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SYNTHESIS OF DIMETHYLAMINE-PYRIDINE-BASED SCHIFF BASE COMPLEXES OF FE(II), CO(II), AND CU(II), STRUCTURAL ELUCIDATION: INVESTIGATION OF BIOLOGICAL ACTIVITIES

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ABSTRACT

This report aims to synthesize a new Schiff base ligand (L) and its Fe(II), Co(II), and Cu(II) metal complexes, analyze their structures, and evaluate their antioxidant activities. The Schiff base was prepared through a condensation reaction between 4-(dimethylamino)benzaldehyde and 6-acetyl-2-amino-4,5,6,7-tetrahydrothieno[2,3-*c*]pyridine-3-carboxamide. Subsequently, complexes of the ligand with Fe(II), Co(II), and Cu(II) were designed and synthesized. The ligand and its metal complexes were characterized using a range of physicochemical and spectroscopic techniques, including elemental analysis, magnetic susceptibility measurements, ^{1}H and ^{13}C NMR, FTIR, UV-Vis, mass spectrometry, and thermogravimetric analysis (TGA). Based on the analytical data, the proposed molecular formulas for the Fe(II), Co(II), and Cu(II) complexes are $[LFe_2(H_2O)_6Cl_3]1.5H_2O$, $[LCo_2(H_2O)_2Cl_3]1.5H_2O$, and $[LCu_2(H_2O)_2Cl_3]3H_2O$, respectively. The ligand coordinates to the metal ions through the azomethine and amine nitrogen atoms, as well as the oxygen atoms of the carbonyl group. Magnetic susceptibility and electronic spectroscopy data indicated that the Fe(II) complex adopts an octahedral geometry, while the Cu(II) and Co(II) complexes display square-planar geometries. TGA results demonstrated that all complexes have greater thermal stability than the free Schiff base ligand. Furthermore, the antioxidant activities of the synthesized compounds were evaluated using the DPPH free radical scavenging assay, the CUPRAC method for cupric ion reducing capacity, and the ABTS assay for overall antioxidant capacity. The antioxidant activities of these compounds were compared to those of standard antioxidants. The results indicated that both the ligand and its metal complexes exhibit significant antioxidant activities.

Keywords: Schiff base, Metal complex, Biological activity, DPPH, Antioxidant.

1 INTRODUCTION

Schiff bases play a key role as ligands in coordination chemistry, typically coordinating with metal ions through the azomethine nitrogen atom. These compounds are crucial for the design and development of biologically active metal complexes because of their wide range of applications, versatile coordination behavior, and structural diversity [1-3]. Modifying the substituents of Schiff bases has facilitated the synthesis of numerous novel metal complexes with diverse and intriguing properties [3-7]. Schiff base ligands containing nitrogen and oxygen donor atoms are of particular interest because of their notable biological activities [8-10]. Owing to the presence of multiple electron-donating sites, these compounds readily form coordination complexes with metal ions in various oxidation states [11-13]. Importantly, the properties of these complexes are significantly influenced by the coordination environment surrounding the central metal ions.

Recent innovations have introduced researchers to various Schiff base synthesis methods, emphasizing factors such as reaction speed, efficiency, and environmental sustainability. The versatility of Schiff bases, especially their ability to donate electrons or protons, has led to their widespread use in many fields. In medicine, they function as metal chelators with potential therapeutic applications. They also serve as catalysts to accelerate the reaction rate. Their metal-binding properties make them essential in materials science for applications in energy storage, chemosensing, biosensing, biomedical fields, nanotechnology, and the development of new compounds with specific features. Additionally, Schiff bases are also used in the dye industry to produce vibrant colors on textiles and other materials. They have also demonstrated promising activity against various pathogens and cancer cells, making them strong candidates for medicinal and pesticide use. Furthermore, their antioxidant properties enable them to stabilize free radicals by donating protons and electrons [14-17].

Antioxidants donate electrons or hydrogen atoms to neutralize reactive species. Schiff base antioxidants and their related complexes serve as electron or hydrogen donors to neutralize free radicals at reactive sites [10].

In this study, a Schiff base (L) and its corresponding metal complexes, $[LFe_2(H_2O)_6Cl_3]1.5H_2O$, $[LCo_2(H_2O)_2Cl_3]1.5H_2O$, and $[LCu_2(H_2O)_2Cl_3]3H_2O$ were successfully synthesized [18]. The structural characterization of these compounds was performed using analytical and spectroscopic techniques to confirm the geometry and coordination modes of the metal centers in the complexes. The antioxidant activities of all synthesized compounds were evaluated using DPPH, ABTS, and CUPRAC methods. The results were compared with the antioxidant activity of the free Schiff base reported in previous studies using the standard antioxidants BHT and BHA as positive controls. This study aimed to develop a biologically active Schiff base incorporating pyridine and carboxamide groups, along with its transition metal complexes, and to focus on their antioxidant potential.

