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SYNTHESIS, STRUCTURAL ELUCIDATION AND ELECTROCHEMICAL BEHAVIOR OF SOME OXIME-PHENYLALANINE MIXED LIGAND COMPLEXES

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ABSTRACT. Four new mixed ligand complexes Me(II)/phenylalanine (phe)/HL [HL =4-(4-bromophenyl-aminoisonitrosoacetyl)biphenyl and Me = Co, Ni, Cu, Zn] were synthesized. These complexes are formulated as: [CoL(phe)(H_2O)$_2$], [NiL(phe)(H_2O)$_2$], [CuL(phe)(H_2O)$_2$] and [ZnL(phe)(H_2O)$_2$]. All the compounds were characterized by elemental analyses, FT-IR, magnetic susceptibility measurements, TG/DTA and cyclic voltammetry (CV) experiments. IR spectral data confirmed the coordination of the oxime ligand to the metal ions through the oxime and carbonyl oxygen. The geometrical structures of the complexes have been found to be octahedral. The measured molar conductance values of the complexes in DMF are in agreement with the non-electrolytic nature ofthe complexes. The elemental analyses confirm a 1:1:1 [metal:HL:L(phenylalanine)] molar ratio. Thermal behavior of the compound was investigated by thermal gravimetric analysis (TG) and differential thermal analysis (DTA) techniques. All the complexes were transformed into metal oxides after thermal degradation. The electrochemical properties of both ligand and their complexes were analyzed by cyclic voltammetry (CV) using glassy carbon electrode in DMF solution containing 0.1 M TBAP as supporting electrolyte.

KEY WORDS: Oxime, electrochemical characterization, mixed ligand complexes, amino acid, phenylalanine

INTRODUCTION

Oximes are noteworthy complexing agents due to the several electron-rich donor centers with unusual structural and chemical properties and they can form different types of coordination compounds with transition metal ions [1-4]. Oxime based ligands and their transition metal complexes are potential analytical, spectrophotometric and bioactive agents [4-9]. A huge body of literature is available on the chemical synthesis of oximes, oxime complexes and their applications [1-9].

Among the numerous organic ligands that have been employed for the formation of metallic complexes, amino acids consist a very important family of ligands, due to their versatility regarding the coordination mode and binding properties towards metal ions [10]. Amino acids are present in all living organisms, which are essential for various biochemical processes that ensure the permanence of life in the individuals, can act as potential oxygen and nitrogen donor ligands, too [11, 12]. Under biological conditions, amino acids bind to transition metal ions via the carboxylate-O and the amino-N donor atoms, thereby forming a thermodynamically stable five-membered chelate ring [13, 14]. The amino acid complexes with biologically active metal

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*Corresponding author. E-mail: fkaripcin@nevsehir.edu.tr ions have received much attention because they proved to be useful antibacterial agents, nutritive supplies for humans and animals, and also as models for metalloproteins [11-17].

L-Phenylalanine, containing non-polar phenyl group, is a common aromatic amino acid in living organisms. It is essential to cross the blood–brain barrier, changes into tyrosine in vivo and makes essential hormones, such as norepinephrine and epinephrine. The derivatives of phenylalanine are important in pharmaceutical field, e.g. in the case of Parkinson's drug L-3,4-dihydroxyphenylalanine (L-DOPA) [12, 14, 18].

The ligand quantity, ligand type, and coordination geometry have important factors on the biological activity and the other properties of metal-based complexes. In recent years, the formation and properties of mixed ligand complexes have received much attention because they can provide new materials with useful properties such as biological activity [14-20], electrical conductivity [21] and photoluminescence [22].

Many mixed amino acid complexes have considerable biological activity, such as antitumor properties, and usually increase the diffusibility of complexes and enhance their biological action inside the cell. Such systems are widely used in the field of chemotherapy [12, 14, 23]. The introduction of amino acid co-ligands such as phenylalanine might affect the planarity, hydrophobicity, and coordination geometry of synthesized complexes [17]. On the basis of stated facts, we have decided to prepare and characterize mixed ligand transition metal [Co(II), Ni(II), Cu(II), Zn(II)] complexes derived from 4-(4-bromophenylamino-isonitrosoacetyl)-biphenyl (HL) as primary ligand and phenylalanine (phe) as coligands. The complexes prepared were characterized particularly by elemental analysis, molar conductance, magnetic moment and FT-IR. The relative thermal stabilities of the complexes and their electrochemical behavior have also been discussed.

EXPERIMENTAL

Materials and measurements

All chemicals used were of reagent grade. All chemicals were purchased from Merck or Aldrich and were used as received. Melting points of all the compounds determined on EZ-Melt Automated Melting Point Apparatus in open glass capillaries. Elemental (C, H, N) analyses were carried out by standard methods with a LECO, CHNS-932 analyzer. The IR spectra of the compounds were recorded on a Perkin Elmer Spectrum 100 FT-IR instrument with the samples in 4000–600 cm^{-1} range. The molar conductivity measurements (Λ_m) were taken in dimethylformamide (DMF) at 25 ^oC, using concentrations of $1.0x10^{-3}$ M for the complexes. Thermal analyses (TG/DTA) were recorded on Shimadzu TG DTA 60 thermal analyzer with a heating rate of 10 K/min in dynamic N_2 atmosphere. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz FT-NMR. The proposed molecular structure of mixed ligand complexes are given in Figure 1.

