ligand charge transfer (MLCT) transition. An octahedral geometry is proposed for this complex based on its analytical, conductance, and spectral data. This is further supported by its diamagnetic nature and absence of d-d band, due to its complete d$^{10}$ electronic configuration [9, 24, 25].

The absence of any band below 10,000 cm$^{-1}$ eliminates the possibility of a tetrahedral environment in these complexes [26]. It can also be concluded that a shift in the spectral bands of the complexes, with respect to the spectrum of the Schiff base ligand, bathochromically or hypsochromically, indicates coordination.

3.3. FT-IR Spectral Analysis. The binding mode of the Schiff base ligand to the metal ions in complexes was determined by comparing the FT-IR spectrum of the free ligand with the spectra of the metal (II) complexes.

The stretching frequency for the azomethine C=N bond, $\nu$(C=N) was observed at 1601.0 cm$^{-1}$ for the free ligand. The C=N stretching frequencies in the metal (II) complexes were observed at 1596.2, 1597.4, 1595.7, 1597.1, and 1596.6 cm$^{-1}$ for Manganese (II), Cobalt (II), Nickel (II), Copper (II), and Zinc (II) complexes, respectively, a shift to lower wave numbers. This indicated coordination of Schiff base through the azomethine nitrogen [27]. Moreover, the appearance of additional weak bands in the region 526.4–530.6 cm$^{-1}$ and 483.8–489.7 cm$^{-1}$ attributed to $\nu$(M-N) and $\nu$(M-O), respectively [28], further confirmed complexation [29]. This showed that the Schiff base ligand coordinated to the metal via “N” and “O” atoms.

The FT-IR spectra of the complexes also showed strong bands in the 3140.3–3446.6 cm$^{-1}$ region, suggesting the presence of coordinated/lattice water in the complexes. This was further confirmed by the appearance of nonligand band in the 692.6–699.7 cm$^{-1}$ region, assignable to the rocking mode of water [29].

In the free Schiff base ligand, the band at 1277 cm$^{-1}$ due to $\nu$(C-O, phenolic) shifted to lower wave number by 62.3–66.2 cm$^{-1}$ in the complexes indicating the coordination of the phenolic oxygen atom to the metal ion [30]. Therefore, it can be concluded that coordination took place via phenolic oxygen and azomethine nitrogen of the Schiff base ligand molecule.

3.4. Elemental Analysis. The microanalysis data suggested that all the complexes were mononuclear where two moles of the ligand and two moles of water molecules were coordinated to the central metal atom. The data, therefore, suggested that the metal to ligand ratio in the complex was 1: 2 and the general formula for the complexes as $[M(L)_2(H_2O)_2]$ ($M =$ Mn (II), Co (II), Ni (II), Cu(II), Zn (II); $L$ = deprotonated imine) [31, 32]. The theoretical (calculated) values were found to be in good agreement with the experimental values.

3.5. NMR Spectral Analysis. The $^1$H and $^{13}$C NMR spectra of the Schiff base ligand and its diamagnetic Ni (II) and Zn (II) complexes were recorded in DMSO- $d_6$.

The $^1$H NMR spectrum of the Schiff base showed a singlet peak at $\delta = 8.92$ ppm corresponding to the azomethine proton (–N=CH–) [30, 31], an indication that the Schiff base was formed during the condensation reaction. Observation of a peak at $\delta = 162.82$ ppm in the $^{13}$C NMR spectrum was further proof that the ligand was successfully synthesized [33].

The azomethine proton peak of Schiff base shifted upfield in the $^1$H NMR spectra of the Ni (II) and Zn (II) complexes.
(δ = 8.87–8.90 ppm and 8.55 ppm, respectively). The upfield shifting of azomethine proton in Ni (II) and Zn (II) complexes was attributed to the discharging of electronic cloud towards the Ni (II) and Zn (II) ion indicating coordination through the azomethine nitrogen to the metallic ion [34]. The expected 1H NMR peak, at δ = 12.85 ppm, assignable to the phenolic proton in the free Schiff base ligand [35] was absent in the spectra of the two complexes. This confirmed the deprotonation of the phenolic group and coordination of the negatively charged oxygen species to the metal cation. This observation further proves the neutral nature of the metal (II) complexes and explains the nonelectrolytic behavior of the complexes. The 13C NMR peaks for the azomethine carbon atom and phenolic group carbons of the coordinated Schiff base ligand were, respectively, observed at δ = 165 ppm and 162 ppm, in the spectra of the Ni (II) complex, a 2 ppm upfield shift from that observed for the free ligand, due to coordination [33, 36]. Thus, the 1H NMR and 13C NMR spectra confirmed the monobasic bidentate nature of the ligand, already suggested by the FT-IR spectral studies. Furthermore, the number of protons calculated from the integration curves and obtained values of the expected C H N analysis agreed well with each other [34, 37].