2 MATERIAL AND METHODS

2.1 Physical Measurements

All chemicals and reagents used in this study were of analytical grade and employed without further purification, unless otherwise specified. FT-IR spectra were measured using a PerkinElmer FT-IR 65 spectrophotometer with KBr discs. ^{1}H and ^{13}C NMR were performed using a Bruker AV 400 MHz spectrometer. UV-Vis spectra were measured using a Shimadzu UV-1800 spectrophotometer. The elemental compositions of C, N, H, and S were determined using a Vario EL III elemental analyzer (GmbH). Thermal analysis was recorded using a Shimadzu TGA-50H instrument under a nitrogen atmosphere. The magnetic susceptibility measurements were performed at room temperature using a Sherwood Scientific model MKI Magnetic Susceptibility Balance. Mass spectrometry data were obtained using an AB Sciex 3200 QTrap mas spectrometer. Melting points (°C) were measured using a Gallen-Kamp melting point apparatus equipped with a hot stage, employing the open capillary method.

2.2 Synthesis of Ligand (L)

A solution of 6-acetyl-2-amino-4,5,6,7-tetrahydrothieno[2,3-*c*]pyridine-3-carboxamide (1.0 g, 4.2 mmol) was prepared in 15 mL of DMF. To this, a solution of 4-(dimethylamino)benzaldehyde (0.62 g, 4.2 mmol) in 15 mL DMF was added dropwise. The mixture was then heated under reflux for 24 h. The progress of the reaction was monitored using thin-layer chromatography (TLC). Upon completion, the crude product was washed with diethyl ether and purified by recrystallization from a methanol/chloroform solvent system (Figure 1).

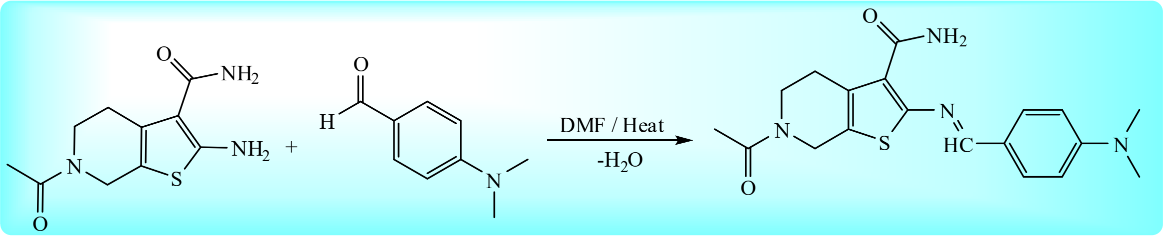


Figure 1. Schiff base ligand (L)

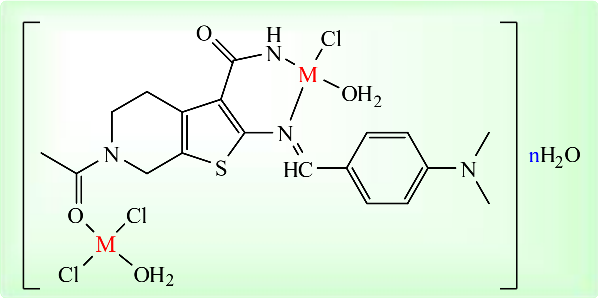
Yield (84%), Color: Dark orange; M.p.: 185 °C. Anal. Calc. for $C_{19}H_{22}N_4O_2S$ (370.29 g/mol): C, 61.62; H, 5.94; N, 15.13; S, 8.66. Found: C, 62.00; H, 5.95; N, 15.12; S, 8.69. FT-IR (ν, cm^{-1}): 3380, 3278 (-NH_2), 3005 (-CH, Ar.), 2907, 2853 (-CH, Alip.), 1653, 1638 (C=O), 1611 (HC=N), 1600, 1566, 1528, 1432 (C=C, Ar.), 1287 (C-N), 743 (C-S-C). ^{1}H-NMR (DMSO-d_6, δ, ppm): 8.27 (s, H, CH=N), 7.69-6.71 (m, 4H, CH, Ar.), 4.72 (s, 2H, NH_2), 3.68-3.19 (m, 4H, CH_2 py), 3.10 (s, 8H, CH_2 py and $N(CH_3)_2$), 2.19 (s, 3H, CH_3). ^{13}C-NMR (DMSO-d_6, δ, ppm): 169.35, 165.87 (C=O), 158.13 (CH=N), 155.81-111.69 (benzene and thiophene rings), 43.97-40.12 (py, $N(CH_3)_2$), 27.59-21.39 (CH_3). UV-Vis. (EtOH, λ_{max} (nm)): 209, 214, 223, 231, 246, 265, 300, 399.

