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Synthesis, Characterization, and Antioxidant Studies of Novel Cu(II) and Ni(II) Homo Binuclear Complexes with N,N'-bis(Benzamidothiocarbonyl) Hydrazine Ligand Derivatives

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***Abstract*—This study presents the synthesis, spectral characterization, and antioxidant evaluation of Cu(II) and Ni(II) homo binuclear complexes derived from three bis(thiourea) hydrazine ligands: N, N′-bis(benzamidothiocarbonyl)hydrazine (L^1), N, N′-bis(*o*-chlorobenzamidothiocarbonyl)-hydrazine (L^2), and N, N′-bis(*p*-methylbenzamidothiocarbonyl)hydrazine (L^3). The ligands were synthesized through condensation reactions and characterized using Carbon, Hydrogen, Nitrogen, and Sulfur elemental analysis, fourier transform infrared spectroscopy, Ultraviolet-Visible, and ^{1}H-NMR and ^{13}C-NMR nuclear magnetic resonance spectroscopy. The metal complexes were prepared in a 2:1 metal-to-ligand molar ratio and characterized by melting point determination, magnetic susceptibility, molar conductivity, and spectral techniques. IR data confirmed coordination through the thiocarbonyl sulfur and amide oxygen atoms, forming neutral bidentate complexes. Magnetic moment values and electronic spectra were consistent with square planar geometries for both Cu(II) and Ni(II) complexes. Molar conductance measurements indicated non-electrolytic behavior in N, N-dimethylformamide. Antioxidant activity was assessed through the 2,2-diphenyl-1-picrylhydrazyl radical scavenging assay, revealing that the metal complexes exhibited enhanced radical scavenging capacity compared to the free ligands, likely due to increased delocalization and metal ion involvement in electron transfer. These findings highlight the potential of bis(thiourea)hydrazine-based metal complexes as antioxidant agents.**

***Index Terms* – Antioxidant, Bis(thiourea)hydrazine ligands, Cu(II) and Ni(II) coordination, Homo binuclear complexes, Square planar geometry.**

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I. Introduction

Transition metal complexes, including nickel and copper, along with nitrogen-, sulfur-, and oxygen-containing compounds, exhibit significant biological activities. Thioureas act as ligands in these important compounds (Sun, et al., 2006a; Arslan, et al., 2009; Binzet, et al., 2007). Several procedures have yielded thiourea derivatives (Lee, et al., 2015; Thiam, et al., 2008; Kang, Cho and Jeon, 2012; Dong, et al., 2008; Odame, et al., 2020), which Neucki initially created (Nencki, 1873). Acyl/aroyl thioureas represent a versatile category of organic compounds that can be synthesized through various synthetic methodologies (Saeed, Flörke and Erben, 2014). However, the predominant method for their synthesis is Douglas Dain's approach (Douglass and Dains, 1934), which involves the reaction of diverse amines with *in situ*-generated acyl isothiocyanates in dry acetone or acetonitrile at a specified temperature (Mukerjee and Ashare, 1991). Thiourea derivatives have extensive applications in health, agriculture, and analytical chemistry. These molecules exhibit a broad spectrum of biological processes, including antioxidant (Ariffin, et al., 2014), antibacterial (Zhong, et al., 2008), herbicidal, analgesic (Xiao, Liu and Li, 2009; Hu, et al., 2006), antiviral (Sun, et al., 2010; Sun, et al., 2006b), plant growth regulating (Ranise, et al., 1991), antihyperlipidemic (Vig, et al., 1998), antiarrhythmic (Claridge, et al., 2008), fungicidal (Wang, Qin and Huang, 2006; Ke and Xue, 2006), local anesthesia (Manjula, et al., 2009), and antiaggregating (Ranise, et al., 2003). Numerous researchers have reported modifications on the N side of thiourea, in which certain N, N'-disubstituted thiourea compounds have shown effective performance as inhibitors of HIV binding (Sivan, Vangala and Manga, 2013). Several dithiourea derivatives have demonstrated cytotoxic effects on various cancer cell lines (Zhang, et al., 2001).

Thiourea derivatives are also utilized as potentiometric sensors due to the presence of C=S and amine groups, which readily form complexes with metal ions (Jumal, et al., 2012).

N-benzoylthioureas serve as versatile bidentate ligands within the realm of coordination chemistry, primarily coordinating with metal ions through O and S interactions. Symmetrical quadridentate bis(N-acyl/aroyl-thioureas) demonstrate the ability to chelate two metal ions because of the functions of both N-acyl and aroylthioureas. These organic molecules, referred to as bipodal derivatives, are also suitable for the synthesis of multinuclear complexes featuring various architectures dictated by their design. Metal ions, such as Cu^{II} and Ni^{II} form stable complexes with bis(N-aroylthioureas) (Jumal, et al., 2012; Rodenstein, et al., 2008; Hallale, Bourne and Koch, 2005). Stable derivatives featuring at least two potential donor atoms, specifically oxygen and sulfur, exhibit notably complex coordination, with the chemistry occurring at the active sites of various metallobiomolecules (Zhang, et al., 2004; Arslan, et al., 2009). Certain dithiourea derivatives show stability and possess a minimum of two potential donor atoms, particularly oxygen and sulfur. These have been observed to demonstrate remarkably specific coordination chemistry at their active sites, especially with transition metals (Hollmann, et al., 2017).

This study aims to uncover, for the 1st time, the coordination chemistry of bis(aroylthiourea)hydrazine derivatives with Cu(II) and Ni(II) ions, resulting in the formation of novel homo-binuclear metal complexes. Given the absence of prior research on this ligand class in transition metal complexation, this work seeks to tackle the synthetic and solubility challenges associated with these ligands by employing appropriate reaction conditions and solvent systems. A comprehensive characterization of the synthesized ligands and their complexes is conducted using Carbon, Hydrogen, Nitrogen, and Sulfur (CHNS) elemental analysis, fourier transform infrared spectroscopy (FT-IR), ^{1}H and ^{13}C NMR, Ultraviolet-Visible (UV-Vis) spectroscopy, and magnetic susceptibility measurements. Furthermore, the antioxidant activity of both the free ligands and their metal complexes is assessed using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging assay to evaluate their potential as bioactive agents. This investigation aims to broaden the application of hydrazine-based ligands in coordination chemistry and establish a foundation for future studies in biological and materials applications.

