



Electrochemical and Spectral Behaviour of Binary and Mixed-Ligand Copper (II) Complexes of Dicyanamide and Pyrazine in Non-Aqueous Solvents

Rachana Shukla, Krishna Srivastava* and Jagdish Prasad

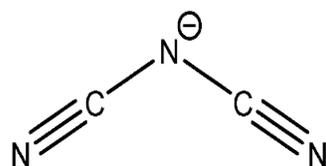
Nanoscience and Electrochemical Research Laboratory, Department of Chemistry,
University of Allahabad, Allahabad-211002 (U. P.), **INDIA**
Email: dr_krishna_s@yahoo.co.in, rshuklachemau@gmail.com

Accepted on 4th March 2018

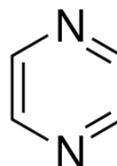
ABSTRACT

The binary copper (II) complex with dicyanamide and mixed ligand copper (II) complex involving dicyanamide and pyrazine were synthesized and characterized by elemental analyses (C,H,N), UV-Visible and FT-IR spectra. The electrochemical behaviour of these complexes were studied in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) containing 0.1M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte at a glassy carbon disc working electrode using cyclic voltammetry. The cyclic voltammograms of binary and mixed ligand complexes in DMF and DMSO showed a quasireversible redox couple corresponding to $\text{Cu}^{2+}/\text{Cu}^+$ with formal potentials $E^{0'} = 263$ mV, $E^{0'} = 285$ mV, $E^{0'} = 175$ mV and $E^{0'} = 166$ mV against Ag/AgCl. The cathodic peak potential shifts negatively and anodic peak potential shifts positively with increasing scan rate and the plot of cathodic peak current (I_{pc}) vs square root of scan rate ($v^{1/2}$) gave a straight line passing through origin, inferring that the reduction process is diffusion-controlled. The UV-Visible spectra of the binary and mixed ligand complexes in DMF and DMSO were also studied.

Graphical abstract



Dicyanamide



Pyrazine

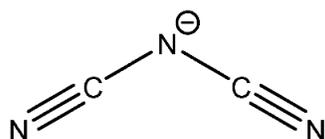
Keywords: Methyl orange, Iron nanoparticles, UV-Visible Spectroscopy, Rate Constant.

INTRODUCTION

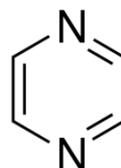
Copper is a biologically relevant element and many enzymes that depend on copper for their activity have been identified. Copper(II) is a substitutionally labile metal ion and multidentate ligands are found to be better than bidentate ligands in keeping the copper (II) ion chelated in solution. Typically, upon association with dioxygen or hydrogen peroxide these copper complexes are reported to perform reactive intermediates [1]. Copper (II)-organic frameworks possess enormous structural diversity due to flexible coordination sphere around the copper (II) ion, in combination with steric and packing forces. Copper(II) is one of the most important transition metal ions, not only because of its relevance as the active-site structure of metalloproteins, but also due to its magnetochemistry [2].

Metal dicyanamide (dca) coordination polymers constitute a hot subject of research, due to their rich structural and topological features along with the magnetic properties [3]. Dicyanamide ligand binds metal ions in various modes: viz. monodentate bonding through a nitrile nitrogen or bridging modes such as μ -1,3 and μ -1,5 bidentate, μ -1,3,5 and μ -1,1,5 tridentate, and μ -1,1,3,5 tetradentate and μ -1,1,3,5,5 pentadentate. In this context, variability of the coordination modes of the dca ligand allows the preparation of compounds of various kinds of architectures: mononuclear, polynuclear, and 1D, 2D and 3D networks. Several studies of dicyanamide in conjugation with other coligands have already been reported extensively for the synthesis of polymetallic complexes with interesting supramolecular architecture [4]. Dicyanamide is used as a curing agent for epoxy resins, and in the manufacture of melamine, fertilizers, explosives, pharmaceuticals and dyestuffs [5].