3.6. Mass Spectra. The mass spectrum of the Schiff base ligand showed a molecular ion peak at m/z 249 (M++1) which is consistent with the molecular weight of the Schiff base ligand 249.

3.7. Antibacterial Activity. The antibacterial activity tests were conducted according to standard procedures using two Gram-positive and two Gram-negative bacterial strains [13, 38]. The results were recorded as shown in Table 1. The ability of the Schiff base ligand and its metal (II) complexes to inhibit the growth of the bacteria was compared to that of the known standard antibacterial drugs, Amoxycilav (AMC), Nalidixic acid (NA), and Gentamicin (GEN). The Schiff base ligand and its metal (II) complexes demonstrated abilities to inhibit bacterial growth. Research has shown that coordination of a ligand, with the potential to inhibit bacterial growth, evokes antibacterial growth inhibition ability [39].

The nickel (II) complex had the highest activity against E. coli and P. aeruginosa, while the manganese (II) complex showed maximum inhibition zone against B. subtilis at 40 µg/mL. The zinc (II) complex was slightly active than the ligand against E. coli. The cobalt (II) complex had a slightly higher activity than the ligand against P. aeruginosa and B. subtilis. The nickel (II) complex performed better than the ligand against S. typhi at 40 µg/mL.

It is worth noting that the Schiff base and its metal (II) complexes inhibited the growth of Amoxycilav-resistant P. aeruginosa, B. subtilis and S. typhi.

Overall, the inhibition zones of the Schiff base ligand and its complexes at different concentrations showed that the complexes had enhanced bactericidal activity than the ligand [40] and the standard drug Amoxycilav (AMC) against all the bacterial strains studied. The antibacterial activities of the metal complexes are directly proportional to their concentration.

The biological activity of various transition metal coordination compounds has been explained using various theories. The increase in the antibacterial activity of the metal (II) complexes may be due to the effect of the metal ion on the normal state of the bacterial cell process [41]. Research has shown that the structural components possessing additional (C=N) bond with nitrogen and oxygen donor systems inhibit enzyme activity due to their deactivation by metal coordination [42, 43]. According to Tweedy’s chelation theory, polarity of the metal ion is greatly reduced as a result of overlap of the ligand orbital and partial sharing of positive charge of metal ion with donor groups [44]. This enhances the delocalization of the pi electrons over the entire complex ring thereby promoting the lipophilicity of the chelate. Therefore, chelation enhances the lipophilic character of the central metal ion, hence increasing the hydrophobic character and liposolubility of the complex. This favors the complex permeation through the lipid layers of the cell membrane of the bacteria. Once it penetrates the cell, the complexes block the metal binding sites on enzymes of microorganisms. This in turn disturbs the respiration process of the cell by curtailing the synthesis of proteins, which restricts further growth of the organism [45, 46]. Thus, there is hope that these complexes could reasonably be used in designing more potent antibacterial agents for the treatment of some common diseases caused by E. coli, P. aeruginosa, B. subtilis, and S. typhi.

4. Conclusions

The Schiff base ligand 4-chloro-2-[(E)-[4-fluorophenyl]imino]methyl]phenol (C13H9ClFNO) and its metal (II) complexes, [M(L)2(H2O)2] (M = Mn, Co, Ni, Cu, and Zn), were successfully synthesized and characterized. The deprotonated bidentate Schiff base ligand coordinated to the metal (II) ion via the azomethine nitrogen and phenolic oxygen resulting in the formation of a stable six-membered chelate ring. An octahedral geometry has been proposed for the metal (II) complexes based on the electronic spectra. The complexes formed are neutral with no free anions outside the coordination sphere. The metal (II) complexes exhibited better antibacterial properties than the parent Schiff base ligand under the same experimental conditions. It can also be deduced from this study that the antibacterial growth inhibition ability of the synthesized compounds increased with increasing concentration.

Data Availability

The data supporting the findings of the study are already given within the text.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.
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