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Trans $[Co(en)_2(CH_3CH_2CH_2)H_2o]^{2+}$:Synthesis, Characterization, Equilibria, Kinetics and DNA-Binding Studies

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ABSTRACT

Pseudo first order reaction kinetics and binding studies of trans-$[Co(en)_2(CH_3CH_2CH_2)H_2O]^{2+}$ complex with imidazole ,substituted imidazoles, glycine and ethyl glycine ester has been investigated using spectrophotometric technique. Equilibrium constants were determined as a function of pH at 25°c. Binding and kinetic studies were correlated based on basicity, steric hindrance. From the equilibrium data, it is found that the entering nucleophile is participating in the transition state, thereby SN^1 mechanism is proposed. The effect of the incoming ligands on the complex is studied by molecular mechanics. The interaction of trans-$[Co(en)_2(CH_3CH_2CH_2)H_2O]^{2+}$with CT DNA has been studied spectrophotometrically.

Key words: B*ioinorganicchemistry, Bioactive compounds, DNA-binding, VitaminB_{12} models*

INTRODUCTION

To understand the mechanistic aspect of coenzyme B_{12}, which actively carries many enzymatic reactions, model complexes of the coenzyme are widely studied. Much of the study with model complexes reveals that the active part of the coenzyme is the Co-C bond cleavage, which initiates the enzymatic reaction. Pentammine (methyl) cobalt (III) complex is the simplest model depicting coenzyme B_{12}[1], where four amine groups are bound to cobalt in equatorial position and one amine and a methyl group in axial positions trans to each other. Later studies on cobalamins and cobaloximes had been extensively carried out. The carbanion co-coordinated to cobalt (III) is influenced by other ligands in co-ordination with the cobalt in the cis or trans way. The cis and trans effect on the Co–C bond was reported with naturally occurring methylcobalamin[2] and various synthetic complexes such as tetrapyrroles, imines, oxime, mixed imine-oximes or amines [3-7]. The data for the *trans*-$[Co(DH)_2(CH_3)L]$ series, the ^{13}C chemical shift and ^{59}Co-^{13}C coupling constant[8] and bond distance are influenced by the *trans* ligand[9]. We have previously studied the *trans* influence in cobaloxime with varying ligands using spectrophotometric methods and molecular mechanics[10-13]. Now, we are reporting in this paper the *trans* and *cis* influence of ligands on *trans*-$[RCo(en)_2OH_2]$ based on the kinetic and binding studies.

EXPERIMENTAL SECTION

Materials ad methods

t-butylCarbazate, acetone, bromoethane, imidazole, 1-methyl imidazole,2-methyl imidazole, glycine and ethylglycine ester , histidine and histamine were purchased from *Sigma-Aldrich Chemicals*. Tetrabutyl ammonium

hydrogen sulfate (TBAHS), potassium hydroxide, magnesium sulfate, conc. HCl, cobalt nitrate, ammonia solution and methanol were obtained from *Merck*.

Synthesis of complex

Trans-$[Co(en)_2(CH_3CH_2CH_2)H_2O]^{2+}$has been prepared according to the previously available literature[1][7b][found C, 21.035; H, 6.532; N, 14.312. Calc. for $C_7N_4H_{25}O_1Co$: C, 21.010; H, 6.297; N, 14.0023 %] UV-Vis peaks at;245,306,437 as given in Fig 1;IR: 1458 (C=C), 1578 (C=N), 80 (Co–N (en)), 578 (Co–N (L))as given in Fig 2. ^{1}H –NMR as given in Fig 3, ^{13}C-NMRas given in Fig.4,LC-MS*:* m/z= 398(APCI-NEG1) in Fig.5, DTA-TG-MS in Fig 6 andmolecularmodelingstructures in Fig 9,10,11. The Propylhydrazine was prepared[14]and as it is used as an alkylating agent. The *Scheme 1* shows the synthesis.

Physical measurements

Elemental analyses (C,H and N) was performed on Flash EA 1112 series Thermofinnigon. The pH of the solution was measured by a DigisunpH meter DI-707. For the calibration of the pH meter, standard buffers of pH 4.0,7.0 and 9.2 were used. Mass spectra was recorded on LC-MS- 2010A Schimadzu with Column- C-18,Detector-UV(254) and MS probe of ESI. Infrared spectra was recorded on a Perkin –Elmer 1600 series-FTIR Spectrometer as KBr discs. NMR spectra on a Bruker ARX-300 NMR Spectrometer with D_2O as a solvent. TG8110thermal analyzer was used to record simultaneous TG,DTA,MS curves in the temperature range of 20-800^{0}c using platinum crucibles. UV-VIS spectra were recorded on a Elico BL 198model spectrophotometer with temperature control, models for molecules are drawn with the help of Hyperchem software and energies are calculated using the same software. Kinetics and binding studies were performed on a Elico SL 171 model single beam spectrophotometer.

