

## Electrochemistry of binary and mixed-ligand copper(II) complexes with pyrazine and dicyanamide bridging ligands in aqueous medium

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The binary copper(II) complexes, viz., [Cu(II) (pyz)<sub>n</sub>(H<sub>2</sub>O)<sub>n</sub>] (**1**), and [Cu(II)(dca)<sub>n</sub>(H<sub>2</sub>O)<sub>n</sub>] (**2**), and, mixed ligand complex, [Cu(II) (dca)<sub>n</sub>(pyz)<sub>n</sub>. nH<sub>2</sub>O (**3**), containing pyrazine (pyz) and dicyanamide (dca) bridging ligands (where n is number of ligand attached and it could be 1 to 6 ) are formed in aqueous medium. The electrochemical behavior of binary complexes in 1:1, 1:2 and 1:10 (Cu : pyz/dca) molar ratios and mixed ligand complex in 1: 1 :1 and 1:2:1 (Cu:dca:pyz) molar ratios have been carried out by cyclic voltammetry. The binary complex **1** undergoes a quasi-reversible single-electron redox process (Cu<sup>2+/+</sup>), while the binary complex **2** exhibits a totally irreversible reduction peak involving two electrons corresponding to Cu<sup>2+/0</sup> change. The reduction potential becomes positive with increasing concentration of pyz/or dca, clearly indicating that reduction becomes easier with increasing concentration of ligand in binary complexes. The mixed ligand complex **3** involving pyz and dca bridging ligands shows an irreversible reduction peak assigned to Cu<sup>2+/0</sup> electrode reactions. The UV-vis spectral properties of all the binary and mixed ligand complexes have been studied in aqueous medium.

**Keywords:** Electrochemistry, UV-visible spectra, Binary complexes, Bridging ligands, Copper, Pyrazine, Dicyanamide

Pyrazine plays a significant role as an intermediate for perfumes, pharmaceuticals and agrochemicals. In particular, amides and sulfonamides derivatives of pyrazine have been used as anti-tuberculosis, oral anti-diabetics, nutrition supplement, insecticides and fungicides<sup>1</sup>.

The presence of the second nitrogen atom in pyrazine increases the electron affinity and lowers the energies of its empty orbitals. Hence, the electrochemical reduction of pyrazine takes place at considerably less negative potentials than that of pyridine. The potential region and the current densities significantly depend on the electrode nature. Pyrazine can be involved in electro-reduction process on Au and Cu electrode in water medium<sup>2</sup>.

The gas phase electron affinity of pyrazine is more positive than that of pyridine. It reduces at modest potentials and serves as a redox-active component to facilitate the two-electron reduction of protons to hydrogen<sup>3</sup>. The lower lying  $\pi^*$  orbitals of pyrazine relative to pyridine would enhance metal-to-ligand backbonding from the metal center and give a more electron-deficient metal with more positive reduction potentials<sup>4</sup>.

Pyrazine and substituted pyrazines have the ability to form linear bridges between metal ions to generate oligomeric species<sup>5-8</sup> or polymeric arrays<sup>9</sup> in the presence of metals atoms containing more than one oxidation state. The electrochemical behavior of pyrazine derivative is highly dependent on the pH<sup>10</sup>.

Xu *et al.*<sup>11</sup> studied the photophysical properties of [Cu(pyrazino-1,10-phenanthroline)<sub>2</sub>]PF<sub>6</sub> complex in solution condition. The electronic absorption spectrum of this complex exhibits the lowest-lying metal-to-ligand charge transfer (MLCT) absorption band at 459 nm and a high-energy ligand-based transition at 275 nm.

Cyclic voltammetry and differential pulsed voltammetry of cobalt pyrazinoporphyrazine complexes show both ligand and metal-based redox processes while its zinc and copper derivatives exhibits only ligand-based redox processes. The redox processes of the pyrazinoporphyrazines significantly shifts towards positive potentials compared to those of the common phthalocyanines<sup>12</sup>.

Mubarak *et al.*<sup>13</sup> studied the electrochemical behavior of chlorinated pyrazines, quinoxaline and pyridazines at carbon and mercury cathodes in

non-aqueous medium and found that both pyrazine and pyridazine exhibit a single reduction wave, whereas unsubstituted quinoxaline shows three cathodic waves.