2.3 Synthesis of the Complexes

To prepare the ligand solution, 0.60 g (1.62 mmol) Schiff base was dissolved in 15 mL of ethanol. A solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.78 g, 3.24 mmol) in 10 mL ethanol was then added dropwise to the ligand solution. The mixture was then refluxed for 4 h. Upon completion of the reaction, the mixture was decanted into a separate vessel and allowed to stand at 25 °C for 2 days. The obtained colored solid was thoroughly washed twice with diethyl ether and dried under reduced pressure. Fe(II) and Co(II) complexes were synthesized using a similar procedure. The proposed structures of the obtained metal complexes are shown in Figures 2 and 3.

Yield (85%); Color: Brown; M.p.: > 250 °C. Anal. Calc. for $C_{19}H_{31}N_4O_7SCuCl_3$ (692.74 g/mol): C, 32.94; H, 4.47; N, 8.10; S, 4.63. Found: C, 32.95; H, 5.00; N, 8.11; S, 4.64. FT-IR (ν, cm^{-1}): 3438 (OH/H_2O), 3256 (NH), 3184, 3092 (-CH, Ar.), 2998, 2907 (-CH, Alip.), 1657, 1645 $(C=O)_{br}$, 1607 (CH=N), 1573, 1519, 1494, 1431 (C=C, Ar.), 1289 (C-N), 863 (H_2O), 743 $(C\text{-}S\text{-}C)_{br}$, 580, 531 (Cu-O), 487, 470 (Cu-N). UV-Vis. (EtOH, λmax (nm)): 213, 228, 247, 257, 266, 274, 287, 297, 301, 359, 376, 387, 396, 402, 600. MS [ESI+]: *m/z* 691.74 (Calc.), 691.737 (Found) $[M\text{-}H]^-$. μ_{eff} (B.M.): 1.84.

Yield (83%), Color: Dark Brown; M.p.: > 250 °C. Anal. Calc. for $C_{19}H_{28}N_4O_{5.5}SCo_2Cl_3$ (656.50 g/mol): C, 35.08; H, 4.30; N, 8.54; S, 4.88. Found: C, 35.04; H, 4.32; N, 8.53; S, 4.90. FT-IR (ν, cm^{-1}): 3388 (OH/H_2O), 3240 (NH), 3161, 3032 (-CH, Ar.), 2956, 2910 (-CH, Alip.), 1657, 1631 $(C=O)_{br}$, 1605 (CH=N), 1590, 1554, 1520, 1459 (C=C, Ar.), 1285 (C-N), 825 (H_2O), 742 $(C\text{-}S\text{-}C)_{br}$, 590, 526, 514 (Co-O), 490, 465 (Co-N). UV-Vis. (EtOH, λmax (nm)): 224, 234, 248, 291, 348, 363, 432, 894. MS [ESI+]: *m/z* 654.50 (Calc.), 654.097 (Found) $[M\text{-}2H]^{2+}$. μ_{eff} (B.M.): 2.13.



M= Cu, Co
n= 3, 1.5

Figure 2. Proposed structure of Cu(II) and Co(II) complexes

Yield (82%); Color: Black; M.p.: > 250 °C. Anal. Calc. for $C_{19}H_{36}N_4O_{9.5}SFe_2Cl_3$ (722.39 g/mol): C, 31.58; H, 4.98; N, 7.76; S, 4.44. Found: C, 32.00; H, 5.00; N, 7.74; S, 4.45. FT-IR (ν, cm^{-1}): 3429 (OH/H_2O), 3259 (NH), 3187, 3089 (-CH, Ar.), 2956, 2925 (-CH, Alip.), 1670, 1647 $(C{=}O)_{br}$, 1607 (CH=N), 1573, 1522, 1495 (C=C, Ar.), 1289 (C-N), 823 (H_2O), 743 $(C\text{-}S\text{-}C)_{br}$, 578, 540, 518 (Fe-O), 495, 468 (Fe-N). UV-Vis. (EtOH, λmax (nm)): 221, 231, 244, 253, 354, 361, 372, 575, 606. MS [ESI+]: *m/z* 720.39 (Calc.), 720.238 (Found) $[M\text{-}2H]^+$. μ_{eff} (B.M.): 4.96.

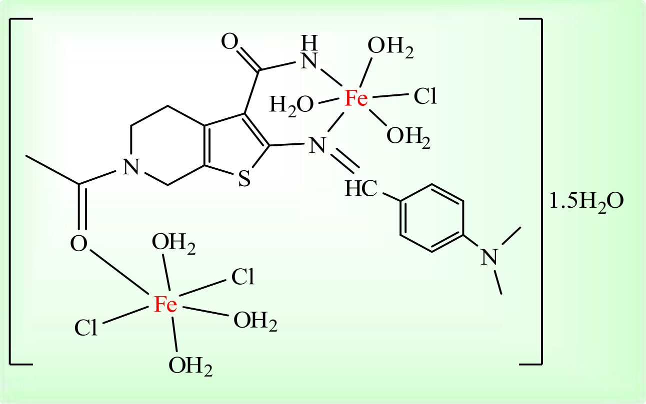


Figure 3. Structure of Fe(II) complex

3 RESULT AND DISCUSSION

3.1 Chemistry

In this study, a novel ligand (L) and its Fe(II), Co(II), and Cu(II) complexes were prepared and characterized. Analytical and spectroscopic data for all the synthesized compounds are provided in the Supplementary Materials. Subsequently, the antioxidant properties of these compounds were assessed.