Spectroscopic characterization

Complex was characterized by UV-Vis peaks at; 245,306,437; IR: 1458 (C=C), 1578 (C=N), 80 Co–N (en)), 578 (Co–N (L)). ^{1}H –NMR peaks at2.825(t)(CH_3), 3.12(m)(CH_2),3.14(t)(CH_2) and 2.63(t) (CH_2en) ppm, ^{13}C-NMR peaks at40.48(CH_2), 39.31(CH_3),44.5(CH_2en) ppm, and LC-MS: (APCI-NEG1) studies with column- C-18,Detector-UV(254) and MS probe of ESI shows that the calculated m/z value was matching with the recorded m/z value (m/z 398).

Thecharacterization of the structure and energies of molecular complexes are essential for understanding many biological functions. To be able to predict the strength of non covalent bonding between molecular and 3D structures of the corresponding complexes has thus been along standing goal in computational chemistry significant progress has been made in computer aided ligand design during the past decade and methodologies based on force field calculations such as Molecular Mechanics, Molecular Dynamics and Monte Carlo simulations have been important for many of these developments [28-31]. Molecular mechanistic studies were performed on complex. The optimized structure of the complex is given in Fig (9),all bond lengths and bond angles are given in table (4 & 5)

Thermal analysis

The thermal analysis curves (TG, DTA, MS) of the studied complex was shown in Fig (6). The Thermogravimetry (TG) and Differential thermal analysis curves showed a three step decomposition pattern. In the first step the on set temp (T_{on}) at 231.6^{0}c and end set temp(T_{en}) at 259.9^{0}c has been attributed to the loss of water molecule with a mass change of -17.65%. In the second step theon set temp (T_{on}) at 350.9^{0}cand end set temp(T_{en})at 387.8^{0}chas been attributed to the mass change of -12.28%. In the third step the on set temp (T_{on}) at 672.1^{0}cand end set temp (T_{en})at 743.7^{0}chas been attributed to the mass change of -21.58%. In the DTA curve, there are three peaks. The first endothermic peak appears at 249.6^{0}c, the second endothermic peak appears at 369.4^{0}c and the third endothermic peak appears at 707.9^{0}c. At the end of decomposition cobalt oxide is present.

Binding and Kinetic Studies

The binding and kinetic studies were carried out using an *Elico* single beam spectrophotometer (*SL-171* model). Spectra were recorded on ElicoBL198 Model. The concentrations were fixed at 480nm. The sample compartment temperature was maintained at25° □1°c.

Determination of Equilibrium Constant

The apparent binding constants (K_{app}) were determined for the axial ligation of *trans*-$[Co(en)_2(CH_3CH_2CH_2)H_2O]^{2+}$complex with different ligands. By taking fixed concentration of complex and by varying the ligand concentration the absorbance was recorded. Solutions containing an appropriate buffer (0.2M) to

maintain pH, KCl to maintain ionic strength (1.0M), varying concentrations of ligand are taken in a 3 ml cuvette and allowed to equilibrate in a thermostat cell holder at 25□0.1°c for 15 min prior to the addition of *trans*-$[Co(en)_2(CH_3CH_2CH_2)H_2O]^{2+}$.

Absorbance's were recorded and the apparent equilibrium constants were calculated from the plot of $\Delta A/[L]_f$ *vs*.ΔA. Thus, for each ligand K_{app} was calculated using *Eq. 1*.

$$\Delta A = \Delta A_{max} [L]_f / (1/K_{app} + [L]_f) \text{ ---------- (1)}$$

The least square fit of the above equation after rearrangement is given by *Eq. 2*:

$$\Delta A = \Delta A_{max} - \{1 / K_{app} (\Delta A / [L]_f)\} \text{ ---------- (2)}$$

Where ΔA = difference in absorbance between solutions containing only complex with and without ligand.

ΔA_{max} = maximum difference in absorbance recorded at high ligand concentration.

