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Synthesis, characterization, electrochemistry and axial ligation properties of macrocyclic divalent metal complexes of acetylacetone buckled with different diamines

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Abstract—A series of macrocyclic nickel(II) copper(II) complexes using acetylacetone and different aliphatic and aromatic diamines (1,2-diamino ethane, 1,2-diamino propane, 1,2-diamino benzene, 1,3-diamino benzene and 3,4-diamino toluene) has been synthesized by the template method. These complexes were characterized by elemental analysis, conductivity measurements, electronic, infrared and NMR spectral data. The molar conductivity data show them to be non-electrolytes. The electronic spectral data in toluene (a non-coordinating solvent) suggest square planar geometry for these complexes. The axial coordination in these complexes is supported by their electronic spectra in dimethylformamide (DMF, a coordinating solvent). Various ESR parameters for all copper complexes have been calculated showing an axial $d_{x^2-y^2}$ ground state. The electrochemical behaviour of these complexes has been studied by cyclic voltammetry. © 1997 Elsevier Science Ltd

Keywords: synthesis; characterization; electrochemistry; axial ligation; macrocyclic metal complexes; acetylacetone; diamines.

Macrocyclic transition metal complexes have been regarded as better model compounds for metalloporphyrins and metallocorrins because of their intrinsic structural properties. Spontaneous self-assembly reactions have been considered as vehicles for reliable and economical preparation of macrocyclic complexes. Hence these reactions hold a fascination for chemists to mimic anabolic reactions without enzymes. Macrocyclic nickel(II) complexes using (substituted) acetylacetone and 1,2-phenylenediamine have been synthesized and (partially) characterized by Jaeger [1]. Woodruff *et al.* reported resonance Raman studies of macrocyclic Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes derived using acetylacetone and 1,2-phenylenediamine [2]. Although several tetraaza macrocyclic nickel(II) complexes have been prepared using acetylacetone and ethylenediamine [3]/1,2-phenylenediamine [1], the studies on macrocyclic nickel(II) and copper(II) complexes derived using acetylacetone and substituted diamines are limited and may be considered incomplete in the absence of resonance (^{1}H-NMR and ESR) spectra and cyclicvoltammetric studies. Recently, we have reported [4,5] the synthesis and characterization of a series of unsymmetrical macrocyclic cobalt(II) complexes. In the light of the lacuna identified and in continuation of our earlier work, herein we report the synthesis, characterization, spectral studies and electrochemistry of macrocyclic nickel(II) and copper(II) complexes derived using acetylacetone and different diamines *viz.* 1,2-diaminoethane, 1,2-diaminopropane, 1,2-diaminobenzene, 1,3-diaminobenzene and 3,4-diaminotoluene (serial numbers of complexes and their structures are given in Scheme 1.

EXPERIMENTAL

All the chemicals used were of AR grade. 1,2-Diaminobenzene, 1,3-diaminobenzene and 3,4-diam-

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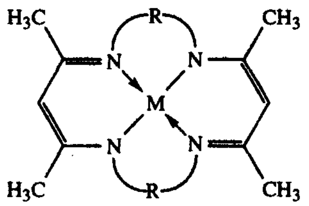

	Where, M = Ni (II)		Where, M = Cu (II)
I	$R = 1,2-C_6H_4$	VI	$R = 1,2-C_6H_4$
II	$R = 1,3-C_6H_4$	VII	$R = 1,3-C_6H_4$
III	$R = 3,4-CH_3C_6H_3$	VIII	$R = 3,4-CH_3C_6H_3$
IV	$R = C_2H_4$		
V	$R = 1,2-C_3H_6$		

Scheme 1.

inotoluene were purified by single recrystallisation from ethanol in the presence of decolorising charcoal. The diamines *viz*, 1,2-diaminoethane (Qualigens), 1,2-diaminopropane (Fluka), 1,2-diaminobenzene (Fluka), 3,4-diaminotoluene (Fluka), 1,3-diaminobenzene (Aldrich) and metal salts ($NiCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$) were used in the present study.