Cyclic voltammetry measurements

Electrochemical measurements were conducted using an Autolab Potentiostat/Galvanostat PGSTAT-302N device controlled by Nova 2.1.4 program on a computer. A standard three electrode electrochemical cell was used for all measurements and main parts of this cell are a glassy carbon (GCE) as working electrode (2.0 mm diameter), platinum wire as counter electrode, and a Ag/AgCl as reference electrode. Previous to each experiment, GCE was polished with 1.0, 0.3 and 0.05 μm alumina powder. Residual alumina particles were removed by an ultrasonic bath. Afterwards, the electrode was dried and washed with pure DMF before use. Cyclic voltammetry studies were performed in DMF containing 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte with an analyte concentration of 2.0 mM. All solutions were purged with nitrogen for 10 min before measurements, and the experiments were carried out at room temperature.

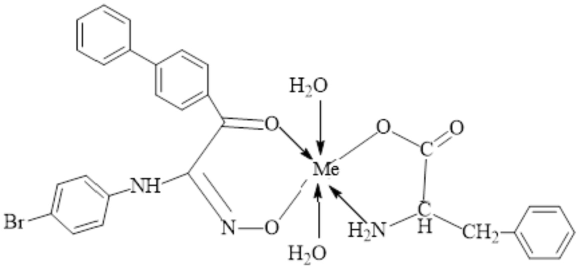
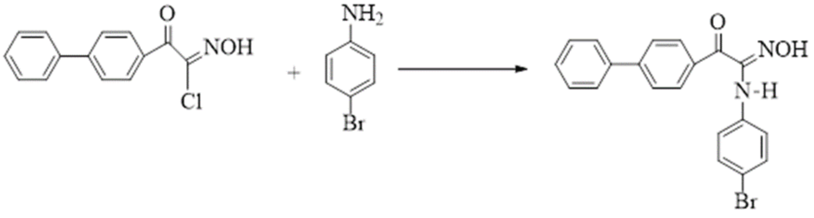


Figure 1. Proposed molecular structure of the mixed ligand complexes.

Synthesis

Synthesis of ligand (HL). 4-(4-Bromophenylaminoisonitrosoacetyl)biphenyl (HL) was prepared according to previously published procedures [3, 4]. First, 4-biphenylhydroximoyl chloride (1.5 mmol; 0.389 g) were dissolved in EtOH (50 mL) and the mixture was cooled 0 °C. Then 4-bromoaniline (3 mmol, 0.51 g) in EtOH (10 mL) was added dropwise to solution of first solution over 15 min with cooling. After that period, the reaction mixture was stirred 1 h at the same temperature. Then it was allowed to stir at ambient temperature for 2 h and diluted 100 mL distilled water. The resulting precipitate was filtered and then recrystallized from ethanol. The product was filtered off, washed distilled water, cold ethanol and dried on P_2O_5. The synthetic route of the ligand is shown in Scheme 1.



HL

Scheme 1. Synthesis of proposed ligand HL.

L. Yellow; yield: 90.5%; mp: 160 °C; mol wt: 395.23; elem. anal. calcd: C, 60.78; H, 3.82; N, 7.09%. Found: C, 61.17; H, 3.83; N, 7.17%; FT-IR (cm^{-1}): 3425 m (O-H), 3034 w, 738 s, 655 m (C-H)$_{Ar}$, 2917 w (C-H)$_{Al}$, 1667 s (C=O) and υ_{as}(COO^{-}), 1586 s (C=N), 1402 m (C=C)$_{Ar}$, 1215 m (C-N), 1172 m (C-C), 1052s (N-O); ^{1}H-NMR (CDCl$_3$): N-OH (s, 1H) 10.86 ppm; Ar(C-H) (m, 13H) 7.32-8.12 ppm; N-H (s, 1H) 6.76 ppm. ^{13}C NMR (CDCl$_3$, ppm): 183 (C=O); 147 (C=NOH); 127-139 C$_{Ar}$.

Synthesis of [CoL(phe)(H$_2$O)$_2$] (1). Complex **1** was prepared by addition of $Co(CH_3COO)_2{\cdot}4H_2O$ (1.5 mmol, 0.37 g) in 50 mL of ethanol to the ligand (1.5 mmol, 0.59 g) in 20 mL of hot methanol. The resulting mixture was refluxed for 30 min. To this solution, L-phenylalanine (1.5 mmol, 0.24 g) dissolved in 4 mL water containing KOH (1.5 mmol, 0.24 g) and 10 mL methanol was added with constant stirring and refluxed for 4 h. On standing, the solid product was collected by filtration, washed several times with cold water, ethanol, anhydrous ether and dried on P_4O_{10}.

