

STUDY OF THE PROPERTIES OF MIXED METAL COMPLEXES (Me - Co, Ni, Cu, Zn) USING DIFFERENT METHODS

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Abstract: The study focused on the synthesis and characterization of mixed-ligand transition metal complexes containing the oxime-based ligand 4-(4-bromophenylaminoisonitrosoacetyl)biphenyl (HL) and the amino acid L-phenylalanine (Phe). Complexes of Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} were prepared, and their physicochemical properties were systematically investigated. Elemental analysis, molar conductivity measurements, infrared (IR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy were employed to elucidate the structural characteristics and coordination modes of the ligands. The results confirmed the formation of stable 1:1:1 metal–ligand–amino acid complexes, with both HL and Phe acting as bidentate ligands. Molar conductivity data indicated the non-electrolytic nature of the complexes in solution. These findings offer valuable insights into the electronic and structural features of the synthesized complexes, underlining their potential applications in catalysis, sensing technologies, and electronic devices.

Keywords: mixed ligand complexes, oxime, coordination chemistry, electrical conductivity, cyclic voltammetry

Introduction

Oximes characterized by the functional group ($-\text{C}=\text{N}-\text{OH}$) have garnered significant attention as complexing agents in coordination chemistry due to their unique electronic properties and the presence of multiple electron-rich donor centres, and these attributes enable them to form a variety of coordination compounds with transition metal ions, which are valuable in applications such as analytical chemistry, spectrophotometry and bioactivity. A substantial body of literature details the chemical synthesis of oximes and their metal complexes, underscoring their importance in both theoretical and practical contexts [1]. Among the wide variety of organic ligands employed in the formation of metal complexes, amino acids are particularly notable due to their versatile coordination modes and strong binding affinity toward metal ions. As fundamental building blocks of proteins in all living organisms, amino acids play vital roles in numerous biochemical processes. Their ability to act as donor ligands arises from the presence of both amino ($-\text{NH}_2$) and carboxylate ($-\text{COO}^-$) functional groups, enabling coordination with transition metal ions through nitrogen and oxygen donor atoms. This interaction often results in the formation of stable five-membered chelate rings which enhance the thermodynamic stability of the resulting metal complexes. These complexes, particularly those involving biologically active metal ions, have gained attention for their potential applications as antibacterial agents, nutritional supplements and models for metalloproteins [2, 3]. L-Phenylalanine, an aromatic amino acid with a non-polar phenyl group, is significant in biological systems due to its ability to cross the blood-brain barrier and convert to tyrosine, a precursor biomolecule (norepinephrine and epinephrine), whose derivatives are exemplified by their role in treating Parkinson's disease with L-3,4-dihydroxyphenylalanine (L-DOPA) [4]. The interactions of phenylalanine within metal complexes are critical for understanding their biomedical implications [5]. The associated planar arrangement of ligands facilitates more efficient electron delocalization compared to twisted geometries. Furthermore, the electronic properties of the ligands play a key role, as their electron-donating capabilities—particularly in the case of oximes and amino acids—significantly influence the overall reactivity and stability of the complexes [6]. The choice of solvent can significantly influence the dissociation behaviour of complexes in solution, thereby affecting their conductivity. Polar solvents, in particular, can enhance ion mobility, leading to increased electrical conductivity. In our study we will emphasise

the creation and depiction of mixed ligand transition metal complexes involving cobalt (II), nickel (II), copper (II), and zinc (II) using 4-(4-bromophenylamino-isonitrosoacetyl)-biphenyl (HL) primary ligand and phenylalanine (phe) co-ligand [7].

Experimental part

Materials and methods. The chemicals utilized in this study were of reagent grade, ensuring high purity and reliability for experimental procedures. All chemicals were sourced from reputable suppliers, specifically Merck and Aldrich, and were utilized without any further purification to maintain their integrity and reactivity. The melting points of the synthesized compounds were determined using an "open glass capillaries" method, providing accurate measurements of melting points, which are critical for assessing the purity and identity of the synthesized compounds. Elemental analysis for carbon, hydrogen, and nitrogen (C, H, N) content was performed using standard analytical methods with a LECO CHNS-932 analyser [8, 9], which allows for precise quantification of the elemental composition of the compounds, facilitating the verification of their molecular formulas and structural integrity. Infrared (IR) spectroscopy was employed to characterize the functional groups present in the synthesized compounds. The IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR instrument, with measurements taken over a range of 4000–600 cm^{-1} . This spectral range provides comprehensive information about the vibrational modes of the molecular bonds, allowing for the identification of key functional groups and insights into ligand coordination to metal centers. Molar conductivity measurements (Λ_m) were conducted in dimethylformamide (DMF) at a temperature of 25°C, using solutions with a concentration of 1.0×10^{-3} M for the metal complexes. Molar conductivity is a crucial parameter for understanding the electrochemical behaviour of compounds, as it indicates the extent of ionic dissociation and provides insights into the nature of the coordination environment surrounding the metal ions [10]. Thermal analyses were performed using a Shimadzu TG DTA 60. Nuclear magnetic resonance (NMR) spectroscopy was used to further characterize the molecular structure of the compounds; ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz FT-NMR spectrometer [11, 12].