Pyrazines play an important role as intermediates for perfumes, pharmaceuticals and agricultural chemicals. Especially, amides and sulfonamides of pyrazines have been used as insecticides, fungicides, nutrition supplements and drugs for tuberculosis/diabetic [6]. The use of trace amounts of pyrazines as flavour and fragrance enhancers in the foodstuffs and tobacco industries was also documented [7]. The substituted pyrazines have the ability to form linear bridges between metal ions to generate oligomeric species or polymeric arrays in the presence of metals atoms containing more than one oxidation state. The electrochemical behaviour of pyrazine derivative is highly dependent on the pH[8]. Structures of dicyanamide and pyrazine ligands are given below:



Dicyanamide



Pyrazine

MATERIALS AND METHODS

Cupric nitrate hemi(pentahydrate) ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$), sodium dicyanamide ($\text{C}_2\text{N}_3\text{Na}$), pyrazine ($\text{C}_4\text{H}_4\text{N}_2$) and tetrabutylammonium perchlorate (TBAP) were procured from Sigma Aldrich Chemicals Pvt. Ltd. Dimethylsulfoxide (DMSO) and Dimethylformamide (DMF) were procured from Merck Specialities Pvt. Ltd. The software driven BAS Electrochemical System, Model EPSILON (Bioanalytical System, Inc, USA) was employed for all the electrochemical studies. 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 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 ± 0.5 °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. Elemental (C,H,N) analyses was carried out with Elemental Analyzers (EUROVECTOR EA 3000).

Synthesis of the binary complex [Cu(dca)₂]: 10-mL aqueous solution of cupric nitrate hemi(pentahydrate) (Cu(NO₃)₂·2.5H₂O), (5.2mM, 1.2 g) was added to a 10-mL aqueous solution of sodium dicyanamide (Nadca) (964mg, 10.8mM) with constant stirring. The result was immediate precipitation of the dark green product. Filtered and washed with ethanol several times. It was dried at room temperature inside a vacuum desiccator over P₂O₅. (yield: 390 mg, 36% based on Cu).

Synthesis of the mixed ligand complex [Cu(dca)₂(pyz)]_n: 10-mL aqueous solution of cupric nitrate hemi(pentahydrate) (Cu(NO₃)₂·2.5H₂O), (5.2 mM, 1.2 g) was quickly added to a 10-mL aqueous solution that contained sodium dicyanamide (Nadca) (0.964 g, 10.8 mM) and pyrazine (0.414 g, 5.2 mM) with constant stirring. The result was immediate precipitation of the blue-green product [9]. The contents were filtered and the precipitate was washed with ethanol several times. It was then dried at room temperature inside a vacuum desiccator over P₂O₅. (yield: 1.260 g, 49% based on Cu).

RESULTS AND DISCUSSION

Elemental analyses and IR spectra: The binary and mixed ligand complexes were characterized by elemental analyses (C,H,N) and FT-IR methods. Anal. Calculated for binary complex [Cu(dca)₂](%): C, 24.237; H, 0.000; N, 40.993; Found: C, 24.48; H, 0.00; N, 42.85 Anal. Calculated for mixed ligand complex [Cu(dca)₂(pyz)]_n (%): C, 34.77; H, 2.19; N, 39.336 Found: C, 33.73; H, 1.40; N, 39.35. The elemental analyses were consistent with their chemical formulae.

FTIR of binary and mixed ligand complexes were recorded in the range of 4000-450cm⁻¹ using a KBr pellet. Band found at 1377cm⁻¹ in binary complex and 1380 cm⁻¹ in mixed ligand complex correspond to (C-N) stretching frequency. In addition to this, in mixed ligand complex the bands found at 2315 cm⁻¹, 2248cm⁻¹ and 2179cm⁻¹ correspond to (C≡N) band of sodium dicyanamide [4]. The bands at 1417cm⁻¹ and 816 cm⁻¹ are due to presence of pyrazine in the mixed ligand complex [10].

Electrochemical behaviour of binary complex [Cu(dca)₂] in DMF and DMSO: Cyclic voltammetric (CV) behaviour of the binary complex were studied in DMF and DMSO containing 0.1M TBAP as a supporting electrolyte at GCE in the scan rate 25 to 500 mVs⁻¹. The cyclic voltammetric data are given in table 1 and their voltammograms at 100 mVs⁻¹ in figs. 1(a) and 1(b). One redox couple appeared between the potential limit of 800 mV to -200mV. The observed formal potentials and anodic to cathodic peak potential difference are: E⁰ = 263mV, ΔE_p = 150mV in DMF, E⁰ = 175mV, ΔE_p = 148mV in DMSO at the scan rate 100 mV/s, assigned to quasireversible 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 increasing the scan rate the cathodic peak potential shifts more negatively showing difficult reduction and easier oxidation. A plot of cathodic peak current (I_{pc}) vs square root of scan rate (v^{1/2}) gave a straight line passing through origin inferring that the reduction process was diffusion-controlled [11-12].