[CoL(phe)(H_2O)$_2$]. Brown; yield: 67.4%; dp: 272 °C; mol wt: 653.35; elem. anal. calcd: C, 53.9; H, 4.32; N, 6.43%. Found: C, 53.71; H, 4.35; N, 6.29%; Λ_M (DMF solution, $\Omega^{-1}cm^2mol^{-1}$): 7.2; μ_{eff} BM: 1.33. FT-IR (cm^{-1}): 3359 b, 834 m (O-H), 3265 w (N-H), 3029 s, 725 m, 659 m $(C\text{-}H)_{Ar}$, 2921 w $(C\text{-}H)_{Al}$, 1653 m (C=O) and $\upsilon_{as}(COO^-)$, 1599 s C=N, 1399 m $(C{=}C)_{Ar}$ and $\upsilon_s(COO^-)$ 1261 m (C-O), 1216 m (C-N), 1179 m (C-C), 1046 m (N-O).

*Synthesis of [NiL(phe)(H_2O)$_2$] (**2**)*. Complex **2** was prepared by addition of $Ni(CH_3COO)_2{\cdot}4H_2O$ (1.5 mmol, 0.37 g) in 50 mL of ethanol to the ligand (1.5 mmol, 0.59 g) in 20 mL of hot methanol. The resulting mixture was refluxed for 30 min. To this solution, L-phenylalanine (1.5 mmol, 0.24 g) dissolved in 4 mL water containing KOH (1.5 mmol, 0.24 g) and 10 mL methanol was added with constant stirring and refluxed for 4 h. On standing, the solid product was collected by filtration, washed several times with cold water, ethanol, anhydrous ether and dried on P_4O_{10}.

[NiL(phe)(H_2O)$_2$]. Light brown; yield: 70.6%; dp: 246°C; mol wt: 653.12; elem. anal. calcd: C, 53.33; H, 4.32; N, 6.43%. Found: C, 52.86; H, 4.64; N, 6.64%; Λ_M (DMF solution, $\Omega^{-1}cm^2mol^{-1}$: 4.2; μ_{eff} BM: 2,70; FT-IR (cm^{-1}): 3354 b, 833 m (O-H), 3290 w (N-H), 3029 s, 720 m, 668 s $(C\text{-}H)_{Ar}$, 2958 w $(C\text{-}H)_{Al}$, 1650 m (C=O) and $\upsilon_{as}(COO^-)$, 1614 s (C=N), 1388 s $(C{=}C)_{Ar}$ and $\upsilon_s(COO^-)$, 1265 m (C-O), 1224 m (C-N), 1160 m (C-C), 1033 m (N-O).

*Synthesis of [CuL(phe)(H_2O)$_2$] (**3**)*. Complex **3** was prepared by addition of $Cu(CH_3COO)_2{\cdot}H_2O$ (1.5 mmol, 0.29 g) in 50 mL of ethanol to the ligand (1.5 mmol, 0.59 g) in 20 mL of hot methanol. The resulting mixture was refluxed for 30 min. To this solution, L-phenylalanine (1.5 mmol, 0.24 g) dissolved in 4 mL water containing KOH (1.5 mmol, 0.24 g) and 10 mL methanol was added with constant stirring and refluxed for 4 h. On standing, the solid product was collected by filtration, washed several times with cold water, ethanol, anhydrous ether and dried on P_4O_{10}.

[CuL(phe)(H_2O)$_2$]. Brown; yield: 62.4%; dp: 223 °C; mol wt: 657.97; elem. anal. calcd: C, 52.94; H, 4.29; N, 6.39%. Found: C, 52.49; H, 4.03; N, 6.78%; Λ_M (DMF solution, $\Omega^{-1}cm^2mol^{-1}$): 3.7; μ_{eff} BM: 1.75. FT-IR (cm^{-1}): 3332 b, 838 s (O-H), 3248 s (N-H), 3032 s, 719 m, 673 m $(C\text{-}H)_{Ar}$, 2961 w $(C\text{-}H)_{Al}$, 1663 w (C=O) and $\upsilon_{as}(COO^-)$, 1615 s (C=N), 1383 s $(C{=}C)_{Ar}$ and $\upsilon_s(COO^-)$, 1273 m (C–O), 1217 m (C-N), 1160 m (C-C), 1033 w (N-O).

*Synthesis of [ZnL(phe)(H_2O)$_2$] (**4**)*. Complex **4** was prepared by addition of $Zn(CH_3COO)_2{\cdot}H_2O$ (1.5 mmol, 0.32 g) in 50 mL of ethanol to the ligand (1.5 mmol, 0.59 g) in 20 mL of hot methanol. The resulting mixture was refluxed for 30 min. To this solution, L-phenylalanine (1.5 mmol, 0.24 g) dissolved in 4 mL water containing KOH (1.5 mmol, 0.24 g) and 10 mL methanol was added with constant stirring and refluxed for 4 h. On standing, the solid product was collected by filtration, washed several times with cold water, ethanol, anhydrous ether and dried on P_4O_{10}.

