

# Synthesis, characterization, and antifungal and antioxidant evaluation of novel ethylenediamine-derived Schiff bases and their Ni(II), Co(II), Cd(II), and Cu(II) complexes

P. D. Iorungwa<sup>ID\*</sup>, M. S. Iorungwa<sup>ID</sup>, S. D. Umoh<sup>ID\*\*</sup>, R. A. Wuana<sup>ID</sup>, E. N. Iornumbe<sup>ID</sup>, A. G. Ugama<sup>ID</sup>, L. T. Tyagher<sup>ID</sup>

*Department of Chemistry, Joseph Sarwuan Tarka University, Makurdi, Nigeria*

## Abstract

Three Schiff base ligands derived from condensation of ethylenediamine with benzaldehyde, salicylaldehyde, and vanillin, namely (1E,1'E)-N,N'-(ethane-1,2-diyl)bis(1-phenylmethanimine) (BBE), 4,4'-((1E,1'E)-(ethane-1,2-diylbis(azanelylylidene))bis(methaneylylidene))bis(2-methoxyphenol) (BHE), and 2,2'-((1E,1'E)-(ethane-1,2-diylbis(azanelylylidene))bis(methaneylylidene))diphenol (BME), were synthesized and complexed with Co(II), Cu(II), Ni(II), and Cd(II) ions. To the best of our knowledge, these specific metal complexes have not been reported previously, and their biological activities have not been evaluated. The ligands and complexes were characterized by melting point determination, solubility tests, molar conductivity, UV-visible and FTIR spectroscopy, magnetic susceptibility, X-ray fluorescence, powder X-ray diffraction (XRD), and thermogravimetric/differential thermal analyses (TGA/DTA). Low molar conductivity values ( $10.5\text{--}12.0\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ ) indicate non-electrolytic behavior, while FTIR and X-ray fluorescence studies indicate coordination through azomethine nitrogen and oxygen donor atoms. XRD patterns show crystalline structures with sharp diffraction peaks, and thermal analyses indicate multistep decomposition and good thermal stability. Biological analysis indicates increased antifungal activity of the metal complexes over the free ligands, with lower minimum inhibitory concentrations; some complexes also showed improved 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity ( $\text{IC}_{50} = 0.68101\ \text{mg/mL}$ ). The first-row transition metals are biologically relevant, while Cd(II) was included only for comparative structure-activity evaluation despite its known toxicity. This study provides insight into Ni(II) and Cd(II) complexes through integrated structural, thermal, and biological characterization.

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## 1. Introduction

Schiff bases are derived from the condensation of primary amines and active carbonyl compounds [1, 2]. They are nitro-

gen analogs of aldehydes or ketones, with an imine or azomethine ( $-\text{CH}=\text{N}-$ ) functional group in place of the carbonyl functional group ( $\text{C}=\text{O}$ ) analog. Aliphatic Schiff bases derived from aldehydes or ketones are generally unstable and readily undergo polymerization, whereas aromatic Schiff bases exhibit greater stability owing to extended conjugation [3]. The azomethine nitrogen has a coordination site with metal ions to allow the development of stable metal complexes [4]. The variable oxidation states of some metal ions enable interactions with

\*Corresponding Author Tel. No.: +234-803-751-3959.

\*\*Corresponding Author Tel. No.: +234-703-134-3987.

Email addresses: [iorungwa.patience@uam.edu.ng](mailto:iorungwa.patience@uam.edu.ng) (P. D.

Iorungwa<sup>ID</sup>), [sampson.umoh@uam.edu.ng](mailto:sampson.umoh@uam.edu.ng) (S. D. Umoh<sup>ID</sup>)

biomolecules, including proteins and amino acids, and interactions with pathogenic microorganisms [5]. Schiff base metal complexes have received much attention due to their tendency to increase the lipophilicity, stability, and reactivity through coordination, making them attractive candidates for biomedical and pharmaceutical investigations [6–8]. These complexes often exhibit greater antimicrobial, antifungal, antioxidant, and anticancer activity than the free ligands [9–11]. Most previous studies have involved Co(II) and Cu(II), and have shown promising antimicrobial and antioxidant properties [12, 13].

Schiff base complexes of transition metals like Co(II), Cu(II), and Ni(II), derived from ethylenediamine and aromatic aldehydes, are notable for their coordination behavior and biological activities. However, most research has been centered on individual ligands, specific metal ions, or limited characterization methods [14–16]. Schiff base complexes of Cu(II), Co(II), and Ni(II) from salicylaldehyde or substituted aromatic aldehydes have primarily been studied for antimicrobial activity, electronic spectroscopy, and coordination analysis, usually lacking comparative evaluation or integrated thermal and biological characterization [17, 18]. Cd(II)-based Schiff base complexes are less explored due to toxicity concerns, although they are valuable for studying coordination chemistry and structure–property relationships in related metal systems [19]. The present study’s novelty lies in the comparative investigation of three ethylenediamine-derived Schiff base ligands (benzaldehyde-, salicylaldehyde-, and vanillin-based) coordinated with Co(II), Cu(II), Ni(II), and Cd(II). This research includes physicochemical, spectroscopic, thermal, structural, antifungal, and antioxidant evaluations under similar conditions, facilitating a clearer understanding of ligand- and metal-dependent structure–activity relationships. The study highlights the limited systematic investigations of Ni(II) and Cd(II) complexes.

