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Synthesis, Characterization, Spectral and Electrochemical Studies of Copper (II) Complexes with Nitrogen and Oxygen Donor Ligands

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ABSTRACT

The mixed- ligand copper (II) complexes [Cu (2-CINA)₂(bipy)] 1; [Cu(2-CINA)(phen)(H₂O)](NO₃) 2, and [Cu(2-CINA)₂(dmp)(H₂O)] 3, were synthesized by using 2-chloronicotinic acid (2-CINA) and the aromatic diimines, viz., 2,2'-bipyridine (2,2'-bipy), 1,10-phenanthroline (1,10-phen) and 2,9-dimethyl-1,10-phenanthroline (dmp) in aqueous / non aqueous media. Synthesized complexes have been characterized by elemental analysis, molar conductance measurements, (FT-IR, UV-Visible) spectroscopic technique and room temperature magnetic susceptibility measurements. Molar conductance measurements have been carried out in DMSO and DMF, complexes 1 and 3 correspond to non electrolyte and complex 2 represents mono cationic nature. The redox properties of the all these complexes were extensively investigated by electrochemical method using cyclic voltammetry (CV). The electrochemical behavior of complex 3, involving dmp as the auxiliary ligand is different from rest of two mixed-ligand Cu (II) complexes. Based on these studies, a distorted square-pyramidal coordination geometry around the Cu (II) ion has been proposed in solid complexes 2 and 3, while complex 1 is square planar. In DMSO and DMF solutions, complexes 2 and 3 possess distorted octahedral and complex 1, shows tetragonally distorted octahedral geometry due to solvent coordination.

Keywords: Mixed-ligand copper (II) complexes, 2-Chloronicotinic acid, 2, 9-dimethyl-1, 10-phenanthroline, cyclic voltammetry

Introduction

Copper belongs to one of the important class of elements known as 3d transition elements. It can occur in various oxidation states but common is +2. Copper (II) complexes continue to receive attention because of chemical, biological and industrial importance ^[1]. Inorganic chemistry of copper (II) is fascinating owing to: (i) copper (II) exhibits a variety of coordination numbers (4–8) with associated geometries, (ii) copper (II) complexes are liable to Jahn–Teller distortion, (iii) the anionic ligand may be non-coordinated or coordinated, (iv) it is one of constituent metal ions in most of superconductors and (v) the copper (II) compounds (e.g. carboxylates) may be monomeric, dimeric or polymeric. Copper is an essential element as it plays a key role in all living organisms, serving as a co-factor for many proteins and enzymes involved in electron transfer, oxidative, oxygenation activities and detoxification of oxygen radicals ^[2, 3].

Copper (II) is known to play a significant role in biological systems and also as pharmacological agents. Synthetic copper (II) complexes have been reported to act as potential anticancer and cancer inhibiting agents ^[4-6], and a number of copper complexes ^[7, 8] have been found to be active both *in-vitro* and *in-vivo*. The mixed- ligand copper (II) complexes of diimines, which bind and cleave DNA and also exhibit anticancer activity that is more efficient than that of cisplatin ^[9]. The use of phen as the coligand in the above ternary complexes is of considerable interest because some of the phen-containing copper complexes exhibit biological as well as pharmacological properties ^[10].

Pyridine carboxylic acid and its derivatives constitute an important group of anthelmintics and vitamins. It is known that the some drugs act via chelation ^[9] or via the inhibition of metalloenzymes ^[11], but little is known about modification of the activities of most drugs that are potential ligands. The structures of many complexes show that with nicotinic acid

(niacin or vitamin B₃) and its derivatives acting as bridging ligands through the carboxylate group and pyridyl-N atom [12]. 2-Chloronicotinic acid and certain of its derivatives show remarkable physiological activity [13]. 6-chloronicotinic acid (6-CINA) is important building blocks for agrochemicals, animal food enrichment, feed additives, reduce plasma cholesterol and pharmaceuticals [14].

Because nicotinic and isonicotinic acids play important roles in the metabolism of all living cells and much interest have been directed towards their metal complexes [15,16]. Redox properties of a drug can give insights into its metabolic fate or pharmaceutical activity [17]. The electron transfer mechanism of the metal complexes is investigated by the aid of cyclic voltammetry.

