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Research Article

Synthesis, spectral, electrochemical and antibacterial studies of tetraaza macrocyclic complexes of Mn(II) and Co(II)

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Abstract

Me_2dibenzo[*b*,*l*]dipyridyl[*g*,*q*][1,5,11,15]-tetraaza-6,10,16,20-tetraoxocycloeicosane macro-cyclic complexes of Mn(II) and Co(II) have been synthesized by the template method. These synthetic macrocycles analysed by various techniques like Molar conductance, FTIR, UV-Vis. and Mass spectra etc. Cyclic voltammetric studies were carried out on Pt disc (tip-06.1204.120.) electrode (2mm diameter) in different solvents. The heterogeneous electron transfer rate constant (K^0) was also determined with the help of Nicholson and Kochi's method in MeOH, Acetonitrile (AN), DMF and found in the order $K^0_{MeOH} > K^0_{AN} > K^0_{DMF}$. The octahedral geometry has been assigned to these macrocycles and attributed the unusual oxidation state of metal ion which is stabilized by macrocyclic cavity. These synthetic macrocycles were also tested for their antibacterial activities against *E. coli, P. aeruginosa, B. cereus, S. aureus* and antifungal against *C. albicans* to assess their inhibition potential and were compared with standard drugs like Gentamycin.

Keywords: Template synthesis, spectroscopic characterisation, cyclic voltammetric studies, antibacterial screening.

1. Introduction

The design and synthesis of macrocyclic complexes performing functions identified with metal containing natural products are of multifaceted importance. The synthetic macrocycles mimic the properties of naturally occurring complicated protein derivatives and provides two principal structural components to the coordination site thereby determining the electronic properties of the metal ion and further aspects of the active site[1-4]. The control of the electronic properties of the metal ions in the heme proteins involved redox processes. It is known that macrocyclic ligands are uniquely convenient for the evaluation of the dependence of redox properties of metal chelates. A variety of processes have been identified depending primarily on the metal ion, the ligand and solvent. These include redox behaviour of the central metal ion and the ligand. It is possible to identify electrode processes that are attributable to some metal ion couple. The influences of various structural features including ring size degree of unsaturation and alkyl substitution have received special attention because of their mixed hard–soft donor character and their redox behaviour for biological and catalytic activities[42]. The heterocyclic unit containing macrocyclic compounds show various biological activities, such as antibacterial[3-4] and anti-inflammatory. The biological activities of the macrocyclic complexes may be associated to their redox properties with a lower reduction potential seems to be related to an increased antifungal activity[5]. The common antifungal drugs currently used in clinics belong to polyenes and azoles. Polyenes (amphotericin B and nystatin) cause serious host toxicity and some peptido-heterocyclic containing macrocycles exhibit a general ionophoric potency towards divalent cations [6-7]. Advanced electrochemical energy storage systems are critical for the future as they could improve the efficiency of electric power grids, stimulate the growth of renewable electricity generation and provide alternatives to fossil fuels for transportation because of their importance as considerable efforts which have been devoted to develop batteries with higher energy density, improved safety and reliability and reduced cost[8-9]. Among the battery technologies, interest in rechargeable magnesium batteries has increased because of their substantial prospective benefits; Mg metal is a low-cost, safe and environmentally benign material[10-13]. Recently 2,6-disubstituted pyridine containing

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macrocycles have been used as biologically active congeners and have also significant interest in electroluminescence from organic materials. The emergence of new materials allows the use for organic light emitting devices (OLEDs). A number of emission materials and hole transport materials have been reported such as metal-chelates complexes having quinolinolato ligands, 1,3,5-oxadiazoles, 1,2,4-triazole, phenanthroline derivatives. Generally heterocyclic macrocycles containing electron deficient nitrogen atoms are suitable for this purpose. Recently the novel series of 6,12,19,25-tetramethyl-7,11,20,24-dinitrilo-dibenzo[b,m]1,4,12,15-tetra-azacyclodocosine (TMCD) serves as electron transporting material for organic EL devices[14-18]. In this communication synthesis antibacterial and cyclic voltammetric studies like electrode kinetics for synthesized pyridine based tetraaza macrocyclic complexes have been carried out.

