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Electronic, cyclic voltammetry, IR and EPR spectral studies of copper(II) complexes with 12-membered N₄, N₂O₂ and N₂S₂ donor macrocyclic ligands

Sulekh Chandra*, Rajiv Kumar

Department of Chemistry, Zakir Husain College, University of Delhi, J. L. Nehru Marg, New Delhi 110002, India

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Abstract

A new series of copper(II) complexes have been synthesized with macrocyclic ligands having three different donating atoms in the macrocyclic ring. It has been shown that the stereochemistry of complexes is dependent on the coordinated anions. These complexes are characterized by various physicochemical techniques, viz. elemental analysis, molar conductance, magnetic susceptibility measurements, IR, electronic, ¹H NMR and EPR spectral studies. Cyclic voltammetric behavior of the complexes has also been discussed. The observed anisotropic *g*-values indicate that the chloro and acetato complexes are six-coordinate tetragonal. Whereas the sulfato and nitrato complexes are found to have five-coordinate square-pyramidal and four-coordinate square-planar geometry, respectively. © 2004 Elsevier B.V. All rights reserved.

Keywords: Macrocyclic ligand; Copper(II); Electronic; IR; EPR; Cyclic voltammetry

1. Introduction

Nature prefers macrocyclic derivatives for many fundamental biological functions such as photosynthesis and transport of oxygen in mammalian and other respiratory systems [1]. Hence the synthesis and studies of model systems are important which show important properties such as thermodynamic, kinetic stability [2], electron transfer and magnetic interaction between metal centers [3]. These are effected by the ring size, coordination sites and electronic effect [4] at aromatic ring of the ligand system. Since the late 1980s, the study of copper(II) complexes has attracted considerable attention due to relevance of copper(II) in biological systems [5]. There have been several attempts to model the active center of biological molecules that includes copper atom on their structure such as haemocyanin or other biological proteins [6]. In view of the above applications, it is highly desirable to synthesize and characterize the copper(II) complexes with such ligands. In this paper we report the synthesis and characterization of copper(II)

* Corresponding author.

E-mail addresses: schandra_00@yahoo.com (S. Chandra), chemistry_rajiv@hotmail.com (R. Kumar).

complexes with N_4 , N_2O_2 and N_2S_2 donor 12-membered macrocyclic ligands.

2. Experimental

All the chemicals used were of AnalaR grade, and procured from Fluka and Sigma Aldrich. Metal salts were purchased from E. Merk and used as received. All solvents were used of spectroscopic grade.

3. Synthesis of diamines

1,2-Di(*o*-aminophenoxy)ethane (Fig. 1a), 1,2-di(*o*-aminophenylamino)ethane (Fig. 1b) and 1,2-di(*o*-aminophenylthio)ethane (Fig. 1c) were prepared and characterized by the procedure as reported earlier [7]. All these diamine are used for the preparation of macrocyclic ligands.

3.1. Characterization of diamines

1,2-Di(*o*-aminophenoxy)ethane, mp 130–132 °C. ¹H NMR (CDCl₃) δ 7.0 (2H, d), δ 6.6 (2H, m), δ 6.3 (2H, d), (2H, m), δ 4.0 (4H, O–CH₂). 1,2-Di(*o*-aminophenylamino)



Fig. 1. Structure of diamines.

ethane, mp 135–136 °C. ¹H NMR (CDCl₃) δ 7.1 (2H, m), δ 6.7 (2H, d), δ 6.6 (2H, m), δ 6.3 (2H, d), δ 3.0 (4H, NH–CH₂). 1,2-Di(*o*-aminophenylthio)ethane, mp 75 °C. ¹H NMR (CDCl₃) δ 7.2 (2H, d), δ 7.1 (2H, m), δ 6.6 (2H, m), δ 6.3 (2H, d), δ 2.8 (4H, S–CH₂).

3.2. Preparation of macrocyclic ligands

2,3-Diphenyl-1,4-diaza-7,10-dioxo-5,6:11,12-dibenzo[e, k]-cyclododeca-1,3-diene[N₂O₂]ane (L₁) (Fig. 2a), 2,3-diphenyl-1,4,7,10-tetraaza-5,6:11,12-dibenzo[e,k]-cyclododeca-1,3-diene[N₄] ane (L₂) (Fig. 2b) and 2,3-diphenyl-1,4-diazo-7,10-dithia-5,6:11,12-dibenzo[e,k]-cyclododeca-1,3-

diene[N_2S_2]ane [L_3] (Fig. 2c) containing aromatic head, and lateral units macrocyclic ligands were prepared by the procedure as reported earlier [7].

