



Electrochemical and Spectral Behaviour of Binary And Mixed Ligand Copper (II) Complexes Involving Various Pyridinedicarboxylic Acids and 2,9-Dimethyl-1,10-Phenanthroline in Dimethylsulfoxide

Alka Srivastava*, Dipiti Porwal, Krishna Srivastava and Jagdish Prasad

*Nanoscience and Electrochemical Research Laboratory, Department of Chemistry,
University of Allahabad, Allahabad-211002 (U. P.), **INDIA**

Email: alka23srivastava@gmail.com

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ABSTRACT

The Electrochemical studies of binary copper (II) complexes with six pyridinedicarboxylic acids (pdcs), viz; 2,3-pdc (A), 2,4-pdc (B), 2,5-pdc (C), 2,6-pdc (D), 3,4-pdc (E) and 3,5-pdc (F) in 3:1 metal to ligand molar ratio and the mixed-ligand copper(II) complexes with six pdcs and dmp (2,9-dimethyl-1,10-phenanthroline), where pdcs = 2,3-pdc 1; 2,4-pdc 2; 2,5-pdc 3; 2,6-pdc 4; 3,4-pdc 5 and 3,5-pdc 6 were made in 3:1:1 metal to ligand molar ratio in dimethylsulfoxide (DMSO) containing 0.2 M sodium perchlorate (NaClO₄) as the supporting electrolyte at a glassy carbon disc working electrode using cyclic voltammetry. It should be mentioned that in all the binary complexes a single quasireversible redox couple (Cu^{2+/+}) is obtained at the scan rate of 25 mV/s. On the other hand the mixed-ligand complexes in 3:1:1 Cu (II): pdcs: dmp metal to ligand molar ratios was involved one irreversible redox process and a second quasireversible couple at the scan rate of 25 mV/s. The UV-visible electronic spectra of the binary complexes in dimethylsulfoxide exhibit only a single broad d-d absorption band at 810, 803, 825, 818, 845 and 842 nm, respectively, clearly indicating a distorted octahedral geometry. The UV-visible spectra of all the mixed-ligand complexes were also studied in respective medium.

Keywords: Binary and mixed-ligand Cu (II) complexes, pyridinedicarboxylic acids, cyclic voltammetry, UV- Visible Spectra.

INTRODUCTION

The carboxylate ligands can have different binding modes and each of them may play role in the formation of supramolecular assembly [1-3]. The compounds having multiple carboxylic acid groups are good synthons for supramolecular architectures and coordination polymers [4-7]. Carboxylate groups display a variety of binding geometries such as monodentate-terminal, chelating, bidentate-bridging and monodentate-bridging in coordination chemistry and the active sites of metalloenzymes[5].Pyridinedicarboxylic acids and their derivatives belong to an interesting series of compounds with biological applications [8] Pyridine-2, 6-dicarboxylic acid (dipicolinic acid) is present in nature as an oxidative degradation product of vitamins, coenzymes and alkaloids and is a component of fulvic acid. It has frequently been cited in the literature as a plant sterilizing and water germicidal agent and an antioxidant

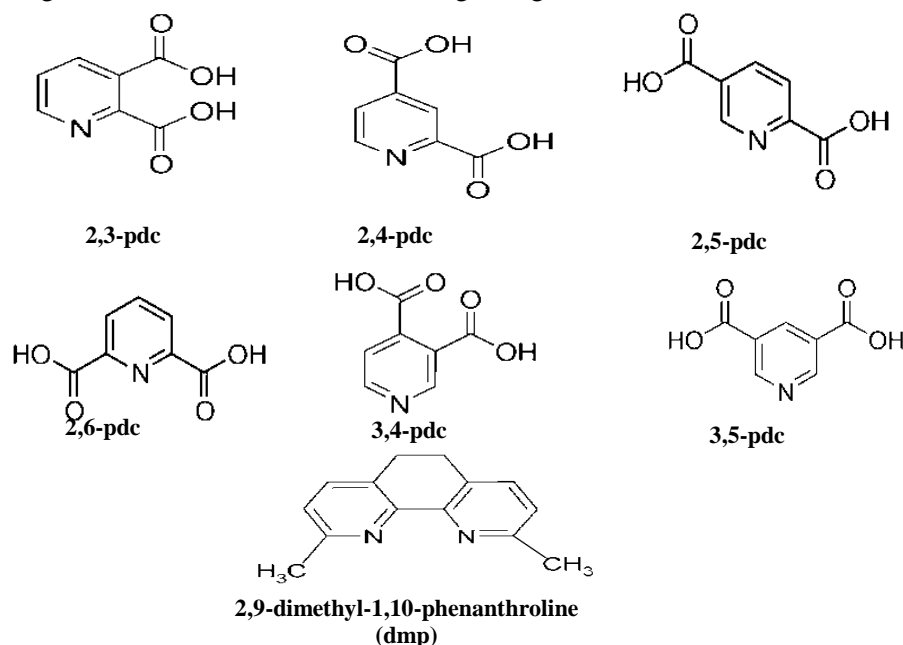
for ascorbic acid in foods [9]. Furthermore, pyridinedicarboxylic acids (2,3-pdc, 2,4-pdc, 2,5-pdc, 2,6-pdc, 3,4-pdc, and 3,5-pdc) have been shown to be interesting and versatile ligands as they exhibit various coordination modes, and have been used to prepare various types of structures with different dimensionalities [10–14].

