FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 10 No. 24, December, 2026, pp 325 – 332
DOI: https://doi.org/10.33003/fjs-2026-1024-5619

Preparation, Characterization and Antibacterial Evaluation of Metal (II) Complexes Derived from Ethylenediamine and Acetophenone Schiff Base

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Received: 27 Jul. 2026
Accepted: 15 Nov. 2026
Published: 17 Nov. 2026

ABSTRACT
This study reports microwave-assisted synthesis, characterization, and antibacterial study of metal complexes derived from ethylenediamine and acetophenone Schiff base using Zinc (II) and Cobalt (II) as central metal ions. The compounds were characterized using melting point determination, solubility test, Ultraviolet visible spectroscopy (UV vis), Fourier transform infrared spectroscopy(FTIR), Elemental analysis and Magnetic susceptibility measurement to determine electronic transitions within the ligand and its complexes. Spectroscopic data indicate the Schiff base coordinates to Zn(II) and Co(II) ion in bidentate mode via N atoms. Magnetic moments and spectral Studies suggest tetrahedral geometry for both complexes. The structural parameters such as bond length, bond angles, HOMO and LUMO orbital, dipole moment, electronegativity, global softness, global hardness and electrophilicity were calculated by the methods based B3LYP on density functional theory (DFT) to establish the geometry and stability of the prepared compounds. Antibacterial screening against Staphylococcus aureus and Escherichia coli revealed that metal complexes exhibited higher inhibitory activity than the free ligand.

Keywords: Ethylenediamine, Acetophenone, Geometry, DFT calculation, Antibacterial

INTRODUCTION

Coordination chemistry is fundamental to contemporary inorganic and bioinorganic sciences, connecting the unique attributes of metal ions with the electronic and structural aspects of organic ligands (Abo-Aly et al., 2015). Transition metals form complexes with diverse coordination numbers, geometries and ligand environments due to their flexible electronic structures (Malav & Ray, 2025; Power, 2023).Schiff bases, first identified by Hugo Schiff in the 19th century, are among the most versatile ligand structures; they form through the condensation of primary amines with aldehydes or ketones, resulting in the imine (azomethine) functional group, –C=N– (Katarzyna and Elzbieta, 2014, Prakash and Adhikari, 2012, Cimerman *et al*., 2000).

Schiff base complexes are widely used in various fields, including catalysis, sensing, materials science, and notably, medicinal chemistry, where they frequently demonstrate antimicrobial, anticancer, and anti-inflammatory properties (Raman *et al,* 2001, Manjunatha, Naik and Kulkarni, 2011, Nagesh and Mruthyunjayaswamy, 2015, Ahmed et al, 2019, Abd El-Hamid et al., 2021, , Alanazi et al., 2022, Kumar *et al.,* 2023). Schiff bases play important roles in biology and pharmacology because they possess ability to coordinate with metal ions to form diverse structures compatible with biological systems (Mendez-Arriage, 2024, Sharma, 2026). The azomethine (C=N) group is pivotal within biological contexts, affecting mechanisms of action and the ability to chelate essential ions (Ali *et al.,* 2021, El-Sonbanti et al., 2025, Behera et al., 2026). Transition metals can engage in various coordination chemistries, redox reactions, and ligand exchange processes, enabling them to interact with biological targets in various ways, including binding to nucleic acids, inhibiting metalloenzymes, and producing reactive oxygen species (ROS) (Mishra *et al.,* 2008, Getzner et al., 2024, Liu, *et al*., 2024). There is an increasing abundance of drug-resistant pathogens despite continuous efforts by researchers to mitigates the resistance. Therefore, this research focuses on synthesis and characterization of Schiff base derive from acetophenone and ethylenediamine complexes as potential candidates to combat drug resistant-pathogens. The synthesized compounds were characterized using spectroscopic techniques and their antibacterial properties were examined. Spectroscopic data confirmed coordination of the ligand to Co(II) and Zn(II) ions via the azomethine nitrogen, with a shift in ν(C=N) from 162 cm^{-1} to 1608 cm^{-1}. UV-Vis and DFT studies supported the proposed geometry of the synthesized compounds. Antibacterial study demonstrated enhanced activity of the complexes compared to the ligand.