To an ethanolic solution (25 ml) of benzil (0.005 mol, 1.05 g) an EtOH solution of (25 ml) of 1,2-di(*o*-aminophenoxy)ethane or 1,2-di(*o*-aminophenylamino)ethane or 1,2di(*o*-amino phenyl thio)ethane (0.005 mol) was added in presence of few drops \sim 1 ml of conc. HCl. The resulting solution was refluxed for 5–7 h. The resulting solution was concentrated to half of its volume under reduced pressure and kept overnight. The white/white off crystals formed, which were filtered, washed with EtOH and dried under vacuum over P₄O₁₀.



Fig. 2. Structure of macrocyclic ligands.

3.3. Characterization of macrocyclic ligands

These ligands are characterized on the basis of elemental analysis, ¹H NMR and infrared spectra.

- Yield 71%, mp 172 °C. Found: C, 80.0; H, 5.0; N, 6.2. C₂₈H₂₂N₂O₂ calculated: C, 80.4; H, 5.3; N, 6.7%. ¹H NMR: δ 7.2–7.3 (10H, m), δ 7.1 (2H, m), δ 7.0 (2H, d), δ 6.9 (2H, d), δ 6.6 (2H, m), δ 4.0 (4H, O–CH₂) for ligand L₁.
- Yield 67%, mp 179 °C. Found: C, 80.1; H, 5.3; N, 13.1. C₂₈H₂₄N₄ calculated: C, 80.7; H, 5.8; N, 13.4%. ¹H NMR: δ 7.2–7.4 (10H, m), δ 7.1 (2H, m), δ 6.9 (2H, d), δ 6.7 (2H, d), δ 6.6 (2H, m), 3.0 (4H, NH–CH₂) for ligand 2.
- Yield 70%, mp 182 °C. Found: C, 74; H, 4.3; N, 6.0. C₂₈H₂₂N₂S₂ calculated: C, 76.6; H, 4.9; N, 6.2%. ¹H NMR: δ 7.2–7.24 (10H, m), δ 7.27(2H, d), δ 7.1 (2H, m), δ 6.9 (2H, d), δ 6.6 (2H, m), δ 4.0 (4H, m, S–CH₂) for ligand 3.

3.4. Preparation of the complexes

A hot EtOH, solution (25 ml) of the corresponding hydrated copper(II) salt $CuX_2 \cdot nH_2O$, 0.005 mol (where $X = Cl^-$, CH_3COO^- , NO_3^- and $(1/2)SO_4^{2-}$) was added to a hot EtOH solution (25 ml) of the corresponding ligand (0.005 mol). The mixture was refluxed on water bath at 80 °C for 5–7 h. On cooling, a colored precipitate was formed. It was filtered, washed with EtOH and dried over P_4O_{10} under vacuum.

4. Physical measurements

Magnetic susceptibility measurements were carried out a CAHN 2000 Faraday balance using Hg[Co(CNS)₄] $(\chi_g = 16.44 \times 10^{-6} \, g \, cm^{-3}$ at 28 °C) as the calibrant. Molar conductance measurements were carried out on a

Table 1				
Analytical	data	of	copper(II)	complexes

Leeds Northrup Conductivity Bridge 4995. IR spectra were recorded on a Perkin Elmer 137 instrument as KBr pellets. The electronic spectra of the complexes were recorded on a Shimadzu UV mini-1240 spectrophotometer in DMF solution. C, H and N analysis were carried out on a carl-Ebra 1106 elemental analyzer. Nitrogen contents was determined by the Kjeldahl's method. ¹H NMR spectra were recorded on a Bruker Avance 300 spectrometer at 100 kHz modulation at room temperature. EPR spectra were recorded at room temperature on a varion E-4 EPR spectrometer at \sim 9.1 GHz and 100 kHz field modulation and phase sensitive detections by using DPPH as marker. The copper content in the complexes was determined gravimetrically as CuSCN. Cyclic voltammograms of the copper(II) complexes in MeCN at 300 K were recorded by using a BAS electrochemical analyses. The electrolyte cell contains a reference Ag/AgCl electrode, Pt wire as auxiliary electrode. Unless otherwise stated all potentials were referred to Ag/AgCl.