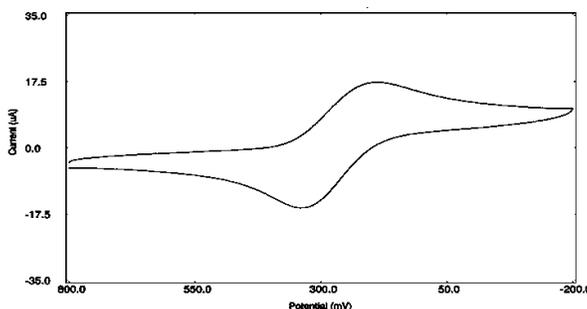


Figure 1(a). CV of binary [Cu(dca)₂] complex in DMF containing 0.1 M TBAP at 100 mVs⁻¹

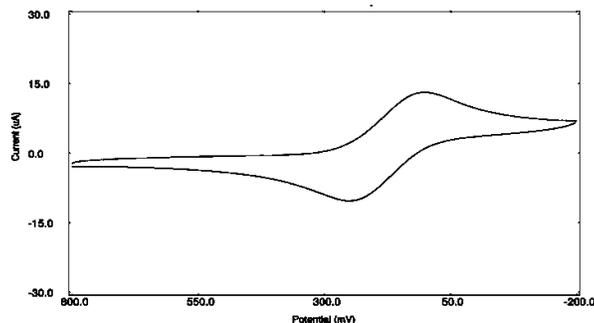


Figure 1(b). CV of binary $[\text{Cu}(\text{dca})_2]$ complex in DMSO containing 0.1 M TBAP at 100 mVs^{-1}

Table 1. -CV data for binary $[\text{Cu}(\text{dca})_2]$ complex in DMF and DMSO containing 0.1 M TBAP

Solvent	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}
DMF	25	201	325	7.1	7.6	263	124	1.0
	50	199	331	10.0	10.1	265	132	1.0
	100	188	338	14.7	15.9	263	150	1.0
	200	175	348	18.9	20.7	261.5	173	1.0
	300	168	351	23.3	24.1	259.5	183	1.0
	400	161	357	27.6	28.5	259	196	1.0
	500	154	358	35.3	37.5	256	204	1.0
DMSO	25	122	236	5.2	5.4	179	114	1.0
	50	111	242	7.1	7.2	176.5	131	1.0
	100	101	249	8.4	8.7	175	148	1.0
	200	88	262	13.5	14.6	175	174	1.0
	300	83	266	16.3	16.9	174.5	183	1.0
	400	78	274	18.0	18.6	176	196	1.0
	500	73	279	19.9	20.6	176	206	1.0

Electrochemical behaviour of mixed-ligand complex $[\text{Cu}(\text{dca})_2(\text{pyz})_n]$ in DMF and DMSO: Cyclic voltammetric (CV) behaviour of the mixed ligand complex were recorded in DMF and DMSO containing 0.1M TBAP as a supporting electrolyte at GCE at the scan rate 25 to 500 mVs^{-1} . The cyclic voltammetric data are given in table 2 and the cyclic voltammograms at 100 mVs^{-1} are shown in figs. 2(a) and 2(b). In the case of mixed ligand Cu(II) complex, one redox couple appeared between the potential limit of 800 mV to -200mV. The observed formal potentials and anodic to cathodic peak potential difference are: $E^0 = 285\text{mV}$, $\Delta E_p = 208\text{mV}$ in DMF and $E^0 = 166\text{mV}$, $\Delta E_p = 116\text{mV}$ in DMSO at the scan rate 100 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

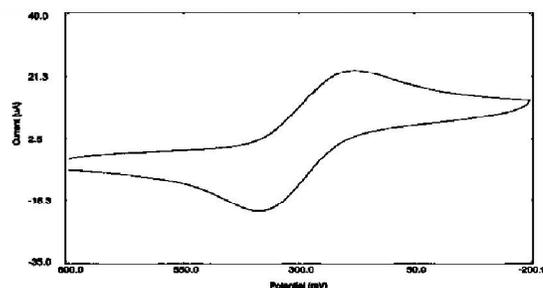


Figure 2(a). CV of mixed ligand complex $[\text{Cu}(\text{dca})_2(\text{pyzy})_n]$ in DMF containing 0.1 M TBAP at 100 mVs^{-1}

