Spectral Studies of Anionic Transition Metal Complexes with Octaaza Protonated 2,3,10,11,18,19,26,27-Octahydroxy-1,4,9,12,17,20,25,28-Octa Azacyclodotriacontane-1,3,9,11,17,19,25,27-Octaene as Cation

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ABSTRACT

Supramolecular chemistry of macrocycles has become vital aspect of biological, industrial, and environmental fields. Recent developments focus on the use of these molecular receptors as membrane transport agents for chloride in biological systems, ion-pair receptors, sensors in the detection of biologically important anionic species. Spectral studies of anionic transition metal complexes with Octaaza Protonated 2,3,10,11,18,19,26,27-Octahydroxy-1,4,9,12,17,20,25,28-Octa azacyclodotriacontane-1,3,9,11,17,19,25,27-Octaene as cation has been elucidated to evaluate it as a potential candidate for biological applications.

INTRODUCTION

Recognition of anionic species is a vigorous research field of supramolecular chemistry due to the important role of these charged molecules in biological, industrial, and environmental fields[1-2]. Recent developments in this field focus on the use of artificial receptors as membrane transport agents for chloride in biological systems, ion-pair receptors, sensors for the detection of biologically important anionic species, anion template reactions, etc.[3] where the design and synthesis of three-dimensional molecular receptors for selective recognition of anions play a crucial role. Electron-deficient, positively charged, or neutral groups can be used as binding sites for the recognition of anionic species. A large number of anionic associations using amine-[4] and amide-based[5] receptors have been structurally characterized. They generally bind the substrate by multiple electrostatic interactions and/or hydrogen bonds. Selectivity is achieved by cooperative effects of geometric fit and strong interactions between partners[6].

Anions play an important role in biological processes. Approximately two third of proteins contain anions[7]. Therefore, sparking efforts towards the understanding of various interactions that contribute to the effective binding of these moieties and selectivity between anions with similar chemical characteristics (charge/ geometry) is required. The macrocycle, 1,4,7-triazacyclononane[8] and derivatives thereof, have been used extensively in binding metal cations, showing a great propensity for tripodal facial co-ordination in positively charged entities, and in the development of model compounds for metal sites in metalloproteins[9-11]. A less-well explored property of the azamacrocycles is the ability of protonated forms of the macrocycle to act as cationic hosts for negatively charged ions. Studies related to the binding of anions by polyazamacrocycles has been subject of research in recent years[12-15], the emphasis being mainly, but not exclusively, on the determination of adduct stoichiometry and binding constants.

Preparation:

Precursor and metal complexes were prepared, synthesized and reported[16].

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Preparation of cyclic product [P1cy]:

1,4-diaminobutane (0.174mL, 1.74mmol) was added to the hot ethanolic solution of precursor [P1] (500mg, 1.74mmol). The solution was stirred for 45 minutes to get a cyclic product [P1$_{cy}$]. Then it was filtered and dried in vacuum (Fig.1).
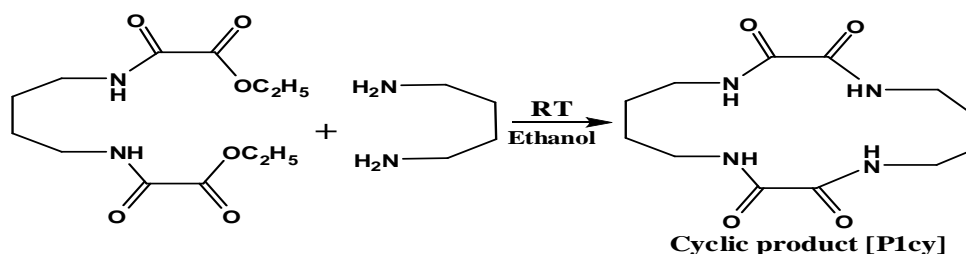

Figure No. 1: Preparation of cyclic product [P1cy]