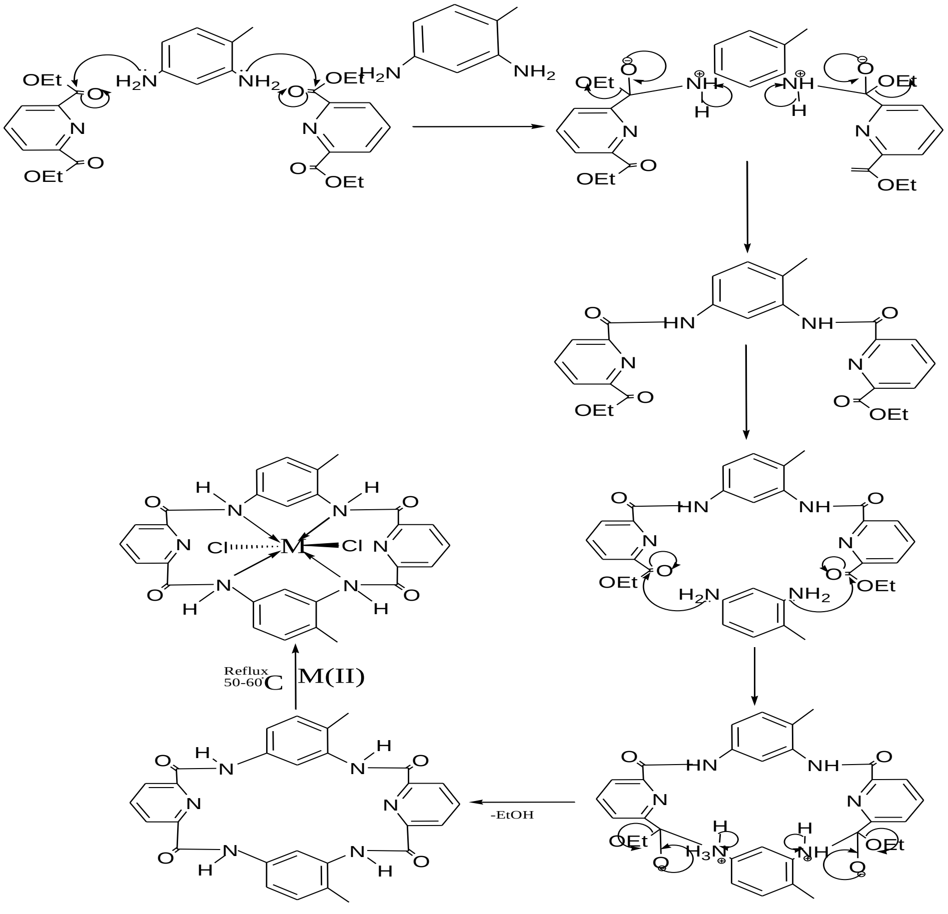
2. Materials and Methods

All the chemicals were used of AR grade. The microanalysis (C, H, N) and mass spectral studies of these compounds were carried out at Central Instrumental Laboratory (CIL) Panjab University Chandigarh (Eager Xperience and TOF MS ES+6018e3). Infrared spectra were recorded using KBr DRS system (Shimadzu 8400S). The electronic spectra were recorded on Double Beam Spectrophotometer (Perkin Elmer 2550) in methanol. The molar conductance of these complexes was recorded on Auto ranging Conductivity/TDS Meter (TCM 15+). The electrochemical studies were carried by using Auto Lab instrument (Metrohm 663 VA Stand) in methanol (MeOH), acetonitrile (AN) and dimethylformaide (DMF) containing TEAP as supporting electrolyte by employing cyclic voltammetric techniques. This system contain three electrode system consists of Pt disc electrode (2mm diameter) as a working electrode, Ag/AgCl (3M KCl) reference electrode and Pt wire electrode as auxiliary electrode. Pre-treatment of electrodes was done before every cyclic voltammetric experiments.

2.1 Preparation of the Macrocyclic complexes:

These macrocyclic complexes have been synthesised according to the literature method[24].

Scheme 1: Synthesis of macrocyclic complexes.



