



Electrochemical and Spectral Behavior of Binary and Mixed Ligand Copper (II) Complexes involving 3,4-Pyridinedicarboxylic Acid and Diimines in Dimethylsulfoxide

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ABSTRACT

The Electrochemical studies of binary copper(II) complexes with 3,4-pyridinedicarboxylic acid (3,4-pdc) in 1:1 **A**; 2:1 **B**; and 3:1 **C**; metal to ligand molar ratios and seven mixed-ligand copper(II) complexes of 3,4-pyridinedicarboxylic acid and diimines [Cu(3,4-pdc)(diimine)], where diimines= bipy **1**; 4,4'-Me₂bipy **2**; 5,5'-Me₂bipy **3**; phen **4**; dmp **5**, bathophen **6**; and bathocuproin **7** were made in 3:1:1 metal-to-ligand molar ratio in dimethylsulfoxide (DMSO) containing 0.2M sodium perchlorate (NaClO₄) as the supporting electrolyte at a glassy carbon disc working electrode using cyclic voltammetry. It should be mentioned that in all binary complex solutions a single quasireversible redox couple (Cu^{2+/+}) was obtained with formal potential E^0 nearly at +80 mV vs Ag/Ag Cl at a scan rate of 25 mV s⁻¹. On the other hand the mixed ligand systems involving bipy, 4,4'-Me₂bipy, 5,5'-Me₂bipy, phen and bathophen showed a single quasireversible redox couple while those involving dmp and bathocuproin displayed one irreversible redox process and a second quasireversible couple at 25 mV s⁻¹. The UV-visible electronic spectra and the X-band EPR spectra of the above copper (II) complexes were studied in DMSO at room temperature and liquid nitrogen temperature respectively.

Keywords: Cu (II) complexes, cyclic voltammetry, UV-visible spectra, EPR spectra.

INTRODUCTION

Copper is an essential trace element for life. Pyridinedicarboxylic acids and their derivatives are belonging to an interesting series of organic compounds with useful biological applications [1]. Pyridinedicarboxylic acids have important biological function in the metabolism such as enzyme inhibitor, plant preservative and food sanitizer [2-4]. These properties have attracted the interest of scientists not only in the field of coordination chemistry but also in inorganic and bioorganic chemistry. Pyridinedicarboxylic acids are good complexing agents. Pyridine 2, 3-, 2, 4-, 2, 5-, 2, 6-, 3, 4- and 3, 5- dicarboxylic acids exhibit various co-ordination modes.

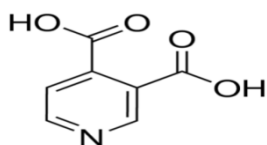
As a ligand, pyridine-3,4-dicarboxylic acid has unique features, the steric hindrance between the two adjacent carboxylic groups, the whole conjugation interaction between the pyridine groups and the carboxylic groups is remarkably weakened, so 3,4-pyridinedicarboxylic acid usually acts as a steric ligand,

therefore, it is more likely that 3,4-pdc will form high dimensional frameworks with metals [5]. Due to steric hindrance between the carboxylic groups in the 3- and 4- positions, the participation of only one carboxylic group in coordination to the metal center is expected. However, the rotational freedom of the carboxylic groups makes them flexible enough to participate in the coordination environment at the same time. 1, 10-phenanthroline and its derivatives are biologically important ligands. A consequence of the planar nature of 1, 10-phenanthroline is its ability to participate as a DNA intercalator [6]. Some metal complexes containing 1, 10-phenanthroline are also known to bind DNA by an intercalative mode. Several metal complexes with 1, 10-phenanthroline and natural products incorporating this heterocyclic nucleus possess interesting anticancer properties [7-9]. 2,9-dimethyl-1,10-phenanthroline, often called neocuproin, is useful as an analytical reagent for the estimation of copper (I), due, in large measure to its formation of the brilliant red copper complex, bis(phenanthroline)copper(I) complex have received much attention for their being less expensive and environment friendly, interesting photochemical and photo physical properties suitable for practical applications such as light harvesting for photovoltaic cells and as molecular sensors [10-16].