The FT-IR spectra of the Schiff base ligand exhibited peaks at 3380 and 3278 cm^{-1}, attributed to the NH_2 group, while peaks at 1653 cm^{-1} and 1638 cm^{-1} were assigned to the carbonyl group (C=O). The peak at 1611 cm^{-1} was attributed to the azomethine group (HC=N), and the peak at 1287 cm^{-1} was ascribed to the $N(CH_3)_2$ group. The band observed at 743 cm^{-1} corresponds to the C-S-C bond of the thiophene ring. In the ^{1}H NMR spectra, the singlet at 8.27 ppm was ascribed to the HC=N proton, while the peaks between 7.69-6.71 ppm correspond to aromatic protons. The singlet at 4.72 ppm was attributed to the NH_2 protons, and the singlet at 3.10 ppm corresponded to the $N(CH_3)_2$ protons [19-21]. The ^{13}C NMR spectra showed peaks at 169.35 and 165.87 ppm corresponding to the carbonyl carbons, a peak at 158.13 ppm for the azomethine carbon, peaks between 155.81 and 111.69 ppm assigned to carbons of the benzene and thiophene rings, and peaks between 43.97 and 21.39 ppm for carbons in the pyridine ring and other aliphatic methyl groups [20]. The appearance of a new azomethine peak in the FT-IR spectra and the shift of one of the NH_2 peaks to a lower wavenumber compared to the starting material, and the presence of the azomethine and NH_2 proton peaks in the NMR spectra confirmed the formation of the ligand.

Comparison of the FT-IR spectra of the ligand and its metal complexes revealed that the nitrogen atoms in the CH=N and NH_2 groups, as well as the oxygen atom in the C=O group, coordinate with the metal ions. The azomethine peak at 1611 cm^{-1} in the Schiff base shifted to 1607 cm^{-1} in both the Fe(II) and Cu(II) complexes and to 1605 cm^{-1} in the Co(II) complex, indicating coordination through the nitrogen atom. The NH_2 stretching bands observed at 3380 cm^{-1} and 3278 cm^{-1} in the ligand shifted to 3259, 3256, and 3240 cm^{-1} in the Fe(II), Cu(II), and Co(II) complexes, respectively, further supporting the involvement of the NH group in metal coordination [6,20,22]. The carbonyl peaks at 1653 and 1638 cm^{-1} in the Schiff base shifted to the range 1670-1631 cm^{-1} in the metal complexes, supporting coordination of the metal ions through the oxygen atom of the carbonyl group. Additionally, the FT-IR spectra of the metal complexes exhibited characteristic M-N (495-465 cm^{-1}) and M-O (590-514 cm^{-1}) bands, indicating coordination via nitrogen and oxygen atoms. The peaks observed at 3438-3388 cm^{-1} and 863-823 cm^{-1} are ascribed to hydration and coordinated H_2O molecules, respectively. These observations are consistent with those of previous studies [23-25]. No significant change was observed in the thiophene peaks, suggesting that the C-S-C group did not participate in the coordination.

The UV-Vis spectra of the ligand showed absorption bands in the 209-265 nm range, which were ascribed to the $\pi\rightarrow\pi^*$ transitions of the carbonyl and aromatic rings. The absorption bands in the 300-399 nm range correspond to $n\rightarrow\pi^*$ transitions associated with the C=O group and N-H of the amine group. The Fe(II), Co(II), and Cu(II) complexes showed absorption peaks in the 213-266 nm range, assigned to $\pi\rightarrow\pi^*$ transitions, and in the 274-396 nm range, corresponding to $n\rightarrow\pi^*$ transitions. Additionally, the Cu(II) and Co(II) complexes exhibited peaks in the 402-894 nm range, which were attributed to $d\rightarrow d$ and ligand-to-metal charge transfer (LMCT) transitions [22,26,27]. The magnetic moment values for the Cu(II) and Co(II) complexes were 1.84 and 2.13 B.M., respectively, consistent with square planar geometries [28,29]. The Fe(II) complex exhibited novel bands at 575 and 606 nm, indicating d→d and ligand-to-metal charge transfer (LMCT) transitions, further confirming complex formation [26,27]. Furthermore, the Fe(II) complex showed a magnetic moment of 4.96 B.M., which, along with the electronic spectral data, supports an octahedral geometry for the Fe(II) complex and square planar geometries for the Cu(II) and Co(II) complexes [30,31].