[ZnL(phe)(H_2O)$_2$]. Light orange; yield: 54.2%; dp: 248 °C; mol wt: 659.81; elem. anal. calcd: C, 52.79; H, 4.27; N, 6.37%. Found: C, 52.58; H, 4.77; N, 6.15%; Λ_M (DMF solution, $\Omega^{-1}cm^2mol^{-1}$): 2.3; μ_{eff} BM: Dia.; FT-IR (cm^{-1}): 3333 b, 836 m (O-H), 3255 s (N-H), 3029 m, 720 m, 681 s $(C\text{-}H)_{Ar}$, 2958 m $(C\text{-}H)_{Al}$, 1675 w (C=O), 1614 s (C=N), 1388 s $(C{=}C)_{Ar}$ and $\upsilon_s(COO^-)$, 1265 m (C-O), 1224 w (C-N), 1160 m (C-C), 1033 m (N-O). ^1H-NMR ($CDCl_3$): Ar(C-H) (m, 13H) 7.34-8.23 ppm; N-H (s, 1H, oxime) 7.04 ppm; N-H (s, 1H, phe) 6.21 ppm; H_2O (coord. s, 4H) 5.82 ppm; CH (m, 1H, phe) 4.41 ppm; CH_2 (d, 2H, phe) 4.08 ppm.

RESULTS AND DISCUSSION

Microanalyses and molar conductance measurements

The synthesized ligand and the mixed ligand complexes were investigated using various physio-chemical properties like melting point (m.p.), color, yield, micro analytical data and molar conductance value are given in the experimental part. The obtained C, H, and N analytical data of the synthesized metal(II) complexes agreed well with the calculated values which confirm a 1:1:1 (metal:HL:L-phenylalanine) molar ratio.

Molar conductivity measurements of the metal complexes were determined using freshly prepared solutions of the complexes in DMF at room temperature.The measured molar conductance values of 10^{-3} M solutions of the mixed ligand complexes werefound to be in the range 2.3–7.2 S cm^2 mol^{-1} which is in agreement with the non-electrolytic nature ofthe complexes [17]. The results of the elemental analysis of the mixed ligand complexesare in good agreement with those required by the proposed formula.

NMR spectra of the oxime ligand (HL) and the mixed ligand Zn complex {$[ZnL(phe)(H_2O)_2]$}

The oxime ligand in $CDCl_3$ was studied by ^1H and ^{13}C NMR spectroscopy. The deuterium-exchangeable proton of the (N–OH) group for the HL showed a chemical shift at 10.86 ppm as a singlet [4]. In the region of 7.32–8.12 ppm, chemical shifts for aromatic hydrogens were assigned as multiplet. The chemical shift of the aromatic amine proton of HL appeared at 6.76 ppm as a singlet. In ^{13}C NMR spectrum, the aromatic carbon resonances were shown in between δ = 127-139 ppm which is corresponding to the bromophenyl and biphenyl rings in the compound. The carbonyl and oxime carbons were clearly observed at δ = 183 and 147 ppm, respectively and more slightly deshielded in the spectra. The increasing electronegativity of oxygen and nitrogen atoms and different environment and conformations cause a deshielding effect for these signals. All of these values prove that the oxime ligand formed and are in good agreement with the values previously reported [4, 24, 25]. Since Co(II), Ni(II) and Cu(II) complexes are paramagnetic, their ^1H and ^{13}C spectra could not be obtained.

The ^1H NMR spectrum of free oxime ligand were compared with the diamagnetic mixed ligand Zn(II) complex taken in $CDCl_3$ medium. Unfortunately, the insolubility of phenylalanine in $CDCl_3$ makes it difficult to obtain ^1H NMR spectrum of phenylalanine to further clarify the binding of phenylalanine ligand to the metal ions. Zn(II) complex are well established in their predictable regions [26]. The absence of COOH proton of phe peak in the Zn(II) complex indicates that this proton is removed during chelation process and this prove that phe ligand is coordinated through bidentate mode with the Zn(II) ion via amino–N and deprotonated carboxylato–O atoms [26]. Also, the disappearance of proton peak of –NOH at 10.86 ppm for HL in the complex prove that oxime ligand is coordinated through bidentate mode with the Zn(II) ion via carbonyl and deprotonated oximato–O atoms. In the region of 7.34–8.23 ppm, chemical shifts for aromatic hydrogens were assigned as multiplet. The chemical shifts of the aromatic amine proton of HL and amine proton of phe appeared at 7.04 and 6.21 ppm as a singlet, respectively. In addition, the spectrum of Zn(II) complex shows a characteristic new peak centered at 5.82 ppm, which confirm the presence of coordinated water molecule [17, 27]. The protons of the CH and CH_2 groups for phe in the Zn(II) complex showed chemical shifts at 4.41 and 4.08 ppm. Thus, the NMR studies reinforce the findings drawn from the vibrational spectral studies about the mode of binding.

FTIR spectroscopy

The IR spectra of the investigated complexes (Figure 3) are compared with those of the free ligand (Figure 2) to determine the coordination sites. The basic theory involved is that the stretching modes of the ligands change upon complexation due to weaking/strengthening of the bonds involved in the bond formation resulting in subsequent change in the position of the bands appearing in the IR spectrum. The spectrum of the oxime ligand exhibits a characteristic band at 3425 cm^{-1} due to the stretching vibration of the OH group. On the other hand, the IR spectra of all the complexes show broad band at 3359–3332 cm^{-1}which have been assigned to υ(OH) stretching vibration of water molecules, in accordance with the results of the elemental analysis listed in Section 2.3 [11, 28-30].

