

Research Article

Synthesis, Characterization, and Antibacterial Activities of 1H-Imidazo [5, 6-f] [1,10] Phenanthroline-2(3H)-Thione and Its Ni(II) and Cu(II) Complexes

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As multidrug resistant pathogens are emerging, the search for novel potent drug candidates is ever going. Heterocycles are known by their broad spectrum of biological activities, so a search for a new drug from heterocycles can elevate the chance of success. The aim of this study was to obtain novel potent antimicrobial compounds. In line with this, 1H-imidazo [5, 6-f] [1,10] phenanthroline-2(3H)-thione and its complexes (Ni(II) and Cu(II)) were synthesized, characterized, and evaluated against bacterial strains. The compounds were characterized by elemental analyses (C, H, N, and S), FT-IR, ¹H-NMR, ¹³C-NMR, AAS, UV-Vis spectra, and molar conductivity measurement. The results showed that the ligand is bidentate, and the molar conductivity measurement indicates that complexes are electrolytic. Electronic spectral study showed octahedral and distorted octahedral geometry for the Ni(II) and Cu(II) complex, respectively. The ligand and its complexes were screened against four bacterial strains using disk diffusion method. The result revealed that the Ni(II) complex showed more bioactivity than gentamicin against *Staphylococcus aureus* and *Escherichia coli*, while the Cu(II) complex is more active than the Ni(II) complex against *Bacillus subtilis*. Both Cu(II) and Ni(II) complexes exhibit higher antibacterial activities than the free ligand.

1. Introduction

Heterocyclic chemistry is a branch of organic chemistry deals with two third of organic compounds, called heterocycles. Heterocycles contain heteroatoms such as sulfur, oxygen, or nitrogen as part of their ring structure. Examples: pyridine (C₅H₅N), pyrimidine (C₄H₄N₂), and dioxane (C₄H₈O₂) [1]. Heterocycles containing more than one nitrogen such as purine, pteridine, and flavin are key structures of biochemical processes, and their metal complexes assist enzymatic reactions. They are also part of biomolecules such as nucleic acids, vitamins, proteins, and other biologically important molecular systems [2]. Among the nitrogen heterocycles, 1,10-phenanthroline derivatives have attracted considerable interest from both synthetic and medicinal chemists being the structural pattern in several natural biologically important compounds [3] and molecular scaffoldings for supramolecular assemblies, building blocks for the synthesis of metallo dendrimers, thin films of luminescent

complexes, and ligands of synthesis of ring-opening metathesis polymerization (ROMP) monomer [4].

Although a large number of antibiotics and chemotherapeutic agents are available, treatment of infectious diseases is still a challenging problem due to the outbreak of new infectious diseases as well as medicinal drug-resistant pathogens [5] which makes the search for a novel potent drug candidate an indispensable strategy to overcome the challenge of drug-resistant pathogens. Reported literatures have suggested that heterocycles and their derivatives have excellent broad spectrum of biological activities [3, 6], so a search for a new drug from heterocycles is supposed to uplift the chance of success. Hence, this research was aimed to synthesize a novel potent ligand and some of its transition metal complexes. From antibacterial bioassay, it was observed that the Ni(II) complex of the new ligand was more active than gentamicin against *S. aureus*, *E. coli*, and *P. aeruginosa*.

2. Materials and Methods

2.1. Chemicals and Instrumentation. Analytical reagent (AR) grade chemicals were used without purification. Copper chloride (Nice Lab reagent Ltd.), nickel chloride (Nice Lab reagent Ltd.), 1,10-phenanthroline (Nice indicator), thiourea (LOBA Chemie PVT.LTD.), potassium bromide (KBr), sodium hydroxide (NaOH), conc. nitric acid (HNO₃), conc. sulphuric acid (H₂SO₄), anhydrous magnesium sulphate (MgSO₄) (Finkem), silver nitrate (Kiran light laboratories), dichloromethane (Blulux Laboratory (p) Ltd.), and dimethyl sulfoxide (DMSO)(Blulux Laboratory (p) Ltd.) were purchased. Solvents such as chloroform, ethanol, petroleum ether, and methanol were purchased from LOBA Chemie Ltd. Company. The bacterial strains were obtained from the Department of Biology, Jimma University.

NMR spectrum of the ligand was recorded using BRUKER 400 MHz (¹H NMR) and the 100.06 MHz (¹³C-NMR) ultrashielded NMR spectrometer in DMSO using TMS as the internal standard. The infrared spectra were recorded in the range of 4000 cm⁻¹–400 cm⁻¹ in KBr medium. The percentage of C, H, N, and S was estimated by using the Flash FA 1112 Elemental analyzer and that of the metal (Cu and Ni) quantity in the complexes by AAS. Electronic absorption spectra were measured on 6705 UV-Vis (JENWAY Spectrometer) in the range of 200–800 nm regions in DMSO at room temperature. The melting point and molar conductivity of the synthesized compounds were determined using Griffin melting point apparatus and HQ 40d (multi) conductivity meter, respectively. TLC was used to ensure reaction completion and purity of the products.