Cyclic Voltammetry Measurements. Cyclic voltammetry (CV) is used to investigate the redox status of chemical species and typify their electrochemical properties [13, 14]. In this study, electrochemical studies were performed utilising Autolab Potentiostat/Galvanostat PGSTAT-302N, controlled by Nova 2.1.4 software. The GCE was chosen for its constructive electrical conductivity, chemical stability, and wide voltage range [15].

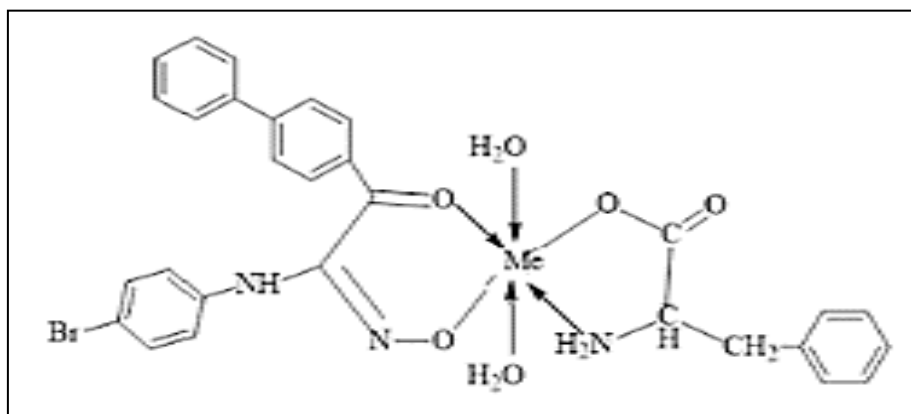


Fig. 1. Suggested molecular structures of mixed transition metal complexes containing oxime and phenylalanine.

Based on a previous protocol, the synthesis of the ligand 4-(4-bromophenylaminoisonitrosoacetyl) biphenyl (HL) (Fig. 2), which depicts optimal yields and purity. The process begins with the preparation of 4-biphenylhydroximoyl chloride. In a controlled

environment, 1 mmol (0.389 g) of 4-biphenylhydroximoyl chloride is dissolved in 50 mL of ethanol. Ethanol serves as a suitable solvent due to its ability to dissolve a wide range of organic compounds while providing a moderate boiling point that facilitates the reaction without excessive evaporation. The solution is then cooled to 0°C, a critical step that helps to slow down the reaction kinetics and allows for more controlled addition of the amine. The next step involves the gradual addition of 4 g of the appropriate amine in 10 mL of ethanol to the chilled solution of 4-biphenylhydroximoyl chloride. This dropwise addition is performed over a period of 15 minutes, allowing for a thorough interaction between the reactants while minimizing the risk of side reactions that could compromise the formation of the desired ligand. The cooling temperature is maintained throughout this addition to further control the reactivity of the components involved [16, 17]. After the addition is complete, the reaction mixture is stirred continuously for 1 h at 0°C to ensure the reaction is complete. Following this step, the temperature is gradually returned to ambient conditions, and the mixture is stirred for a further 2 hours, resulting in the successful binding of the target oxime [18, 19]. Once the synthesis is complete, the reaction mixture is diluted with 100 mL of distilled water followed by washing with cold ethanol to enhance purity. The use of cold ethanol is particularly effective [20, 21].

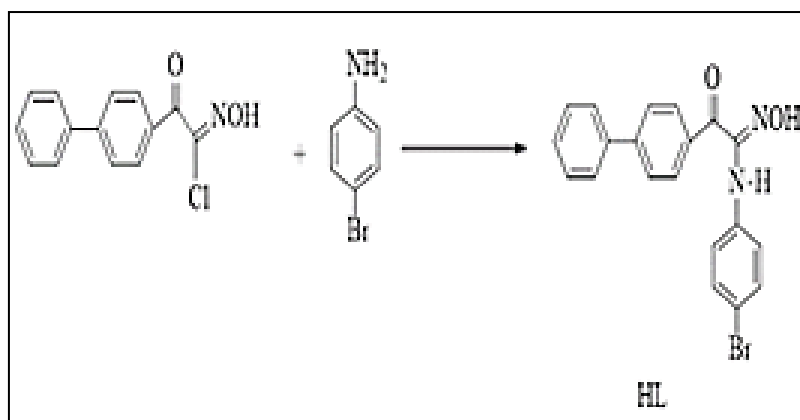


Fig. 2. Synthesis of the proposed ligand HL.

