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Cu(II), Zn(II), and Cd(II) Complexes of L-Asparagine: Preparation, Characterization, and Electrochemical Properties

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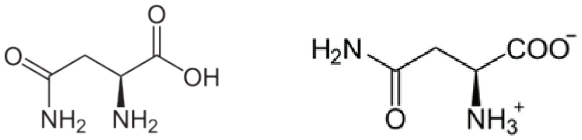
Abstract

L-asparaginato complexes of Copper(II), Zinc(II) and Cadmium(II) were synthesized from their respective metal oxide and L-asparagine. These prepared complexes were characterized by their metal content analysis, infrared, and ultraviolet-visible spectral studies, magnetic susceptibility measurement, thermal analysis, and cyclic voltammetric measurement. Physico-chemical investigations reveal that $[M(OOCCHNH_2CH_2CONH_2)_2]$, (M = Cu(II), Zn(II), and Cd(II)) is the general formula for the complexes. L-asparagine combines with metal oxides to form bis(L-asparaginato)metal(II) complexes in which the metal(II) ion is hexa-coordinated by the O^- anion of the carboxylate ion, the N atom of the amino group, and the O atom of the side chain carboxamide group from each of the two asparaginato species. The statement is corroborated by the analyses conducted for these complexes. The redox behaviours of the metal ion, both in its free state and when complexed, exhibit notable differences, as demonstrated by voltammetric investigations. Both peak currents and peak potentials respond sensitively to the complexation process, as it is expected.

Keywords: Biomolecule, Asparagine, Anti-cancer drugs, Spectral analysis, Cyclic voltammetry.

I. Introduction

Amino acids are the major building wedges of protein and nitrogenous backbones of many biomolecules such as neurotransmitters and hormones. They exhibit various functions in enabling life on earth and its emergence[1]. Among 22 proteinogenic amino acids, L-asparagine is a non-essential α-amino acid that is used in the biosynthesis of proteins. An α-amino group, an α-carboxylic acid group, and a side chain carboxamide make up this aliphatic amino acid (Scheme I). At physiological pH, the α-amino group is in the protonated $-NH_3^+$ form and the α-carboxylic acid group is in the deprotonated $-COO^-$ form, designating it as a polar[2]. The amino side chain groups are involved for formation of metal center and its catalytic reaction in proteins. Microenvironment around the metal center is essential for molecular recognition, substrate fixation and catalytic functions of enzymes[1].



Scheme I: The Skeletal structure of L-asparagine along with its zwitterionic form.

Amino acids and their metal complexes play a wide range of roles in both prokaryotic and eukaryotic systems, researchers are therefore interested in these compounds[3]. The fundamental aspects of complex formation between various metal ions and amino acids are well established. Transition metals are fascinating for developing anti-cancer drugs because of their variable oxidation states, coordination numbers and capability to bind with bioactive ligands including various amino acids. Asparagine has the potential to function as a ligand for Zn(II), Cd(II), and Pb(II) ions, as documented in a consistent ionic medium within the solution phase[4]. The crystal structure of the bis(L-asparaginato)copper(II) complex was determined using the film data collection method[5], and a subsequent report by Vencato *et al*[6], provided a more precise redetermination. The neutralization reaction between NaOH and L-asparagine yielded the L-asparaginato anion, which then reacted with $CuSO_4.5H_2O$ in an aqueous medium, resulting in the formation of royal-blue $Cu(L\text{-asparaginato})_2$ single crystals. The formation constants for the interactions of Zn(II) and Cd(II) with L-asparagine were assessed, and the existence of the M(II)-L-asparagine-creatinine mixed-ligand complex was proven by potentiometric studies[7]. Additionally, the complex formation equilibria of the ternary complexes Cu(II)-isoniazid-L-asparagine and Zn(II)-isoniazid-L-asparagine were evaluated using the potentiometric titration method[8].

The investigation of the mixed-ligand complex containing asparagine in combination with different metal ions has been conducted by Willims[9] as a potential antimetabolite in neoplastic cells. W. Kreis[10], reported the role of amino acid for tumor-cell treatment by depletion and antagonists actions of amino acid. The preparation, characterization, and thermal study of few mixed ligand complexes of urea and asparagine with various metal ions was also studied by Jamil *et al*[11]. The literature has also addressed the antibacterial investigation of mixed-ligand complexes formed by bivalent metal ions along with L-asparagine and Schiff bases[12]. Although there have been limited previous studies on asparagine-metal complexes, most of these investigations were conducted in solution phase, and the mixed-ligand complexes were synthesized using various methods. This report outlines

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a straight forward synthetic approach for Metal(II)-L-asparaginato complexes, along with their physico-chemical characterization and cyclic voltammetric properties.

II. Experimental

Chemicals

L-asparagine monohydrate (BDH Chemical Ltd. England), $CuCl_2.2H_2O$ (Peking Chemical Works, China), ZnO (MERCK, India), $ZnCl_2$ (MERCK, India), CdO (MERCK, Germany), $CdCl_2$ (MERCK, Germany), KCl (BDH, UK), N_2 (99.99% pure, BOC, Bangladesh) were used to carry out the experimental works. Solvents employed throughout this research included methanol, ethanol, acetone, hexane, and deionized water. All chemicals are used as purchased and are of analar grade.