2.2. Experimental Procedures

2.2.1. Preparation of 1,10-Phenanthroline-5, 6-Dione (PD). A reported procedure, Calderazzo et al. [7], was followed to prepare 1,10-phenanthroline-5, 6-dione (PD). In a three-necked flask, solid ice cold 1,10-phenanthroline (10.0 g, 50.5 mmol) and KBr (10 g, 84 mmol) were dissolved in a mixture of ice cold 96% H₂SO₄ (90 mL) and 68% HNO₃ (45 mL) through adding drop wise from a dropping funnel with stirring at 0°C (addition time 20 min) (Scheme1). The resulted red to orange suspension was allowed to warm up to room temperature and then refluxed for 10 h at 150°C, monitoring with TLC until the starting materials completely reacted. The yellow suspension was cooled at room temperature and poured on to ice water. The pH of the mixture was carefully raised to 6 by adding 30% NaOH and extracted with CH₂Cl₂. The extract was dried over MgSO₄, the solvent was removed by rotary evaporator, and the product was dried in an oven at 80°C. Finally, the product was recrystallized from hot methanol to give a yellow crystalline solid. Yield: 50.47%; MP (°C): 258–260.

2.2.2. Synthesis of 1H-Imidazo [5, 6-f] [1,10] Phenanthroline-2(3H)-Thione (1,10-PDTU). An equimolar of thiourea (1.55 g, 0.0204 mol) in 40 mL hot methanol was added drop wise to 1,10-phenanthroline-5, 6-dione (4.29 g, 0.0204 mol) in 40 mL hot methanol stirring with a magnetic stirrer. The

reaction mixture was refluxed for 10 h at 70°C, monitoring by TLC test. The precipitate was filtered, washed successively with petroleum ether, and dried in an oven at 80°C [8]. Yield: 68.5%; MP 264–267(°C).

2.2.3. Synthesis of Complexes. The Ni(II) complex was synthesized by slowly adding the ligand (0.81 g, 3.2 mmol) in hot ethanol (40 mL) into a 250 mL two-necked flask containing NiCl₂·6H₂O (0.38 g, 1.6 mmol) solution in ethanol (40 mL) with magnetically stirring. The mixture was refluxed for 11 h at 60°C, monitoring the reaction progress by TLC. The resulting brown precipitate was filtered, washed with petroleum ether and chloroform, and finally dried in an oven at 80°C [9–11].

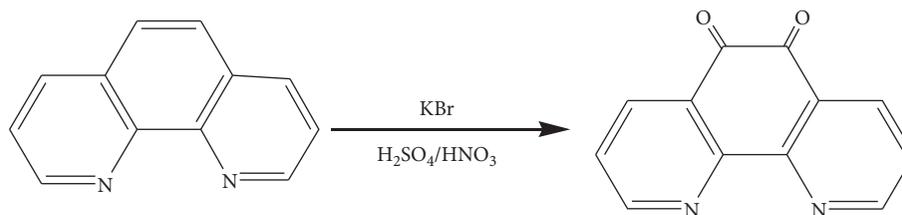
Yield: 36.45%; MP (°C): 313–314. The Cu(II) complex was synthesized with the same approach but in this case the reflux was done for 12 h which gave a green precipitate. Yield: 82.33%; MP (°C): 289–291.

2.2.4. Antibacterial Activity. The antibacterial activity studies were conducted using agar disc diffusion method as described by Shaik et al. [12, 13]. The *in-vitro* antibacterial screening of the new synthesized compounds was tested against four bacterial strains, *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis*, and *Pseudomonas aeruginosa*, by disc diffusion method using Mueller–Hinton agar (MHA) as a medium. The discs measuring 6 mm in diameter were prepared from whatman No. 1 filter paper sterilized by dry heat at 121°C for 1 h. The solution of 100 mg/mL of each test compounds was prepared by dissolving the compound in DMSO, and the solutions were loaded on the wall of the culture and incubated at 37°C for 24 h. The efficiency was evidenced by measuring the zone of inhibition. Gentamycin and DMSO were used as a positive and negative control, respectively.

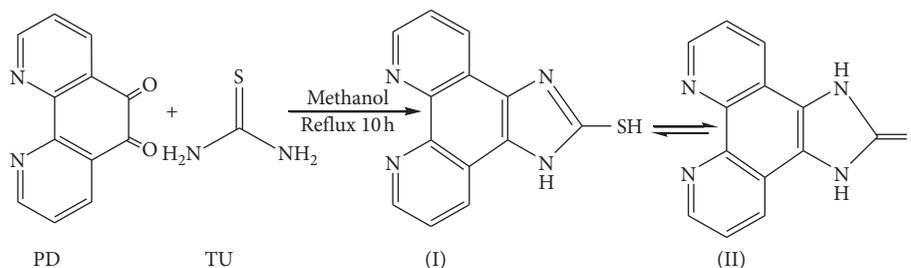
3. Results and Discussion

3.1. Synthesis and Physical Characteristics of the Ligand and Its Complexes. The synthesis of the new ligand is illustrated in Scheme2. Combination of thiourea solution with 1,10-phenanthroline-5, 6-dione (PD) solution in hot methanol under reflux afforded orange precipitate which indicates the formation of a new compound. Reported literatures suggested that such reactions might form structure I or II [14–16]. However, the IR spectrum of the free ligand shows a broad band at 3232 cm⁻¹ which arises from the ν (N-H) stretching. The result of DEPT also suggests the presence of three CH-groups on the benzene rings which would be possible only if the ligand becomes symmetrical that in turn reveals that structure (II) is the major product (Scheme2). The ligand was reacted with hexahydrated metal chlorides to synthesize complexes (Scheme3). However, the result of elemental analysis of the complexes displayed zero signals for sulfur which implies that the ligand has undergone desulphurization during metal-ligand coordination [17, 18].