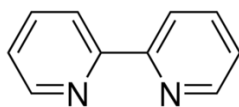
It is noteworthy that copper(II) complexes with diimine ligand almost exclusively formed five- or six-coordinate complexes in the solid state and in coordinating solvents and most likely the formation of a trigonal bipyramidal coordination geometry. Complexes containing the $[\text{Cu}(\text{dpp})_2]^{2+}$ moiety (with or without ligand substituent) only $[\text{Cu}(\text{phen})_2](\text{PF}_6)_2$ and $[\text{Cu}(\text{dpp})_2](\text{ClO}_4)_2$ are four coordinate [17-18]. The tendency for bis(diimine) Cu(II) complexes to be five-coordinate is further demonstrated by the structure of $[\text{Cu}(\text{tmbp})_2](\text{ClO}_4)_2$ and $[\text{Cu}(\text{tmbp})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (tmbp=4,4',6,6'-tetramethyl-2,2'-bipyridyl) both of which are five-coordinate with ClO_4 and H_2O coordination, respectively [19].

In our earlier paper [20] we have reported the Electrochemical and spectral behaviors of binary and mixed-ligand complexes of oxovanadium (IV) with dipicolinic acid and diimines in dimethylsulfoxide. In the present article, the electrochemical and spectral properties of binary and mixed-ligand copper (II) complexes involving 3,4-pyridinedicarboxylic acid and diimines formed in dimethylsulfoxide are reported. The structures of 3, 4-pdc and diimines are given below-

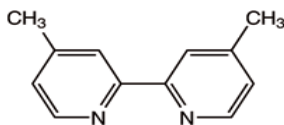
Structure of Ligands:



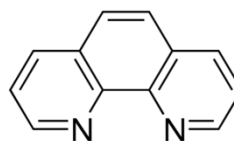
3,4-pyridinedicarboxylic acid
(3,4-pdc)



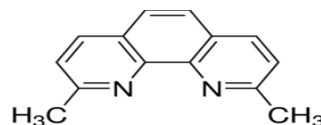
2,2'-bipyridine
(bipy)



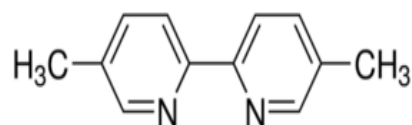
4,4'-dimethyl-2,2'-bipyridine
(4,4'-Me₂bipy)



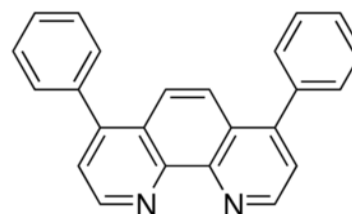
1,10-phenanthroline
(phen)



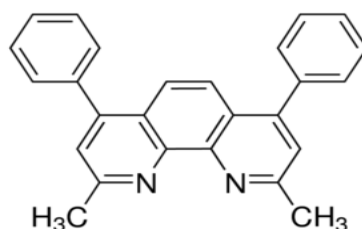
2,9-dimethyl-1,10-phenanthroline
(dmp)



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



4,7-diphenyl-1,10-phenanthroline
(bathophen)



2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline
(bathophen)

MATERIALS AND METHODS

All the chemicals, Copper Perchlorate hexahydrate $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, 3,4-pyridinedicarboxylic acid (3,4-Pdc), diimines= 2,2'-bipy, 4,4'-Me₂bipy, 5,5'-Me₂bipy, phenanthroline, dmp, bathophenanthroline, bathocuproin, Sodium Perchlorate and dimethylsulfoxide (DMSO) purchased from Sigma-Aldrich Chemicals Pvt. Ltd., and were used as such. All the cyclic voltammograms were recorded in dimethylsulfoxide (DMSO) containing 0.2 M sodium perchlorate (NaClO_4) as a supporting electrolyte. 1mM solution of copper perchlorate in DMSO was used in both the binary and mixed ligand complexes of copper (II).

The software driven BAS Electrochemical System, Model EPSILON (Bioanalytical System, Ind, USA) was employed for all the electrochemical studies. The working electrode was glassy carbon disc electrode (GCE), the counter electrode was platinum wire and reference electrode Ag/Ag Cl in saturated K Cl ($E^0 = +199$ 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 pretreatment. 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.

The X-band EPR spectra of Cu (II) complexes in DMSO were recorded at Liquid Nitrogen Temperature (77K) on JES-FA200 ESR Spectrometer Model JEOL.