5. Results and discussion

All the complexes are found to have the composition $CuLX_2 \cdot nH_2O$ (where L = Ligand L₁, L₂, or L₃, and X = Cl^- , CH_3COO^- , NO_3^- and $(1/2)SO_4^{2-}$). Chloro, acetato and sulfato complexes of Cu(II) show molar conductances in the range of $0-20 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (Table 1) corresponding to non-electrolytes whereas, the nitrato complexes were found to be 1:2 electrolytes. Therefore, these complexes may be formulated as [Cu(L)X₂], [Cu(L)SO₄] and [Cu(L)](NO₃)₂, respectively.

6. IR spectra

There is no absorption bands at 3380–3400 and 1640–1720 $\rm cm^{-1}$ in the IR spectra of the ligands show the absence of free amino (–NH₂) and kenotic (>C=O) group. This indicates that complete condensation takes

Complexes	Yield	mp (°C)	Molar conductance $(\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1})$	Color	Elemental analysis calculated (found) (%)				
	(%)				Cu	С	Н	N	
[Cu(L ₁)(CH ₃ COO) ₂], CuC ₃₂ H ₂₈ N ₂ O ₆	40	210	7.00	Dark blue	10.58 (10.25)	64.05 (63.75)	4.70 (4.35)	4.67 (4.52)	
$[Cu(L_1)(CI_2)], CuC_{28}H_{22}N_2O_2Cl_2$	42	235	13.00	Blue	11.50 (11.26)	60.82 (60.61)	4.00 (3.75)	5.06 (4.82)	
$[Cu(L_1)](NO_3)_2, CuC_{28}H_{22}N_4O_8$	47	217	205	Blue	10.49 (10.21)	55.50 (55.21)	3.65 (3.26)	9.25 (8.72)	
$[Cu(L_1)SO_4], CuC_{28}H_{22}N_2O_6S$	50	219	19	Light blue	10.99 (10.71)	58.18 (57.71)	3.84 (3.51)	4.85 (4.35)	
[Cu(L ₂)(CH ₃ COO) ₂], CuC ₃₂ H ₃₀ N ₄ O ₄	55	235	6.00	Green	10.62 (10.52)	64.26 (63.99)	5.05 (4.91)	9.37 (9.17)	
$[Cu(L_2)(Cl_2)], CuC_{28}H_{24}N_4Cl_2$	58	238	8.00	Dark green	11.53 (11.21)	61.04 (60.96)	4.39 (4.21)	10.17 (9.88)	
$[Cu(L_2)](NO_3)_2, CuC_{28}H_{24}N_6O_6$	61	240	210	Light green	10.52 (10.26)	55.68 (55.28)	4.00 (3.72)	13.91(12.96)	
$[Cu(L_2)(SO_4)], CuC_{28}H_{24}N_4O_4S$	63	221	11.0	Green	11.03 (10.90)	58.38 (57.91)	4.20 (4.01)	9.73 (9.62)	
[Cu(L ₃)(CH ₃ COO) ₂], CuC ₃₂ H ₂₈ N ₂ S ₂ O ₄	52	240	17	Shiny blue	10.05 (9.75)	60.79 (60.61)	4.46 (4.11)	4.43(4.10)	
$[Cu(L_3)(Cl_2)], CuC_{28}H_{22}N_2S_2Cl_2$	57	219	11	Light blue	10.86 (10.62)	57.48 (57.40)	3.78 (3.52)	4.80 (4.53)	
[Cu(L ₃)](NO ₃) ₂ , CuC ₂₈ H ₂₂ N ₄ S ₂ O ₆	68	241	215	Sky blue	9.95 (9.82)	52.71 (52.30)	3.47 (31.16)	8.78 (8.52)	
$[Cu(L_3)(SO_4], CuC_{28}H_{22}N_2S_3O_{4a}]$	61	250	16	Blue	10.41 (10.32)	55.12 (54.91)	3.63 (3.22)	4.60 (4.31)	

place between the NH₂ and >C=O In the IR spectrum of (L₂) a sharp band is appeared at 3320 cm^{-1} corresponding to ν (NH) group. New characteristic band due to (>C=N) in the ligands are appeared at 1627 (L₁), 1628 (L₂) and 1607 cm⁻¹ (L₃). The position of this band is shifted to lower frequency in the complexes as compared to free macrocyclic ligands, suggesting that the coordination takes place through the nitrogen of ν (C=N) group [8].