M= Mn(II) and Co(II)

Table 1: **Physical properties of Mn(II) and Co(II) complexes.**

Complexes (Molecular Formula)	Colour	Molar Conductance ($ohm^{-1}\,cm^2\,mol^{-1}$)	M.P (^0C)	Mol. Wt.	C (%)	H (%)	N (%)
I.[$Mn(C_{28}H_{22}N_6O_4)Cl_2$]	Dark Brown	32	235	632	53.17 (55.64)	03.48 (5.57)	13.29 (10.13)
II.[$Co(C_{28}H_{22}N_6O_4)Cl_2$]	Reddish Brown	27	218	636	52.83 (53.23)	03.46 (05.12)	13.21 (10.73)

3. Results and Discussion

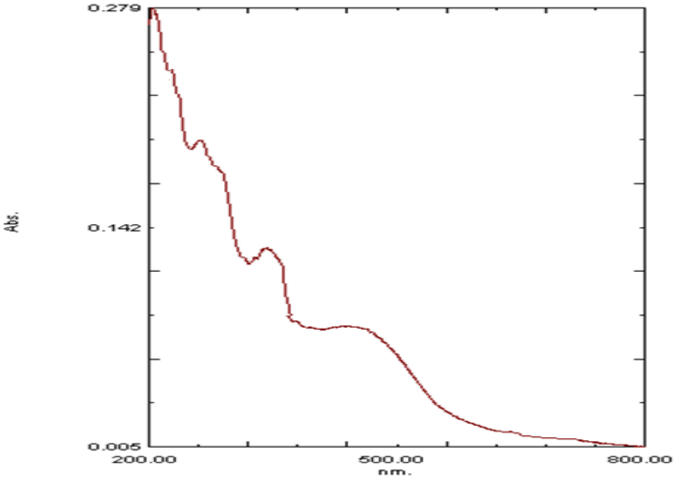
3.1 Infrared Spectral Studies

The synthesized complexes were characterised by the FTIR spectra. The spectra of Mn(II) and Co(II) complexes show characteristic absorption bands for ν(N-H) at 3225 cm^{-1} and at 3235 cm^{-1}, for ν(C=O) at 1643 cm^{-1} and at 1658 cm^{-1} and for ν(C-N) at 1451 cm^{-1} and at 1445 cm^{-1} respectively [19]; moreover the bands due to ν(Mn-N) and ν(Co-N) obtained at 525 cm^{-1} and at 565 cm^{-1}[20-21].

3.2 Electronic spectra

Mn (II) complex exhibits two very weak bands at 33,575 and 25,070 cm^{-1}, these bands may be assigned to the transitions: $^6A_{1g} \rightarrow {}^4T_{1g}$ (G) and $^6A_{1g} \rightarrow {}^4E_g$, $^4A_{1g}$ (G) transition respectively. These observations reveal that the stereochemistry of this complex is consistent with the six coordinated octahedral geometry. The electronic spectrum of Co(II) complexes **[Fig.1]** shows bands at 21,978, 29,411 and 36,496 cm^{-1}, these bands are assignable to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively. The data is consistent to the octahedral environment [22-24].

Fig. 1 Electronic spectrum of Co(II) complex



3.3 Study of Ligand Field Parameters

The ligand field parameters D_q, B', β were calculated for these complexes from Tanabe-Sugano diagram since Tanabe-Sugano diagram include both weak and strong fields using ν_2/ν_1 ratio. The nephelauxetic parameters β is readily obtained using the relation. $\beta = B' / B$ where B (free ion) is Mn (II) = 960 Cm^{-1}, Co(II) =1120 Cm^{-1} [25] and calculated B' values for Mn(II) and Co(II) are 533.3 and 968.8 respectively. The calculated values of β for Mn (II) and Co (II) are 0.555 and 0.995 respectively[26].

Table 2: **Magnetic moment, Electronic Spectra and Ligand Field Parameter**

Complexes	Magnetic moment (B.M.)	Electronic Spectra		Stereochemistry	Ligand Field Parameter			
		Energy (cm^{-1})	Transition		D_q (cm^{-1})	ν_3/ν_1	B' (cm^{-1})	β
I. [$Mn(C_{28}H_{22}N_6O_4)Cl_2$]	5.83	25070	$^6A_{1g} \rightarrow {}^4T_{1g}$ (G)	Octahedral	463.7	1.3	533.3	0.55
II. [$Co(C_{28}H_{22}N_6O_4)Cl_2$]	4.87	21978	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	Octahedral	919.7	1.6	968.8	0.99

3.4 Mass Spectra

The mass spectra of these macrocyclic complexes showed a more intense molecular ion peak $(M)^{+\cdot}$ at m/z 632and 635 for Mn(II) and Co(II) complexes respectively which are in good agreement with respect to the molecular formula. The mass spectrum of Co (II) complex **[Fig.3]** showed a molecular ion peak $(M)^{+\cdot}$ at m/z 635 and other at m/z 214, 212, 71. The possible cleavage given in **Scheme 2**.