Synthesis of complexes

A 250-cm^3 Erlenmeyer flask was charged with spin bar, metal chloride (0.0097 mol), diamine (0.0194 mol), acetylacetone (0.0194 mol) added by syringe and dry butanol (30 cm^3). The mixture was brought to a brisk reflux which was continued for 8 h. On cooling, the addition of small quantity of methanol (15 cm^3) caused an oily layer to separate out. This was treated with water and stirred vigorously to obtain a solid substance which was collected by filtration, washed with hot water, cold methanol and finally dried *in vacuo*. The yield, colour and melting points together with analytical data for all complexes are given in Table 1.

Physical measurements

The elemental analyses were performed by the HERAEUS (Mikro standard 8304071) carbon and hydrogen analyzer. The IR spectra were recorded in the range 4000–400 cm^{-1} with Perkin-Elmer 983 G Spectrophotometer. The absorbance measurements in DMF and toluene were carried out on a Schimadzu UV-160A spectrophotometer using 10-mm quartz cells. Conductance measurements of $\simeq 10^{-3}$ M solutions were made using the solvent DMF and a Systronic 303 direct reading conductivity cell. ESR spectra were obtained using a Varian E-112 X-band spectrophotometer at room temperature and liquid nitrogen temperature (LNT) in DMF. The ^{1}H-NMR spectra were obtained using a JEOL, GSX-400 NMR instrument at room temperature. The cyclic voltammetry was performed with BAS model CV-27 controller and a conventional three electrode configuration with glassy carbon working electrode, silver/silver chloride reference electrode and platinum counter electrode. Nitrogen was used as a purge gas and all solutions were of 0.1 M concentration in $TBAClO_4$.

RESULTS AND DISCUSSION

Attempts to isolate the free ligands using acetylacetone and different diamines that are used in the present study were unsuccessful. The ability of certain transition metals, especially nickel(II), to promote intramolecular Schiff base reaction into macrocyclic formation is well known. Hence the corresponding macrocyclic metal complexes were prepared using the template synthesis. All the complexes are insoluble in water but readily soluble in methanol, ethanol, DMF and dimethylsulphoxide (DMSO). The analytical and physico-chemical data for all the complexes are given in Table 1. The analytical data are consistent with the proposed molecular formulae and given in Table 1. The molar conductivity measurements show their non-electrolytic nature and molecular weights of the nickel and copper complexes showed that they are monomeric.

Electronic spectra

Both nickel(II) and copper(II) complexes are soluble in DMF. While nickel complexes are soluble in toluene, the corresponding copper complexes are insoluble in this solvent.

In the electronic spectrum of nickel tatraaza macro-

Table 1. Analytical data of complexes

Complex	Colour	Yield (%)	M.p. (°C)	Percentage of Carbon found (calc.)	Percentage of Hydrogen found (Calc.)
I [Ni($C_{22}H_{22}N_4$)]	Dark green	75	239–241	65.8 (65.9)	5.5 (5.5)
II [Ni($C_{22}H_{22}N_4$)]	Black	65	> 300	65.7 (65.9)	5.4 (5.5)
III [Ni($C_{24}H_{26}N_4$)]	Dark green	65	168–170	67.1 (67.2)	6.1 (6.0)
IV [Ni($C_{14}H_{22}N_4$)]	Red	85	196–198	55.2 (55.1)	7.1 (7.2)
V [Ni($C_{16}H_{26}N_4$)]	Red	80	190–192	57.6 (57.7)	7.8 (7.8)
VI [Cu($C_{22}H_{22}N_4$)]	Dark brown	65	220 D	65.0 (65.1)	5.4 (5.4)
VII [Cu($C_{22}H_{22}N_4$)]	Dark brown	50	> 300	65.1 (65.0)	5.3 (5.4)
VIII [Cu($C_{24}H_{26}N_4$)]	Dark brown	62	190–192	66.4 (66.4)	6.0 (5.9)