RESULTS AND DISCUSSION

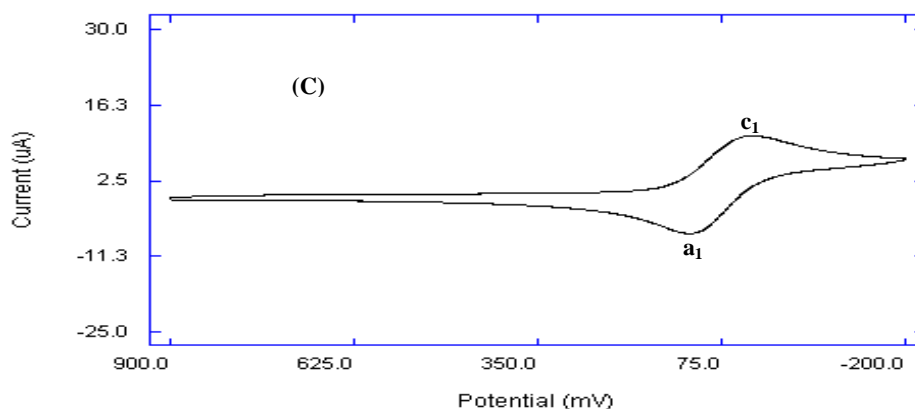
Electrochemical behaviour of binary copper (II)-3,4-pdc complex species formed in 1:1 (A), 2:1 (B) and 3:1 (C) molar ratios: The electrochemical behavior of binary copper(II) : 3,4-pdc complex species formed in 1:1, 2:1 and 3:1 molar ratios were studied in DMSO containing 0.2 M NaClO_4 as a supporting electrolyte at a glassy carbon disc working electrode. The cyclic voltammogram (CV) of binary copper(II) : 3,4-pdc complex species formed in 3:1 molar ratio at scan rate 25 mV/s is displayed in **figure 1** and the CV data for all the above three complexes are given in **table 1**. It should be noted that in the case of all

three binary complex solutions, one redox couple appeared between the potential limit of 900 mV to -200mV. The observed formal potentials $E_0' = 82.5$ mV for 1:1 molar ratio, 80 mV for 2:1 molar ratio and 75 mV for 3:1 molar ratio at the scan rate 25 mV/s, assigned to quasireversible $\text{Cu}^{2+}/\text{Cu}^{+}$ one electron transfer electrochemical reactions. The values of peak potential difference (ΔE_p) was greater than 60 mV also justified the quasi-reversible nature of redox couple. On increasing the scan rate the cathodic peak potential shifts more negatively in the sequence: **A.** ($E_{pc}=38\text{mV}$) \rightarrow **B.** ($E_{pc}=35\text{mV}$) \rightarrow **C.** ($E_{pc}=29\text{mV}$) at 25mV/s. It was observed from the cathodic peak potential that the complex **C** showed easier reduction step comparison to other binary complexes **A** and **B**. A plot of cathodic peak current (I_{pc}) vs square root of scan rate ($v^{1/2}$) relationship gave a straight line passing through origin showed that the reduction process was diffusion-controlled [21]. It is noteworthy that the peak current ratio, I_{pa}/I_{pc} is greater than 1.0 in 1:1 (**A**) binary complex, suggesting the adsorption of the complex species at the surface of working electrode [22, 23] (Table 1).

Table 1: CV data for binary complexes of Cu(II) with 3,4-pdc (A, B and C) formed in 1:1, 2:1 and 3:1 $\text{Cu}(\text{ClO}_4)_2$: pdc molar ratio in DMSO containing 0.2 M NaClO_4

Systems	Scan rate (mV/s)	E_{pc} (mV)	E_{pa} (mV)	E_0' (mV)	ΔE_p (mV)	I_{pa}/I_{pc}
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: 3,4-pdc (1:1) (A)	25	38	127	82.5	89	1.1
	50	34	130	82	96	1.2
	100	28	134	81	106	1.2
	200	16	138	77	122	1.3
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: 3,4-pdc (2:1) (B)	25	35	125	80	90	1.0
	50	30	128	79	98	1.0
	100	20	134	77	114	1.0
	200	8	144	76	136	1.0
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: 3,4-pdc (3:1) (C)	25	29	121	75	92	1.0
	50	22	128	75	106	1.0
	100	14	134	74	120	1.0
	200	-2	146	72	148	1.0