In this present paper, we have reported the synthesis and characterization of three mixed-ligand Cu(II) complexes viz; [Cu(2-CINA)₂(bipy)] 1; [Cu(2-CINA)(phen)(H₂O)](NO₃) 2, and [Cu(2-CINA)₂(dmp)(H₂O)] 3.

2. Experimental Part

2.1 Materials and methods

All the chemicals viz., copper (II) nitrate trihydrate, 2-chloronicotinic acid and diimines (bipy, phen and dmp) were purchased from Sigma Aldrich Chemicals Pvt. Ltd. and were used as such. Analar grade methanol, dimethylsulfoxide (DMSO) and dimethylformamide (DMF) were procured from E. Merk India Ltd. The C, H, N microanalysis were carried out at Central Drug Research Institute (CDRI) Lucknow. For each complex the C, H, N analyses were carried out twice. The FT-IR spectra were performed on Perkin Elmer 577 FT-IR Spectrophotometer from KBr pellets in the range 4000-400 cm⁻¹ and room temperature magnetic susceptibility measurements were carried out using Hg[Co(NCS)₄] as a calibrating standard at Banaras Hindu University, Varanasi. The UV-VIS spectra of the complexes were recorded in DMSO and DMF solutions with a Perkin-Elmer Model Lambda 35 Spectrophotometer. Melting point was recorded on a Metrex melting point apparatus.

2.2 Cyclic voltammetric measurements

The software driven BAS Electrochemical System, Model EPSILON (Bioanalytical Systems, Inc; U.S.A.) was employed for all the electrochemical studies. 1×10⁻² M stock solutions of these complexes were prepared in the desired solvent. More dilute (1×10⁻³ M) solutions were prepared by accurate dilution. 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°=

+199mV vs NHE). Purging and blanketing of nitrogen (99.999% pure) were done for analyte solution placed in the electrochemical cell of 15 ml capacity for 20 min. Great care was taken in the electrode pretreatment. Mechanical polishing of the working electrode (GCE) was done over a velvet microcloth with an alumina suspension. The electrode was rinsed with doubly distilled water after each polishing, and ultrasonicated in ethanol and water for 5 min, respectively. Then, the bare GCE was subjected to electrochemical deposition. Controlled Potential Electrolysis (CPE) was carried out for calculating the number of electrons involved in the reduction process. Electrolysis was done in 1×10⁻³ M DMSO solution of a complex containing 0.2M NaClO₄ in a BASi Bulk electrolysis cell, consisting of Reticulated Carbon Working Electrode, coiled platinum auxiliary electrode dipped in a separate cell containing 0.2M NaClO₄ in DMSO solution only and Ag/AgCl as a reference electrode. Nitrogen gas was initially purged for 30 min with constant stirring of solution and then N₂ was blanketed over the constantly stirred cell solution during the electrolysis. All the electrochemical experiments were performed at a constant temperature 25±0.5°C.

2.3 Synthesis of mixed-ligand complexes (1-3)

To the aqueous solution (30ml) of Cu (NO₃)₂.3H₂O (3.33 mmol), the methanolic solutions of 2-chloronicotinic acid (6.66 mmol in 50ml methanol) and appropriate diimine (3.33 mmol) in 20ml methanol were slowly added with constant stirring for 2hr. The pH of the resulting solution was adjusted to 4.5 with 1.0 M aqueous sodium hydroxide, then the solution was heated over water bath for 1hr. The solution was cooled to room temperature and then it was filtered off and the filtrate was kept for crystallization at room temperature (25°C). Blue polycrystalline complexes (1 and 2) and green coloured complex 3 were isolated by filtration, washed with diethylether and dried inside a vacuum desiccator. Yield ≈ 65-70%.

