Electrochemical Study of Benzimidazole Complexes with Copper (II) Ions in Organic Solvents

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Abstract: *The electrochemical behaviours of copper (II) benzimidazole complex species have been studied in varying concentrations of benzimidazole using cyclic voltammetry. The cyclic voltammetric parameters were calculated. The complex species described involved two or more redox steps. The first step ($Cu^{2+/+}$) involved a single electron, diffusion-controlled quasi-reversible electrode process (EC mechanism), while the second step(s) involved an irreversible reduction of the Cu(I) species to metallic copper.*

Keywords: copper (II) complexes, benzimidazole, organosolvent, cyclic voltammogram, electroreduction, electrooxidation

1.   INTRODUCTION

Benzimidazoles are classified as drugs[1] based on the possible substitutions at different positions on the benzimidazole nucleus. Benzimidazole is extensively used in industrial processes as a corrosion inhibitor for metal and alloy surfaces.[2–5] It is also known to play a fundamental role in many biological systems.[2] As interest in exploring benzimidazole derivatives and their metal complexes has continually increased, it has been recognised that these materials may serve as models that mimic both the structure and reactivity of metal ions in complex biological systems.[6]

Synthesis, thermal profiles,[2] spectral and magnetic[7] studies of copper (II) complexes of the general formula $Cu(B_ZIm)X_2$ have been performed. Nickel (II) benzimidazole bromide complexes with the formula $NiL_4Br_2(acetone)_2$ have also been investigated[8] using thermoanalytical techniques coupled with a Fourier transform infrared (FT–IR) system supported by spectral techniques. The molecular structure of the dichlorobis(benzimidazole)Zn(II) complex was also investigated[9] by X-ray diffraction and infrared (IR) spectroscopy. The Zn atom was found to coordinate tetrahedrally with two Cl⁻ anions and two benzimidazole ligands.

A literature review revealed that electrochemical studies of complexes with benzimidazole or its derivatives have received little attention.[10] Cyclic voltammograms (CVs) of ruthenium and iron complexes with benzimidazole derivatives were described previously[10] and displayed a single wave couple, which was reversible over all pH ranges investigated. The relationship between the acid-base equilibria and electrochemistry was explored by focusing on their proton-couple electron transfer (PCET) reactions. Earlier, electroreduction of copper complexes with chelating ligands (benzimidazole, phenanthroline) in organic lithium containing an aqueous electrolyte was studied.[11] Electrochemical and spectral methods were used to test models for the energy transforming device, which contained electrode materials based on the complexes studied.

The aim of this study was to extend the cyclic voltammetric investigation of benzimidazole complexes from the first redox step to the second redox step. Copper was used as the metal ion in organic solvents and electrode mechanisms were proposed when necessary.

2.   EXPERIMENTAL

The electrochemical parameters were obtained with a BAS Model CV-IB (Indiana, USA) cyclic voltammograph instrument having an electrochemical cell with a three-electrode system. The working electrode was a glassy carbon electrode (GCE). Platinum (Pt) wire was used as an auxiliary electrode, while a saturated calomel electrode (SCE) was used as a reference electrode with $E^0 = 0.242$ V vs. NHE. The voltammograms were recorded on an X-Y recorder. Benzimidazole (B_ZIm) and tetrabutylammoniumphosphate (TBAP) were obtained from Aldrich (USA). Dimethysulfoxide (DMSO) and acetonitrile (AN) were spectroscopy grade and were used as received. Ethyl alcohol was supplied by Calcutta Chemical Company, India. Copper chloride ($CuCl.2H_2O$) was analytical reagent grade.

All cyclic voltammetric experiments were performed in an inert atmosphere. This was achieved by purging the cell solutions with nitrogen gas for approximately 20 minutes. The atmosphere was maintained over the cell solution during the recording of the voltammograms. The nitrogen gas was purified by bubbling through an alkaline vanadous sulfate solution and by passing it through a calcium sulfate drying tube before bubbling the gas through the cell solution(s).

The experiments were carried out at 25°C ± 1°C in 0.1 M tetrabutylammoniumphosphate-supporting electrolyte. Stock solutions of 0.01 M in 100 cm^3 of solvent were prepared for $CuCl_2.2H_2O$ and B_ZIm in dimethylsulfoxide, acetonitrile and ethyl alcohol. For a total working volume of

20 cm^3, 2.0 cm^3 of CuCl$_2$.2H$_2$0 was placed in a clean dry beaker for each experiment. To make 0.002 M, 0.004 M and 0.006 M B$_Z$Im solutions, 4.0 cm^3, 8.0 cm^3 and 12.0 cm^3 were respectively mixed with the copper salt solution in the same beaker to obtain a total of 20 cm^3 of each of the non-aqueous solvents. The 0.01 M and 0.1 M B$_Z$Im solutions were prepared by dissolving 0.236 g and 2.362 g, respectively, in a beaker containing 2.0 cm^3 CuCl$_2$.2H$_2$0 to obtain 20 cm^3 of each non-aqueous solvent. These were specified as 1:2, 1:4, 1:6, 1:10 and 1:100 copper:ligand molar ratios. All experiments were carried out with freshly prepared solutions.