Preparation of protonated cyclic product [PP1cy]:

1,4-diaminobutane (0.174mL, 1.74mmol) was added to the hot ethanolic solution of precursor [P1] (500mg, 1.74mmol). 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 [PP1$_{cy}$]. The PP1$_{cy}$ (Fig.2) was washed with ether, filtered and dried in vacuum over anhydrous CaCl$_2$.
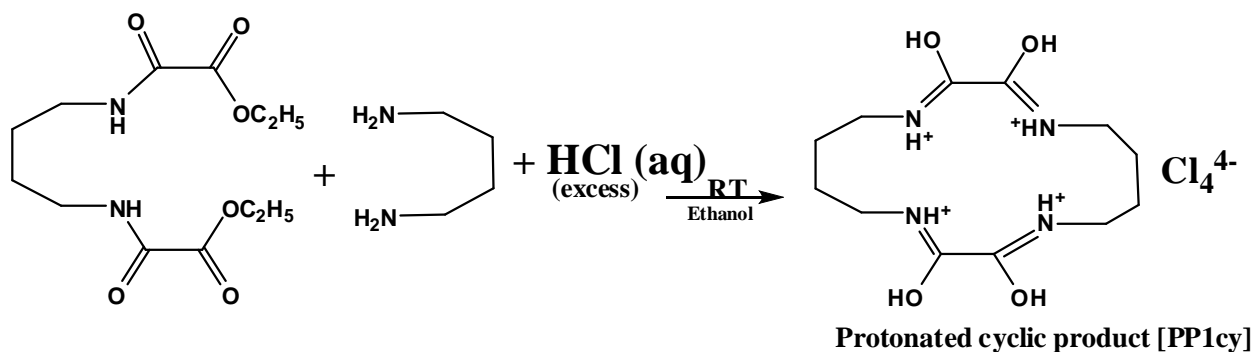

Figure No. 2: Preparation of protonated cyclic product [PP1cy]

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

The acyclic nature of the precursor is evident from the band at 1751cm^{-1} (data no.12) in the IR spectrum of precursor [P1] (Fig.3), corresponding to ester carbonyl group. The appearance of the bands at 1648 cm^{-1} (data no.13) [amide I (C=O stretching)] and 1535 cm^{-1} (data no.14) [amide II (NH deformation)] confirms the presence of amide moiety in the precursor.

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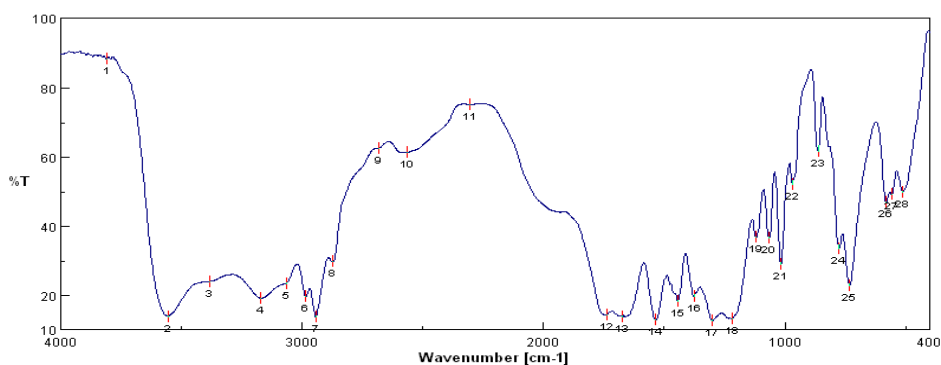
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Figure No. 3: IR spectrum of precursor