Figure 1: CV of binary $[\text{Cu}(\text{pdc})]^{2+}$ complex species formed in 3:1 (C) $\text{Cu}(\text{ClO}_4)_2$:3,4-pdc molar ratio in DMSO containing 0.2 M NaClO_4 at 25 mVs^{-1}



Electrochemical behavior of mixed-ligand copper (II) complexes with 3, 4-pdc and diimines [Cu(3,4-pdc) (diimines)] 1-7: The electrochemical properties of mixed-ligand Cu(II): 3,4-pdc : diimines complexes formed in 3:1:1 molar ratios (where diimines = bipy **1**; 4,4'-Me₂bipy **2**; 5,5'-Me₂bipy **3**; phen **4**; dmp **5**; bathophen **6** and bathocuproin **7**) were studied in DMSO by cyclic voltammetry at 25°C containing 0.2 M NaClO_4 as a supporting electrolyte. All CV experiments were performed in the scan rate range from 25 to 200 mV s^{-1} . The cyclic voltammetric data are given in **table 2**. The cyclic voltammograms of mixed-ligand Cu (II) complex species **1**, **2**, **3** and **4** showed one cathodic peak with

peak potential $E_{pc1} = -19$ mV in complex **1**, $E_{pc1} = -49$ mV in complex **2**, $E_{pc1} = -11$ mV in complex **3** and $E_{pc1} = 7$ mV in complex **4** in forward scan and one corresponding anodic peak in the reverse scan with anodic peak potentials $E_{pa1} = 115$ mV, $E_{pa1} = 117$ mV, $E_{pa1} = 119$ mV and $E_{pa1} = 126$ mV, respectively at scan rate 25 mV/s between the potential range of 900 mV to -200 mV, their peak potentials separation ΔE_p was 134 mV, 166 mV, 130 mV and 119 mV respectively, which was more than 60 mV corresponding to quasireversible one electron transfer reaction and the ΔE_p values increase with increasing scan rate, clearly indicated that the electron transfer processes are quasireversible (**Figures 2**). A plot of peak current (I_{pc1}) vs square root of scan rate ($v^{1/2}$) gives a straight line passing through origin in all the cases showed that the reduction process is diffusion-controlled [21]. It should be noted that the electrochemical behavior and magnitudes of peak potentials in the case of mixed ligand complex **6** are almost similar to that of complex **4** (**Table 2**). In the cyclic voltammograms of complexes **5** and **7**, two cathodic and two anodic peaks were appeared. In the forward cycle, a negative scan revealed two reduction processes c_1' and c_1 in the potential region +1000 to -200 mV while the reverse scan showed the corresponding anodic processes a_1 and a_1' . The two cathodic peaks c_1' with $E_{pc1}' = 315$ mV, and c_1 with $E_{pc1} = 38$ mV for complex **5** and $E_{pc1}' = 303$ mV, and c_1 with $E_{pc1} = 33$ mV for complex **7** and anodic peaks a_1 with $E_{pa1} = 124$ mV and a_1' with peak potential $E_{pa1}' = 618$ mV for complex **5** and $E_{pa1} = 127$ mV and a_1' with peak potential $E_{pa1}' = 613$ mV for complex **7** were observed at a scan rate of 25 mV/s (**Figure 3, Table 2**). The peak potential separations ΔE_{p1} at 25 mV/s for mixed-ligand complexes **5** and **7** were 86 mV and 94 mV, respectively, indicating that the electrochemical reaction was quasireversible one electron transfer process. A plot of cathodic peak current (I_{pc}) Vs square root of scan rate gave a straight line with positive intercept, showing that the electron transfer is preceded by a chemical reaction (**CE mechanism 24**).