The ligand 4-(4-bromophenylaminoisonitrosoacetyl)biphenyl was synthesized in 90.5% yield and melting point 160°C, and the molecular weight was determined to be 395.23 g/mol. Elemental analysis indicated a composition of 60.78% carbon, 3.82% hydrogen and 7.09% nitrogen, with experimental values found to be 61.17% carbon, 3.83% hydrogen and 7.17% nitrogen, showing good agreement with calculated values. The IR spectra revealed large absorption bands, including a broad O-H stretch at 3425 cm^{-1} , a strong C=O stretch at 1667 cm^{-1} and distinct C=N and C=C stretch bands at 1586 cm^{-1} and 1402 cm^{-1} . In the NMR spectra the ligand showed a single N-OH group at 10.86 ppm in the ^1H NMR spectrum, while the aromatic protons were in the range of 6.76 ppm. The ^{13}C NMR spectrum showed a noticeable signal at 183 ppm corresponding to carbon C=O. The synthesis of metal complexes with the ligand HL involved several steps for each metal ion. The cobalt complex $[\text{CoL}(\text{phe})(\text{H}_2\text{O})_2]$ was synthesized by adding $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ to the ligand in ethanol followed by addition of L-phenylalanine and KOH. The cobalt complex showed a yield of 67.4% and a decomposition point of 272°C, with elemental analysis showing carbon 53.9%, hydrogen 4.32% and nitrogen 6.43%. The molar conductivity in DMF was measured at 7.2 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and the effective magnetic moment was 1.33 BM. The FT-IR spectrum showed peaks at 3359 cm^{-1} for O-H stretching and 1599 cm^{-1} for C=N stretching. Nickel complex $[\text{NiL}(\text{phe})(\text{H}_2\text{O})_2]$ was synthesized under similar conditions, and the yield was 70.6% with a decomposition point of 246°C. Elemental analysis indicated carbon 53.33%, hydrogen 4.32% and nitrogen 6.43% with conductivity in DMF measured at 4.2 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and an effective magnetic moment of 2.70 BM. Copper complex $[\text{CuL}(\text{phe})(\text{H}_2\text{O})_2]$ was prepared using $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. The complex formed a brown solid with a yield of 62.4% and a decomposition point of 223°C. Elemental analysis revealed 52.94% carbon, 4.29% hydrogen and 6.39% nitrogen with a molar conductivity of

3.7 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and an effective magnetic moment of 1.75 BM. Zinc complex $[\text{ZnL}(\text{phe})(\text{H}_2\text{O})_2]$ was synthesized in a yield of 54.2% and a decomposition point of 248°C. Elemental analysis indicated 52.79% carbon, 4.27% hydrogen and 6.37% nitrogen with a molar conductivity of 2.3 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and an effective magnetic moment indicating d^{10} formation and successful synthesis and characterization of the HL ligand [22-24].

Results and discussion

Microanalyses and Molar Conductance Evaluation. The manufactured ligand 4-(4-bromophenylaminoisonitrosoacetyl)biphenyl and its corresponding mixed ligand complexes were subjected to a series of physico-chemical evaluations to characterize their properties. Key parameters, such as melting point, colour, yield, microanalytical data, and molar conductance, were meticulously documented and are elaborated upon in the experimental section, and the microanalytical data for carbon (C), hydrogen (H), and nitrogen (N) in the synthesized metal (II) complexes demonstrated a strong correlation with the calculated values, supporting the stoichiometry of a 1:1:1 molar ratio between the metal ion, the ligand (HL), and L-phenylalanine. This ratio signifies the formation of a stable coordination complex, affirming the successful integration of the ligand with the metal ions. To further investigate the nature of the synthesized complexes, molar conductivity measurements were conducted on instantly formulated dimethylformamide (DMF) complex solutions at ambient temperature, and the measured molar conductance values for the 10^{-3} M solutions complexes ranged from 2.3 to 7.2 $\text{S cm}^2 \text{ mol}^{-1}$.