Further to ascertain the mode of coordination of amide in complexes a cyclic polyamide [P1$_{cy}$] was prepared by condensing the precursor [P1] with 1,4-diaminobutane in the absence of metal. IR spectrum of the amide [P1$_{cy}$] **(**Fig.4) shows amide I and amide II bands at 1660 cm^{-1} (data no.7) and 1535 cm^{-1} (data no.8) respectively.
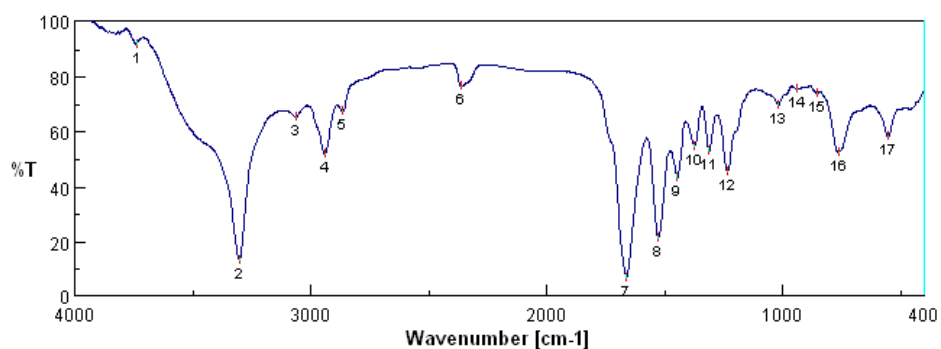

Figure No. 4: IR spectrum of cyclic product

The formation of imine-based protonated cyclic product and anionic metal complexes were investigated by FTIR. As shown in Fig. 5, new peak appears[17] 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 cyclic product. These sharp peaks could be assigned to the deformation of NH^{+} group in protonated cyclic product and metal complexes.

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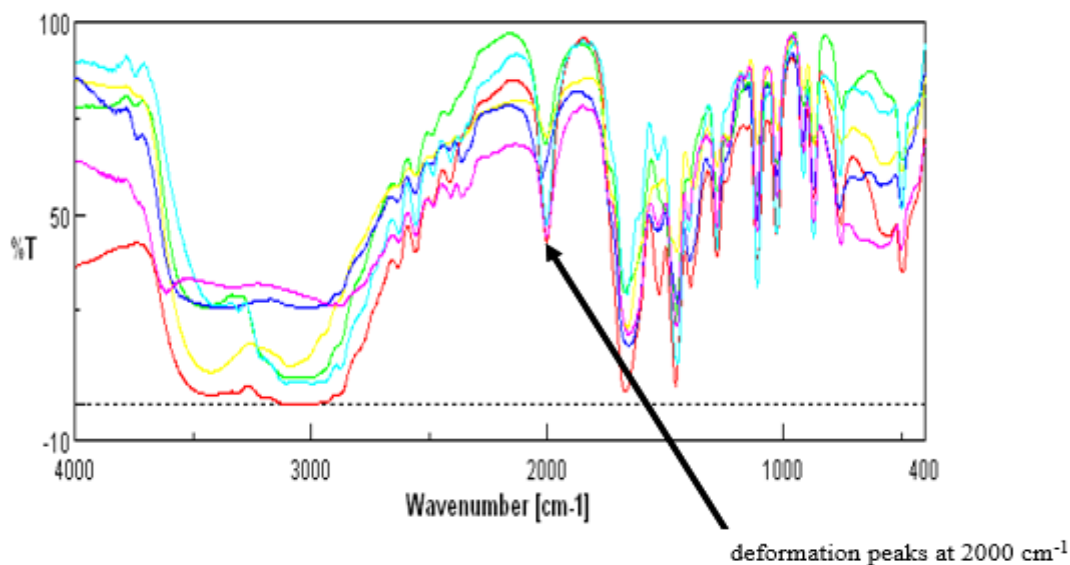
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deformation peaks at 2000 cm⁻¹

Figure No. 5: IR spectra of metal complexes (yellow for copper, red for protonated cyclic product, cyan for cobalt, blue for Nickel, pink for manganese, and green for zinc)