Table 1 reveals that the newly synthesized ligand and complexes are colored compounds, stable at room temperature, and possess melting point (>264°C). They are slightly soluble in



SCHEME 1: Preparation of 1,10-phenanthroline-5, 6-dione [7].



SCHEME 2: Synthesis of 1H-imidazo [5, 6-f] [1,10] phenanthroline-2(3H)-thione.

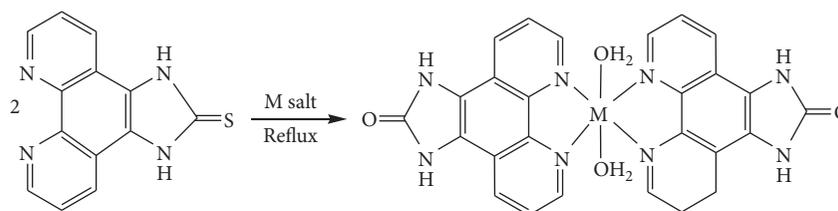
SCHEME 3: Formation of *M* (II) complex, where *M* = Ni and Cu.

TABLE 1: Physical properties of newly synthesized ligand and complexes.

Compound	Molecular formulae	Mol. wt (g/mol)	Color	% yield	MP (°C)	Elemental compositions found (Cal)					Λ_M ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)	Electrolytic nature
						C%	H%	N%	S%	M%		
Ligand	$[\text{C}_{13}\text{H}_8\text{N}_4\text{S}]$	252	Orange	68.5	264–267	59.78 (61.91)	3.19 (3.17)	21.72 (22.22)	11.71 (12.69)	—	—	—
NiL ₂	$[\text{NiC}_{26}\text{H}_{20}\text{N}_8\text{O}_4\text{Cl}_2]$	637.693	Brown	36.45	313–314	47.25 (48.93)	3.09 (3.14)	17.89 (17.56)	0 (-)	8.78 (9.20)	119.5	✓
CuL ₂	$[\text{CuC}_{26}\text{H}_{20}\text{N}_8\text{O}_4\text{Cl}_2]$	642.564	Green	82.33	289–291	48.05 (48.56)	3.01 (3.12)	16.82 (17.43)	0 (-)	10.32 (9.89)	139.6	✓

methanol, ethanol, and water, while completely soluble in DMSO but insoluble in petroleum ether and chloroform which indicates their polar nature. The complexes had electrolytic nature as discussed in the result of molar conductivity.

3.2. ¹H-NMR Spectrum of the 1,10-PDTU. For more clear illustration, atoms in the structure of the ligand are denoted by numbers as depicted in Figure 1, and the ¹H NMR spectrum of the ligand is illustrated in Figure 2. Figure 2 shows peaks at δ (6.99–8.72 ppm) which may assign for protons in the aromatic ring. The peak observed at δ (8.72 ppm) is assignable to protons denoted by H(2) and

H(9). The peak appearing at δ (8.25 ppm, d) stands for the protons H(4) and H(7). Another peak appearing at δ (7.55 ppm, d) refers to two equivalent protons denoted by H(3) and H(8). The spectrum also showed long intense singlet peak at δ (9.5 ppm) assigned to the protons H(16) and H(17) which is also supported by the presence of a broad peak at 3433 cm^{-1} in the IR spectrum. The integration values from the ¹H-NMR spectra for the ligand agreed with the number of protons proposed for the respective structures. However, the peak appearing at δ (3.5 ppm) may be from undeuterated DMSO [19], while the peak observed at δ (2.5 ppm) may arise from (S-H) suggesting the presence resonance structure I in Scheme2.

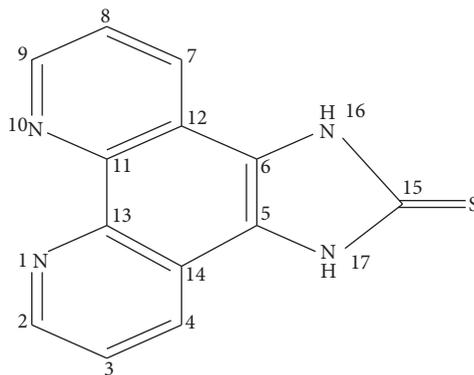


FIGURE 1: The structure of the synthesized ligand 1,10-PDTU.

