



Metal(II) Complexes of Pyridine-Carboxamide Schiff Base: Synthesis, Characterization, and Antioxidant Activities Evaluation

Piridin-Karboksamid Schiff Bazinin Metal(II) Kompleksleri: Sentez, Karakterizasyon ve Antioksidan Aktivitelerinin Değerlendirilmesi

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ABSTRACT

This research introduces two novel Schiff base complexes: $[LNi(H_2O)_2]H_2O$ and $[LCu]_3H_2O$, where L represents (E)-2-(5-bromo-2-hydroxybenzylideneamino)-6-methyl-4,5,6,7-tetrahydrothieno[2,3-c]pyridine-3-carboxamide. These complexes were synthesized by reacting of Schiff base ligand (L) containing ON donor atoms with an equimolar amount of $NiCl_2 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ salts. The compounds were extensively characterized using various analytical and spectroscopic techniques, including elemental analysis, FT-IR, 1H -NMR, ^{13}C -NMR, UV-Vis spectroscopy, mass spectrometry, magnetic susceptibility measurements, molar conductivity, and thermogravimetric analysis. Additionally, the antioxidant properties of both the ligand and metal complexes were evaluated in vitro using three methods: DPPH free radical scavenging activity, ABTS+ cation radical scavenging activity, and CUPRAC reducing power. From the analytical data, it was observed that the Ni(II) complex has an octahedral structure and the Cu(II) complex has a square planar structure. Antioxidant activity results revealed that the starting material and Cd(II) complex exhibited higher activity than the ligand according to the CUPRAC method.

Key Words

Schiff base, metal complex, spectroscopic method, DPPH, ABTS, CUPRAC.

Öz

Bu çalışmada, iki yeni Schiff bazı kompleksi verilmektedir: $[LNi(H_2O)_2]H_2O$ ve $[LCu]_3H_2O$, burada L (E)-2-(5-bromo-2-hidroksibenzilidenamino)-6-metil-4,5,6,7-tetrahidrotiyeno[2,3-c]piridin-3-karboksamid'i göstermektedir. Bu kompleksler, ON donör atomları içeren Schiff bazı ligandının (L) eşit miktarda $NiCl_2 \cdot 6H_2O$ ve $Cu(NO_3)_2 \cdot 3H_2O$ tuzlarıyla reaksiyona sokulmasıyla sentezlendi. Bileşikler elementel analiz, FT-IR, 1H -NMR, ^{13}C -NMR, UV-Vis spektroskopisi, kütle spektrometrisi, manyetik süseptibilite ölçümleri, molar iletkenlik ve termogravimetrik analiz olmak üzere çeşitli analitik ve spektroskopik teknikler kullanılarak kapsamlı bir şekilde karakterize edilmiştir. Ayrıca, hem ligandın hem de metal komplekslerinin antioksidan özellikleri üç yöntem kullanılarak in vitro olarak değerlendirilmiştir: DPPH serbest radikal giderme aktivitesi, ABTS+ katyon radikal giderme aktivitesi ve CUPRAC indirgeme kapasitesi. Analitik verilerden Ni(II) kompleksinin oktahedral yapıya, Cu(II) kompleksinin ise kare düzlem bir yapıya sahip olduğu görülmüştür. Antioksidan aktivite sonuçları, başlangıç maddesi ve Cd(II) kompleksinin CUPRAC metoduna göre, ligandan daha yüksek bir aktivite sergilediğini ortaya koymuştur.

Anahtar Kelimeler

Schiff bazı, metal kompleks, spektroskopik metod, DPPH, ABTS, CUPRAC.

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INTRODUCTION

Schiff base complexes are molecules of interest due to their unique chemical and physical properties, and wide-range of applications in various scientific disciplines. The Schiff base and pyridine-3-carboxamide (nicotinamide) structural systems are extensively utilized and continuously studied as pharmaceuticals and bioactive compounds [1-3]. Nevertheless, there remains a demand for the synthesis of novel ligand and complex compounds with better properties.