The oxime ligand HL shows strong absorption band at 1667 cm^{-1} due to υ(C=O) and 1586 cm^{-1} due to υ(C=N). The (C=N) band is shifted to 1615-1599 cm^{-1} in the complexes indicating the involvement of the nitrogen atom of the azomethine group in the coordination to the metal ion [11, 28-32]. The (C=O) band is located in the same region (1675-1650 cm^{-1}) with $\upsilon_{as}(COO^-)$ stretching bands of amino acidsor disappeared indicating the participation of carbonyl oxygen atom in coordination [26].

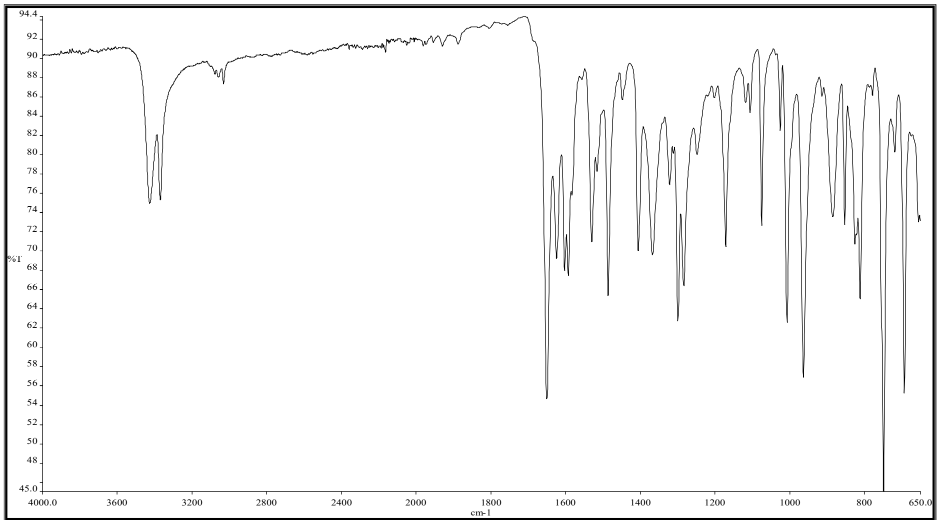


Figure 2. FT-IR spectrum of 4-(4-bromophenylaminoisonitrosoacetyl)biphenyl (HL).

The strong absorption at 1052 cm^{-1}due to υ(N=O)of the oxime group in the free HL ligand is shifted towards lower frequency regions 1046-1033 cm^{-1}in all the complexes [3, 33, 34]. Allthese features indicate that the HL is coordinated to the metal ion through the oxygen of the oxime group.

The $\upsilon(NH_3^+)$ of free amino acids is observed in the range 2933-3369 cm^{-1} [11]. In the complexes, NH_3^+ gets deprotonated and binds to metal through the neutral NH_2 group. The NH_2 symmetric stretching is recorded at 3344 cm^{-1} in the IR spectrum of free phenylalanine [35]. The IR spectra of complexes show characteristic bands of $\upsilon(NH_2)$ in the region 3290–3248 cm^{-1} [11, 36]. The spectra of amino acids display $\upsilon_{as}(COO^-)$ and $\upsilon_s(COO^-)$ frequency in the 1551-1634 cm^{-1} and 1379-1420 cm^{-1} range, respectively. In the metal complexes, $\upsilon_{as}(COO^-)$ and $\upsilon_s(COO^-)$ stretching bands are located in the region 1675-1650 cm^{-1} and 1399-1383 cm^{-1}, respectively [11, 23]. The ligand L-phenylalanine coordinates with M(II) ions through amino-N of NH_2 group and deprotonated carboxylato-O of COOH group to form a stable 5-membered chelate ring [17, 29, 30].

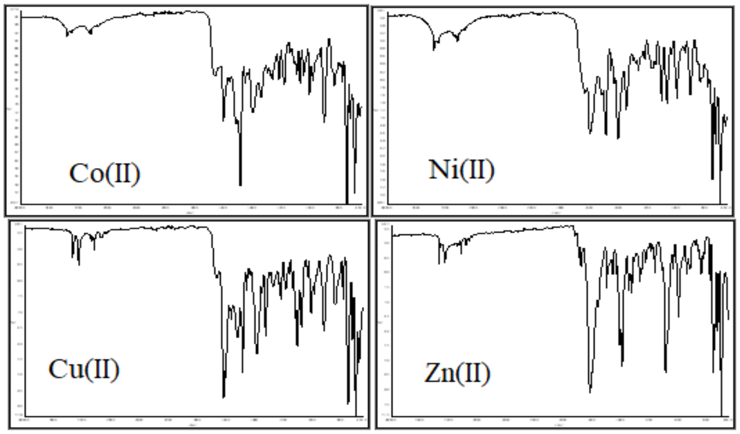


Figure 3. FT-IR spectra of the mixed ligand complexes [MeL(phe)(H_2O)$_2$].

The infrared spectra of the oxime ligand and the mixed ligand complexes are very much consistent with the structural data presented in this paper and these absorption data are in agreement with those previously reported for similar compounds [23, 28-36]. From this study, both the ligands HL and phe are bidentate which form stable metal chelates through the oxygen of deprotonated oxime group and carbonyl oxygen and amino-NH_2 and deprotonated carboxylato-O atoms, respectively.