Equipments and Methods

The STUART, Model SMP11 melting point apparatus from VWR, International Ltd. UK was used to measure the melting points of the complexes, which has up to 300°C recordable temperatures. The standard procedure was followed to qualitatively assess the complexes, solubility using a range of solvents, viz. water, methanol, ethanol, hexane, and acetone. To quantify the metal contents into the complexes, the complexometric titrimetric method was used. Before performing the titration with the standard Na_2EDTA solution in the presence of a suitable metal indicator, the solution was buffered to the appropriate pH. Infrared spectra (IR) of the complexes were recorded on a Shimadzu (Japan) infrared spectrometer model IR-470 in the range of 400-4000 cm^{-1} using KBr pellets. Using distilled water or methanol as reference solvents, the UV-visible recording spectrometer, model UV-160A, Shimadzu (Japan), was used to record the UV-visible spectra (electronic spectra) of the complexes in the wavelength range of 200-1100 nm. The SHERWOOD SCIENTIFIC Magnetic Susceptibility (MSB), Cambridge (England), Model: Magway MSB Mkl, was used to measure the magnetic susceptibility of these complexes. The quasi-static thermogravimetric (QSTG) analysis was performed in a CARBOLITE calibrated muffle furnace of the type CWF 11/5. The weight loss for each sample was recorded at intervals of 50°C in a dry, clean porcelain crucible, up to a maximum temperature of 750°C. The present study employed a custom-made potentiostat Model 2040 for cyclic voltammetry, developed by Advanced Analytics (AA), Virginia, USA. The potentiostat voltage compliance is ±12 V and the maximum current output is 20 mA. The voltammetric cell was a three-electrode system including a glassy carbon working electrode, Ag(s)/AgCl(s) (Satd. KCl) reference electrode, and a platinum wire counter electrode. The cell system is connected to a C_3-cell stand procured from BAS, USA.

Synthesis of the complexes

(i) Bis(L-asparaginato)copper(II), $[Cu(OOCCHNH_2CH_2CONH_2)_2]$

Black powdery CuO was first prepared by heating $CuCl_2.2H_2O$ for an hour at a temperature of approximately 600°C in a calibrated muffle furnace. To an aqueous solution of $NH_2COCH_2CHNH_2COOH.H_2O$ (0.60 g in 50 mL) an excess amount of CuO was added. The resulting solution was heated slowly for about an hour while a deep blue solution was formed. It was then filtered to remove undissolved CuO. The volume of the solution was then reduced and kept at room temperature for crystallization. A royal blue powdery product was then obtained, which were filtered, washed with distilled water and dried in the air first and then over silica gel.

$$CuO + 2\ NH_2COCH_2CHNH_2COOH.H_2O \xrightarrow{H_2O}$$
$$[Cu(OOCCHNH_2CH_2CONH_2)_2] + H_2O$$

Yield (g): 0.86; m.p. (°C): >300; FTIR (cm^{-1}): 3350-3420 (s, br), 2925 (w), 2240 (w), 1686 (s), 1408 (m), 1350 (w), 1299 (w), 1209 (m), 1156 (s), 1016 (w), 958 (w), 932 (w), 892 (w), 801 (m), 661 (s), 602 (m), 560 (w), 516 (w, sh), 452 (s).

(ii) Bis(L-asparaginato)zinc(II), $[Zn(OOCCHNH_2CH_2CONH_2)_2]$

To an aqueous solution of $NH_2COCH_2CHNH_2COOH.H_2O$ (1.00 g in 50 mL) an excess amount of ZnO was added and the mixture was heated slowly for about an hour. It was filtered to remove the undissolved ZnO and the filtrate was kept at room temperature for crystallization while a white crystalline product was formed. The product was filtered, washed with distilled water, and dried in the air first and then over silica gel.

$$ZnO + 2\ NH_2COCH_2CHNH_2COOH.H_2O \xrightarrow{H_2O}$$
$$[Zn(OOCCHNH_2CH_2CONH_2)_2] + H_2O$$

Yield (g): 1.02; m.p. (°C): >300; FTIR (cm^{-1}): 3395 (s), 3340 (w), 2920 (w, sh), 2340 (m), 2250 (w), 1656 (s), 1600 (m), 1402 (s), 1224 (s), 1124 (w), 1092 (w), 1008 (s), 990 (w), 944 (w), 914 (w), 904 (w), 890 (m), 792 (s), 785 (w), 640 (s), 604 (m), 568 (s), 448(m), 416 (w).

(iii) Bis(L-asparaginato)cadmium(II), $[Cd(OOCCHNH_2CH_2CONH_2)_2]$

An excess amount of CdO was added to an aqueous solution of $NH_2COCH_2CHNH_2COOH.H_2O$ (1.00 g in 50 mL). The mixture was heated for an hour and filtered to remove the undissolved CdO. The filtrate was kept at room temperature. White crystalline product was formed which was then filtered, washed with water and dried over silica gel.

$$CdO + 2\ NH_2COCH_2CH(NH_2)COOH.H_2O \xrightarrow{H_2O}$$
$$[Cd(OOCCHNH_2CH_2CONH_2)_2] + H_2O$$

Yield (g): 1.25; m.p. (°C): >300; FTIR (cm^{-1}): 3360-3200 (s, br), 2920 (w), 2790 (w), 2550 (w), 2360 (w), 2260 (w), 1684 (s), 1570 (w), 1392 (m), 1340 (w), 1210 (s), 1112 (w), 1092 (w), 1056 (s), 998 (s), 944 (m), 932 (w), 904 (m), 884 (m), 872 (s), 790 (s), 768 (m), 742 (w), 668 (s), 605 (m), 564 (w), 448 (s), 412 (w).