The electrochemical reduction of pyrazine was carried out by Irish *et al.*<sup>14</sup> in 1.0 M KBr aqueous medium at silver electrode. The reduction was irreversible and observed at potentials more negative than -900 mV (vs SCE)<sup>14</sup>.

Dicyanamide is a versatile ligand with three nitrogen donor atoms; it may act as a uni-, bi-, or tridentate ligand. It can coordinate to metal ions as a terminal ligand through a nitrile or amide nitrogen<sup>15</sup>. Dicyanamide metal complexes are of great interest because of potential application in functional materials. Most of the reports on dicyanamide bridged transition metal complexes are on low-oxidation state systems<sup>16</sup>. Dicyanamide is used as a curing agent for epoxy resins, and in the manufacture of melamine, fertilizers, explosives, pharmaceuticals and dyestuffs<sup>17</sup>.

Vanderaspoilden *et al.*<sup>18</sup> studied the electrochemical behaviour of Cu(I) and Cu(II) ions in 1-butyl-3-methylimidazolium dicyanamide. The comproportionation reaction occurring between Cu(II) and Cu(0) was investigated by different electrochemical techniques such as chronopotentiometry, chronoamperometry and electrochemical quartz crystal microbalance (EQCM). Chronopotentiometry and EQCM experiments conclusively show the existence of a comproportionation reaction,  $\text{Cu(II)} + \text{Cu(0)} \rightarrow 2\text{Cu(I)}$ <sup>18</sup>.

The spectroscopic and electrochemical studies of Cu(II)—dicyandiamide (DCDA) complex were carried out by Kołodziej *et al.*<sup>19</sup>. The spectroscopic behaviour suggests that DCDA is a monodentate ligand forming a bond with  $\text{Cu}^{2+}$  via the nitril nitrogen. Electroreduction of this complex is a two-step process occurring through a Cu(I)—DCDA intermediate<sup>19</sup>.

Zhang *et al.*<sup>20</sup> synthesized chloride-containing dicyanamide/tricyanomethanide-bridged binuclear organometallic complexes involving Fe and Ru metal. Cyclic voltammograms of the dicyanamide/tricyanomethanide-bridged binuclear complexes show stepwise reversible one-electron oxidation waves with the potential separation of the two redox couples in the range 0.14–0.25 V<sup>20</sup>.

The electrochemical and spectral studies on metal complexes of pyrazine, dicyanamide and its derivatives have been carried out previously<sup>21–26</sup>.

The electrochemical and spectral studies of metal complexes formed in non-aqueous medium have been accomplished previously<sup>27,28</sup>. However, the electrochemical and electronic absorption spectral studies of binary and mixed ligand copper complexes with pyrazine and dicyanamide in aqueous medium is rare. Herein, the electrochemical and spectral properties of binary and mixed ligand Cu(II) complexes involving pyrazine and dicyanamide bridging ligands have been examined by cyclic voltammetry under different solution conditions.

### Materials and Methods

The chemicals used in the complexes preparation, such as copper perchlorate hexahydrate ( $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ), dicyanamide ( $\text{C}_2\text{N}_3^-$ ), pyrazine ( $\text{C}_4\text{H}_4\text{N}_2$ ) and sodium perchlorate ( $\text{NaClO}_4$ ) were procured from Sigma Aldrich Chemicals Pvt. Ltd. The stock solutions ( $1 \times 10^{-2}$  M) of these binary and mixed ligand complexes were prepared in doubly distilled water. Further, dilute ( $1 \times 10^{-3}$  M) solutions were prepared by accurate dilution.

The binary and mixed ligand complexes **1**, **2** and **3** were freshly prepared by mixing the aqueous solutions of copper perchlorate hexahydrate and aqueous solution of ligands pyrazine/ dicyanamide in different molar ratios. In the case of binary complexes, the metal-to-ligand molar ratios were kept as 1:1, 1:2 and 1:10, while in the case of mixed ligand complexes the molar ratios of metal:dca:pyz were 1:1:1 and 1:2:1. For the UV-visible spectral studies, 5 mM  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  was used, while the concentration of the ligand depended on the molar ratios of the binary and mixed ligand complexes.