Magnetic measurements

In a magnetic field, the paramagnetic compounds will be attracted while the diamagnetic compounds repelled. Therefore, paramagnetic substances will have positive susceptibilities. Thus, the magnetic susceptibility measurements provide information regardingthe geometric structure of the complexes. The room temperature magnetic moment measurements show that the Zn(II) complex is diamagnetic and are likely to octahedral. The Ni(II) complex is paramagnetic with magnetic susceptibility value of 2.70 B.M., which fits the d^8 metal ion in an octahedral structure, the two-spin value of 2.83 B.M. [3, 36]. Cu(II) and Co(II) complexes are paramagnetic with magnetic susceptibilities of 1.75 B.M. and 1.33 B.M., respectively. Measured value of the magnetic moment for the cobalt complex, which corresponds to one unpaired electron and falls within the range normally observed for low-spin octahedral Co^{2+} complexes. The Cu(II) complex fits the spin value of 1.73 B.M. indicating an octahedrald^9-system [26, 33, 36-38].

Thermal studies

Thermal analysis (DTA/TG) for themetal complexes was carried out within the temperature range from ambient temperature up to 1000 °C. The correlations between the different decomposition steps of the complexes with the corresponding weight losses are discussed in terms of the proposed formula of the complexes. Initially, first weight losses correspond to the removal of coordinated water molecule. All the complexes (**1**–**4**) in the first stage show the weight loss of 5.90–6.40% within the temperature range 21–238 °C. These weight losses correspond to the removal of water molecule from the complexes [17]. Amino acid ligand, L-phenylalanine moiety elimination occurred the second stage. In the final stage, decomposition of primary oxime ligand leading to the formation of MO (metal oxide) as residue [17, 39-43]. DTA/TG profiles of these complexes are given in Figures 4-7.

The Co(II) complex (**1**) with the general formula [$C_{29}H_{28}N_3O_6BrCo$] is thermally decomposed in two successive decomposition steps. The first step with estimated mass loss of 6.20% was found within the temperature range 21–182 ^{o}C and corresponds to loss of two H_2O molecules (calculated mass loss = 5.51%). The second step occurs within the temperature range 182–850 ^{o}C with an estimated mass loss 81.28% (calculated mass loss = 83.02%) are reasonably accounted for the decomposition of the ligand molecules leaving CoO residue.

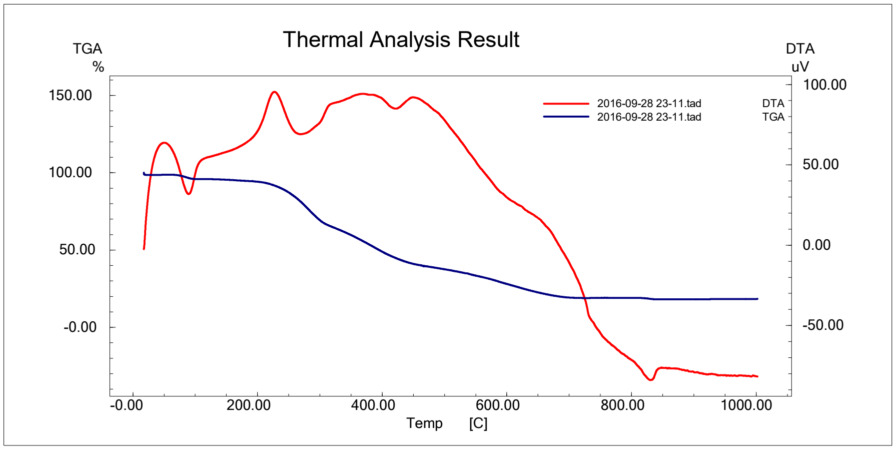


Figure 4. DTA/TG diagram of [CoL(phe)(H_2O)$_2$].

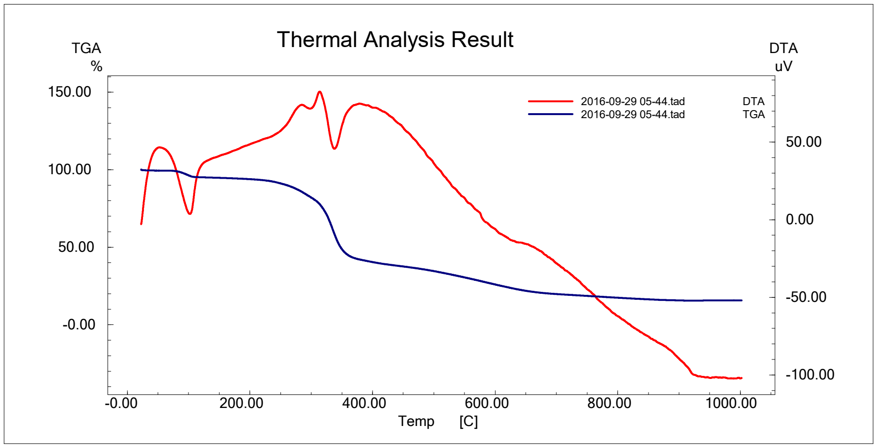


Figure 5. DTA/TG diagram of [NiL(phe)(H_2O)$_2$].