III. Results and Discussion

In the current study, all complexes were prepared by an acid-base reaction involving heating of L-asparagine and the corresponding MO (M = Cu(II), Zn(II) and Cd(II)) in aqueous media. Crystalline and air stable complexes of each were collected from the clear solution on standing after filtering the unreacted metal oxide. The complexes are only soluble in hot water and are insoluble in methanol, ethanol, acetone, and n-hexane. They have relatively high melting point, exceeding 300°C, suggesting their predominantly ionic nature. Complexometric analysis showed that the Cu(II), Zn(II) and Cd(II) content in the complexes is 18.75, 19.62, and 29.23 % respectively, while the calculated values are 19.50, 19.95, and 30.01 % respectively.

Infrared Spectral Analysis

The presence of the water (H_2O) molecule in asparagine monohydrate is indicated by a broad band at 3620 cm^{-1}, which corresponds to the O–H stretching vibration. The significant broadening of this peak suggests the possibility of involvement of intermolecular hydrogen bonding of water molecule to some extent. The stretching vibration of the O–H within the –COOH group occurs at a lower frequency of 3570 cm^{-1}[13-15]. The N–H stretching of the -NH_2 group vibrates at 3470 cm^{-1}, while the N–H stretching of the amide group occurs at 3340 cm^{-1}. The (C–H) stretching of –CH_2CO– group exhibits a peak at 2925 cm^{-1}. A strong peak observed at 1725 cm^{-1} is attributed to the >C=O stretching of the carboxylic acid group. The N–H deformation peak of the amide group appears at 1680 cm^{-1}. The –CH(NH_2)– group exhibits a strong peak at 1140 cm^{-1} due to the stretching of C–N bond.

The metal complexes under this study exhibit a broad band around 3353 cm^{-1} due to N–H stretching vibration of both the –NH_2 and –$CONH_2$ groups present in the complexes. The broadening of the peak also suggests that the nitrogen from either the –$NH_2$and/or –$CONH_2$ group is involved in bonding with the M(II) cation. The (C=O) stretching of the amide group vibrates at 1662 cm^{-1}, exhibiting a shift of approximately 20 cm^{-1}, indicating its involvement in coordination with metal(II) ions. In contrast, the (C=O) stretching of the carboxylic acid group of L-asparagine disappears in the spectra of the complexes. In fact, the carboxylic acid group undergoes deprotonation, resulting in the appearance of the –COO^- anion, which stretches asymmetrically and symmetrically at 1618 and 1408 cm^{-1}, respectively. A slight shifting of the –COO^- anion's stretching vibrations in the lower frequency region indicates its participation in coordination with M(II) through oxygen donor site. The –CH(NH_2)– group shows a peak at 1156 cm^{-1} due to >C–N bond stretching. The peaks observed below 600 cm^{-1} in the spectra of the complexes are assigned to the stretching vibrations of M–N and M–O bonds. This ascertains the complexation of M(II) with asparaginato anion occurs through its N and O donor sites.

Ultraviolet-Visible Spectral Analysis

The L-asparagine exhibits two strong electronic absorption bands at 206 and 302 nm and assigned as the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the major chromophores, –NH_2 and –COO^- present in the ligand moiety. A comparative UV-visible spectra of L-asparagine and prepared M(II)-L-asparagine complexes as recorded are given in Fig. 1. The distorted octahedral copper(II) complex shows two absorption bands: one at 234 nm due to the $\pi \rightarrow \pi^*$ transition and a broad one at 622 nm with a tail in the near IR region due to the $d \rightarrow d$ transition. This $d \rightarrow d$ band is caused by the merging of three components, identified as transitions from the $^2B_1g \rightarrow {}^2A_1g$, $^2B_1g \rightarrow {}^2B_2g$, and $^2B_1g \rightarrow {}^2Eg$, suggesting the possible elongated tetragonal coordination of Cu(II) by the ligands. The absorption bands of zinc(II) complex occur at 200 and 371 nm as a result of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$electronic transitions. Zn(II) is a d^{10} ion, i.e. all five *d*-orbitals are paired up with electrons that exclude the possibility of $d \rightarrow d$ transition. Cadmium complex reveals only one absorption band at 203 nm due to the combining effect of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Cd(II) is also a d^{10} ion, the $d \rightarrow d$ transition is likewise impossible.