$[L]_f$ = the unbound ligand concentration and is calculated from *Eq. 3*

$$[L]_f = [L]_T - (C_T \Delta A / \Delta A_{max}) \text{ ---------- (3)}$$

$[L]_T$ = the total volume of ligand added

C_T = the total concentration of *trans*-$[Co(en)_2(CH_3CH_2CH_2)H_2O]^{2+}$

The pH independent equilibrium constants are then calculated from *Eq. 4*:

$$K_{eq} = K_{app} / a_L \text{ ---------- - (4)}$$

Where a_L (fraction of ligand as free base) was calculated from *Eq. 5*:

$$a_L = K_a / (K_a + [H^+]) \text{ ---------- (5)}$$

Kinetic Studies

Wehave investigated the ligand substitution reactions of *trans*-$[Co(en)_2(CH_3CH_2CH_2)H_2O]^{2+}$with imidazole, substituted imidazoles at 25°c. The reaction rates were determined by maintaining pseudo-first order conditions by taking 10-fold excess of ligand concentration with respect to the complex concentration. The kinetics was studied by varying the concentration of the ligand at 486nm and using appropriate buffer at pH below the pK_a of the ligand. The absorbance was monitored at λ_{max} 480 nm.

The first order rate constants (k_{obs}) are obtained by least square fits of the data to *Eq. 6* below.

$$\ln A_t - \ln A\infty = k_{obs} t \text{ ---------- (6)}$$

Where $A_t$is the absorbance at time't' and $A\infty$ is the final absorbance.

RESULTS AND DISCUSSION

The ligand substitution reactions of *trans*-$[Co(en)_2(CH_3CH_2CH_2)H_2O]^{2+}$with imidazole, substituted imidazoles,histidine, histamine, glycine and ethyl glycine esterare given . The UV-Vis scan of *trans*-$[Co(en)_2(CH_3CH_2CH_2)H_2O]^{2+}$is given in *Fig. 1*. Depending on the pK_a values of the ligands, the binding studies are made in the pH range above and below the pK_a values. The K_{app} values were determined as a function of pH by spectrophotometry. The dependence of logK_{app} for ligation of *trans*-$[Co(en)_2(CH_3CH_2CH_2)H_2O]^{2+}$with different ligands upon pH is given in *Fig. 7* and the data given in *Table 1*. Up to pK_a of the ligand, the log K_{app} increases with pH but above pK_a the log K_{app} is independent of pH. It is observed that the K_{app} value below the pK_a value is very low due to the protonation of the ligand and as the pH increases, ligand gets deprotonated and binds strongly to Co

(III) and K_{app} increases. The Keq values for the binding of Imidazoles to $[Co(en)_2(CH_3CH_2CH_2)H_2O]^{2+}$follow the order:

1-MeIMD > IMD > 2-MeIMD

Where as the binding of aminoacids follow the order

Glycine>Glycine ethyl ester

The stability order can be explained by considering the HSAB principle, basicity of ligands and their ability of π-bonding and σ-donation. Considering imidazole series for 1-MeIMD and IMD the formation constants are high for higher pK_a values*i.e.* they follow the basicity order. Though 2-Me-Imidazole is more basic than Imidazole, the Keq is smaller. This can be attributed to the steric hindrance due to the preference of methyl group at C_2position. Among glycine and glycine ester, both are σ-donors but glycine has more binding constant as it is more basic than ethyl glycine ester. Though amino acids are more basic than Imidazoles they form less stable complexes. The stability order of Imidazoles is attributed to the ability of imidazoles to bind with Co(III) through d_{Π}-p_{Π} back bonding. Glycine and ethyl glycine ester are only σ donors,cannot accept electrons in a similar way.

The rate of ligand substitution is pH dependent. The rate of the reaction increases drastically near the pK_a of the ligand. The slope of the plot of k_{obs}*vs.* concentration of the ligands is given in Fig (8) and the data for the plot is given in *Table 2*. The comparison of second order rate constantk_{on}' at a given pH is given in table 3.

The slopes of the least square fit of the *Eq. 7* gives the second order rate constant.

$$k_{obs} = k_{on}'[L]_T + k_{off} \quad \text{----------} \quad (7)$$

$[L]_T$ =Total ligand concentration

The pH independent second order rate constants, k_{on} are obtained by using the *Eq. 8.*

$$k_{on} = k_{on}' / a_L \quad \text{----------} \quad (8)$$

The second order rate constants increase as the nucleophilicity of the ligand increases. This is in accordance with the order of K_{eq} values. The kinetics of substitution of the axial base in alkylcobaloximes and related cobalt complexes has been studied under a variety of conditions[15,16]. The studies on cobalt complexes and adenosylcobaloxime provide evidences for the mechanism of substitution to be dissociative[16,17] (Id or D). In view of the evidence presented above, for the existence of pentacoordinate alkylcobaloximes and the ligation kinetic studies of others, both on alkyl cobalt complexes and on cobaloxime complexes [18,19] with other equatorial ligand system[20], an SN1 mechanism may be suggested.