In the IR spectrum of the copper complex (Fig.5, yellow color), the absence of the expected strong peak for >C=O stretching of protonated amide around 1751 cm⁻¹ implies that the macrocyclic cation exists in protonated iminol form. The peak appearing at 1660 cm⁻¹ is corresponding to >C=N stretching, while a series of bands observed at 2366, 2557, 2624 cm⁻¹ in the region 2700 – 2250 cm⁻¹ are assignable to the NH stretching of >C=N⁺HR groups. The peak appearing at 2002 cm⁻¹ could be assigned to the NH deformation of >C=N⁺HR groups. These observations together with the appearance of a new peak at 3423 cm⁻¹ due to OH stretching confirm the complex exists predominantly in the iminol form. The OH deformation peak appearing[17] at 1448 cm⁻¹ in the complex also augments that macrocycle is in iminol form. Similar analysis of the IR spectra of protonated cyclic product and other complexes reveals that all the complexes exist in iminol form (Fig. 5, Table 1).

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Table No. 1: IR spectral 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})	
[PP1$_{cy}$]	2412	1668	2002	3421	-	-	-
{(Mac.1) [CuCl$_6$] Cl$_4$. 1.5H$_2$O}	2400	1660	2002	3423	22472 & 10917	361 & 172	2.06
{(Mac.1) [CoCl$_6$] Cl$_4$. 1.5H$_2$O}	2408	1614	2002	3419	16340 & 17240	92 & 76	4.83
{(Mac.1) [NiCl$_6$] Cl$_4$. 1.5H$_2$O}	2414	1656	2011	3417	24510 & 20619	105 & 46	2.93
{(Mac.1) [MnCl$_6$] Cl$_4$. 1.5H$_2$O}	2362	1656	2002	3473	-	-	5.99
{(Mac.1) [ZnCl$_6$] Cl$_4$. 1.5H$_2$O}	2420	1673	2007	3457	-	-	-

Electronic spectra of {(Mac.1) [MCl$_6$] Cl$_4$. 1.5H$_2$O} complexes

The magnetic moment for {(Mac.1) [CuCl$_6$] Cl$_4$. 1.5H$_2$O} is found to be 2.06 B.M. (Table 1) corresponding to one unpaired electron. The electronic spectrum of copper (II) complex (Fig. 6) shows bands at 22472 cm^{-1} and 10917 cm^{-1}. The earlier studies in the literature on electronic spectra of Cu(II) complexes indicate that the band at 22472 cm^{-1} in this complex may be arising due to the transition $^2B_{1g} \rightarrow {}^2E_g$ (ν_3); the 10917 cm^{-1} band is attributable to the transition $^2B_{1g} \rightarrow {}^2A_{1g}$ of a tetragonally distorted octahedral Cu(II) complex.
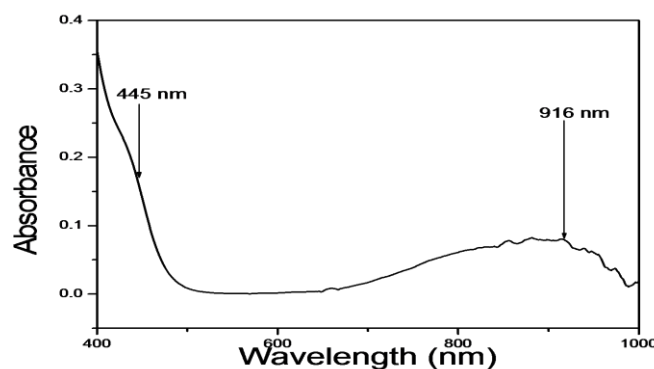