Table 2: CV data for 1-7 mixed-ligand complexes $[Cu^{2+}(pdc)(diimine)]$ formed in 3:1:1 $Cu(ClO_4)_2 : pdc : diimine$ molar ratio in DMSO containing 0.2 M $NaClO_4$

Mixed-ligand complexes with diimines	Scan rate (mV/s)	E_{pc1} (mV)	E_{pa1} (mV)	E^0_1 (mV)	ΔE_{p1} (mV)	I_{pa1}/I_{pc1}	E_{pc1}' (mV)	E_{pa1}' (mV)
(bipy) (1)	25	-19	115	48.0	134	0.8		
	50	-19	120	50.5	139	0.9		
	100	-22	127	52.5	149	0.8		
	200	-29	135	53.0	164	0.8		
(4,4'-Me ₂ bipy) (2)	25	-49	117	34.0	166	0.9		
	50	-51	121	35.0	172	0.9		
	100	-52	129	38.5	181	0.9		
	200	-54	140	43.0	194	0.8		
(5,5'-Me ₂ bipy) (3)	25	-11	119	54.0	130	0.8		
	50	-13	121	54.0	134	0.8		
	100	-18	127	54.5	154	0.8		
	200	-22	136	57.0	158	0.8		
(phen) (4)	25	7	126	66.5	119	0.9		
	50	4	128	66.0	124	0.8		
	100	2	132	67.0	130	0.8		
	200	1	145	73.0	143	0.8		
(dmp) (5)	25	38	124	81	86	0.8	315	618
	50	33	126	79.5	93	0.9	307	629
	100	26	132	79.0	106	0.9	296	641
	200	14	140	77.0	126	0.9	287	651
(bathophen) (6)	25	7	120	63.5	113	0.9		
	50	1	125	63.0	124	0.9		
	100	-4	131	63.5	135	0.9		
	200	-13	140	63.5	153	0.8		
(bathocuproin) (7)	25	33	127	80	94	0.9	303	613
	50	27	133	80	106	0.9	301	618
	100	19	139	79	120	0.9	289	631
	200	3	147	75	144	0.9	278	637