6.1. Bands due to anions

IR spectra of nitrato complexes show sharp absorption bands at 1382 (L₁), 1380 (L₂) and 1384 cm⁻¹ (L₃) corresponding to free nitrate group [9]. The sulfato complexes show bands at 1180–1120 (ν_3) and 760–690 cm⁻¹ (ν_4) corresponding to unidentate nature [10]. Acetato complexes exhibit bands at 1565–1557 (ν_1) and 1410–1420 cm⁻¹ (ν_2). This indicates unidentate nature of acetate group [11].

7. Magnetic moments

All the complexes show magnetic moments in the range of 1.90–2.00 B.M. indicating monomeric nature of the complexes.

8. Electronic spectra

Electronic spectra of six coordinate copper(II) complexes have either D_{4h} or C_{4v} symmetry, and the e_g and t_{2g} level of the ²D free ion term will split in to B_{1g} , A_{1g} , B_{2g} and E_g level, respectively Thus the three spin allowed transitions are expected in the visible and IR region. But only few complexes are known in which such bands are resolved either by Gaussian analysis or single crystal polarization studies. These bands may be assigned to following transitions: ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g} (d_{x^2-y^2} \rightarrow d_{z^2}), {}^{2}B_{1g} \rightarrow {}^{2}B_{2g} (d_{x^2-y^2} \rightarrow d_{xy})$ and ${}^{2}B_{1g} \rightarrow {}^{2}E_g (d_{x^2-y^2} \rightarrow d_{xz}d_{yz})$ in order of increasing energy. The energy level sequence will depend on the amount of distortion due to ligand field and Jahn–Teller effect [12].

8.1. Acetato and chloro copper(II) complexes

All the complexes show two characteristic bands in range of 13,899–15,600 and 16,722–18,860 cm⁻¹. These may be assigned to ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ and ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ transitions, respectively [13] according to tetragonal geometry.

8.2. Nitrato complexes

Nitrato complexes of all ligands display three electronic spectral bands in the range of 15,600-16,920, 18,832-18,867 and 31,526-33,783 cm⁻¹ indicating four-coordinated square-planar geometry [13] (Fig. 3).

8.3. Sulfato complexes

Sulfato complexes all ligands show electronic bands at 8500 and 10,100 cm⁻¹ corresponding to five-coordinate square-pyramidal geometry.

9. EPR spectra

The EPR spectrum of copper(II) complexes provides information about hyperfine and super hyperfine structures. It is very important to understand the metal ion environment in the complexes, i.e. the geometry, nature of the donating atoms from the ligands and degree of covalency of the copper(II)–ligands bonds.

9.1. Chloro and acetato complexes

All the complexes show anisotropic EPR spectra (Figs. 4–7) characteristic to a tetragonal geometry for copper(II) complexes.

g-Tensor values have been calculated by Kneiibuhl's method and results are presented in Table 2.

g-Tensor values of copper(II) complexes can be used to derive the ground state. In an elongated octahedron the 3d unpaired electrons for copper(II) ions lies in $d_{x^2-y^2}$ orbital (²B₁ as ground state). The *g*-values were given by $g_{\parallel} = 2(1 - 4\lambda/\Delta_1)$ and $g_{\perp} = 2(1 - \lambda/\Delta_2)$. In a compressed octahedron, on the other hand, the 3d unpaired electron lies in the d_{z^2} orbital (²A_{1g} ground state). The *g*-values were given by $g_{\parallel} = 2$ and $g_{\perp} = 2(1 - 3\lambda/\Delta_3)$ where Δ_1 , Δ_2 and Δ_3

Table 2 Ligand field (cm^{-1}) parameters of acetate and chloro copper(II) complexes

Complex	g_{\parallel}	g_{\perp}	$g_{ m iso}$	A_{\parallel}	A_{\perp}	$A_{\rm iso}$	G	α^2	β^2
[Cu(L ₁)(CH ₃ COO) ₂]	2.21	2.08	2.12	175	76	109	2.6	0.79	0.91
$[Cu(L_1)(CI_2)]$	2.20	2.06	2.10	177	74	108	3.3	0.80	0.90
$[Cu(L_2)(CH_3COO)_2]$	2.19	2.05	2.09	170	68	102	3.8	0.69	0.96
$[Cu(L_2)(Cl_2)]$	2.11	2.06	2.09	166	67	100	3.8	0.72	0.99
$[Cu(L_3)(CH_3COO)_2]$	2.17	2.07	2.10	168	65	99.0	2.4	0.73	0.93
$[Cu(L_3)(Cl_2)]$	2.15	2.05	2.08	165	72	103	3.0	0.78	0.98