cyclic complexes in DMF, three bands are observed at *ca* 9970–11,074 cm^{-1} (ν_1), 15,528–17,483 cm^{-1} (ν_2) and 24,096–28,249 cm^{-1} (ν_3) assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions [6], respectively. The ratio of $\nu_2 : \nu_1$ lies in between 1.40–1.75 as required for an octahedral Ni^{II} complex. The ligand field parameters, field splitting energy (10 Dq), Racah inter-electronic repulsion parameter β, covalent factor and ligand field stabilization energy (LFSE) have been calculated and presented in Table 2. The β and β^0 values have been calculated for nickel complexes following standard equations [7,8]. The value of the Racah inter-electronic repulsion parameter (β) for these complexes is less than the value of the free ion. This is due to decreased inter-electronic repulsion resulting from electron delocalization thereby suggesting the considerable covalent character of the bond [6]. The electronic spectral data (in DMF) suggest an octahedral geometry for these nickel complexes. DMF is a known coordinating solvent and presumably coordinates nickel in the axial positions to complete the octahedral structure.

The electronic spectra of the nickel complexes were also recorded in toluene and two bands were observed at 20,095–24,125 cm^{-1} (ν_2) and 27,026–31,546 cm^{-1} (ν_3). All of these complexes do not show any significant absorption bands in the energy range less than 15,000 cm^{-1}. Hence the spectral behaviour in toluene is in agreement with the square-planar coordination of nickel.

The electronic spectra of copper complexes are recorded in DMF, covering in the range of 50,000–25,000 cm^{-1} area. The spectral features are analogous to one another. The absorption bands observed above 20,000

Table 2. Electronic spectral data and ligand field parameters of nickel complexes

Complex	Method of evaluation	ν_1	ν_2	ν_3	β	β_{35}^{b}	$\delta\nu^{a}$	10 Dq	$\nu_2-\nu_1$	ν_2/ν_1	β^0
I	Observed	10,026	17,153	25,445	—	—	—	10,026	7127	1.71	
	Calculated	10 Dq	16,546	26,052	835	0.79	607	10,026	6520	1.65	21.0
II	Observed	9970	17,483	24,096	—	—	—	9970	7513	1.75	
	Calculated	10 Dq	15,715	25,863	778	0.74	1767	9970	5745	1.58	26.4
III	Observed	11,050	16,892	25,381	—	—	—	11,050	5842	1.53	
	Calculated	10 Dq	17,000	25,273	608	0.58	−107	11,050	5949	1.54	42.5
IV	Observed	11,074	15,528	28,249	—	—	—	11,074	4454	1.40	
	Calculated	10 Dq	17,381	26,393	703	0.67	−1852	11,074	6307	1.57	33.5
V	Observed	10,953	15,848	26,882	—	—	—	10,953	4895	1.45	
	Calculated	10 Dq	17,049	25,681	658	0.62	−1201	10,953	6096	1.56	37.7

[a] Difference in the observed and calculated value of frequencies.

[b] Ratio of the free ion and of the complex.

cm^{-1} are due to $\pi \rightarrow \pi^*$ (or) charge transfer transitions. However, the low intensity bands in the range 16,000–20,000 cm^{-1} are observed. These bands are assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition [9,10] suggesting the presence of square-planar geometry.