The d^9 configuration of Cu (II) in an octahedral field leads to a significant John-Teller distortion that usually manifests itself as an axial elongation, consistent with the lability and geometric flexibility of Cu(II) complexes [15]. Ternary complexes of oxygen-donor ligands and heteroaromatic N-bases have attracted much interest as they can display exceptionally high stability [16–18]. The use of transition metal complexes of iminodiacetic acid and nitrilotriacetic acid have been widely adopted in biology, and are gaining increasing use in biotechnology, particularly in the protein purification technique known as Immobilized Metal-ion Affinity Chromatography (IMAC) [19]. Many drugs possess modified pharmacological and toxicological properties when administered in the form of metallic complexes. Probably the most widely studied cation in this respect is Cu^{2+} , since a host of low-molecular-weight copper complexes have been proven beneficial against several diseases such as tuberculosis, rheumatoid, gastric ulcers, and cancers [20–23]. The benefits of copper over other transition metals is that only very mild conditions are necessary for binding reactions to occur, facilitating *in vivo* studies of DNA structure [24].

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 [19], bis(phenanthroline)copper(I) complex have received much attention for their being less expensive and environment friendly, interesting photochemical and photophysical properties suitable for practical applications such as light harvesting for photovoltaic cells and as molecular sensors [25–31].

Keeping in my mind the above points, we have therefore investigated the electrochemical and spectral behaviour of binary and mixed ligand copper (II) complexes involving various pyridinedicarboxylic acids and 2,9-dimethyl-1,10-phenanthroline in dimethylsulfoxide. The structures of various pdc's and dmp ligands are illustrated below:

Structure of ligands: The structures of different ligands given below-



MATERIALS AND METHODS

All the chemicals, copper perchlorate hexahydrate $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, pyridinedicarboxylic acids, viz; 2,3-pdc, 2,4-pdc, 2,5-pdc, 2,6-pdc, 3,4-pdc, 3,5-pdc, 2,9-dimethyl-1,10-phenanthroline (dmp), sodium perchlorate purchased from Sigma-Aldrich Chemicals Pvt. Ltd. and DMSO was obtained from E-Merck 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 (Bio analytical 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/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 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.

RESULTS AND DISCUSSION

Electrochemical behaviours of binary copper (II) complexes with six pyridinedicarboxylic acids in 3:1 metal to ligand molar ratio in dimethylsulfoxide: The cyclic voltammetric data for Cu (II) complexes with pdc's are given in table 1 and CVs are shown in figure. 1. It should be noted that Cu^{2+} complexes with all the six pdc's show similar behavior, i.e. one redox couple appeared between the potential limit of 1000 mV to -200mV. The observed formal potentials $E^0 = 73.5$ mV, 67.5 mV, 76 mV, 77 mV, 75 mV and 78 mV for complexes A, B, C, D, E and F, respectively at the scan rate 25 mV/s, assigned to quasireversible $\text{Cu}^{2+/+}$ 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 the basis of cathodic peak potentials (E_{pc}) of all the six Cu (II) complex solutions with pyridinedicarboxylic acids (pdc's) (table 1), the ease of reduction for binary complexes increase in the order: F (41 mV) \rightarrow C=D (33 mV) \rightarrow E (29 mV) \rightarrow A (28 mV) \rightarrow B (20 mV) at 25mV/s. It was observed from the cathodic peak potential that the complex A, B and E showed easier reduction step in comparison to the other binary complexes C, D and F. 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 demonstrated that the reduction process was diffusion-controlled [32, 35].

