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Spectral Studies of Anionic Transition Metal Complexes with Tetraaza Protonated 2,15-Dihydroxy-3,7,10,14-Tetraaza Bicyclo [14.3.1] Icosane-1(20),2,7,9,14,16,18-Heptaene

S. RAJESHWARI[1], N. LAVANYA[2], R. JAYAKUMARARAJ[3], A. SELVAN[4*]

[1]*Department of Chemistry, Prist University School of Law, Arasanoor, Sivagangai*

[2]*Department of Chemistry, Latha Mathavan Engg. College, Kidaripatty, Madurai*

[3]*Department of Botany, Government Arts College, Melur – 625 106*

[4]*Department of Chemistry, Govt. Arts College for Women, Nilakottai – 624 208, India*

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ABSTRACT

Macrocycle architecture with extended supramolecular assembly can potentially be exploited for their catalytic properties as chemotherapeutic agents and complexes as sensors, PET, receptors, radioisotope. Further, fabrication of microelectronic devices using macrocycles has increased during recent times. Due to their overwhelming applications, extensive research is being carried out on macrocycles and their complexes with potential prospects for biomedical applications on commercial scale. In the present study, a new macrocyclic ligand anionic transition metal complexes with tetraaza protonated 2,15-Dihydroxy-3,7,10,14-Tetraaza bicyclo [14.3.1] Icosane-1(20),2,7,9,14,16,18-Heptaene has been analyzed for anion coordination behavior.

INTRODUCTION

Nowadays great impetus has been given to fabricating functional macrocycles for a wide array of applications. These functionalized macrocycles can be effectively be tuned for the architecture of extended supramolecular assembly suitable for optical, electronic[1], functions and potentially exploited for their catalytic properties[2]. In addition, they aid in the preparation of homo/ hetero polymetallic complexes. These complexes enable the study of magnetic interaction between homo/hetero paramagnetic centers [3-5] which facilitates the design and development of molecular materials.

Studies on macrocycles have disclosed their functional applications. Macrocyclic complexes, compared to their open chelating analogues, are kinetically and thermodynamically more stable. This enables chemists to probe many subtle aspects of reactivity of coordination compounds that would not be possible with acyclic ligands. Further, macrocycles, being cyclic in nature, are exploited for selective extraction of metals through molecular recognition.

Recently, amide based macrocycles have been reported to act as anion/cation receptors[6,7] as well as sensors[8] while their complexes are used as MRI[9] and chemotherapeutic agents[10]. Receptor based on isophthalamide receptors of Crabtree was found to be selective for both monohydrogen sulfate and dihydrogen phosphate over other oxo-anions and halides[11].

Among the a range of functional groups that can be conceived as potential anion binder, amide is an interesting class of ligand for it readily involves in hydrogen bonding. Indeed the resonance in the amide group and intermolecular hydrogen bonding between various amide groups in polypeptides dictate the protein structure that in turn leads to a specific bioactivity, especially catalysis of very many biochemical reactions with high efficiency. Researchers exploit the structural chemistry for studying the anion coordination.

Preparation:

Precursor, metal precursor complexes and metal complexes were prepared, synthesized and reported[12,13].

Preparation of protonated cyclic product [PP2cy]:

Isophthaloylchloride (299mg, 1.47mmol) was dissolved in ethanol and added to hot ethanolic solution of precursor [P2] (250mg, 1.47mmol). To this mixture, an excess of hydrochloric acid (3ml, 10N) was added and stirred for 30 minutes. Then the solution was evaporated completely over water bath to get a protonated cyclic product [$PP2_{cy}$]. The $PP2_{cy}$ (Fig.1) was washed with ether, filtered and dried in vacuum over anhydrous $CaCl_2$.