NMR Spectra of the Oxime Ligand (HL) and the Mixed Ligand Zn Complex. The characterization of the oxime ligand 4-(4-bromophenylaminoisonitrosoacetyl) biphenyl (HL) and its corresponding zinc complex was performed using nuclear magnetic resonance (NMR) spectroscopy, and the studies were conducted in deuterated chloroform (CDCl_3), allowing for a detailed analysis of the proton and carbon environments in both the ligand and the complex, and the ^1H NMR spectrum of the oxime ligand (HL) revealed several key features. In the aromatic region, chemical shifts for the aromatic hydrogens were observed between 7.32 and 8.12 ppm, assigned as multiplet signals reflecting the complex interactions within the aromatic rings, and the "aromatic amine proton" of HL appeared further supporting the structural integrity of the ligand. The ^{13}C NMR spectrum showed "aromatic carbon resonances" in the range of $\delta = 127\text{-}139$ ppm corresponding to the bromophenyl and biphenyl moieties present in the ligand, and the carbonyl carbon was distinctly observed at $\delta = 183$ ppm, while the oxime carbon resonated at $\delta = 147$ ppm. Due to the paramagnetic nature of the Co(II), Ni(II), and Cu(II) complexes, obtaining ^1H and ^{13}C NMR spectra for these metal complexes was not feasible, and therefore the NMR analysis focused on the diamagnetic zinc complex.

FTIR Spectroscopy. Fourier Transform Infrared (FTIR) spectroscopy elucidated the coordination sites of the synthesized metal complexes involving the oxime ligand and phenylalanine. In contrast, the IR spectra of the metal complexes show a broad band in the range of 3359–3332 cm^{-1} , assigned to the $\nu(\text{OH})$ stretching vibration of water molecules.

Additionally, the C=O band remains in a similar range, observed at 1675-1650 cm^{-1} , and the presence of $\nu(\text{COO}^-)$ stretching bands from amino acids or the disappearance of this band indicates that the carbonyl oxygen atom also participates in coordination, and this observation emphasizes the bidentate coordination mode of the oxime ligand.

Fig. 3 presents the FT-IR spectrum of the synthesized ligand 4-(4-bromophenylaminoisonitrosoacetyl) biphenyl HL. The spectrum displays a prominent absorption band at around 3425 cm^{-1} , which corresponds to the stretching vibration of the hydroxyl OH group, indicating the presence of hydrogen bonding that can influence the overall stability and solubility of the ligand in various solvents. This peak reflects the electronic environment around the carbonyl group, which may change upon complexation with metal ions. Another notable peak is observed at around 1586 cm^{-1} corresponding to the C=N stretching vibration indicative of the presence of an azomethine group in the ligand structure. The region between 1400 cm^{-1} and 1600 cm^{-1} contains

several bands associated with aromatic CC stretching vibrations confirming the presence of aromatic rings in the ligand. The FT-IR spectrum and its analysis are directly related to the electrical conductivity of the synthesized complexes. This stable coordination reduces the likelihood of dissociation into free ions in solution. The molar conductance values observed for the metal complexes suggest a non-electrolytic nature, as indicated by their relatively low conductivity measurements.

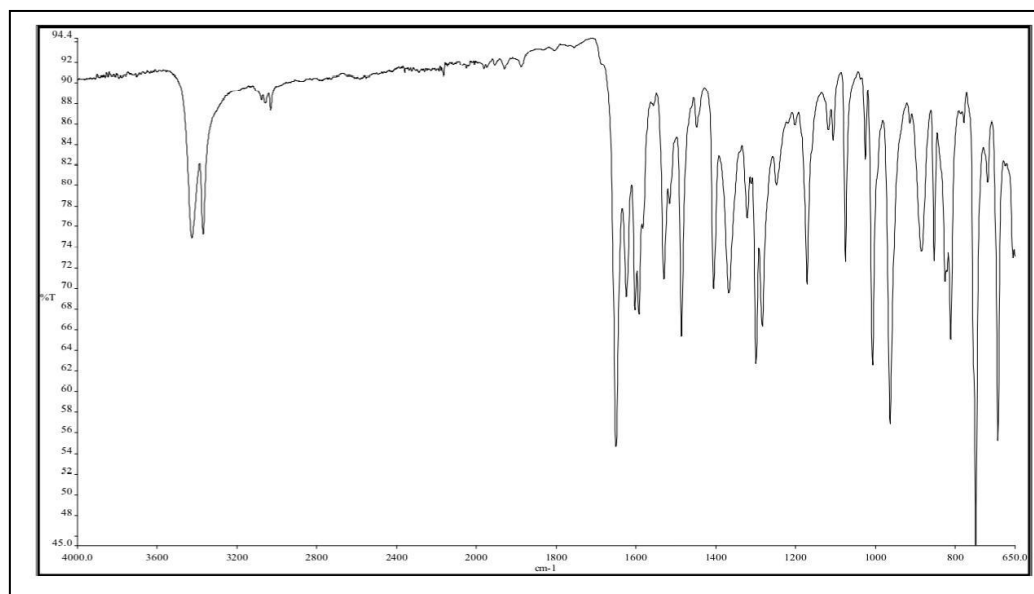


Fig. 3. FT-IR spectrum of 4-(4-bromophenylaminoisonitrosoacetyl) biphenyl (HL).