Molecular Mechanistic Studies

The structural investigation of coordination and organometallic chemistry has been advanced using molecular mechanics[21-24]. Using MM2 parameterization, the optimized structure was deduced using Hyperchem software in*Fig.9* shows ball and stick representation of complex.The optimized structure of Complex with imidazole has been given in Fig 10, the Complex with Glycine has been given in Fig 11. Bond lengths and bond angles are given in tables 4 & 5.

DNA Binding. Absorption Spectral Studies

The application of electronic absorption spectroscopy in DNA-binding studies is one of the most useful techniques[25, 26] metal complex binding with DNA through groove mode usually results in hypochromism and bathochromism, due to the groove mode involving a strong stacking interaction between an aromatic chromophore and the base pairs of DNA. The extent of the hypochromism commonly parallels the groove binding strength. The absorption spectra of the complex in absence and presence of calf thymus DNA using *Tris* buffer are illustrated in *Fig. 12* . In the UV region, the intense absorption bands observed in Co(III) complexes are attributed to intraligand d_{Π}–p_{Π}transition of the coordinated groups. Addition of increasing amounts of CT DNA results in hypochromism and moderate bathochromic shift in the UV spectra of the complex -$[Co(en)_2(CH_3CH_2CH_2)H_2O]^{2+}$. These spectral data

may suggest a mode of binding that involves a stacking interaction between the complex and the base pairs of DNA. In order to quantitatively compare the binding strength of the two complexes, the intrinsic binding constants *K* of the complexes with CT DNA were determined according to the following equation [27] through a plot of [DNA] / ($å_b$-$å_f$) *vs.* [DNA] (*Eq. 9*).

[DNA] / ($å_a$ – $å_f$) = [DNA] / ($å_b$ – $å_f$) + 1/(K ($å_b$ – $å_f$)) (9)

Where [DNA] is the concentration of DNA in base pairs, the apparent absorption coefficient $å_a$, $å_f$ and $å_b$ correspond to A_{obs} / [Co], the extinction coefficient for the cobalt complex in the free and fully bound form, respectively. In plots DNA] / ($å_b$-$å_f$) *vs.* [DNA]. *K* is given by the ratio of slope to intercept. DNA binding constant*K* was about 1.6 x 10^4 Mrespectively from the decay of the absorbance. The binding constants indicate that the complex binds more strongly.

Fluorescence Studies

The complexes can emit luminescence in Tris buffer (pH 7.0) with the emission maxima at 619nm. Binding of complexto DNA was found to increase the fluorescence intensity. The emission spectra of complex in the absence and presence of CT DNA are shown in Fig 13. The plots of the emission quenching intensity versus the ratio of [DNA]/[Co] are also inserted in Fig 14. Upon addition of CT DNA, the emission intensity increases steadily. The increase in emission intensity of complex is that these results were strengthened by viscosity studies.

Table1: Formation constants(K_{app}) for the axial ligation of the aqua bis (ethylene diamine) propyl cobalt(III) complex by different ligands at 25^0 C for different pH Values

pH	1-MeImd	Imd	2-MeImd	Gly	Gly-OEt	Hist	Histmn
5.0			–	–		1.27	1.09
5.5			–	–			1.57
6.0	1.456	1.32	0.563		0.556	2.1	1.96
6.5	1.916	1.77	1.052		1.044	2.34	2.26
7.0	2.312	2.144	1.521		1.484	2.4	2.42
7.5	2.59	2.39	1.93	0.203	1.832	2.5	2.5
8.0	2.735	2.512	2.225	0.697	2.05	2.52	2.5
8.5	2.793	2.56	2.38	1.153	1.145	2.52	2.5
9.0	2.813	2.57	2.45	1.635	2.18	2.53	2.5
10.0	2.821	2.58	2.48	2.26	2.2	2.53	2.5
11.0	2.823	2.58	2.48	2.424		2.53	2.5
K_{eq}	664.31	381.54	304.51	280	158	336.88	328.68

Table 2 : Dependence of the rate constants (k_{obs}) for the axial ligation of aqua bis(ethylene diamine) propyl cobalt(III) on the concentration of the ligand at 25^0 C