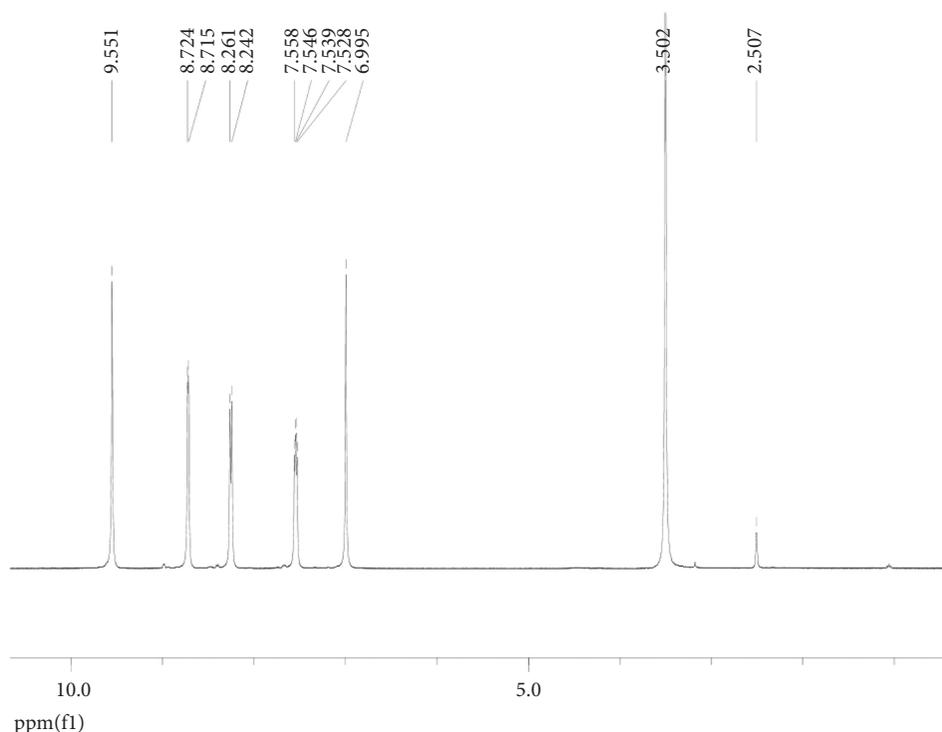


FIGURE 2: ^1H NMR spectrum of ligand 1,10-PDTU in DMSO.

3.3. ^{13}C NMR Spectrum of 1,10-PDTU. The ^{13}C -NMR results are summarized in Table 2, and the spectra are depicted in Figure 3. The ^{13}C NMR spectrum was observed in agreement with previously published literatures for the ligand [18, 20]. ^{13}C -NMR spectrum of the ligand indicates seven carbon resonances, out of which four of them with δ 182.2 ppm, 147.0 ppm, 132.5 ppm, and 85.8 ppm are quaternary carbons and attributed to C(15), C(5), C(11), and C(12), respectively. The peak at δ 150.7 ppm, 136.6 ppm, and 125.1 ppm are, respectively, due to C(2), C(3), and C(4) which are in agreement with the structure of the ligand. However, the peak at δ 39.1 ppm may be due to DMSO present as impurity.

3.4. Infrared Spectra Studies of 1,10-PDTU and Complexes. The IR bands of the characteristic groups in the ligand and the complexes are summarized in Table 3. In order to reveal

the functional groups as well as binding mode of the ligand, the IR spectrum of the free ligand was compared with those of the complexes (Figures 4–6). Figure 4 shows IR spectra of the free ligand, displaying a broad band at 3433 cm^{-1} attributed to ν (N-H) stretching in the imidazole. This band is overshadowed by intermolecular hydrogen bonding and is not clearly observed in the Ni(II) complex, while it shifted to 3074 cm^{-1} in the Cu(II) complex due to electron flow caused by coordination [20]. The strong broad bands observed at 3232 cm^{-1} in the Ni(II) complex and at 3378 cm^{-1} of in the Cu(II) complex indicate intermolecular hydrogen bonding as well as ν (O-H) stretching vibration of the water molecules [21]. The appearance of weak band at 814 cm^{-1} in the Ni(II) and at 813 cm^{-1} in the Cu(II) complex also confirms the presence of the (-N-H) group in the complexes. The bands were observed at 2972 and 2713 cm^{-1} in the ligand spectrum due to ν (C-H) in aromatic ring. The strong band observed at

TABLE 2: ^1H -NMR, ^{13}C NMR, and DEPT 135 of the ligand as depicted in Figure 1.

Proton (assigned)	^1H NMR δ (ppm)	Carbon (assigned)	^{13}C NMR δ (ppm)	Group (assigned)	DEPT δ (ppm)
H(2), H(9)	8.72	C(2), C(9)	150.7	C-H	150.7
H(4), H(7)	8.25	C(5), C(6)	147.0	C	—
H(3), H(8)	7.55	C(4), C(7)	136.6	C-H	136.6
H(16), H(17)	9.55	C(11), C(13)	132.5	C	—
		C(3), C(8)	125.1	C-H	125.1
		C(12), C(14)	85.8	C	—
		C(15)	182.2	—	—

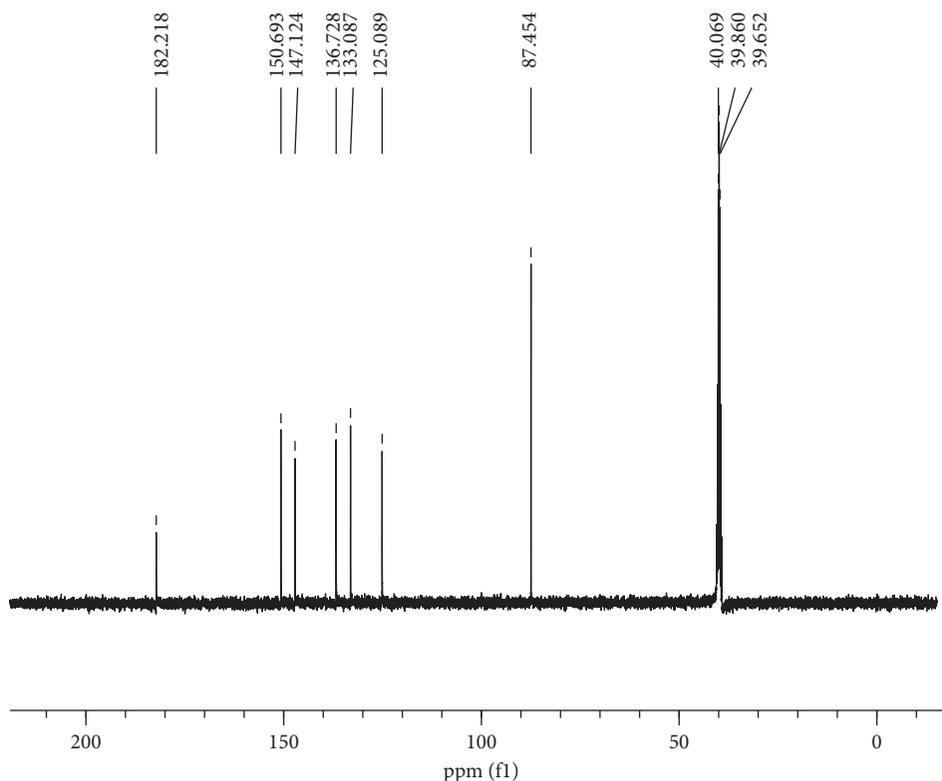
FIGURE 3: ^{13}C NMR spectrum of ligand 1,10-PDTU in DMSO.