3. Results and Discussion

The formula, formula weight, elemental analyses (Cu, C, H and N %), M.P. and room temperature magnetic moments are given in Table 1. On the basis of elemental analyses, spectral (FT-IR and UV-VIS), magnetic moments and conductance measurements the formulae for complexes 1-3 are proposed. The observed magnetic moments at room temperature (25°C) for these complexes 2.02 BM (Table 1) showing that complexes are mononuclear [18]. The Electronic absorption spectral data for complexes (1-3) are tabulated in Table 2.

Table 1: Formula, Formula Weight, Elemental Analyses and Room temperature Magnetic Moments (μ_{eff}) of the Mixed-Ligand Copper (II) Complexes 1-3.

Complex No.	Formula	Empirical Formula	Mol. Weight	Colour	M.P. (°C)	Elemental Analyses, % Cal. (Found)				μ_{eff} RT (B.M.)
						Cu	C	H	N	
1	[Cu(2-CINA) ₂ (bipy)]	Cu ₂ C ₂₂ H ₁₄ N ₄ O ₄ Cl ₂	532.5	Dark Blue	215±1	11.92 (11.80)	49.57 (49.64)	2.62 (2.70)	10.51 (10.72)	1.74
2	[Cu(2-CINA)(phen)(H ₂ O)](NO ₃)	Cu ₂ C ₁₈ H ₁₃ N ₄ O ₆ Cl	480	Blue	198±1	13.22 (13.32)	45.00 (44.90)	2.71 (2.67)	11.67 (11.70)	1.74
3	[Cu(2-CINA) ₂ (dmp)(H ₂ O)]	Cu ₂ C ₂₆ H ₂₀ N ₄ O ₅ Cl ₂	602.5	Green	175±1	10.53 (10.59)	51.78 (51.72)	3.31 (3.26)	9.29 (9.25)	1.74

Table 2: UV-Vis Spectral Data for Copper (II) Complexes 1-3.

Complex	Colour of Solid Compound	DMSO		DMF		Assignments of bonds
		Colour	λ_{max} (nm) (ϵ , Lmol ⁻¹ cm ⁻¹)	Colour	λ_{max} (nm) (ϵ , Lmol ⁻¹ cm ⁻¹)	
[Cu(2-CINA) ₂ (bipy)] (1)	Dark Blue	Blue	682 (63)	Blue	660 (115)	d-d
[Cu(2-CINA)(phen)(H ₂ O)](NO ₃) (2)	Blue	Blue	696 (50)	Blue	678 (75)	d-d
[Cu(2-CINA) ₂ (dmp)(H ₂ O)] (3)	Green	Green	742 (58)	Orange	789 (105)	d-d

3.1 IR spectra and molar conductance studies of mixed-ligand Cu (II) complexes

IR spectra firmly support the formation of these complexes. The IR bands of all these copper (II) complexes are assigned on comparing with the free ligands data [19, 20]. The infrared spectrum of complex 1 exhibits characteristic strong bands at 1641 and 1365 cm⁻¹, assignable as antisymmetric stretching $\nu_{\text{asym}}(\text{COO}^-)$ and symmetric stretching $\nu_{\text{sym}}(\text{COO}^-)$, respectively. The difference between ν_{asym} and ν_{sym} ($\Delta\nu$) thus comes 276 cm⁻¹, indicating that the carboxylato group (COO⁻) of 2-CINA⁻ is unidentately coordinated through its one oxygen atom only [17, 20, 21-23]. In addition to these peaks, a weak band in the region 1573-1579 cm⁻¹ may be correlate to the pyridyl C=N stretching vibration due to the 2-CINA⁻ and 2,2'-bipyridine [24, 25]. The peak at 463 cm⁻¹ of medium intensity may be assigned to γ (py) of pyridine ring [24, 20].

