



## Electrochemical and Spectral Investigations of Copper in Different Mixed Ligand Complex Solutions in Non- Aqueous Solvents

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### ABSTRACT

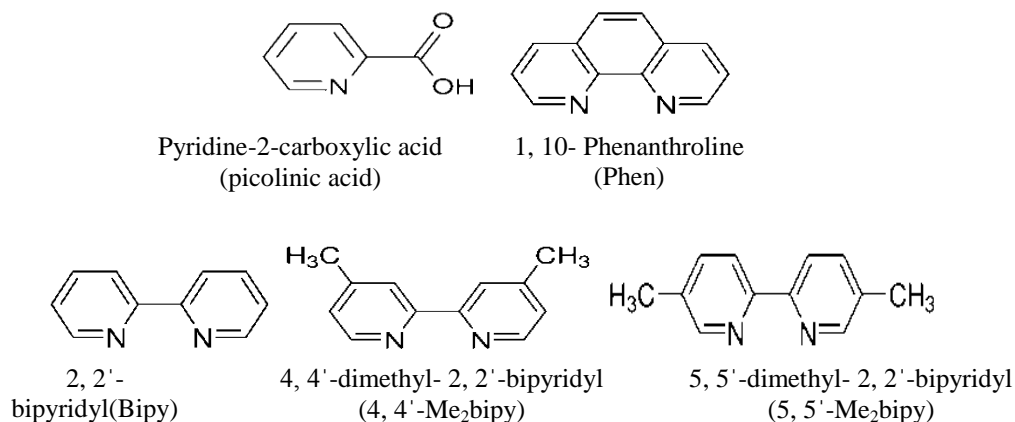
*Electrochemical behaviour of copper in its mixed ligand complexes of picolinic acid with diimines {where diimines =1, 10- Phenanthroline(phen)1; 2, 2'-bipyridyl(bipy)2; 4, 4'-dimethyl 2, 2'-bipyridyl(4,4'-Me<sub>2</sub>bipy)3; 5, 5'-dimethyl 2, 2'-bipyridyl(5,5'-Me<sub>2</sub>bipy)4}[Cu<sup>2+</sup>(diimine)pic] in 1:2:10 metal to ligand molar ratio have been studied in dimethylsulfoxide (DMSO) and dimethyl formamide (DMF) separately containing 0.2 M sodium perchlorate (NaClO<sub>4</sub>) as a supporting electrolyte at a glassy carbon disc working electrode using cyclic voltammetry. It should be mentioned that the complexes displayed a single quasireversible redox couple (Cu<sup>2+/+</sup>). It is observed that the cathodic peak potential shift more negatively and anodic peak potential shifts more positively with increasing scan rate. Anodic to cathodic peak potential difference, ΔE<sub>p</sub> values are more than 60 mV, clearly showing the quasireversible nature of redox process. The UV-visible electronic spectra of the above Cu(II) complexes were also studied in DMSO and DMF at room temperature.*

**Keywords:** Cu (II) complexes, diimines, picolinic acid, cyclic voltammetry, UV-visible spectra.

### INTRODUCTION

Copper is an important trace element in living organisms that plays very vital roles in different enzymatic processes; superoxide dismutase, cytochrome oxidase, tyrosinase, azurin and ceruloplasmin all involving oxidation and reduction [1]. Pyridine-2-carboxylic acid (picolinic acid) which is a naturally occurring product of the degradation of tryptophan is a biologically important ligand found in some enzymes. It has metal ion-chelating activity and is an active agent in some drugs [2]. The crystal structures of 2-picolinic acid complexes with Ni(II), Zn(II), Co(III), and Cu(II) have been reported[3]. The presence of nitrogen and oxygen donor atoms in the picolinic acid has provided binding sites to various metals during the formation of various monomeric and polymeric coordination complexes [4]. Metal complexes of pyridine-2-carboxylic acid (picolinic acid) have been widely studied as well as those of its derivatives with electron-withdrawing substituent, such as hydroxyl groups or halogen atoms, due to their great coordination flexibility and wide variety of physiological properties, especially insulinomimetic activity [5].

In the present paper, electrochemical and spectral behaviour of mixed ligand Cu(II) complexes with diimines and picolinic acid in 1:2:10 metal to ligand molar ratio have been reported. The structures of the ligands taken are shown below.