This creates a considerable gap in the knowledge of the structure–activity relationship and the biomedical application of these complexes.

Microbial resistance to traditional antibiotics is a significant global health issue [20], and thus novel therapeutic agents are urgently needed. To address this challenge, metallodrugs have emerged as promising candidates because of their structural diversity, distinctive biological reactivity, and therapeutic potential [21]. One proposed approach to bypass microbial resistance and reduce the toxicity of free metal ions is to coordinate biocompatible metal ions with Schiff bases [9]. Schiff base complexes of transition metals like Co(II), Cu(II), and Ni(II), derived from ethylenediamine and aromatic aldehydes, have been extensively studied due to their coordination behavior and biological properties. However, most research has concentrated on specific ligands or individual metal systems, primarily focusing on antimicrobial or spectroscopic characterization [15]. Comparative studies on ethylenediamine-derived Schiff base ligands with multiple metal ions are limited, especially regarding their physicochemical, thermal, structural, antifungal, and antioxidant properties. Cd(II)-based systems are notably underexplored due to toxicity concerns, despite their relevance in understanding structure–property relationships.

This study aims to compare benzaldehyde-, salicylaldehyde-, and vanillin-derived Schiff base complexes of Co(II), Cu(II), Ni(II), and Cd(II) through spectroscopic, thermal, structural, antifungal, and antioxidant evaluations. Three Schiff base ligands derived from ethylenediamine were synthesized and coordinated with Co(II), Ni(II), Cu(II), and Cd(II) ions to evaluate their physicochemical, structural, thermal, antifungal, and antioxidant properties. Cd(II), despite its toxicity and lack of therapeutic application, served as a contrast to biologically relevant metals for analyzing coordination behavior and biological responses. The study provides insights into structure–property and structure–activity relationships among the complexes, which should be viewed as comparative models rather than pharmaceutical candidates. Characterization was performed using various techniques, including UV–visible and FTIR spectroscopy, X-ray fluorescence, and thermal analysis, while assessing the influence of metal coordination on biological activity.

## 2. Materials and methods

### 2.1. Materials and reagents

All chemicals (obtained from World Corsica Ltd and Emole Nig. Ltd.) used in the study were of analytical grade and included nickel(II) chloride hexahydrate, copper(II) chloride hexahydrate, cobalt(II) chloride hexahydrate, cadmium(II) chloride hemihydrate, various aldehydes, solvents, and reagents sourced from commercial suppliers. Distilled water was used in the study.

### 2.2. Instrumentation

Melting points were determined using a Barnstead Electrothermal 9100 apparatus. FTIR spectra were recorded using Cary 630 and ProRaman-L-785-B1S spectrophotometers, UV–visible spectra were recorded with a Shimadzu 1800 spectrophotometer, magnetic susceptibility was assessed using a Sherwood Scientific balance, thermogravimetric analysis was conducted with a Setsys 18A (Setaram, France), and conductivity was measured using a HACH Sension5 meter.

### 2.3. Synthesis of Schiff base ligands

All Schiff base ligands were synthesized by condensation of ethylenediamine with the appropriate aldehydes following reported procedures [1, 2] with slight modifications.

#### 2.3.1. Synthesis of (1*E*,1'*E*)-*N,N'*-(ethane-1,2-diyl)bis(1-phenylmethanimine)

Ethylenediamine (0.67 mL, 10 mmol) was dissolved in 10 mL of ethanol, followed by the dropwise addition of benzaldehyde (2.04 mL, 20 mmol) in 15 mL of ethanol. The mixture was refluxed for 3 hours at 78 °C with constant stirring. The resulting precipitate was filtered after cooling, recrystallized, and dried.

### 2.3.2. Synthesis of salicylaldehyde- and vanillin-based Schiff bases

The same procedure was used for the condensation of ethylenediamine with salicylaldehyde or vanillin in methanol or ethanol, respectively, using a 1:2 molar ratio. The condensate was filtered out and recrystallized in ethanol.

### 2.4. Synthesis of metal complexes

The metal complexes were synthesized from the Schiff base ligand following the procedure described by Rao et al. [1]. Each ligand (4.0 mmol) was dissolved in hot ethanol (65 °C) and mixed with an equimolar amount of Ni(II), Cu(II), Cd(II), or Co(II) chloride salt dissolved in ethanol (25 mL). The mixture was stirred for 2 hours, and the resulting precipitate was filtered, washed with hot ethanol and ether, and dried under vacuum at 70 °C.

### 2.5. Physicochemical characterization

The determination of melting point, solubility, colour, molar conductivity (in dimethyl sulfoxide (DMSO)), and magnetic susceptibility was done following standard procedures. To establish coordination and electronic transitions, FTIR and UV-visible spectra were taken. Thermogravimetric and differential thermal analysis were performed under synthetic air (25 to 800 °C) and controlled temperature (10 °C/min).