MATERIALS AND METHODS

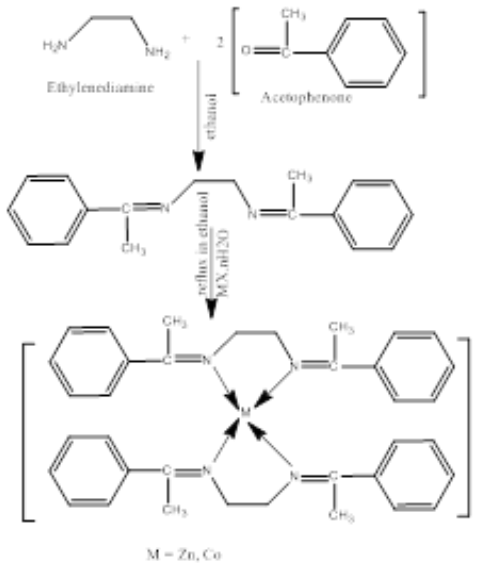
FTIR spectra(4000-400cm^{-1}) using KBr discs were recorded with Cary 630 FTIR. Magnetic susceptibility measurements were carried out at room temperature on a Gouy balance using Swissmake-H-1640 with maximum capacity of 80 g. Electronic spectra were recorded using Spectra Lab 7525 spectrophotometer in the range of 0-400, 400-900 nm for ligand and complexes. Elemental analysis was determined using Perkin Elmer, USA 2400 series II. The theoretical study of B is [N,N^1(phenylethylidene) ethane 1,2,diamine] cobalt / zinc (II) complexes as antibacterial agents was carried out using Density Functional Theory (DFT) with B3LYP functional 6-31+G* bases sets. All calculations were performed using the Spartan 10 software package. Microorganisms (*Staphylococcus aureus*, *Escherichia coli)* were obtained from Biological Lab, Bamidele Olumilua University of Education, Science and Technology. Ikere - Ekiti).

Preparation of Schiff Base Ligand

The Schiff base was prepared by general method (Prakash *et al*., 2012). Ethylenediamine (0.02495 mol, 1.5 g) with acetophenone (0.0499 mol, 5.99 g) in a 50 ml flask was stirred in 20ml ethanol at room temperature for 20 minutes, two drops of conc. H2SO4 was added to the mixture to aid the condensation process, the mixture was subjected to microwave irradiation for 5 minutes. The resulting white precipitate formed was separated by filtration, washed with absolute ethanol and dried under oven.

Synthesis of Schiff Base with Zn(II) and Cu(II)

1 mol (0.54 g) of $ZnSO_4$ .7H_2O was dissolved in 20 ml ethanol in a 50ml flask and added to an ethanolic solution containing 0.001 mol (0.8 g) of Schiff base ligand in molar ratio (2:1). The reaction mixture was stirred for 20 minutes, then subjected to microwave irradiation for 8 minutes. The resulting white precipitate formed was filtered, washed with absolute ethanol and dried overnight in air. 0.001mol (0.55 g) of $Co(NO_3)_2$ .6H_2O was dissolved in 20 ml ethanol in a 50ml flask and added to an ethanolic solution containing 0.001mol (0.8 g) of Schiff base in molar ratio (2:1). The reaction mixture was stirred for 20 minutes, then subjected to microwave irradiation for 8minutes. The resulting pink coloured precipitate formed was filtered, washed with absolute ethanol and dried overnight in air.



Scheme 1: Synthesis of Schiff base metal complexes

RESULTS AND DISCUSSION

Elemental Analysis

Elemental analysis of the Schiff base in Table 1, shows that the observed values are in agreement with the calculated values based on the proposed molecular formula. The result also confirmed the purity of the prepared ligand.