One millimole aqueous solution of copper perchlorate hexahydrate was used to prepare the binary and mixed ligand complex solutions for the cyclic voltammetric studies. The software driven BAS electrochemical systems, (model Epsilon, Bioanalytical Systems, Inc, USA) was employed for all the cyclic voltammetric studies. The working electrode was glassy carbon disc electrode (GCE), the counter electrode was a platinum wire and reference electrode Ag/AgCl in saturated KCl ( $E^\circ = +199$  mV vs NHE). Purging and blanketing of nitrogen (99.999% pure) in the complex solution were done for 30 minutes before running the sample. Sufficient care was taken in the electrode pretreatment. Mechanical polishing of the working electrode (GCE) was done

over a velvet microcloth with alumina suspension. All the electrochemical experiments were performed at a constant temperature  $25 \pm 0.5$  °C. IR compensation and background subtraction were also done. All the cyclic voltammograms were recorded in aqueous 0.1 M NaClO<sub>4</sub> as supporting electrolyte at the glassy carbon working electrode.

The electronic absorption spectra of complexes were recorded in the range 400–1100 nm and 200–500 nm on a Perkin–Elmer UV-visible spectrophotometer (model Lambda 35).

## Results and Discussion

### Cyclic voltammetric studies of binary complexes 1 and 2

The electrochemical properties of binary complexes **1** and **2** in 1:1, 1:2 and 1:10 Cu(II):pyz/dca molar ratios, containing 0.1 M NaClO<sub>4</sub> as a supporting electrolyte were examined by cyclic voltammetry at 25–500 mV s<sup>-1</sup> scan rate ( $\nu$ ) and 500 to –200 mV potential limit. The cyclic voltammograms of complexes **1** and **2** in 1:2 and 1:1 molar ratios at  $\nu = 500$  mV s<sup>-1</sup> are shown in Figs 1 and 2, respectively. It is noteworthy that the electrochemical behavior of complexes **1** and **2** are different from each other. Complex **1** undergoes a quasi-reversible single-electron redox process (Cu<sup>2+/+</sup>), while complex **2** is reduced totally irreversibly involving two electrons (Cu<sup>2+/0</sup>). The coulometric analyses for complexes **1** and **2** were carried out at ~100 mV. The cathodic peak potential observed at –125 mV for complex **1** and at +120 mV for complex **2** in 1:10 metal: ligand ratio, also confirm the involvement of one and two electrons per molecule in the reduction steps of complexes **1** and **2**, respectively. The plots of cathodic peak current ( $I_{pc}$ )

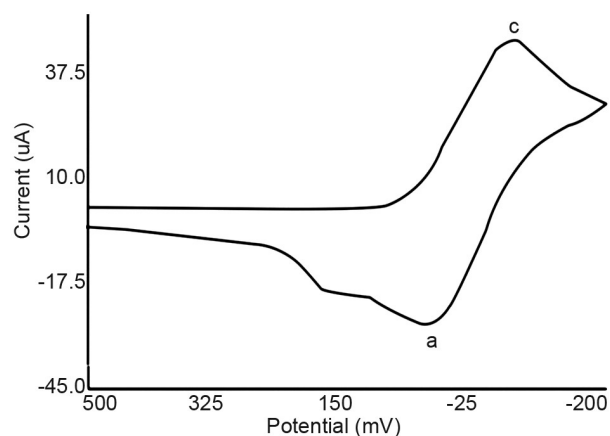


Fig. 1 — Cyclic voltammograms of binary complexes **1** in 1:2 Cu:pyz molar ratio at  $\nu = 500$  mV s<sup>-1</sup>.