### 2.6. Antifungal activity

The antifungal activity was assessed by the agar well diffusion method against *Aspergillus niger*, *Rhizopus flavus*, *Fusarium* spp., *Candida* spp., and *Mucor* spp. Fluconazole was used as the reference drug. Zones of inhibition were measured after incubation at 30 °C for 72 h. The minimum inhibitory concentration (MIC) and minimum fungicidal concentration (MFC) were determined by the agar dilution method with concentrations ranging from 6.25–50% (v/v), following the reported procedure [22]. All antifungal experiments, including zone of inhibition, MIC, and MFC, were conducted in triplicate ( $n = 3$ ), with results reported as mean  $\pm$  standard deviation. MIC and MFC values were determined through concentration-dependent growth inhibition assays (6.25–50%, v/v). MIC is the lowest concentration preventing visible fungal growth, while MFC is the lowest concentration achieving fungicidal activity after incubation.

### 2.7. Antioxidant activity (DPPH assay)

DPPH radical scavenging activities were evaluated using the methods of Girgih et al. [23]. Samples (0.0156–1.0 mg/mL) were mixed with DPPH solution (100  $\mu$ M in methanol) and incubated in the dark for 30 minutes. Reduced glutathione (GSH) served as the positive control, and the absorbance was measured at 517 nm. Radical scavenging activity (%) was calculated, and IC<sub>50</sub> values were obtained from concentration–response plots. All antioxidant measurements were conducted in triplicate, with data expressed as mean  $\pm$  standard deviation. IC<sub>50</sub> values were derived from concentration–response plots to enhance reproducibility and minimize experimental bias.

## 3. Results and discussion

### 3.1. Physical properties and molar conductivity

The physical properties of the Schiff base ligands (BBE, BHE, and BME) and their metal complexes are presented in Table 1. All compounds were obtained as crystalline solids with distinct colours, confirming the formation of new coordination compounds. The ligands are yellow solids with melting points in the range 120–125 °C, while their metal complexes show slightly higher melting points (125–130 °C). The increase in melting point upon complexation indicates enhanced thermal stability due to chelation and formation of more rigid structures, as commonly reported for Schiff base metal complexes [4]. All the compounds are soluble or slightly soluble in acetone, ether, chloroform, and DMSO. The molar conductivity values of all complexes fall in the narrow range of 10.5–12.0  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , indicating that the complexes are non-electrolytes in solution. This strongly suggests the absence of ions outside the coordination sphere and that the complexes are neutral, in agreement with earlier reports on Ni(II), Co(II), Cd(II), and Cu(II) neutral Schiff base complexes [6, 24].

### 3.2. Solubility behaviour

The solubility data (Table 2) show that most ligands and complexes are soluble or slightly soluble in DMSO and selected organic solvents, whereas BBE, BHE-Co, BME-Cu, and BME-Ni are insoluble in DMF or distilled water. Such solubility behaviour is commonly observed for Schiff base metal complexes because of their predominantly organic ligand framework and limited affinity for aqueous media. The good solubility in DMSO (and, where applicable, DMF) facilitates their spectroscopic characterization and biological evaluation [7, 9].

### 3.3. Electronic spectral (UV-visible) studies

The electronic spectra of the ligands and complexes are shown in the stacked spectra in Figure 1. The free ligands show intense bands in the UV region around 250–300 nm, assigned to  $\pi \rightarrow \pi^*$  transitions of the aromatic system, and bands around 320–380 nm attributed to  $n \rightarrow \pi^*$  transitions of the azomethine (C=N) group. These features are characteristic of Schiff bases and confirm successful condensation [25, 26]. The Cd(II) complexes ( $d^{10}$  system) show no d–d transitions but display metal-to-ligand charge-transfer (MLCT) bands in the visible region in addition to ligand-centered transitions. The Co(II) complexes display absorption bands in the 500–650 nm range linked to d–d transitions. Together with magnetic susceptibility, conductivity, and ligand donor traits, these findings suggest a tentative octahedral or distorted octahedral coordination environment [27], though single-crystal X-ray diffraction is needed for definitive structural confirmation. This agrees well with studies for octahedral Co(II) Schiff base complexes [7, 12]. The Ni(II) complexes show weak but distinct bands in the visible region corresponding to spin-allowed transitions of octahedral Ni(II), confirming six-coordinate environments [7, 12].

The Cu(II) complexes exhibit broad bands typical of  $d^9$  systems, assigned to d–d and ligand-to-metal charge-transfer

Table 1: Some physical constants of the ligands and metal complexes, highlighting their coordination properties.

| Compound | Colour of the crystal | Melting point (°C) | Molar conductivity ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) |
|----------|-----------------------|--------------------|--------------------------------------------------------------------|
| BBE      | yellow                | 120                |                                                                    |
| [BBE-Cd] | yellow                | 125                | 10.5                                                               |
| [BBE-Co] | green                 | 125                | 12.0                                                               |
| [BBE-Cu] | brown                 | 129                | 11.7                                                               |
| [BBE-Ni] | yellow                | 127                | 11.6                                                               |
| BHE      | yellow                | 125                |                                                                    |
| [BHE-Cd] | yellow                | 128                | 10.6                                                               |
| [BHE-Co] | green                 | 127                | 10.8                                                               |
| [BHE-Cu] | brown                 | 130                | 11.8                                                               |
| [BHE-Ni] | yellow                | 130                | 12.0                                                               |
| BME      | yellow                | 120                |                                                                    |
| [BME-Cd] | yellow                | 125                | 10.9                                                               |
| [BME-Co] | green                 | 127                | 11.3                                                               |
| [BME-Cu] | brown                 | 128                | 12.0                                                               |
| [BME-Ni] | yellow                | 130                | 12.0                                                               |