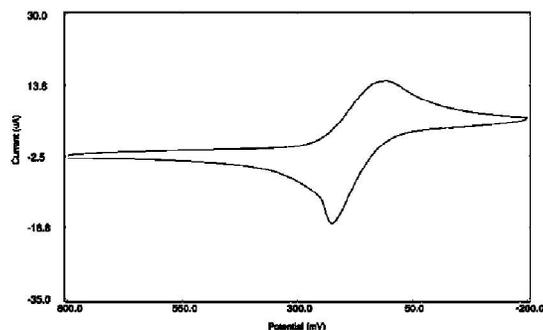


Figure 2(b). CV of mixed ligand complex $[\text{Cu}(\text{dca})_2(\text{pyz})]_n$ in DMSO containing 0.1 M TBAP at 100 mVs^{-1}

also justified the quasi-reversible nature of redox couple. On increasing the scan rate the cathodic peak potential shifts more negatively shows difficult reduction. A plot of cathodic peak current (I_{pc}) vs square root of scan rate ($v^{1/2}$) gave a straight line passing through origin showed that the reduction process was diffusion-controlled [11-12].

Table 2. CV data for mixed ligand complex $[\text{Cu}(\text{dca})_2(\text{pyz})]_n$ in DMF and DMSO containing 0.1 M TBAP

Solvent	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}
DMF	25	206	370	9.04	9.5	288	164	1.0
	50	192	377	11.8	12.9	284.5	185	1.0
	100	181	389	17.5	18.8	285	208	1.0
	200	170	403	24.6	25.4	286.5	233	1.0
	300	170	403	29.9	30.8	286.5	233	1.0
	400	165	414	34.8	35.6	289.5	249	1.0
	500	165	420	37.8	38.9	292.5	255	1.0
DMSO	25	123	205	6.8	7.6	164	82	1.0
	50	116	218	9.3	14.2	167	102	1.0
	100	108	224	12.1	19.2	166	116	1.0
	200	107	235	16.8	25.4	171	128	1.0
	300	103	238	20.1	30.7	170.5	135	1.0
	400	100	241	21.5	33.3	170.5	141	1.0
	500	96	244	23.5	35.5	170	148	1.0

Table 3. UV-Visible spectra of binary $[\text{Cu}(\text{dca})_2]$ and mixed ligand $[\text{Cu}(\text{dca})_2(\text{pyz})]_n$ complexes in DMF and DMSO

Solvent	System	Colour	λ_{max} (nm)	ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)
DMF	Pyrazine (ligand)	Colourless	316	53
	$[\text{Cu}(\text{dca})_2]$ (a)	Light blue	812	45
	$[\text{Cu}(\text{dca})_2(\text{pyz})]_n$ (b)	Light blue	811	47
DMSO	Pyrazine (ligand)	Colourless	317	78
	$[\text{Cu}(\text{dca})_2]$ (a)	Light blue	814	40
	$[\text{Cu}(\text{dca})_2(\text{pyz})]_n$ (b)	Light blue	845	45

Electronic absorption spectral studies of binary and mixed ligand complexes in DMF and DMSO: The electronic absorption spectra of binary and mixed ligand complexes were studied in DMF and DMSO (table 3). The spectrum of pyrazine ligand shows one absorption band at 316nm in DMF and at 317nm in DMSO in UV- region and are assigned to ligand-centered (π - π^*) transitions. A broad band appeared at 811nm in DMF and at 845nm in DMSO for mixed ligand complex and at 812nm in DMF and at 814nm in DMSO for binary complex which are attributed to d-d transitions. A new charge transfer bands appeared at 332nm in DMF and 372nm in DMSO medium of mixed ligand complex and are due to ligand to metal charge transfer (LMCT). On the basis of electronic absorption spectral band, it could be clear that a six coordinated copper complex species are predominantly present in the binary and mixed ligand complex solutions.

APPLICATION

Form the results of absorption spectral band, it could be clear that six coordinated copper complex is predominant species present in the binary and mixed ligand complex solutions and are is useful to find the structure of the complexes.

CONCLUSIONS

The binary complex $[\text{Cu}(\text{dca})_2]$ and mixed ligand complex $[\text{Cu}(\text{dca})_2\text{pyz}]_n$ were synthesized in aqueous medium and their electrochemical investigations show that both the complexes undergo a quasi-reversible single-electron redox process ($\text{Cu}^{2+/+}$) with formal potentials $E^0 = 263$ mV and 285 mV in DMF and 175 mV and 166 mV in DMSO. The formal potential is more positive in DMF than that in DMSO, showing easier oxidation in DMF. The electronic absorption spectral band corresponds to a six- coordinated copper complex in the binary and mixed ligand complex solutions.