3.   RESULTS AND DISCUSSION

Table 1 shows the electrochemical results for the Cu(II)-B$_Z$Im complexes with [Cu(II)]:[B$_Z$Im] = 1:2, 1:4, 1:6, 1:10 and 1:100 molar ratios and 0.001 M CuCl$_2$.2H$_2$0 in DMSO. The CVs for the 1:2, 1:4, 1:6 and 1:10 ratios scanned in the potential range of +0.80 to –0.90 V vs. SCE were similar. They were characterised by a redox couple (c$_I$/a$_I$) and an irreversible reduction c$_2$ at $\cong$ –0.67 V at 25 mV/s (Figure 1). The peak current for the second reduction (Ipc$_2$) was, however, very small relative to that for first step (Ipc$_1$). When scanning in the negative direction from +0.80 to –1.40 V, the 1:100 molar ratio showed a redox couple c$_I$/a$_I$ corresponding to Cu$^{2+/I+}$ with E$^{0'}$ = +165 mV. A second irreversible reduction (c$_2$) was attributed to the Cu$^{+/o}$ at –1.09 V followed by a stripping peak (a$_2$) at –0.32 V in the reverse sweep (Figure 2). Analysis of Table 1 for the first couple indicated that the Cu(II)-B$_Z$Im complexes underwent a diffusion controlled (1:2 and 1:4 ratios excepted) quasi-reversible single-electron transfer reduction.[12]

Figure 3 shows that CVs of a Cu(II)-B$_Z$Im system in acetonitrile with 1:2 (A) and 1:4 (B) molar ratios scanned in the potential range of +0.80 to –0.20 V have features similar to SCE. Quasi-reversible reduction was displayed at +365 and +325 mV and had an irreversible reduction at $\cong$ 20 mV and $\cong$ 150 mV, respectively, at 25 mV/s. The peak current Ipc$_2$ was drastically reduced in the 1:4 molar ratio.

The CVs (Figure 4) scanned in the potential range of +0.80 to –0.90 V also showed similar features with one more reduction steps at a more negative potential. This involved two waves marked as c'$_3$ and c$_3$ at –0.64 (–0.67) and –0.73 (–0.79) V, respectively. They were assigned to a Cu$^{+/0}$ change in the 1:2 (1:4) molar ratio at 25 mV/S with a stripping peak at $\cong$ –0.27 (0.25) V.

Table 1: Cyclic Voltametric Parameters for [M]: [L] Cu(II)-B$_Z$Im Complexes, 0.001 M CuCl$_2$.2H$_2$0 in 0.1 M TBAP/DMSO.

Scan Rate mVs^{-1}	First Step							Second Step	
	Epc$_1$/mV	Epa$_1$/mV	Ipc$_1$/µA	Ipa$_1$/µA	E$^{0'}$/mV	ΔEp/mV	$\frac{Ipa_1}{Ipc_1}$	Epc$_2$(Ipc$_2$)	Epa$_2$(Ipa$_2$)
L=0.002M									
10	+265	+365	3.0	2.0	+315	100	0.66		
25	+260	+365	4.0	3.0	+313	105	0.75	−670(N/M)	
50	+250	+375	6.0	4.5	+313	125	0.75	−690(N/M)	
100	+230	+390	7.0	6.0	+310	160	0.85	−700(N/M)	
150	+225	+400	8.0	7.0	+313	175	0.87		
200	+220	+405	9.0	8.0	+313	185	0.88		
250	+215	+410	10.0	9.0	+313	195	0.90		
L=0.004M									
10	+260	+350	2.5	2.0	+305	90	0.80		
25	+240	+360	3.5	3.0	+300	120	0.80	−670(N/M)	
50	+225	+365	5.0	4.0	+295	125	0.80	−690(N/M)	
100	+220	+380	7.0	5.0	+300	160	0.71	−700(N/M)	
150	+210	+390	8.0	6.0	+300	180	0.75		
200	+200	+395	9.2	7.0	+298	195	0.76		
250	+200	+400	10.0	8.0	+300	200	0.80		
300	+195	+405	11.2	8.5	+300	210	0.75		
L = 0.006M									
10	+245	+335	2.0	2.0	+290	90	1.0		
25	+230	+335	3.0	2.5	+283	105	0.83	−670(N/M)	
50	+225	+345	4.5	4.0	+285	120	0.88	−690(N/M)	
100	+215	+355	6.0	5.0	+285	140	0.83	−700(N/M)	
150	+205	+365	7.5	6.0	+285	160	0.80		
200	+195	+370	8.0	7.0	+283	175	0.87		
250	+190	+380	9.0	7.5	+285	190	0.83		
300	+185	+385	10.0	8.2	+285	200	0.82		