Table 2: Solubility properties of the ligands and complexes in different solvents at 24 °C.

| Compound | DMF | Distilled water | Acetone | Ether | Chloroform | DMSO |
|----------|-----|-----------------|---------|-------|------------|------|
| BBE      | S   | INS             | S       | S     | S          | S    |
| [BBE-Cd] | S   | S               | S       | S     | S          | S    |
| [BBE-Co] | S   | S               | SS      | S     | S          | S    |
| [BBE-Cu] | S   | S               | S       | S     | S          | SS   |
| [BBE-Ni] | S   | S               | SS      | S     | S          | SS   |
| BHE      | S   | S               | SS      | S     | S          | S    |
| [BHE-Cd] | S   | S               | S       | S     | S          | S    |
| [BHE-Co] | INS | S               | S       | S     | S          | S    |
| [BHE-Cu] | SS  | S               | S       | S     | S          | S    |
| [BHE-Ni] | SS  | S               | S       | S     | S          | S    |
| BME      | SS  | SS              | S       | S     | S          | S    |
| [BME-Cd] | S   | S               | S       | S     | S          | S    |
| [BME-Co] | S   | S               | S       | S     | S          | S    |
| [BME-Cu] | INS | S               | S       | S     | S          | S    |
| [BME-Ni] | INS | S               | S       | S     | S          | S    |

DMF = dimethylformamide; DMSO = dimethyl sulfoxide; S = soluble; SS = slightly soluble; INS = insoluble.

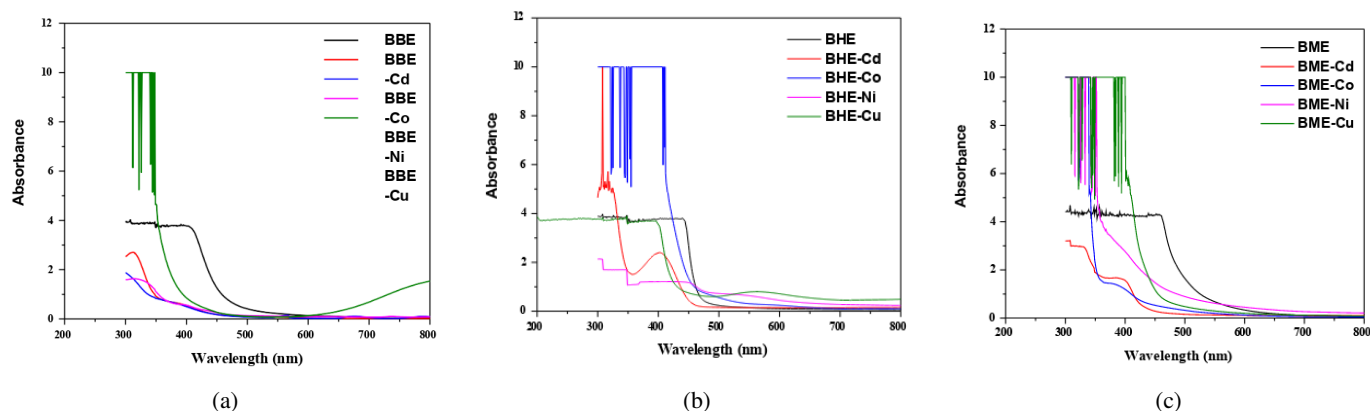


Figure 1: Stacked electronic spectra showing systematic shifts upon complexation for (a) BHE series, (b) BME series, and (c) BBE series.

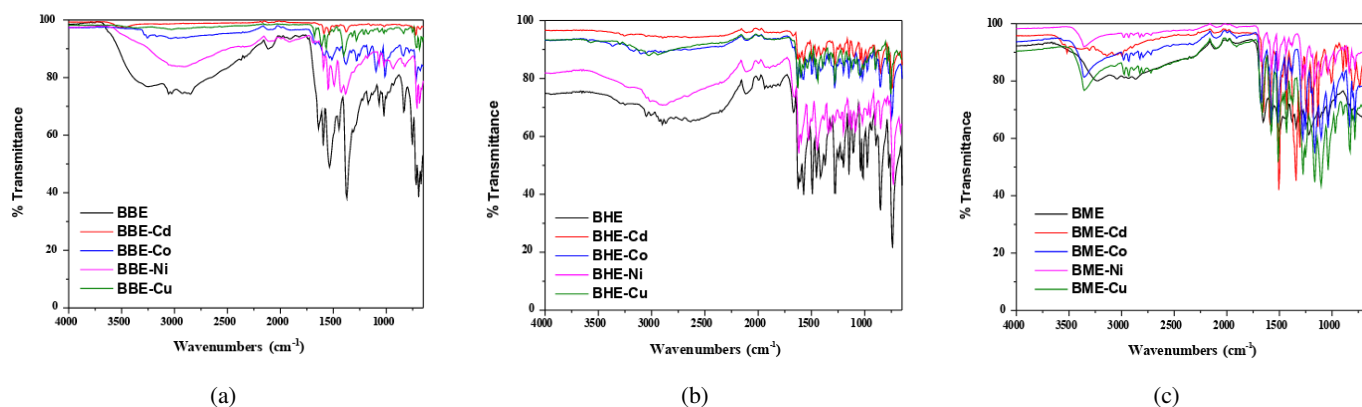


Figure 2: Stacked FTIR spectra of the (a) BBE series, (b) BHE series, and (c) BME series.