	M/L	1-MeImd	Imd	2-MeImd	Gly	Gly-Oet	Hist	Histmn
k_{obs} (S^{-1})	1:50	2×10-5	1×10-5	2×10-5	2×10-5 (1:10)	2×10-5 (1:10)	2×10-5 (1:10)	2×10-5 (1:10)
	1:100	2×10-5	2×10-5	2×10-5	3×10-5 (1:20)	2×10-5 (1:20)	2×10-5 (1:20)	2×10-5 (1:20)
	1:150	2×10-5	3×10-5	6×10-5	7×10-5 (1:30)	2×10-5 (1:30)	2×10-5 (1:30)	2×10-5 (1:30)
	1:200	5×10-5	3×10-5	8×10-5	9×10-5 (1:50)	5×10-5 (1:50)	4×10-5 (1:50)	4×10-5 (1:50)
$k_{on'}$		$3.62x10^{-4}$	$3x10^{-4}$	$2.3x10^{-4}$	$9x10^{-5}$	8×10-5	$2.82x10^{-4}$	$2.64x10^{-4}$
pH		7.5	7.5	7.5	11.0	8.0	9.0	9.0
α		0.586	0.645	0.28	0.948	0.707	0.856	0.856
k_{on} ($dm^3mol^{-1}sec^{-1}$)		$6.17x10^{-4}$	$4.65x10^{-4}$	$8.2×10^{-4}$	$9.5×10^{-5}$	$1.1×10^{-4}$	$3.3x10^{-4}$	$3.1x10^{-4}$

Table 3 : Comparison of second order rate constants k_{on} for the formation of $[CH_3CH_2CH_2Co(en)_2OH_2]^{2+}$at 25^0C obtained from trans aquo and amino cobalt (III) complex.

Complexes	1-MeImd	Imd	2-MeImd	Gly	Gly-Oet	Hist	Histmn
$[CH_3CH_2CH_2Co(en)_2OH_2]^{2+}$	$6.17x10^{-4}$	$4.65x10^{-4}$	$8.2×10^{-4}$	$9.5×10^{-5}$	$1.1×10^{-4}$	$3.3x10^{-4}$	$3.1x10^{-4}$

Table- 4: Bond lengths of $[CH_3CH_2CH_2Co(en)_2L]^{2+}$

Complex		Imidazole	1-Me-Imidazole	2-Me-Imidazole	Glycine	Ethyl glycine ester	Histidine	Histamine
$[CH_3CH_2CH_2Co(en)_2OH_2]^{2+}$	Co_1- N_2	2.2421	2.17804	2.2869	1.9005	1.9112	2.19146	1.88312
	Co_1- N_3	2.05996	2.20704	2.2047	1.9112	1.88635	2.0337	1.8859
	Co_1- N_4	2.32152	2.08436	1.92763	1.9092	1.8838	2.0676	1.9009
	Co_1- N_5	1.8615	1.72366	1.92579	1.9041	1.89938	1.8622	1.9012
	Co_1- C_{10}	2.11777	2.1604	2.26403	1.9642	1.9667	2.0968	1.95606
	Co_1- N_{13}	2.33593	2.1604	2.3734	1.8495	1.8962	1.9053	2.3756
	C_6- N_2	1.5252	1.4939	1.5492	1.4792	1.46720	1.52573	1.4678
	C_7- N_3	1.5438	1.46364	1.54518	1.4688	1.4681	1.5403	1.4678
	C_8- N_4	1.62573	1.56896	1.5022	1.4717	1.47107	1.5745	1.4691
	C_9- N_5	1.49938	1.72434	1.53297	1.4712	1.4747	1.66001	1.4638
	C_6- C_7	1.50174	1.8443	1.49789	1.5263	1.49767	1.8587	1.5054
	C_8- C_9	1.55662	1.3727	1.58613	1.532	1.50315	1.5544	1.4999
	C_{10} -C_{11}	1.61806	1.0804	1.67774	1.5532	1.5313	1.5902	1.5368
	C_{11} -C_{12}	1.5863	1.58446	1.61282	1.5424	1.5319	1.5821	1.53035

Table- 5: Bond angles of $[CH_3CH_2CH_2Co(en)_2L]^{2+}$

Complex		Imidazole	1-Me- Imidazole	2-Me-Imidazole	Glycine	Ethyl glycine ester	Histidine	Histamine
$[CH_3CH_2CH_2Co(en)_2OH_2]^{2+}$	4-1-8	72.5564	51.9972	166.254	85.2259	50.0819	70.822	72.72
	5-1-9	35.093	85.8293	37.703	85.4454	66.6631	81.7452	84.992
	8-4-1	118.554	124.958	126.239	110.93	110.853	127.503	123.202
	1-5-9	144.798	122.872	165.364	112.255	111.487	125.273	109.11
	6-2-1	125.121	141.69	123.24	113.607	112.014	128.453	111.634
	7-3-1	124.499	144.923	129.043	110.844	112.014	126.621	110.311
	4-8-9	106.009	98.1917	106.57	109.885	102.085	98.978	106.693
	5-9-8	65.1412	108.149	68.3373	104.673	104.78	106.502	105.50
	2-6-7	103.639	102.803	106.57	110.526	101.061	101.377	111.908
	3-7-6	114.184	98.5872	113.964	107.153	115.231	112.728	104.33
	10-1-13	157.949	159.784	166.254	129.991	159.87	150.721	115.908