(continued)

Table 1: (continued)

Scan Rate mVs⁻¹	First Step							Second Step	
	Epc_1/mV	Epa_1/mV	Ipc_1/μA	Ipa_1/μA	$E^{0'}$/mV	ΔEp/mV	$\frac{Ipa_1}{Ipc_1}$	$Epc_2(Ipc_2)$	$Epa_2(Ipa_2)$
L = 0.01M									
10	+235	+325	2.0	2.0	+280	90	1.0		
25	+225	+335	3.0	2.5	+280	110	0.83		
50	+220	+340	4.5	3.5	+280	120	0.77	−675(N/M)	
100	+205	+345	6.0	5.0	+275	140	0.83	−690(N/M)	
150	+200	+350	7.0	6.0	+275	150	0.85		
200	+195	+355	8.2	7.0	+275	160	0.85		
250	+190	+360	9.2	8.0	+275	170	0.86		
300	+175	+365	10.0	8.5	+270	190	0.85		
L=0.1M									
10	+120	+210	1.5	1.5	+165	90	1.0		
25	+120	+210	2.5	2.0	+165	90	0.80	−1090(2.0)	−320(10.5)
50	+115	+225	3.0	3.0	+170	110	1.0	−120 (11.0)	−310 (3.0)
100	+100	+230	4.5	4.0	+165	130	0.88		
150	+100	+230	5.0	4.5	+165	130	0.90		
200	+95	+235	6.0	5.0	+165	140	0.83		
250	+85	+240	7.0	5.5	+163	155	0.78		
300	+80	+245	7.2	6.0	+163	165	0.83		

Notes: N/M not measurable
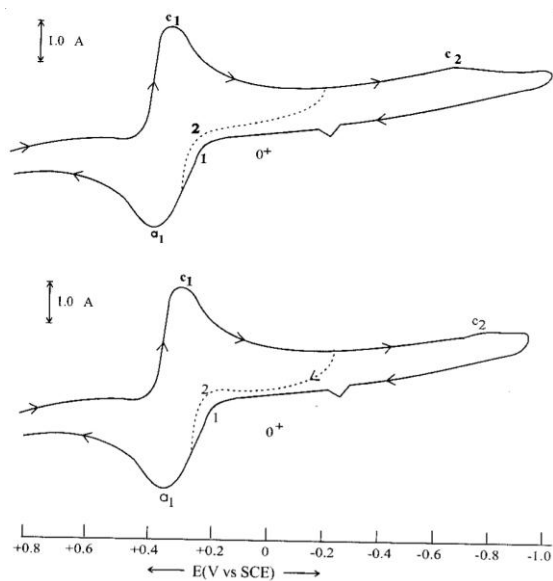   All potentials are given in mV vs SCE

Figure 1: CVs of 1:2 (A) and 1:4 (B) Cu(II)-B_ZIm system at υ = 25 mV/s, 0.001 M $CuCl_2$ in DMSO/0.1 M TBAP.
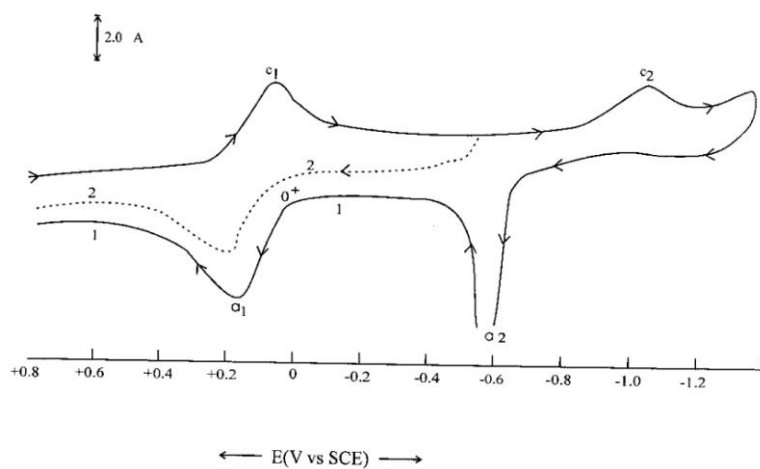