Figure No. 6: Electronic spectrum of Copper complex

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. than spin only value

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due to spin orbit coupling. In the present study, nevertheless, the nickel complex shows magnetic moment 2.93 B.M. (Table 1) that is nearly spin only value expected for octahedral nickel(II) complex. Further, electronic spectrum of the complex (Fig. 7) displays bands with lower ε values. The near spin only magnetic moment and the electronic bands with lower ε values suggest that the formed nickel(II) halide complex in the present study may have octahedral geometry. Recently a crystallographic study[18] has established the formation of octahedral nickel(II) halide complex. Hence the bands at 20619cm^{-1} and 24510 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.
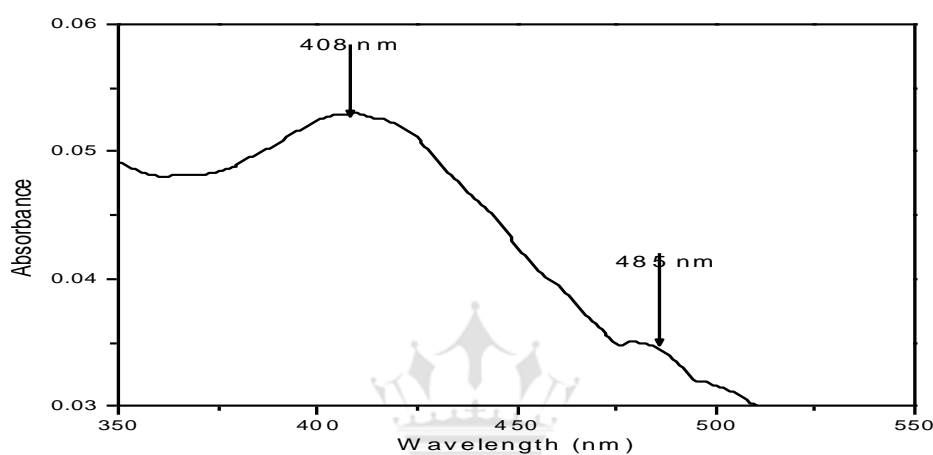

Figure No. 7: Electronic spectrum of Nickel complex

Generally, cobalt(II) forms tetrahedral halide complexes. The ground state for tetrahedral cobalt(II) complex is $^4A_2$ and a low magnetic moment of 3.87 B.M. might be expected. However, in the present study, cobalt(II) complex shows magnetic moment of 4.83 B.M. (Table 1) (higher than spin only value) expected for octahedral cobalt(II) halide complex. Further, electronic spectrum of the complex (Fig. 8) display bands with lower ε values. The observed higher magnetic moment than spin only value and the electronic bands with lower ε values suggest that the formed cobalt(II) halide complex in the present study may have octahedral geometry. The formation of octahedral cobalt(II) halide complex is recently studied by crystallographic study[19]. Hence the present observed bands at 16340 cm^{-1} and 17240 cm^{-1} may be attributable to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ of an octahedral Co(II) halide complex.

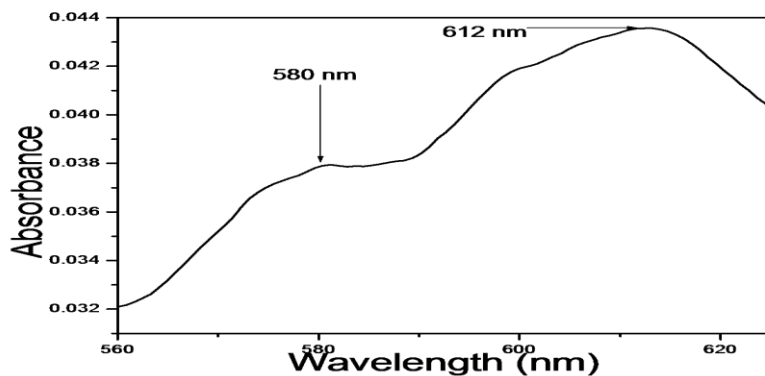*Citation: A. SELVAN et al. Ijsrm.Human, 2020; Vol. 14 (3): 86-98.*

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Figure No. 8: Electronic spectrum of Cobalt comple

Crystal studies[20] indeed illustrate the existence of octahedral manganese(II) halide complex. The magnetic moment value for manganese(II) complex was found to be 5.99 B.M. (Table 1). 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.1) [CuCl₆] Cl4. 1.5H₂O}