The characteristic band for the carboxylate group of 2-CINA⁻ anion at 1634-1589 cm⁻¹ due to the asymmetric stretching and at 1634-1589 cm⁻¹ due to the symmetric stretching are observed in the case of complex 2. The peak separations between $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ are 245 and 237 cm⁻¹, respectively. The splitting of the $\nu_{\text{asym}}(\text{COO}^-)$ peak indicates two different coordination modes [16, 26-29] for the carboxylate group. A broad band at 3416 cm⁻¹, assigned to the ν_{OH} stretching vibration of water molecule [24, 27, 25]. Moreover, the characteristic band at 848 cm⁻¹, attributed to the rocking mode of coordinated water molecule [30]. A sharp peak of medium intensity at 648 cm⁻¹ may be assignable to $\nu_{\text{C=N}}$ of phen ring. However, in complex 2, the carboxylate groups may be considered in a chelating mode. The $\Delta\nu$ values for a complex(215 and 235 cm⁻¹) which are close to the ionic

values confirmed that 2-CINA⁻ anion as a ligand is most probably coordinated via a bridging carboxyl group [24]. The greater $\Delta\nu$ values for complexes which contain 2, 6-Cl₂NA⁻ and 5-BrNA⁻ anions, respectively, (242 to 260cm⁻¹) are rather typical for asymmetrically chelating carboxylate groups. However, in these cases $\Delta\nu$ values are comparable to those of unidentate complexes.

The FT-IR spectrum of complex 3 shows two strong absorption bands at 1634 and 1378 cm⁻¹ corresponding to asymmetric and symmetric stretching vibrations of the carboxylato group. The value of $\Delta\nu$ ($\nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)$) is 256 cm⁻¹, clearly showing that the mode of coordination of COO⁻ group is mono dentate through one of the oxygen atoms. The presence of weak band in the region 1549-1579 cm⁻¹ may be assigned to pyridyl C=N stretching vibrations due to the 2-CINA⁻ and dmp ligands [24, 27] and a peak at 471cm⁻¹ may be attributed [24] to γ (py). A weak broad band is observed at 3211 cm⁻¹, assigned [20, 24, 27] to the ν_{OH} -stretching vibration of water molecule. Moreover, the IR spectrum also exhibits characteristic band at ca. 855 cm⁻¹, assigned to rocking mode of coordinated water molecule [30].

The molar conductance data for complexes 1 and 3 indicate that they are non-electrolyte nature (neutral complexes) in DMSO, while complex 2 correspond to 1:1 electrolyte type mono cationic nature. The room temperature magnetic moments of these complexes suggest the presence of one unpaired electron and it is believed to be indicative of mononuclear nature of these complexes. The elemental analyses (Cu, C, H and N %) also support the proposed formulae for complexes 1-3, (Table 1).

Table 3: CV data for 1mM mixed-ligand Cu (II) complexes in DMSO containing 0.2 M NaClO₄

Scan rate (mVs ⁻¹)	Epc(mV)	Epa(mV)	E ⁰ (mV)	ΔE_p (mV)	Ipa/Ipc		
[Cu(2-CINA) ₂ (bipy)], 1							
25	-94	28	-33	122	1.1		
50	-94	26	-34	120	1.1		
100	-94	18	-38	112	1.1		
200	-96	16	-40	112	1.3		
300	-98	14	-42	112	1.4		
400	-100	12	-44	112	1.6		
500	-101	11	-45	112	1.6		
[Cu(2-CINA)(phen)(H ₂ O)](NO ₃), 2							
25	-57	70	6.5	127	0.9		
50	-57	70	6.5	127	1.0		
100	-59	76	8.5	135	1.0		
200	-62	87	12.5	149	1.2		
300	-62	87	12.5	149	1.3		
400	-65	88	11.5	153	1.3		
500	-67	88	10.5	155	1.7		
[Cu(2-CINA) ₂ (dmp)(H ₂ O)], 3							
Scan rate (mVs ⁻¹)	Epc ₁ (mV)	Epc ₂ (mV)	Epa ₂ (mV)	E ⁰ (mV)	$\Delta E_p(2)$ (mV)	Epa' ₂ (mV)	Ipa' ₂ (μ A)
10	245	-1	57	+28.0	58	570	0.6
25	224	-3	59	+28.0	62	582	1.0
50	206	-4	59	+27.5	63	595	1.5
100	188	-6	61	+27.5	67	607	2.2
200	174	-13				623	3.0
300	175					627	3.3