II. Materials and Methods

A. Materials

The compounds included benzoyl chloride, 2-chlorobenzoyl chloride, 4-methylbenzoyl chloride, and ethanol, which were procured from Shanghai Macklin. Nickel(II) chloride anhydrous and copper(II) chloride anhydrous were purchased from 3A Materials. Methanol and dichloromethane (DCM) from Biochem. Tetrahydrofuran (THF) (lab-scan). DPPH (SISCO). Ammonium thiocyanate (Merck). Acetone, N, N-dimethylformamide (DMF), and hydrazine monohydrate (Scharlau). Deionized water (GAMBRO CWP 800 SYSTEM). All chemicals were purchased from commercial suppliers and were of analytical (reagent) grade; they were used without further purification.

B. Characterization Techniques

FT-IR analysis was performed using a Shimadzu ATR-FTIR spectrometer (single bounce diamond ATR) at a resolution of cm^{-1}. UV-Vis analysis was performed in DMF using a UV-6100 EMCLAB double-beam spectrophotometer in the 200-1000 nm range. The magnetic susceptibility of the samples was measured with a Sherwood Scientific magnetic susceptibility balance at 296.15 K. Conductivity of all 10^{-3} M metal complexes was measured by a TRANAS INSTRUMENTS BC3020 Professional Benchtop Conductivity Meter in DMF solution at 296.15 K. Melting points of the compounds were determined in one open-end glass capillary tube using an AELAB Colorful Touch Screen Melting Point device DMP-800. ^{1}H-NMR and ^{13}C-NMR spectra were recorded using a Bruker Analytic 300 MHz spectrometer at room temperature in DMSO-d^6, concerning tetramethylsilane (TMS) as an internal standard. The C, H, and N analyses were performed using a CHNS Thermo Fisher Eager 300 Analyzer.

III. Synthesis of Ligands and Their Complexes

A. General Procedure for Synthesis of Ligands (L^1–L^3)

A solution of substituted benzoyl isothiocyanate **(2)** (10 mmol) was prepared by reacting substituted benzoyl chloride **(1)** with ammonium thiocyanate in dry acetone under reflux at 55°C for 1 h. After filtration, hydrazine monohydrate (5 mmol) was added to the filtrate, and the mixture was refluxed for an additional 3 h. The mother liquor was allowed to stand overnight in a fume hood. The precipitate was then filtered and washed several times with DCM and a 1:1 mixture of ethanol and deionized water, after which it was dried in a vacuum desiccator to obtain the target compound N, N'-bis(benzamidothiocarbonyl)hydrazine (L^1) **(3)** in good to excellent yields. For further purification, the product was recrystallized from a THF/water (8:2) solution. The same procedure was repeated for ligands L^2 and L^3.

N, N'-bis(benzamidothiocarbonyl)hydrazine, L^1

Yield 70%; white crystal; mass: 358.43; m.p. 340°C; FT-IR (cm^{-1}): ν(N-H) 3222, ν(C=O) 1672, ν(C=S) 1269; UV-vis. Spectrum, λ_{max} nm, (εM, M^{-1} cm^{-1}): 231(3230), 359(2718); ^{1}H NMR (300 MHz, DMSO) δ 14.28 (s, 1H), 12.20 (s, 1H), 8.08–7.98 (m, 2H), 7.77–7.63 (m, 1H), 7.56 (dd, J = 8.3, 6.9 Hz, 2H). ^{13}C NMR (75 MHz, DMSO) δ 172.00, 168.89, 133.83, 132.04, 129.36, 128.97. Anal. Calcd. for $C_{16}H_{14}N_4O_2S_2$: C, 53.62; H, 3.94; N, 15.63; S, 17.89. Found: C, 50.49; H, 3.49; N, 14.61; S, 18.76.

N, N'-bis(o-chlorobenzamidothiocarbonyl)hydrazine, L^2

Yield 73%; white crystal; mass: 427.32; m.p. 291°C; FT-IR (cm^{-1}): ν(N-H) 3229, ν(C=O) 1682, ν(C=S) 1294; UV-vis. Spectrum, λ_{max} nm, (εM, M^{-1} cm^{-1}): 234(3093), 345(2565); ^{1}H NMR (300 MHz, DMSO) δ 13.97 (s, 1H), 12.60 (s, 1H), 7.76–7.65 (m, 1H), 7.65–7.54 (m, 2H), 7.49 (ddd, J = 7.4, 6.3, 2.3 Hz, 1H). ^{13}C NMR (75 MHz, DMSO) δ 171.44, 168.22,

134.17, 132.86, 130.47, 130.10, 129.95, 127.67. Anal. Calcd. For $C_{16}H_{12}N_4O_2S_2Cl_2$: C, 44.97; H, 2.83; N, 13.11; S, 15.01. Found: C, 43.34; H, 2.46; N, 12.88; S, 15.34.

N, N'-bis(p-methylbenzamidothiocarbonyl)hydrazine, L^3

Yield 75%; white crystal; mass: 386.49; m.p. 381°C; FT-IR (cm^{-1}): ν(N-H) 3213, ν(C=O) 1672, ν(C=S) 1295; UV-vis. Spectrum, λ_{max} nm, (εM, M^{-1} cm^{-1}): 232(3125), 353(2609); ^{1}H NMR (300 MHz, DMSO) δ 14.28 (s, 1H), 12.08 (s, 1H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 2.40 (s, 5H). Anal. Calcd. For $C_{18}H_{18}N_4O_2S_2$: C, 55.94; H, 4.69; N, 14.50; S, 16.59. Found: C, 54.67; H, 4.23; N, 14.24; S, 15.44.

B. General Procedure for Synthesis of Cu(II) Complexes

A solution of $CuCl_2$ (2 mmol) in deionized water was added to a solution of bis(aroylthiourea)hydrazine ligands (1 mmol) in THF. The mixture was refluxed for 4 h at 40°C. The solid product formed was filtered, washed with THF and diethyl ether to remove unreacted bis(aroylthiourea)hydrazine ligands, and dried under a vacuum.

(N, N'-bis(benzamidothiocarbonyl)hydrazine)copper(II) chloride complex, $[Cu_2(L^1)Cl_4]$, (C^1)

Yield 86%; dark green solid; mass: 627.33; m.p. >400°C; FT-IR (cm^{-1}): ν(N-H) 3421 and 3220, ν(C=O) 1630, ν(C=S) 1279; UV-vis. spectrum, λmax nm, (εM, $M^{-1}cm^{-1}$): 233(3201), 382(2890), 644(285); Anal. Calcd. for $C_{16}H_{14}Cl_4Cu_2N_4O_2S_2$: C, 30.63; H, 2.25; N, 8.93; S, 10.22. Found: C, 30.12; H, 2.01; N, 8.45; S, 9.82.