Infrared Spectra

The relevant FTIR band assignment of the ligand and its metal complexes of Zn(II) and Co(II) are presented in Table 2 and the spectra in Figure 1- 3. The identified bands are categorized by those emanating from the ligand and those evolving from the bonds established between metal ion and the ligand coordinating sites. The spectra of the free ligand showed band in the region 1625 cm^{-1} assignable to v(C=N) (Khedr *et al*., 2011; Ajibulu *et al*., 2023). The HC=N stretching frequencies in the complexes were observed at 1608 cm^{-1} for both zinc (II) and cobalt (II) respectively. This shift in azomethine stretching frequency showed that the Schiff base coordinated with metal ion via 'N' atom (Shelke *et al*., 2012). The FTIR spectrum of the free Schiff base ligand showed no v(H_2O) vibration, indicating that the ligand was anhydrous and contained no water molecules. The bands at 3369 and 3218 cm^{-1} in the spectrum of Zn(II) and Co(II) are assigned to v(N-H) stretching vibrations of the amine moiety (Kargar, *et al*, 2018, Nakamato, 2009). The appearance of new bands at 449 cm^{-1} Zn(II) and 493 cm^{-1} Co(II) confirmed the participation of azomethine nitrogen atom in the formation of the complexes (Ali and *et al*., 2020, Abdulkarim *et al*., 2023).

Table 1: Analytical and Physical Properties of Schiff Base and its Complexes

Compound	Empirical formula	Colour	Yield (%)	M.P (°C)	M.w t(g)	Solubility	Elemental analysis(found/calc)			
							C	H	N	O
Ligand	C18 H20N2	White	69	250	264	DMSO/Water	82.17 (81.81)	7.64 (8.00)	10.52 (10.60)	-
[Co(L)2]	[$Co(L)_2$]	Pink	75	260	587	DMSO/Water				
[Zn(L)2]	[$Zn(L)_2$]	White	65	262	593	Water				

Electronic Spectroscopy

The UV-vis absorption bands of the Schiff base and its metal (II) complexes with proposed geometry are shown Table 2. The absorption of the ligand is characterized by two bands at 226 and 324 nm. In Co(II) complex, three bands are observed at 220, 594 and 696 nm. These are due to $\pi \rightarrow \pi^*$, $^4A_{2(F)} \rightarrow {}^4T_{2(F)}$, and $^4A_{2(F)} \rightarrow {}^4T_{1(F)}$, suggesting tetrahedral geometry around the Co(II) with the observed magnetic susceptibility value 4.6 BM indicating d^7 high-spin system (Raman *et al,* 2001; Hamza and Slaheddine, 2026). The electronic spectra

of Zn(II) complex exhibited three bands 246, 356, 425 nm which is due to π→π*, n→π* and LMCT transitions. This suggests tetrahedral geometry coupled with the observed magnetic susceptibility value of o) because zinc is paramagnetic (Qian, 2021).

Table 2: Electronic Data of Ligand 0 (Zero) (L) and its Complexes

Compound	Wavelength λmax(nm)	μeff (B.M)	Transition(s) band assignment	Geometry
Ligand	265, 310	___	π→π*,n→π*	___
[Co(L2)]	220, 594, 696	4.5	π→π*,d→d	Tetrahedral
[Zn(L2)]	264, 356, 425	___	π→π*, n→π*, LMCT	Tetrahedra