Absorption band at 1052 cm^{-1} , in the FT-IR spectrum of the free ligand 4-(4-bromophenylaminoisonitrosoacetyl)biphenyl (HL), attributed to the stretching vibration of the $\text{N}=\text{O}$ bond in the oxime group, shifts to a lower frequency region of $1046\text{--}1033\text{ cm}^{-1}$ in all synthesized metal complexes. This shift indicates effective coordination between the oxime group and the metal ion, specifically through the oxygen atom. In the case of amino acids, the stretching vibration of the ammonium ion (NH_3^+) is typically found in the range of $2933\text{--}3369\text{ cm}^{-1}$. During the complexation process, this ammonium ion becomes deprotonated, allowing the amino group (NH_2) to coordinate with the metal ion and the symmetric stretching of NH_2 is recorded. The complexes exhibit characteristic NH_2 stretching bands in the region of $3290\text{--}3248\text{ cm}^{-1}$, and this shift suggests that the phenylalanine ligand coordinates with metal ions through the nitrogen atom of the amino group, enhancing the stability of the complex. The FT-IR spectra of amino acids show asymmetric ($\nu_{as}(\text{COO}^-)$) and symmetric ($\nu_s(\text{COO}^-)$) stretching frequencies in the ranges of $1551\text{--}1634\text{ cm}^{-1}$ and $1379\text{--}1420\text{ cm}^{-1}$, respectively. In the metal complexes, these bands shift to $1675\text{--}1650\text{ cm}^{-1}$ and $1399\text{--}1383\text{ cm}^{-1}$, indicating the involvement of the deprotonated carboxylate oxygen atom in the coordination with the metal ion and the formation of stable five-membered chelate rings, facilitated by the coordination of the amino-N from the NH_2 group and the deprotonated carboxylate-O, significantly enhances the stability of the metal complexes. This strong coordination not only stabilizes the structure of the complexes but also positively influences their electrical conductivity and the stabilization provided by the chelation process reduces the likelihood of ionic dissociation in solution, which is beneficial for the conductivity of the synthesized compounds and the measured low molar.

IR spectra of the oxime ligand and the "mixed ligand complexes" align with the data that support structural conclusions of this study, confirming that both the oxime ligand (HL) and L-phenylalanine (phe) act as bidentate ligands and they form stable metal chelates. Furthermore, the results indicate that the Zn(II) complex adopts an octahedral geometry (Fig. 4). Stable coordination environments and efficient ligand-metal interactions can facilitate electron transfers, making these compounds suitable for various applications, including sensors and electronic devices, and the

presence of coordinated water and stable ligand solubility contributes to a controlled conduction profile, reducing the potential for ionic dissociation and thus enhancing the overall electrical stability of the compounds.