Scheme 2: Scheme of fragmentation of Co (II) macrocyclic complex

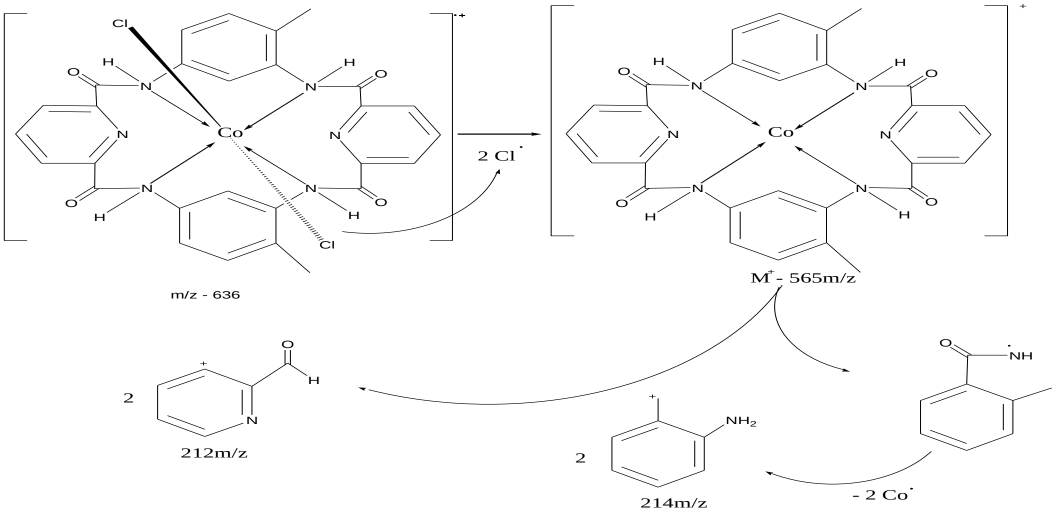
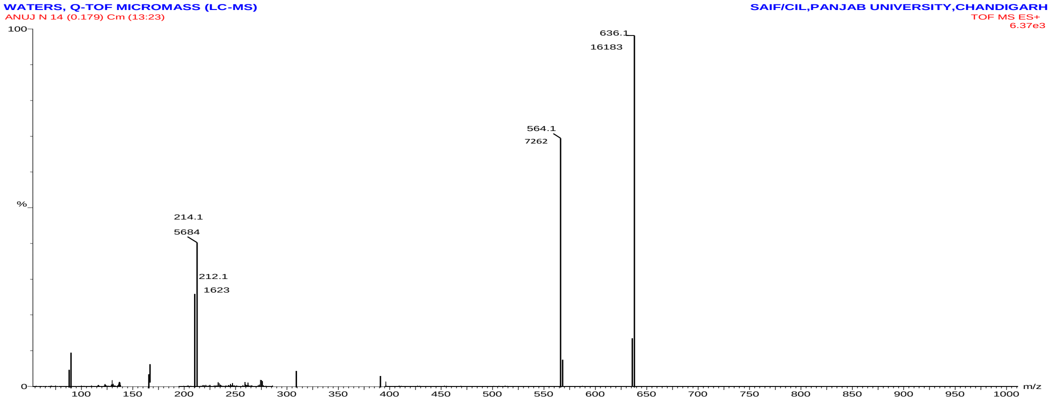


Fig.3 Mass spectrum of Co (II) macrocyclic complexes



3.5 Electrochemical Studies

Electrochemical studies of these macrocycles been carried out in the CH_3OH, CH_3CN, DMF. There is specific correlation between $E_{1/2}$ and solvent and depends on the interaction between the solvent and macrocyclic complexes[26]. In this communication Nicholson, Kochi and Nicholson-Shain equation, Randles-Sevcik equation methodology are used to calculate the heterogeneous electron transfer rate constants and diffusion coefficients respectively for these complexes considering the one electron quasirreversible redox process on the of basis solvent effect on peak separation.