3.2 Thermal Analysis

Thermal analysis of the metal complexes showed that the Fe(II) complex decomposed in a single step. The observed mass loss was 58.20% (calc. 57.98%), corresponding to the removal of 7.5 moles of water, 3 moles of chlorine, and $C_{10}H_{12}NS$ fragments. The remaining residue consisted of 40.50% $C_9H_7N_3$ and 2 moles of FeO. The Cu(II) complex decomposed in two steps. In the first step, a mass loss of 18.11% (calc. 17.61%) was observed, corresponding to the removal of 5 moles of water and 1 mole of chlorine. The second step showed a mass loss of 34.10% (calc. 34.46%), which was attributed to the elimination of 2 moles of chlorine and the organic $C_9H_{11}S$ fragment. The remaining residue contained 47.13% $C_{10}H_{10}N_3$ and 2 moles of CuO. The Co(II) complex also decomposed in two steps. The first step showed a mass loss of 17.78% (calc. 16.91%), corresponding to the removal of 3.5 moles of water, one chloride ion, and one CH_2 units. The second step exhibited a mass loss of 38.74% (calc. 37.55%), attributed to the elimination of 2 chloride ions and the organic $C_9H_{11}NOS$ fragment. The residue contained 40.53% $C_{10}H_{10}ON_3$ and 2 moles of metallic cobalt. These findings agree with the experimental and theoretical results presented in Table 1.

Table 1. Thermogravimetric data of metal complexes

Compounds	**Step**	**Temp. Range (°C)**	**Weight loss (%)**		**Evolved components**
			Calc.	**/Found**	
$[LCu_2(H_2O)_2Cl_3]3H_2O$	1	50-260	18.11	17.61	$5H_2O$, Cl
	2	260-740	34.10	34.46	$C_9H_{11}SCl_2$
	Residue	740-		47.13	$C_{10}H_{10}N_3 + 2CuO$
$[LCo_2(H_2O)_2Cl_3]1.5H_2O$	1	50-320	17.78	16.91	$3.5H_2O$, Cl, CH_2
	2	320-800	38.74	37.55	$C_9H_{11}NOSCl_2$
	Residue	800		40.53	$C_{10}H_{10}ON_3Co_2$
$[LFe_2(H_2O)_6Cl_3]1.5H_2O$	1	50-800	58.20	57.98	$7.5H_2O$, $C_{10}H_{12}NSCl_3$
	Residue	800-		40.50	$C_9H_7N_3 + 2FeO$

The mass spectra of the Fe(II), Cu(II), and Co(II) complexes showed molecular ion peaks at *m/z* values of 720.238, 691.737, and 654.097, respectively. The principal ion peaks were observed at 473.274, 619.617, and 367.308 for the Fe(II), Cu(II), and Co(II) complexes, respectively, supporting the formation of the expected structures [29].

3.3 Antioxidant Activity

3.3.1 Scavenging Activity of DPPH Radical

The antioxidant activity of the samples was assessed using a modified DPPH (2,2-diphenyl-1-picrylhydrazyl) assay, as described in a previous study [30]. A 0.1 mM DPPH solution was prepared by dissolving 38 mg of DPPH in 100 mL of ethanol and stirring for approximately 12 h to ensure complete dissolution. The synthesized compounds were diluted to 1 mg/mL, and different volumes (10, 20, and 30 µg/mL) were compared with standard antioxidants (BHT, ascorbic acid, and α-tocopherol). Each sample received 300 µL of the DPPH solution, and the final volume was adjusted to 2000 µL with ethanol. After incubation in the dark at 25 °C for 30 min, the absorbance was measured at 517 nm using a UV-Vis spectrophotometer. A control sample containing 1700 µL of ethanol and 300 µL of DPPH solution was used. The control absorbance (1.500-2.000) was adjusted as needed by modifying the ethanol-to-DPPH ratio [33].

The DPPH free radical scavenging activity was determined by observing the decrease in absorbance, as DPPH-H did not show any absorbance at 517 nm. Antioxidant activity is shown. Compared with the standard antioxidants (ascorbic acid, α-tocopherol, and BHT), the absorbance values of the synthesized starting material, ligand, and Fe(II), Co(II), and Cu(II) metal complexes decreased with increasing concentrations. The starting material, Fe(II), and Co(II) complexes showed antioxidant properties similar to those of the standard BHT, whereas the ligand and Cu(II) complex showed increasing absorbance with increasing concentrations and did not exhibit antioxidant properties compared to the standards (Figure 4). These results suggest that the newly synthesized compounds exhibit different antioxidant properties.