## MATERIALS AND METHODS

All the chemicals, copper perchlorate hexahydrate  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ , picolinic acid, diimines (phen, bipy, 4,4'-Me<sub>2</sub>bipy, 5,5'-Me<sub>2</sub>bipy) and sodium perchlorate were purchased from Sigma-Aldrich Chemicals Pvt. Ltd., dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) from Merck, India and were used as such without further purification. All the cyclic voltammograms were recorded in DMSO and DMF separately containing 0.2 M sodium perchlorate ( $\text{NaClO}_4$ ) as a supporting electrolyte. 1mM solution of copper perchlorate (both in DMSO and in DMF) was used.

The software driven BAS Electrochemical System, Model EPSILON (Bioanalytical System, Inc, USA) was employed for all the electrochemical measurements. The working electrode was glassy carbon disc electrode (GCE), the auxiliary electrode was platinum wire and reference electrode was Ag/AgCl in saturated KCl ( $E^{0'} = +199$  mV vs. NHE). Purging and blanketing of nitrogen (99.999% pure) were done for analytical solution placed in the electrochemical cell of 15mL capacity for 20 min. Great care was taken in the electrode pre-treatment. Mechanical polishing of the working electrode (GCE) was done over a velvet micro cloth with an alumina suspension. All the electrochemical experiments were performed at a constant temperature of  $25 \pm 0.5^\circ\text{C}$ . IR compensation and background subtraction have also been done. Electronic absorption spectra of the complexes have been recorded in DMSO and DMF at room temperature by Perkin-Elmer UV-Visible Spectrophotometer Model Lambda-35.

## RESULTS AND DISCUSSION

### Electrochemical behaviour of mixed-ligand copper (II) complexes with diimines and picolinic acid

**[Cu(diimines)(pic)] in DMSO and DMF:** The electrochemical properties of Cu(II): diimines: pic complexes formed in 1:2:10 molar ratios were studied separately in DMSO and DMF containing 0.2 M  $\text{NaClO}_4$  as a supporting electrolyte using cyclic voltammetry. All CV experiments were performed in the scan rate range from 25 to  $200\text{mVs}^{-1}$  in the potential limits +1000 to -300mV. The CV data are given in Table 1 and cyclic voltammograms are shown in Fig1(a) and 1(b) at  $25^\circ\text{C}$ . At scan rate  $25\text{mVs}^{-1}$ , cathodic peak potentials,  $E_{pc}$  (in DMSO) = 14 mV, -89 mV, -121 mV and -117 mV and  $E_{pc}$  (in DMF) = 58 mV, -75 mV, -114 mV and -101mV in forward scan and one corresponding anodic peak in the reverse scan with anodic peak potentials,  $E_{pa}$  (in DMSO) = 101mV, 50 mV, 31mV and 10mV and  $E_{pa}$  (in DMF) = 130 mV, 83 mV, 31mV and 61 mV were obtained. At scan rate  $25\text{mVs}^{-1}$ , their peak potential separation  $\Delta E_p$  was 87 mV, 139 mV, 152 mV and 127 mV in DMSO and 72 mV, 158 mV, 145 mV and 162 mV, respectively in DMF, which are more than 60 mV corresponding to quasireversible one electron transfer reaction and the

$\Delta E_p$  values increase with increasing scan rate, clearly indicated that the electron transfer processes are quasireversible. In DMSO, a plot of cathodic peak current ( $I_{pc}$ ) vs square root of scan rate ( $v^{1/2}$ ) gave a straight line passing through origin showing that the reduction process was diffusion-controlled (EC-Mechanism)[6- 8], while in DMF, it gave a straight line with positive intercept indicating that the electron transfer is preceded by a chemical reaction (CE mechanism)[9, 10].

It should be noted that the cathodic peak potential ( $E_{pc}$ ) for [Cu(phen)(pic)] mixed ligand complex species formed is more positive as compared to that of [Cu(bipy)(pic)] complex species in a given solvent, indicating that the reduction of phen complex is easier (Table 1). This is because of the fact that the  $\pi$ -acceptor property of 1, 10- phenanthroline is better as compared to 2, 2'- bipyridyl ligand.