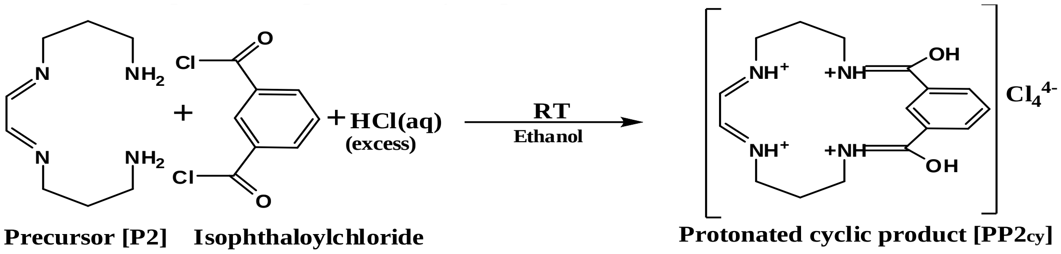

Figure No. 1: Preparation of protonated cyclic product [PP2cy]

IR spectra of precursor, metal precursor complexes, protonated cyclic product and metal complexes

IR spectrum of precursor [P2] (Fig.2) shows peak at 3349 cm^{-1}(data no.1) and 1563 cm^{-1} (data no.7) corresponding to -NH stretching and bending respectively. The imine (>C=N) peak appearing at 1634 cm^{-1} (data no.6) while C-N stretching shows a band at 1157 cm^{-1} (data no.13).

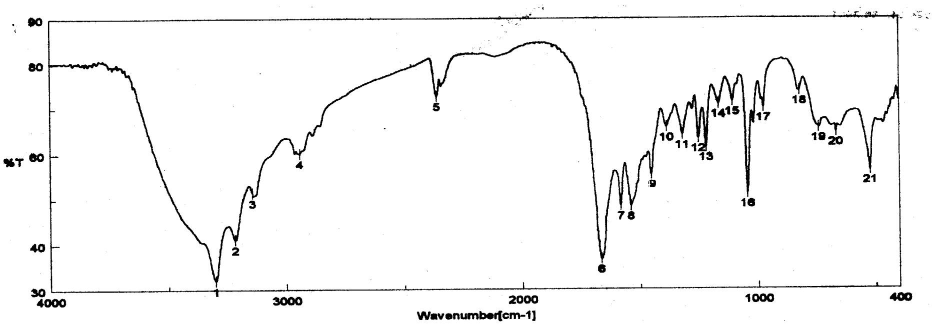

Figure No. 2: IR spectrum of precursor

From the IR spectrum of Cu precursor complex (Fig.3), it is seen that >C=N band occurs at 1641 cm^{-1} (data no.4) and NH bending occurs at 1579 cm^{-1} (data no.5). Shift of these peaks relative to that of ligand indicates that metal coordinates with both amine and imine groups.

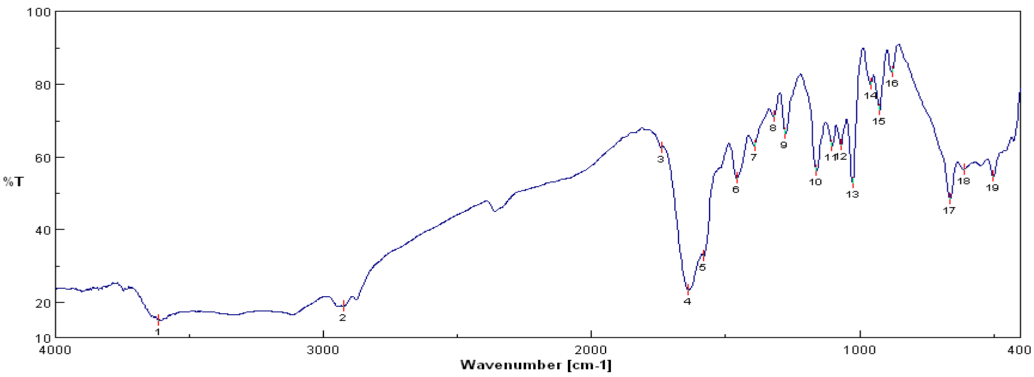

Figure No. 3: IR spectrum of Copper precursor

From the IR spectrum of Mn precursor complex (Fig.4), it is seen that >C=N band occurs at 1641 cm^{-1} (data no.3) and NH bending occurs at 1543 cm^{-1} (data no.4). Shift of these peaks relative to that of ligand indicates that metal coordinates with both amine and imine groups.