(N, N'-bis(o-chlorobenzamidothiocarbonyl)hydrazine) copper(II) chloride complex, $[Cu_2(L^2)Cl_4]$, (C^2)

Yield 87%; olive green solid; mass: 696.21; m.p. >400°C; FT-IR (cm^{-1}): ν(N-H) 3191, ν(C=O) 1651, ν(C=S) 1317; UV-vis. spectrum, λmax nm, (εM, M^{-1} cm^{-1}): 233(3195), 385(2926), 623(330); Anal. Calcd. for $C_{16}H_{12}Cl_6Cu_2N_4O_2S_2$: C, 27.60; H, 1.74; N, 8.05; S, 9.21. Found: C, 26.82; H, 1.54; N, 7.89; S, 9.01.

(N,N'-bis(p-methylbenzamidothiocarbonyl)hydrazine) copper(II)chloride complex, $[Cu_2(L^3)Cl_4]$, (C^3)

Yield 89%; deep green solid; mass: 655.38; m.p. >400°C; FT-IR (cm^{-1}): ν(N-H) 3173, ν(C=O) 1630, ν(C=S) 1300; UV-vis. spectrum, λmax nm, (εM, $M^{-1}cm^{-1}$): 233(2155), 380(2880), 658(301); Anal. Calcd. for $C_{18}H_{18}Cl_4Cu_2N_4O_2S_2$: C, 32.99; H, 2.77; N, 8.55; S, 9.78. Found: C, 32.12; H, 2.56; N, 8.32; S, 9.58.

C. General Procedure for Synthesis of Ni(II) Complexes

A solution of $NiCl_2$ (2 mmol) in methanol was added to a solution of bis(aroylthiourea)hydrazine ligands (1 mmol) in THF. The mixture was refluxed for 4 hs at 50°C. The solid product formed was filtered, washed with THF and diethyl ether to remove unreacted bis(aroylthiourea)hydrazine ligands, and dried under a vacuum.

(N, N'-bis(benzamidothiocarbonyl)hydrazine) nickel chloride complex, $[Ni_2(L^1)Cl_4]$, (C^4)

Yield 81%; yellowish-green solid; mass: 617.62; m.p. 302°C; FT-IR (cm^{-1}): ν(N-H) 3400 and 3263, ν(C=O) 1639, ν(C=S) 1298; UV-vis. spectrum, λmax nm, (εM, M^{-1} cm^{-1}): 236(3117), 358(2583), 404(2915), 588(14); Anal. Calcd. for $C_{16}H_{14}Cl_4N_4Ni_2O_2S_2$: C, 31.12; H, 2.28; N, 9.07; S, 10.38. Found: C, 30.87; H, 2.08; N, 8.91; S, 9.65.

(N,N'-bis(o-chlorobenzamidothiocarbonyl)hydrazine)nickel chloride complex, $[Ni_2(L^2)Cl_4]$, (C^5)

Yield 84%; olive green solid; mass: 686.50; m.p. 250°C; FT-IR (cm^{-1}): ν(N-H) 3212, ν(C=O) 1646, ν(C=S) 1272; UV-vis. spectrum, λmax nm, (εM, M^{-1} cm^{-1}): 237(3132), 359(2573), 406(2953), 586(31); Anal. Calcd. for $C_{16}H_{12}Cl_6N_4Ni_2O_2S_2$: C, 27.99; H, 1.76; N, 8.16; S, 9.34. Found: C, 27.12; H, 1.65; N, 7.98; S, 9.12.

(N,N'-bis(p-methylbenzamidothiocarbonyl)hydrazine)nickel chloride complex, $[Ni_2(L^3)Cl_4]$, (C^6)

Yield 85%; bright green solid; mass: 645.67; m.p. 353°C; FT-IR (cm^{-1}): ν(N-H) 3412 and 3219, ν(C=O) 1616, ν(C=S) 1279; UV-vis. spectrum, λmax nm, (εM, M^{-1} cm^{-1}): 238(3118), 358(2617), 408(3001), 586(21); Anal. Calcd. for $C_{18}H_{18}Cl_4N_4Ni_2O_2S_2$: C, 33.48; H, 2.81; N, 8.68; S, 9.93. Found: C, 32.85; H, 2.65; N, 8.48; S, 9.78.

IV. Results and Discussion

A. General Comments

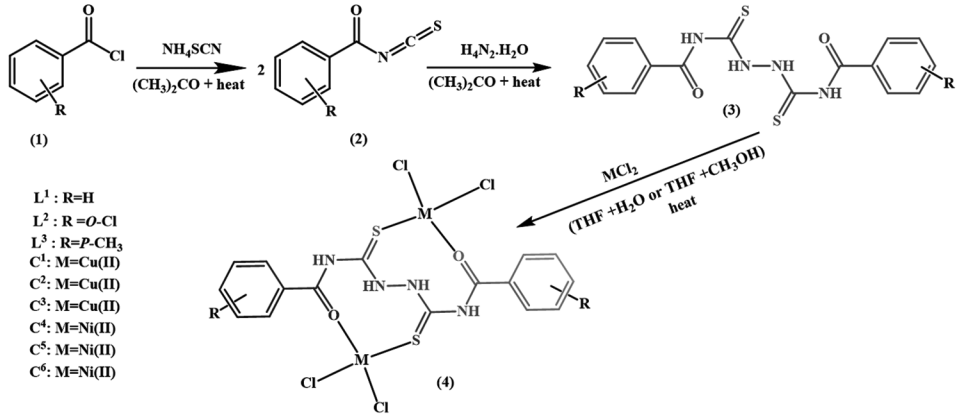
The synthesis pathway for the synthesized compounds, bis(aroylthiourea)hydrazine ligands (L^1–L^3), is shown and detailed in Scheme 1, and their structure is presented in Fig. 1, according to the literature with some modification (Firdausiah, Hasbullah and Yamin, 2018). The synthesis pathways and proposed structure for Cu(II) and Ni(II) complexes **(4)** are presented in Scheme 1. The synthesis of bis(aroylthiourea) hydrazine ligands (L^1–L^3) was conducted by a two-step reaction process. The initial step involved the nucleophilic replacement of a chlorine atom **(1)** with a thiocyanate ion, forming the isothiocyanate molecule **(2)**. The following step was the nucleophilic addition of hydrazine nitrogen to the carbon atom of isothiocyanate, resulting in the formation of bis(aroylthiourea)hydrazine ligands **(3)**. The target ligands (L^1–L^3) were purified by recrystallization from a THF/water (8:2) solution and were characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR, and elemental analysis. Cu(II) and Ni(II) complexes **(4)** were prepared by adding the solution of ligands (1 mmol) to metal solutions (2 mmol). The mixture was refluxed for 4 h. Analytical and physical data of ligands and their homo-binuclear complexes are shown in Table 1. The resulting products formed were filtered, washed with THF and diethyl ether, and dried. All resulting complexes were characterized with FT-IR, conductivity measurement, elemental analysis, magnetic moment measurement, and UV-Vis.