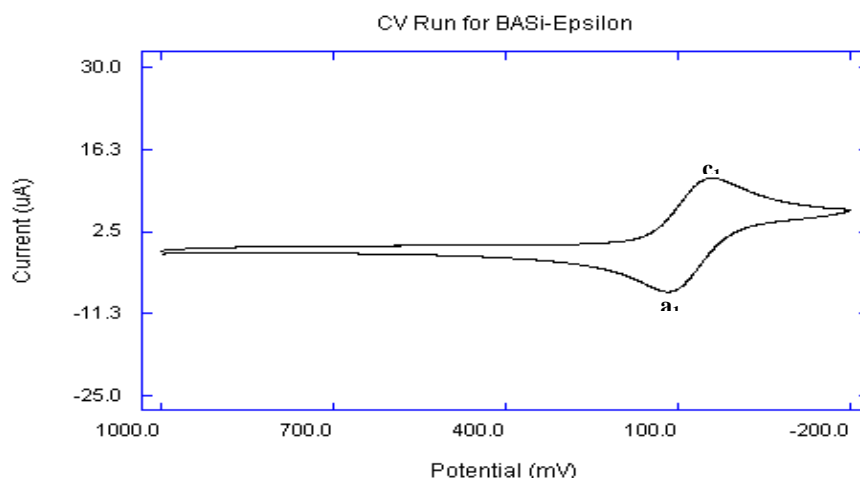


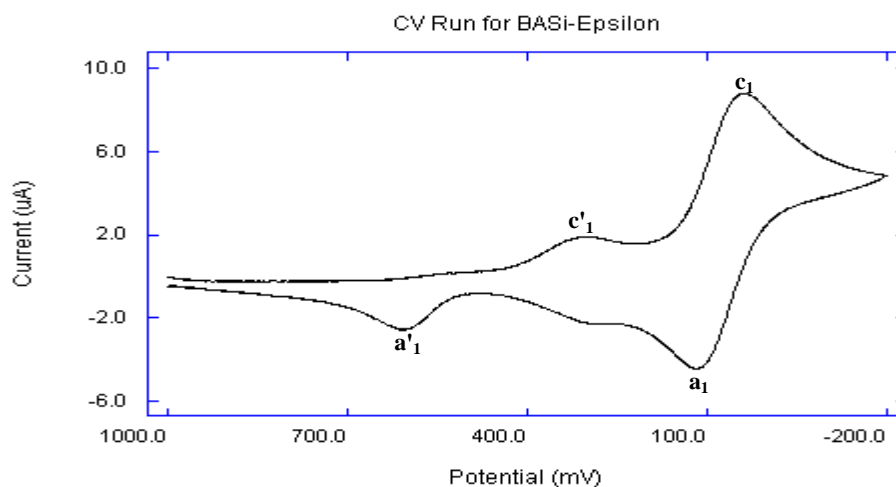
Table 1: CV data for binary complexes of Cu (II) with pdc's formed in 3:1 Cu(ClO₄)₂ : pdc's molar ratio in DMSO containing 0.2M NaClO₄ (A-F)