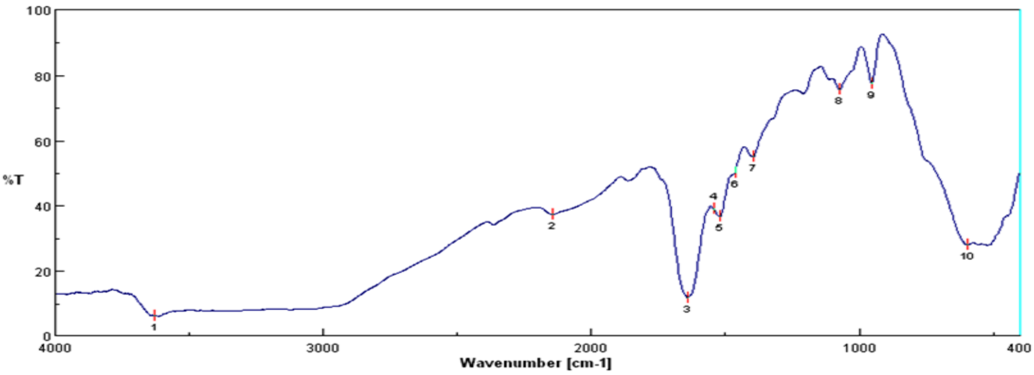

Figure No. 4: IR spectrum of Manganese precursor

The formation of imine-based protonated cyclic product and anionic metal complexes were investigated by FTIR. As shown in Fig. 5, a new peak appears[14] at about 2000 cm^{-1} in the FTIR spectra of protonated cyclic product and metal complexes, which were not observed in the FTIR spectra of precursor and metal precursor. These nice sharp deformation peaks could be assigned to the presence of NH$^+$ group in protonated cyclic product and metal complexes.

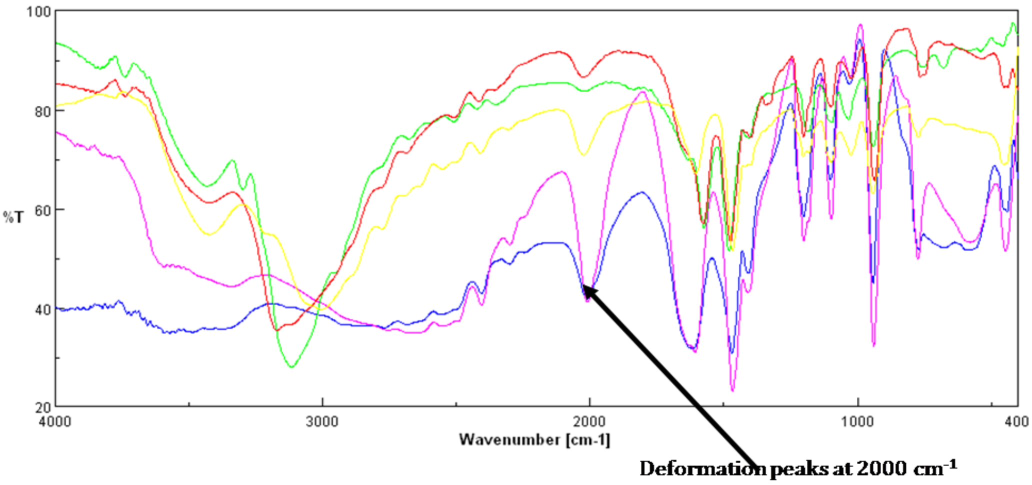

Figure No. 5: IR spectra of metal complexes (pink for protonated cyclic product, Green for Copper, Red for Zinc and Blue for Cobalt and Yellow for Nickel complexes)

In the IR spectrum of the copper complex (Fig.5 – green color), the absence of the expected strong peak for >C=O stretching of protonated amide around 1725 cm^{-1} implies that the macrocyclic cation exists in protonated iminol form. A series of bands at 2352, 2426, 2510 cm^{-1} in the region 2700 – 2250 cm^{-1} are assignable to the NH stretching of >C=N^{+}HR groups while its NH deformation is appearing at 2000 cm^{-1}. The >C=N^{+} stretching is occurring at 1635 cm^{-1}. The appearance of a new peak at 3434 cm^{-1} suggests that the complex exists predominantly in iminol form. The OH deformation peak appearing[14] at 1481 cm^{-1} in the complex also augments that macrocycle is in iminol form. Similar analysis of the IR spectra of other complexes reveals that all the complexes exist in iminol form (Fig.5, Table 1).