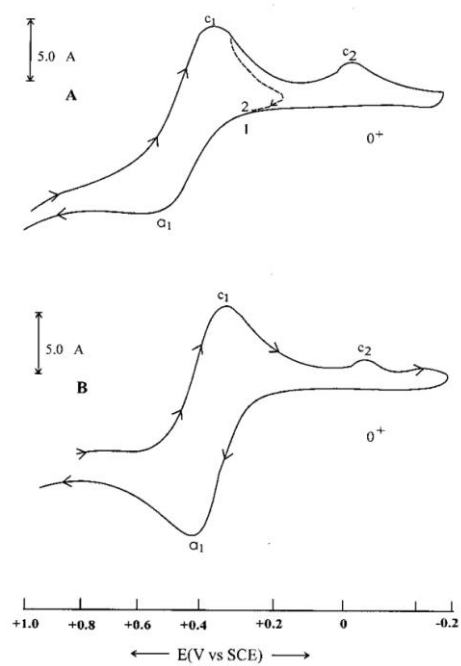Figure 2: CV of 1:100 Cu(II)-B_ZIm system at υ = 25 mV/s, 0.001 M $CuCl_2$ in DMSO/0.1 M TBAP.

Figure 3: CVs of 1:2 (A) and 1:4 (B), Cu(II)-B_ZIm system at $\upsilon = 25$ mV/s, 0.001 M CuCl$_2$ in AN/0.1 M TBAP.
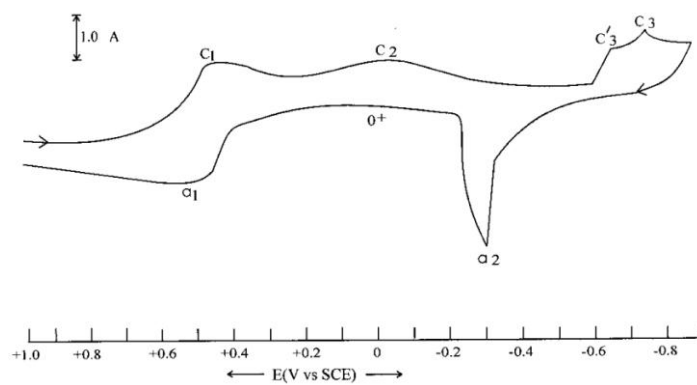

Figure 4: CV of 1:2 Cu(II)-B_ZIm system at $\upsilon = 25$ mV/s, 0.001 M CuCl$_2$ in AN/0.1 M TBAP.
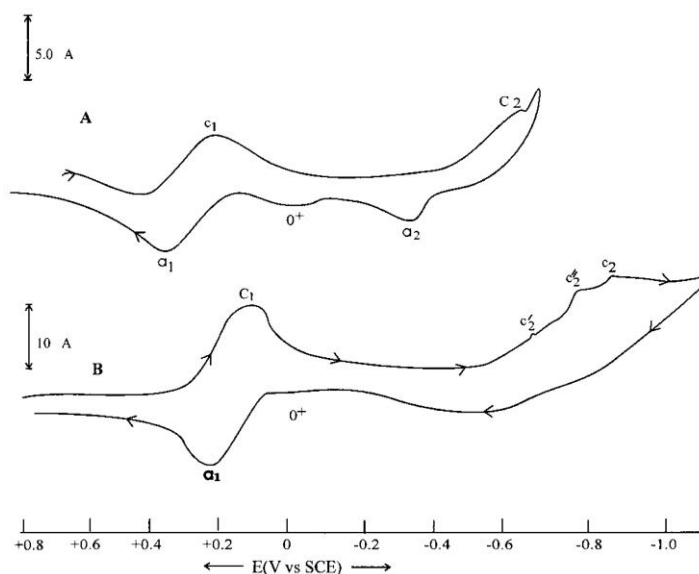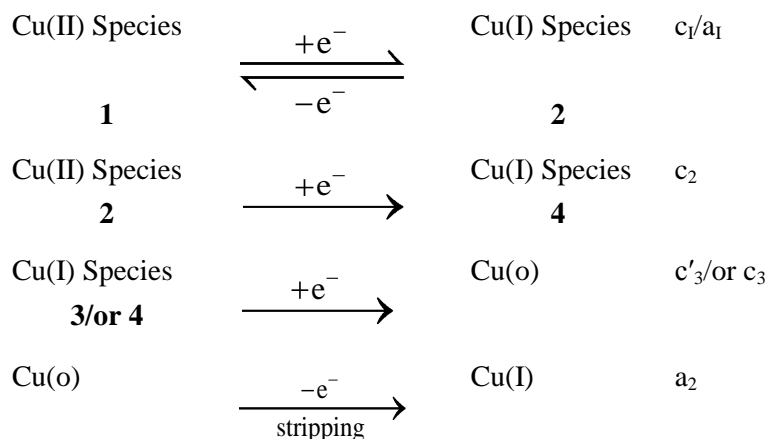
Figure 5: CV of (A) 1:10, (B) 1:100 Cu(II)-B_ZIm system at υ = 25 mV/s, 0.001 M CuCl$_2$ in AN/0.1 M TBAP.

