



Electrochemical and Spectral Behavior of Some Copper(II) Mixed Ligand Complexes involving Pyridine-3,5-dicarboxylic acid and Diimines in Dimethylsulfoxide

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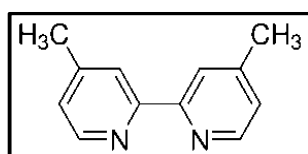
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ABSTRACT

Electrochemical behaviour of copper in its mixed ligand complexes of pyridine-3, 5-dicarboxylic acid(3,5-pdc)with diimines {where diimines =1, 10- Phenanthroline(phen)**1**; 2, 2'-bipyridyl(bipy)**2**;4, 4'-dimethyl 2, 2'-bipyridyl(4,4'-Me₂bipy)**3**;5, 5'-dimethyl 2, 2'-bipyridyl(5,5'-Me₂bipy)**4**}[Cu²⁺ (diimine) 3,5-pdc] in 2:1:1 metal to ligand molar ratio have been studied in dimethylsulfoxide (DMSO) containing 0.2 M sodium perchlorate (NaClO₄) as a supporting electrolyte at a glassy carbon disc working electrode using cyclic voltammetry. It should be mentioned that the complexes displayed a single quasi reversible redox couple (Cu^{2+/+}).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_p values are more than 60 mV, clearly showing the quasi reversible nature of redox process. The UV-visible electronic spectra of the above Cu(II) complexes were also studied in DMSO at room temperature.

Graphical Abstract



4, 4'-dimethyl- 2, 2'-bipyridyl
(4, 4'-Me₂bipy)

Highlights:

- Mixed ligand copper (II) complexes with pyridine-3, 5-dicarboxylic acid and diimines in DMSO are investigated by electrochemical and spectral studies.
- All the complexes show single quasi reversible redox couple.
- UV-visible studies indicate the presence of distorted octahedral six coordinated copper (II) complex species in DMSO.

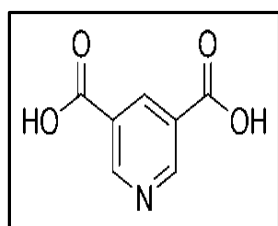
Keywords: Cu (II) complexes, diimines, pyridine-3, 5-dicarboxylic acid, cyclic voltammetry, UV-Visible spectra.

INTRODUCTION

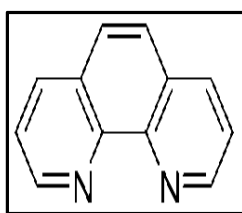
In living organisms, copper is an important trace element and plays very significant roles in different enzymatic processes; superoxide dismutase, cytochrome oxidase, tyrosinase, azurin and ceruloplasmin all involving oxidation and reduction [1]. Pyridinedicarboxylic acids have important biological function in the metabolism such as enzyme inhibitor, plant preservative and food sanitizer [2-5]. Pyridine 2, 3-, 2, 4-, 2, 5-, 2, 6-, 3, 4- and 3, 5- dicarboxylic acids exhibit various co-ordination modes. Pyridine-3, 5-dicarboxylic acid (3,5-pdc) is a multifunctional ligand which can bridge metal centres through different bridging modes with M–O and M–N bonds [6-8].

1, 10- phenanthroline and its derivatives are biologically important chelating ligands. Due to the planar nature of 1, 10- phenanthroline, it has an ability to participate as a DNA intercalators [9]. Some metal complexes containing 1, 10-phenanthroline is also known to bind to DNA by an intercalative mode [10-12]. Several metal complexes with 1,10-phenanthroline and natural products incorporating this heterocyclic nucleus process interesting anticancer properties [13-15].

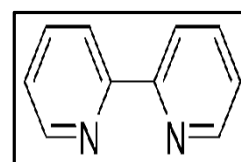
In the earlier work [16], we have investigated the electrochemical and spectral behaviours of mixed ligand complexes of copper (II) with picolinic acid and diimines in non- aqueous solvents (DMSO and DMF). In the present work, electrochemical and spectral behaviour of mixed ligand Cu(II) complexes with diimines and pyridine-3, 5-dicarboxylic in 2:1:1 metal to ligand molar ratio have been reported. The structures of the ligands taken are shown below.



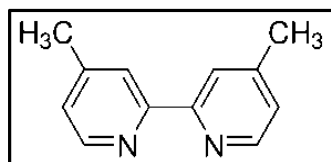
Pyridine-3, 5-dicarboxylic acid
(3, 5-pdc)



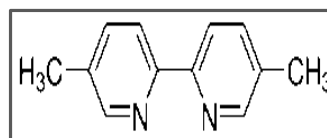
1, 10- Phenanthroline
(Phen)



2, 2'-bipyridyl
(Bipy)



4, 4'-dimethyl- 2, 2'-bipyridyl
(4, 4'-Me₂bipy)



5, 5'-dimethyl- 2, 2'-bipyridyl
(5, 5'-Me₂bipy)

MATERIALS AND METHODS

All the chemicals, copper perchlorate hexahydrate $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, pyridine-3, 5-dicarboxylic acid, diimines (phen, bipy, 4,4'-Me₂bipy, 5,5'-Me₂bipy) and sodium perchlorate were purchased from Sigma-Aldrich Chemicals Pvt. Ltd., dimethylsulfoxide (DMSO) from Merck, India and were used as such without further purification. All the cyclic voltammograms were recorded in DMSO containing 0.2 M sodium perchlorate (NaClO_4) as a supporting electrolyte. 2mM solution of copper perchlorate was used.