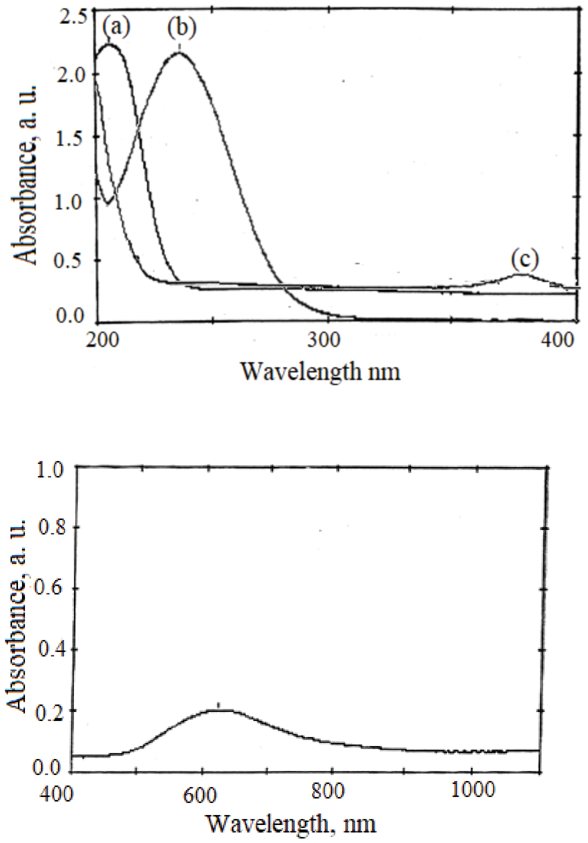


Fig. 1. Comparative UVspectra of (a) $H_2NCOCH_2CHNH_2COOH.H_2O$, (b) $[Cu(OOCCHNH_2CH_2CONH_2)_2]$, (c) $[Zn(OOCCHNH_2CH_2CONH_2)_2]$, and visible spectrum of $[Cu(OOCCHNH_2CH_2CONH_2)_2]$

Magnetic Susceptibility

The copper-L-asparaginato complex has a paramagnetic moment of 1.52 BM corresponding to the presence of one unpaired electron in the 3*d* orbital. This indicates that the copper in this complex is in the bivalent state, Cu(II), a d^9 system and has octahedral geometry. Conversely, it is found that the complexes of zinc and cadmium have negative magnetic susceptibility values. This is expected, as the metals in both complexes are in the divalent state and exist as d^{10} ions. Consequently, Zn(II) and Cd(II) have ten electrons paired with each of their five *d*-orbitals.

Thermal Analysis

The quasi-static thermogravimetric (QSTG) analysis reveals that the asparagine monohydrate starts losing weight at 50°C (Fig. 2(a)). Within the temperature range of 100°C, the weight loss percentage is about 11.94%, which corresponds to the loss of water (calcd. loss of 11.99%). After 250°C, the weight loss process is rapid and continuous, resulting in no residue left at 650°C, i.e., the entire ligand molecule decomposes into CO_2, CO, NO, NO_2, H_2O, and other by products. All three synthesized bis(L-asparaginato) complexes of Cu(II), Zn(II) and Cd(II) exhibit thermal stability up to 250°C, suggesting the absence of any loosely bound lattice component. Beyond this temperature, the species start losing weight rapidly and continuously. The approximate weight loss percentage within the temperature range of 250 to 450°C is 76.51% for Cu(II) complex (Fig. 2(b)), 250 to 550°C is 75.39% for Zn(II) complex (Fig. 2(c)), and 250 to 500°C is 66.59% for Cd(II) complex (Fig. 2(d)), due to the loss of two L-asparaginato anions (calcd. loss of 74.97% for Cu(II), 74.55% for Zn(II), and 65.19% for Cd(II) complexes). CuO, ZnO, or CdO make up the residue that is left over during thermal treatment of the complexes under ambient condition.

During the thermal heating process, the colour changes observed for the complexes are as follows: The bis(L-asparaginato)copper(II) complex changes from blue to deep blue at 300°C, and from deep blue to black residue at 400°C; The bis(L-asparaginato)zinc(II) complex changes from white to ash at 300°C, from ash to violet at 350°C, from violet to black at 500°C, and finally from black to white at 550°C; and the bis(L-asparaginato)cadmium(II) complex changes from white to yellow at 300°C, from yellow to violet at 350°C, and from violet to deep brown at 500°C.