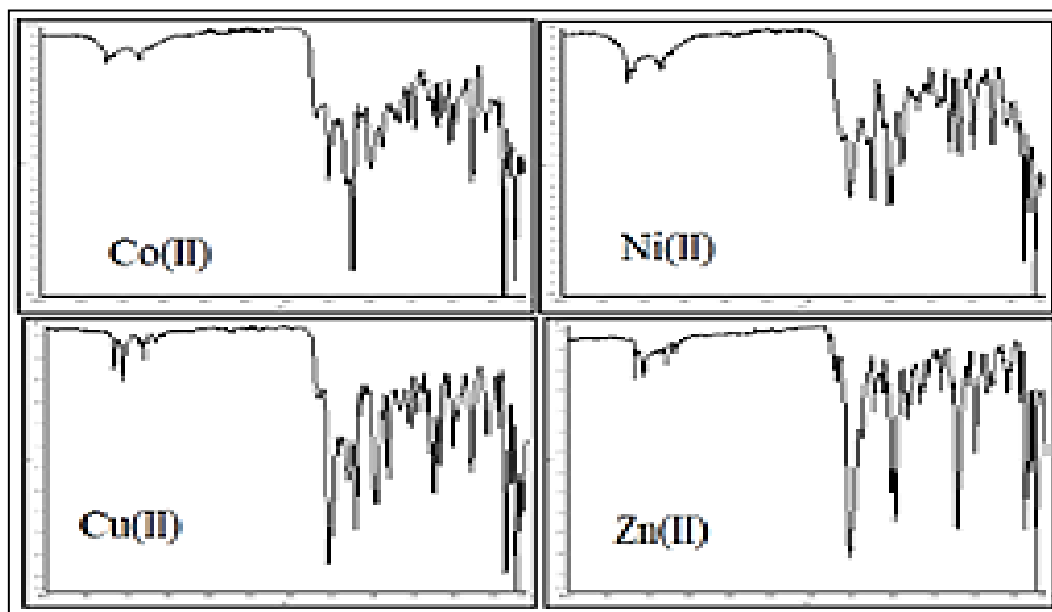
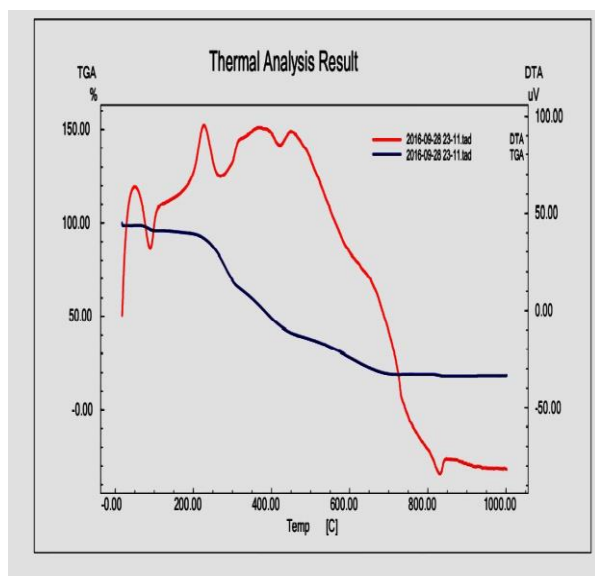


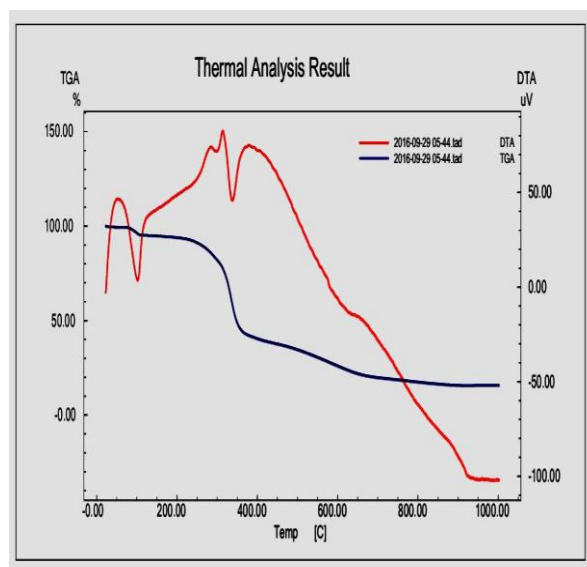
Fig. 4. FT-IR spectra of mixed ligand complexes [MeL(phe)(H₂O)₂]

As a result, the favourable thermal and magnetic properties observed enhance the potential of these metal compounds in electrochemical applications, where conductivity is a key performance factor (Fig. 5).

The thermal decomposition behavior of the Ni (II) complex [C₂₉H₂₈N₃O₆BrNi], reveals a two-step process at 21 to 920°C. In the first step, which occurs between 21°C and 194°C, there is an estimated mass loss of 6.12%, the second step involves a significant mass loss of 82.05% (calculated mass loss = 83.04%) and corresponds to the breakdown of the ligand, resulting in nickel oxide (NiO) and the cupric complex with the structure [C₂₉H₂₈N₃O₆BrCu]. Last exhibits a comparable two-stage decomposition pattern: the initial mass loss of 6.40% occurs from 21°C to 181°C, which is attributed to the decomposition of the ligand molecules, yielding copper oxide (CuO) as the final residue (calculated mass loss = 82.43%) and the Zn(II) complex, denoted as [C₂₉H₂₈N₃O₆BrZn].



a)



b)