vs square root of the scan rate ( $\nu^{1/2}$ ) for complexes **1** in different Cu(II):pyz molar ratios were linear with positive intercept, suggesting that the electrochemical processes are not completely diffusion-controlled<sup>29,30</sup>. The anodic to cathodic peak potential difference,  $\Delta E_p$  ( $= E_{pa} - E_{pc}$ ) was greater than the theoretical value for an electrochemically reversible one-electron transfer process ( $\approx 60$  mV) and was dependent on the scan rate, suggesting that the electron process was quasi-reversible<sup>30</sup> (Table 1). Anodic to cathodic peak current ratio ( $I_{pa} / I_{pc}$ ) was less than 1.0 for 1:1 and 1:2 Cu(II)-pyz ratio in complex **1** (Table 1), showing that the electron transfer is followed by a chemical reaction (EC mechanism), while it is close to unity (1.0) for 1:10 ratio, indicating that it was a simple electron transfer in the presence of excess ligand (Table 1). It should be noted that  $E_{pc}$  shifts towards more positive value with increasing concentration of both pyrazine and dca, in the complexes **1** and **2** respectively, indicating that the reduction becomes easier at higher concentration of ligand (Tables 1 and 2). As expected, the cathodic peak potential also becomes more negative (or less positive) with increasing scan rate in both these binary complex systems (Tables 1 and 2). The reduction of binary complex **2** is easier than that of complex **1** (Tables 1 and 2). It should be also mentioned that both pyz and dca ligands are electro-inactive in the potential range studied.

The effect of scan rate on the cyclic voltammetric behaviour of binary complexes **1** and **2** in different Cu: pyz/dca molar ratios (1:1, 1:2 and 1:10) were studied in scan rates from lower value 25 mV s<sup>-1</sup> to higher value 500 mV s<sup>-1</sup>. The time taken to complete

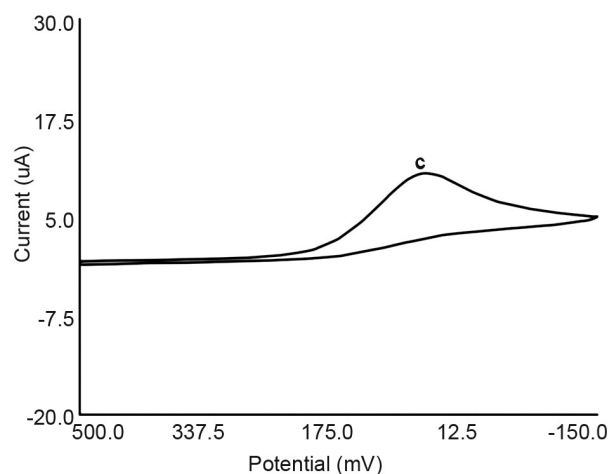


Fig. 2 — Cyclic voltammograms of binary complex **2** in 1:1, Cu:dca molar ratio at  $\nu = 500$  mV s<sup>-1</sup>.

Table 1 — Cyclic voltammetric data for binary complex **1** formed in different Cu:pyz molar ratios in aqueous medium

Metal: ligand molar ratio	Scan rate (mV s <sup>-1</sup> )	$E_{pc}$ (mV)	$E_{pa}$ (mV)	$I_{pc}$ (μA)	$I_{pa}$ (μA)	$E^0$ (mV)	$\Delta E_p$ (mV)	$I_{pa}/I_{pc}$
1 : 1	25	-51	19	11.1	9.6	-16.0	70	0.8
	50	-56	24	13.8	10.3	-16.0	80	0.7
	100	-68	36	18.9	11.9	-16.0	104	0.6
	200	-71	39	27.1	15.7	-16.0	110	0.5
	300	-76	44	32.2	18.5	-16.0	120	0.5
	400	-77	45	35.7	19.4	-16.0	122	0.5
	500	-87	54	37.8	20.2	-16.5	141	0.5
1 : 2	25	-32	48	20.2	9.2	8.0	80	0.4
	50	-34	51	22.9	10.6	8.5	85	0.4
	100	-35	52	28.5	12.3	8.5	87	0.4
	200	-37	53	35.5	19.9	8.0	90	0.5
	300	-40	54	38.0	24.3	7.0	94	0.6
	400	-41	55	44.3	28.1	7.0	96	0.6
	500	-70	56	48.8	36.2	7.0	116	0.9
1 : 10	25	-23	74	11.3	10.3	25.0	97	0.9
	50	-23	75	14.6	12.8	26.0	98	0.8
	100	-24	76	19.3	15.4	26.0	100	0.8
	200	-24	78	27.2	23.5	27.0	102	0.8
	300	-24	79	32.7	29.8	27.5	103	0.9
	400	-25	80	37.7	33.8	27.5	105	0.9
	500	-29	80	40.1	37.0	25.5	109	0.9