IR spectra

In the IR spectra of the complexes, strong bands appearing in the range 1610–1585 cm^{-1} are assigned [11–14] to the coordinated and conjugated νC=N group present in all the complexes. The bands characteristic of the acetylacetone moiety are present in all the complexes. This contention is supported by the presence of bands in 1400–1430 cm^{-1} and 1353–1380 cm^{-1} regions respectively assigned to ν_{asy}(C—CH$_3$) and ν_{sym}(C—CH$_3$). The absence of bands at 1525 [ν(C–O) stretching] and 1280 cm^{-1} [δ(C–O) bending] suggest the disappearance of the C—O moiety in all the complexes [15]. In the spectra of all the complexes, bands are observed in the region 440–485 cm^{-1} assigned to ν(Co–N) vibration which substantiate the participation of the conjugated nitrogen in the complexation.

ESR spectra

The ESR spectra of the complexes **VI**, **VII**, and **VIII** are recorded in DMF at liquid nitrogen temperature. A typical ESR spectrum of complex **VI** is given in Fig. 1. The spin Hamiltonian orbital reduction and bonding parameters of these complexes are given in Table 3. The $g_\parallel$ and $g_\perp$ are computed from the spectrum using the TCNE free radical as g marker. Kivelson and Neiman [16] have reported that the $g_\parallel$ value is less than 2.3 for the covalent character of the metal ligand bond and greater than 2.3 for the ionic character. Applying this criterion, the covalent character of metal–ligand bond in **VI** and **VII** complexes can be inferred. For complex **VIII** the $g_\parallel$ value is slightly higher than 2.3, suggesting the presence of a small amount of ionic character. The trend $g_\parallel > g_\perp > g_e$ (2.0023) observed for these complexes suggests that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital [17] of the copper(II) ion. The G value (>4) for all the complexes may support the idea that these have elongated axial symmetry. The ESR parameters $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ of complexes and the energies of *d-d* transitions are used [16–22] to calculate the orbital reduction parameters ($K_\parallel, K_\perp$), the bonding parameters (α^2), the dipolar interaction term (P) and Fermi contact interaction term (K), are incorporated in Table 3. The observed $K_\parallel > K_\perp$ relation indicates the absence of significant in-plane π-bonding. The α^2 values for these complexes suggest the presence of covalent bonding in them. Giordano and Bereman [23] suggest the identification of bonding groups from the values of dipolar term, P. The reduction of P values from the free ion value (0.036 cm^{-1}) might be attributable to the strong covalent bonding. The lower P and α^2 values for **VII** and **VIII** complexes suggest the presence of stronger in-plane π-bonding. The dimensionless quantity K which is found to have a value of $\simeq 0.30$ compares well with those calculated for other copper complexes [24,25]. ESR spectral data [26] suggest square-planar for all the copper complexes.

NMR spectra

The ^{1}H-NMR spectra of complexes **I**–**V** in CDCl$_3$ were recorded with a JEOL, GSX-400 NMR instrument. ^{1}H-NMR signals, assignment (number) and shift in ppm (multiplicity) for complexes **I**–**V** are as follows: (**I**) phenyl (8H) 6.69–6.56 (d), methine (2H) 4.85 (s), methyl (12H) 2.34 (d); (**II**) phenyl (8H) 6.33–6.91 (m), methine (2H) 5.1 (s); methyl (12H) 2.02–2.85 (m); (**III**) phenyl (6H) 6.36–6.99 (m); methine 4.52 (d), methyl (12H) 2.05–2.52 (m); Ar-CH$_3$ (6H) 2.58 and 2.90 (m); (**IV**) methylene (8H) 3.01 (s), methine (2H) 4.89 (s); methyl (12H) 1.86 (s); (**V**) methylene (4H) 2.62 (d), methine (2H) 3.07 (q), methine (2H) 4.87 (d), methyl (12H), 1.85 (m), R-CH$_3$ (6H) 1.31 (d) and 1.88 (d). Hence the ^{1}H-NMR spectra of the complexes (**I**–**V**) are consistent with the proposed structures.