Table 3: Some standard properties of MeOH, AN, DMF

Solvents	B.P.	Dielectric constant	Z-value	Density	Dipole moment
A- MeOH	65 °C	33.0	0.857	0.791 g/ml	1.70 D
B- AN	82 °C	37.5	0.895	0.786 g/ml	3.92 D
C- DMF	153 °C	38.0	0.954	0.944 g/ml	3.82 D

The cyclic voltammetric behaviour of these macrocyclic complexes were studied in the range -2.0V to +2.0V. The cyclic voltammograms of these complexes show quasirreversible wave couples peaks. The $E_{1/2}$ values are also comparable with the reported values for the analogous complexes under the identical conditions [28] and given in **Table 4**. The difference between the E_{pc} and E_{pa} peak potential for these complexes are very close to 58mV which may be assigned to a one electron quasirreversible process: Co(II)/Co(III) and Co(III)/Co(II) with respect to the anodic and cathodic peaks respectively. The value of I_{pa}/I_{pc} ratio is also close to unity suggesting that these complexes show quasirreversible electrochemical process [29-30]. The observation in the different solvents shows a very little difference in their diffusion coefficient (D_0) and heterogeneous electron transfer rate constant (K^0).

Table 4: **$E_{1/2}$ and ΔE where $E_{1/2}= (E_{pc}+ E_{pa})/2$, $\Delta E=E_{pa}-E_{pc}$**

Compounds	E_{Pa} (V)	E_{Pc} (V)	$E_{1/2}$ (V)	ΔE (V)	I_{Pc}/I_{Pa}
$[Mn(C_{28}H_{22}N_6O_4)Cl_2]$	0.68 1.10	0.88 1.37	0.78 1.23	-0.20 -0.27	1.03
$[Co(C_{28}H_{22}N_6O_4)Cl_2]$	0.98 -1.22	0.70 -1.46	0.82 -1.46	0.28 0.48	0.98
10^{-3}M complex and 0.1M TEAP in CH_3OH as the supporting electrolyte at -2V to +2V range at 200 mV/s scan rate.					
$[Mn(C_{28}H_{22}N_6O_4)Cl_2]$	0.62 1.30	0.90 1.09	0.76 1.19	-0.28 -0.21	1.07
$[Co(C_{28}H_{22}N_6O_4)Cl_2]$	1.00 -1.07	0.65 -1.55	0.82 -1.31	0.35 0.24	1.11
10^{-3}M complex and 0.1M TEAP in CH_3CN as the supporting electrolyte at -2V to +2V range at 200 mV/s scan rate.					
$[Mn(C_{28}H_{22}N_6O_4)Cl_2]$	1.30 -0.60	1.10 -0.50	1.20 0.55	-0.20 -0.10	0.95
$[Co(C_{28}H_{22}N_6O_4)Cl_2]$	1.03 -1.18	0.83 -1.63	0.93 -1.45	0.20 0.45	1.05
10^{-3}M complex and 0.1M TEAP in DMF as the supporting electrolyte at -2V to +2V range at 200 mV/s scan rate.					

3.5.1 Nicholson's Method

This methodology relates 'K^0' to the peak separation (ΔE) through the dimensional parameter Ψ (Kinetic Factor) by the following equation.

$$\Psi = \gamma K^0 /(\pi a D_0)^{1/2}$$

Where $\gamma = D_0/D_R$, the ratio of diffusion constants of oxidized and reduced forms. $a = n F\nu/ R T$ and ν is scan rate.

If $\gamma = 1$ then $\Psi = K^0 /(\pi a D_0)^{1/2}$. The method is applicable peak separation in the range of 57 mV to 250 mV[30,32]

3.5.2 Kochi's Method

Kochi and Klinger derived another correlation between ΔE and heterogeneous rate constant (K^0).

$$K^0= (2.18)[\alpha D_0 nF\nu/RT]^{1/2}\exp[-\alpha^2 nF/RT(E_{pa}-E_{pc})],$$

Where α is calculated by $E^0= (1-\alpha)E_{pc}+ \alpha E_{pa}$, $E^0 = E_{1/2} = E_{p/2} - 1.09\, RT/nF$.