3.2 Electronic Absorption Spectra

Electronic spectrum of the mononuclear copper(II) complex recorded at room temperature, in DMSO and DMF solution, shows weak absorption d-d band in the range 660-789 nm, which may be assign to ${}^2B_{1g} \rightarrow {}^2A_{1g} (dx^2-y^2 \rightarrow dz^2)$ ($\sqrt{1}$), ${}^2B_{1g} \rightarrow {}^2B_{2g} (dx^2-y^2 \rightarrow dzy)$ ($\sqrt{2}$), and ${}^2B_{1g} \rightarrow {}^2E_g (dx^2-y^2 \rightarrow dzx, dyz)$ ($\sqrt{3}$) transition and it is in conformity with distorted octahedral geometry^[18], an indication of the most probable geometric configuration of the synthesized complexes is their magnetic moment values. So, additional confirmed by the magnetic moment measurements at room temperature values lie at 2.02 B.M corresponding to the presence of one unpaired electron and it supports an octahedral geometry^[18].

3.3 Electrochemical behavior of complexes 1- 3 in DMSO / DMF solution

The electrochemical behaviours of mixed-ligand complexes of Cu(II) -2-chloronicotinic acids with diimines (diimine = 2,2'-bipyridine (bipy), 1,10- phenanthroline (phen) and 2,9-dimethyl- 1,10-phenanthroline (dmp)), 1 to 3 have been studied in 0.2 M NaClO₄ in DMSO and DMF at a glassy carbon working electrode using cyclic voltammetry. CV data for complexes 1-3 in DMSO and DMF are given in Tables 3 and 4, respectively and the representative cyclic voltammograms are displayed in Figures 1 and 2.

The cyclic voltammogram of complex 1 in DMSO showed a single well-defined quasi-reversible one-electron reduction couple (c/a) associated with Cu^{2+/+} change, with E_{pc} = -94 mV, E_{pa} = +18 mV, E⁰ = -38 mV and ΔE_p = 112 mV at 100 mVs⁻¹. The peak current ratio (I_{pa}/I_{pc}) is greater than unity (Table 3), clearly indicating that the reduced complex species is adsorbed at the surface of electrode^[31-37]. Complex 2 in DMSO also shows similar behaviour with E_{pc} = -59 mV, E_{pa} = +76 mV, E⁰ = 8.5 mV and ΔE_p = 135 mV. The peak current ratio is 1.0 at scan rate ≤100 but greater than 1.0 at higher scan rates (Table 3).

It should be noted that the electrochemical behaviour of complex 3 is different from those of complexes 1 and 2. A negative scan in the potential range +1000 to -170 mV for 3 in DMSO showed two reduction peaks at E_{pc1} = 224 mV and E_{pc2} = -3 mV in the forward cycle, while the reverse scan exhibited two oxidation peaks at E_{pa2} = +55 mV, E⁰ = 27.5 mV and ΔE_p = 58 mV and E_{pa1} = 582 mV at 25 mVs⁻¹ (Table 3 and Fig. 1). Furthermore, CV with a negative scan in the potential range +1000 to +110 mV shows only the irreversible cathodic peak at E_{pc1} = +224 mV, clearly indicating that two complex species exist in solution and that one of the complex species is irreversibly reduced at c₁ (Cu^{2+/+}) and the second complex species is reduced quasi-reversibly involving a single-electron (Cu^{2+/+}). The anodic peak a₂' is dependent on the reduction process c₂, and that this redox process also involves EC mechanism^[31-37]. Cyclic voltammogram of 1 in DMF showed a diffusion-controlled quasi-reversible one-electron transfer reaction with E_{pc} = -107 mV, E_{pa} = +40 mV, ΔE_p = 147 mV and I_{pa}/I_{pc} = 0.25 at 100 mVs⁻¹ (Table 4), corresponding to Cu^{2+/+} change with EC mechanism^[31-37]. However, at scan rates ≥400 mVs⁻¹, an additional oxidation peak a' appeared at E_{pa}' = +135 mV at 500 mVs⁻¹ (Table 3 and Figure 2), suggesting that complex 1 is unstable and that

the electron transfer is followed by a chemical reaction (EC mechanism)^[31-37]. The electrochemical behaviour of 2 is similar to 1 (Figure 2).