EPR spectrum of the Cu(II) complex (Fig. 9) was recorded at room temperature in solid state. Analysis of the spectrum indicates that $\mu = 1.82$ and it is in good agreement with the usual observed value for Cu(II) system corresponding to one unpaired electron.
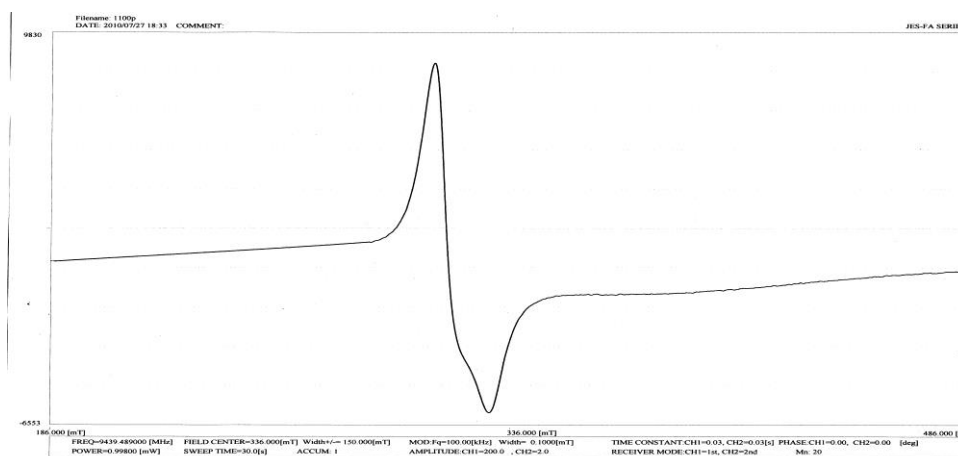

Figure No. 9: ESR spectrum of Copper complex

Electrochemical behavior of {(Mac.1) [MCl₆] Cl₄. 1.5H₂O} complexes

The cyclic voltammograms of the {(Mac.1) [MCl₆] Cl₄.1.5H₂O} complexes were taken in DMSO medium with three electrode assembly using Pt working electrode, Ag/AgNo₃

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reference electrode and Pt wire auxiliary 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: Cyclic voltammetric measurement of $\{(Mac.1)[MCl_6]Cl_4.1.5H_2O\}$ complexes

Complex	Figure	ep_c (mv)	ep_a (mv)	Δep (mv)
DMSO	10	-1272	-317	955
$[PP1_{cy}]$	11	-611	-	-
$\{(Mac.1) [CuCl_6] Cl_4 \ 1.5H_2O\}$	12	-745	-123	622
$\{(Mac.1) [CoCl_6] Cl_4 \ 1.5H_2O\}$	13	-461	-31	430
$\{(Mac.1) [MnCl_6] Cl_4 \ 1.5H_2O\}$	14	-448	-258	190

