

Electrochemical and EPR spectral investigations of mixed-ligand copper(II) complexes involving 2,2'-bipyridine and aminoacids

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The redox behaviours of some mixed-ligand copper(II) complexes, viz. [Cu(bipy)(gly)]Cl.1.5H₂O (1), [Cu(bipy)(ala)]Cl.1.5H₂O (2), [Cu(bipy)(val)]Cl.3H₂O (3), [Cu(bipy)(ser)]Cl.H₂O (4) and [Cu(bipy)(IDA)H₂O].5H₂O (5) have been investigated in 0.1 M NaClO₄ in aqueous medium at glassy carbon electrode using cyclic voltammetry. The cyclic voltammograms of these complexes display a quasi-reversible couple corresponding to Cu²⁺/Cu⁺ redox change with formal potential, $E^0 = -95 \pm 5$ mV in the potential range +0.40 to -0.40 V vs SCE. A second irreversible cathodic peak is also observed corresponding to Cu⁺/Cu⁰ in the potential region +0.40 to -0.65 V at scan rate 50 mV s⁻¹. The EPR spectra of these polycrystalline complexes at room temperature and liquid nitrogen temperature display a single signal with g values in the range 2.063 to 2.076, which are greater than the free electron g value of 2.0023.

Complexation with copper enhances the biological activity of a wide variety of organic ligands¹. There are a series of ligands for which the biological activity is markedly influenced by metal complexation is that related to 2,2'-bipyridyls and 1,10-phenanthrolines². Some of these ligands were shown to be bactericides, and they exhibit numerous biological activities, e.g. antifungal, antiviral and antimycoplasmal. Antiviral activity was also studied for a range of divalent metals with substituted phenanthrolines³. There has been considerable interest in the solution chemistry of mixed-ligand complexes particularly those containing copper(II)⁴ as a metal ion because copper is a very important biological element essential to healthy life of plants⁵ and animals⁶.

Cyclic voltammetric and electron paramagnetic resonance (EPR) spectral properties of some mixed-ligand complexes of copper(II) involving 2,2-bipyridyl as a primary ligand and aminoacids as secondary ligands are described in this report. The secondary ligands taken in the present study are : glycine (gly) NH₂CH₂COOH; alanine (ala) CH₃CH(NH₂)COOH; valine (val) (CH₃)₂CH. CH(NH₂)COOH; serine (ser) OHCH₂CH(NH₂)COOH and iminodiacetic acid (IDA) COOH.CH₂NH.CH₂COOH. The following complexes were chosen for the cyclic voltammetric and EPR investigations : [Cu(bipy)(gly)]Cl.1.5H₂O (1), [Cu(bipy)(ala)]Cl.1.5H₂O (2), [Cu(bipy)(val)]Cl.3H₂O (3), [Cu(bipy)(ser)]Cl.H₂O (4), [Cu(bipy)(IDA)H₂O].5H₂O (5).

Results and discussion

The electrochemical behaviours of 1 mM aqueous solution of each of the complexes, 1 to 5 in 0.1 M sodium perchlorate were preliminarily investigated in deaerated aqueous medium at glassy carbon electrode (GCE) by means of cyclic voltammetry (CV) with scan rate (v) ranging from 10 to 250 mV s⁻¹. Fig. 1(a, b) displays the typical cyclic voltammograms of 1 mM [Cu(bipy)(gly)]Cl.1.5H₂O and [Cu(bipy)(IDA)H₂O].5H₂O in 0.1 M NaClO₄ in aqueous medium, respectively. The initial negative scan exhibited a cathodic peak c_1 at -130 mV vs SCE (Cu^{2+/+}) in the forward potential range from +0.40 to -0.40 V vs SCE, with a directly associated almost reversible anodic peak a_1 at -50 mV (Cu^{+/2+}) in the reverse scan at $v = 50$ mV s⁻¹. On extending the negative potential limit to -0.65 V, a second totally irreversible reduction peak c_2 is observed at -0.50 V vs SCE (Cu^{+/0}). Reversal of the negative-voltage scan after this -0.50 V peak results in an anodic voltammogram without the peak(s) for c_2 and with a new stripping anodic peak a_2 at +35 mV vs SCE (Cu^{0/2+}) at scan rate of 50 mV s⁻¹ (Fig. 1a). The cyclic voltammogram of [Cu(bipy)(IDA)H₂O].5H₂O complex exhibits one reversible and one irreversible reduction peaks c_1 and c_2 (at -135 mV and -440 mV vs SCE, respectively) as well as an almost reversible oxidation peak a_1 at -50 mV ($E_\lambda = -0.25$ V vs SCE) and two irreversible oxidation peaks a'_1 and a_2 at 0.0 and +50 mV vs SCE, respectively in the potential range +0.60 to -0.52 V vs SCE at 50 mV s⁻¹ (Fig. 1b).