Isomers are possible for complexes **III** and **V**. The chemical shift values for **III** at 2.58 and 2.90 correspond to methyl groups on phenylenediiminato moieties of the macrocycle. The symmetrical peak position of methyl groups indicates the *trans*-configuration of the ring system. Chemical shift values for complex **V** at 1.30 and 1.88 which corresponds to two methyl groups of propane diiminato moiety are well separated from each other. This observation suggests that two methyl groups may be in the *cis*-configuration of the ring system.

Electrochemical studies

Cyclic voltammograms for the nickel and copper complexes were recorded in DMF in tetrabutylammonium perchlorate supporting electrolyte *vs* Ag/AgCl reference electrode. The CV data of all complexes are given in Table 4. Cyclic voltammograms of **III** and **VI** complexes are presented in Fig. 2.

The CV of **I** and **III** complexes of nickel shows two reversible reduction waves, one at the $E_{1/2}$ of -0.47 V, -0.42 V and another at the $E_{1/2}$ of -1.12 V and -1.15 V respectively. These two (**I** and **III**) complexes also have quasi-reversible reduction waves at the $E_{pc} = -1.1$ V. Complex **III** is reduced at more negative potential in comparison with complex **I**. This is due to the presence of an electron donating group (—CH$_3$) on the macrocyclic ligand of complex **III** [25]. The CV of complex **II** shows a irreversible reduction wave at the $E_{pc} = -0.88$ V. The CV of complex **IV** shows two reversible reduction waves at