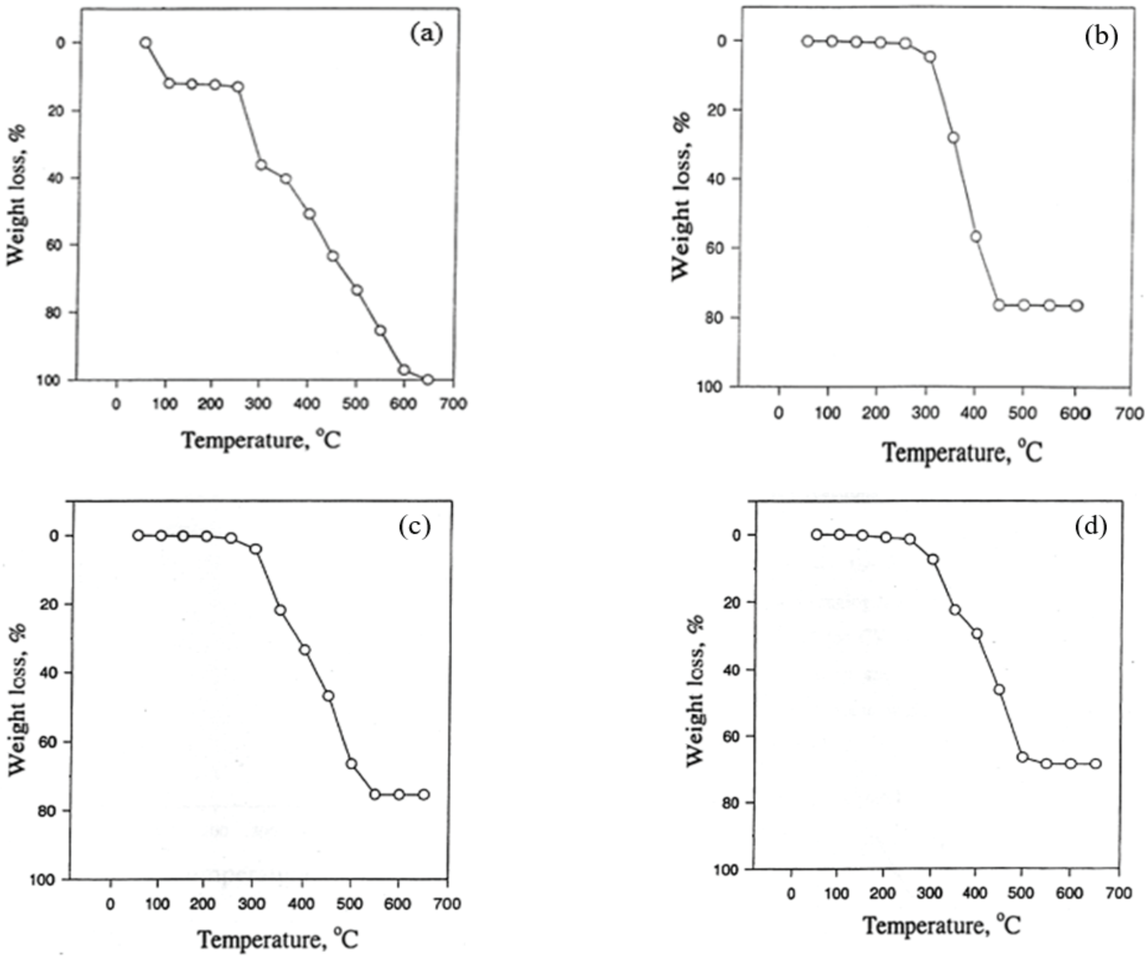


Fig. 2. QSTG graph of (a) $H_2NCOCH_2CHNH_2COOH.H_2O$ (b) $[Cu(OOCCHNH_2CH_2CONH_2)_2]$, (c) $[Zn(OOCCHNH_2CH_2CONH_2)_2]$, and (d) $[Cd(OOCCHNH_2CH_2CONH_2)_2]$

Cyclic Voltammetric (CV) Studies

Solutions of 2 mM $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2$, L-asparagine, and bis(asparaginato) complexes of Cu(II), Zn(II), and Cd(II) in 0.1 M KCl supporting electrolyte were prepared for cyclic voltammetric measurement. Glassy carbon electrode (GCE) was used as a working electrode in a three electrode system of electrochemical cell for cyclic voltammetric study of them at various scan rates of 25, 50, 75, 100, 150, and 200 mVs^{-1} within the appropriate potential windows.

CV of L-asparagine

The cyclic voltammogram of 2 mM L-asparagine in 0.1 M KCl solution at a scan rate of 100 mVs^{-1} in the potential window from -1200 mV to +1200 mV at GCE does not exhibit any redox peak in either the cathodic or anodic regions.

CV of 2 mM Cu(II) and $[Cu(OOCCHNH_2CH_2CONH_2)_2]$ complex

Fig. 3 illustrates the cyclic voltammogram of $CuCl_2$ (2 mM) in supporting electrolyte of 0.1 M KCl solution at 20°C within the potential window from -1200 mV to +750 mV at the scan rate of 100 mVs^{-1}. It displays two cathodic peaks i_{pcl} and i_{pc2} at +190.6 mV and -255.7 mV respectively, and their corresponding anodic peaks i_{pal} and i_{pa2} at +269.6 mV and -79 mV, respectively. The cathodic peaks corresponds to the reduction of Cu(II) to Cu(I) and Cu(I) to Cu(0) species, whilst the anodic peaks are due to the oxidation of Cu(0) to Cu(I) and Cu(I) to Cu(II) ions. The peak current ratio of peaks i_{pa1}/i_{pcl} is nearly unity indicating reversibility of this couple. Another couple with the ratio i_{pa2}/i_{pc2} is far from unity and quasi-reversible. Additionally, the peak potential separation of the first redox couple, $\Delta E_p = (E_{pal}-E_{pcl})$ 0.059 V, is well consistent with one electron transfer reversible couple, while for second couple the peak potential separation does not reflect reversibility. The CV of $[Cu(OOCCHNH_2CH_2CONH_2)_2]$ complex solution with scan rate of 100 mVs^{-1} within the potential window from -1200 mV to +750 mV shows a cathodic peak, i_{pc} at -595.6 mV and an anodic peak, i_{pc} at -21.8 mV. The cathodic peak is associated with the reduction of Cu(II) to Cu(0) species, while the anodic peak is related to the oxidation of Cu(0) to Cu(II) ion. Voltammograms of L-asparagine, $CuCl_2$, and $[Cu(OOCCHNH_2CH_2CONH_2)_2]$ complex are shown in Fig. 3. In comparison to the Cu(II) voltammogram, the complex exhibits a significant shifting of the cathodic peak towards the negative potential, a slight shift of the anodic peak towards the positive potential, and a reduction in the peak heights. The substantial cathodic peak shifting can be attributed to strong participation of copper(II) in the complex formation with L-asparagine, which makes its reduction process more difficult[16,17]. Conversely, the anodic peak shifted a little to the positive, suggesting that the presence of ligand has aided in oxidation of copper. The above statement is in good agreement with the observation of copper-catechol complex reported by Berg *et al*[18]. This is to be expected, as hard acid like copper(II), has more tendency to participate in complexation with hard bases like the N of $–NH_2$ group, O of $–CONH_2$ group, and $–O^-$ of $–COO^-$ anion.