The Ni(II) complex **(2)**, [$C_{29}H_{28}N_3O_6BrNi$], is thermally decomposed in two successive decomposition steps within the temperature range 21–920 ^{o}C. The first step with estimated mass loss of 6.12% was found within the temperature range 21–194 ^{o}C and corresponds to loss of two

H_2O molecules (calculated mass loss = 5.52%). The second decomposition step of estimated mass loss 82.05% (calculated mass loss = 83.04%) which is responsibly accounted for the decomposition of the ligand molecules with a final oxide residue of NiO.

The Cu(II) complex **(3)**, with the general formula [$C_{29}H_{28}N_3O_6BrCu$], shows decomposition pattern of two stages. The first steps with estimated mass loss of 6.40%, found within the temperature range 21–181 °C. Corresponding to loss of two H_2O molecules (calculated mass loss = 5.48%). The second steps with estimated total mass loss of 81.20%, found within the temperature range 181–910 °C corresponding to decomposition of the ligand molecules (calculated mass loss = 82.43%) leaving CuO residue.

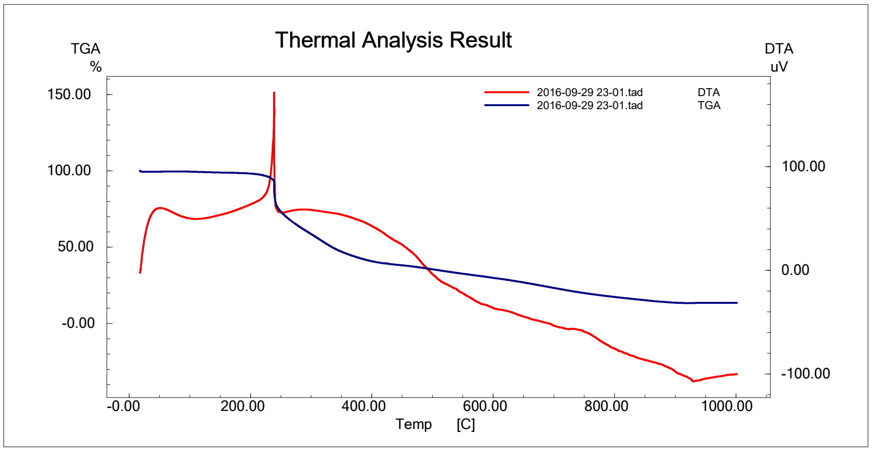


Figure 6. DTA/TG diagram of [CuL(phe)(H_2O)$_2$].

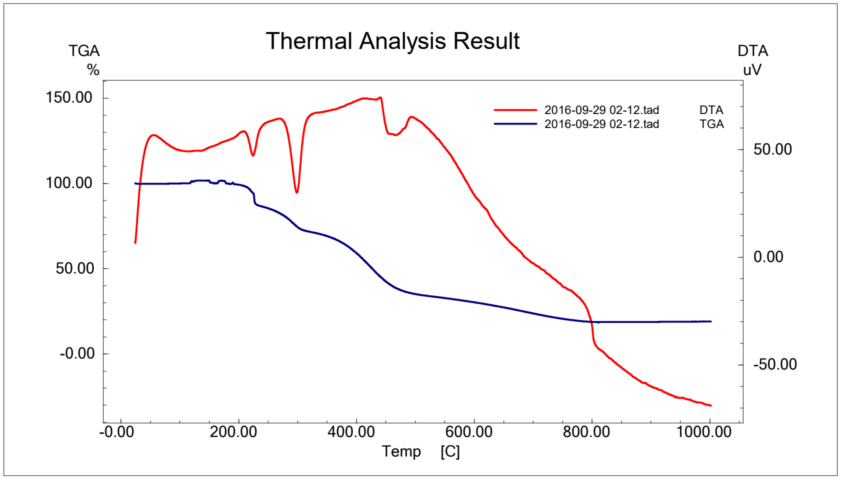


Figure 7. DTA/TG diagram of [ZnL(phe)(H_2O)$_2$].

The Zn(II) complex **(4)**, with the general formula [$C_{29}H_{28}N_3O_6BrZn$], also shows decomposition pattern of two stages. The first step with estimated mass loss of 5.90%, found within the temperature range 21–238 °C. Corresponding to loss of two H_2O molecules (calculated mass loss = 5.46%). The second step with anestimated total mass loss 81.63% which is due to loss of theligand molecules leaving ZnO residue occurring withinthe temperature range 238–840°C (calculated mass loss = 82.20%).

Cyclic voltammetry

The application of electrochemical methods to study of the coordination of metal ion provides a helpful complement to the previously used methods of investigations such as spectroscopy. The electrochemical properties of ligands and their complexes were investigated by cyclic voltammetry. The potential was scanned in the range -2.0 V to +2.0 V at a scan rate 100 mVs^{-1}. The cyclic voltammogram of phenylalanine showed one anodic wave and one cathodic wave located at +0.75 V and -0.87 V. In the voltammogram of HL, one anodic wave is observed at +0.95 V which can be attributed to the oxidation of the oxime group [44]. The results of cyclic voltammetric investigations of all the complexes are summarized in Table 1 and the cyclic voltammogram of complex **2**, HL and DMF are presented in Figure 8. The anodic wave seen around +0.95 V in the CVs for all metal complexes are presumed to be ligand based oxidation. The voltammograms of the metal complexes, in addition to the ligands peak, also have oxidation and reduction peaks. The peaks of the complexes confirm the presence of metal cations and ligands in the complexes.