Schiff bases are the products of condensation reactions between primary amines and ketones or aldehydes under specific conditions. These compounds form an important category of ligands owing to their capacity to stabilize various transition metals in different oxidation states, their numerous catalytic and industrial uses, and their extensive range of biological activities (including antioxidant, antiviral, antimalarial, antibacterial, antifungal, antitubercular, antimicrobial, antiproliferative, anti-inflammatory, antipyretic, and anticancer properties) [4-6]. Schiff bases form stable complexes with metal ions because the nitrogen in the azomethine ($-N=CH$) bond has a lone pair of electrons that can coordinate with metal ions [7-11]. These stable complexes play crucial role in many significant biological processes, supramolecular chemistry, bioinorganic, and molecular magnetism [2, 12-14].

In recent years, chemists have shown great interest in the coordination chemistry of compounds with heterocyclic Schiff base ligands containing oxygen, nitrogen, and sulfur as donor atoms. These ligands can coordinate with metal atoms in different ways. Schiff base ligands are widely used in medicine, industry, and agriculture because of their ability to form chelates. Currently, research focus has shifted towards the synthesis of macrocyclic ligands and their metal complexes, which have potential applications in cancer diagnosis and tumor therapy [15-18]. Transition metal ions play a vital role in various biological processes within the body. Metals such as zinc (II), nickel (II), and copper (II) are present in high concentrations and are often found at the active sites of enzymes or as part of their structural framework [19]. Polyamines, including diamines and triamines, serve as potent chelating agents capable of binding to various transition metal ions. By forming complexes with these metal ions, polyamines enhance the biological functions of organic molecules containing nitrogen

donors. Consequently, the coordination of transition metals is essential for many biological activities [20].

Pyridine and various heterocyclic compounds with aromatic rings are excellent ligands, benefiting from a nitrogen atom with a localized electron pair. Many thiopyridines have been evaluated pharmacologically and they have been used as analgesics and anti-inflammants and showed activity against diabetes mellitus [21,22]. Carboxamide group found in the primary structure of proteins plays a crucial role as a ligand in coordination chemistry. The carboxamide compounds are commonly used in the synthesis of coordination complexes and show strong binding to transition metal ions. These compounds are particularly valued for their diverse applications, with carboxamide ligands and their metal complexes being important in many fields, particularly in biological contexts. Certain carboxamide compounds have even been identified as having potential therapeutic uses in the treatment of cancer and infectious diseases [23].

Molecules that neutralize free radicals, which can harm cells and tissues in organisms, are known as antioxidants. They also prevent oxidation processes that occur during metabolic pathways' chemical reactions. Consequently, researchers extensively study the antioxidant properties of synthetic compounds. A crucial area of investigation involves finding active chemicals that can mitigate or prevent the effects of oxidative stress on cells. Furthermore, it is established that free radical oxidative processes play a significant harmful role in the progression of numerous human diseases and the aging process [24,25].

Antioxidants are molecules that destroy free radicals that can damage cells and tissues in organisms and prevent oxidation processes that occur during chemical processes in metabolic pathways. Therefore, the antioxidant properties of synthetic substances are extensively investigated. An important area of research is the search for active chemicals that can prevent or reduce the effects of oxidative stress on cells. In addition, it is known that free radical oxidative processes play a significant detrimental role in the development of many human diseases as well as aging.

In this research, the Schiff base ligand (L) was synthesized by reacting 2-amino-6-methyl-4,5,6,7-tetrahydrothieno[2,3-c]pyridine-3-carboxamide with

5-bromo-2-hydroxybenzaldehyde. Subsequently, metal complexes of the Schiff base ligand were prepared using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ metal salts. The Schiff base and its complexes were characterized using various analytical techniques, including FT-IR, ^1H and ^{13}C NMR, UV-Vis, elemental analysis, mass spectrometry, magnetic susceptibility, molar conductivity, and thermal analysis methods. Lastly, the antioxidant properties of the Schiff base and its complexes were examined through in vitro studies.

EXPERIMENTAL

Materials and instruments

The chemicals and solvents used in this study were sourced from Merck, Alfa Aesar, or Sigma Aldrich chemical companies and were used as received without further purification. Micro analysis for carbon, hydrogen, nitrogen and sulfur (C, H, N, S) was recorded at Inonu University's Center Research Laboratory with a LECO CHNS-932 Vario Elemental Analyzer. Fourier transform infrared (FT-IR) spectra were recorded in the $4000\text{--}400\text{ cm}^{-1}$ range using KBr on a Perkin-Elmer 65 spectrometer. UV-Vis. spectra of the compounds were obtained in ethanol solution with a Shimadzu UV-1800 UV/Vis.