TABLE 3: Major IR spectral frequencies of the ligand and its complexes.

Compound	ν (N-H) cm^{-1}	ν (O-H) cm^{-1}	ν (C-H) cm^{-1}	ν (C=O) cm^{-1}	ν (C=N) cm^{-1} (phenring)	ν (C=C) cm^{-1}	ν (C-N) cm^{-1}	ν (C=S) cm^{-1}	(C-H) bending cm^{-1}	ν (M-N) cm^{-1}
L[C ₁₃ H ₈ N ₄ S]	3433b	—	2972–2713w	—	1617s	1422s	1315s	1019s	731s	—
[NiC ₂₆ H ₂₀ N ₈ O ₄] Cl ₂	—	3232s,b	—	1701w	1626s	1426s	1319w	—	730s	616w
[CuC ₂₆ H ₂₀ N ₈ O ₄] Cl ₂	—	3378s,b	3074w	1698s	1630s	1430s	1301m	—	725s	548w

b = broad; s = strong; m = medium; w = weak.

731 cm^{-1} in the free ligand, at 730 cm^{-1} in the Ni(II) complex, and at 725 cm^{-1} in the Cu(II) complex indicate the presence of aromatic rings [22, 23]. The ν (C=N) (phenanthroline ring) group showed a strong band at 1617 cm^{-1} in the free ligand which shifted to 1626 cm^{-1} and 1630 cm^{-1} in nickel (II) and Cu(II) complexes, respectively

(Figures 5 and 6), which ascribed the participation of the ν (C=N) (phenanthroline ring) group in coordination [24]. The strong absorption band at 1019 cm^{-1} assigned to be the ν (C=S) thiocarbonyl group disappeared in complexes implying the absence of the ν (C=S) group due to oxidation. In both complexes, the appearance of a new strong

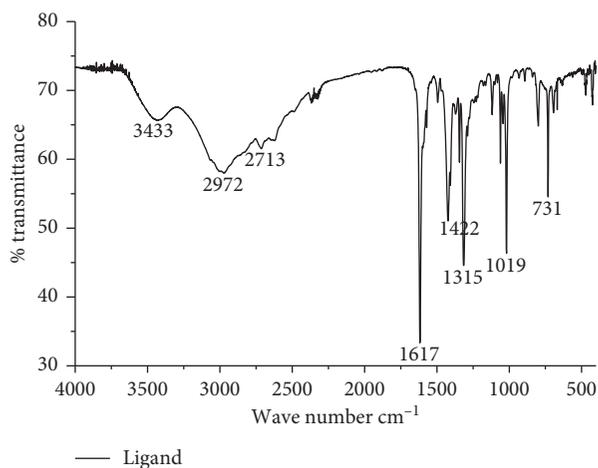


FIGURE 4: IR spectra of ligand 1,10-PDTU.

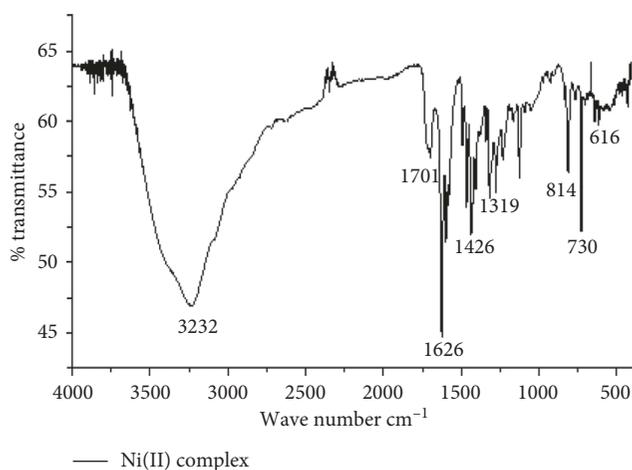


FIGURE 5: IR spectra of Ni(II) complex.