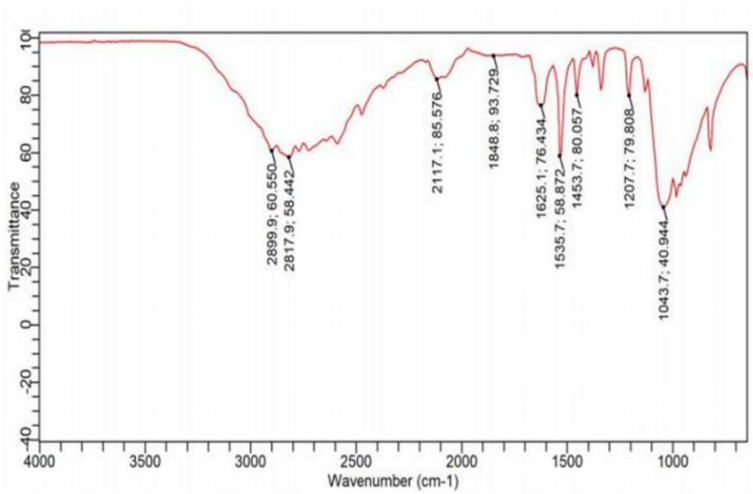


Figure 1: FTIR spectrum of the ligand

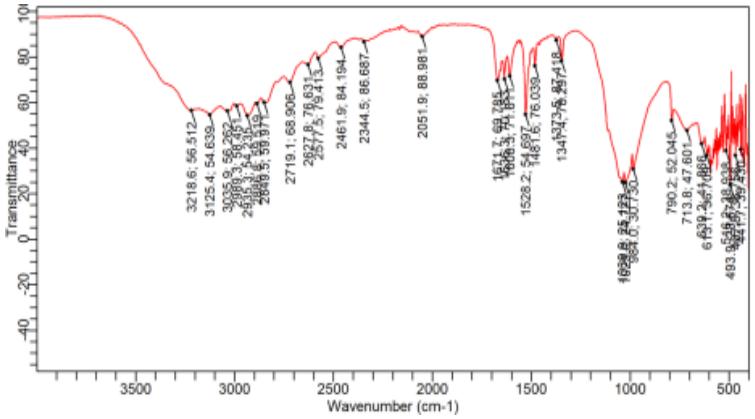


Figure 2: FTIR spectrum of [Co(L_2)]

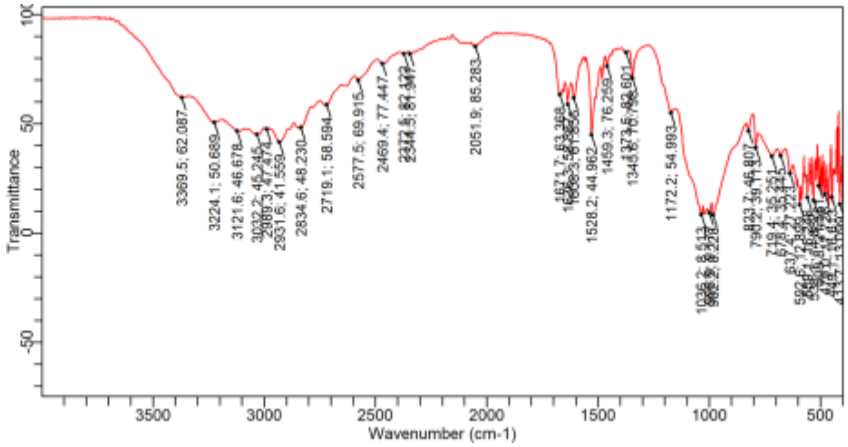


Figure 3: FTIR spectrum of [Zn(L2)]

Computational Studies

DFT is widely applied because it provides accurate electronic properties (Minakshee, 2024 & Jones, 2015). All calculations were performed using the Spartan 10 software package. The term HOMO-LUMO energies have been used frequently in quantum Chemistry. Literatures have shown that these orbitals are important in the growth of a wide variety of chemical processes and charge transfer in metal complexes (Bhanuka & Singh, 2017; Anupama et al., 2022). The HOMO and LUMO orbitals' respective energies have been linked to ideas of hard and soft nucleophiles and electrophiles. The HOMO-LUMO gap is a critical measure of a molecule's kinetic stability (Anupama et al., 2022).

Molecular Geometry

The bond length and bond angle parameters provide important insights into the molecular geometry and electronic characteristics of the studied compounds. Bond lengths and bond angles for two closely related compounds or molecular configurations (possibly structural isomers or substituted derivatives) are selected. Examining these values provides insights into how substitution, resonance, and hybridization influence the molecular geometry and electronic distribution of each system.