It is also interesting to note that the magnitude of cathodic potentials for bipyridyl mixed ligand complexes become less negative in the order 3→4→2 in both the solvents taken in the present investigation. This clearly shows that the reduction of the complexes become easier in the order mentioned above (Table 1). This can be understood on the basis of +I (inductive effect) effect of the substituent methyl groups in the complex species 3 and 4 with respect to unsubstituted 2, 2'-bipyridyl ligand. Furthermore, the cathodic peak potential ( $E_{pc}$ ) for a given complex at a given scan rate is more negative in DMSO as compared to that in DMF due to larger donor number (DN) of DMSO as compared to DMF.

**Table 1:** CV data for mixed-ligand complexes formed in 1:2:10  
Cu(ClO<sub>4</sub>)<sub>2</sub>: diimines: picolinic acid molar ratio in DMSO and DMF containing 0.2 M NaClO<sub>4</sub>

Solvent	Mixed-ligand Complexes with diimines	scan rate (mVs <sup>-1</sup> )	E <sub>pc</sub> (mV)	E <sub>pa</sub> (mV)	I <sub>pc</sub> (μA)	I <sub>pa</sub> (μA)	E <sup>0</sup> (mV)	ΔE <sub>p</sub> (mV)	I <sub>pa</sub> /I <sub>pc</sub>
DMSO	Cu(ClO <sub>4</sub> ) <sub>2</sub> :phen:pic <b>1</b>	25	14	101	2.7	1.9	57.5	87	0.7
		50	13	101	3.9	2.9	57.0	88	0.7
		100	13	104	5.5	4.2	58.5	91	0.8
		200	10	105	7.7	5.9	57.5	95	0.8
	Cu(ClO <sub>4</sub> ) <sub>2</sub> : bipy:-pic <b>2</b>	25	-89	50	2.4	2.1	-19.5	139	0.9
		50	-94	55	3.4	3.0	-19.5	149	0.9
		100	-96	58	4.7	4.4	-19.0	154	0.9
		200	-106	67	6.7	6.3	-19.5	173	0.9
	Cu(ClO <sub>4</sub> ) <sub>2</sub> :4,4'-Me <sub>2</sub> bipy:pic <b>3</b>	25	-121	31	2.5	2.1	-45.0	152	0.8
		50	-122	35	3.5	3.1	-43.5	157	0.9
		100	-128	42	5.0	4.4	-43.0	170	0.9
		200	-130	48	7.0	6.4	-41.0	178	0.9
	Cu(ClO <sub>4</sub> ) <sub>2</sub> :5,5'-Me <sub>2</sub> bipy:pic <b>4</b>	25	-117	10	2.4	2.2	-53.5	127	0.9
		50	-118	12	3.4	3.2	-53.0	130	0.9
		100	-118	13	4.9	4.6	-52.5	131	0.9
		200	-120	17	6.9	6.5	-51.5	137	0.9
DMF	Cu(ClO <sub>4</sub> ) <sub>2</sub> :phen:pic <b>1</b>	25	58	130	3.6	2.6	94.0	72	0.7
		50	46	134	4.2	3.3	90.0	88	0.8
		100	36	136	5.0	4.3	86.0	100	0.9
		200	23	138	6.1	5.6	80.5	115	0.9
	Cu(ClO <sub>4</sub> ) <sub>2</sub> :bipy:pic <b>2</b>	25	-75	83	3.8	2.6	4.0	158	0.7
		50	-75	87	5.0	3.8	6.0	162	0.8
		100	-76	90	6.7	5.2	7.0	166	0.8
		200	-76	95	9.0	7.2	9.5	171	0.8
	Cu(ClO <sub>4</sub> ) <sub>2</sub> :4,4'-Me <sub>2</sub> bipy:pic <b>3</b>	25	-114	31	3.6	2.7	-41.5	145	0.8
		50	-117	34	4.9	3.7	-41.5	151	0.8
		100	-122	40	6.5	5.2	-41.0	162	0.8
		200	-126	44	8.5	7.5	-41.0	170	0.9
	Cu(ClO <sub>4</sub> ) <sub>2</sub> :5,5'-Me <sub>2</sub> bipy:pic <b>4</b>	25	-101	61	3.2	1.9	-20.0	162	0.6
		50	-102	65	4.1	2.6	-18.5	167	0.6
		100	-105	70	5.3	3.5	-17.5	175	0.7
		200	-108	78	7.0	4.8	-15.0	186	0.7