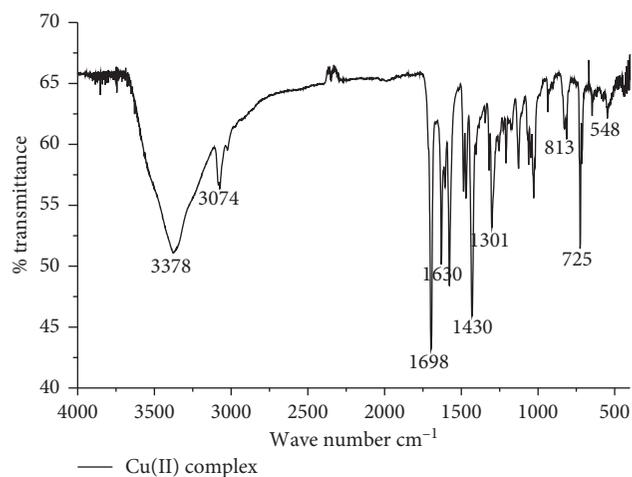


FIGURE 6: IR spectra of Cu(II) complex.

band at 1698–1701 cm^{-1} implies the formation of $\nu(\text{C}=\text{O})$ as a consequence of oxidation [18, 25, 26]. The IR spectra bands observed at 1422 cm^{-1} and 1315 cm^{-1} were assigned

for the stretching of (C=C) and (C-N) groups. In the complexes, these bands shifted which may be due to participation of the nitrogen atom of the phenanthroline ring. The formation of the complex is confirmed by the appearance of new weak intensity bands at 616 cm^{-1} and 548 cm^{-1} in the spectra of both complexes which are assigned to frequencies of $\nu(\text{Ni-N})$ and $\nu(\text{Cu-N})$ stretching vibrations, respectively. This indicates that coordination has occurred through the nitrogen atoms of C=N (phenanthroline ring) of the ligand [27, 28]. Therefore, from the IR spectra, it can be deduced that the ligand behaves as bidentate.

3.5. Elemental Analysis: CHNS. The result of elemental analysis provides that the percentage of carbon, hydrogen, nitrogen, and sulfur (Table 3) is in agreement with the theoretical values. These values were used to devise the empirical formulae of the ligand. However, the percentage of sulfur in both complexes was found to be zero which may be due to desulfurization [17, 27]. The result of elemental analysis also suggests that both complexes contain 1:2 metals to ligand ratio.

3.6. AAS Analysis of Metal Ions. The metal content of complexes was determined by atomic absorption spectroscopy (AAS). In a dry clean beaker, 30 mg of complex was digested in 10 mL of conc. HNO_3 with gently heating in a hood until a few drops remain in the beaker which was further heated with additional 10 mL conc. HNO_3 till the content gets colorless. The residue was dissolved and diluted using distilled water in a 50 mL flask. The solution was subjected to AAS study. Then, the percentage of metal was determined using the following relation:

$$\%M = \frac{\text{concentration (ppm)} \times \text{volume diluted} \times 100}{\text{mass of sample taken} \times 1000} \quad (1)$$

The percentage of nickel in the complex was determined experimentally to be 8.78%, while the calculated value is 9.20%. The percentage of Cu was found to be 10.32%, whereas the calculated one is 9.89%. This small deviation between the calculated and experimentally found values may be due to the presence of impurities or instrumental error. The metal-ligand ratio was estimated to be 1:2 based on the combination of AAS and elemental analysis. Based on these data the chemical formula of the Ni(II) and Cu(II) complexes were proposed to be $[\text{NiC}_{26}\text{H}_{20}\text{N}_8\text{O}_4]\text{Cl}_2$ and $[\text{CuC}_{26}\text{H}_{20}\text{N}_8\text{O}_4]\text{Cl}_2$, respectively.

3.7. Molar Conductivity of the Complexes. The conductivity measurements were carried out at room temperature by dissolving 20 mg of each complex in 30 mL of DMSO. Specific conductance (K) of the Ni(II) and Cu(II) complexes was obtained as 119.5×10^{-6} and 139.6×10^{-6} S/cm, respectively. The molar conductance (Λ_M) of the complexes was calculated using the relation $\Lambda_M = 1000 \text{ K/C}$ (where C is the molar concentration of the metal complex solution

and K is specific conductance); the molar conductivity of the Ni(II) complex and Cu(II) complex was obtained as 119.5 and $139.6 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, respectively, which suggests these complexes have electrolytic nature in a 1 : 2 ratio. This was in line with the chloride test [29, 30].

3.8. Electronic Spectra of the Ligand and Its Complexes.

Electronic spectra were used to assign the stereochemistry of a metal complex [31]. The UV-Vis spectra of the ligand and the complexes were recorded in DMSO in the range of 200–800 nm at room temperature as summarized in Table 4. The electronic spectra of the ligand (Figure 7) showed two strong bands at 260 nm (38461 cm^{-1}) and at 291 nm (34364 cm^{-1}). The band at 260 nm (38461 cm^{-1}) is assigned to $\pi \rightarrow \pi^*$ transition. The band observed at 291 nm (34364 cm^{-1}) is attributed to $n \rightarrow \pi^*$ transitions of the C=N chromophores [32]. The electronic spectrum of the Ni(II) complex (Figure 8) shows four major spectral bands at 260 nm (38461 cm^{-1}), 302 nm (33112 cm^{-1}), 391 nm (25575 cm^{-1}), and at 495 nm (20202 cm^{-1}). The spectrum exhibits a band at 302 nm (33112 cm^{-1}), which is assigned to a charge transfer band [33]. From the expected three d-d transitions, two of them appeared in this complex. The spectra of Ni(II) complex show the transition bands at 391 nm (25575 cm^{-1}) and 495 nm (20202 cm^{-1}) are assignable to the transitions ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F), respectively, indicating an octahedral geometry [34, 35]. The third transition [${}^3A_{2g} \rightarrow {}^3T_{2g}$ (F)] band often tails into the ultraviolet region, supposed to be covered by charge transition spectral bands. The Cu(II) complex displayed three electronic spectral bands at 260 nm (38461 cm^{-1}), 300 nm (33333 cm^{-1}), 342 nm (29240 cm^{-1}), and at 445 nm (22472 cm^{-1}) (Figure 9). The band observed at 300 nm (33333 cm^{-1}) assigned to be charge transfer, while the shoulder peak at 342 nm (29240 cm^{-1}) arise from distortion. The Cu(II) complex also shows a band at 445 nm (22472 cm^{-1}) attributed to ${}^2E_g \rightarrow {}^2T_{2g}$ transition, so distorted octahedral geometry was suggested to the Cu(II) complex [28, 36].