Scanning Spectrophotometer at $25\text{ }^\circ\text{C}$. Proton and carbon NMR spectra (^1H , ^{13}C) were recorded at 300 MHz and 75.47 MHz, respectively, using a Bruker 300 Merkur spectrometer with DMSO-d_6 as the solvent and SiMe_4 as the internal standard. Magnetic susceptibility measurements were conducted using the Gouy method, with $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant. Thermal analysis, including thermogravimetric (TG) and differential thermal analysis (DTA), was performed under nitrogen from $25\text{ }^\circ\text{C}$ to $900\text{ }^\circ\text{C}$ using a Shimadzu TGA-50H thermal analyzer. Mass spectra were recorded on an AB Sciex 3200 QTrap spectrometer. Melting and decomposition points were determined with a STUART SMP30 apparatus. The molar conductivities of 10^{-3} M solutions of the complexes in DMF were measured using a Jenway conductivity meter.

Synthesis of metal(II) complexes

The Schiff base ligand (L) and its $\text{Cd}(\text{II})$ complex were synthesized following the methodology described in a previous report [26]. Yield: 85%, m.p. $235\text{ }^\circ\text{C}$. Color: Yellow. Anal. Calc. for $\text{C}_{23}\text{H}_{19}\text{Br}_2\text{N}_3\text{O}_3\text{S}$: C, 47.86; H, 3.29; N, 7.28; S, 5.55%. Found: C, 47.88; H, 3.30; N, 7.27; S, 5.56%.

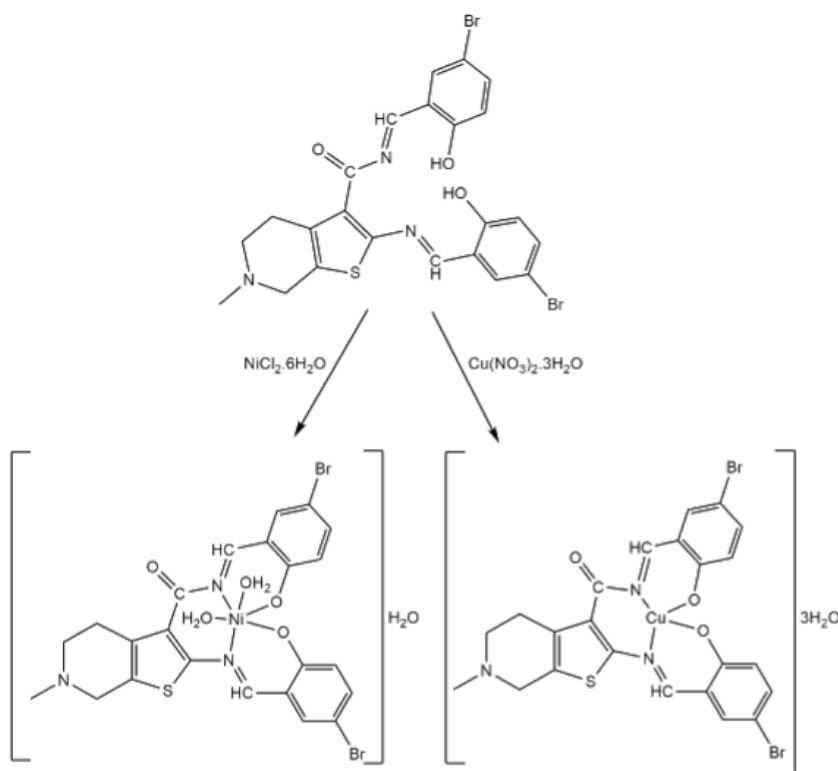


Figure 1. Structure of metal complexes.

Table 1. Thermal analysis data.