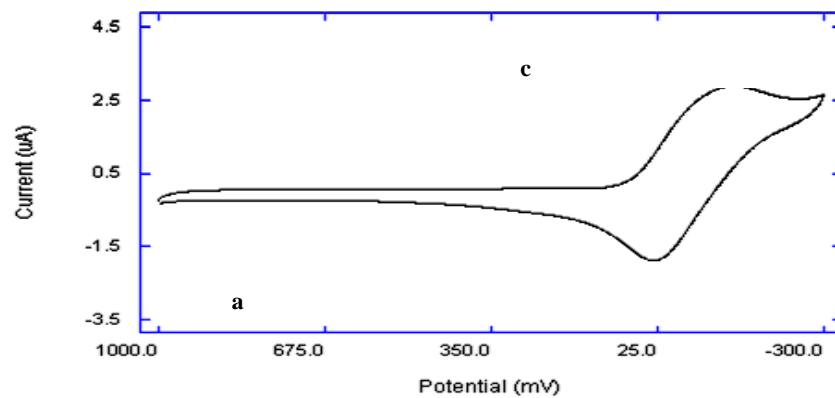


Figure 1(a). CV of mixed ligand complex 3 formed in DMSO containing 0.2 M NaClO<sub>4</sub> at 25mVs<sup>-1</sup>

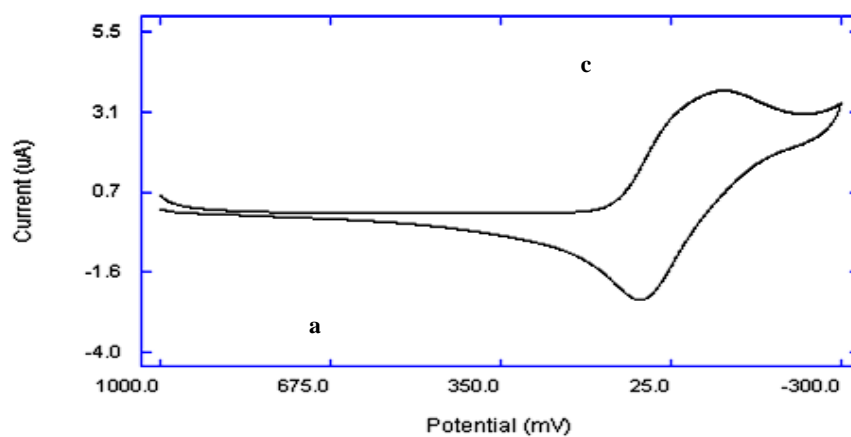


Figure 1(b). CV of mixed ligand complex 2 formed in DMF containing 0.2 M NaClO<sub>4</sub> at 25mVs<sup>-1</sup>

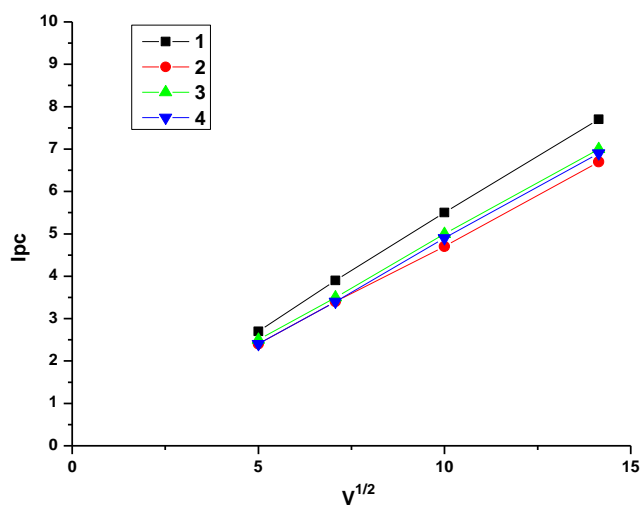


Figure 2(a): Plot of I<sub>pc</sub> Vs  $v^{1/2}$  for mixed ligand complexes 1- 4 in DMSO