B. ^{1}H and ^{13}C NMR spectra of ligands

The ^{1}H and ^{13}C NMR characterization for the investigated ligands (L^1–L^3) is listed in the experimental section and Figs. 2-4. They have been recorded in DMSO-d^6. ^{1}H NMR spectrum of all ligands exhibited singlet signals at 14.28–13.97 ppm and 12.6–12.08 ppm, which were assigned to the CONH and CSNH protons. The aromatic protons appear

TABLE 1: Analytical and Physical Data of Ligands and their Metal Complexes

Comp.	Molecular formula molecular weight (g/mol)	Color	Melting point °C	Elemental analysis calculated (Found)				Yield %
				%C	%H	%N	%S	
L^1	$C_{16}H_{14}N_4O_2S_2$ (358.43)	White	340	53.62 (50.49)	3.94 (3.49)	15.63 (14.61)	17.89 (18.76)	70
L^2	$C_{16}H_{12}N_4O_2S_2Cl_2$ (427.32)	white	291	44.97 (43.34)	2.83 (2.46)	13.11 (12.88)	15.01 (15.34)	73
L^3	$C_{18}H_{18}N_4O_2S_2$ (386.49)	white	381	55.94 (54.67)	4.69 (4.23)	14.50 (14.24)	16.59 (15.44)	75
C^1	$C_{16}H_{14}Cl_4Cu_2N_4O_2S_2$ (627.33) $[Cu_2(L^1)\ Cl_4]$	Dark green	>400	30.63 (30.12)	2.25 (2.01)	8.93 (8.45)	10.22 (9.82)	86
C^2	$C_{16}H_{12}Cl_6Cu_2N_4O_2S_2$ (696.21) $[Cu_2(L^2)\ Cl_4]$	Olive green	>400	27.60 (26.82)	1.74 (1.54)	8.05 (7.89)	9.21 (9.01)	87
C^3	$C_{18}H_{18}Cl_4Cu_2N_4O_2S_2$ (655.38) $[Cu_2(L^3)\ Cl_4]$	Deep green	>400	32.99 (32.12)	2.77 (2.56)	8.55 (8.32)	9.78 (9.58)	89
C^4	$C_{16}H_{14}Cl_4N_4Ni_2O_2S_2$ (617.62) $[Ni_2(L^1)\ Cl_4]$	Yellowish green	302	31.12 (30.87)	2.28 (2.08)	9.07 (8.91)	10.38 (9.65)	81
C^5	$C_{16}H_{12}Cl_6N_4Ni_2O_2S_2$ (686.50) $[Ni_2(L^2)\ Cl_4]$	Olive green	250	27.99 (27.12)	1.76 (1.65)	8.16 (7.98)	9.34 (9.12)	84
C^6	$C_{18}H_{18}Cl_4N_4Ni_2O_2S_2$ (645.67) $[Ni_2(L^3)\ Cl_4]$	Bright green	353	33.48 (32.85)	2.81 (2.65)	8.68 (8.48)	9.93 (9.78)	85



Scheme 1: Synthesis of bis(aroylthiourea)hydrazine ligands (L^1–L^3) and their Cu(II) and Ni(II) complexes.

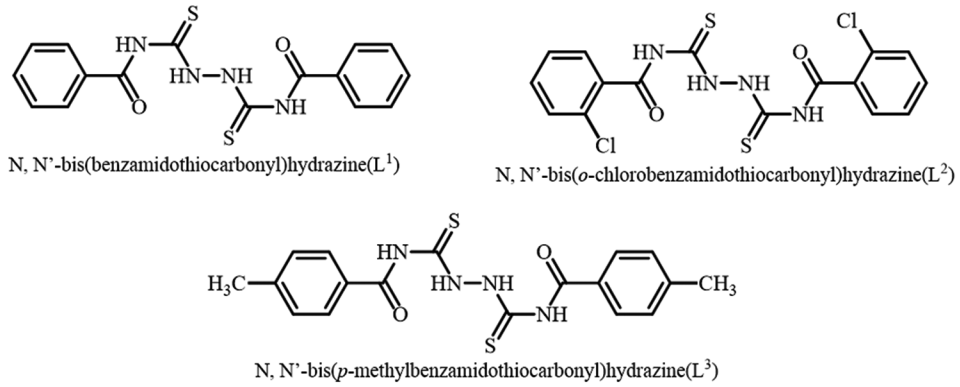


Fig. 1. Chemical structure of bis(aroylthiourea)hydrazine ligands (L^1–L^3).

for all ligands between 8.03 and 7.36 ppm, and the methyl protons of L^3 appear at 2.4 ppm. Their high chemical shift values are consistent with intramolecular hydrogen bonding and solvent interactions, which are known to deshield exchangeable protons significantly (Wilson, et al., 2010). The integration values of the CONH and CSNH protons each correspond to one proton, further supporting the molecule's symmetrical nature across the N–N bond.

This symmetry is reflected in the consistent chemical environments on both sides of the molecule. The ^{13}C NMR spectra of ligands L^1 and L^2 exhibited characteristic signals at 172.0 and 171.44 ppm, respectively, corresponding to the C=S groups, and at 168.89 and 168.22 ppm, respectively, for the C=O groups. Signals for aromatic carbons were observed in the range of 134.17–127.67 ppm. The ^{13}C NMR spectrum of ligand L^3 was not obtained due to its low solubility in DMSO solvent.

C. Infrared Spectra

The key vibrational bands of the free ligands and their corresponding copper(II) and nickel(II) complexes are shown in Fig. 5-7 and summarized in Table 2. The IR spectra of the uncoordinated ligands (L^1–L^3) display characteristic absorption bands at 3229–3213 cm^{-1} (N–H stretching), 1682 and 1672 cm^{-1} (C=O stretching), and 1269–1269 cm^{-1} (C=S stretching). Upon complexation, notable shifts in these bands are observed. In the IR spectra of the metal complexes, the C=O stretching bands appear at lower frequencies