Systems	Scan rate (mV/s)	E _{pc} (mV)	E _{pa} (mV)	I _{pc} (μA)	I _{pa} (μA)	E ^{o'} (mV)	ΔE _p (mV)	I _{pa} /I _{pc}
Cu(ClO ₄) ₂ .6H ₂ O: 2,3,-pdc (A)	25	28	119	6.2	4.0	73.5	91	0.6
	50	21	119	7.5	6.1	70.0	98	0.8
	100	15	126	10.2	8.8	70.5	111	0.9
	200	0	134	12.9	11.7	67.0	134	0.9
Cu(ClO ₄) ₂ .6H ₂ O: 2,4-pdc (B)	25	20	115	5.5	4.0	67.5	95	0.7
	50	13	121	7.0	5.6	67.0	108	0.8
	100	6	127	8.9	8.2	66.5	121	0.9
	200	-15	135	10.8	11.0	60.0	150	1.0
Cu(ClO ₄) ₂ .6H ₂ O: 2,5-pdc (C)	25	33	119	6.9	6.9	76	86	1.0
	50	27	125	9.4	9.0	76	98	0.9
	100	19	129	11.8	12.6	74	110	1.0
	200	7	139	15.1	15.9	73	132	1.0
Cu(ClO ₄) ₂ .6H ₂ O: 2,6-pdc (D)	25	33	121	7.9	7.7	77	88	0.9
	50	32	126	10.6	10.5	79	94	1.0
	100	21	132	13.5	13.9	76.5	111	1.0
	200	8	140	17.8	18.6	74	132	1.0
Cu(ClO ₄) ₂ .6H ₂ O: 3,4-pdc (E)	25	29	121	8.8	9.0	75	92	1.0
	50	22	128	12.0	12.3	75	106	1.0
	100	14	134	15.4	15.4	74	120	1.0
	200	-2	146	18.5	19.0	72	148	1.0
Cu(ClO ₄) ₂ .6H ₂ O: 3,5-pdc (F)	25	41	115	10.0	9.7	78	74	1.0
	50	38	120	13.7	13.3	79	82	1.0
	100	32	125	17.5	17.8	78.5	93	1.0
	200	23	132	23.9	23.3	77.5	109	1.0

Electrochemical behaviour of mixed-ligand copper (II) complexes with six pyridinedicarboxylic acids and 2,9-dimethyl-1,10-phenanthroline in 3:1:1 metal to ligand molar ratio in dimethyl sulfoxide: The Electrochemical studies of mixed-ligand Cu (II): pdc : dmp complexes formed in 3:1:1 metal to ligand molar ratio in DMSO were studied by cyclic voltammetry at 25^oC containing 0.2 M NaClO₄ as a supporting electrolyte . All CV experiments were performed in the scan rate range from 25 to 200 mV/s. The cyclic voltammetric data are given in table 2. The cyclic voltammograms of all the six mixed-ligand Cu (II) complex species 1, 2, 3, 4, 5, and 6 showed two cathodic and two anodic peaks. In the forward cycle, a negative scan revealed two reduction processes c₁' and c₁ in the potential region +1000 to -200 mV while the reverse scan showed the corresponding anodic processes a₁ and a₁'. The two cathodic peaks c₁' with E_{pc1}'= 303 mV, and c₁ with E_{pc1}=-1 mV for complex 1, E_{pc1}'= 303 mV, and c₁ with E_{pc1}= 9 mV for complex 2, E_{pc1}'= 316 mV, and c₁ with E_{pc1}= 32 mV for complex 3, E_{pc1}'= 305 mV, and c₁ with E_{pc1}= 23 mV for complex 4, E_{pc1}'= 315 mV, and c₁ with E_{pc1}= 38 mV for complex 5 and E_{pc1}'= 303 mV, and c₁ with E_{pc1}= 39 mV for complex 6 and anodic peaks a₁ with E_{pa1}=125 mV and a₁' with peak potential E_{pa1}'= 597 mV for complex 1, E_{pa1}=127 mV and a₁' with peak potential E_{pa1}'= 607 mV for complex 2, E_{pa1}=120 mV and a₁' with peak potential E_{pa1}'= 616 mV for complex 3, E_{pa1}=127 mV and a₁' with peak potential E_{pa1}'= 618 mV for complex 4, E_{pa1}=124 mV and a₁' with peak potential E_{pa1}'= 618 mV for complex 5 and E_{pa1}=119 mV and a₁' with peak potential E_{pa1}'= 604 mV for complex 6 were observed at a scan rate of 25 mV/s (figure 2, table 2), their peak potentials separation ΔE_p was 126 mV, 118 mV, 88 mV, 104 mV, 86 mV and 80 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 indicating that the electron transfer processes are quasireversible (figure 2). A plot of cathodic peak current (I_{pc}) Vs square root of scan rate (v^{1/2}) gave a straight line with positive intercept in all the cases, showing that the electron transfer is preceded by a chemical reaction (CE mechanism) [33,34].