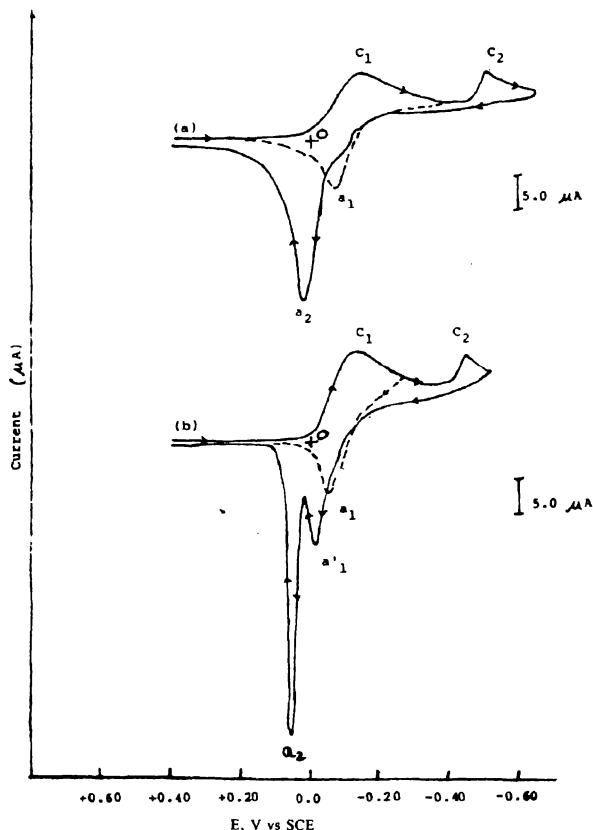
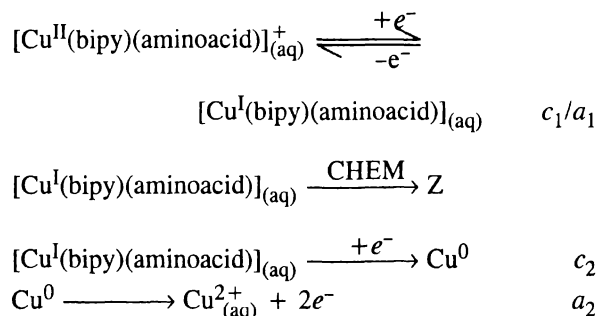


Fig. 1. Cyclic voltammograms of 1 mM [Cu(bipy)(gly)]Cl.1.5H₂O (a) and Cu(bipy)(IDA)H₂O.5H₂O (b) in 0.1 M NaClO₄ in aqueous medium at scan rate $\nu = 50 \text{ mV s}^{-1}$; dashed curve (a), $E^0 = -0.40 \text{ V vs SCE}$; solid curve, $E^0 = -0.65 \text{ V vs SCE}$; dashed curve (b), $E^0 = -0.25 \text{ V vs SCE}$; solid curve, $E^0 = -0.52 \text{ V vs SCE}$.

The reduction peak potential, $E_{p_{c1}}$ varies slightly and shifts negatively with the increasing scan rate and the peak potential separation, $\Delta E_p (E_{p_{a1}} - E_{p_{c1}})$ varies from 70–110, 80–150, 65–100, 120–290 and 65–110 mV vs SCE for complexes 1, 2, 3, 4 and 5, respectively in the scan rate range 10 to 250 mV s^{-1} . Constant potential coulometry at about -0.40 V vs SCE has confirmed the involvement of one electron per molecule of each of these complexes. These observations clearly show that the voltammetric behaviour corresponds to a quasi-reversible one-electron charge transfer reaction^{7,8}. The plots of $I_{p_{c1}}$ vs square root of the scan rate ($\nu^{1/2}$) produce a straight line passing through origin, indicating that the electrode process is diffusion controlled^{7,8}. The ratio of anodic-to-cathodic peak current ratio ($I_{p_{a1}}/I_{p_{c1}}$) is 1.0 for complexes 1 and 4, less than 1.0 for complexes 3 and 5 and more than 1.0 for complex 2, indicating that the electrode process involves a single-electron transfer with-