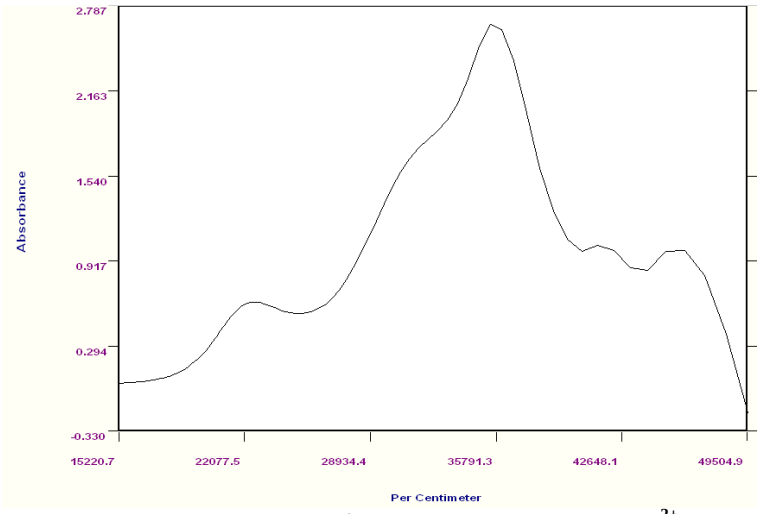

Fig 1:U.V.Visible scan of $[CH_3CH_2CH_2Co(en)_2OH_2]^{2+}$

This observation is further supported by the emission quenching experiments using $[Fe(CN)_6]^{4-}$ as a quencher. The ion $[Fe(CN)_6]^{4-}$ has been shown to be able to distinguish differentially bound cobalt (III) species and positively charged free complex ions. The complex binding to DNA can be protected from the quencher, because highly negatively charged $[Fe(CN)_6]^{4-}$ would be repelled by the negative DNA phosphate backbone, hindering quenching of the emission of the bound complex. The method essentially consists of titrating a given amount of DNA-metal complexes with increasing concentrations of $[Fe(CN)_6]^{4-}$ and measuring the change in fluorescence intensity. The

ferro-cyanide quenching curves of the complex in the presence and absence of CT DNA are shown in Fig (14). The absorption and fluorescence spectroscopy studies determine the binding of complexes with DNA.