Figure 5A displays the CV of the 1:10 Cu(II)-B_ZIm system in the potential range of +0.80 to –0.80 V at ν = 25 mV/s; a quasi-reversible couple (c_I/a_I) and an irreversible reduction (c_2) at $\cong$ –0.69 V is shown. Interestingly, the second anodic peak (a_2) at –0.37 V did not appear as a stripping peak and its potential was shifted cathodically relative to lower Cu(II)-B_ZIm molar ratios. Further, CV features observed for the 1:100 Cu(II)-B_ZIm system with respect to second reduction step differed greatly. The second step consisted of three overlapping waves displayed as c'_2, c''_2 and c_2 at about –0.63, 0.73 and –0.815 V. However, the anodic peak, a_2, disappeared completely (Figure 5B). Analysis of Table 2 indicated that the Cu(II)-B_ZIm complexed with [Cu(II)]: [B_ZIm] (1:2 to 1:100 molar ratios) underwent a diffusion-controlled[12] quasi-reversible single-electron redox reaction Cu$^{2+/+}$ and an irreversible Cu$^{+/o}$ reduction (c_2) at a more negative potential in acetonitrile.

The suggested redox process[14, 15] for copper (II) complexes at low molar ratios of 1:2 and 1:4 may be represented as follows:

Cu(II) Species $\xrightarrow[-e^-]{+e^-}$ Cu(I) Species c_I/a_I

1   **2**

Cu(II) Species $\xrightarrow{+e^-}$ Cu(I) Species c_2

2   **4**

Cu(I) Species $\xrightarrow{+e^-}$ Cu(o) $c'_3/or\ c_3$

3/or 4

Cu(o) $\xrightarrow[stripping]{-e^-}$ Cu(I) a_2

The CV features were similar for the 1:2 Cu(II)-B_ZIm system in ethyl alcohol (Figure 6A) with those in AN (Figure 3). A quasi-reversible[12] couple (c_I/a_I) corresponding to the $Cu^{2+/+}$ reduction step at +350 mV and an irreversible reduction peak (c_2) at +190 mV were observed in alcohol in the potential range +0.70 to –0.20 in contrast to SCE. However, when extending the potential region to –1.10V, a second reduction step composed of two overlapping waves (c'_3 and c_3) at $\cong$ –0.773 and –0.96 V at 50 mV/s (Figure 6B) were observed. Interestingly, the second anodic peak (a_2) did not appear in the reverse scan, which differed more than in AN (Figure 4). The peak current ratio (Ipa_I/Ipc_I) was greater than unity for the 1:2 and 1:4 Cu(II): B_Z/Im system, suggesting that the copper (II) species was weakly absorbed at the surface of the working electrode. It should be noted that the reduction peak, c_2, appeared at $v \geq 50$ mV/s while the reduction peak, c_3, was centred at $\cong$ –0.68 V (Table 3). It appears that the concentration of the second reducible species was appreciably low in solution in the 1:4 molar ratio.

In the 1:6 molar ratio, an ill-defined second wave (c_2) appeared only at a higher scan rate in the sweep limit from +0.70 to –0.20 V as in the 1:4 molar ratio. However, when extending the potential range to –1.0 V, a reduction peak (c_3) appeared at a relatively more negative potential ($\cong 0.67$ V) corresponding to $Cu^{+/0}$ reduction and a well-known anodic stripping peak (a_2) at $\cong$ –0.09 V at 25 mV/s (Figure 7). Similar CV features can be noted for both 1:10 and 1:100 molar ratios, although the anodic peak (a_2) did not appear in the latter case (Figure 8).