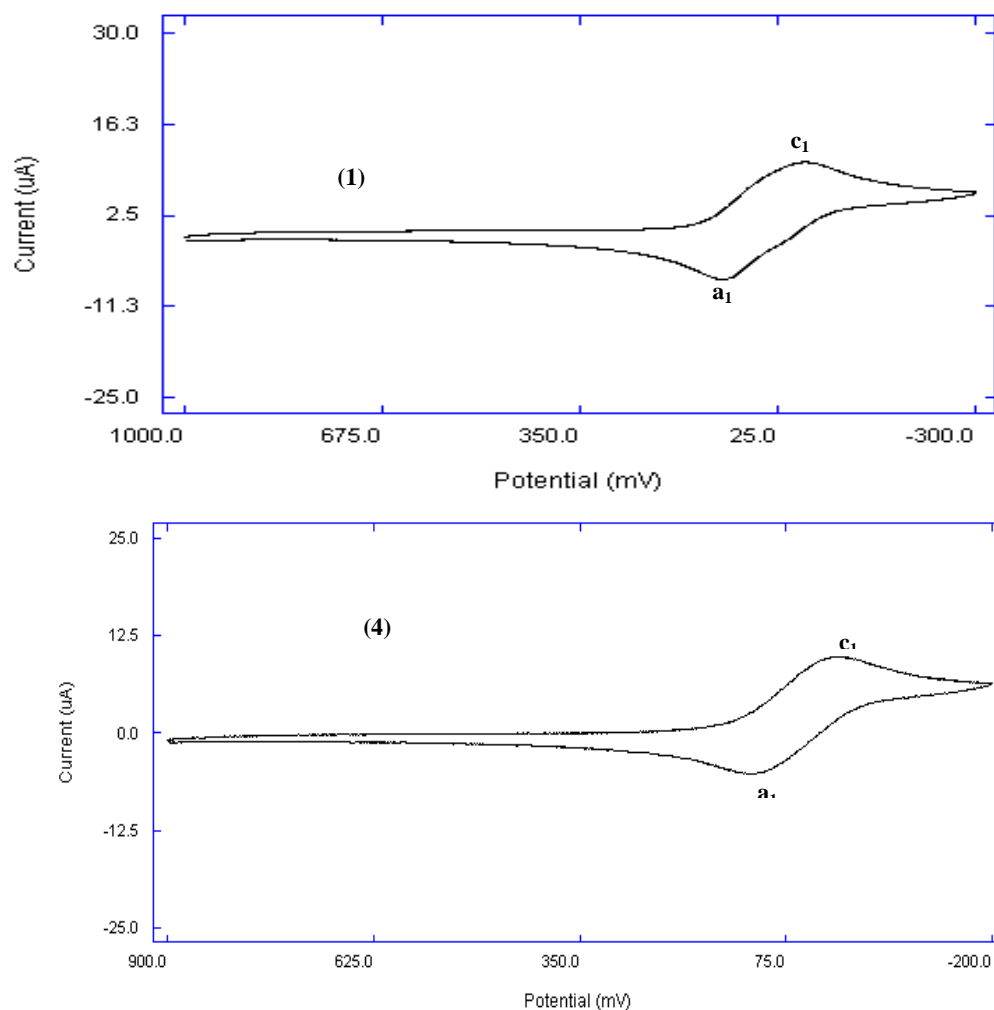


Figure 2. CVs of $[Cu^{2+}(pdc)(diimine)]$ mixed-ligand complexes **1** and **4** in DMSO containing 0.2 M $NaClO_4$ at 25 mVs^{-1} (diimine = 2,2'-bipy **1** and phen **4**).

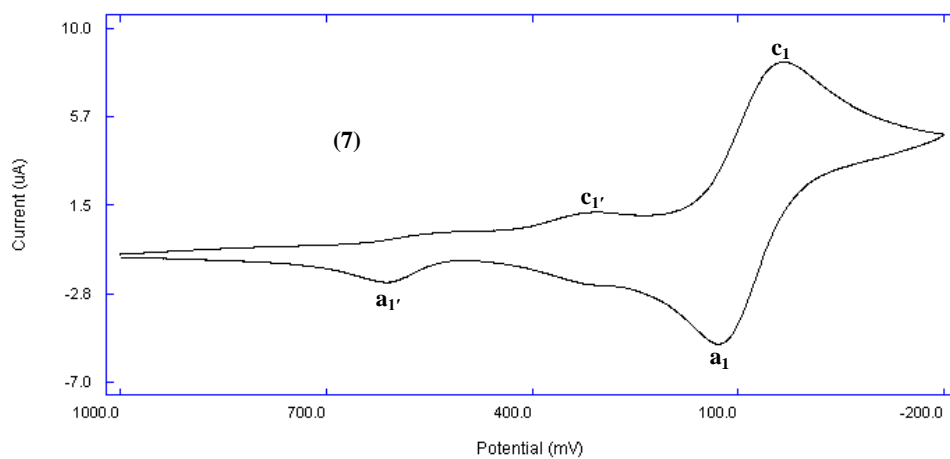


Figure 3. CVs of $[Cu^{2+}(pdc)(bathocuproin)]$ mixed-ligand complex **7** in DMSO containing 0.2M $NaClO_4$ at 25 mVs^{-1}

Electronic absorption spectral properties of binary Cu(II) : 3,4-pdc complex species formed in 1:1 (A), 2:1 (B) and 3:1 (C) molar ratios: The electronic absorption spectral data for the binary complexes formed in 1:1, 2:1 and 3:1 molar ratios are presented in **Table 3 (a)**. The electronic absorption spectra of all these complexes in the above molar ratios showed a single broad d-d absorption band at 814 nm respectively assigned to metal-based ligand field (d-d) transitions. On the basis of electronic absorption spectral band it could be clear that a six coordinated copper complex predominant species are present in all the binary complex solutions.

Electronic absorption spectral properties of mixed-ligand copper (II) complexes with 3,4-Pdc and diimines, 1-7: The electronic absorption spectral data for mixed ligand complexes are presented in **Table 3 (b)**. The electronic absorption spectra of light blue colored mixed ligand Cu (II) complex showed a broad d-d absorption bands at 782 nm for complex **1**, at 786 nm for complex **2**, at 786 nm for complex **3**, while complex **4** exhibited a single broad d-d absorption band at 817 nm. The color of complex **5** solution was yellow which showed two absorption bands one at 782 nm due to the d-d transitions while second other at 454 nm due to the strong charge transfer. The complex **6** was light yellow in color which showed two absorption bands at 781 nm due to the d-d transitions, and 480 nm due to the charge transfer. The color of complex **7** was dark red showed two absorption bands at 842 nm and 480 nm because of d-d transition and charge transfer, respectively. It could be clear that six coordinated species was present in mixed-ligand complex solutions.