Compounds	Decomp. stages	TG range (°C)	Mass loss (%) calc./found		Assignment
[LNi(H ₂ O) ₂]H ₂ O	1	30-800	58.65	57.62	3H ₂ O, C ₁₅ H ₉ B ₁₂
	Residue	800-	41.41	42.29	C ₈ H ₈ N ₃ O ₂ S + NiO
[LCu]3H ₂ O	1	50-160	30.86	31.15	3H ₂ O, 2Br
	2	160-340	39.73	38.58	C ₁₉ H ₁₇ ON
	3	340-760	29.40	26.57	C ₄ ON ₂ S + CuO
	Residue	760-		2.96	

In separate methanol solutions, Ni(II) and Cu(II) metal salts were dissolved (0.25 g, 1.04 mmol and 0.30 g, 1.21 mmol, respectively, in 20 mL). These solutions were then slowly introduced into a 30 mL methanol solution containing the ligand (0.60 g (1.04 mmol) and 0.70 g (1.21 mmol)), while constantly stirring. The resulting mixture underwent reflux for 10 hours. Subsequently, the precipitates were collected through filtration, thoroughly washed with ethanol, and dried under vacuum. Despite efforts, single crystals of the complexes could not be obtained. The reaction process is illustrated in Fig. 1.

Dark copper, m.p. 300 °C. yield: 80%. C₂₃H₂₃Br₂N₃O₆Sn (M.W. 687.81 g/mol): Anal. Calc. for C, 40.16; H, 3.34; N, 6.11; S, 4.66%. Found C, 40.17; H, 3.38; N, 6.13; S, 4.67%. IR (KBr, ν , cm⁻¹): 3427 (OH/H₂O)_{br}, 3066 (CH)_{Ar}, 2963, 2925, 2857 (CH)_{Aliph}, 1689 (C=O)_{br}, 1660, 1628 (CH=N), 1598, 1537, 1514, 1453 (C=C)_{Ar}, 1173, 1158 (C-O), 827 (H₂O), 775 (C-S-C), 586-535 (Ni-O), 482, 476, 457 (Ni-N). UV-Vis. (λ_{max} , nm) (ϵ in parenthesis, M⁻¹ cm⁻¹): 205 (3772), 215 (4571), 225 (3237), 235 (4427), 280 (2135), 295 (2217), 325 (1403), 360 (1603), 370 (1582), 395 (1674), 445 (1304), 475 (1493), 652 (60), 715 (23). μ_{eff} (B.M.): 3.20. ESI-MS (m/z): 687.810 (Calc.), 687.085 (Found) [M]⁺.

Light brown, m.p. 280-285 °C, yield: 75%. C₂₃H₂₃Br₂N₃O₆S-Cu (M.W. 692.67 g/mol): Anal. Calc. C, 39.87; H, 3.32; N, 6.07; S, 4.63%. Found C, 40.00; H, 3.33; N, 6.10; S, 4.62%. IR (KBr, ν , cm⁻¹): 3415 (OH/H₂O)_{br}, 3134, 3048, 3001 (CH)_{Ar}, 2922 (CH)_{Aliph}, 1683 (C=O), 1663, 1622 (CH=N), 1596, 1537, 1497 (C=C)_{Ar}, 1179 (C-O), 816 (H₂O), 777 (C-S-C), 554-508 (Cu-O), 499, 463 (Cu-N). UV-Vis. (λ_{max} , nm) (ϵ in parenthesis, M⁻¹ cm⁻¹): 205 (3564), 215 (3905), 230 (3979), 240 (3864), 255 (10000), 330 (3873), 345 (3334), 352 (3662), 369 (3522), 375 (3124), 663 (169). μ_{eff}

(B.M.): 1.86. ESI-MS (m/z): 694.670 (Calc.), 694.223 (Found) [M+2H]⁺.

DPPH radical scavenging method

The samples' free radical scavenging activity was evaluated using a recently developed variation of the DPPH (1,1-diphenyl-2-picrylhydrazyl) method [27]. A 0.1 mM DPPH solution served as the free radical source. To prepare this, 38 mg of DPPH was dissolved in 100 mL ethanol by magnetic stirring for about 12 hours. The synthesized Schiff base (L) and its Ni(II), Cu(II), and Cd(II) complexes were prepared as 1 mg/mL solutions. In a cuvette, 250 μ L of DPPH solution was combined with sample solutions at varying concentrations (10, 20, and 30 μ g/mL), and their absorbance was measured. The procedure was repeated using standard antioxidant solutions (BHT, ascorbic acid, α -tocopherol) in place of the synthesized samples. The total volume was adjusted to 2000 μ L with ethanol. Following a 30-minute incubation at room temperature in darkness, absorbance readings were taken at 517 nm using a UV-Vis spectrophotometer. 1750 μ L of ethanol and 250 μ L of DPPH radical solution were used as control. To achieve the desired control absorbance (1.500-2.000), the ethanol and DPPH radical ratio were adjusted through dilution with ethanol.