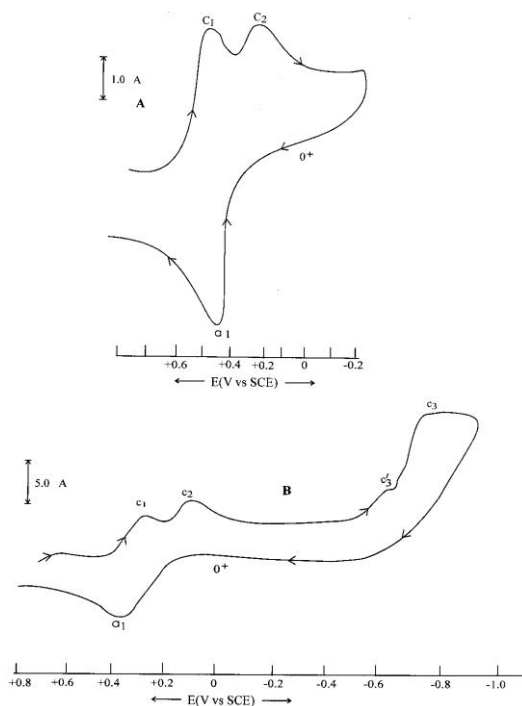Figure 6: CV of 1:2 Cu(II)-B_ZIm system at υ = 50 mV/s, 0.001 M CuCl$_2$ in ethylalcohol/0.1 M TBAP.
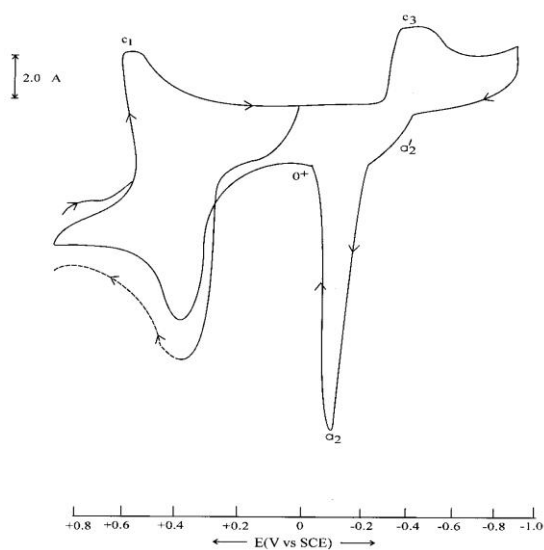

Figure 7: CV of 1:6 Cu(II)-B_ZIm system at υ = 25 mV/s, 0.001 M CuCl$_2$ in ethylalcohol/0.1 M TBAP.

Table 2: Cyclic Voltametric Parameters for [M]:[L] Cu(II)-B$_Z$Im Complexes, 0.001 M CuCl$_2$.2H$_2$0 in 0.1 M TBAP/Acetonitrile.

Scan Rate mVs-1	First Step								Second Step		
	Epc$_I$/mV	Epa$_I$/mV	Ipc$_I$/µA	Ipa$_I$/µA	E^0'/mV	ΔEp/mV	$\frac{Ipa_I}{Ipc_I}$	irr Epc$_2$/mV (Ipc$_2$/µA)^a	Epc$_2$/mV (Ipa$_2$/µA)	Epc$_3$'/mV (Ipa$_3$'/µA)	Epc$_3$'/mV (Ipa$_3$/µA)
L=0.002M											
10	+375	+515	5.0	4.0	+445	140	0.80	+30	−270 (19.5)	−640 (3.0)	−730 (8.0)
25	+365	+505	8.0	6.0	+435	140	0.75	+20			
50	+365	+510	11.0	8.5	+437	145	0.77	−5			
100	+355	+505	15.5	12.0	+430	150	0.77	−50			
150	+345	+510	19.0	15.0	+427	165	0.78	−90			
200	+340	+515	22.0	17.0	+427	175	0.77	−120			
250	+335	+515	24.5	18.5	+425	180	0.75	−140			
L=0.004M											
10	+325	+425	6.0	5.0	+375	100	0.83	−140		−670 (8.5)	−690 (9.0)
25	+325	+425	9.0	7.5	+375	100	0.83	−150			
50	+325	+430	13.0	11.0	+377	105	0.84	−160			
100	+310	+430	18.0	15.0	+370	120	0.83	−170			
150	+310	+440	22.0	18.0	+375	130	0.81	−180			
200	+310	+440	25.0	21.0	+375	130	0.82	−180			
250	+305	+445	28.0	23.5	+375	140	0.83	−185			
300	+295	+450	31.0	25.5	+372	155	0.82	−210			
L=0.006M											
10	+305	+395	7.5	5.5	+350	90	0.73				
25	+305	+400	10.5	8.5	+353	95	0.80				
50	+305	+400	15.0	11.5	+353	95	0.76				
100	+300	+400	19.5	16.5	+350	100	0.84				
150	+290	+405	24.0	21.0	+347	115	0.87				
200	+285	+405	28.0	24.0	+345	120	0.85				
250	+285	+410	31.0	27.0	+348	125	0.87				
300	+285	+415	33.5	29.5	+350	130	0.88				