Table 3(a). Electronic absorption spectral data for binary and mixed-ligand Cu(II) complex Species formed in different molar ratios

System	Ratio	Colour	λ_{\max} (nm)	ϵ (L mol ⁻¹ cm ⁻¹)
Cu(ClO ₄) ₂ :3,4- pdc (A)	1:1	Light blue	814	40
Cu(ClO ₄) ₂ :3,4- pdc (B)	2:1	Light blue	814	40
Cu(ClO ₄) ₂ :3,4- pdc (C)	3:1	Light blue	814	40

Table 3(b). Electronic absorption spectral data for mixed-ligand Cu(II) complex Species formed in different molar ratios

System	Ratio	Colour	λ_{\max} (nm)	ϵ (L mol ⁻¹ cm ⁻¹)
Cu(ClO ₄) ₂ :3,4- pdc :2,2'-bipy (1)	3:1:1	Light blue	782	23
Cu(ClO ₄) ₂ :3,4-pdc:4,4'-Me ₂ bipy (2)	3:1:1	Light blue	786	23
Cu(ClO ₄) ₂ :3,4-pdc:5,5'-Me ₂ bipy (3)	3:1:1	Light blue	786	23
Cu(ClO ₄) ₂ :3,4-pdc:phen (4)	3:1:1	Light blue	817	33
Cu(ClO ₄) ₂ :3,4-pdc:dmp (5)	3:1:1	Yellow	782 454	24 190
Cu(ClO ₄) ₂ :3,4-pdc: bathophen (6)	3:1:1	Light yellow	781 480	20 43
Cu(ClO ₄) ₂ :3,4-pdc: bathocuproin (7)	3:1:1	Dark red	842 480	20 740

Electron paramagnetic resonance spectral studies: X-band EPR Spectra of the binary and mixed – ligand copper (II) complexes were studied at liquid nitrogen temperature (77K) in dimethylsulfoxide (DMSO). The EPR spectra of binary Cu (II) complexes are shown in **figure 4(a)** and mixed ligand complexes are shown in **figure 4(b)**. The relevant EPR spectral parameters of binary and mixed-ligand complexes are given in **tables 4a and 4b**, respectively. The Cu^{2+} ion has $3d^9$ electronic configuration with one unpaired electron and $S=1/2$ with nuclear spins: ^{63}Cu , $I=3/2$ (69%) and ^{65}Cu , $I=3/2$ (31%) gives characteristics hyperfine splitting, resulting in 4-lines. The frozen solution spectra of mixed-ligand complex solutions are of axial type ($g_{\parallel} > g_{\perp} > 2.0023$) with dx^2-y^2 as the ground state, indicating that tetragonally distorted octahedral complex species is maintained in frozen solution.

Table 4(a): EPR data for binary complexes of Cu(II) with 3,4-pdc (A, B and C) formed in 1:1, 2:1 and 3:1 $\text{Cu}(\text{ClO}_4)_2 : 3,4\text{-pdc}$ molar ratios in DMSO at 77K

Systems	g_1	g_2	g_3	g_4	g_{\perp}
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} :$ 3,4-pdc (1:1) (A)	2.54039	2.41887	2.30572	2.20391	2.07142
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} :$ 3,4-pdc (2:1) (B)	2.55988	-	-	-	2.07452
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} :$ 3,4-pdc (3:1) (C)	2.56162	2.45107	2.35040	-	2.07505

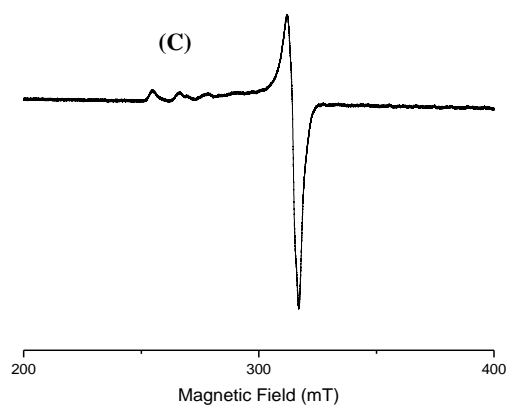


Figure 4(a). X-band EPR spectra of binary $[\text{Cu}(\text{pdc})]^{2+}$ complex species formed in 3:1 **(C)** $\text{Cu}(\text{ClO}_4)_2 :$ 3,4-pdc molar ratio In DMSO at 77K

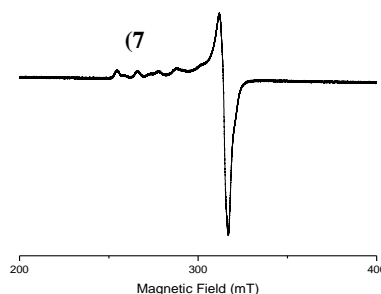


Figure 4(b). X-band EPR spectra of $[\text{Cu}^{2+}(\text{pdc})(\text{bathocuproin})]$ mixed-ligand complex species **7** formed in 3:1:1 $\text{Cu}(\text{ClO}_4)_2 : 3,4\text{-pdc} :$ bathocuproin molar ratio in DMSO at 77K.