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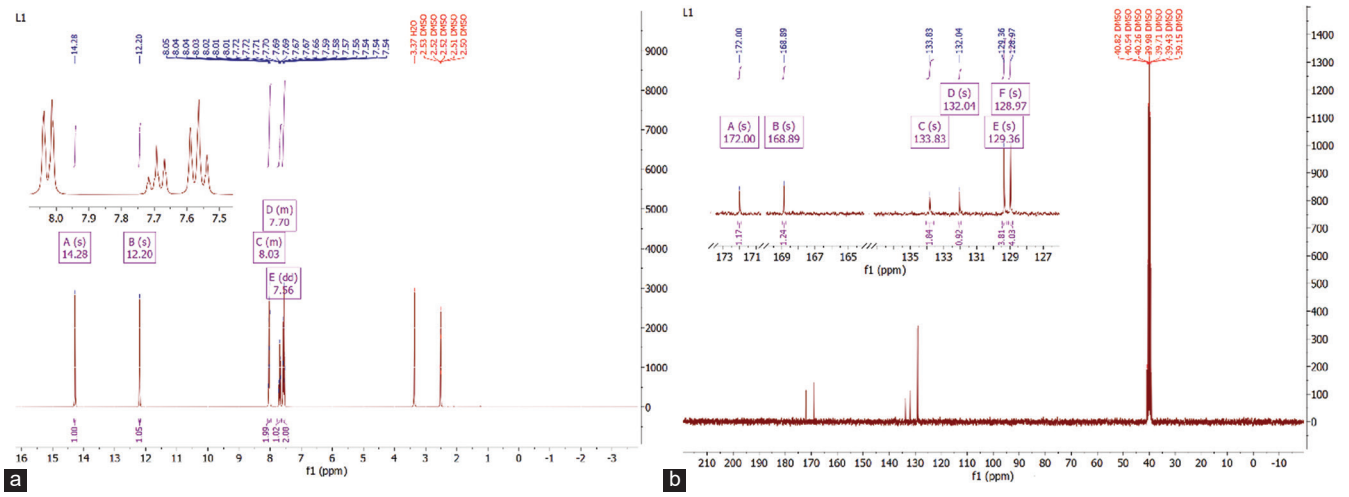

Fig. 2. (a) ^{1}H-NMR and (b) ^{13}C-NMR of N, N'-bis(benzamidothiocarbonyl)hydrazine (L^{1}).

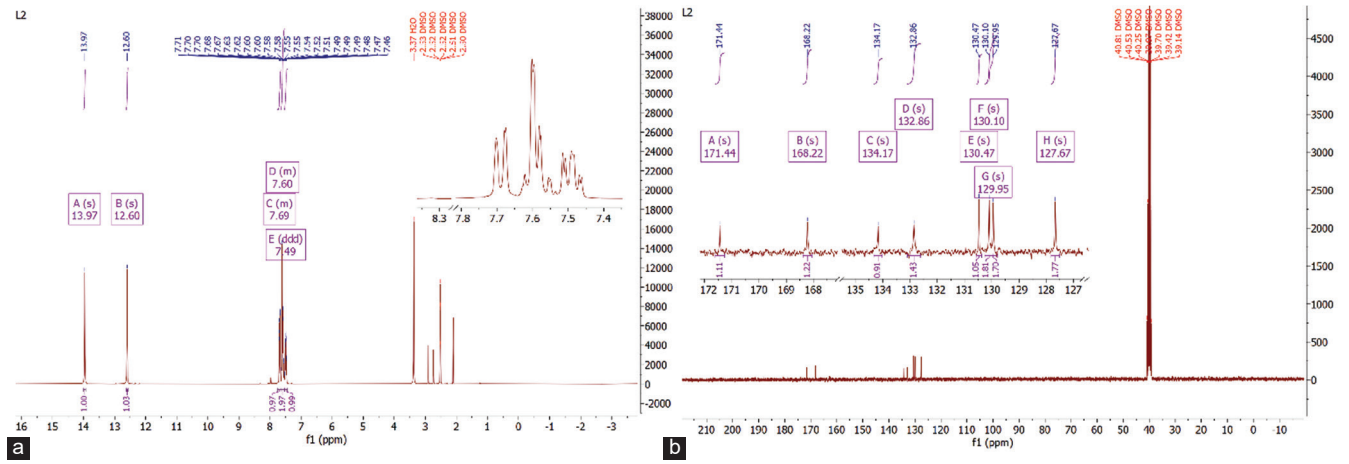

Fig. 3. (a) ^{1}H-NMR and (b) ^{13}C-NMR of N, N'-bis(*o*-chlorobenzamidothiocarbonyl)hydrazine (L^{2}).

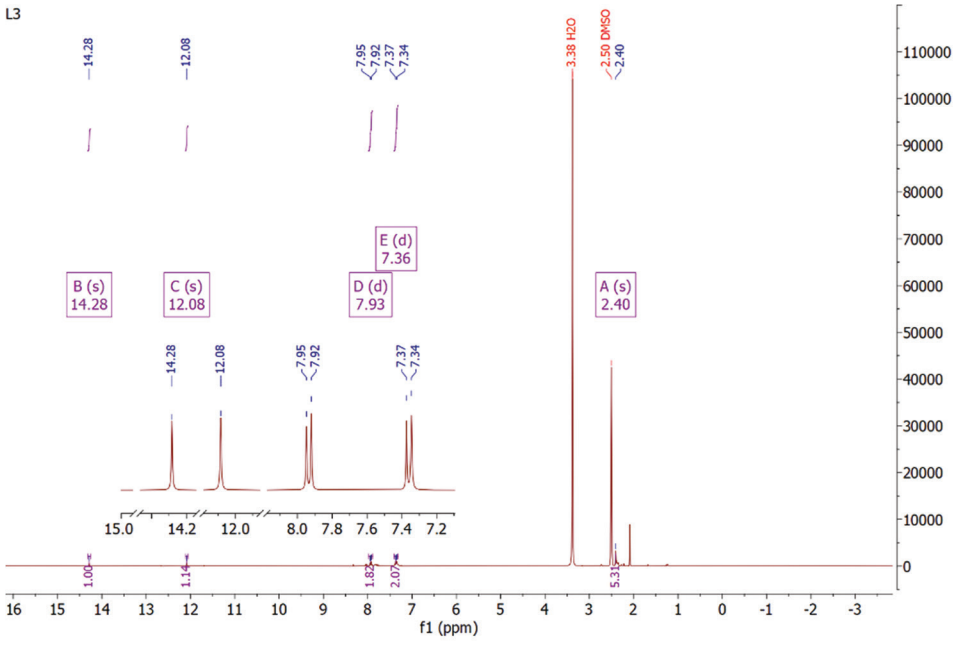

Fig. 4. ^{1}H-NMR of N, N'-bis(*p*-methylbenzamidothiocarbonyl)hydrazine (L^{3}).