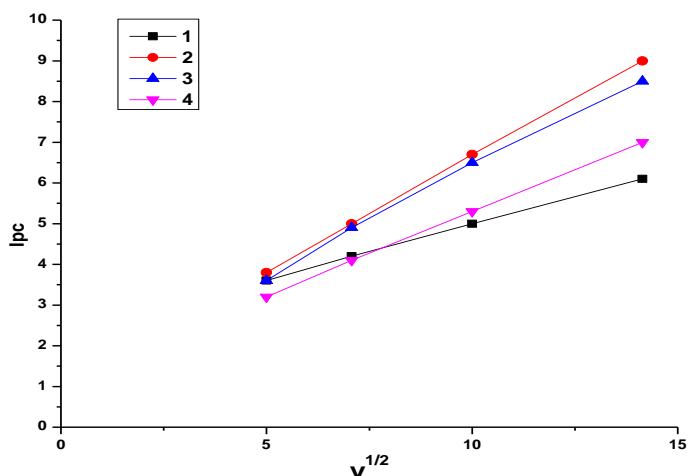


Figure 2(b): Plot of  $I_{pc}$  Vs  $v^{1/2}$  for mixed ligand complexes 1- 4 in DMF

**Electronic absorption spectral properties of mixed-ligand copper (II) complexes with diimines and picolinic acid [Cu (diimines) (pic)] in DMSO and DMF:** The electronic absorption spectral data for Cu(II) complexes are presented in Table 2. The electronic absorption spectra of Cu (II) complexes 1- 4 showed a broad d-d absorption band at 672 nm, 646 nm, 655 nm and 655 nm in DMSO and 677 nm, 638 nm, 655 nm and 648 nm in DMF, respectively suggested that 6- coordinated octahedral species were present in the mixed ligand complex solution [11, 12].

Table 2. Electronic absorption spectral data for mixed-ligand Cu(II) complex species formed in 1:2:10 molar ratio in DMSO and DMF

Solvent	System	Colour	$\lambda_{max}$ (nm)	$\epsilon$ (Lmol <sup>-1</sup> cm <sup>-1</sup> )
DMSO	Cu(ClO <sub>4</sub> ) <sub>2</sub> :phen:pic <b>1</b>	Light blue	672	40
	Cu(ClO <sub>4</sub> ) <sub>2</sub> :bipy:pic <b>2</b>	Light blue	646	60
	Cu(ClO <sub>4</sub> ) <sub>2</sub> :4,4'-Me <sub>2</sub> bipy:pic <b>3</b>	Light blue	655	40
	Cu(ClO <sub>4</sub> ) <sub>2</sub> :5,5'-Me <sub>2</sub> bipy:pic <b>4</b>	Light blue	655	50
DMF	Cu(ClO <sub>4</sub> ) <sub>2</sub> :phen:pic <b>1</b>	Light blue	677	60
	Cu(ClO <sub>4</sub> ) <sub>2</sub> :bipy:pic <b>2</b>	Light blue	638	60
	Cu(ClO <sub>4</sub> ) <sub>2</sub> :4,4'-Me <sub>2</sub> bipy:pic <b>3</b>	Light blue	655	70
	Cu(ClO <sub>4</sub> ) <sub>2</sub> :5,5'-Me <sub>2</sub> bipy:pic <b>4</b>	Light blue	648	60

### Highlights:

- Mixed ligand copper (II) complexes with picolinic acid and diimines in DMSO and DMF are investigated by electrochemical and spectral studies.
- All the complexes show single quasireversible redox couple.
- UV-visible studies indicate the presence of distorted octahedral six coordinated copper (II) complex species in nonaqueous solvents.

## CONCLUSIONS

In both the solvents (DMSO and DMF) all the mixed ligand copper (II) complexes with diimines and picolinic acid formed in 1:2:10 metal to ligand molar ratio displayed a single quasireversible redox couple ( $\text{Cu}^{2+/+}$ ) in the potential range +1000 to -300 mV. On increasing the scan rate the cathodic peak potential shift more negatively and anodic peak potential shifts more positively. The difference between anodic to cathodic peak potential,  $\Delta E_p$  values are more than 60 mV, clearly showing the quasireversible nature of redox couple. The electronic absorption spectra of mixed-ligand complexes showed one broad absorption band in the region 640-680 nm. On the basis of electronic absorption spectral band it could be clear that distorted octahedral copper (II) complex predominant species was present in complex solutions.

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