Table 2 — Cyclic voltammetric data for binary complex **2** formed in different Cu:dca molar ratios in aqueous medium

Scan rate (mV s <sup>-1</sup> )	Cu:dca molar ratio					
	1:1		1:2		1:10	
	$E_{pc}$ (mV)	$I_{pc}$ (μA)	$E_{pc}$ (mV)	$I_{pc}$ (μA)	$E_{pc}$ (mV)	$I_{pc}$ (μA)
25	74	6.5	124	7.4	219	9.6
50	73	7.2	117	9.1	207	13.0
100	66	9.0	107	11.3	194	17.5
200	49	12.2	93	15.5	179	24.1
300	46	14.4	88	20.1	175	30.6
400	40	17.2	84	23.2	173	34.8
500	33	18.2	78	25.8	165	34.3

one cycle of voltammogram during the CV experiment depended on the scan rate. When the scan rate was slow, the CV experiments took longer time to complete one cycle, while at high scan rate the cycle of voltammogram was completed rapidly. The electrochemical parameters such as cathodic peak current ( $I_{pc}$ ), anodic peak current ( $I_{pa}$ ), cathodic peak potential ( $E_{pc}$ ), anodic peak potential ( $E_{pa}$ ), peak potential difference ( $\Delta E_p$ ) were influenced by the scan rates. The effect of scan rate on these cyclic voltammetric (CV) parameters was determined by simple plot between scan rate and the studied CV parameter.

In the case of binary complex **1**, the cathodic peak current ( $I_{pc}$ ) increased with increase in scan rate. It was noted that the 1:1 and 1:10 Cu: pyz complexes exhibit similar enhancement of  $I_{pc}$  while the 1:2 Cu: pyz complex shows comparatively higher  $I_{pc}$  values. The relationship between anodic peak current ( $I_{pa}$ ) vs scan rate ( $v$ ) was plotted and it was observed that the anodic peak current ( $I_{pa}$ ) increased with increasing scan rate. A higher value of anodic peak current ( $I_{pa}$ ) was observed in the cyclic voltammogram of 1:10 Cu: pyz complex solution. The decreasing order of  $I_{pa}$  values, i. e., 1:10 > 1:2 > 1:1 were observed in complex **1**. It was found that the  $I_{pa}$  values increased with increasing concentration of pyz ligand. The anodic peak current of the complex was proportional to the scan rate, which indicates that the electrode process is surface-controlled<sup>31</sup>.

The cathodic peak potentials values ( $E_{pc}$ ) were shifted in a more negative direction with increasing scan rate, clearly indicating that the reduction became difficult with increasing scan rate. It was found that the cathodic peak potential values shifted more negatively in 1:1 Cu/pyz complex solution. The trend of  $E_{pc}$  shifting (negatively) and reduction behavior of all the Cu:pyz binary complexes was observed in the

following order: 1:1 > 1:2 > 1:10 ( most difficult reduction (1:1) > less difficult reduction (1:2) > easier reduction (1:10).

The anodic peak potential ( $E_{pa}$ ) values shifted more positively with increasing scan rate which indicates that oxidation became more difficult at higher scan rate. It was noted that the 1:1 Cu:pyz complex solution showed easier oxidation while 1:10 Cu/pyz complex solution was difficult to oxidise. The trend of oxidation from easier to difficult is: Cu:pyz (1:1) → Cu:pyz (1:2) → Cu:pyz (1:10). The peak potential differences ( $\Delta E_p$ ) were also affected by scan rate. The  $\Delta E_p$  values increased with increasing scan rates. The redox behavior of binary complex **1** in all Cu:Pyz molar ratios changed from quasi-reversible to irreversible with increasing scan rate.