Table No. 1: Spectral and magnetic moment data of the complexes

Complex	**Vibrational frequency (cm^{-1})**				**Electronic Spectral Data**		**Magnetic Moment Data**
	ν_{NH}	**$\nu_{C=N}$**	**δ_{N^+H}**	**ν_{OH}**	**λ_{max} (cm^{-1})**	**ε (L mol^{-1} cm^{-1})**	
[PP2cy]	2406	1629	2009	3340	-	-	-
{(Mac.2) [$CuCl_6$]}	2426	1635	2026	3434	22573, 10941	382, 217	2.19
{(Mac.2) [$NiCl_6$]}	2410	1604	2024	3424	25253, 20704	310, 80	2.82
{(Mac.2) [$CoCl_6$]}	2405	1620	2013	3359	14663, 16340	783, 518	4.91
{(Mac.2) [$MnCl_6$]}	2418	1687	2009	3332	-	-	5.73
{(Mac.2) [$ZnCl_6$]}	2414	-	2024	3428	-	-	-

Electronic spectra of {(Mac.2) [MCl_6]} complexes

The magnetic moment for {(Mac.2) [$CuCl_6$]} is found to be 2.19 B.M. (Table 1) corresponding to one unpaired electron. The electronic spectrum of copper (II) complex (Fig. 6) shows bands at 22573 $cm^{-1}$and 10941 cm^{-1}. From the literature on electronic spectra of Cu(II) complexes (octahedral) indicate that the band at 22573 cm^{-1} in this complex may be arising due to the transition $^2B_{1g} \rightarrow {}^2E_g$ (ν_3); similarly the 10941 cm^{-1} band is attributable to the transition $^2B_{1g} \rightarrow {}^2A_{1g}$ of a tetragonally distorted octahedral Cu(II) complex.

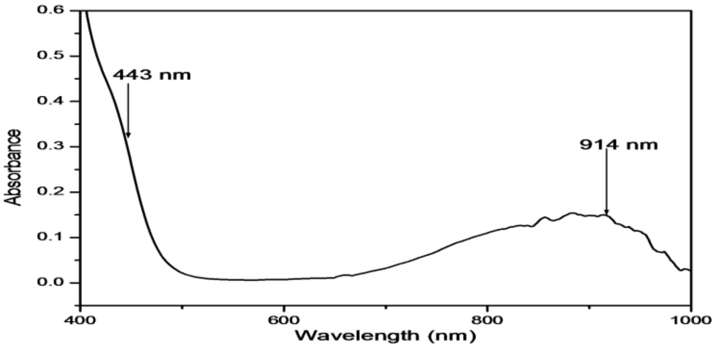

Figure No. 6: Electronic spectrum of Copper complex

Generally, cobalt (II) forms tetrahedral halide complexes. The ground state for tetrahedral cobalt (II) complex is $^4A_2$ and hence a low magnetic moment of 3.87 B.M. (Table 1) might be expected. However, in the present study, cobalt (II) complex shows magnetic moment of 4.91 B.M. (higher than spin only value) expected for octahedral cobalt (II) complex. Further, electronic spectrum of the complex (Fig. 7) display bands with lower ε values. Both the magnetic moment and electronic spectral data imply the formation of octahedral cobalt (II) halide complex which is also recently established unequivocally by a crystallographic study[15]. Hence the bands observed at 14663 cm^{-1} and 16340 cm^{-1} in the present work may be attributable to the transitions $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ of an octahedral Co(II) complex.