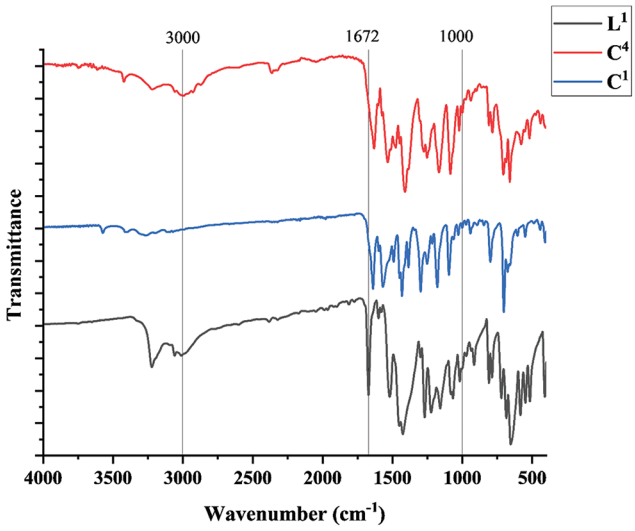

Fig. 5. Fourier transform infrared spectroscopy spectrum of L^1 and its Cu(II) and Ni(II) homo binuclear complexes.

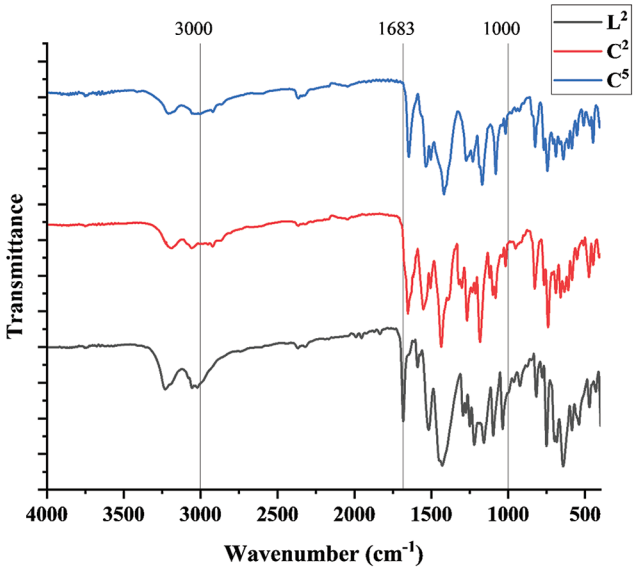

Fig. 6. Fourier transform infrared spectroscopy spectrum of L^2 and its Cu(II) and Ni(II) homo binuclear complexes.

(1651–1616 cm^{-1}), indicating a red shift relative to the free ligands. This shift is consistent with coordination through the carbonyl oxygen atom, as supported by literature, which places the amide C=O stretching frequency typically between 1630 and 1690 cm^{-1} (Coates, 2000). The observed red shift is attributed to electron donation from the oxygen lone pair to the metal center. This reduces the double bond character of the C=O group, weakens the bond, and subsequently lowers its force constant, resulting in a shift to lower wavenumbers.

Similarly, the C=S stretching vibrations are observed at 1271–1294 cm^{-1} in the free ligands and shift to higher frequencies (1317–1272 cm^{-1}) upon complexation. According to previous studies, where the structures of analogous complexes were confirmed by single-crystal X-ray diffraction, such a shift to higher frequency suggests that the C=S group

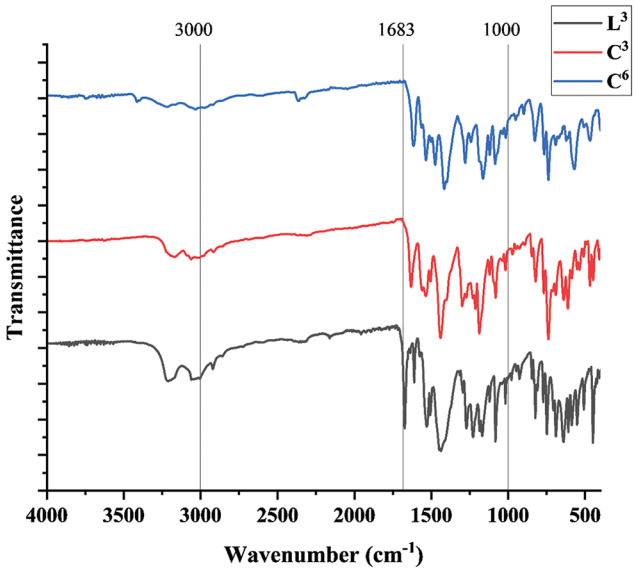

Fig. 7. Fourier transform infrared spectroscopy spectrum of L^3 and its Cu(II) and Ni(II) homo binuclear complexes.

TABLE 2: Fourier Transform Infrared Spectroscopy Characterization (ν_{MAX}, cm^{-1}) of the Free Ligands (L^1–L^3) and their Copper and Nickel Complexes

Compound	ν(N-H)	ν(C=O)	ν(C=S)
L^1	3222	1672	1269
L^2	3229	1682	1294
L^3	3213	1672	1271
$[Cu_2(L^1)Cl_4]$	3421 and 3220	1630	1279
$[Cu_2(L^2)Cl_4]$	3191	1651	1317
$[Cu_2(L^3)Cl_4]$	3173	1630	1300
$[Ni_2(L^1)Cl_4]$	3400 and 3263	1639	1298
$[Ni_2(L^2)Cl_4]$	3212	1646	1272
$[Ni_2(L^3)Cl_4]$	3413 and 3219	1616	1279

is involved in coordination with the metal. However, due to the position of the C=S band within the fingerprint region, its exact assignment may be less definitive (Teixeira, et al., 2020; Costa and Gushikem, 1984).

These spectral features provide compelling evidence that both Ni(II) and Cu(II) complexes involve bidentate coordination through the C=O and C=S donor atoms of the ligand, without N–H deprotonation. The emergence of metal-ligand vibrational modes and the shifts in donor group frequencies strongly support the formation of square planar geometries around the Ni(II) (d^8) and Cu(II) (d^9) centers – geometries that are typical and well-documented for these electronic configurations.