The effect of scan rate on the CV behavior of complex **2** in different Cu:dca molar ratios was examined. As known from Fig. 2, only one irreversible cathodic peak appeared in the voltammogram of complex **2**. The cathodic peak potential ( $E_{pc}$ ) shifted negatively with scan rate. The  $E_{pc}$  values of Cu:dca (1:1) complex shifted more negatively in compared to the  $E_{pc}$  values of 1:2 and 1:10 Cu:dca complexes. It was found that 1:1 Cu: dca complex solution was reduced easily, while 1:10 Cu: dca complex solution was difficult to reduce. The cathodic peak current ( $I_{pc}$ ) increased with increasing scan rates. The maximum enhancement in  $I_{pc}$  was observed in 1:10 Cu:dca complex solution. The sequence of cathodic peak current values in complex **2** is as follows: 1:10 (Cu:dca) > 1:2 (Cu:dca) > 1:10 (Cu:dca). The plot between cathodic peak current ( $I_{pc}$ ) vs square root of scan rates ( $v^{1/2}$ ) of complexes **1** and **2** are linear (Supplementary Data, Figs S1 and S2), indicating that the electrode reaction is controlled by diffusion.

#### UV-visible spectral studies of binary complexes **1** and **2**

The electronic spectra of binary Cu(II) complexes **1** and **2** in 1:1, 1:2 and 1:10 Cu(II): ligand (pyz/dca) molar ratios were studied in aqueous medium (Supplementary Data, Table S1). The spectrum of pyrazine ligand shows two absorption bands in UV region. The intense absorption bands centered at 260 nm and 301 nm are assigned to ligand-centered ( $\pi-\pi^*$ ) transitions. These intra-ligand bands (at 260 and 301 nm) remain unaffected on complexation, while a new charge transfer band appears at 266 nm in the all three metal: ligand molar ratios of binary

complex **1**. In addition, a broad ligand field band due to the  $d-d$  transition appeared at 808 nm (in 1:1 and 1:2 Cu/Pyz complexes) and at 791 nm (in 1:10 Cu/Pyz complex). Furthermore, the binary complex **2** showed only two absorption bands; the broad absorption band at  $\approx 795$  nm attributed to  $d-d$  transitions and the relatively intense band at  $\approx 306$  nm assigned to charge transfer transitions.

Previous report on UV spectral studies of pyrazine (Pz), pyrazine carboxamide (PzCA) and pyrazinic carboxylic acid (PzAM) show an absorption band at around 260 nm, which may be attributed to  $\pi-\pi^*$  transition of the pyrazine ring. This absorption band remains unchanged in their complexes<sup>32</sup>. The band around 245 nm may be due to  $n-\pi^*$  of Pz, PzCA and PzAM. A shoulder at around 330 nm may be due to the ligand to metal charge transfer (LMCT). This LMCT peak was found to disappear upon reduction of the cobalt(III) by Fe(II) or Cr(II)<sup>33,34</sup>.

#### Cyclic voltammetric studies of mixed-ligand complex **3**

The electrochemical behavior of the mixed ligand complex **3** formed in 1:1:1 and 1:2:1 (metal: dca: pyz) molar ratios was studied in aqueous 0.1 M NaClO<sub>4</sub>. The cyclic voltammograms of the complexes **3** in these two molar ratios showed a totally irreversible cathodic peak similar to that observed for the complex **2** (Fig. 3). It was observed that the cathodic peak potential ( $E_{pc}$ ) for the complex **3** in 1:1:1 ratio, at a given scan rate, was less positive as compared to complex **2** in 1:1 ratio, while it was more positive than complex **1** in 1:1 ratio. Furthermore, the values of  $E_{pc}$  in complex **3** formed in 1:2:1 molar ratio was more positive than that formed in 1:1:1 molar ratio (Table 3), indicating that the reduction of mixed-

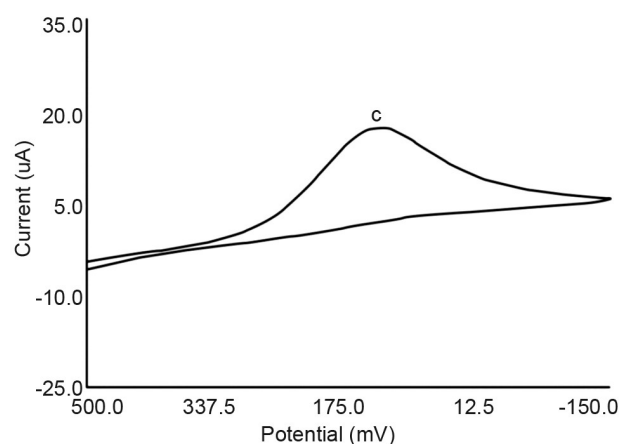


Fig. 3 — Cyclic voltammograms of mixed ligand complex **3** in 1:2:1, Cu:dca:pyz molar ratio at  $v = 500 \text{ mV s}^{-1}$ .

