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# Cyclic voltammetric and spectral studies of some mixed-ligand copper(II) complexes involving 2,2′-bipyridine/1,10-phenanthroline and amino acids

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**Abstract : Cyclic voltammetric and electronic spectral studies of some mixed ligand copper(II) complexes, viz. [Cu(bipy)(glu)], 1; [Cu(bipy)(tyro)]Cl, 2; [Cu(phen)(asp)], 3; [Cu(phen)(glu)].2$H_2O$, 4 and [Cu(phen)(tyro)]Cl.$H_2O$, 5 (where, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, asp = L-aspartate dianion, glu = L-glutamate dianion and tyro = L-tyrosinate anion) have been studied in aqueous medium at pH 5.0. All these complexes displayed a single-electron redox couple ($Cu^{2+/+}$) in the potential range +1000 to –400 mV vs Ag/AgCl. The cathodic peak potential shifts positively with increasing scan rate (v) and peak current ratio ($I_{pa}/I_{pc}$) is greater than 1.0, representing a decrease in dissolved $Cu^{I}$ species near the electrode surface because of weak adsorption of the reduced species at the surface of working electrode in the case of phen mixed ligand complexes, 3 to 5. It is important to note that for a given amino acid, the reduction potential ($E_{pc}$) of these mixed ligand $Cu^{II}$ complexes is less negative for the phen complex than the bipy complex (1 vs 4 and 2 vs 5), owing to the stronger π-acceptor character of phen over bipy.**

**Keywords : Electrochemistry, cyclic voltammetry, bipyridine, phenanthroline, mixed ligand $Cu^{II}$ complexes, amino acids.**

## Introduction

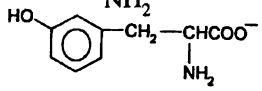
Mixed-ligand complexes containing an amino acid as a second ligand are of significance as they are not only potential models for enzyme-metal ion-substrate complexes but also related to $Cu^{II}$-mixed amino acid complexes such as those containing L-histidine and L-threonine, which occurs[1] to a significant proportion among the copper(II) mixed amino acid complexes found[2] in human serum. In this mixed amino acid complex, the coordination geometry around $Cu^{II}$ as revealed by X-ray crystal structure study[3], is one in which histidine forms two strong Cu–N bonds and an irregular Cu–O bond while threonine bonds glycine like to $Cu^{II}$.

Over the past decade, there has been substantial increase in interest in the design and study of DNA binding properties of potential redox and spectroscopically active $Cu^{II}$, $Co^{III}$ and $Ru^{II}$ complexes[4] as new chemical nucleases[5] as they appear to be less readily repaired by DNA repair mechanism[6]. Copper(II) complexes containing heterocyclic bases have received considerable interest in nucleic acid chemistry due to their diverse applications following the discovery of the "chemical nuclease" activity of the $[Cu(phen)_2]^+$ (phen =1,10-phenanthroline) complex in the presence of hydrogen peroxide and a reducing agent by Sigman *et al.*[7a]. A strong relationship between metals or their complexes, and antibacterial, antitumour and anticancer activities is also known[7b]. A number of *in vivo* studies have indicated that biologically active compounds become more bacteriostatic and carcinostatic upon chelation. Such interaction of transition metal ions with amino acids and peptides is of immense importance. It has been reported that metal complexes of amino acid derived ligands possess anticancer activity[7b].

X-Ray crystal structure studies of [Cu(phen)(L-glu)($H_2O$)].3$H_2O$[8a] and [Cu(phen)(L-tyro).$H_2O$]Cl[8b] complexes have shown that each copper(II) ion coordinates to two nitrogen atoms of phen and the amino nitrogen and carboxylato O atoms of L-$glu^{2-}$/L-$tyro^{-}$ in the equatorial positions and one water oxygen at an apical position, giving an approximate square pyramidal geometry. In contrast, Kwick *et al.*[8c] have proposed square planar geometry for cationic complexes [Cu(bipy)(tyro)]Cl, **2** and [Cu(phen)(tyro)]Cl.$H_2O$, **5** on the basis of conductance and spectral measurements. The crystal structure of [Cu(bipy)(L-glu)][8a], **1** is built up of two crystallographically independent one-dimensional polymeric chains. Each copper atom exhibits slightly distorted square-pyramidal five coordination, with bipy and the L-$glu^{2-}$ ion acting as bidentate ligands in the equatorial plane and a γ-carboxylate O atom from a second glutamate ion in the apical position. The crystal lattice of [Cu(phen)(asp)].3.5$H_2O$[8d,e] is composed of two types of copper complexes, the

coordination geometries around the copper atoms in both complexes are approximately square pyramidal. The equatorial ligands of both the $Cu^{II}$ ions are the nitrogen atoms of the phen and the N and O atoms of the amino acid group of the asp molecules. The apical position is occupied by an O atom of a neighbouring aspartic acid molecule in one complex while in the second complex this position is occupied by the O atom, from the same aspartic acid molecule. Furthermore, complex [Cu(phen)(asp)($H_2O$)].4$H_2O$ has been reported to involve octahedral geometry around the $Cu^{II}$ ion[8f].