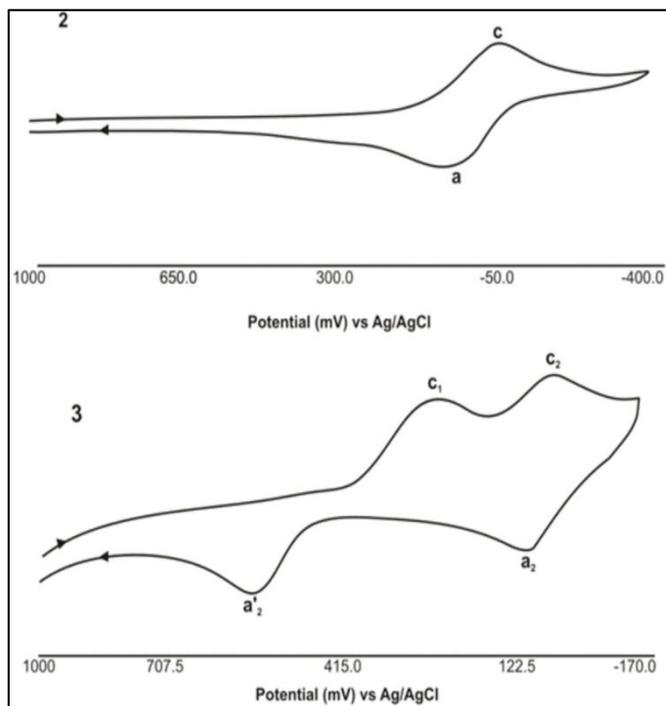


Fig 1: Cyclic voltammograms of complexes 2 (100mVs⁻¹) and 3 (25mVs⁻¹) in DMSO

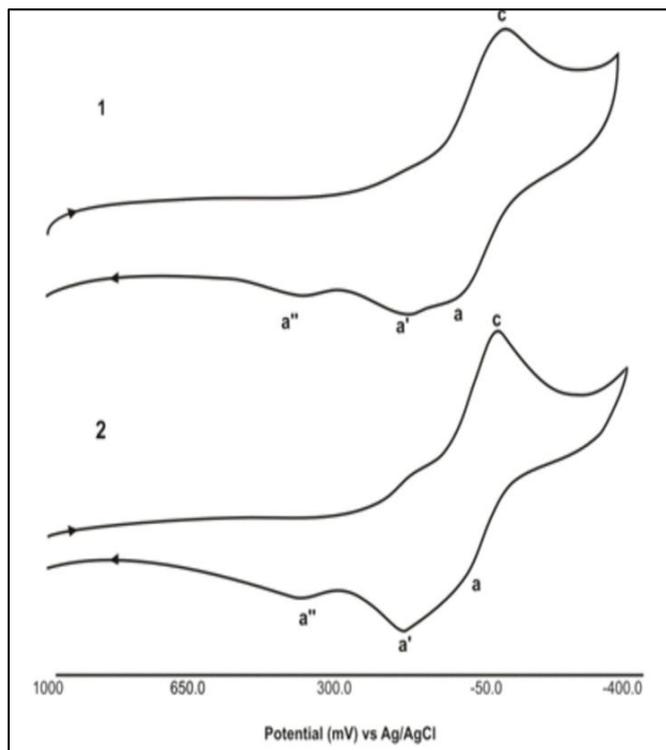


Fig 2: Cyclic voltammograms of complexes 1 and 2 500mVs⁻¹ in DMSO

Table 4: CV data for 1mM mixed-ligand Cu (II) complexes in DMF containing 0.2 M NaClO₄