Table 3 — Cyclic voltammetric data for mixed ligand complex **3** formed in different Cu:dca:pyz molar ratios in aqueous medium

Scan rate (mV s <sup>-1</sup> )	Cu:dca:pyz molar ratio			
	1 : 1 : 1		1 : 2 : 1	
	<i>E</i> <sub>pc</sub> (mV)	<i>I</i> <sub>pc</sub> ( μA)	<i>E</i> <sub>pc</sub> (mV)	<i>I</i> <sub>pc</sub> ( μA)
25	72	8.7	160	6.4
50	71	10.0	151	8.1
100	51	10.3	137	11.3
200	31	12.3	117	17.0
300	20	14.7	111	20.2
400	7	15.4	104	23.3
500	-4	15.8	96	25.5

ligand complex in 1:2:1 ratio is easier than in 1:1:1 ratio. On the basis of CV results it may, therefore, be concluded that different types of mixed-ligand complex species were formed in 1:1:1 and 1:2:1 molar ratios. In 1:1:1 ratio, each Cu(II) ion is expected to be coordinated through two nitrogen atoms of the two *trans* dca and two nitrogen atoms of the two *trans* pyz ligands.

Two previous studies<sup>35,37</sup> based on the electrochemistry of dicyanamide bridging complex have been reported. However, the cyclic voltammetric response of the both complexes is totally different. Konar *et al.*<sup>35</sup> synthesized a polymeric dicyanamide bridged hexa-coordinated copper(II) complex [Cu(2-carboxypyrazine)(dicyanamide)<sub>2</sub>]<sub>n</sub> from the reaction of Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 2-pyrazinecarbonitrile and sodium dicyanamide in methanolic medium. The electrochemical behavior of this complex was studied by cyclic voltammetry in the range of +1.00 V to -0.50 V at a scan rate of 100 mV s<sup>-1</sup> in DMF at platinum electrode versus SCE using tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. Dicyanamide ion is a stronger electron donor<sup>36</sup> and behaves as an oxidant, thereby favouring the oxidation of the metal center. The metal center is oxidised first at *E*<sub>pa</sub> = 0.228 V and then reduced at *E*<sub>pc</sub> = 0.0418 V in a one electron redox system. The cyclic voltammogram for the complex was found to be quasi-reversible in nature with Δ*E*<sub>1/2</sub> = 0.186 V.

Mitra *et al.*<sup>37</sup> synthesized a seven coordinated pentagonal bipyramidal manganese complex [Mn(acetate)(2,4,6-tris(2-pyridyl)-1,3,5-triazine)(dicyanamide)(H<sub>2</sub>O)].(H<sub>2</sub>O)<sub>2</sub>. An electrochemical study of this complex was performed using dimethylformamide as solvent and tetrabutylammonium perchlorate as the supporting electrolyte at a scan rate of 50 mV s<sup>-1</sup>. One irreversible reductive response at -1.05 V versus SCE was observed, which

is attributed to a ligand-centered reduction. No oxidation response was found on the positive side of SCE.

[Cu(2-carboxypyrazine)(dicyanamide)<sub>2</sub>]<sub>n</sub> shows quasi-reversible behaviour while the [Mn(acetate)(2,4,6-tris(2-pyridyl)-1,3,5-triazine)(dicyanamide)(H<sub>2</sub>O)].(H<sub>2</sub>O)<sub>2</sub> complex shows totally irreversible redox behavior. In the present case, complexes **1** and **2** showed quasi-reversible and irreversible redox behavior respectively while the mixed ligand complex **3** exhibited a totally irreversible redox nature in aqueous medium. Similar redox behavior was observed in complexes **2** and **3**.