Table 1. Electrochemical data of the complexes[a].

Complex	E_{pa} (V)	E_{pc} (V)	ΔE_p (mV)
1	-	-1.56	-
2	+1.35	-1.65	300
3	- 0.07	-0.52	450
4	+ 0.21	-0.09	120

[a]Supporting electrolyte, TBAP (0.1 M) in DMF; Scan rate, 100 mVs^{-1}; $\Delta Ep = (Epa - Epc)$, where Epa and Epc are anodic and cathodic potentials, respectively.

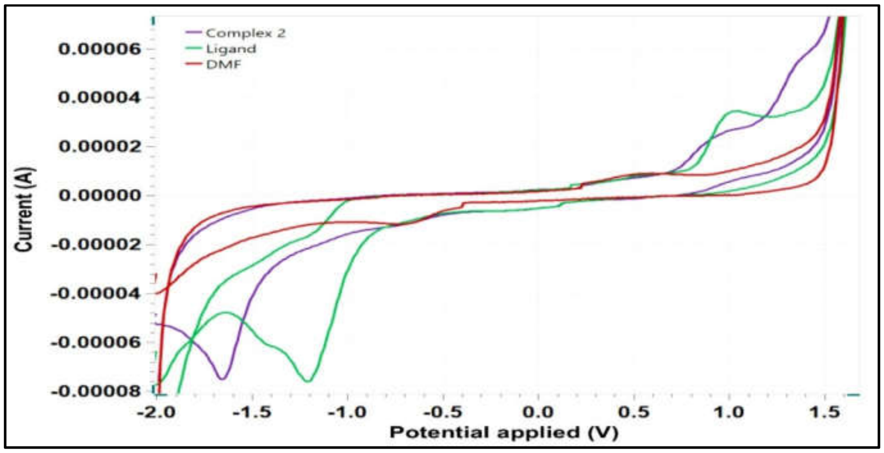


Figure 8. Cyclic voltammograms of complex **2**, HL and DMF (0.1 M TBAP) at scan rate of 100 mV s^{-1} versus Ag/Ag + electrode.

Through the analysis of the CV voltammograms obtained at various scanning speeds, the transfer of electrons and the way of transporting the substance to the electrode surface are known. The cyclic voltammetric behaviors of the ligand and complexes were studied by varying the sweep rate from 20 mVs^{-1} to 500 mVs^{-1}. Linear correlations were obtained between square root of scan rate (v$^{1/2}$) and peak current ($I_{pc)}$ (Figure 9). On the other hand, the slope values of the correct equations between the logarithm of the potential scanning speed (log v) and the logarithm of the peak current (log I_{pc}) were found in values ranging from 0.75 to 1.0. These values confirmed that the process was adsorption controlled.

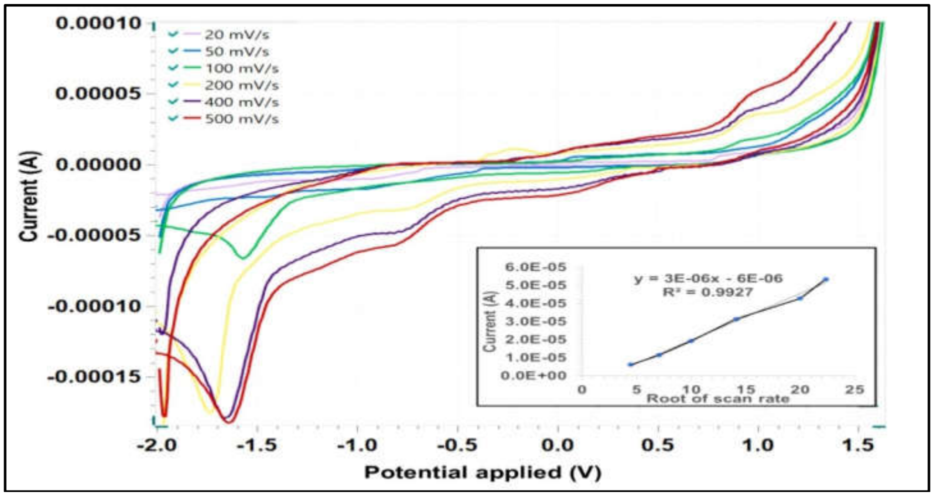


Figure 9. Cyclic voltammograms of complex 1 in DMF solution (0.1 M TBAP) at differentscan rates.

CONCLUSION

In conclusion, a new (4-(4-bromophenylaminoisonitrosoacetyl)biphenylligand (HL) and their mixed ligand Co(II), Ni(II), Cu(II) and Zn(II) complexes with L-phenylalanine were synthesized and were characterized by elemental analysis, magnetic susceptibility measurements, CV, FT-IR, and ^{1}H NMR. Elemental analysis, stoichiometric and spectroscopic data of the metal complexes indicated that the complexes can be formulated as [MeL(phe)(H_2O)$_2$]. The results obtained by CV method pointed out that the electrode reaction was adsorption controlled.

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