The present work stems from our continued interest in defining and evaluating the electrochemical and spectral behaviour of simple and mixed ligand $Cu^{II}$ complexes of diimines. In our earlier paper[8g], we reported the electrochemical and EPR spectral investigations of mixed-ligand copper(II) complexes involving 2,2′-bipyridine and amino acids. In this report, we explore the electrochemical and electronic absorption spectral properties of some mixed ligand copper(II) complexes containing bipy/phen and amino acidates, viz. [Cu(bipy)(glu)], **1**; [Cu(bipy)(tyro)]Cl, **2**; [Cu(phen)(asp)], **3**; [Cu(phen)(glu)].2$H_2O$, **4** and [Cu(phen)(tyro)]Cl.$H_2O$, **5**, where, bipy = 2,2′-bipyridine, phen = 1,10-phenanthroline, asp = L-aspartate dianion, $^-OOC–CH_2–\underset{\underset{NH_2}{|}}{C}HCOO^-$, glu = L-glutamate dianion, $^-OOC–CH_2–CH_2–\underset{\underset{NH_2}{|}}{C}HCOO^-$ and tyro = L-tyrosinate anion,



have been studied in aqueous 0.2 *M* potassium chloride as a supporting electrolyte at pH 5.0 at a glassy carbon working electrode (GCE) using cyclic voltammetry (CV) with scan rate (v) ranging from 25 to 500 mV $s^{-1}$.

## Results and discussion

Typical cyclic voltammogramms of 1 mM aqueous solutions of complexes **1** and **3** containing 0.2 *M* KCl at pH 5.0, respectively at a scan rate of 100 mV $s^{-1}$ are displayed in Fig. 1(a,b) and the CV data for the complexes are given in Table 1. These complexes in aqueous solution showed a weak broad *d-d* absorption maximum ($\lambda_{max}$) at 601–660 nm at pH 5.0. The value of $\lambda_{max}$ for these complexes is found to increase in the order: **2** (601 nm) > **1** (624 nm) > **4** (637 nm) > **3** (649 nm) > **5** (660 nm). The negative scan initiated from 1000 mV in the potential range +1000 to –400 mV vs Ag/AgCl resulted a single couple (c/a) corresponding to $Cu^{2+/+}$ change in all the complexes (Table 1).

**Table 1.** CV data for [Cu(diimine)(amino acid)]$^{0/+}$ complexes in aqueous 0.2 *M* KCl at pH 5.0

| Scan rate (mV $s^{-1}$) | $E_{pc}$ (mV) | $E_{pa}$ (mV) | $E^{0'}$ (mV) | $\Delta E_p$ (mV) | $I_{pa}/I_{pc}$ |
|---|---|---|---|---|---|
| | | [Cu(bipy)(glu)], **1** | | | |
| 25 | –121 | –52 | –86.5 | 69 | 0.4 |
| 50 | –121 | –50 | –85.5 | 71 | 0.5 |
| 100 | –122 | –50 | –86.0 | 72 | 0.7 |
| 200 | –121 | –48 | –84.5 | 74 | 0.8 |
| 300 | –121 | –47 | –84.0 | 74 | 0.8 |
| 400 | –121 | –46 | –83.5 | 75 | 0.8 |
| 500 | –122 | –46 | –84.0 | 76 | 0.8 |
| | | [Cu(bipy)(tyro)]Cl, **2** | | | |
| 25 | –145 | –50 | –97.5 | 95 | – |
| 50 | –145 | –48 | –96.5 | 97 | 0.8 |
| 100 | –146 | –40 | –93.0 | 106 | 0.9 |
| 200 | –146 | –36 | –91.0 | 110 | 0.9 |
| 300 | –148 | –33 | –90.5 | 115 | 0.9 |
| 400 | –165 | –33 | –99.0 | 132 | 0.9 |
| 500 | –166 | –24 | –95.0 | 142 | 1.0 |
| | | [Cu(phen)(asp)], **3** | | | |
| 25 | –113 | –46 | –79.5 | 67 | 1.5 |
| 50 | –108 | –45 | –76.5 | 63 | 1.7 |
| 100 | –107 | –38 | –72.5 | 69 | 1.9 |
| 200 | –106 | –30 | –68.0 | 76 | 1.8 |
| 300 | –96 | –32 | –64.0 | 64 | 1.9 |
| 400 | –95 | –27 | –61.0 | 68 | 1.9 |
| 500 | –94 | –24 | –59.0 | 70 | 1.9 |
| | | [Cu(phen)(glu)].2$H_2O$, **4** | | | |
| 25 | –83 | 83 | 0.0 | 166 | 2.5 |
| 50 | –74 | 84 | 5.0 | 158 | 1.8 |
| 100 | –70 | 84 | 7.0 | 154 | 1.9 |
| 200 | –70 | 80 | 5.0 | 150 | 1.5 |
| 300 | –69 | 78 | 4.5 | 147 | 1.3 |
| 400 | –69 | 74 | 2.5 | 143 | 1.2 |
| 500 | –69 | 72 | 1.5 | 141 | 1.2 |
| | | [Cu(phen)(tyro)]Cl.$H_2O$, **5** | | | |
| 25 | –95 | –35 | –65.0 | 60 | 1.6 |
| 50 | –94 | –29 | –61.5 | 65 | 1.6 |
| 100 | –93 | –22 | –57.5 | 71 | 1.6 |
| 200 | –91 | –17 | –54.0 | 74 | 1.4 |
| 300 | –89 | –17 | –53.0 | 72 | 1.4 |
| 400 | –87 | –15 | –51.0 | 72 | 1.5 |
| 500 | –87 | –13 | –50.0 | 74 | 1.4 |