The mixed ligand complexes formed in 1:1:1 and 1:2:1 Cu:dca:pyz showed only one reduction peak in their voltammogram. It was found that cathodic peak potentials (*E*<sub>pc</sub>) decrease with increasing scan rates. The cathodic peak potentials (*E*<sub>pc</sub>) of 1:1:1 Cu:dca:pyz complex shifted more negatively as compared to 1:2:1 Cu:dca:pyz complex. It was also observed that reduction is easier with increasing scan rate. The cathodic peak current (*I*<sub>pc</sub>) increased with scan rates. The *I*<sub>pc</sub> value shifted towards more positive values in the case of 1:2:1 Cu:dca:pyz complex as compared to the 1:1:1 Cu:dca:pyz complex. In the case of complex **3**, linearity was observed in the graph plotted between square root of scan rate vs cathodic peak current (Supplementary Data, Fig. S3).

#### UV-visible spectral studies of mixed ligand complex **3**

The electronic spectra of mixed ligand complexes **3** in 1:1:1 and 1:2:1 molar ratios were also recorded in aqueous solution (Supplementary Data, Table S2). The spectra shows three absorption bands with one broad *d-d* band at 799 nm in the visible region and two relatively intense bands at 301 and 260 nm in the UV region, assigned to intraligand (pyrazine-based) π - π\* transitions. The electronic spectral properties of the mixed ligand complexes **3** formed in 1:1:1 and 1:2:1 (metal: dca: pyz) molar ratios were almost similar.

Konar *et al.*<sup>35</sup> reported that the mixed ligand complex, [Cu(2-carboxypyrazine)(dicyanamide)<sub>2</sub>]<sub>n</sub> in dimethyl formamide (DMF), shows two band at 298 nm and 468 nm. The first one at 298 nm is due to the ligand-to-metal charge transfer transition (LMCT) and the second band at 468 nm is due to *d-d* transition of Cu(II) center. These two absorption bands can be assigned to the *S*<sub>0</sub>-*S*<sub>11</sub> and *S*<sub>0</sub>-*S*<sub>20</sub> transitions, respectively<sup>35,38</sup>. According to Mitra *et al.*<sup>37</sup> the mixed ligand complex, [Mn(acetate)(2,4,6-tris(2-pyridyl)-1,3,5-triazine)(dicyanamide)(H<sub>2</sub>O)].(H<sub>2</sub>O)<sub>2</sub> in dimethylformamide shows three strong bands at ~240,

265 and 295 nm due to charge transfer from the coordinated ligand to Mn(II). The complex does not show any *d-d* transitions<sup>39</sup>.

### Conclusions

Binary copper(II) complexes, viz., [Cu(II)(pyz)<sub>n</sub>(H<sub>2</sub>O)<sub>n</sub>] (**1**) and [Cu(II)(dca)<sub>n</sub>(H<sub>2</sub>O)<sub>n</sub>] (**2**), and, mixed ligand complex, [Cu(II)(dca)<sub>n</sub>(pyz)<sub>n</sub>].nH<sub>2</sub>O (**3**) containing pyrazine (pyz) and dicyanamide (dca) bridging ligands (where n is number of ligand attached, value from 1–6) are formed in aqueous medium. The binary complex **1** undergoes a quasi-reversible single-electron redox process (Cu<sup>2+/+</sup>) while the binary complex **2** exhibits a totally irreversible reduction peak involving two electrons corresponding to Cu<sup>2+/0</sup> change. The reduction potential becomes positive with increasing concentration of pyz/or dca, clearly indicating that reduction becomes easier with increasing concentration of ligand in complexes **1** and **2**. The mixed ligand complex **3** shows an irreversible reduction peak assigned to Cu<sup>2+/0</sup> changes. Pyrazine and dicyanamide ligands are electro-inactive within the studied potential limit. The intense absorption bands at 260 and 301 nm are assigned to ligand-centered ( $\pi - \pi^*$ ) transitions, while a charge transfer band appears at 266 nm in all molar ratios of complex **1**. A broad ligand field band at 808 nm (in 1:1 and 1:2 ratio) and at 791 nm (in 1:10 ratio) also appears due to *d-d* transitions. The binary complex **2** shows only two absorption bands at  $\approx 792$  nm and  $\approx 305$  nm, attributed to *d-d* transitions and charge transfer transitions respectively. The electronic spectra for the mixed ligand complex **3** in all the metal:ligands molar ratios are almost similar.

### Supplementary Data

Supplementary data associated with this article, viz., Table S1 and S2 and Figs S1-S3, are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA\\_56A\(06\)585-591\\_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_56A(06)585-591_SupplData.pdf)

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