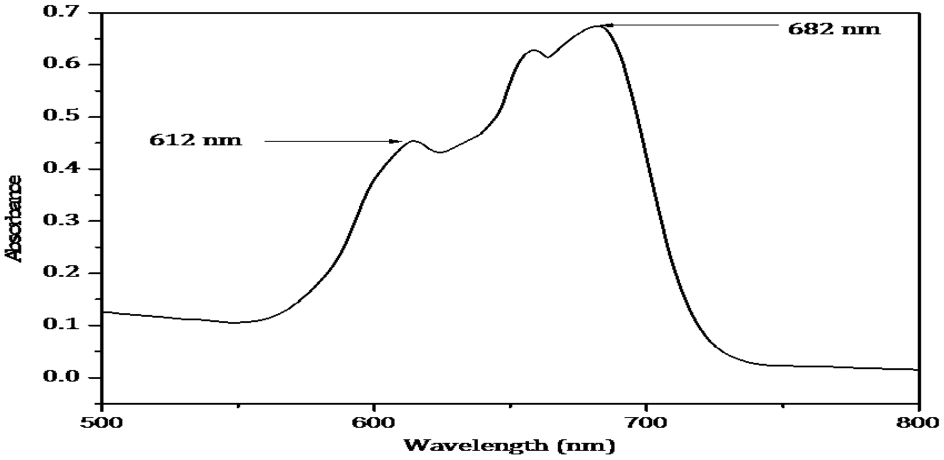

Figure No. 7: Electronic spectrum of Cobalt complex

Usually, Nickel (II) forms tetrahedral halide complexes. Nickel (II) possessing e^4 t^4 configuration in tetrahedral field, has higher magnetic moment of 4 B.M. (Table 1) than spin only value due to spin orbit coupling. In the present study, the nickel complex shows magnetic moment 2.82 B.M. (nearly spin only value) expected for octahedral nickel complex. Further, electronic spectrum of the complex (Fig. 8) display bands with lower ε values. Both the magnetic moment and electronic spectral data imply the formation of octahedral nickel(II) halide complex which is also recently established unequivocally by a crystallographic study[16]. Hence the bands at 20704 $cm^{-1}$and 25253 cm^{-1} may be attributable to the transitions $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) (ν_3) of an octahedral Ni(II) complex.

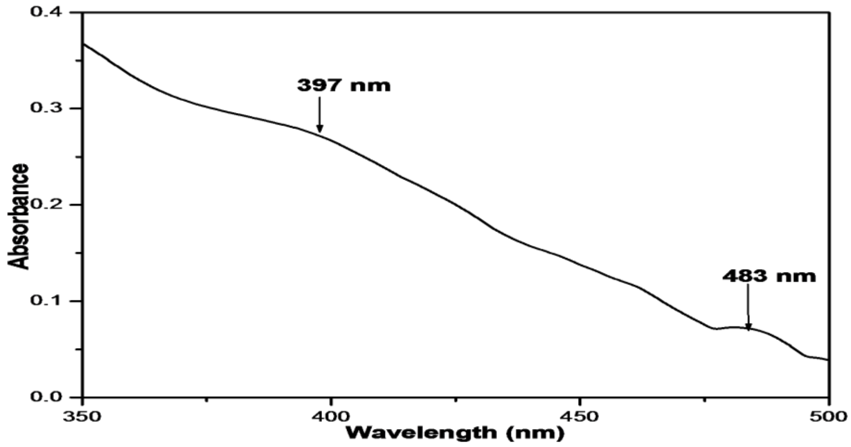

Figure No. 8: Electronic spectrum of Nickel complex

Crystal studies [17] of Manganese (II) halide complexes shows the existence of octahedral structure. The magnetic moment value for Manganese was found to be 5.73 B.M. From magnetic moment data value, similar to previously described complexes the structure of Manganese (II) complex is proposed to be octahedral.

ESR spectrum of Copper complex for {[Mac.2] [$CuCl_6$]}

ESR spectrum of the Cu (II) complex (Fig.9) was recorded at room temperature in solid state. Analysis of the spectrum indicates that μ = 1.79 and it is in good agreement with the usual observed value for Cu(II) system corresponding to one unpaired electron.