CUPRAC method

The CUPRAC (cupric ion reducing antioxidant capacity) method was employed to determine the Cu²⁺ ion reduction abilities of the samples. The procedure involved adding 500 μ L each of 0.01 M CuCl₂, 7.5 mM neocuprine solutions, and 1 M potassium acetate buffer to microplate wells. Subsequently, varying concentrations (10, 20, and 30 μ g/mL) of the initial material, L, Ni(II), Cu(II), and Cd(II) complexes, and standard substances were introduced. The solutions were diluted to 2000 μ L with pure water and incubated for 30 minutes. Finally, absorbance

measurements were taken at 450 nm using a Shimadzu UV-1800 spectrophotometer and documented [28].

ABTS⁺ radical scavenging method

The ABTS (2,2-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)) method began with the production of ABTS cation radicals. This was achieved by combining 2.45 mM K₂S₂O₈ and 2 mM ABTS⁺ solutions in equal proportions and stirring them with a magnetic stirrer for 6 hours in darkness. The control sample of this radical solution exhibited an absorbance value of 1.0 ± 0.2 at 734 nm. Various concentrations (10, 20 and 30 µg/mL) of the initial material, L, Ni(II), Cu(II), and Cd(II) complexes, or standard antioxidants (BHA, BHT, ascorbic acid, α -tocopherol) were placed in cuvettes. To these, 500 µL of ABTS radical solution and distilled water were added, bringing the total volume to 2000 µL. The mixture was then incubated for 30 minutes. Following incubation, the absorbances of the samples at 734 nm were measured using a UV-Vis spectrophotometer. For control purposes, 500 µL of ABTS radical was applied to 1500 µL of pure water [29].

RESULTS and DISCUSSION

Characterization

Metal complexes exhibit different colors, are stable at ambient temperatures, and dissolve effectively in solvents such as DMF and DMSO. The microanalysis results of the prepared metal complexes indicated a good agreement between the experimentally obtained percentages and the theoretically calculated values. The ligand-to-metal ratio in the complexes was determined to be 1:1. Our group previously characterized the prepared ligand using various spectroscopic techniques, including FT-IR, elemental analysis, UV-Vis, ¹H-NMR, and ¹³C-NMR [26].

The most valuable IR bands of the metal complexes are detailed in the experimental section and illustrated in Fig. S2 and Fig. S3. The ligand's FT-IR spectra showed azomethine group stretching vibrations at 1668 and 1609 cm⁻¹. In the metal complexes, these bands shifted to 1663-1622 cm⁻¹, indicating coordination of the azomethine nitrogen to metal ions [30,31]. The ligand's C-O stretching vibrations at 1204 and 1188 cm⁻¹ shifted to lower frequencies (1173, 1158, and 1179 cm⁻¹) in Ni(II) and Cu(II) complexes [32]. The phenolic OH vibration of the ligand at 3426 and 3350 cm⁻¹ disappeared in the complexes, supporting the role of the deprotonated

phenolic hydroxyl group in metal ion binding [33]. New bands appeared in the complexes' spectra at 499-457 and 586-508 cm⁻¹, attributed to ν (M-N) and ν (M-O) respectively, which were absent in the Schiff base [34,35]. Broad strong bands at 3427 and 3415 cm⁻¹ in the complexes' IR spectra suggesting the presence of coordinated water molecules [16,36]. This coordination was further confirmed by additional strong, sharp bands at 827 and 816 cm⁻¹, arising from -OH rocking vibration. The IR analysis demonstrated that the ligand coordinates to metal ions through the azomethine nitrogen and phenolic oxygen.