The reduction peak potential, $E_{pc}$ varies slightly and shifts negatively in bipy mixed ligand complexes **1** and **2** in the scan rate range 25–500 mV $s^{-1}$. Constant potential coulometry at –325 and –350 mV vs Ag/AgCl in aqueous 0.2 *M* KCl at pH 5.0 for complexes **1** and **2** has confirmed the involvement of one electron per molecule of each of these complexes. These observations clearly demonstrate that the electrochemical behaviour corresponds to a quasi-reversible one-electron charge transfer reaction[9]. The plot of $I_{pc}$ vs square root of the scan rate ($v^{1/2}$) gives a straight

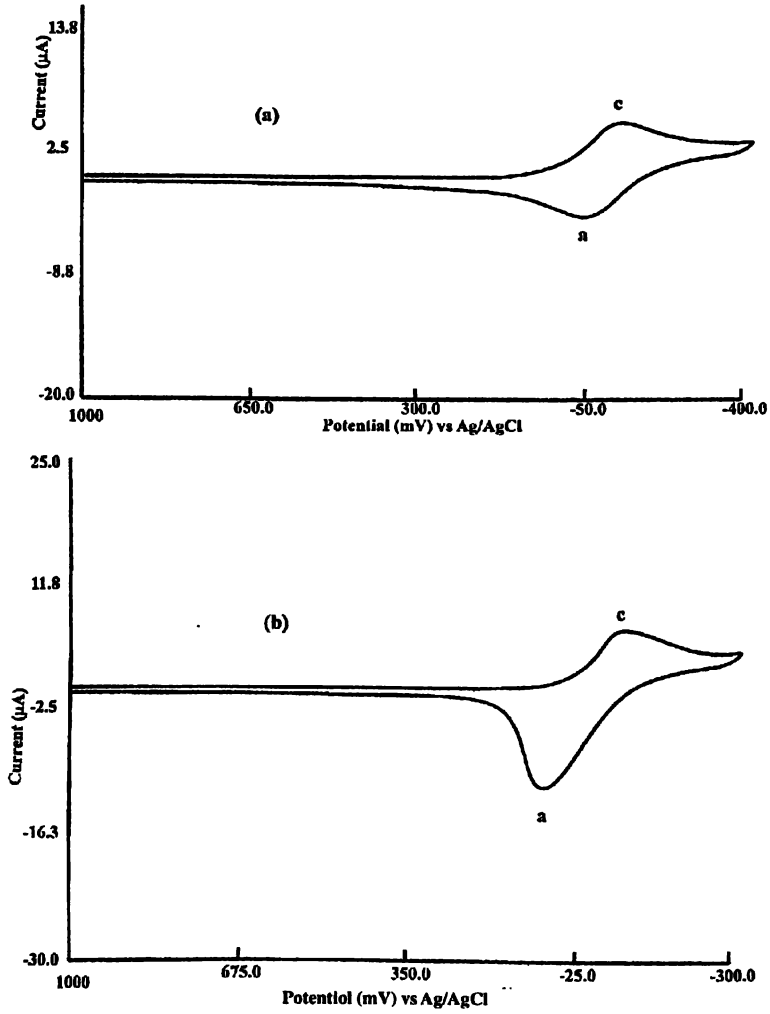



**Fig. 1.** Cyclic voltammograms of [Cu(bipy)(glu)], (a) and [Cu(phen)(glu)].$H_2O$, (b) in aqueous 0.2 *M* KCl at pH 5.0, scan rate (v) = 100 mV $s^{-1}$.