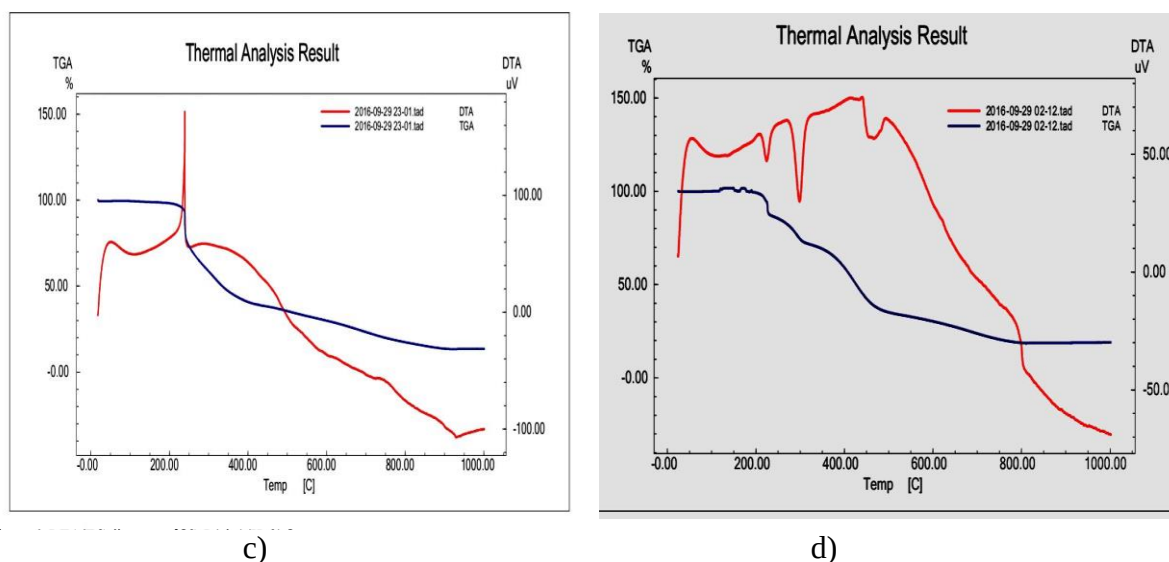


Fig. 5. Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TG) results. (A) DTA/TG analysis of the $[\text{CoL}(\text{phe})(\text{H}_2\text{O}_2)]$ complex; (B) DTA/TG analysis of the $[\text{NiL}(\text{phe})(\text{H}_2\text{O}_2)]$ complex; (C) DTA/TG analysis of the $[\text{CuL}(\text{phe})(\text{H}_2\text{O}_2)]$ complex; (D) DTA/TG analysis of the $[\text{ZnL}(\text{phe})(\text{H}_2\text{O}_2)]$ complex

Electrochemical investigation of phenylalanine-metal oxime ligand complexes using cyclic voltammetry. Cyclic voltammetry (CV) is used to study the redox status of ligands and their metal complexes. This method allows for the detailed investigation of the electrochemical properties and coordination interactions between metal ions and ligands, providing complementary information to other analytical techniques such as spectroscopy. In this study, the electrochemical behavior of phenylalanine and the oxime ligand (HL) was analyzed along with their metal complexes through cyclic voltammetry. The scanning potential was conducted in the range of -2.0 V to +2.0 V at a scan rate of 100 mV/s. The cyclic voltammogram of phenylalanine exhibited a clear anodic peak at +0.75 V, along with a cathodic peak at -0.87 V. These peaks indicate the redox processes occurring within the ligand, demonstrating its electroactive nature, especially for the oxime ligand (HL) (Table 1).

For example, the second complex (with the formula $[\text{C}_{29}\text{H}_{28}\text{N}_3\text{O}_6\text{BrNi}]$) showed an anodic peak at +1.35 V and a cathodic peak at -1.65 V, with a peak separation of 300 mV. This behavior indicates a reversible electrochemical reaction, highlighting the complex's ability to undergo both oxidation and reduction processes, and the presence of both the ligand and metal cations in the complexes confirms their coordination, which is essential for their electrochemical behaviour, and the HL ligand and DMF, recorded at a scan rate of 100 mV/s. The voltammogram features distinct anodic and cathodic peaks, which represent the electrochemical activity of the ligands and the associated metal ions.

Table 1. Electrochemical Data of the Complexes

Complex	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)
1	-	-1.56	-
2	+1.33	-1.64	301
3	-	+0.07	-0.525
4	+0.212	-0.07	121.2

E_{pa} : Anodic potential

E_{pc} : Cathodic potential

ΔE_p : Peak separation, calculated as $\Delta E_p = E_{pa} - E_{pc}$

Fig. 6 serves as a visual representation of the redox processes and highlights the potential applications of these complexes in electrochemical sensors or catalysts. The cyclic voltammetry experiments were conducted at varying scan rates from 20 mV/s to 500 mV/s to analyze the electron transfer dynamics and the transport of species to the electrode surface. The analysis revealed linear correlations between the square root of the scan rate ($v^{1/2}$) and the peak current (I_{pc}), which suggests that the processes are controlled by the adsorption of reactants onto the electrode surface (Fig. 6 b).