The wavelengths and their corresponding extinction coefficients for the absorption bands are provided in the experimental section. The ligand exhibited significant absorption bands in the UV region, specifically around 197-285 nm and 340-395 nm. These bands, based on their extinction coefficients, were likely associated with π - π^* and n - π^* transitions, respectively. These π - π^* transitions were also observed in the metal complex spectra, though with altered intensities. The complexes also displayed a new absorption band at 445-715 nm for the Ni(II) complex and 663 nm for the Cu(II) complex. The Ni(II) complex's electronic spectrum revealed intense bands, with one at 445 nm due to charge transfer transition and three others exhibiting d-d transition in the visible region at 475 and 652, 715 nm, indicating octahedral geometry [37,38]. The copper complex's absorption spectrum showed a band at 663 nm, corresponding to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, characteristic of square planar geometry [39], further confirmed by its magnetic moment value of 1.86 B.M. [40,41]. The Ni(II) complex has a magnetic moment of 3.20 B.M., suggesting two unpaired electrons in the Ni ion and an octahedral configuration [38].

Mass spectra results of the Ni(II) and Cu(II) complexes showed molecular ion peaks aligning with the empirical formula. Additional peaks indicated fragmentation products separated from the molecular ion. The complexes' molecular weights and molecular ion masses were in agreement, confirming their structure and successful synthesis [42,43]. The Ni(II) complex's mass spectrum showed a main peak at 687.085, corresponding to the molecular ion [M]⁺ peak. For the Cu(II) complex, the main peak was observed at 389.460, with a peak at m/z : 685.057 corresponding to a molecular ion such as [M+2H]⁺.

The molar conductivity of the complexes was measured at a concentration of (1×10^{-3}) molar using DMF solvent at room temperature. Results indicated molar conductivity values of 10.06 and 9.48 $\text{ohm}^{-1} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$ for the Ni(II) and Cu(II) complexes, respectively. These relatively low values demonstrate that the prepared complexes were not electrolytes.

Thermogravimetric study

Thermogravimetric analysis (TGA) was employed to evaluate the thermal stability of both complexes, with their TGA curves shown in Fig. S5. For $[\text{LNi}(\text{H}_2\text{O})_2]\text{H}_2\text{O}$, the TGA profile revealed an initial weight loss of approximately 57.62% between 30-800 °C, attributed to the elimination of hydrate and coordination waters, along with the $\text{C}_{15}\text{H}_9\text{Br}_2$ organic group. The final residue at 800°C, comprising about 42.29%, was identified as $\text{C}_8\text{H}_8\text{N}_3\text{O}_2\text{S} + \text{NiO}$. In contrast, the TGA profile of $[\text{LCu}]\text{3H}_2\text{O}$ exhibited a loss of hydrate waters and 2Br atoms, amounting to roughly 31.15%, within the 50-160 °C range. The subsequent stage, occurring between 160-340 °C, demonstrated a weight loss associated with the decomposition of the $\text{C}_{19}\text{H}_{17}\text{ON}$ organic group. The final residue, observed at 340-760 °C and constituting approximately 26.57%, was identified as $\text{C}_4\text{ON}_2\text{S} + \text{CuO}$ (Table 1).

Antioxidant Studies

DPPH radical scavenging activity

The DPPH free radical scavenging activity is determined by examining the relationship between absorbance at 517 nm and concentration in $\mu\text{g/mL}$. As DPPH-H does not absorb at 517 nm, the reduction in absorbance indicates the extent of free radical scavenging and antioxidant activity. A comparison was made between the DPPH free radical scavenging activity of the synthesized starting material (2-amino-6-methyl-4,5,6,7-tetrahydrothieno[2,3-c]pyridine-3-carboxamid), L, Cu(II), Ni(II), and Cd(II) complexes, and the standards α -tocopherol, BHT, and vitamin C. The standards exhibited decreasing absorbance values as concentration increased, with α -tocopherol and vitamin C demonstrating the highest antioxidant effects, followed by BHT. The starting material and its metal complexes also showed concentration-dependent decreases in absorbance, surpassing the antioxidant properties of standard BHT. The graph reveals that the starting material, L, and its Cd(II), Cu(II), and Ni(II) complexes possess antioxidant properties comparable to the standard substances (vitamin C and α -tocopherol). The findings (Fig. 2a) in-

dicate that the newly synthesized compounds exhibit notable antioxidant properties across various ranges, as determined by the DPPH method.