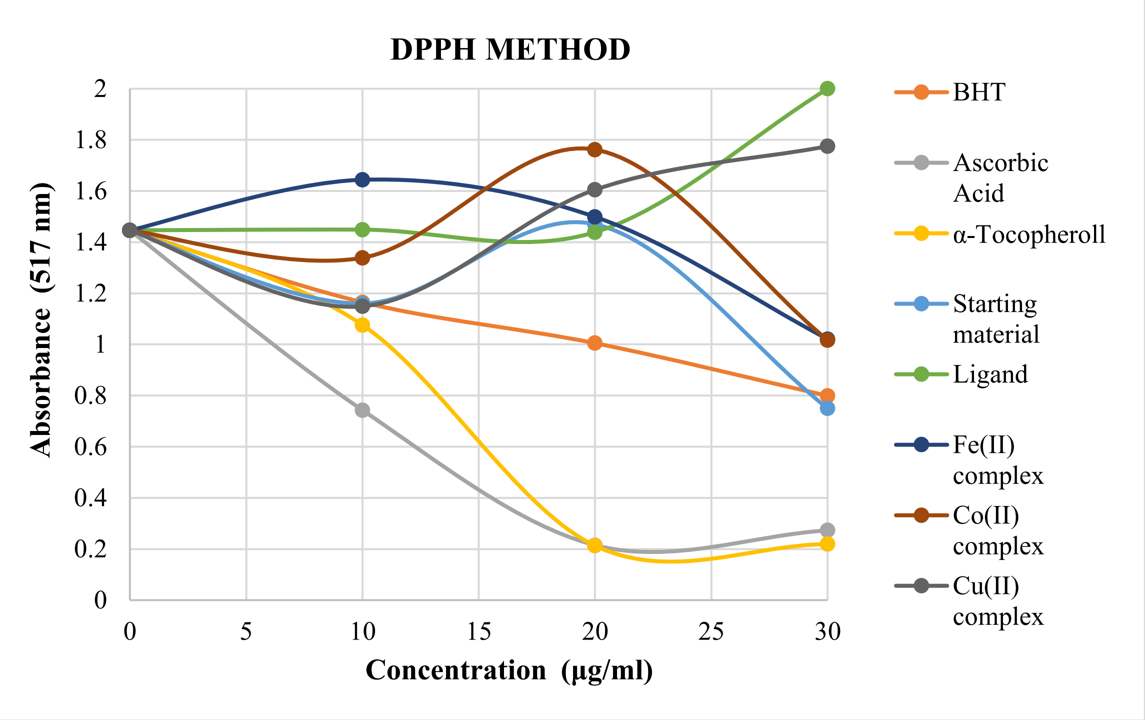


Figure 4. DPPH free radical scavenging activity graph

3.3.2 ABTS Radical Scavenging Assay

In the ABTS (2,2'-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid) assay, free radicals were generated by mixing equal volumes of 2.45 mM potassium persulfate ($K_2S_2O_3$) and 2 mM ABTS solutions, followed by stirring in the dark for 6 h. The resulting ABTS radical solution was then diluted with distilled water to achieve an absorbance of 1.0 ± 0.2 at 734 nm, as measured using a UV-Vis spectrophotometer [34]. For the antioxidant evaluation, 500 µL of the ABTS radical solution and distilled water were added to cuvettes containing 10, 20, or 30 µg/mL of the test compounds, including the starting material, ligand, and its Fe(II), Co(II), and Cu(II) complexes, along with reference antioxidants (BHA, BHT, ascorbic acid, and α-tocopherol). The final volume was adjusted to 2000 µL using distilled water. After 30 min of incubation at room temperature, the absorbance was measured at 734 nm. A control was prepared using 500 µL of ABTS solution and 1500 µL of ethanol [33].

In this method, the ABTS radical reacts with antioxidant compounds by accepting an electron, thereby reducing it to a non-radical ABTS form. The decrease in absorbance at 734 nm, corresponding to the degree of radical scavenging, was used to evaluate the antioxidant activity.

The antioxidant activities of the synthesized starting compound, ligand, and Fe(II), Co(II), and Cu(II) complex compounds were evaluated using the ABTS scavenging method, and the results were compared with those of standard antioxidant substances such as α-tocopherol, BHA, BHT, and vitamin C (ascorbic acid). The absorbance values of the standard antioxidants decreased with increasing concentration, indicating that the antioxidant activity increased in a concentration-dependent manner. According to the ABTS assay, the antioxidant effectiveness of the standard compounds followed the order: BHA > BHT > ascorbic acid > α-tocopherol.

Among the synthesized compounds, the Fe(II) complex exhibited the highest antioxidant activities. As its concentration increased, the absorbance values were consistently lower than those of both α-tocopherol and ascorbic acid, indicating significantly stronger radical scavenging ability. The starting compound also showed a decrease in absorbance with increasing concentration, suggesting antioxidant properties comparable to those of ascorbic acid but weaker than those of α-tocopherol. The ligand and Cu(II) complex similarly demonstrated decreasing absorbance values, indicating moderate antioxidant activity. In contrast, the Co(II) complex displayed an increase in absorbance at higher concentrations, indicating relatively poor antioxidant performance. Overall, based on the ABTS cation radical scavenging assay, the Fe(II) complex exhibited the strongest antioxidant activity, followed by the starting compound, the Cu(II) complex, and the ligand, with the Co(II) complex showing the weakest activity (Figure 5).