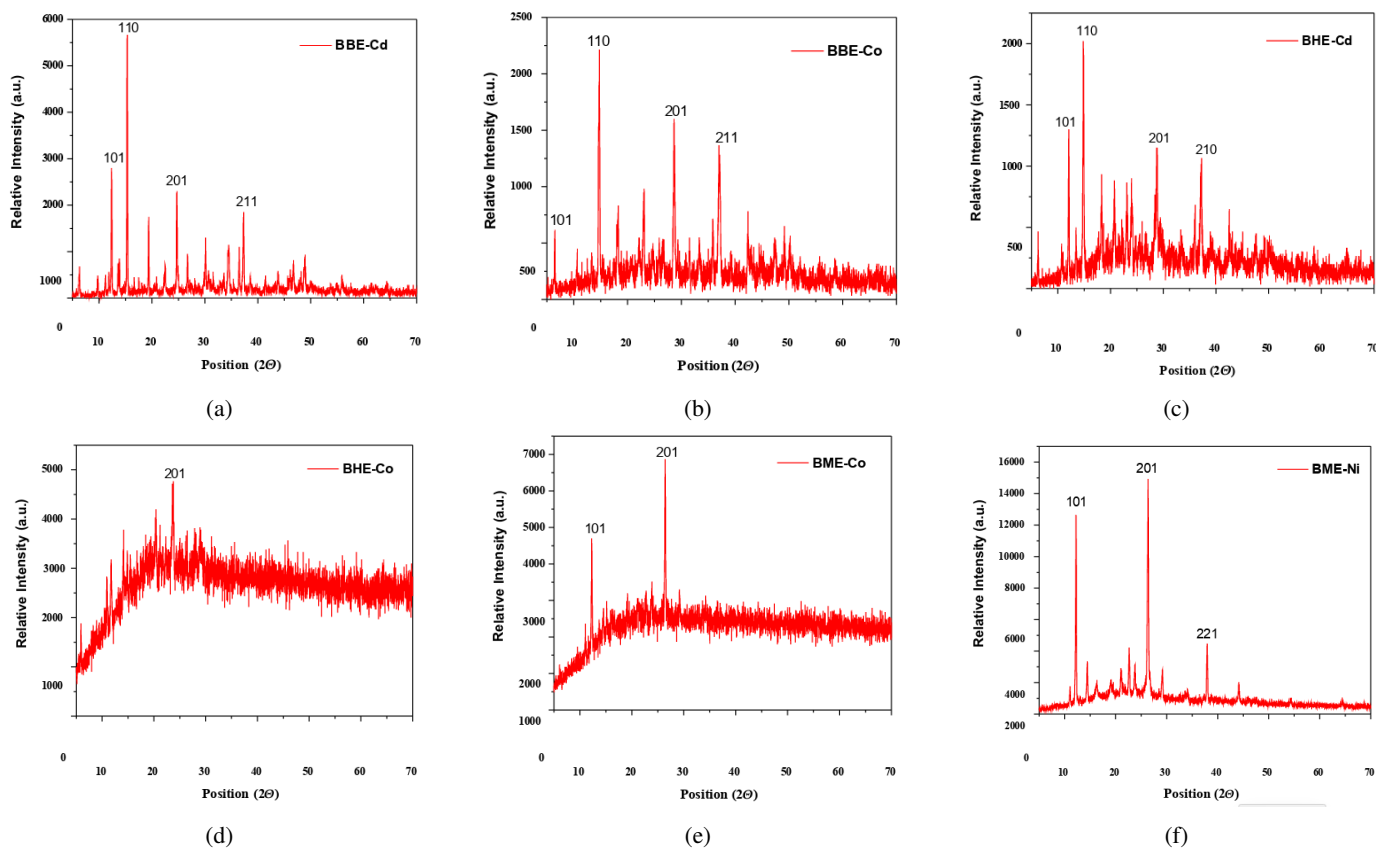


Figure 3: X-ray diffractogram of BHE-Cd, BHE-Co, BME-Co, BME-Ni, BBE-Cd, and BBE-Co.

(LMCT) transitions, consistent with distorted octahedral geometry [7, 12]. The stacked spectra (Figure 1) clearly show systematic shifts and new bands upon complexation, confirming coordination.