The software driven BAS Electrochemical System, Model EPSILON (Bioanalytical System, Ind, 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 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 pyridine-3, 5-dicarboxylic acid [Cu(diimines)(3, 5- pdc)]: The electrochemical properties of Cu(II): diimines: 3, 5-pdc complexes formed in 2:1:1 molar ratios were studied in DMSO containing 0.2 M NaClO_4 as a supporting electrolyte using cyclic voltammetry. All CV experiments were performed in the scan rate range from 25 to 500 mVs^{-1} in the potential limits +1000 to -300mV. The CV data are given in table 1 and cyclic voltammogram is shown in figure 1 at 25°C . At scan rate 25 mVs^{-1} , cathodic peak potentials, $E_{pc} = -6 \text{ mV}$, -13 mV , -49 mV and -17 mV in forward scan and one corresponding anodic peak in the reverse scan with anodic peak potentials, $E_{pa} = 101 \text{ mV}$, 112 mV , 115 mV and 115 mV were obtained. At scan rate 25 mVs^{-1} , their peak potential separation ΔE_p was 107 mV, 125 mV, 164 mV and 132 mV which are more than 60 mV corresponding to quasi reversible one electron transfer reaction and the ΔE_p values increase with increasing scan rate, clearly indicated that the electron transfer processes are quasi reversible. A plot of cathodic peak current (I_{pc}) and anodic peak current (I_{pa}) vs square root of scan rate ($v^{1/2}$) gave a straight line with positive intercept (Figure 2a and 2b) indicating that the electron transfer is preceded by a chemical reaction (CE mechanism)[5, 16, 17].

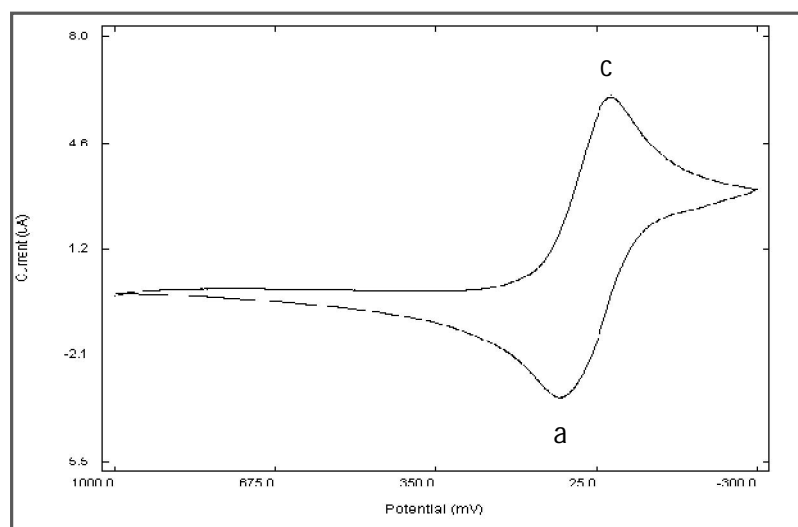


Figure 1. CV of mixed ligand complex 1 formed in DMSO containing 0.2 M NaClO_4 at 25 mVs^{-1}

It should be noted that the cathodic peak potential (E_{pc}) for [Cu(phen)(3,5-pdc)] mixed ligand complex species formed is more positive as compared to that of [Cu(bipy)(3,5-pdc)] 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 π -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 $3 \rightarrow 4 \rightarrow 2$. 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.

Table 1. CV data for mixed-ligand complexes formed in 2:1:1 Cu(ClO₄)₂: diimines: 3, 5-pdc molar ratio in DMSO containing 0.2 M NaClO₄