line passing through origin, showing that the reduction process is diffusion-controlled[9] for these complexes. The anodic to cathodic current ratio ($I_{pa}/I_{pc}$) is less than 1.0 for **1** and nearly equal to 1.0 for **2**, indicating that the electrode processes involve a single electron transfer without any chemical complication for complex **2** and EC mechanism[9] for **1** (Table 1). It is interesting to note that the cathodic peak potential shifts positively with increasing scan rate (v) and the peak current ratio ($I_{pa}/I_{pc}$) is > 1.0 at all scan rates studied for complexes **3-5** (Table 1), representing a decrease in dissolved R near the electrode surface because of weak adsorption[9] of $Cu^{I}$ species at the surface of GCE in all these phen mixed ligand $Cu^{II}$ complexes.

It should be noted from Table 1 that for a given amino acid, the reduction potential ($E_{pc}$) of these mixed ligand $Cu^{II}$ complexes is less negative for the phen complex than the bipy complex (distorted square pyramidal complexes **1** vs **4** and square planar complexes **2** vs **5**). These observations seem to imply that an amino acid is bonded more covalently to $Cu^{II}$ in the phen series than in the bipy series, conceivably owing to the stronger π-acceptor character of phen over bipy[10]. It should be mentioned that the redox potentials of complexes are affected by various factors[10] such as types of ligands, nature of donar atoms, geometry of the complex, electron density on the central metal ion, solvent etc. Furthermore, the reduction potential ($E_{pc}$) of [Cu(phen)(asp)], **3** is more negative than for [Cu(phen)(glu)].$2H_2O$, **4**, indicating that the reduction of **3** is more difficult as compared to that of **4**. A perusal of Table 1 shows that the ease of reduction of these

complexes decreases in the order : **4** > **5** > **3** > **1** > **2**. It should be noted that no simple correlation between the crystal field parameter ($\lambda_{max}$) and the formal redox potential ($E^{0\prime}$, Table 1) has been found for these complexes.

## Experimental

All the complexes (**1** to **5**) were prepared according to procedure reported earlier[8c] and their purity was checked by elemental analyses. All reagents used were of analytical grade. The aqueous solutions of the complexes under investigation were freshly prepared in double distilled water. The tyrosine mixed ligand complexes, **2** and **5** are less soluble in water and therefore their solutions were filtered through gravimetric filter paper before purging nitrogen gas and recording of CVs and also absorption spectra. The pH of the complex's solutions was adjusted by adding NaOH solution and measuring the pH with the help of pH meter.

The software driven BAS Electrochemical System, Model EPSILON (Bioanalytical Systems, Inc, USA) was employed for all the electrochemical studies. $1 \times 10^{-2}$ *M* stock solutions of these complexes were prepared in double distilled water except **2** and **5**. More dilute ($1 \times 10^{-3}$ *M*) solutions were prepared by accurate dilution. The working electrode was glassy carbon disc electrode (GCE), the counter electrode was a platinum wire and reference electrode Ag/AgCl in saturated KCl ($E^0$ = +199 mV vs NHE). Purging and blanketing of nitrogen (99.999% pure) were done for analyte solution placed in the electrochemical cell of 15 ml capacity for 20 min. Great care was taken in the electrode pretreatment. Mechanical polishing of the working electrode (GCE) was done over a velvet microcloth with an alumina suspension. Controlled Potential Electrolysis (CPE) was carried out for calculating the number of electrons involved in the reduction process. Electrolysis was done in $1 \times 10^{-3}$ *M* aqueous solution of a complex containing 0.2 *M* KCl in a BASi Bulk electrolysis cell, consisting of Reticulated Carbon Working Electrode, coiled platinum auxiliary electrode dipped in a separate cell containing 0.2 *M* KCl solution only and Ag/AgCl as a reference electrode. Nitrogen gas was initially purged for 30 min with constant stirring the solution and then $N_2$ was blanketed over the stirred cell solution during the electrolysis. All the electrochemical experiments were performed at a constant temperature 27 ± 0.5 °C. Room temperature electronic absorption spectra were measured in the range 800–400 nm with a Perkin-Elmer UV-Visible spectrophotometer Model Lamda 35 available in our laboratory, for 2 mM aqueous solutions of the complexes at pH 5.0.

*Conclusion* :

For a given amino acid, the reduction potential ($E_{pc}$) of these mixed ligand copper(II) complexes is less negative for the phen complex (distrorted square pyramidal complexes **1** vs **4** and square planar complexes **2** vs **5**) owing to stronger π-acceptor character of phen over bipy.

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