 $[Cu(ligand)(X_2)]$ Where $Z = O(L_1) S(L_3)$ and $NH(L_2)$ and $X = CI^{-}_{1} CH_3 COO^{-1}_{2}$



[Cu(ligand)SO₄] Where $Z = O(L_1) S(L_3)$ and $NH(L_2)$



 $[Cu(ligand)](NO_3)_2$ Where $Z = O(L_1) S(L_3)$ and $NH(L_4)$

Fig. 3. Suggested structure of copper(II) complexes.

are $d_{x^2-y^2} \rightarrow d_{xy}$, $d_{x^2-y^2} \rightarrow d_{xz}$, d_{yz} and $d_{x^2-y^2} \rightarrow d_{z^2}$ excitation energy, respectively, and λ is the spin orbit coupling constant [14]. From the observed *g*-values it is evident that the unpaired electron lies predominantly in $d_{x^2-y^2}$ orbital. Different EPR parameters are calculated and given in Table 2.

9.2. Nitrato complexes

The EPR spectra of $[Cu(L)](NO_3)_2$ complexes (Fig. 8) were also recorded as polycrystalline sample and in DMSO, which suggests that the complexes have square-planar geometry. Related data are listed in Table 3.

The results also indicate that the exchange couplings are not effective in nitrato complexes of all ligands [15]. Molecular orbital coefficients π bonding (β^2) and σ bonding (α^2), are calculated [16]. α^2 and β^2 values indicate that there is a substantial interaction in-plane σ bonding whereas in-plane π bonding is almost ionic.

9.3. EPR spectra of sulfato complexes

Since the IR spectra of these complexes show monodentate behavior of sulfato group, a five coordinated geometry may be assigned to these complexes. The two configurations square-pyramidal and trigonal bipyramidal are characterized by ground state $d_{x^2-y^2}$ and d_{z^2} , respectively [17]. EPR spectra of copper(II) (Fig. 9) provide a very good basis for distinguish between these two general states. For systems with $g_3 > g_2 > g_1$ the ratio of $(g_2 - g_1/g_3 - g_2)$ (here after







Fig. 5. EPR spectrum of copper(II) complexes in aqueous solution (A) $[Cu(L_1)CI_2]$, (B) $[Cu(L_1)(CH_3COO)_2]$, (C) $[Cu(L_2)CI_2]$, and (D) $[Cu(L_2)(CH_3COO)_2]$.

Table 3 EPR spectra data copper(II) nitrato complexes

Complex	81	g_{\perp}	giso	A_{\parallel}	A_{\perp}	Aiso	G	A	α^2	β^2
[Cu(L ₁)](NO) ₃	2.10	2.02	2.09	158	55	89.3	5.43	0.58	0.78	1.95
$[Cu(L_2)](NO)_3$	2.12	2.05	2.07	145	58	87.0	4.36	0.62	0.85	1.99
$[Cu(L_1)](NO)_3$	2.16	2.03	2.07	149	65	93.0	4.50	0.68	0.90	2.00



Fig. 6. EPR spectrum of copper(II) complexes in forezen solution (77 K) (A) $[Cu(L_1)CI_2]$, (B) $[Cu(L_1)(CH_3COO)_2]$, (C) $[Cu(L_2)CI_2]$, (D) $[Cu(L_2)(CH_3COO)_2]$, (E) $[Cu(L_3)CI_2]$, (F), $[Cu(L_3)(CH_3COO)_2]$. Scan mang. 150 mT, $\nu = 100$ kHz, microwave frequency 9.51–9.54.



Fig. 7. (A) EPR spectrum of $[Cu(L_1)(CH_3COO)_2]$, and (B) $[Cu(L_2) (CH_3COO)_2]$. $\nu = 9.49$ GHz.

called the parameter *R*) is a very useful for this purpose. If the ground state is d_{z^2} the value of *R* is greater than 1. On the other hand, for the ground state being predominantly $d_{x^2-y^2}$ the value of *R* is less than 1. The complexes under study show the value of *R* (Table 4) less than 1, thus indicating five-coordinate trigonal bipyramidal geometry.