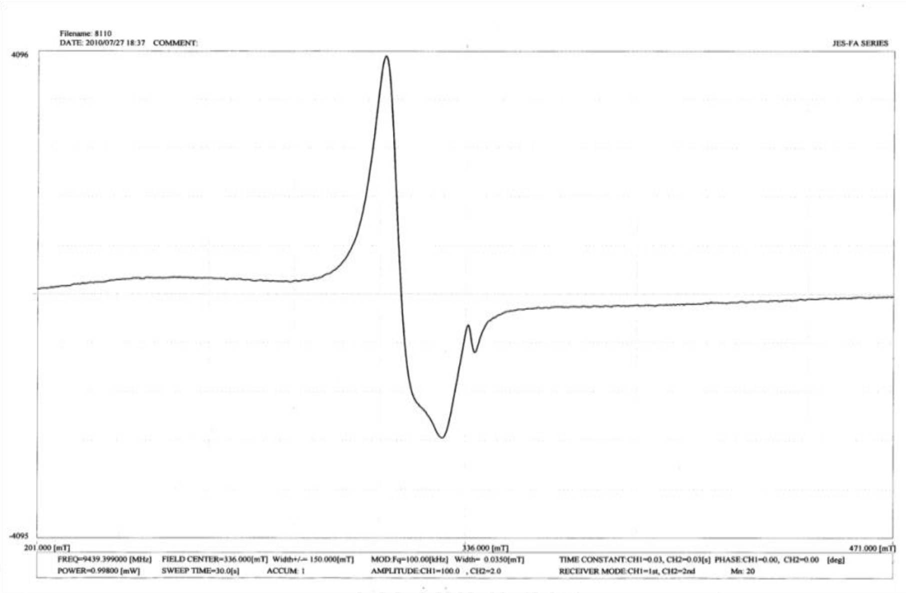

Figure No. 9: ESR spectrum of Copper complex

Electrochemical behavior of {[Mac.2] [MCl_6]} complexes

The cyclic voltammogram of the {[Mac.2] [MCl_6]} complexes were taken in DMSO medium with three electrode assembly using Pt working electrode, Ag/$AgNo_3$ reference electrode and Pt wire auxillary electrode. All the complexes were used as 1×10^{-3} M solution in DMSO using tetrabutylammonium tetrafluoroborate (0.05M) as supporting electrolyte.

Table No. 2: Data of cyclic Voltammetric measurement of {(Mac.2) [MCl_6]} complexes

Complex	Figure	Ep_c (mV)	Ep_a (mV)	ΔEp (mV)
DMSO	10	-1217	-317	900
[$PP2_{cy}$]	11	-611	-	-
{(Mac.2)[$CuCl_6$]}	12	-917	-8	909
{(Mac.2) [$NiCl_6$]}	13	-679	-569	110
{(Mac.2) [$CoCl_6$]}	14	-749	-219	530
{(Mac.2) [$MnCl_6$]}	15	-479	-89	390

The cyclic voltammogram of DMSO (Fig.10, Table 2) exhibits a different cathodic peak (Epc) at -1217 mV and an anodic peak (Epa) at - 317 mV when compared to all other metal complexes of cyclic voltammograms. Further, cyclic voltammogram of $PP2_{cy}$ exhibits only a cathodic peak (Epc) at -611 mV (Fig.11, Table 2). The difference between cathodic and anodic peak potentials for Copper (Fig.12, Table 2), Nickel (Fig.13, Table 2), Cobalt (Fig.14, Table 2) and Manganese (Fig.15, Table 2) metal complexes (Δ_{Ep})□ were higher than 59 mV and the peak currents rise with increasing scan rate. These show all the complexes have a quasi-reversible character.