All the two tables (3-5) show N_3-Co_1 (1.960 Å) (A), N_3- Zn_1 (1.977 Å) (B) bond lengths of N_1-Co_1 (1.930 Å) (A), N_1-Zn_1 (6.409 Å) (B), are in this range. This indicates that partial double-bond character exists in all compounds, which gave a proof that there is a presence of conjugation or delocalized π-electrons including nitrogen atoms. The Carbon–Carbon double bond lengths through all the tables range approximately between 1.37–1.47Å, which is an indication that confirmed conjugated carbon systems discovered in a structure of semi-aromatic or aromatics structures. The results from these tables of the bond length revealed that all the compounds considered possess SP^2 hybridized carbon atoms, leading to partial planarity. In each case, there is an alternation between shorter and longer C–C or C–N bonds, which confirms resonance and π-delocalization in the molecular framework for example C1-C2 (1.524 and 1.535) and N1=C4 (1.326 and 1.478). The bond angles of the selected atoms of all the compounds in the range between 87° and 110°, which indicated that the compound has sp3 hybridization with some angular distortions (Cramer & Truhlar, 2009). Angles that are nearer to 110° leads in all compounds, reflecting a distorted tetrahedral geometry (Cotton et al., 1999). There are some angles that deviate from the normal given above (angles110° - 145°), showing substituent effect around nitrogen and carbon centers.

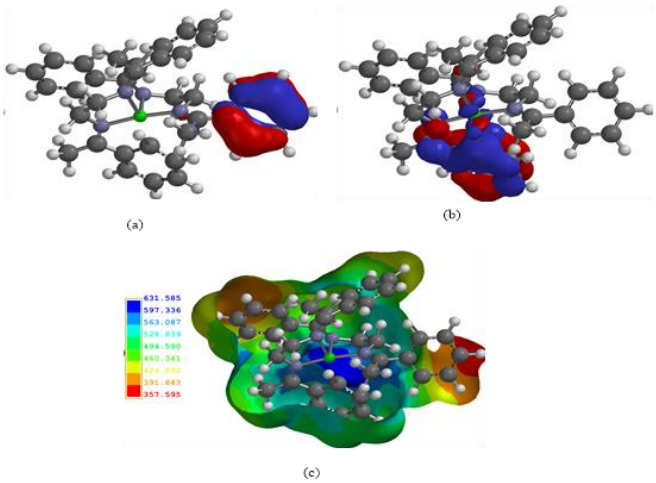


Figure 4: Optimized Geometry of Homo (a) Lumo (b) and Electro potential map (c) of Co
Complex (A)

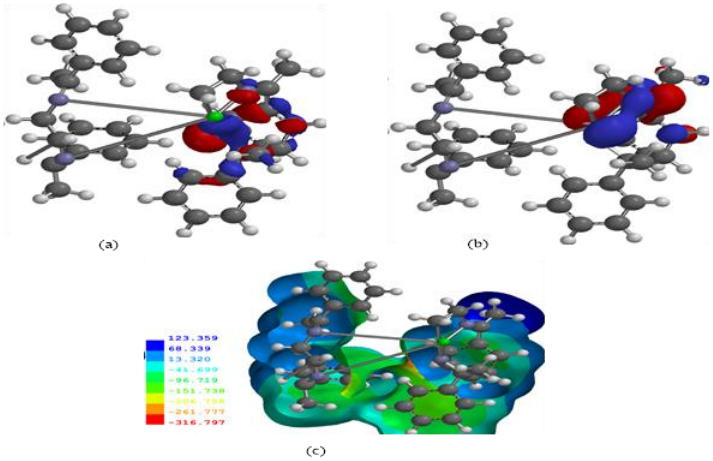


Figure 5: Optimized Geometry of Homo (a) Lumo (b) and Electro potential map (c) of Zn
Complex B