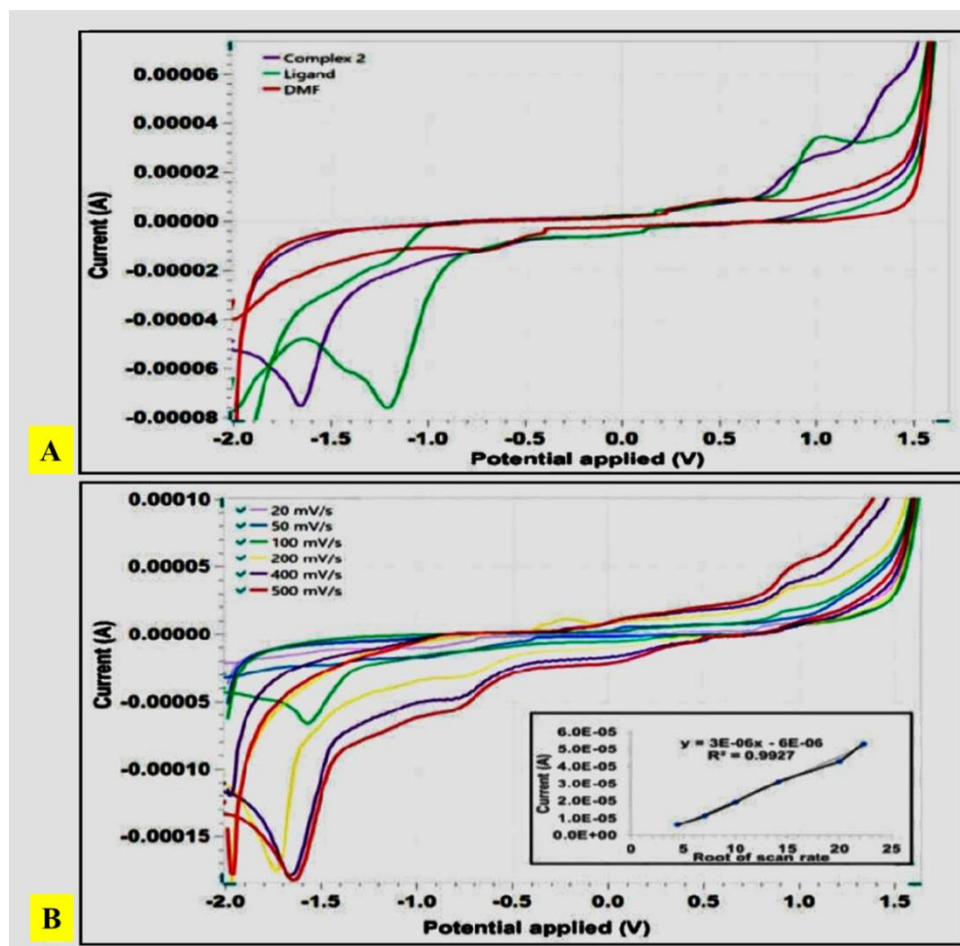


Fig. 6. Electrochemical investigation of phenylalanine-metal oxime ligand complexes using cyclic voltammetry. (A) Cyclic voltammograms of complex 2. (B) Cyclic voltammograms of complex 1 in DMF solution (0.1 M TBAP) at different scan rate

Conclusion

The present study synthesized and characterized a series of Co^{+2} , Ni^{+2} , Cu^{+2} and Zn^{+2} complexes with mixed ligands incorporating the oxime-based ligand 4-(4-bromophenylaminoisonitrosoacetyl)biphenyl and the amino acid L-phenylalanine. Their physicochemical properties were extensively investigated. The structural features and coordination modes of the ligands within the metal complexes confirmed the formation of stable 1:1:1 metal-ligand-amino acid complexes, where the ligands coordinated to the metal centres in a bidentate fashion. The molar conductivity data suggested the non-electrolytic nature of the complexes in solution, indicating the presence of coordinated water molecules and the absence of significant ionic dissociation. The NMR studies further substantiated the vibrational spectral findings, supporting the proposed coordination geometries. These findings contribute to a deeper understanding of the electronic and structural properties of the mixed-ligand complexes, paving the way for their potential applications in diverse fields such as catalysis, sensors, and electronic devices. The successful synthesis and characterization of these complexes highlight their significance in

coordination chemistry and their potential for development into functional materials with tailored properties.

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