(continued)

Table 2: (continued)

Scan Rate mVs-1	First Step							Second Step			
	Epc₁/mV	Epa₁/mV	Ipc₁/µA	Ipa₁/µA	$E^{0'}$/mV	ΔEp/mV	$\frac{Ipa_1}{Ipc_1}$	irr Epc₂/mV (Ipc₂/µA)ᵃ	Epc₂/mV (Ipa₂/µA)	Epc₃'/mV (Ipa₃'/µA)	Epc₃'/mV (Ipa₃/µA)
L=0.01M											
10	+275	+360	7.0	6.0	+318	85	0.85				
25	+265	+360	11.0	8.5	+313	95	0.77			−690(7.5)	−370(5.0)
50	+260	+360	15.0	12.0	+310	100	0.80			−870(14.5)	−390(2.5)
100	+250	+365	21.0	17.0	+308	115	0.80			−850(17.0)	−370ᵇ(5.0)
150	+250	+370	26.0	21.0	+310	120	0.80				
200	+225	+380	29.0	24.0	+303	155	0.82				
250	+225	+385	32.0	26.0	+305	160	0.81				
300	+215	+395	34.0	28.0	+305	180	0.81				
L=0.1M											
10	+155	+225	6.0	5.0	+190	70	0.83				
25	+140	+225	9.0	7.5	+183	85	0.83				
50	+130	+255	12.0	10.5	+192	125	0.87	−630 (3.0)	−730(12.5)	−815(20.0)	
100	+110	+235	18.0	15.0	+173	125	0.83				
150	+105	+235	22.0	18.0	+170	130	0.81				
200	+105	+240	25.0	20.0	+173	135	0.80				
250	+115	+240	27.0	23.0	+178	125	0.85				
300	+115	+245	29.5	25.0	+180	130	0.84				

Notes: a not measurable
irr irreversible
b = broad
All potentials are given in mV vs SCE
All currents are given in µA

Table 3: Cyclic Voltametric Parameters for [M]: [L] Cu(II)-B$_Z$Im Complexes, 0.001 M CuCl$_2$.2H$_2$0 in 0.1 M TBAP/Absolute Alcohol.

Scan Rate mVs-1	First Step								Second Step		
	Epc$_1$/mV	Epa$_1$/mV	Ipc$_1$/µA	Ipa$_1$/µA	E°/mV	ΔEp/mV	$\frac{Ipa_1}{Ipc_1}$	Epc$_2$/mV (Ipc$_2$/µA)	Epa$_2$/mV (Ipa$_2$/µA)	Epc$_3$'/mV (Ipc$_3$'/µA)	Epc$_3$/mV (Ipc$_3$/µA)
L=0.002M											
10	+350	+460	3.0	3.5	+405	110	1.16	+230 (N/M)			
25	+350	+470	4.0	5.0	+410	120	1.25	+190 (0.30)			
50	+335	+485	5.0	7.0	+410	150	1.40	+150 (2.0)		−775 (6.5)	−960 (12.5)
100	+320	+510	7.0	9.2	+415	190	1.31	+100 (3.0)			
150	+320	+500	9.0	11.0	+410	180	1.22	+80 (4.0)			
200	+315	+510	10.0	13.0	+412	195	1.30	+65 (5.0)			
250	+305	+520	11.0	14.5	+412	215	1.31	+50 (5.5)			
300	+300	+530	12.0	15.0	+415	230	1.25	+40 (6.0)			
L=0.004M											
10	+315	+425	3.0	3.5	+370	110	1.16	N/A			
25	+320	+435	4.5	5.0	+377	115	1.10	N/A			
50	+300	+455	6.0	6.2	+377	155	1.03	+150[a]		−680 (8.0)	
100	+290	+470	8.0	9.2	+380	180	1.15	+100[a]			
150	+280	+480	9.5	11.0	+380	200	1.15	+95[a]			
200	+265	+495	11.0	12.5	+380	230	1.13	+70[a]			
250	+245	+515	12.0	14.0	+380	270	1.16	+40[a]			

Table 3: (continued)