The values of heterogeneous electron transfer rate constant (K^0) was also calculated with the help of the following relation.

$$I_p = 0.227\, nFA\, C_0\, K^0 \exp\{-\alpha n_a f(E_p-E^f)\}$$

Where, I_p = Peak current (µA), n = No. of electron involving in the process, F = Faraday constant, A = Area of the electrode, C^0 = Concentration of the electro active species (mM), $\alpha n_a = 0.048/E_p - E_{p/2}$, Where, $E_{p/2}=E_{1/2}-1.09RT/nF$ [31].

Generally in quasireversible systems current is controlled by charge transfer as well as mass transfer the Nernst equation satisfied, the standard heterogeneous rate constant (K^0) lies in the range $10^{-1}>K^0>10^{-5}$ cm/s. According to the Nicholson method, if kinetic factor $\Psi>7$, the process is reversible and ΔE is independent on Ψ but $\Psi<0.001$, the process is irreversible and ΔE may not be measured and the intermediate value of Ψ tends to the quasirreversible process [33-34]. The calculation of diffusion Coefficient (D_0) is carried out with help of Nicholson-Shain-equation.

$$D_0 = (I_p)^2\, RT/(0.4463\, n\, C_0\, A\, F)^{1/2}\, n\, F\, v$$

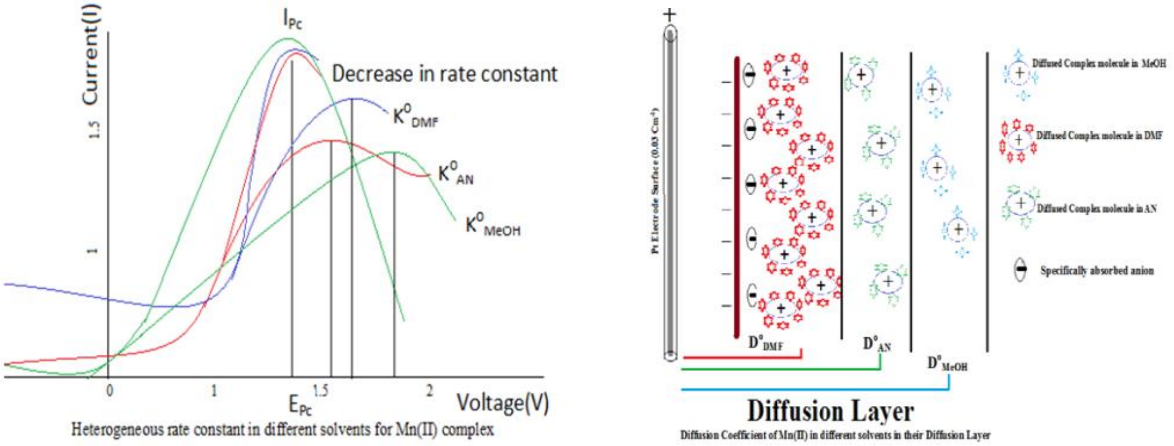
Where, I_p = Peak current (µA), n = No. of electron involving in the process, F = Faraday constant (c-mol^{-1}), A = Area of the electrode (cm^2), C^0 = Concentration of the electro active species (mM), v = Scan rate (mV/s).

Heterogeneous rate constants and diffusion coefficients as determined by considering one electron quasirreversible process $I_p^f=I_p^b$(µA), C_0=1mM, A= 0.031Cm^2, v=0.200Vs^{-1}, at different calculated values of αn_a slope are given in **Table 5**.

Table 5: Cyclic voltammetric determination for heterogeneous rate constant and diffusion coefficient

Complexes	$K^0\times10^{-3}$ (cm/s)			$D_0\times10^{-6}$(cm^2/s)		
	CH_3OH	CH_3CN	DMF	CH_3OH	CH_3CN	DMF
$[Mn(C_{28}H_{22}N_6O_4)Cl_2]$	0.14	0.59	1.81	7.02	4.49	8.81
$[Co(C_{28}H_{22}N_6O_4)Cl_2]$	0.96	0.38	1.39	2.8	4.49	5.14

Fig.4: Peak separation dependence of Heterogeneous rate constant corresponding to their diffusion layer phenomenon