3.9. Proposed Structure of the Complexes. Based upon the results of spectral and analytical analysis as well as molar conductivity, a general structure is proposed for both complexes (Figure 10).

3.10. Antibacterial Activity Test. The newly synthesized ligand and its complexes (Ni^{2+} and Cu^{2+}) were screened against four bacterial strains, namely, *Staphylococcus aureus* and *Bacillus subtilis* (Gram positive) and *Escherichia coli* and *Pseudomonas aeruginosa* (Gram negative) through disc diffusion method [37]. The antibacterial activities of the compounds were described measuring their inhibition zone (mm) in comparison with gentamicin (standard drugs).

The results of antibacterial activity of the ligand and its complexes are found to be comparable with standard drugs, presented in Table 5 and Figures 11(a)–11(d). The inhibition zone of metal complexes is higher than that of the ligand

TABLE 4: Electronic spectra of the complexes.

Compound	Wave number (cm^{-1})	Transition	Suggested geometry
Ligand (L)	38461	$\pi \rightarrow \pi^*$	—
	34364	$n \rightarrow \pi^*$	—
[NiC ₂₆ H ₂₀ N ₈ O ₄] Cl ₂	38461	Intraligand	Oh
	33112	CT	
	25575	${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P)	
	20202	${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F)	
[CuC ₂₆ H ₂₀ N ₈ O ₄] Cl ₂	38461	Intraligand	Distorted Oh
	33333	CT	
	22472	${}^2E_g \rightarrow {}^2T_{2g}$	

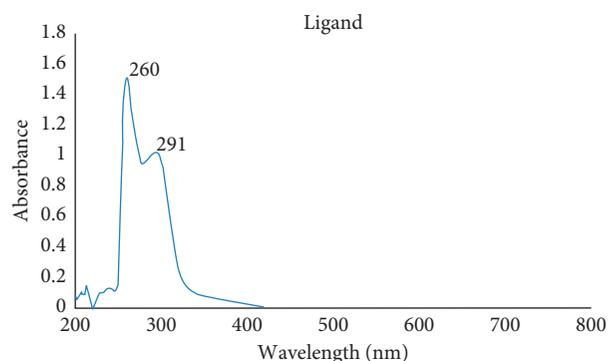


FIGURE 7: UV-visible spectrum of the ligand.

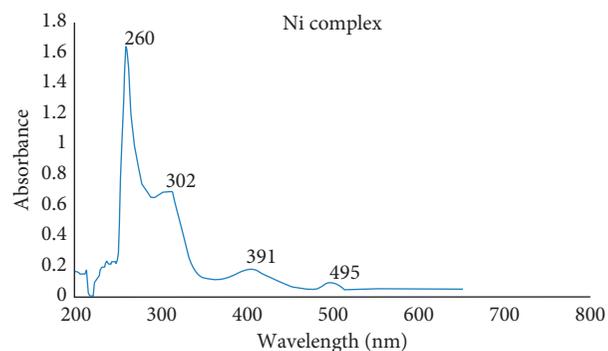


FIGURE 8: UV-visible spectrum of Ni(II) complex.

which indicates that complexes exhibit higher antibacterial activities than the free ligand due to chelation which enhance lipophilicity and so favors permeation into the bacterial membrane to cause the death of the organisms [38]. The Ni(II) complex shows higher activity than gentamicin against *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas aeruginosa*, while the Cu(II) complex is more active than the Ni(II) complex against *Bacillus subtilis*. This evidence implies the Ni(II) complex can be a potential candidate drug towards *Staphylococcus aureus*, *Escherichia coli*, and *Pseudomonas aeruginosa*.

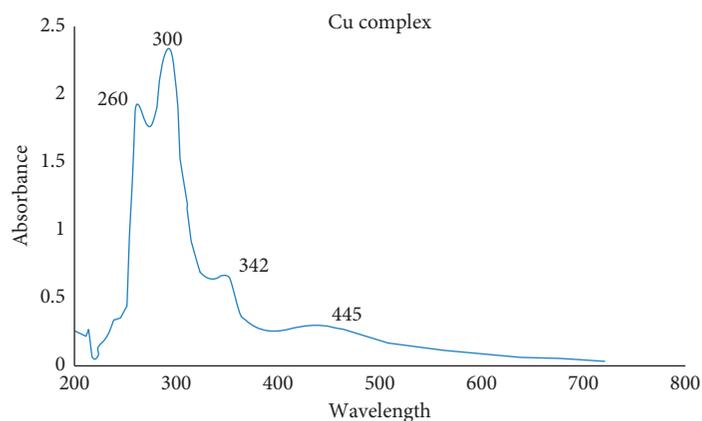


FIGURE 9: UV-visible spectrum of Cu(II) complex.