Scan rate (mVs ⁻¹)	E _{pc} (mV)	E _{pa} (mV)	E ⁰ (mV)	Δ E _p (mV)	I _{pa} /I _{pc}	E _{pa} '(mV)	E _{pa} ''(mV)	I _{pa} '(μA)
[Cu(2-CINA) ₂ (bipy)], 1								
25	-105	51	-27.0	156	0.3	-	-	-
50	-106	46	-30.0	152	-	-	-	-
100	-107	40	-33.5	147	-	-	-	-
200	-114	35	-39.5	149	-	-	-	-
300	-114	30	-42.0	144	-	-	-	-
400	-119	28	-45.5	147	-	130	375	-
500	-121	28	-46.5	149	-	135	386	-
[Cu(2-CINA)(phen)(H ₂ O)](NO ₃), 2								
25	-76	20	-28.0	96	0.5	110	-	2.2
50	-76	20	-28.0	96	0.5	110	-	3.5
100	-78	20	-29.0	98	0.5	112	-	5.8
200	-81	24	-28.5	105	0.6	119	-	8.7
300	-83	24	-29.5	107	0.6	122	-	10.7
400	-84	29	-27.5	113	0.7	124	350	12.8
500	-87	29	-29.0	116	0.7	131	360	14.0

Conclusion

In the present work, synthesis, characterization and electrochemistry of mixed-ligand Cu (II) complexes of 2-chloronicotinic acid with aromatic diimines have been performed. Elemental analyses, spectral (FT-IR, UV-Vis), room temperature magnetic susceptibility and molar conductance measurements have been used for structural characterization of these complexes (1-3). For complex 1, square planar and the complexes 2 and 3 are the distorted square pyramidal in solid and distorted octahedral (in DMSO and DMF) geometries have been proposed. The observed magnetic moments correspond to mononuclear complexes with one unpaired electron (2.02) B.M. [18]. The electrochemical behaviors of these complexes have also been studied in DMSO and DMF solutions containing 0.2 M NaClO₄. The DMSO solutions of complexes 1 and 2 showed a well defined quasi-reversible Cu^{2+/+} redox couple except that complex 3. The DMSO solution of complex 3 exhibited one irreversible cathodic peak at E_{pc} = +224 mV (Cu^{2+/+} and one quasi-reversible reduction couple (Cu^{2+/+}), clearly supporting the existing of two complex species in solution. It is concluded that the reduction of 2-chloronicotinic acid-Cu (II)-diimines mixed ligand complex becomes easier in the sequence 1→2→3 in a given solvent. This can be better understood on the basis of electronic and steric effects of the substituents on the diimines. As the positive charge on the central atom of a complex increase, the reduction becomes easier.