out any chemical complication for complexes 1 and 4, while electrogenerated copper(I) species of complex 2 is weakly adsorbed at the surface of the electrode^{7,8}. However, the electrode processes of complexes 3 and 5 involve EC mechanism^{7,9}. The following reaction pathway may be proposed to explain the observed electrochemical data :



Furthermore, the cathodic peak potentials $E_{p_{c1}}$ for all the complexes except complex 4 are almost similar at a given scan rate. This may be due to the fact that in aqueous solution all these complexes involve similar geometry and similar coordination environment, i.e. tetragonally distorted octahedral structure⁹ in which the copper(II) ion is coordinated through two nitrogen atoms of 2,2'-bipyridyl, one amino nitrogen and one oxygen of the carboxylic group of the amino acid in addition to two oxygens of two water molecules (3N, 3O). [Cu(bipy)(IDA)H₂O].5H₂O complex, however, involves one imido nitrogen, two oxygens of the two carboxylate groups, one oxygen from water molecule and two N atoms of bipy ligand around the central metal ion¹⁰.

Polycrystalline, solution and frozen solution EPR spectral studies :

EPR spectra of powdered sample of the complexes investigated were recorded both at room temperature (298 K) and liquid nitrogen temperature (77 K) and the corresponding g values are listed in Table 1 (Fig. 2). [Cu(bipy)(aminoacid)]⁺ complexes show a single signal (with g values in the range 2.063 to 2.076 which are

Table 1. g -Tensor values of some polycrystalline [Cu(bipy)(amino acid)]⁺ complexes

Complex	at RT (298 K)		at LNT (77 K)
	G		g
[Cu(bipy)(gly)]Cl.1.5H ₂ O	2.076		2.067
[Cu(bipy)(ala)]Cl.1.5H ₂ O	2.076		2.073
[Cu(bipy)(val)]Cl.3H ₂ O	2.067		2.063
[Cu(bipy)(ser)]Cl.1.H ₂ O	2.076		2.067

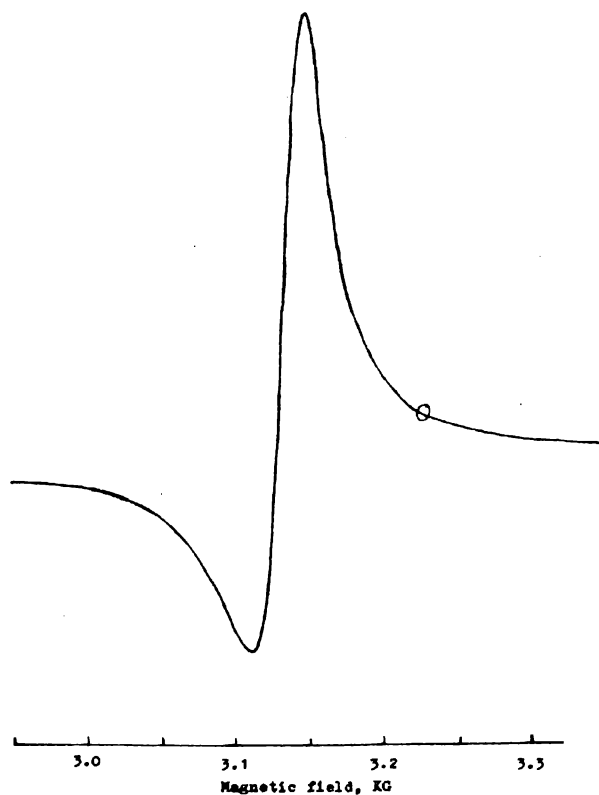


Fig. 2. Polycrystalline EPR spectrum of [Cu(bipy)(val)]Cl.3H₂O at 77 K.