Scan Rate mVs-1	First Step							Second Step			
	Epc/mV	Epa_1/mV	$Ipc/\mu A$	$Ipa/\mu A$	$E^{o\prime}/mV$	$\Delta Ep/mV$	$\dfrac{Ipa1}{Ipc1}$	Epc_2/mV $(Ipc_2/\mu A)$	Epa_2/mV $(Ipa_2/\mu A)$	$Epc_3\prime/mV$ $(Ipc_3\prime/\mu A)$	Epc_3/mV $(Ipc_3/\mu A)$
L=0.006M											
10	+310	+390	4.2	3.5	+350	80	0.83	−670 (3.5)			
25	+295	+405	5.5	5.0	+350	110	0.90		−90 (9.0)		
50	+285	+420	7.0	7.0	+353	135	1.0				
100	+270	+440	9.0	9.0	+355	170	1.0				
150	+260	+460	10.5	11.0	+360	200	1.04				
200	+255	+460	12.0	12.5	+358	205	1.04				
250	+255	+465	13.0	14.0	+360	210	1.07				
L=0.01M											
10	+275	+375	4.0	4.0	+325	100	1.0				
25	+275	+380	6.0	6.0	+327	105	1.0	−660 (1.0)	−215 (6.0)		
50	+255	+395	8.0	8.0	+325	140	1.0				
100	+235	+415	11.0	11.0	+325	180	1.0				
150	+215	+430	13.0	13.0	+323	215	1.0				
200	+210	+435	15.0	15.0	+323	225	1.0				
250	+190	+440	17.0	17.0	+315	250	1.0				

(continued)

Table 3: (continued)

| Scan Rate mVs^{-1} | First Step | | | | | | | | Second Step | | |
	Epc$_1$/mV	Epa$_1$/mV	Ipc$_1$/µA	Ipa$_1$/µA	E$^{o'}$/mV	ΔEp/mV	Ipa$_1$/Ipc$_1$	Epc$_2$/mV (Ipc$_2$/µA)	Epa$_2$/mV (Ipa$_2$/µA)	Epc$_3$'/mV (Ipc$_3$'/µA)	Epc$_3$mV (Ipc$_3$/µA)
L=0.1M											
10	+175	+270	4.0	3.0	+223	95	0.75				
25	+165	+280	5.0	4.5	+223	115	0.90	−668 (7.5)			
50	+145	+285	7.0	6.0	+215	140	0.85				
100	+135	+300	9.0	8.5	+218	165	0.94				
150	+115	+310	10.5	10.0	+213	195	0.95				
200	+100	+320	12.0	11.5	+210	220	0.95				
250	+90	+325	13.0	13.0	+208	235	1.0				

Notes: a, corresponding current (Ipc$_2$) is not measurable
N/M not measurable
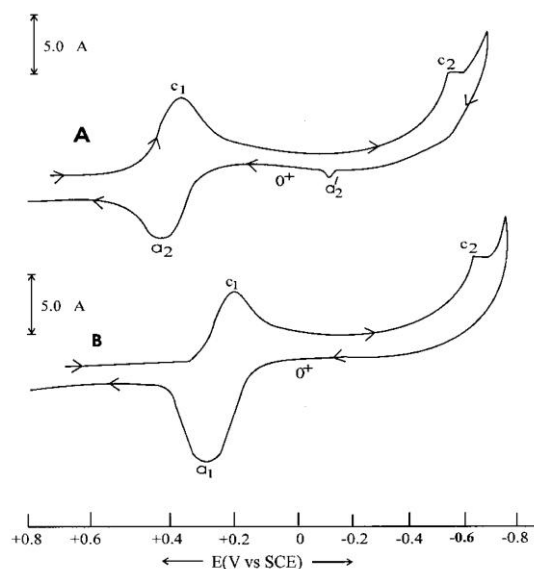N/A not appeared
All potentials are given in mV vs SCE

Figure 8: CVs of 1:10 (a) and (B) 1:100 Cu(II)-B_ZIm system at υ = 25 mV/s, 0.001 M CuCl$_2$ in ethylalcohol/0.1 M TBAP.

The peak current ratio for Ipa$_I$/Ipc$_I$ was determined to be $\cong$ 1.0 for 1:6, 1:10 and 1:100 Cu(II)-B_ZIm systems (Table 3), which indicated chemical reversibility. However, ΔEp increased with a scan rate indicating chemical quasi-reversibility (slow electron transfer).[12] A common observation in these solvents was that the first reduction potential (Epc$_I$) shifted cathodically with an increased concentration of the ligands; an opposite trend was observed for the corresponding anodic peak (Epa$_I$). These observations indicated that the higher order complexes of Cu(B_ZIm)nX$_2$ (n = 2, 4) were formed with an increased concentration of the ligand.

4.   CONCLUSION

Cyclic voltammetry of Cu(II)-B_ZIm complexes in organic solvents (dimethylsulfoxide, acetonitrile and ethyl alcohol) was complex because it was comprised of electrooxidation and electroreduction of copper (0), copper (I) and copper (II) species.

5.   ACKNOWLEDGEMENTS

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