Table 3: Chemical Quatum Calculation Parameters

Properties	Co Ligands	Zn Ligands
EHomo (Ev	-14.60	-8.76
ELumo (eV)	-7.33	-0.75
Energy Gap (ΔE) ev	7.27	8.01
Dipole Moment (debye)	6.33	7.19
Molecular Weight (amu)	587.677	594.134
Ionization Potential(l)ev	14.60	8.76
Electron Afinity (A) ev	7.33	0.75
Global Hardness	3.635	4.005
Global Softness	0.275	0.249
Absolute Electronegativity	10.96	4.755

Table 4: Selected Bond lengths and Bond-Length Alterations of Ligand (L) of Co(L) and Zn (L) Complexes

Bond Length	Co(L) (A)	Zn(L) (B)
N3- Co1, N3-Zn1	1.960	1.977
N2-Co1, N2-Zn1	1.957	1.894
N4-Co1, N4-Zn1	1.886	5.985
N1-Co1, N1-Zn1	1.930	6.409
C1- C2	1.524	1.535
N1-C1	1.486	1.285
N2-C2	1.489	1.456
N1=C4	1.326	1.478
N3=C22	1.327	1.305
N4=C21	1.329	1.294
N2=C3	1.323	1.515
C3-C7	1.478	1.405
C21 –C25	1.454	1.395
C22 –C31	1.477	1.405
C3-C7	1.478	1.455
C9-C12	1.390	1.400
C15- C18	1.391	1.405
C33-C36	1.392	1.399
C25-C28	1.387	1.387
H1-C5	1.101	1.102
H2-C23	1.101	1.103
H11-C24	1.099	1.099
H- C6	1.01	1.111

Table 5: Selected Bond Angles (º) and Bond angles alteration of the ligand (L), Co(L) and Zn (L) Complexes

Bond Angle		Co(L) (º)	Zn(L) (º)
N1-Co1-N3	N1-Zn1-N3	94.73	104.64
N2-Co1-N1	N2-Zn1-N1	87.56	97.56
N3-Co1-N4	N3-Zn1-N4	97.20	107.54
Co1-N2-C6	Zn1-N2-C6	106.64	107.64
Co1-N3-C12	Zn1-N3-C12	140.47	145.45
Co1-N5-C47	Zn1-N5-C47	115.40	125.40
N2-Co1-N4	N2-Zn1-N4	94.71	104.71
N2-C6-H8		108.83	108.83
N3-C12-C14		124.76	126.66
N4-C44-H46		108.76	107.96
C6-C9-H10		111.67	121.67
H7-C6-C9		108.76	118.76
C12-C14-H15		112.806	112.806
C24-C27-H31		119.86	121.86
C37-C34-C38		119.86	119.86
H39-C35-C38		120.04	121.04
H46-C44-H45		104.69	114.69
C50-C60-C63		124.56	114.56
C51-C52-H54		111.07	112.07

Chemical Quantum Parameter

HOMO and LUMO orbitals are important quantum molecular orbitals in chemical processes. The molecule's interactions with other species can be ascertained. The orbital functions as an electron donor in HOMO and an electron acceptor in LUMO. The molecule chemical stability is characterized by the gap between HOMO and LUMO (Maurya et al., 2015). The HOMOs and LUMOs, sometimes referred to as quantum molecular orbitals, are crucial for assessing the chemical stability, reactivity, hardness, and softness of molecules (Xiaohan *et al*., 2014 & Fukui, 1982) Figures 4 and 5 display the compounds' highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

Table 3 lists the orbital energy levels of the HOMO and LUMO of ligands and their complexes. A bigger HOMO-LUMO gap should make an electronic system less reactive than one with a smaller gap. The LUMO-HOMO energy gap values for Co(L) and Zn(L) in the current work are 7.27 and 8.01 eV, respectively. The last charge-transfer interaction occurring within the molecules would be explained by the lower values of the HOMO and LUMO energy gaps. This molecule has low ionization energies, indicating that it could lose electrons readily, as demonstrated by the low HOMO values for ligands.