greater than the free electron g value of 2.0023), which may be due to spin-spin interaction between the neighbouring paramagnetic cupric ions. It must be emphasized that these [Cu(bipy)(aminoacid)]⁺ complexes have the similar geometry and similar coordination donor environment about the central metal ion¹⁰. The solution EPR spectra recorded with 3 mM aqueous solutions of these complexes in 1.0 M NaClO₄ exhibited the four line isotropic spectra showing hyperfine interaction between the unpaired electron and copper nucleus ($I = 3/2$). The frozen solution EPR spectra of these complexes are anisotropic with $g_{||}$ (= 2.224 to 2.239) > g_{\perp} (=

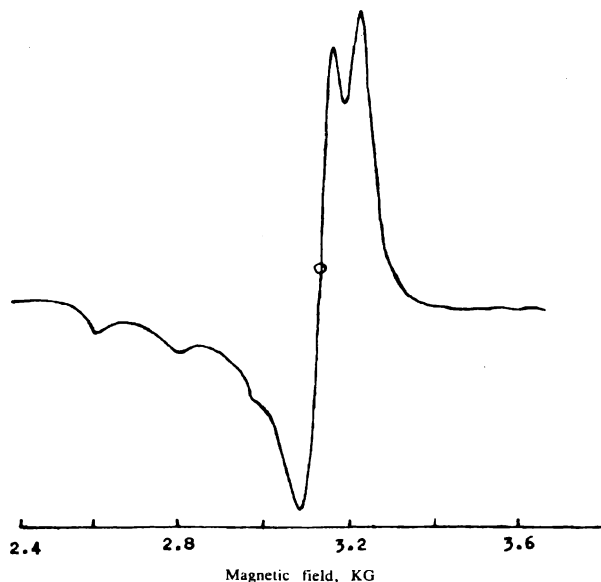


Fig. 3. Frozen solution EPR spectrum of 3 mM [Cu(bipy)(ala)]Cl.1.5H₂O in 1.0 M NaClO₄.

2.054 to 2.060) and $A_{||}$ (= 180 to 200G, Table 2 and Fig. 3). These spectra are characteristic of the tetragonally elongated octahedral copper(II) complexes with the ground state $d_{x^2-y^2}$.

Experimental

All the complexes are prepared as previously reported¹⁰ and their purity was checked by elemental analyses. All reagents used were of analytical grade. Cyclic voltammetric study was performed on a BAS model CV-1B instrument having an electrochemical cell with a three electrode system. The working electrode was a glassy carbon electrode (GCE), platinum wire was used as an auxiliary electrode and saturated calomel electrode (SCE) was used as a reference electrode. ($E^0 = 0.242$ V vs NHE). The cyclic voltammograms were recorded on an X-Y recorder. All the cyclic voltammetry experiments were done in an inert atmosphere achieved by purging the cell solution with extra pure nitrogen for about 20 min. An inert atmosphere of nitrogen was also maintained over the cell solution during recording of the voltammograms. 0.1 M Sodium perchlorate was used as the supporting electrolyte. Fresh solutions were prepared in double distilled water. The working electrode was polished with alumina polish after recording of each cyclic voltammogram. All the experiments were performed at 25°C.

The EPR spectra were recorded on a Varian E-line X-

Table 2. EPR parameters for 3 mM [Cu(bipy)(aminoacid)]⁺ complexes in 1.0 M NaClO₄ in aqueous medium

Complex	at RT (298 K)		at LNT (77 K)		
	g_0	A_0 (G)	$g_{ }$	g_{\perp}	$A_{ }$ (G)
[Cu(bipy)(gly)]Cl.1.5H ₂ O	2.115	73.3	2.239	2.060	180
[Cu(bipy)(ala)]Cl.1.5H ₂ O	2.119	73.3	2.231	2.060	190
[Cu(bipy)(val)]Cl.3H ₂ O	2.116	73.3	2.224	2.054	200
[Cu(bipy)(ser)]Cl.H ₂ O	2.116	73.3	2.231	2.054	180

band spectrometer equipped with a dual cavity and operating in the 9.152–9.232 GHz range. The g -values were calibrated with tetracyanoethylene, TCNE ($g = 2.0028$) used as a field marker. The EPR spectra were recorded both in solid and in solution state (3 mM solution of each of the complexes **1** to **4** in 1.0 M aqueous NaClO₄ at room temperature (298 K) and at liquid nitrogen temperature (77 K)). $g_{||}$ values were measured according to standard procedure.

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