Mixed-ligand Complexes with diimines	scan rate (mVs ⁻¹)	E _{pc} (mV)	E _{pa} (mV)	I _{pc} (μA)	I _{pa} (μA)	E ⁰ (mV)	ΔE _p (mV)	I _{pa} /I _{pc}
Cu(ClO ₄) ₂ :phen:3,5-pdc 1	25	-6	101	6.4	4.4	47.5	107	0.7
	50	-8	104	8.8	5.8	48.0	112	0.7
	100	-12	108	12.7	8.0	48.0	120	0.6
	200	-20	120	17.7	11.3	50.0	140	0.6
	300	-22	122	21.7	13.4	50.0	144	0.6
	400	-23	124	24.9	15.5	50.5	147	0.6
	500	-25	127	28.0	17.2	51.0	152	0.6
Cu(ClO ₄) ₂ :bipy: 3,5-pdc 2	25	-13	112	12.4	9.4	49.5	125	0.8
	50	-18	117	17.9	13.4	49.5	135	0.7
	100	-19	119	25.3	19.1	51.0	140	0.8
	200	-21	126	36.3	26.7	52.5	147	0.7
	300	-23	130	44.6	32.5	53.5	153	0.7
	400	-26	134	51.5	37.5	54.0	160	0.7
	500	-31	140	57.4	41.8	54.5	171	0.7
Cu(ClO ₄) ₂ :4,4'-Me ₂ bipy: 3,5-pdc 3	25	-49	115	6.4	4.9	33.0	164	0.8
	50	-49	115	8.8	6.7	33.0	164	0.8
	100	-51	122	13.0	9.2	35.5	173	0.7
	200	-54	125	18.4	12.4	35.5	179	0.7
	300	-55	130	22.8	15.1	37.5	185	0.7
	400	-57	133	26.9	17.2	38.0	190	0.6
	500	-57	136	29.7	19.0	39.5	193	0.6
Cu(ClO ₄) ₂ :5,5'-Me ₂ bipy: 3,5-pdc 4	25	-17	115	7.0	5.2	49.0	132	0.7
	50	-18	119	9.8	7.0	50.5	137	0.7
	100	-19	128	13.8	9.7	54.5	147	0.7
	200	-25	136	20.1	13.0	55.5	161	0.6
	300	-25	138	24.8	15.8	56.5	163	0.6
	400	-25	140	28.8	18.3	57.5	165	0.6
	500	-28	144	32.0	20.0	58.0	172	0.6

Electronic absorption spectral properties of mixed-ligand copper (II) complexes with diimines and pyridine- 3, 5-dicarboxylic acid [Cu (diimines) (3, 5-pdc)]: 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 bands at 769 nm, 770 nm, 772 nm and 782 nm in DMSO, respectively suggested that 6- coordinated octahedral species were present in the mixed ligand complex solution [18, 19].

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

Solvent	System	Colour	λ _{max} (nm)	ε(Lmol ⁻¹ cm ⁻¹)
DMSO	Cu(ClO ₄) ₂ :phen:3,5-pdc 1	Light blue	769	60
	Cu(ClO ₄) ₂ :bipy: 3,5-pdc 2	Light blue	770	60
	Cu(ClO ₄) ₂ :4,4'-Me ₂ bipy: 3,5-pdc 3	Light blue	772	60
	Cu(ClO ₄) ₂ :5,5'-Me ₂ bipy: 3,5-pdc 4	Light blue	782	60

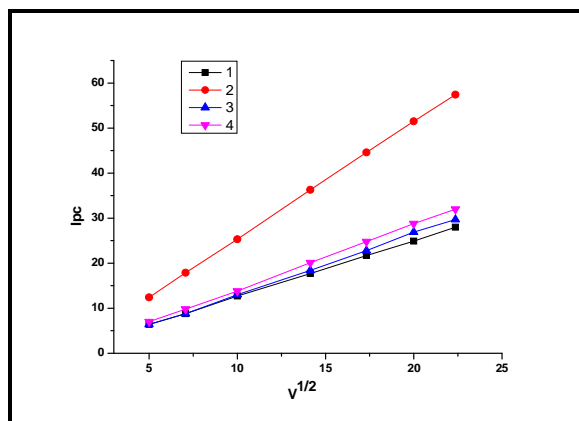


Figure 2(a). Plot of Ipc Vs $v^{1/2}$ for mixed ligand complexes 1- 4 in DMSO

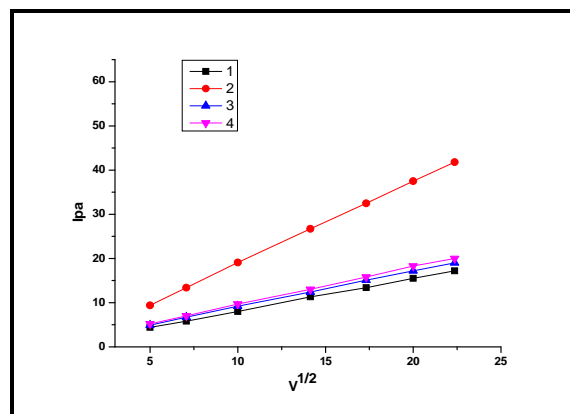


Figure 2(b). Plot of Ipa Vs $v^{1/2}$ for mixed ligand complexes 1- 4 in DMSO

Highlights:

- Mixed ligand copper (II) complexes with pyridine-3, 5-dicarboxylic acid and diimines in DMSO are investigated by electrochemical and spectral studies.
- All the complexes show single quasi reversible redox couple.
- UV-visible studies indicate the presence of distorted octahedral six coordinated copper (II) complex species in DMSO.

APPLICATION

The study of electronic absorption spectral bands, the geometry of complexes can be assessed.

CONCLUSION

In DMSO all the mixed ligand copper(II) complexes with diimines and pyridine-3, 5-dicarboxylic acid formed in 2:1:1 metal to ligand molar ratio displayed a single quasi reversible 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, ΔE_p values are more than 60 mV, clearly showing the quasi reversible nature of redox couple. The electronic absorption spectra of mixed-ligand complexes showed one broad absorption band in the region 760-790 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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