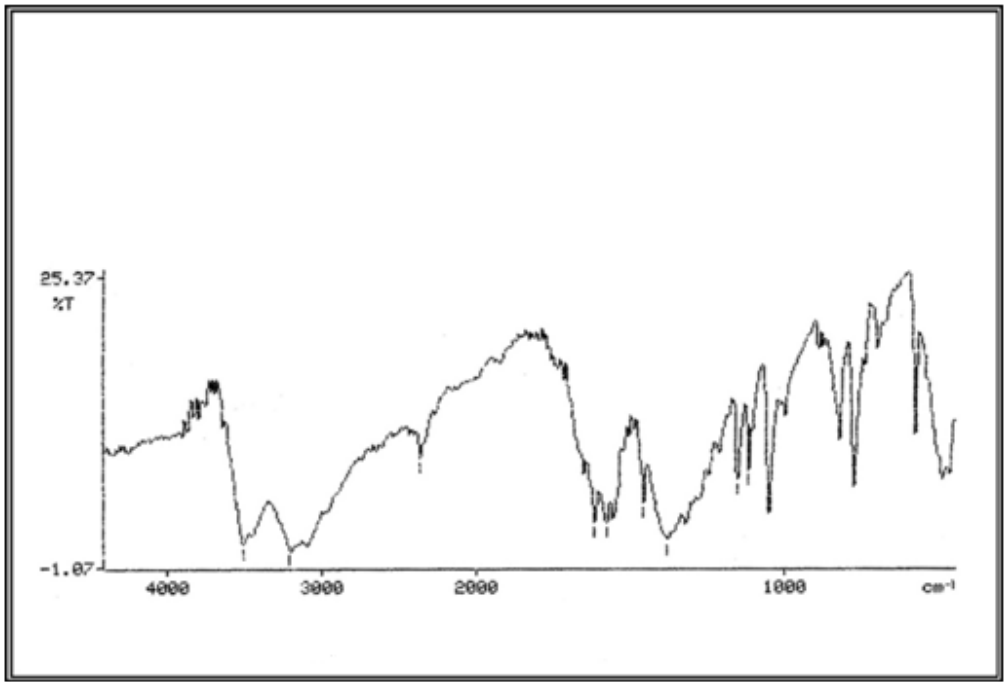

Fig2: IR Spectrum of $[CH_3CH_2CH_2Co(en)_2OH_2]^{2+}$

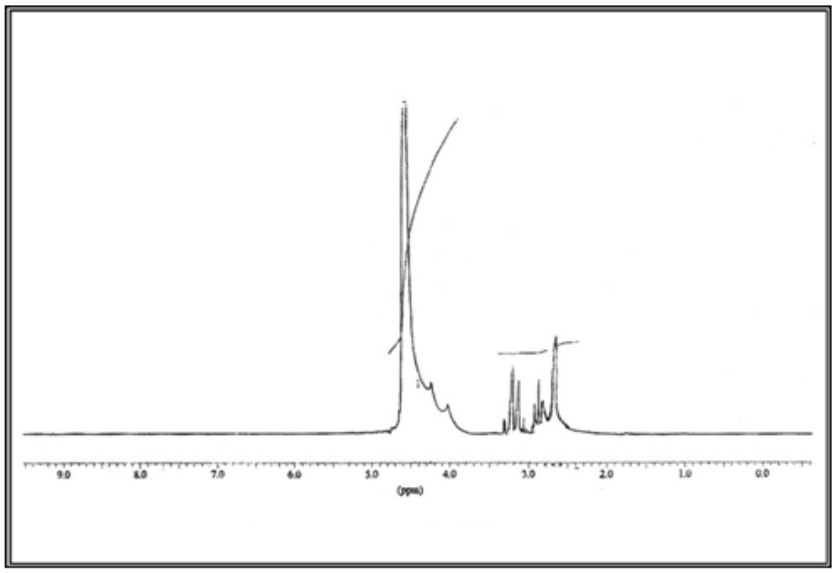

Fig3: ^{1}H NMR Spectrum of $[CH_3CH_2CH_2Co(en)_2OH_2]^{2+}$

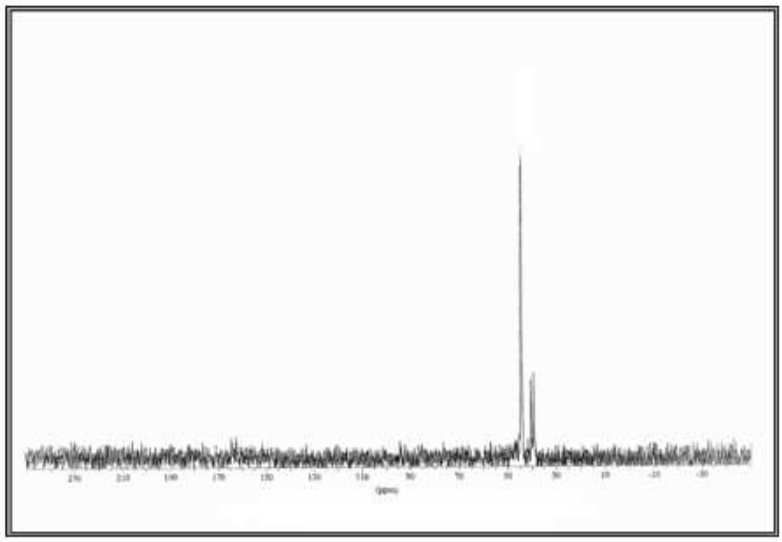

Fig 4 : ^{13}C [^{1}H] NMR Spectrum of $[CH_3CH_2CH_2Co(en)_2OH_2]^{2+}$