### 3.4. FTIR spectral studies

The FTIR spectra (Figure 2) of the ligands showed azomethine  $\nu(\text{C}=\text{N})$  stretching bands typical for Schiff bases, which shifted to lower frequencies upon coordination, suggesting azomethine nitrogen involvement in metal coordination. Ligands with phenolic oxygen donors (BHE and BME) exhibited

changes in  $\nu(\text{O}-\text{H})/\text{C}-\text{O}$  regions, indicating oxygen coordination. Additionally, new low-frequency bands in the  $400\text{--}600\text{ cm}^{-1}$  range were likely associated with  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{O})$  vibrations, confirming chelation through nitrogen and oxygen donor atoms [26, 28]. Schiff base formation was inferred from evidence including azomethine  $\nu(\text{C}=\text{N})$  vibrational bands, UV-visible ligand transitions, and melting behaviour, despite not performing NMR characterization of the free ligands.

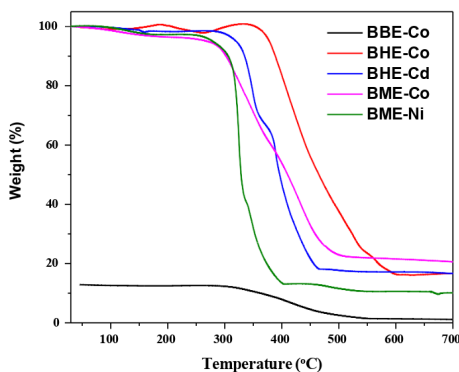


Figure 4: Stacked TGA thermograms of selected metal complexes.

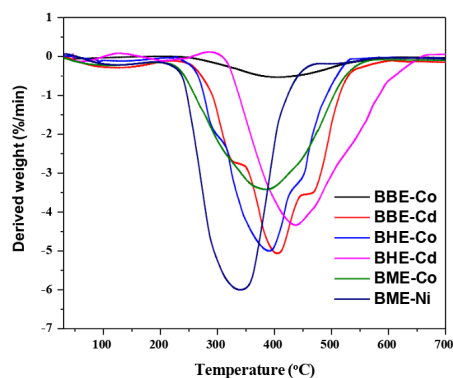


Figure 5: Stacked DTG plots of some selected metal complexes.

### 3.5. X-ray diffraction (XRD) studies

The powder XRD patterns of selected complexes (Figure 3) display sharp and well-defined peaks, confirming their crystalline nature. The appearance of new diffraction peaks and the disappearance of ligand peaks verify the formation of new coordination phases. The calculated lattice parameters (Table 3) differ from those of the free ligands, confirming the structural reorganization that occurs upon complexation. Similar crystalline behavior has been reported for Schiff base metal complexes [29, 30]. New peaks indicated the formation of new coordination compounds and structural changes upon metal coordination. The most intense peaks were indexed with Miller indices, revealing ordered crystalline domains. Differences in  $2\theta$  values and interplanar spacings reflect variations in crystal packing and metal–ligand interactions. Calculated crystallite sizes ranged from 26.50 to 59.82 nm (Table 3), suggesting nanocrystalline characteristics. Variations in peak positions suggest that coordination of Schiff base ligands alters the structural environment. Relatively narrow FWHM values further support well-ordered domains. However, definitive crystal system assignments require more detailed crystallographic analysis.

### 3.6. Thermogravimetric analysis (TGA)

Figure 4 demonstrates the decomposition patterns of the stacked TGA curves in three phases: the initial phase shows

the loss of a lattice or solvent molecule; the second phase reflects partial degradation of the Schiff base structure; and the final phase indicates complete degradation, resulting in metal oxide residues. The thermal stability observed is typical of chelated metal complexes, evidenced by high decomposition temperatures [31]. Figure 4 displays the stacked plot showing that Co(II) and Ni(II) complexes are slightly more thermally stable than Cd(II) complexes.

### 3.7. Differential thermal analysis (DTA)

The endothermic peaks in the DTA curves (Figure 5) imply the loss of moisture and/or solvent. The exothermic peaks are related to the oxidative breakdown of the organic ligands. These peaks are easily associated with TGA mass-loss steps, which validates the multi-stage decomposition. The absence of sharp melting peaks indicate that the complexes decompose rather than melt, which is typical for strongly chelated systems [29].

### 3.8. Antifungal activity

The antifungal findings indicate that the complexes exhibit greater biological activity compared to the free ligands (Figure 6), which is attributed to the enhancement resulting from the chelation theory [32]. Chelation decreases the polarity of metal ions and increases lipophilicity, thereby enhancing the permeability of fungi to the cell membrane. There is an apparent structure-activity relationship with the antifungal efficacy decreasing in the order Cu(II) > Co(II) > Ni(II) > Cd(II) > free ligands, indicating that the Cu(II) and Co(II) complexes are even better. The antifungal responses exhibited low replicate variability, as demonstrated by the standard deviation values and error bars, indicating acceptable measurement reproducibility.

#### 3.8.1. Minimum inhibitory concentration (MIC)

The MIC data in Figure 7 confirm that metal complexes exhibit lower concentrations required to inhibit fungal growth compared to free ligands. For BME complexes, similar MIC values suggest comparable potency across metal ions. In contrast, for BHE complexes, Ni(II) and Co(II) showed the weakest MIC values, while BBE complexes displayed equal MIC values. These findings are consistent with previous research on Schiff base metal complexes [33].