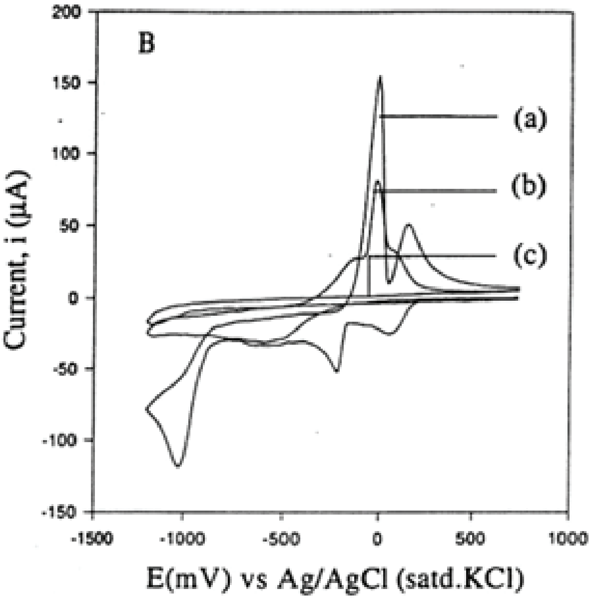


Fig. 3. CV of 2mM (a) Cu(II), (b) $[Cu(OOCCHNH_2CH_2CONH_2)_2]$ complex and (c) L-asparagine in 0.1 M KCl at GCE with scan rate of 100 mVs^{-1}

CV of Zn(II) and $[Zn(OOCCHNH_2CH_2CONH_2)_2]$ complex

The CV of 2 mM $ZnCl_2$ in 0.1 M KCI solution at GCE with the scan rate of 100 mVs^{-1} within the potential window -200 mV to -1300 mV (Fig. 4)) shows one cathodic peak i_{pc} at -1199.9 mV and one anodic peak i_{pa} at -1000.6 mV. The cathodic peak is attributed to the Zn(II) → Zn(0) while the anodic peak is for Zn(0) → Zn(II) conversions[19]. At different scan rates, the voltammograms demonstrate the i_{pa}/i_{pc} ratio deviates from unity indicating that a quasi-reversible nature of the redox process on the GCE surface. The peak potential difference, $\Delta E_p = (E_{pa}- E_{pc})$ further supports the quasi-reversible characteristic of the redox process.

The CV of $[Zn(OOCCHNH_2CH_2CONH_2)_2]$ under the experimental condition exhibits a cathodic peak, i_{pc} at -1277.2 mV for Zn(II) → Zn(0) and a anodic peak, i_{pa} at -1081.7 mV for Zn(0) → Zn(II). However, the peak current ratio i_{pa}/i_{pc} is near to unity indicating that the redox system is quasi-reversible, one step, and two-electron transfer process. Some irreversibility of the redox process also corroborates with the $\Delta E_p = (E_{pa}-E_{pc})$ values observed at different scan rates.

Fig. 4 illustrates the comparison of the cyclic voltammograms for (a) $ZnCl_2$, (b) $[Zn(OOCCHNH_2CH_2CONH_2)_2]$ complex, and (c) L-asparagine. In comparison to the cyclic voltammogram of Zn(II), the peaks of the complex show significant shift, accompanied by reduced peak heights. These findings suggest a strong involvement of Zn(II) in complex formation with L-asparagine.