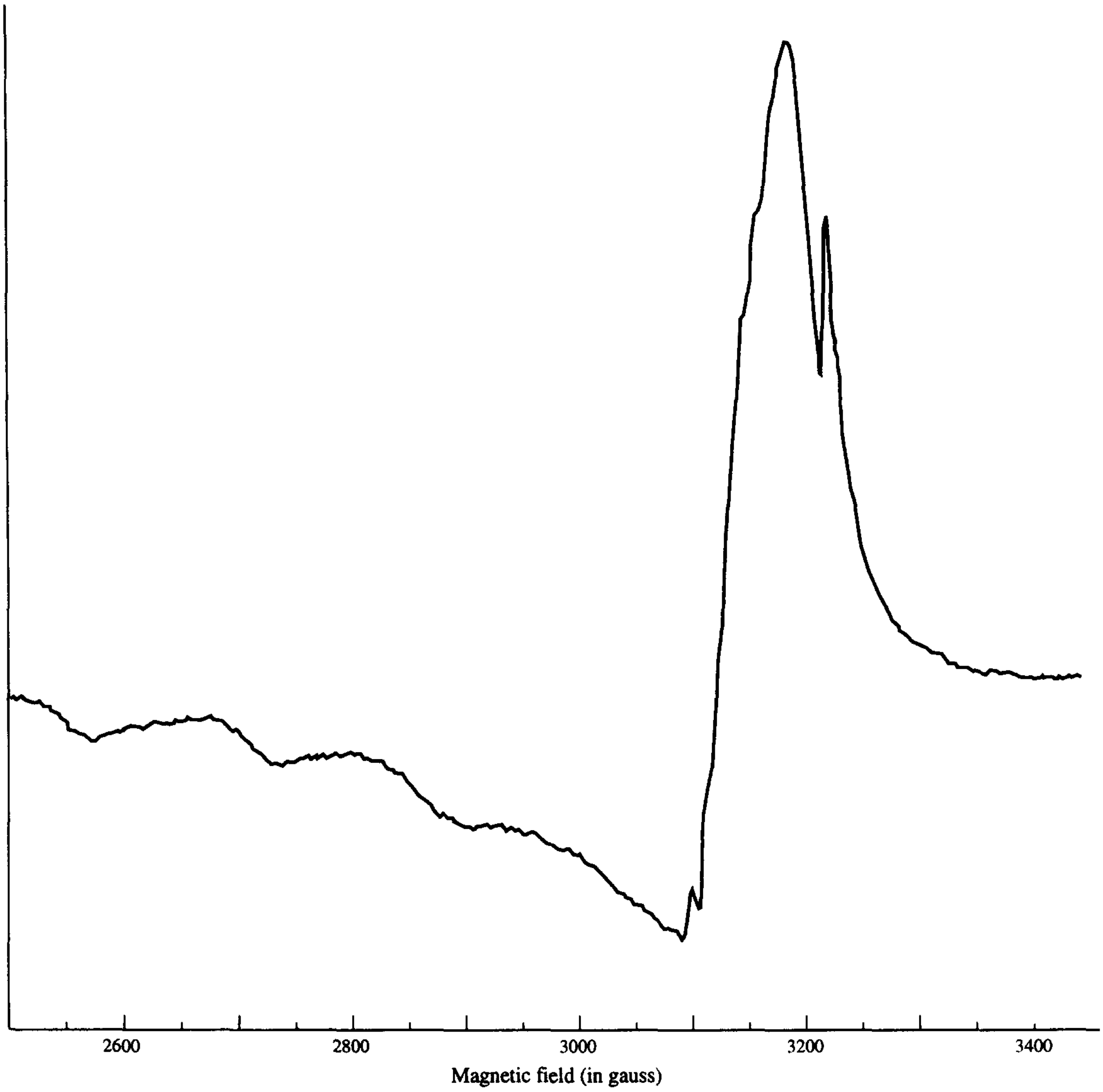

Fig. 1. ESR spectrum of complex **VI** in DMF at liquid nitrogen temperature (LNT).

Table 3. Spin Hamiltonian and orbital reduction parameters of copper complexes

Parameter	[Cu($C_{22}H_{22}N_4$)] VI	[Cu($C_{22}H_{22}N_4$)] VII	[Cu($C_{24}H_{26}N_4$)] VIII
$g_\parallel$	2.301	2.219	2.327
$g_\perp$	2.061	2.053	2.071
g_{av}	2.141	2.108	2.156
G	5.09	4.27	4.73
$A_\parallel$	0.016	0.0122	0.0121
$A_\perp$	0.003	0.002	0.003
A_{av}	0.0073	0.0054	0.006
$K_\parallel$	0.946	0.805	0.825
$K_\perp$	0.837	0.779	0.694
α^2	0.702	0.508	0.425
P	0.0224	0.0155	0.0162
K	0.347	0.243	0.246

Table 4. Cyclic voltammetric data of nickel and copper complexes (10^{-3} M) in DMF containing 0.1 M $TBAClO_4$ at 1.0 V/s at glassy carbon electrode, Temp. 26°C

Complex	Gain	E_{pc} (V)	E_{pa} (V)	$E_{1/2}$	E (mV)
I	0.01	−0.62	−0.31	−0.47	310
		−1.13	−1.10	−1.12	30
	0.02	−0.60	−0.33	−0.47	270
		−1.13	−1.1	−1.12	30
II	0.01	−0.88	—	—	—
	0.02	−0.80	—	—	—
III	0.02 &	−0.50	−0.33	−0.42	170
	0.05	−1.19	−1.10	−1.15	90
IV	0.01	−0.64	−0.04	−0.34	600
	0.02	−0.60	−0.33	−0.47	270
V	0.02 &	−0.80	−0.62	−0.71	180
	0.05				
VI	0.02 &	+0.41	+0.55	+0.48	140
	0.05	−1.25	—	—	—
VII	0.10 &	+0.41	+0.56	+0.48	150
	0.20	−1.25	—	—	—
VIII	0.02 &	+0.42	+0.53	+0.48	110
	0.05	−1.21	—	—	—