ABTS radical scavenging activity

The ABTS radical, which interacts with antioxidants, undergoes an electron transfer and converts to non-radical ABTS. The resulting decrease in absorbance at a specific wavelength is utilized to calculate antioxidant activity. The ABTS cation radical scavenging activity is determined by examining the relationship between absorbance (734 nm) and concentration ($\mu\text{g/mL}$), where a reduction in absorbance indicates free radical scavenging and antioxidant activity. A comparison of the synthesized starting material, L, Cu(II), Ni(II), and Cd(II) complex compounds, and standards (α -tocopherol, BHA, BHT, and vitamin C) revealed that the standard substances exhibited decreasing absorbance values as concentration increased (Fig. 2b). The antioxidant effect, as indicated by the decrease in absorbance, was observed in the following order: BHA, BHT, α -tocopherol, and vitamin C. BHA and BHT demonstrated the strongest antioxidant effects. Among the synthesized compounds, the starting material showed relatively better antioxidant activity according to the ABTS method compared to the other compounds and vitamin C standard. This suggests that the newly synthesized starting material, L, Cu(II), Ni(II), and Cd(II) complexes do not possess strong antioxidant properties based on the ABTS cation radical scavenging method.

CUPRAC reducing method

The CUPRAC method demonstrates that higher absorbance values indicate an increased capacity for reducing cupric ions (Cu^{2+}) in the reaction mixture. The free radical scavenging and antioxidant activities are determined from the rising absorbance amount, as shown in the absorbance (450 nm)-concentration ($\mu\text{g/mL}$) graph (Fig. 2c). When comparing the reducing activity of the synthesized starting material, L, Cu(II), Ni(II), and Cd(II) complexes with α -tocopherol, BHA, BHT, and vitamin C standards, the absorbance values of the standard substances increased proportionally with concentration. The antioxidant effect, indicated by the increase in absorbance values, was observed for BHA, BHT, vitamin C (ascorbic acid), and α -tocopherol, in that order. BHA and BHT exhibited the strongest antioxidant effect. The starting material, L, Cu(II), Ni(II), and Cd(II) complexes showed minor increases in absorbance values as concentration increased. Among the synthesized samples,