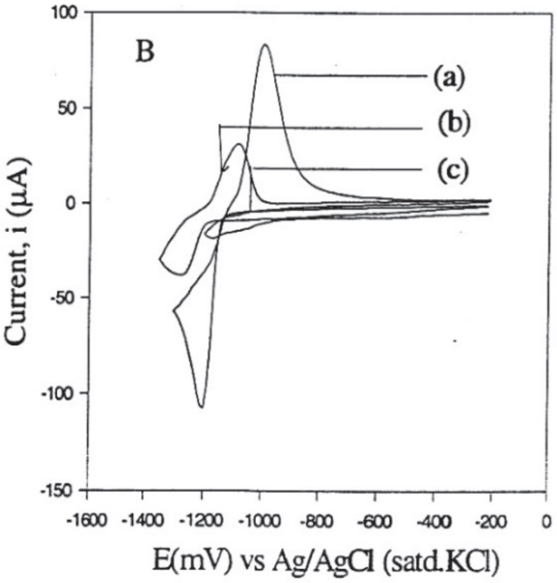


Fig. 4. CV of 2 mM (a) Zn(II), (b) $[Zn(OOCCHNH_2CH_2CONH_2)_2]$ complex, and (c) L-asparagine in 0.1 M KCl at GCE with scan rate of 100 mVs^{-1}

CV of Cd(II) and $[Cd(OOCCHNH_2CH_2CONH_2)_2]$ complex

The CV of 2 mM solution of $CdCl_2$ at a scan rate 100 mVs^{-1} within the potential window -1200 to 0 mV (as depicted in Fig. 5) reveals a cathodic peak at -815.0 mV and an anodic peak at -670.0 mV. These peaks correspond to the reduction of Cd(II) to Cd(0) and the oxidation of Cd(II) to Cd(0), representing a diffusion-controlled irreversible, one step, two-electron transfer process[19]. As the scan rate increases, the peaks shift and the peak separation (ΔE) increases. The peak current ratio i_{pa}/i_{pc} deviates from unity, indicating an irreversible system[20].

Under the same experimental conditions, the voltammogram of $[Cd(OOCCHNH_2CH_2CONH_2)_2]$ displays a cathodic peak at -876.0 mV and an anodic peak at -710.4 mV. When comparing the CV for (a) $CdCl_2$, (b) $[Cd(OOCCHNH_2CH_2CONH_2)_2]$ complex, and (c) L-asparagine, (Fig. 5), it is evident that both the cathodic and anodic peaks of the complex are significantly shifted,with reduced the peak heights. These observations suggest a strong interaction between the Cd(II) ion and L-asparagine under the experimental conditions.

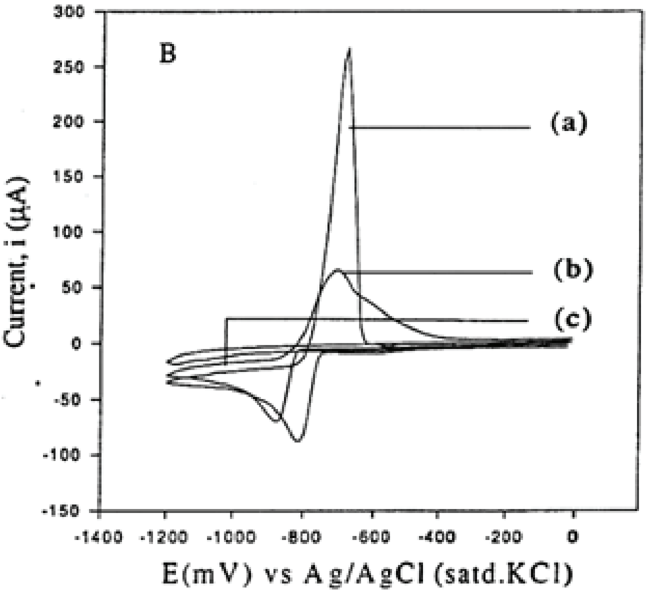
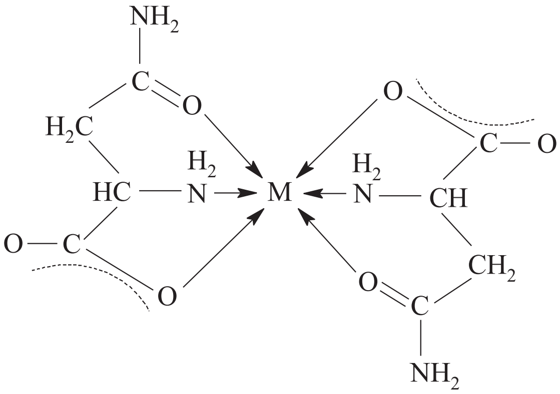


Fig. 5. CV of 2 mM solution of (a) $CdCl_2$, (b) $[Cd(OOCCHNH_2CH_2CONH_2)_2]$ complex, and (c) L-asparagine in 0.1 M KCl at GCE with scan rate of 100 mVs^{-1}

IV. Conclusion

Three bis(L-asparaginato) complexes of Copper(II), Zinc(II) and Cadmium(II) were synthesized by heating an aqueous solution of L-asparagine and their respective metal oxide for an hour. Air-stable needles-shaped crystals of metal(II)-L-asparaginato complexes of various color are collected. The copper(II) complex is royal blue, while zinc, and cadmium complexes are white. They have high melting points (>300°C) and are only soluble in hot water. The complexes were characterized using various physico-chemical techniques. The suggested general formula of the complexes to be $[M(OOCCHNH_2CH_2CNH_2)_2]$, where M = Cu(II), Zn(II), and Cd(II). The reaction between L-asparagine and the metal oxide is essentially an acid-base type, resulting in the formation of water and metal-amino acid complex. In these complexes, each metal(II) ion is hexa-coordinated by two asparaginato anions, with coordination occurring through the N atom from the $–NH_2$ group, the O from the $–CONH_2$ group, and the $–O^-$ from the $–COO^-$ group. The Cu(II) complex is paramagnetic, while the Zn(II) and Cd(II) complexes are diamagnetic. The CV studies of the complexes reveal shifted anodic and cathodic peaks, indicating that the formation of a complex with L-asparagine by each metal(II) ion. Based on the results of various physico-chemical studies described and discussed in this research work, the most probable structures for the complexes are proposed below:



[$M(OOCCHNH_2CH_2CONH_2)_2$], M = Cu(II), Zn(II), and Cd(II)

It is important to note here that determining the precise geometry of the complex structures is challenging until single crystal X-ray diffraction studies are conducted.