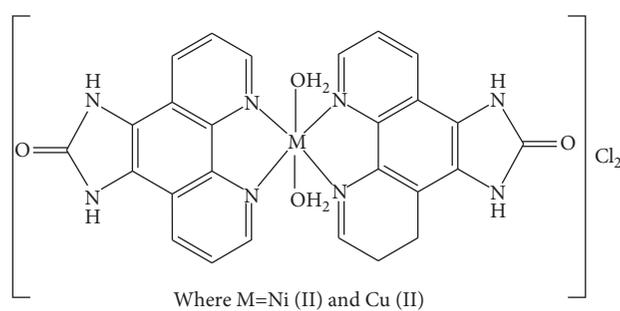


FIGURE 10: The proposed structure of complexes.

TABLE 5: Inhibition zones of the as-synthesized compounds against four bacterial strains.

Compound	Zone of inhibition in diameter (mm)			
	<i>S. aureus</i>	<i>B. subtilis</i>	<i>E. coli</i>	<i>P. aeruginosa</i>
Ligand (L)	11	15	16	12
Ni(II) complex	21	22	23	24
Cu(II) complex	17	24	19	16
Gentamicin	20	24	21	22
DMSO	—	—	—	—

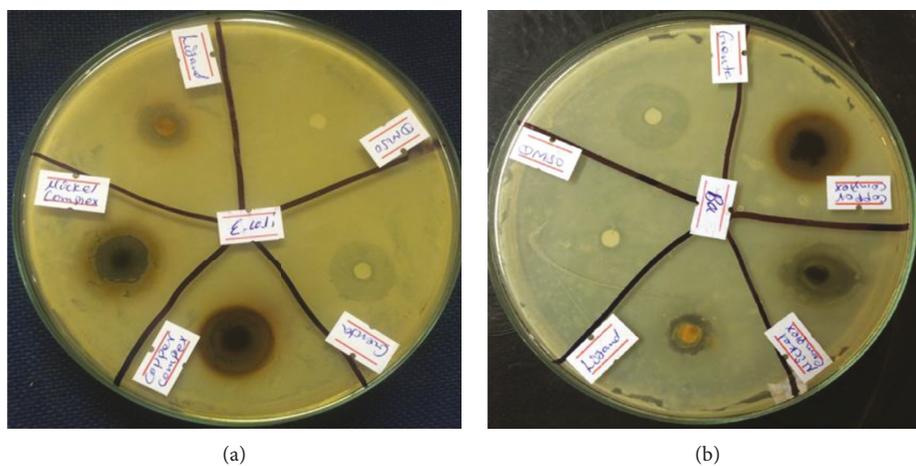


FIGURE 11: Continued.

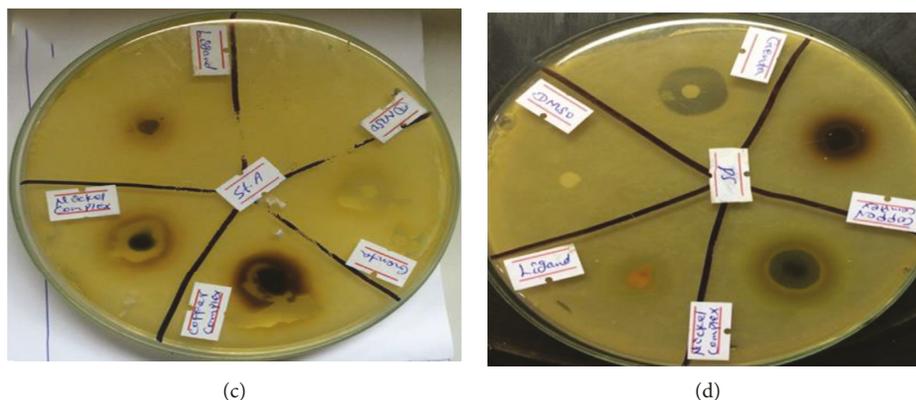


FIGURE 11: Inhibition of *Escherichia coli* (a), *Bacillus subtilis* (b), *Staphylococcus aureus* (c), and *P. aeruginosa* (d).

4. Conclusions

The ligand, 1H-imidazo [5, 6-f] [1,10] phenanthroline-2(3H)-thione (1,10-PDTU) was synthesized from 1,10-phenanthroline-5, 6-dione (PD) and thiourea (TU), and its complexes were synthesized by reacting the ligand with metal chlorides. The as-synthesized compounds were characterized by spectro-analytical techniques which suggested bidentate ligand. The result of conductivity measurement reveals electrolytic nature of both complexes. The analytical data showed that stoichiometry of both complexes to be 1:2 metals to ligand ratio and formulated as $[\text{NiC}_{26}\text{H}_{20}\text{N}_8\text{O}_4]\text{Cl}_2$ and $[\text{CuC}_{26}\text{H}_{20}\text{N}_8\text{O}_4]\text{Cl}_2$. On the basis of the combined analytical results, distorted octahedral geometry of Cu(II) and octahedral geometry of Ni(II) complexes were achieved. Antibacterial activities of the prepared ligand and complexes have also been studied. From the comparative study, both metal complexes showed significantly enhanced antibacterial activity against selected bacterial strains in comparison to the free ligand.

Data Availability

Previously reported figures and reaction schemes were used to support this study and are cited at relevant places within the text as references [7, 17, 18].

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Radiet Anbessie Tirkeso and Tilahun Wubalem Tsega contributed equally during lab work.

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