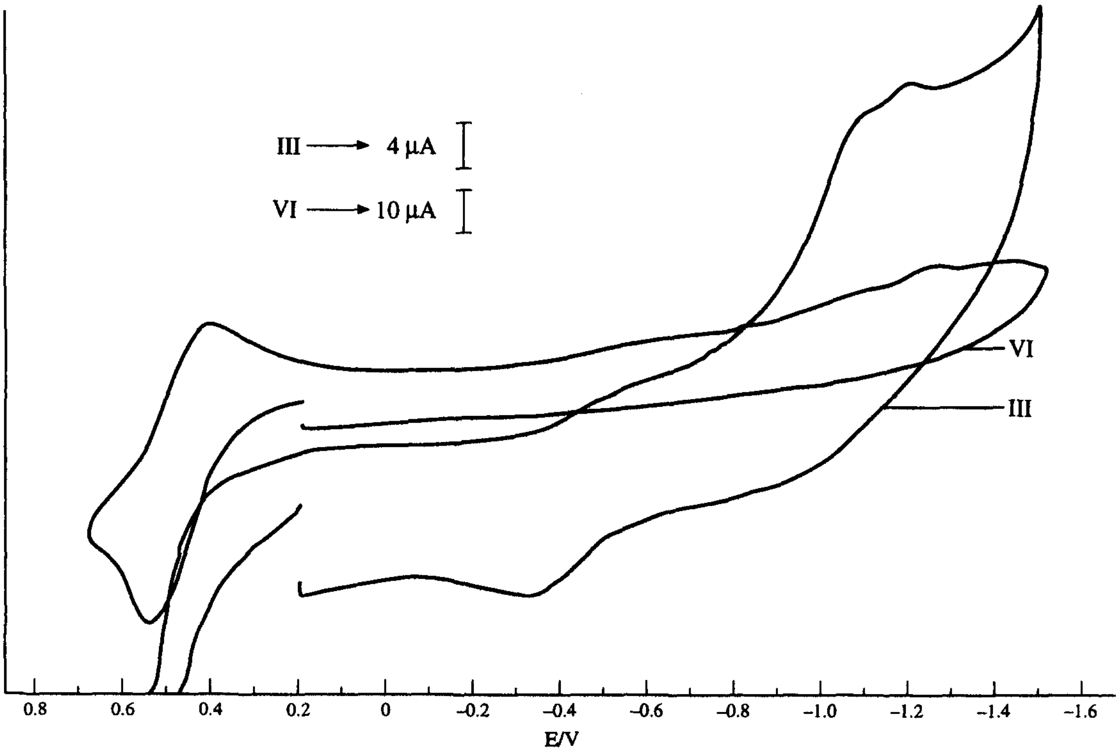

Fig. 2. Cyclic voltammograms for complexes **III** and **VI** in DMF (0.001 M, 0.1 M $TBAClO_4$) GC electrode, Ag/AgCl reference electrode (scan rate, 100 mV s^{-1}).

the $E_{1/2} = -0.34$ V and -0.47 V. The complex **V** has a reversible reduction at the $E_{1/2} = -0.71$ V. It also suggests an irreversible reduction wave at $E_{pc} = -1.35$ V. The complex **V** also reduced at more negative potentials in comparison with complex **IV**. It appears that the electron donating group present in complex **V** may help to stabilize nickel(II) complex [25].

The CV of copper tetraaza macrocyclic complexes of **VI**, **VII** and **VIII** show a single reversible reduction wave at the $E_{1/2} = +0.48$ V. The reversible couple is assigned to the $Cu^{2+} \rightleftharpoons Cu^{+}$ couple. The Cu^{II}/Cu^{I} $E_{1/2}$ values for all the complexes studied are similar to the value reported for copper(II) laccase [26]. The half-wave potential shows a systematic variation in their values with size. These three complexes also suggest an irreversible reduction wave at $E_{pc} = -1.25$ V.

The results presented above suggest that although macrocyclic copper complexes prefer to have a square-planar structure, the corresponding nickel complexes essentially have an octahedral structure in the presence of a coordinating solvent. Thus, there is a discernible difference in the ligation properties of nickel and copper complexes as evidenced by their electronic spectral data.

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