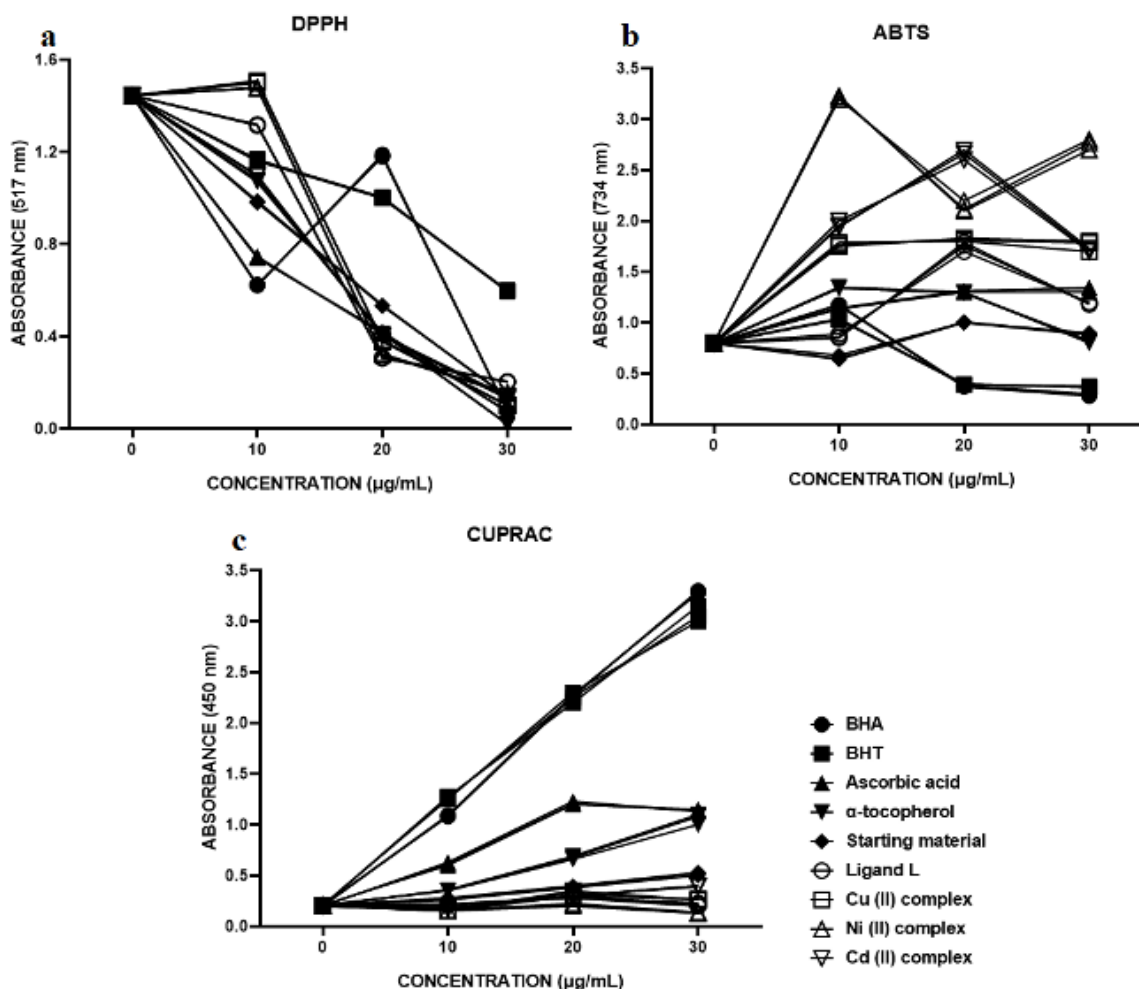


Figure 2. a) DPPH free radical scavenging potentials of samples and standard compounds, b) ABTS cation radical scavenging potentials of samples and standard compounds, c) Cupric reducing antioxidant capacities of samples and standard compounds

the starting material and Cd(II) complex demonstrated the best activity, with absorbance values lower than the standard materials but higher than the other compounds. The Cu(II) complex, L, and Ni(II) complex displayed less activity than the standard materials, the starting material, and Cd(II) complex, respectively. The Ni(II) complex showed the least activity. These results suggest that the newly synthesized compounds do not possess strong antioxidant properties according to the CUPRAC method.

There are various studies in the literature on the antioxidant activities of metal complexes of Schiff bases.

Studies show that Schiff bases are generally strong antioxidants and metal complexes generally increase these activities [44-46]. Vivekanand et al. reported that the DPPH radical scavenging activity of the Cu(II) complex is stronger than that of the Co(II), Ni(II) complexes and the ligand [47]. Savcı et al. also reported that the Ni(II) complex has stronger antioxidant activities than that of the Fe(II), Co(II) complex and the ligand [48]. However, in the current study, it is seen that the ligand and metal complexes do not increase the antioxidant activities. Since the mechanisms regarding the antioxidant activities of the ligand and metal complexes are not yet clear, this situation cannot be explained.

CONCLUSION

In our earlier research, we formed a pyridine-3-carboxamide (nicotinamide) substituted Schiff base (L) by combining 2-amino-6-methyl-4,5,6,7-tetrahydrothieno[2,3-c]pyridine-3-carboxamide and 5-bromo-2-hydroxybenzaldehyde, along with its Cd(II) complex. The current study focuses on the synthesis of Cu(II) and Ni(II) complexes. We employed analytical and spectroscopic techniques to characterize the synthesized compounds. Based on our findings and existing literature, we observed that in all complexes, the Schiff base chelated with the metal ion through azomethine nitrogen and carbonyl oxygen. We proposed the geometry of Ni(II) and Cu(II) complexes using elemental, spectral, and thermogravimetric data. Magnetic moment measurements strongly corroborated the spectral results. Lastly, we examined the antioxidant activity of the ligand and Cd(II) complex from the previous study, as well as the Cu(II) and Ni(II) complexes from this study. Our findings revealed that the metal complexes exhibited superior antioxidant effects compared to the Schiff base.

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