D. Electronic Absorption Spectra

The electronic spectra of the free ligands and their corresponding Cu(II) and Ni(II) complexes were recorded at room temperature in DMF solution. The free ligands exhibit intense absorption bands in the region of 230–363 nm, which are attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

For the Cu(II) complexes, additional absorption bands are observed in the visible region at 644 nm

(ε = 285 $M^{-1}\cdot cm^{-1}$), 623 nm (ε = 330 $M^{-1}\cdot cm^{-1}$), and 658 nm (ε = 301 $M^{-1}\cdot cm^{-1}$), which are assigned to the d-d transitions. These features, in conjunction with magnetic moment values ranging from 1.86 to 1.96 Bohr magnetons (B.M.) and molar conductivity values of 7.5–16.8 Ω^{-1} cm^2/mol, strongly support a transition of $^2B_1g \rightarrow {}^2A_2g$ or $^2B_1g \rightarrow {}^2A_2g$ for the Cu(II) complexes (Lever and Rice, 1969; Ajayeoba, Akinyele, and Oluwole, 2017). Similarly, the Ni(II) complexes display absorption bands at 404 nm (ε = 2915 M^{-1}/cm), 406 nm (ε = 2953 M^{-1}/cm), and 408 nm (ε = 3001 M^{-1}/cm), which are also attributed to MLCT transitions. In addition, weak bands observed at 588 nm (ε = 14 M^{-1}/cm), 586 nm (ε = 31 M^{-1}/cm), and 586 nm (ε = 21 $M^{-1}\cdot cm^{-1}$) are assigned to d–d transitions, specifically the $d\text{-}d^2$ transition. The presence of these transitions, along with the diamagnetic nature and low molar conductivity of the Ni(II) complexes, confirms a transition of $^1A_1g \rightarrow {}^1A_2g$ or $^1A_1g \rightarrow {}^1B_1g$ for Ni(II) complexes (Jamil, et al., 2013). Fig. 8 and Table 3.

As shown in Table 3, the magnetic moment values for the Cu(II) complexes $[Cu_2(L^1)Cl_4]$, $[Cu_2(L^2)Cl_4]$, and $[Cu_2(L^3)Cl_4]$ fall within the range of 1.86–1.96 B.M., which is consistent with the presence of one unpaired electron per Cu(II) center (d^9, S = 1/2). These values typically indicate mononuclear Cu(II) species. However, based on the 2:1 metal-to-ligand stoichiometry, elemental analysis, and the ligand's symmetrical bidentate nature, the formation of homo-binuclear complexes is strongly supported. The magnetic data suggest that the two Cu(II) centers in each complex are magnetically non-interacting, likely due to the absence of bridging ligands or significant spatial separation. In such cases, each Cu(II) ion behaves independently, and spin–spin coupling is negligible, resulting in a μ_{eff} close to that of a mononuclear center. This interpretation is further supported by the electronic spectra and IR data, which confirm square planar coordination around each Cu(II) center. Thus, the magnetic behavior aligns with structurally binuclear but magnetically isolated Cu(II) centers.

E. Evaluation of Antioxidant Activity

Scavenging Activity of DPPH Radical. The study of DPPH radical scavenging activity constitutes a common assay in antioxidant activity studies. It serves as an expedited method for evaluating the radical scavenging activity of specific chemicals (Al-Amiery, Kadhum, and Mohamad, 2012). The free radical scavenging effects of all compounds and ligands on the DPPH radical were assessed using various concentrations (100, 200, 300, and 400 μg/mL) of the test compound in 1 mL of DMF, which was then combined with 1.0 mL of a 0.4 mM methanol solution of DPPH and agitated thoroughly. Following a 30-min incubation period at room temperature, the scavenging capacity was assessed according to the literature (Ejidike and Ajibade, 2015), with some modifications. The antiradical efficacy of an antioxidant is quantified by measuring the reduction in absorbance of DPPH at 518 nm (Firdausiah, Hasbullah and Yamin, 2018). Ascorbic acid (vitamin C) is utilized as a conventional pharmaceutical agent. The absorbance diminished due to a colour shift when the antioxidant scavenged DPPH upon accepting an

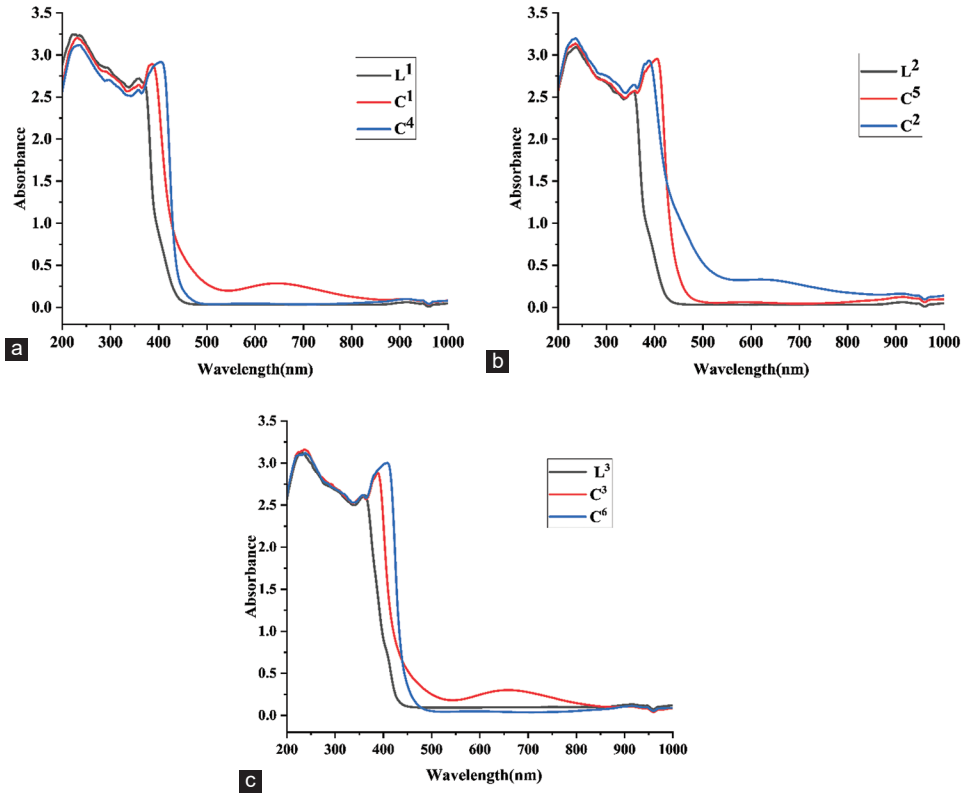

Fig. 8. (a-c) Electronic spectra of free ligands (L^1–L^3) and their homo binuclear Cu(II) and Ni(II) complexes in N, N-dimethylformamide.