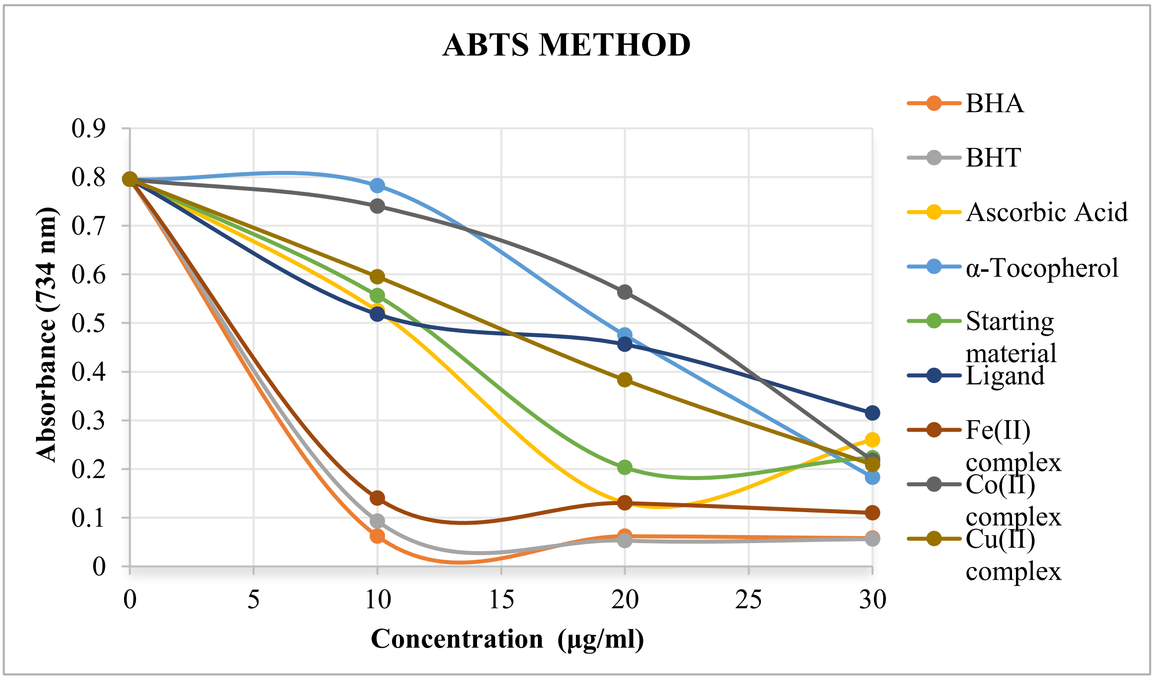


Figure 5. ABTS cation radical scavenging activity graph

3.3.3 CUPRAC Assay

The cupric ion (Cu^{2+}) reducing capacities of the samples were evaluated using the cupric ion reducing antioxidant capacity (CUPRAC) assay. To each well of a microplate, 500 µL of 0.01 M $CuCl_2$, 500 µL of 7.5 mM neocuproine, and 500 µL of 1 M potassium acetate buffer were added sequentially. This was followed by the addition of various concentrations (10, 20, and 30 µg/mL) of the synthesized compounds, including the precursor, ligand, and their Fe(II), Co(II), and Cu(II) complexes, along with standard antioxidants. The final volume in each well was adjusted to 2000 µL using distilled water. After incubating the mixtures for 30 min, the absorbance was measured at 450 nm using a UV-Vis spectrophotometer [35].

An increase in absorbance indicates a stronger Cu^{2+} reducing activity. The antioxidant potential was evaluated based on the absorbance-concentration curves. Among the standards, antioxidant activity increased with concentration in the following order: BHA > BHT > ascorbic acid > α-tocopherol. BHA and BHT demonstrated the highest activity (Figure 6). Among the synthesized compounds, the starting material and Co(II) complex exhibited the highest absorbance values, although these were still lower than those of BHA and BHT. These two compounds exhibited stronger reducing capacities than the other synthesized structures. The ligand showed antioxidant properties comparable to those of α-tocopherol. Although the Fe(II) and Cu(II) complexes also exhibited a concentration-dependent increase in absorbance, their activities remained lower than those of the standard antioxidants and other synthesized compounds, such as the starting material, ligand, and Co(II) complex.

These results indicate that the newly synthesized compounds possess moderate to low antioxidant capacities according to the CUPRAC method. While some compounds, particularly the starting material and Co(II) complex, exhibited promising reducing activity, the overall antioxidant potential of the synthesized derivatives was low in this assay system.