Heterogeneous rate constant in different solvents for Mn(II) complex

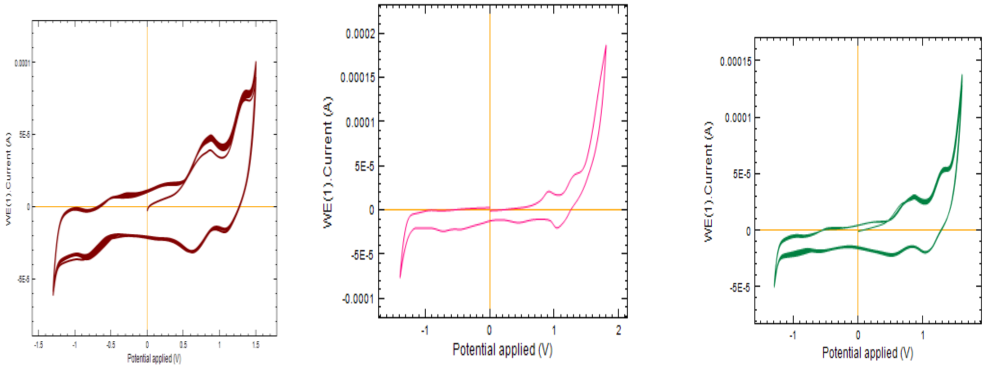
Diffusion Coefficient of Mn(II) in different solvents in their Diffusion Layer

The diffusion coefficient of these complexes has also been calculated with the help of Randles-Sevcik equation.

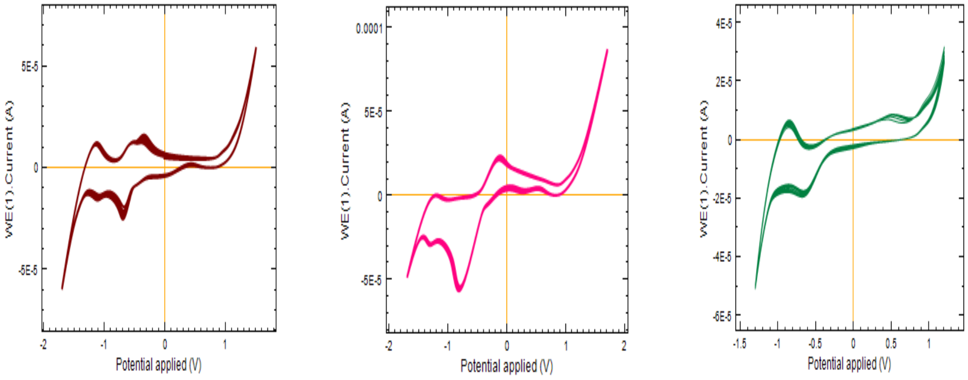
$$I_p = \text{Constant } nFAC\,(nFvD_0/RT)^{0.5}$$

In general electroactive species interact with the solvent in polarization mode[35], a solvent of high polarity favoured for electron transfer and controlled by dielectric constant of the solvent[36-37]. Z-value of a solvent is a measure of polarity and exhibit markedly fast rate of electron transfer reaction[38-39]. This fact is also cleared on the basis of dielectric constant which directly affects the diffusion of the electroactive species and thus is directly related to the heterogeneous rate constant (K^o). The rate of diffusion is faster in DMF compared to other solvents, adsorption of ion solvent pair on the surface of the electrode favoured more in DMF which leads to the high diffusion coefficient of electroactive species in DMF for the same complex[40]. Diffusion coefficients for both complexes showed a little difference corresponding to different solvents for Mn(II) complex $D_0^{DMF} > D_0^{MeOH} > D_0^{AN}$ and for Co(II) complex $D_0^{DMF} > D_0^{AN} > D_0^{MeOH}$.