Table 4(b): EPR data for 1-7 mixed-ligand complexes $[\text{Cu}^{2+}(\text{pdc})(\text{diimine})]$ formed in 3:1:1 $\text{Cu}(\text{ClO}_4)_2$: pdc : diimine molar ratio in DMSO at 77K

Systems	g_1	g_2	g_3	g_4	g_L
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: 3,4-pdc:bipy (1)	2.564553	2.448214	2.36286	2.23717	2.07374
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: 3,4-pdc: 4,4'- Me₂bipy (2)	2.55864	2.453699	2.36175	2.23182	2.07547
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: 3,4-pdc:5,5'- Me₂bipy (3)	2.56082	2.453602	2.36527	2.23789	2.07314
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: 3,4-pdc:phen (4)	2.565961	2.450203	2.36847	2.24668	2.07182
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: 3,4-pdc:(dmp) (5)	2.55900	2.45260	2.38793	2.26829	2.07492
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: 3,4-pdc :bathophen (6)	2.56022	2.45158	2.36320	2.24494	2.07421
$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$: 3,4-pdc :bathocuproin (7)	2.56882	2.45438	2.34967	2.26699	2.07447

Highlights:

- Binary and mixed ligand copper (II) complexes with 3, 4-pdc and diimine investigated by electrochemical and spectral studies.
- All the binary and mixed ligand complex solutions showed quasireversible redox reactions except mixed-ligand complexes **5** and **7**.
- UV-visible studies indicated the presence of distorted octahedral six coordinated copper (II) complex species in binary and mixed ligand complex solution.
- EPR spectra suggested the distorted octahedral geometry of the complexes.

CONCLUSIONS

On the basis of above discussion it is concluded that for binary copper (II) complexes of 3,4-pyridinedicarboxylic acid in 1:1 (**A**), 2:1 (**B**) and 3:1 (**C**) metal to ligand molar ratios show a single quasireversible redox couple. The complex **C** exhibited easier reduction step compared to complexes **A**

and **B**. The electronic absorption spectra of all these binary complexes **A** to **C** showed a broad absorption band at 814 nm, respectively, assigned to metal based d-d transitions.

The mixed-ligand complexes **1,2,3,4** and **6** showed a single quasireversible redox couple while complexes **5** and **7** showed one irreversible redox process and a quasireversible redox couple at 25mV/s. The cathodic peak potentials of all these mixed-ligand complexes in 3:1:1 metal to ligand molar ratio become more negative and anodic peak shifted towards more positive potentials on increasing scan rates. The electronic absorption spectrum of mixed-ligand complex **4** showed a single broad d-d absorption band at 817nm while complexes **1, 2 and 3** showed one absorption bands in the region 750-790 nm. Complex **5** showed two d-d absorption bands at 782nm and 454nm and in complex **6** two absorption bands were found at 781 and 480 nm and in complex **7** two absorption bands are found at 842 and 480 nm. On the basis of above electronic absorption spectral results it may be concluded that distorted octahedral six-coordinate copper (II) complex predominant species was present in binary and mixed-ligand systems.

X-band EPR Spectra of the binary and mixed –ligand copper (II) complexes were studied at liquid nitrogen temperature (77K) in dimethylsulfoxide (DMSO). The frozen solution spectra of copper (II) complexes of 3,4-pyridinedicarboxylic acid in 1:1 (**A**), 2:1 (**B**) and 3:1 (**C**) metal to ligand molar ratios show axial type EPR spectra with $g_{\parallel} > g_{\perp}$ with dx^2-y^2 as the ground state. The mixed-ligand frozen solution spectra are also axial type with dx^2-y^2 as the ground state, indicating that tetragonally distorted octahedral complex species is maintained in frozen solution.

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