The cyclic voltammogram of DMSO (Fig.10, Table 2) exhibits a different cathodic peak (Epc) at -1272 mV and an anodic peak (Epa) at - 317 mV when compared to all other metal complexes of cyclic voltammograms. Further, cyclic voltammogram of protonated cyclic product $[PP1_{cy}]$ 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), Cobalt (Fig.13, Table 2) and Manganese (Fig.14, 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.
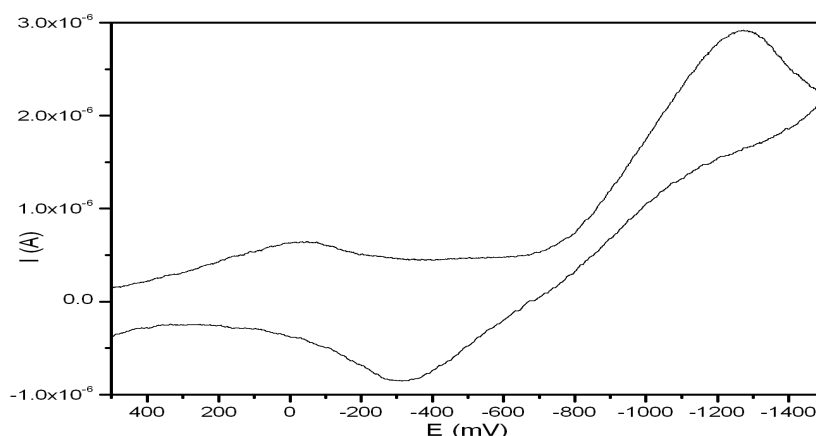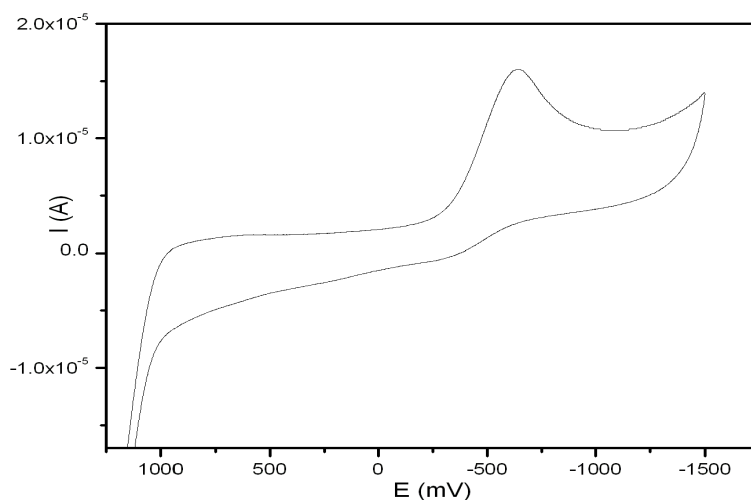

Figure No. 10: Cyclic voltammogram of DMSO

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Figure No. 11: Cyclic voltammogram of protonated cyclic product

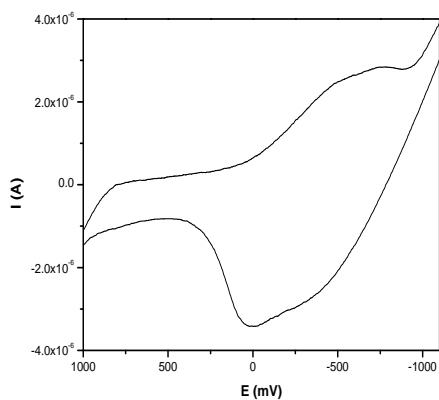**Figure No. 12: Cyclic voltammogram of Copper complex**

Figure No. 13: Cyclic voltammogram of Cobalt complex

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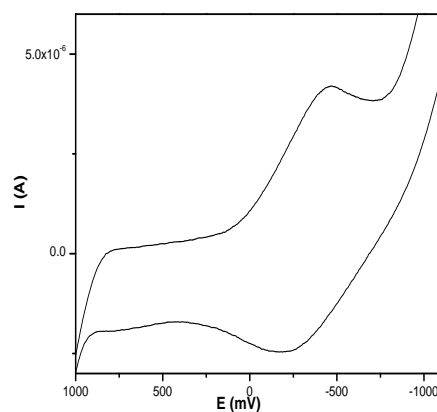
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Figure No. 14: Cyclic voltammogram of Manganese complex

CONCLUSION

In the present study, anionic transition metal complexes with Octaaza Protonated 2, 3, 10, 11, 18, 19, 26, 27-Octahydroxy-1, 4, 9, 12, 17, 20, 25, 28-Octa azacyclodotriacontane-1, 3, 9, 11, 17, 19, 25, 27-Octaene as cation has been prepared and characterized. Results indicated that the metal complex synthesized is a potential candidate for biomedical applications.

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