ACKNOWLEDGEMENTS

One of the authors (Rachana Shukla) is thankful to University Grant Commission (UGC), New Delhi for the financial support.

REFERENCES

- [1]. R. Elayaperumal, M. Kiruthika, P. Dharmalingam, Mixed ligand copper(II) complexes: Synthesis, characterization and DNA cleavage activities, *J. Pharm. Research*. **2013**, 7, 281-285.
- [2]. S. K. Singh, A. K. Srivastava, K. Srivastava, R. Banerjee, J. Prasad, Synthesis, characterization and electrochemical investigations of mixed-ligand copper(II)-organic supramolecular frameworks, *J. Mol. Struc.* **2017**, 1147, 549-557.
- [3]. S. Jana, R. C. Santra, S. Das, S. Chattopadhyay, Variation in DNA binding constants with a change in geometry of ternary copper(II) complexes with N_2O donor Schiff base and cyanate or dicyanamide, *J. Mol. Struc.* **2014**, 1074, 703-712.
- [4]. S. P. Devi, N. S. Devi, L. J. Singh, R. K. B. Devi, W. R. Devi, C. B. Singh, R. K. H. Singh, Spectroscopic and DNA interaction studies on mixed ligand copper(II) complexes of dicyanamide with ethylenediamine or 1,3-diaminopropane, *Inorg. Nano-metal Chem.* **2017**, 47(2), 223-233.
- [5]. M. D. Serna, F. Legaz, M. E. Primo, Improvement of N fertilizer efficiency with dicyandiamide (dcd) in citrus trees, *Fertilizer Res.* **1996**, 43, 137-142.
- [6]. Y. Higashio, T. Shoji, Heterocyclic compounds such as pyrrole, pyridines, pyrrolidine, piperidine, indole, imidazol and pyrazines, *Appl. Catal. A: Gen.* **2004**, 260, 251-259.
- [7]. C. Baillie, J. F. Bickley, P. Branton, J. Chadwick, P. Wan, R. Whyman, Coordination complexes of functionalized pyrazines with metal ions: reagents for the controlled release of flavourant molecules at elevated temperatures, *Flavour Fragr. J.* **2006**, 21, 202-206.

- [8]. V. Prakash, K. Srivastava, J. Prasad, Electrochemistry of binary and mixed-ligand copper(II) complexes with pyrazine and dicyanamide bridging ligands in aqueous medium, *Indian J. Chem.* **2017**, 56A, 585-591.
- [9]. J. L. Manson, T. Lancaster, S. J. Blundell, Y. Qiu, J. Singleton, P. Sengupta, F. L. Pratt, J. Kang, C. Lee, M. H. Whangbo, Spin fluctuations and orbital ordering in quasi-one-dimensional α -Cu(dca)₂(pyz) {dca = dicyanamide = N(CN)₂ ; pyz = pyrazine}, a molecular analogue of KCuF₃, *Polyhedron*, **2010**, 29, 514-520.
- [10]. F. Billes, H. Mikosch, S. Holly, A comparative study on the vibrational spectroscopy of pyridazine, pyrimidine and pyrazine, *J. Mol. Struct. (Thermochem)*. **1998**, 423, 225-234.
- [11]. V. Prakash, K. Srivastava, J. Prasad, Electrochemical and spectral investigation of various pyridinedicarboxylic acids and their complexes with oxovanadium(IV) in dimethyl sulfoxide, *J. Mol. Liquids*. **2014**, 198, 164-168.
- [12]. V. Prakash, K. Srivastava, J. Prasad, Electrochemical and spectral behaviour of binary and mixed-ligand complexes of oxovanadium(IV) with dipicolinic acid and diimines in dimethylsulfoxide, *J. Mol. Liquids*. **2015**, 204, 1-9.
- [13]. P. Jensen, S. R. Batten, G. D. Fallon, D. C. R. Hockless, B. Moubaraki, K. S. Murray, R. Robson, Synthesis, Structural Isomerism, and Magnetism of Extended Framework Compounds of Type [Cu(dca)₂(pyz)]_n, Where dca = Dicyanamide (N(CN)₂⁻) and pyz = Pyrazine, *J. Sol. State Chem.* **1999**, 145, 387-393.