Table 2: CV data for mixed-ligand Cu (II) complexes formed in 3:1:1 Cu(ClO₄)₂ : pdc_s : dmp molar ratio in DMSO containing 0.2 M NaClO₄

Systems	Scan rate (mV/s)	E _{pc1} (mV)	E _{pa1} (mV)	E ^o ₁ (mV)	ΔE _{p1} (mV)	I _{pa1} /I _{pc1}	E _{pc1} ' (mV)	E _{pa1} ' (mV)
Cu(ClO ₄) ₂ .6H ₂ O: 2,3,-pdc:dmp (1)	25	-1	125	62.0	126	0.3	303	597
	50	-4	127	61.5	131	0.4	291	607
	100	-18	134	58.0	152	0.4	283	616
	200	-20	144	62.0	164	0.5	267	629
Cu(ClO ₄) ₂ .6H ₂ O: 2,4- pdc:dmp (2)	25	9	127	68.0	118	0.5	303	607
	50	2	129	65.5	127	0.6	296	617
	100	-16	137	60.5	153	0.6	288	628
	200	-16	147	65.5	163	-	279	638
Cu(ClO ₄) ₂ .6H ₂ O: 2,5- pdc:dmp (3)	25	32	120	76	88	0.8	316	616
	50	25	127	76	102	0.8	303	626
	100	13	131	72	118	0.9	294	637
	200	-1	141	70	142	0.8	283	647
Cu(ClO ₄) ₂ .6H ₂ O: 2,6- pdc:dmp (4)	25	23	127	75.0	104	0.8	305	618
	50	15	132	73.5	117	0.8	297	626
	100	1	140	70.5	139	0.8	294	638
	200	-18	151	66.5	169	0.6	282	652
Cu(ClO ₄) ₂ .6H ₂ O: 3,4- pdc: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
Cu(ClO ₄) ₂ .6H ₂ O: 3,5- pdc:dmp (6)	25	39	119	79	80	0.9	303	604
	50	32	126	79	94	1.5	292	615
	100	27	129	78	102	0.8	284	630
	200	18	131	74.5	113	0.8	269	642

**Figure 2:** CV of mixed-ligand complex species formed in 3:1:1 Cu (ClO₄)₂:3,5-pdc:dmp (6) molar ratio in DMSO containing 0.2 M NaClO₄ at 25 mV s⁻¹

Electronic absorption spectral studies of binary copper (II) complexes with six pdc acids (A) to (F) in 3:1 metal to ligand molar ratio in dimethylsulfoxide: The electronic absorption spectral data for the binary copper (II) complexes with pdc_s (2,3-pdc, 2,4-pdc, 2,5-pdc, 2,6- pdc, 3,4-pdc and 3,5- pdc)formed

in 3:1 molar ratios in DMSO are presented in table 3. The electronic absorption spectra of all these complexes showed a single broad d-d absorption band at 810, 803, 825, 818, 845 and 842 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 six binary complex solutions [36, 37].

Electronic absorption spectral properties of mixed-ligand copper (II) complexes with six pdc acids and 2,9-dimethyl-1,10-phenanthroline 1 to 6 in 3:1:1 metal to ligand molar ratio in dimethyl sulfoxide: The electronic absorption spectral data for mixed ligand complexes are presented in table 4. The electronic absorption spectra of yellow coloured mixed ligand Cu (II) complexes showed two absorption bands at 772 nm due to the d-d transitions and 457 nm due to the charge transfer for complex 1, at 777 nm and 457 nm for complex 2, at 791 nm and 457 nm for complex 3, at 785 and 457nm for complex 4, at 807 and 456 nm for complex 5 and at 802 nm due to the d-d transitions and 457 nm due to the charge transfer for complex 6. It seems clear that six coordinated species are present in mixed-ligand complex solutions [36, 37].

Table 3: Electronic absorption spectral data for (A) to (F) binary complexes of Cu(II) with pdcs formed in 3:1 Cu(ClO₄)₂ : pdcs molar ratio in DMSO

Systems	Ratio	Colour	$\lambda_{\max}(\text{nm})$	$\epsilon (\text{L mol}^{-1} \text{cm}^{-1})$
Cu(ClO ₄) ₂ .6H ₂ O:2,3-pdc(A)	3:1	Light blue	810	37
Cu(ClO ₄) ₂ .6H ₂ O: 2,4-pdc(B)	3:1	Light blue	803	37
Cu(ClO ₄) ₂ .6H ₂ O: 2,5-pdc(C)	3:1	Light blue	825	33
Cu(ClO ₄) ₂ .6H ₂ O: 2,6-pdc(D)	3:1	Light blue	818	43
Cu(ClO ₄) ₂ .6H ₂ O: 3,4-pdc(E)	3:1	Light blue	845	30
Cu(ClO ₄) ₂ .6H ₂ O: 3,5-pdc(F)	3:1	Light blue	842	33