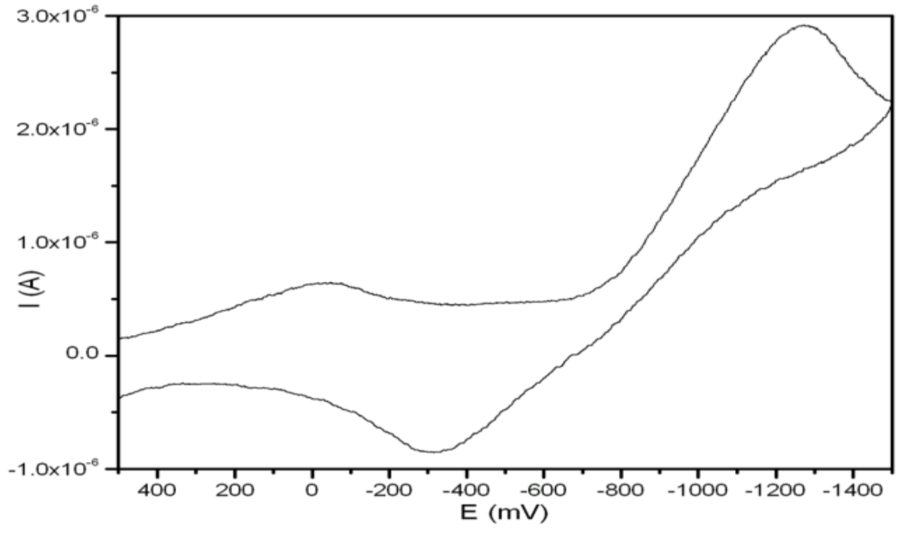

Figure No. 10: Cyclic Voltammogram of DMSO

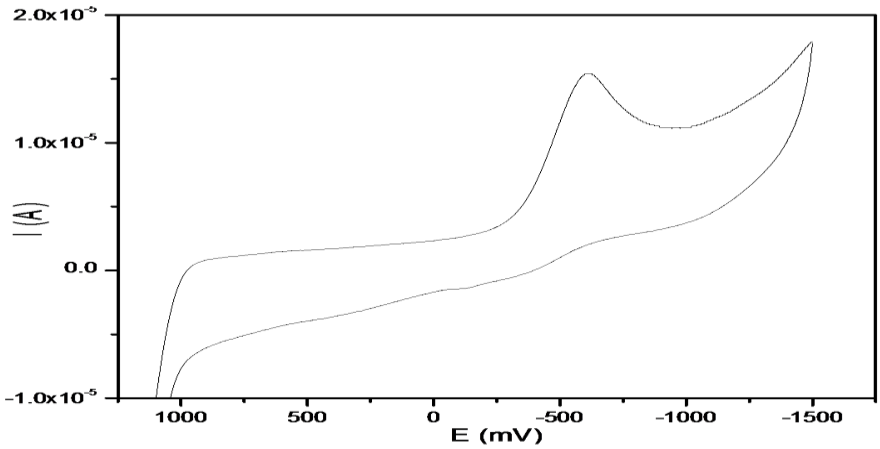

Figure No. 11: Cyclic Voltammogram of protonated cyclic product

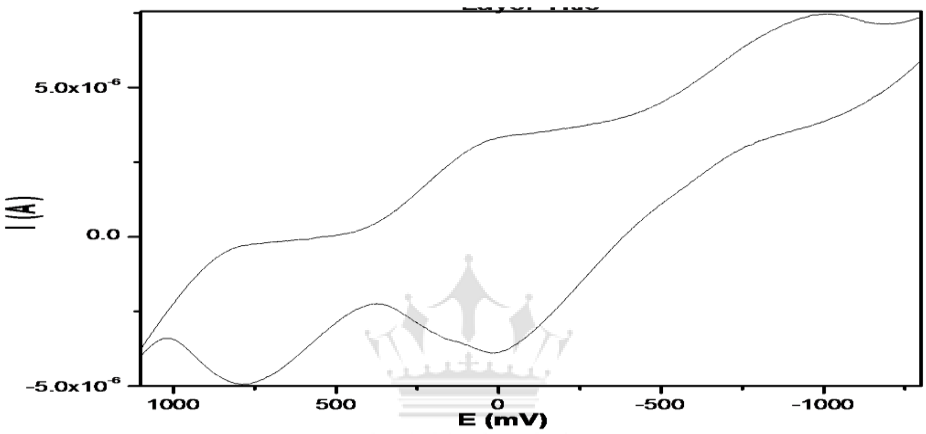

Figure No. 12: Cyclic Voltammogram of Copper complex

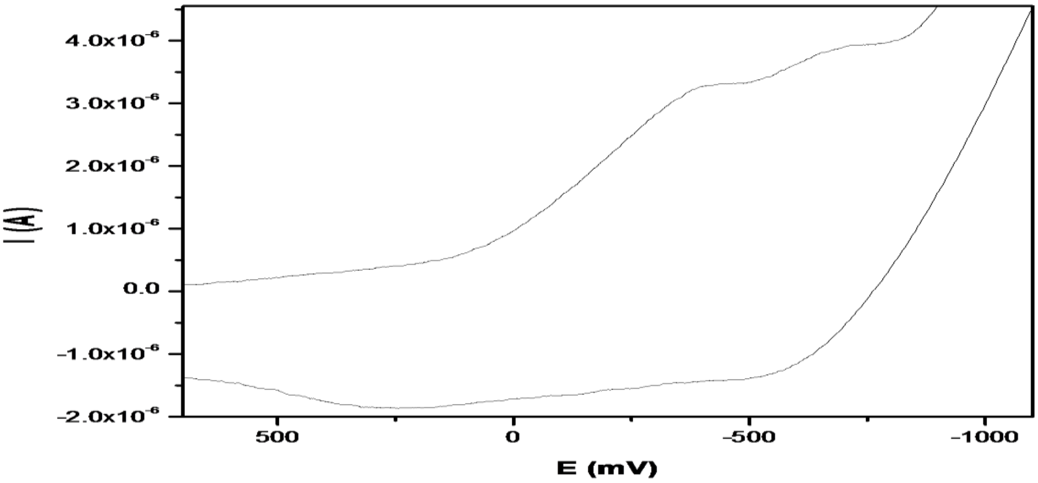

Figure No. 13: Cyclic Voltammogram of Nickel complex

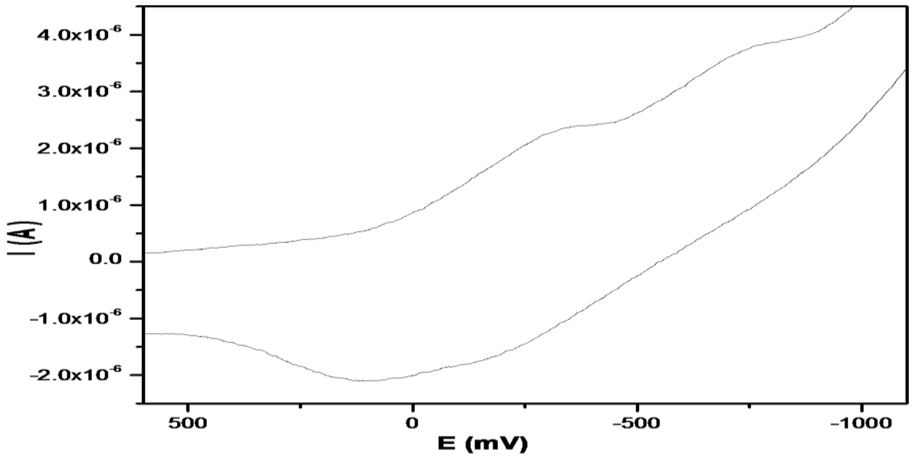

Figure No. 14: Cyclic Voltammogram of Cobalt complex

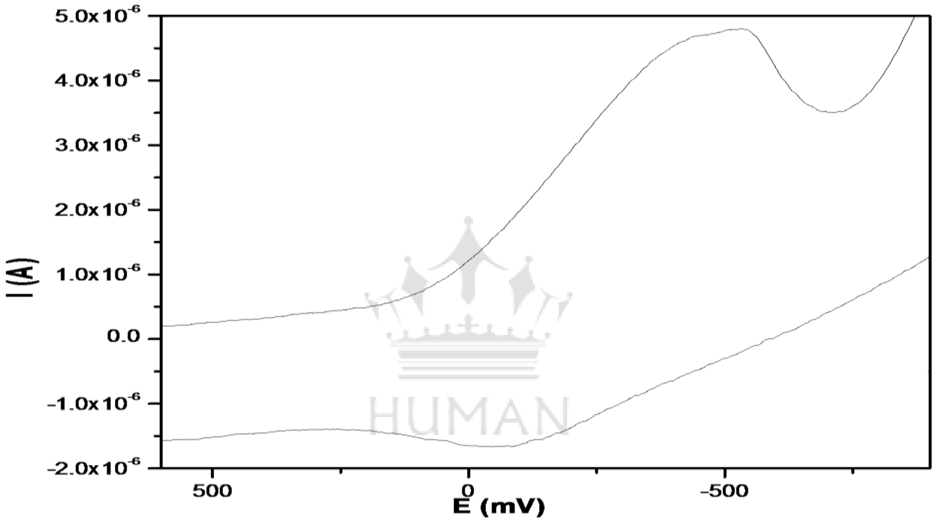

Figure No. 15: Cyclic Voltammogram of Manganese complex

CONCLUSION

Spectral studies of anionic transition metal complexes with tetraaza protonated 2,15-dihydroxy-3,7,10,14-tetraaza bicyclo [14.3.1] icosane-1(20),2,7,9,14,16,18-heptaene has been carried out. Data obtained indicate that the metal complex synthesized is a potential candidate for biomedical applications.

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	**Dr. A. SELVAN** Associate Professor Department of Chemistry, Govt. Arts College for Women, Nilakottai – 624 208, India
NA	**N. LAVANYA** Assistant Professor Department of Chemistry, Latha Mathavan Engg. College, Kidaripatty, Madurai Dist. TamilNadu, India
NA	**S. RAJESHWARI** Assistant Professor Department of Chemistry, PRIST University School of Law, Arasanoor, Sivagangai Dist. TamilNadu, India
	**Dr. R. JAYAKUMARARAJ** Associate Professor in Botany Department of Botany, Government Arts College, Melur – 625 106, Madurai Dist. TamilNadu, India