10. Cyclic voltammetry

The synthesized macrocyclic ligands and their complexes have two dissimilar saturated and unsaturated N_4 , N_2O_2 and N_2S_2 macrocyclic cavity. The reduction of the metal ion was effected in the presence of unsaturated macrocyclic cavity and first its reduction start. It was observed that the change in the reduction potential was observed with change in macrocyclic chelate ring size in the presence of unsaturated macrocyclic cavity. If we compare two macrocyclic rings one of them was containing saturated ring and other has unsaturated ring then the metal ion present in the saturated macrocyclic ring is oxidized first. This may be influenced from the fact that the change in ring size did not affect the first oxidation

Table 4 EPR spectra data of copper(II) sulfato complexes

Complex	<i>g</i> ₃	<i>g</i> ₂	<i>g</i> ₁	R
$[Cu(L_1)SO_4]$	2.11	2.06	2.01	0.50
$[Cu(L_2) SO_4]$	2.18	2.13	2.06	0.58
$[Cu(L_3) SO_4]$	2.15	2.12	2.08	0.55



Fig. 8. (A) EPR spectrum of [Cu(L₁)](NO₃)₂, DMSO solution 300 K. (B) EPR spectrum of [Cu(L₂)](NO₃)₂, DMSO solution 17 K.

potential of the metal ion. This indicates that small changes in the electronic and structural co-ordination environment, affect the redox potential of the complexes.

The redox of the metal complexes was studied in the potential range +1.20 to -1.80. Cl⁻ < MeCOO⁻ complexes of L₁, L₂ and L₃ show a reversible Cu(II)/Cu(I) in the range of -1.40 to -1.475 V versus Ag/AgCl during the reverse sweep potential at -1.65 V.

This region shows oxidation waves of the complexes. Coulometric studies confirmed that each reduction is associated with a single electron transfer process. When the potential is swept below -1.65 V, an irreversible wave at -1.790 V was found and the Cu(II)/Cu(I) couple also become irreversible. This behavior, consistent with that of the copper(II) complexes of all 12-membered different donating macrocyclic complexes [18]. It is attributed to the electrochemical demetalation of the complexes.

This statement is also supported by the appearance of a Cu(II)/Cu(I) stripping wave at -0.78 V to -0.65 Ag/AgCl on the return oxidative sweep. For $[Cu(L_2)]^{2+}$, the Cu(I) redox couple is anodic ally shifted by 0.35 V and appeared at -1.10 V to 0.96 Ag/AgCl. The significantly greater case of reduction can be attributed to the more Cu–N bonds of the complexes relative to those of $[Cu(L_1)]^{2+}$ and $[Cu(L_3)]^{2+}$.

Most of the complexes have higher ($\Delta E_{\rm p} = E_{\rm pc} - E_{\rm pa}$) values. It is due to the differences between the original complex and the reduced species. After the second reduction the complexes may under go ligand replacement reaction and form new species. Due to this the oxidation peak is not related to the corresponding reduction peak of the original complexes. Hence, these reduction processes are not reversible. The same interpretation holds good for the redox process of the complexes in the anodic potential region.



Complexes $[Cu(L_2)]^{2+}$ give two distinct irreversible redox couples in the oxidative sweep. The first, at +0.94 V versus Ag/AgCl, was attributed to the oxidation involving the >NH lone pairs. The second appears at +1.18 V versus Ag/AgCl. It may be assigned to the Cu(III)/Cu(II) redox couple [19].

We are studying here three different donating atoms macrocyclic ligands. These have two unsaturated nitrogen (azomethine) as a donating group and other groups are oxygen, nitrogen and sulfur atoms. Mandal et al. [20] have reported that the first one electron reduction potential is shifted towards more cathodic waves with increase in the saturation of the azomethine linkage in macrocyclic systems. Hence, it is reasonable to believe that in the macrocyclic complex the first one electron reduction occurs at Cu(II) ion coordinated to unsaturated nitrogen atoms and second at the ion coordinated to saturated nitrogen, oxygen and sulfur atoms.

The oxidation potential of the metal center is influenced by the axial anions, e.g. Cl^- , CH_3COO^- , NO_3^- or $(1/2)SO_4^{2-}$. The axial chloro complexes are oxidized at less positive potentials than those of other anion containing complexes. This may be due to the higher basicity of the chloride than the other anion [21].

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