The global hardness represents the Band gap (Eg) values that are directly related to the molecule; in order to improve the molecule's desorption, hardness must be suitably low. According to Table 3, the global softness is 0.275ev (6-31 G*), and 0.249ev (6-31 G*) as the hardness tends toward zero (very soft), whereas the global hardness is 3.635ev (6-31 G*) and 4.005ev (6-31 G*). It suggests that the complexes can interact easily with other chemical species.

Additionally, a system's resistance to charge transfer is implied by its chemical hardness,

whereas its polarizability is directly correlated with its global softness (Table 3). The obtained global softness and chemical hardness values for the complexes under study suggest that the complexes resist the charge transfer and hence possess low polarizability. (Esan et al., 2022). The electrophilicity index (ω), which characterizes the systems' capacity to take electrons, is another characteristic of chemical quantum orbitals. The molecules' capacity to receive electrons is enhanced by high electrophilicity index values. Complexes' capacity to receive electrons is therefore organized as follows: Co(L) > Zn(L).

Antibacterial Screening

The antibacterial screening results as shown in Table 6 indicated that the metal complexes derived from Schiff base ligands exhibited varying degrees of inhibition against both Gram-positive and Gram-negative organisms. The higher zones of inhibition observed in both metal complexes against *Staphylococcus aureus* and *Escherichia coli* suggest that the complexes are more effective against Gram- positive bacteria compared to the free ligand (Vijayalakhmi, 2016, Diab et al, 2022). Zn complex displayed higher zone of inhibition against Gram-negative bacterial compare to Co complex and the free ligand. Zn complex shows higher activity against both *Staphylococcus aureus* and *Escherichia coli*. The higher activity of Zn(II) complexcompared to Co(II) despite computational results indicating that Co(II) has greater ability to accept electron, could be attributed Tweedy's chelation theory. Zn complex may penetrate the bacterial cell wall more efficiently resulting to enhanced activity (Omotade *et al.,* 2018). This variation can also be attributed to the differences in the structural composition of the bacterial cell walls (Awolope, Ejidike and Clayton, 2023: Hossain, 2017). The overall results showed that metal complexation enhances the antimicrobial activity of the Schiff base ligands which is in agreement with previous studies (Kumar & Dhar, 2011; Gabano *et al,* 2022, Ajibulu et al., 2023 and Vijayalakshini, 2025). The results were compared with standard antibiotics (positive controls).

Table 6: Antimicrobial Activity of Ligand and its Metal Complexes at 10mg/ml

	Zone of inhibition (mm)	
	Gram- positive	Gram- negative
Compounds	***Staphylococcus aures***	***Escherichia coli***
Ligand	9	7
[Co(L2)]	16	15
[Zn(L2)]	24	20
Ciprofloxacin	30	28

Conclusion

Schiff base and metal complexes from ethylenediamine and acetophenone were synthesized and characterized. The findings indicated, coordination of the ligand to the metal ions occurs through azomethine nitrogen atoms, forming stable chelates. Compared to the free ligand, the metal complexes exhibited enhanced antimicrobial activity, confirming the advantageous effects of metal coordination on biological properties. The proposed structures of the prepared compounds were elucidated with: FTIR, UV-vis, spectroscopy and Magnetic susceptibility measurement, Zn(II) and Co(II) complexes indicating tetrahedral geometries. The Co-N bond lengths (1.886-1.96 A^o) and Zn-N (1.894-1.977A^o) are in agreement with tetrahedral coordination ranges. HOMO and LUMO calculations indicated the complexes are kinetically more stable than the ligand. The prepared compounds possessed good antimicrobial activity against the tested organisms. In all, Zn(II) complex displayed more antimicrobial activity than Co(II) and Schiff base ligand, but less than the standard drug.

Acknowledgements

The authors are grateful to the Department of Chemistry and Department of Microbiology, Bamidele Olumilua University of Education, Science and Technology, for providing facilities for conducting this research.

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