### 3.9. Antioxidant activity (DPPH/IC<sub>50</sub>)

Table 4 of the DPPH results shows that antioxidant activity varies with the ligand and metal, with Ni(II) and Cd(II) complexes of BBE and BHE demonstrating lower IC<sub>50</sub> values than their free ligands, signifying improved antioxidant activity due to metal coordination. Conversely, the majority of the Cu(II) and Co(II) complexes exhibit higher values of IC<sub>50</sub>, indicating a decreased antioxidant activity with coordination. This indicates that metal coordination does not always increase antioxidant activity but is highly dependent on the nature of the metal ion and the ligand structure. Analogous ligand-dependent effects have been observed in corresponding Schiff base systems

Table 3: Important lattice parameters of selected synthesized complexes.

| Complex  | Hkl | $2\theta$ (°) | $d_{hkl}$ | FWHM (°) | FWHM (rad) | D (nm) |
|----------|-----|---------------|-----------|----------|------------|--------|
| [BBE-Cd] | 201 | 26.35         | 3.379     | 0.236    | 0.0041     | 36.12  |
| [BBE-Co] | 201 | 26.43         | 3.370     | 0.170    | 0.0030     | 50.16  |
| [BHE-Cd] | 110 | 14.83         | 5.960     | 0.231    | 0.0040     | 36.24  |
| [BHE-Co] | 201 | 23.69         | 3.752     | 0.320    | 0.0056     | 26.50  |
| [BME-Co] | 110 | 14.74         | 6.006     | 0.245    | 0.0043     | 34.16  |
| [BME-Ni] | 110 | 15.30         | 5.785     | 0.140    | 0.0024     | 59.82  |

FWHM = full width at half maximum; D = average crystallite size; hkl = Miller index of the most prominent peak; rad = radians.

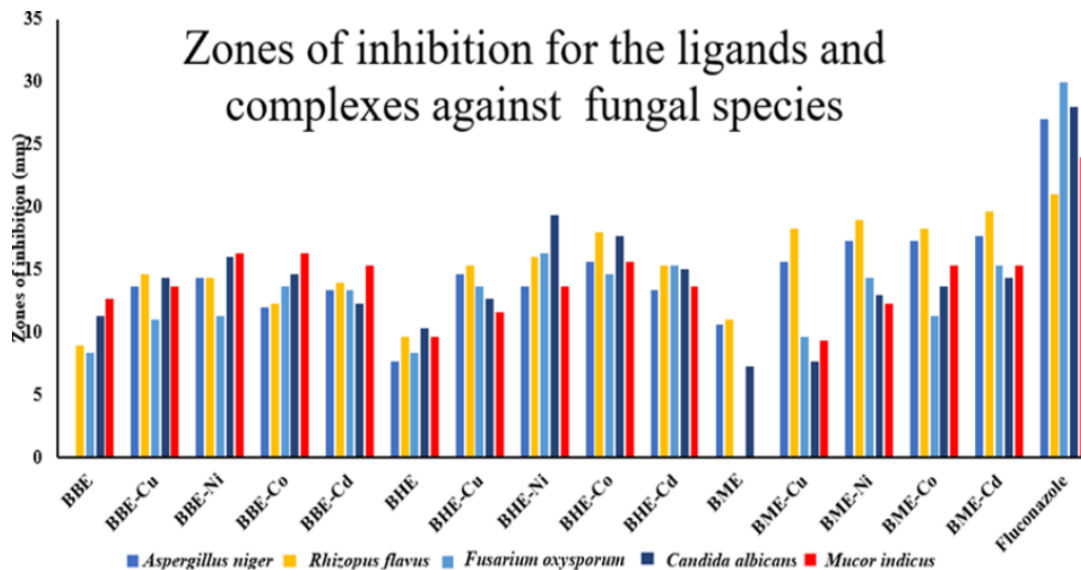


Figure 6: Comparative antifungal activity of Schiff base ligands and their metal complexes against five fungal species (zone of inhibition in mm).

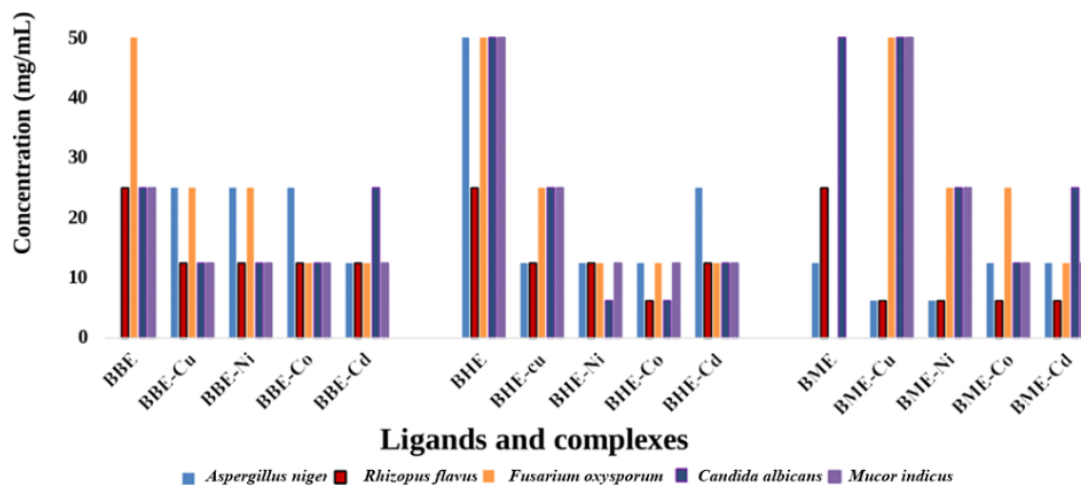


Figure 7: Minimum inhibitory concentration (in mg/mL) of Schiff base ligands and their metal complexes against five fungal species.