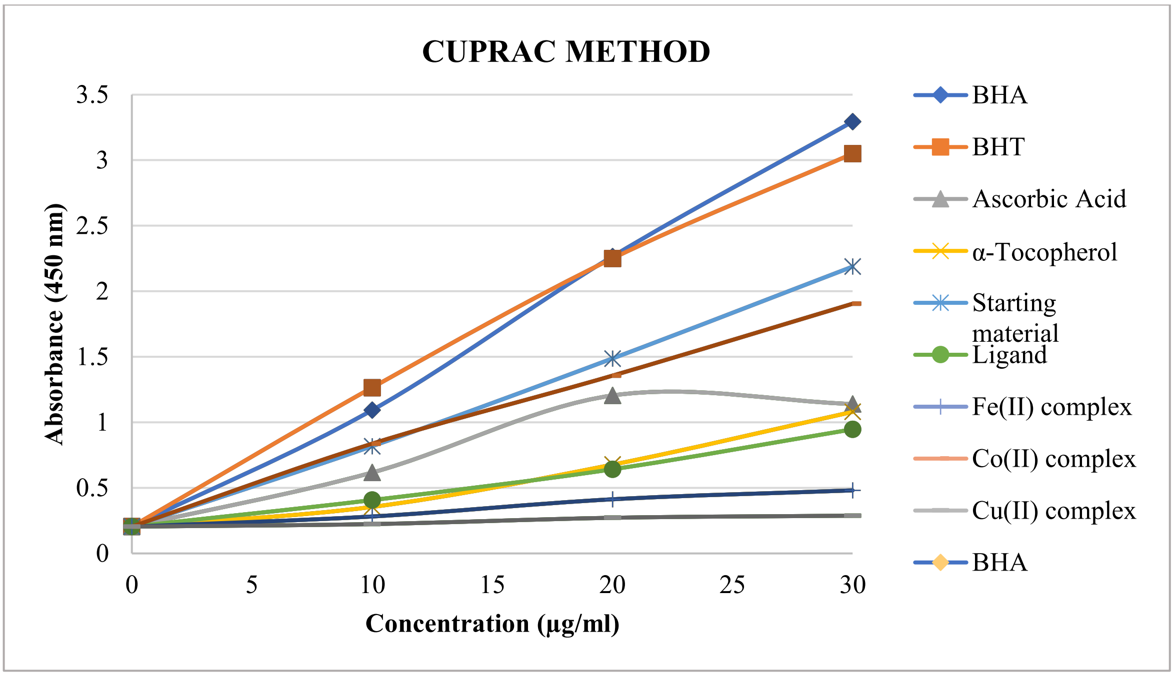


Figure 6. Reduction activity graph according to the CUPRAC method

4 CONCLUSION

The ligand and its corresponding Fe(II), Co(II), and Cu(II) metal complexes have been extensively analyzed using a range of spectroscopic methods, such as FT-IR, NMR, TGA, UV-Vis, mass spectrometry, and microanalysis. The results of these analyses indicate that the Schiff base acts as a bidentate ligand, coordinating with metal ions in a 2:1 metal-to-ligand ratio. Consequently, the general formulas for the synthesized complexes were proposed as $[LCu_2(H_2O)_2Cl_3]3H_2O$, $[LCo_2(H_2O)_2Cl_3]1.5H_2O$, and $[LFe_2(H_2O)_6Cl_3]1.5H_2O$ for the Cu(II), Co(II), and Fe(II), respectively. Thermal analysis confirmed the presence of both coordinated and lattice water molecules, providing additional structural insights. The antioxidant activities of the ligand and its metal complexes were evaluated using DPPH, ABTS, and CUPRAC assays, with the CUPRAC method demonstrating the highest antioxidant capacity, highlighting the potential of these compounds as effective antioxidants. The ligand and its Cu(II), Co(II), and Fe(II) complexes were novel and consistent with previous findings. Schiff bases containing dimethylamine and thiophene rings with ONS donor atoms have been reported to exhibit significant anticancer, optoelectronic, and catalytic properties. Building on these promising findings, future research should explore the synthesis of alternative aldehyde derivatives and their metal complexes. Subsequent investigations will focus on evaluating the anticancer and photocatalytic activities of these compounds, contributing to the development of new materials with potential therapeutic and technological applications.

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Conflict of Interest Statement

The authors declare no conflicts of interest.

Statement of Research and Publication Ethics

This study complied with research and publication ethics.

Artificial Intelligence (AI) Contribution Statement

"This manuscript was entirely written, edited, analyzed, and prepared without the assistance of any artificial intelligence (AI) tools. All content, including text, data analysis, and figures, was solely generated by the authors."

Contributions of the Authors

K. Buldurun: Conceptualization, methodology, formal analysis, software, validation, project administration, writing–original draft, supervision.

H. İnan: Data curation, investigation, methodology, writing, resources, formal analysis, software.

N. Turan: Methodology, writing-original draft, review and editing, visualization, formal analysis, validation.

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