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References

- (1) Stephan H, Juran S, Born K, Comba P, Geipel G, Hahn U *et al.*, 2008; 32:2016. (b) Stamatatos TC, Tangoulis V, Raptopoulou CP, Terzis A, Papaefstathiou GS, Perlepes SP *et al.*, 2008; 47:7969. (c) Armentano D, Mastropietro TF, Julve M, Rossi R, Rossi P, Munno GD. *J Am Chem Soc.* 2007; 129:2740. (d) Ding F, Peng WJ, Photochem Photobiol B. 2015; 147:24. (e) Gaur A, Srivastava BD, Srivastava K, Prasad J. *J Appl Phys.* 2013, 113:073701.
- Holm RH, Kennepohl P, Soloman EI. *Chem. Rev.* 1996; 96:2239.
- Murphy ME, Lindley PF, Adman ET. *Protein Sci.* 1997; 6:76.
- May PM, Williams DR, Sigel H. In *Metallons in Biological Systems*; Ed.; Marcel Dekker: New York, 1981; 12:7.
- Sigel H, Miura T, Hori-i A, Mototani H, Takeuchi H. Ed, *Metal Ions in Biological System*; Marcel Dekker: New York, 1981.
- Fernandes C, Parrilha GL, Lessa JA, Santiago LJM, Kanashiro MM, Boniolo FS *et al.* *Chim. Acta*, 2006; 359:3167.
- Bales BC, Kodama T, Weledji YN, Pitie M, Meunier B, Greenberg MM. *Nucleic Acid Res.* 2005; 33:5371.
- Rajendiran V, Karthik R, Palaniandavar M, Evans HS, Periasamay VS, Akbarsha MA *et al.* *Chem.* 2007; 46:8208.
- Farrell N. *Transition Metal Complexes as Drug, Chemotherapeutic Agents*; Kluwer Academic: Dordrecht, The Netherlands. 1989, 2777.
- Albert, *Selective Toxicity, the Physico Chemical Basis of Therapy*, 6th ed.; Chapman, Hall, London, 1979.
- Hughes MN. *The Inorganic Chemistry of Biological Process*, 2nd ed.; Wiley, New York, 1981.
- Gao S, Liu J, Huo L, Sum Z, Gao J, SW Ng. *Acta Cryst.* 2004, 363.
- Dogra SK. *J Luminescence*, 2005; 114:213.
- Ross WCJ. *Biochem. Pharmacol.* 1967; 16:675.
- Xu D, Xie A, Xu Y, Zhang C, Chen W. *J Coord Chem.* 1996; 39:273.
- Xu D, Xie A, Xu Y, Nishikawa K, Yasuoka N. *J Coord Chem.* 1998; 43:115.
- Shiekh RA, Rahma IA, Malik MA, Masudi SM, Luddin N. *Int J Electrochem Sci.* 2012; 7:12829.
- Dinda J, Sinha C. *Trans. Met. Chem.* 2003; 28:864.
- Infrared Spectra of Inorganic and Coordination Compounds*, Ed. Nakamoto K., Wiley-Interscience, New York, London, Second Edition, 1970.
- Melnik M, Potacnak I, Macáškova L, miklos CE. *Holloway, Polyhedron*, 1996; 15:2159.
- Hokelek T, Budak K, Neefoglu H. *Acta Crystallogr. Sect.* 1997; C53:1049.
- Melnik M, Koman M, Macaskova L, Glowiak T. *J Coord Chem.* 1988; 44:163.
- Mancol J, Korabik M, Segla P, Koman M, Miklos D, Jskova J *et al.* *Chem.*, 2007; 633:298.

24. Inorganic Electronic Spectroscopy, Ed. A.B.P. Lever, Elsevier, Amsterdam-Oxford- New York, Second Edition, 1984.
25. Madaln AM, Paraschiv C, Sutter JP, Schmidtman M, Müller A, Andruh M. Cryst. Growth. Des. 2005; 5:707.
26. Das A, Pilet G, Luneau D, Salah El Fallah M, Ribas J, Mitra S. Inorg. Chim. Acta, 2005; 358:2005; (b) Slint S, Chakraborty J, Sen SG, Pilet C. Desplanches and Mitra S. J Mol. Struct, 2008, 891:19.
27. Bakalbassis EG, Mrozinski J, Tsipis CA. Inorg. Chem. 1986; 25:3684.
28. Hadadzadeh H, Jamil S, Fatemi A, Haseinian SR, Khavasi HR, Pottgen R. Polyhedron, 2008; 27:249.
29. Moncol J, Palicova M, Segla P, Koman M, Melnik M, Valko M, Glowiak T. Polyhedron, 2002; 21:365. and references therein.
30. Bard AJ, Faulkner LR. Electrochemical Methods, John Wiley and Sons, Inc; U.S.A. 1980, 229-235, 530; (b) Martins M, Boas MV, Castro B. de, Hillman AR, Freire C, Electrochem. Acta, 2005; 51:304.
31. Srivastava Krishna, Srivastava Ashish Kumar, Prasad Jagdish. J Indian Chem Soc. 2007; 84:1195.
32. Khare Subhasni, Prasad Jagdish, Kumari Mala, Srivastava Krishna. J. Indian Chem Soc. 2005; 82:829.
33. Srivastava Krishna, Srivastava Divya, Kumari Mala, Khare Subhasni, Prasad Jagdish. J Indian Chem. Soc. 2005; 82:824.
34. Srivastava K, Kumari M, Srivastava A, Prasad J, Pandeya KB. J Indian Chem Soc. 2007; 84:51.
35. Srivastava Krishna, Singh Nutan, Srivastava Ashish Kumar, Prasad Jagdish. J Indian Chem Soc. 2009; 86:189.
36. Srivastava K, Srivastava AK, Singh SK, Prasad J. J Indian Chem Soc. 2012; 89(8):1135.