TABLE 3: Electronic Spectral Assignment, Magnetic Moment, and Conductivity for Cu (II) and Ni (II) Complexes of L^1–L^3

Compounds	Band Position λ nm	Electronic transition (cm^{-1})	ε max ($dm^3 \geq mol^{-1}cm^{-1}$)	Assignment	μ_{eff} (Bohr magnetons)	Conductivity Λm (Ω^{-1} cm^2 mol^{-1})
L^1	231	43290	3230	π→π*		
	359	27855	2718	n→π*		
L^2	234	42735	3093	π→π*		
	345	28986	2565	n→π*		
L^3	232	43103	3125	π→π*		
	353	28329	2609	n→π*		
$[Cu_2(L^1)Cl_4]$	233	42918	3201	π→π*	1.86	16.8
	382	26178	2890	n→π*		
	644	15528	285	$^2B_1g \rightarrow {}^2A_1g$		
$[Cu_2(L^2)Cl_4]$	233	42918	3195	π→π*	1.96	7.5
	385	25974	2926	n→π*		
	623	16051	330	$^2B_1g \rightarrow {}^2A_1g$		
$[Cu_2(L^3)Cl_4]$	233	42918	3155	π→π*	1.9	9.2
	380	26316	2880	n→π*		
	658	15198	301	$^2B_1g \rightarrow {}^2A_1g$		
$[Ni_2(L^1)Cl_4]$	236	42373	3117	π→π*	Diamagnetic	8.37
	358	27933	2583	n→π*		
	404	24752	2915	LMCT		
	588	17007	14	$^1A_1g \rightarrow {}^1A_2g$		
$[Ni_2(L^2)Cl_4]$	237	42194	3132	π→π*	Diamagnetic	9.5
	359	27855	2573	n→π*		
	406	24631	2953	LMCT		
	586	17065	31	$^1A_1g \rightarrow {}^1A_2g$		
$[Ni_2(L^3)Cl_4]$	238	42017	3118	π→π*	Diamagnetic	12.1
	358	27933	2617	n→π*		
	408	24510	3001	LMCT		
	586	17065	21	$^1A_1g \rightarrow {}^1A_2g$		

electron or hydrogen radical from another molecule. DPPH is transformed into a non-radical molecule. All test samples were conducted with three replicates. The percentage of inhibition (%) of free radical generation from DPPH was determined using the following equation:

$$\text{DPPH scavenging ability } (\%) = \frac{\text{Abs}_{\text{Control}} - \text{Abs}_{\text{sample}}}{\text{Abs}_{\text{control}}} \times 100$$

The percentages of DPPH radical scavenging activity and half-maximal inhibitory concentration (IC_{50}) values for vitamin C, ligands, and their complexes are presented in Table 4 and illustrated in Figs. 9 and 10. Generally, compounds often show dose-dependent radical scavenging action, indicated by rising percentages of DPPH inhibition with increasing concentration. Bis(aroylthiourea)hydrazine ligands stabilized the DPPH radical by two mechanisms involving hydrogen donation and electron transfer (Sharma and Bhat, 2009; Ariffin, et al., 2014). The ligand L^3 and its corresponding metal complexes exhibited lower IC_{50} values, approaching those of ascorbic acid, indicating superior antioxidant activity. This enhanced performance may result from structural features that facilitate stabilization of radical intermediates, thereby promoting more efficient hydrogen atom or electron transfer to the DPPH radical. Such interactions increase the radical scavenging capacity of these compounds relative to other ligands and complexes (Nguyen, et al., 2013).

TABLE 4: 2,2-Diphenyl-1-Picrylhydrazyl Scavenging Activity % and IC_{50} Values of Ligands and their Complexes

µg/mL	L^1	L^2	L^3	C^1	C^2	C^3	C^4	C^5	C^6	Vitamin C
100	90.12	83.62	92.36	67.96	89.36	80.42	88.36	81.51	95.28	95.29
200	92.30	89.41	92.62	88.41	95.85	92.68	90.02	85.61	95.42	95.63
300	94.66	91.19	92.94	86.05	89.96	91.10	91.65	85.22	95.69	96.03
400	94.95	91.83	95.09	86.99	94.26	92.59	94.46	85.43	95.72	96.19
	159.84	166.05	160.10	176.30	161.65	156.88	162.81	176.42	156.88	156.34

IC_{50}: Half-maximal inhibitory concentration

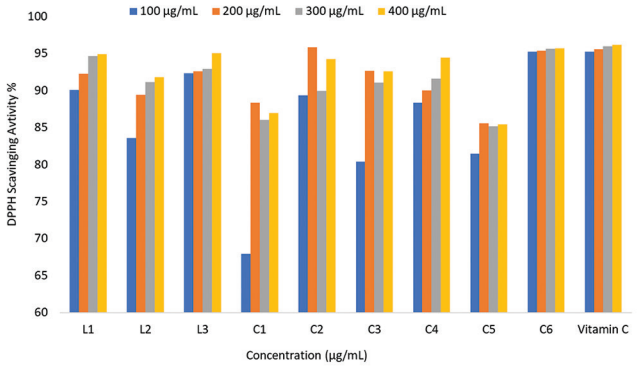

Fig. 9. 2,2-diphenyl-1-picrylhydrazyl scavenging activity of ligands L^1, L^2, and L^3 and their homo binuclear metal complexes with standard antioxidant vitamin C at different concentrations.

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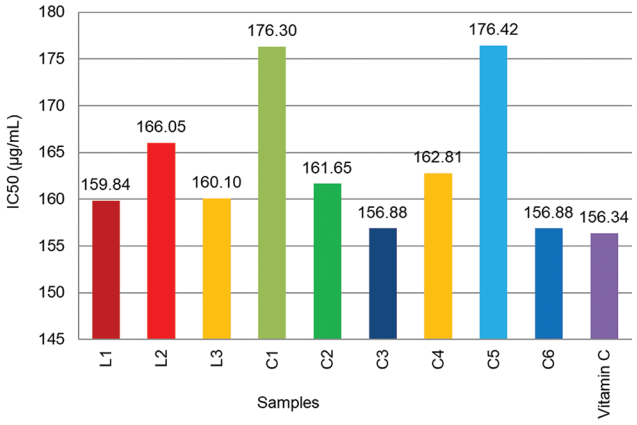

Fig. 10. Half-maximal inhibitory concentration values of ligands L^1, L^2, and L^3 and their homo binuclear metal complexes with standard antioxidant vitamin C.

V. Conclusion

The present work demonstrates the successful synthesis of bis(thiourea)hydrazine ligands and their Cu(II) and Ni(II) complexes, which were comprehensively characterized using elemental and spectral techniques. The ligands acted as neutral bidentate donors, coordinating through sulfur and oxygen atoms. The square planar geometries of the metal complexes were confirmed by magnetic susceptibility and UV-Vis spectral analysis. Molar conductance data supported their non-electrolytic nature in solution. Antioxidant studies using the DPPH assay revealed that the metal complexes exhibited improved radical scavenging activity compared to their corresponding ligands, attributed to enhanced delocalization and potential redox activity of the metal centers. These results underscore the promising role of metal coordination in modulating the biological activity of thiourea-based compounds and provide a foundation for future exploration of their therapeutic and pharmacological applications.

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