[34]. The antioxidant behavior of Schiff base metal complexes is influenced by factors such as electron distribution and metal-centred redox properties [35]. Ni(II) and Cd(II) complexes of BBE and BHE exhibit lower IC<sub>50</sub> values, indicating enhanced radical scavenging activity compared to free ligands. This im-

provement is attributed to chelation, which increases electron delocalization and stabilizes radical intermediates during the DPPH scavenging process [? ].

Coordination alters the electron-donating ability of donor atoms, promoting hydrogen atom or electron transfer to the

Table 4: Inhibitory concentration at 50% (IC<sub>50</sub>) for DPPH scavenging of the ligands and complexes.

| Ligands/Complexes | I     | II    | III   |
|-------------------|-------|-------|-------|
| BBE               | 0.987 | 0.977 | 0.982 |
| BHE               | 0.993 | 0.989 | 0.987 |
| BME               | 0.683 | 0.686 | 0.681 |
| BBE-Cu            | 1.114 | 1.117 | 1.119 |
| BBE-Ni            | 0.913 | 0.914 | 0.919 |
| BBE-Co            | 1.015 | 1.012 | 1.017 |
| BBE-Cd            | 1.012 | 1.009 | 1.013 |
| BHE-Cu            | 0.953 | 0.951 | 0.946 |
| BHE-Ni            | 0.712 | 0.717 | 0.715 |
| BHE-Co            | 1.054 | 1.056 | 1.056 |
| BHE-Cd            | 0.697 | 0.698 | 0.692 |
| BME-Cu            | 1.103 | 1.108 | 1.113 |
| BME-Ni            | 0.693 | 0.697 | 0.692 |
| BME-Co            | 0.984 | 0.985 | 0.989 |
| BME-Cd            | 0.685 | 0.688 | 0.691 |

I, II, and III are the triplicate experimental trials conducted.

DPPH radical [? ]. The metal centre aids in radical stabilization through electron density redistribution. Ni(II) complexes enhance electron transfer processes due to their partially filled d-orbitals, while Cd(II), as a  $d^{10}$  metal ion, indirectly boosts activity via ligand rigidity and electronic delocalization [? ]. These findings show that antioxidant activity is contingent on both ligand and structure and the electronic characteristics of the metal centre, with coordination enhancing scavenging efficiency through increased conjugation and stabilization of reactive intermediates.

Generally, the results of physicochemical analysis indicate successful coordination of the Schiff base ligands to the metal ions, with the formation of neutral, crystalline, and thermally stable complexes due to the presence of azomethine nitrogen and oxygen donor atoms. Based on spectroscopic, magnetic, and XRD data, the Ni(II), Cu(II), and Co(II) complexes are likely to have mainly octahedral or distorted octahedral structures, while the Cd(II) complexes are diamagnetic, as expected for a  $d_{10}$  system. Thermal analysis shows multistep decomposition patterns that ultimately produce metal oxide residues, confirming good thermal stability. Biological tests reveal that metal coordination generally enhances antifungal activity compared to free ligands, as indicated by the MIC values, and often increases antioxidant activity, especially in some Cd(II) and Ni(II) complexes of BBE and BHE ligands.

## 4. Conclusion

This study reports the synthesis, characterization, and biological testing of three Schiff base ligands, BBE, BHE, and BME, and their Co(II), Cu(II), Ni(II), and Cd(II) complexes. The physicochemical characterization of the ligands and complexes using molar conductivity, UV-visible, FTIR, magnetic susceptibility, XRF, XRD, and thermal analysis confirms the coordination of the ligands by the azomethine nitrogen and

oxygen donor atoms to give neutral, stable, mostly octahedral ligand-complexes. The complexes are thermally stable, crystalline, and structurally more rigid than the free ligands. Biological studies generally showed improved antifungal activity after metal coordination, as indicated by the MIC results, together with improved antioxidant (DPPH) activity for some Ni(II) and Cd(II) complexes of the BBE and BHE ligands. The enhanced biological activity is attributed to the chelation effect, which increases lipophilicity, enhances structural rigidity, and promotes electronic delocalization. Despite the observed biological activity of Cd(II) complexes, their known toxicity and environmental persistence limit direct biomedical applications. Instead, they serve as comparative coordination systems providing insights into metal-dependent behavior.

Conversely, Co(II), Ni(II), and Cu(II) complexes may hold greater relevance for future bioinorganic studies due to their higher biological significance. These findings suggest that the complexes are structurally stable and have biological potential for further bioinorganic and pharmaceutical research. Definitive structural confirmation of the proposed coordination behavior would be enhanced by complementary characterization methods, such as ligand nuclear magnetic resonance (NMR) and single-crystal X-ray diffraction, despite existing support from combined spectroscopic and physicochemical data.

## Data availability

All data related to this work are presented herein.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this manuscript.

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