Fig 5: **The typical cyclic voltammograms for both complexes in various solvents**



Mn(II)-MeOH Mn(II)-AN Mn(II)-DMF

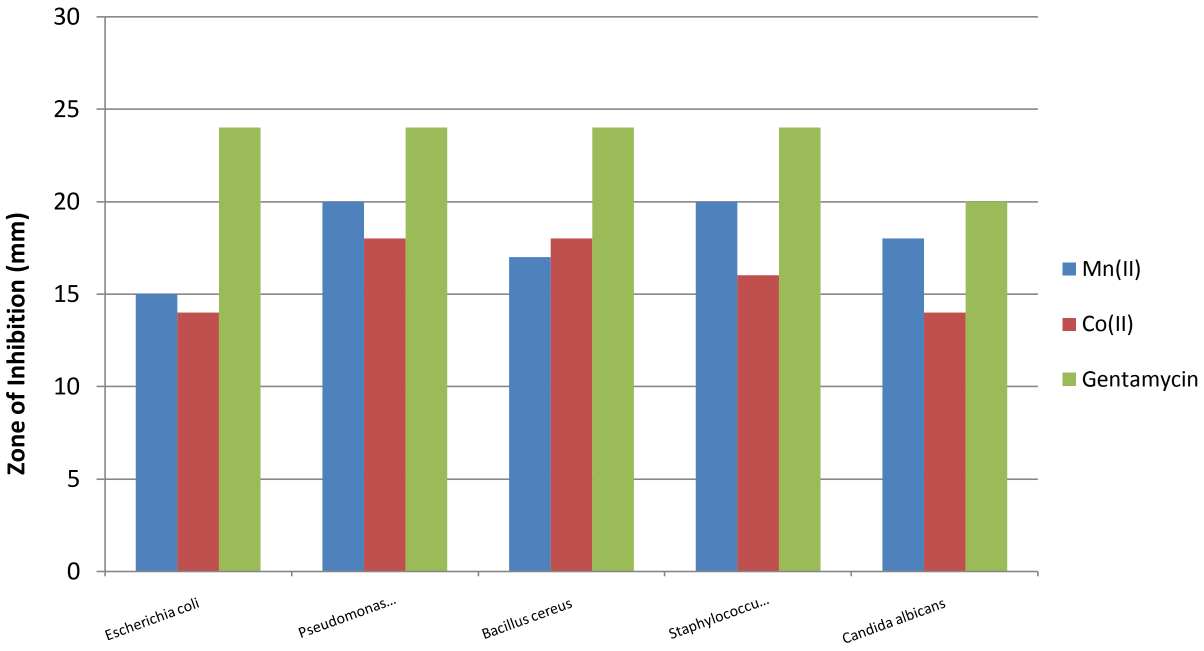


Co(II)-MeOH Co(II)-AN Co(II)-DMF

3.6 Biological Activity

The antibacterial assay for these synthetic macrocyclic complexes was performed by agar well diffusion method for solvent extract. Autoclaved molten Mueller Hinton agar, kept at 45 ^{0}C, was inoculated with 100 µl of the inoculums (1x10^8 cfu/ml) and poured into the Petri dish (Hi-media). After solidification using a cork-borer, well of 6 mm diameter was prepared in the plates and 100 µl of each complex to be tested were loaded into the wells[41]. The plates were then incubated overnight at 37°C. The Microbial growths were determined by measuring the zone of inhibition against *E. coli, P. aeruginosa, B. cereus, S. aureus and C. albicans* and controls were maintained using pure solvents instead of the extract. The zone of inhibition thus formed around each well containing the test compounds was measured accurately in mm with respect to Gentamycin. These complexes were found to be inhibitory against both Gram +ve and Gram –ve bacteria. The data revealed that Mn(II) complex has the best bactericidal properties against *P. aeruginosa* and *S. aureus* while Co(II) complex showed better activity against *B. cereus*. The mode of action of the complexes is not clear. It may involve different targets in pathogens, e.g. inhibition of cell wall synthesis and deterioration of the cytoplasmic membrane, as a result of which cell permeability may be altered leading to cell death. (**Fig. 6**).

Fig. 6: **Antibacterial and antifungal activity of complexes**



4. Conclusion

Electronic and IR spectral analysis have confirmed octahedral geometry for both the complexes. Voltammetric studies also showed the interesting results for their unusual oxidation state and also showed the heterogeneous rate constant in the order $K^0_{DMF} > K^0_{AN} > K^0_{MeOH}$ which is a good agreement between solvents and redox reaction, highest value of K^0_{DMF} is expected for the DMF solvent as it is more polar and has high value of dielectric constant compare to other used solvents. Both the complexes have shown good promise for antibacterial activity against both Gram +ve and Gram –ve bacteria.

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