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References

1. Yamauchi, O., A. Odani and M. Takani, 2002. Metal–amino acid chemistry. Weak interactions and related functions of side chain groups, *J. Chem. Soc*., Dalton Trans. 3411-3421.
2. Martin, R. B., 1961. Metal ion binding to peptides and proteins. *Fed. Proc.* **20(3)**Pt 2:54-57. PMID: 14470438.
3. Ayon, N. J., 2020. Features, roles and chiral analyses of proteinogenic amino acids, AIMS *Mol. Sci.*, **7(3)**, 229-268.
4. Bottari, E. and M. R. Festa,1996. Asparagine as a ligand for cadmium(II), lead(II) and zinc(II), *Chem. Speciation Bioavailability*, **8(3-4)**, 75-83.
5. Stephens, F. S., R. S. Vagg and P. A. Williams, 1975.The crystal and molecular structure of bis(L-asparaginato)copper(II), [$Cu(OOCCHNH_2CH_2CONH_2)_2$]$_n$, *Acta Cryst.*, **B31**, 841-845.
6. Vencato, I., C.Lariucci, K. D. Ferreira, R. C. Santana and J. F. Carvalho, 2004. Redetermination of bis(L-asparaginato) copper(II), *Acta Cryst*., **E60**, m1428-m1430.
7. Karaderi, S. and D. Bilgic, 2006. Zinc(II) and Cadmium(II) Binary Complexes with Creatinine and Their Mixed-Ligand Complexes with L-Asparagine or L-Glutamic Acid: Potentiometrie Studies, *Main Group Met. Chem*., **29(3)**, 145-155.
8. Alkava, D. B., S. Karaderi and G. Erdogan, 2013. Ternary complex formation of isoniazid with some transition metals and amino acids, *Trakya Univ. J. Nat. Sci.*, **14(1)**, 1-14.
9. Williams, D. R., 1972. Metals, Ligands and Cancer, *Chem. Rev.*, **72(3)**, 203-213.
10. Kreis,W., 1983. Chemotherapy Based on Amino Acid Depletion and Amino Acid Antagonists, Cancer Chemotherapy 1 edited by F. M. Muggia, Springer link, 219-248.
11. Jamil, Y. M., M. A. Al-Maqtari, F. M. Al-Azab, M. K. Al-Qadasy, and A. A. Al-Gaadbi, 2018. Synthesis, characterization and comparative thermal degradation study of Co(II), Ni(II) and Cu(II) complexes with asparagine and urea as mixed ligands, *Eclética Química J.*, **43(4)**,11-24.
12. Al-Noor, T. H., R. T. Mahdi and A. H. Ismail, 2015. Synthesis, spectroscopic characterization and evaluation (antibacterial & (GOT, G pT) enzyme) activity of mixed ligand complexes of M(II) with amino acid (L-Asparagine) and Schiff bases derived from (Sulfamethoxazo Drug with 2,4 Dimethoxybenzaldehyde), *Chem. and Process Eng. Res.*, **31,** 18-26.
13. Dyke, S. F., A. J. Floyd, M. Sainsbury and R. S. Theobald, 1978. Organic Spectroscopy - An Introduction, 2nd ed., 61-85.
14. Pavia, D. L., G. M. Lampman and G. S. Kriz, 2001. Introduction to Spectroscopy,a Guide for Students of Organic Chemistry, 3rd ed., Thomson Learning, Boston, 22-368.
15. Akther, S., S. Islam, M. S. Rahman, H. A. Simol, A. H. M. S. I. M. Jamal, D. Islam and P. K. Bakshi, 2024. Synthesis, Characterization and Biological Activities of Tolfenamic Acid Alkaline Earth Metal Complexes, *Appl. Organomet. Chem*., e7779.
16. Quentel, F. and C. Madec, 1990. Voltammetric study of the copper-1,10-phenanthroline complex.,*Anal. Chem. Acta*, **230**, 83-90.
17. Drissi-Daoudi, R., A. Irhzo and A. Darchen, 2003. Electrochemical investigations of copper behaviour in different cupric complex solutions: Voltammetric study, *J. Appl. Electrochem.*, **33**, 339-343.
18. Berg, V.and M.G. Constant, 1984. Determination of copper in sea water by cathodic stripping voltammetry of complexes with catechol, *Anal. Chem. Acta*, **164**, 195-207.
19. Gosser, Jr., D.K., 1993. Cyclic Voltammetry: Simulation and Analysis of Reaction Mechanism, Wiley-VCH, New York.
20. Bard, A. J. and L.R. Faulkner, 198. Electrochemical method: Fundamentals and Applications, New York, 228.