Table 4: Electronic absorption spectral data for 1 to 6 mixed-ligand complexes formed in 3:1:1 Cu(ClO₄)₂ : pdcs : dmp molar ratio in DMSO containing 0.2 M NaClO₄

Systems	Ratio	Colour	$\lambda_{\max}(\text{nm})$	$\epsilon (\text{L mol}^{-1} \text{cm}^{-1})$
Cu(ClO ₄) ₂ .6H ₂ O: 2,3-pdc:dmp (1)	3:1:1	Yellow	772, 457	43, 170
Cu(ClO ₄) ₂ .6H ₂ O: 2,4- pdc:dmp (2)	3:1:1	Yellow	777,457	47, 110
Cu(ClO ₄) ₂ .6H ₂ O: 2,5- pdc:dmp (3)	3:1:1	Yellow	791,457	40,153
Cu(ClO ₄) ₂ .6H ₂ O: 2,6- pdc:dmp(4)	3:1:1	Yellow	785,457	50, 133
Cu(ClO ₄) ₂ .6H ₂ O: 3,4- pdc:dmp (5)	3:1:1	Yellow	807, 456	40, 80
Cu(ClO ₄) ₂ .6H ₂ O: 3,5- pdc:dmp (6)	3:1:1	Yellow	802,457	37, 193

Highlights:

- Binary copper (II) complexes with various pyridinedicarboxylic acids (pdc) viz, 2,3-pdc; 2,4- pdc; 2,5-pdc; 2,6- pdc; 3,4-pdc; 3,5- pdc and mixed ligand copper (II) complexes with six pdc and 2,9-dimethyl-1,10-phenanthroline (dmp) in dimethylsulfoxide are investigated by electrochemical and spectral studies.
- All the binary copper (II) complexes with six pdc show quasireversible redox reactions and mixed ligand complexes show one irreversible redox process and a second quasireversible redox couple.
- UV-visible studies indicate the presence of distorted octahedral six coordinated copper (II) complex species in binary and mixed ligand complex solution.

CONCLUSIONS

On the basis of above discussion it is concluded that for all binary copper (II) complexes of six pyridinedicarboxylic acids (pdc) viz; 2,3-pdc (A), 2,4-pdc (B), 2,5-pdc (C), 2,6-pdc (D), 3,4-pdc (E) and 3,5-pdc (F) formed in 3:1 metal to ligand molar ratio show a single quasireversible redox couple. It was observed from the cathodic peak potentials that copper (II) complexes with 2,3-pdc, 2,4-pdc and 3,4-pdc showed easier reduction step in comparison to the other binary copper (II) complexes. The electronic absorption spectra of all these complexes showed a single broad d-d absorption band at 810, 803, 825, 818, 845 and 842 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 distorted octahedral six coordinated copper (II) complex predominant species are present in all the six binary complex solutions. The mixed-ligand copper (II) complex species 1, 2, 3, 4, 5 and 6 showed one irreversible redox process at more positive potential and a quasireversible redox couple at less positive potential 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 rate. The electronic absorption spectrum of all the mixed-ligand Cu (II) complexes showed two absorption bands. The λ_{\max} with lower wave length is due to the charge transfer transitions and λ_{\max} with higher wave length is assigned to d-d transitions. It is important to note that distorted octahedral six-coordinate copper (II) complex predominant species are present in mixed-ligand systems in dimethylsulfoxide.

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AUTHORS' ADDRESSES

- Alka Srivastava**
Research Scholar (SRF-UGC), Department of Chemistry,
University of Allahabad, Uttar Pradesh, India.
E-mail: alka23srivastava@gmail.com, Mob No.: 08005316192
- Dipiti Porwal**
Post Doctoral Fellow (UGC), Department of Chemistry,
University of Allahabad, Uttar Pradesh, India.
E-mail: dipiti.porwal@gmail.com, Mob No.: 09450509342
- Krishna Srivastava**
Professor, Department of Chemistry,
University of Allahabad, Uttar Pradesh, India.
E-mail: dr_krishna_s@yahoo.co.in, Mob No.: 08874668888
- Jagdish Prasad**
Professor, Department of Chemistry,
University of Allahabad, Uttar Pradesh, India.
E-mail: dr_jagdish_p@yahoo.co.in, Mob No.: 09415247536