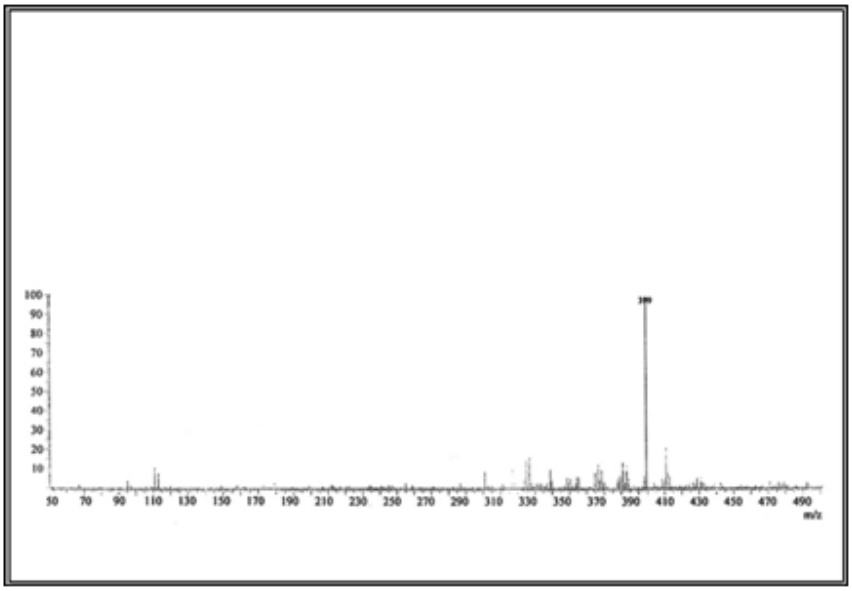

Fig 5 : LC- MS Spectrum of $[CH_3CH_2CH_2Co(en)_2OH_2]^{2+}$

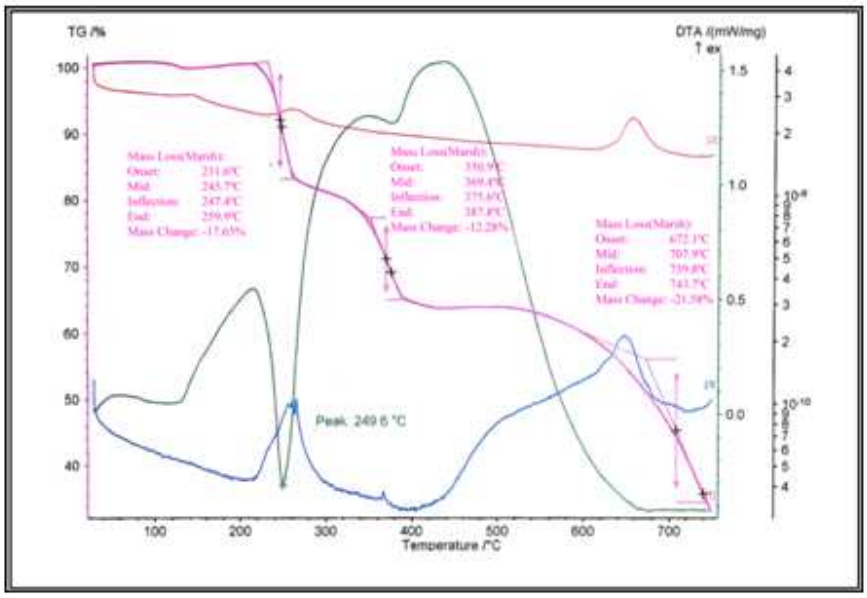

Fig 6 : Thermogram of$[CH_3CH_2CH_2Co(en)_2OH_2]^{2+}$

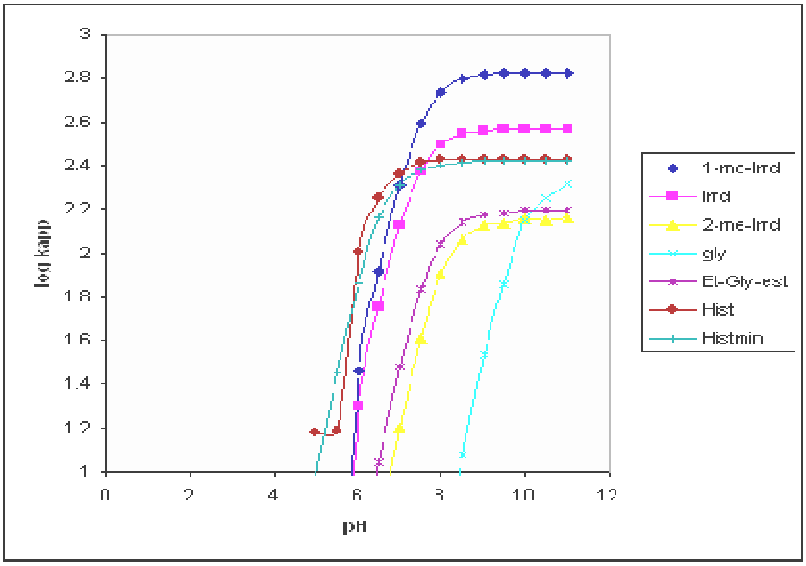

Fig 7: Dependence of formation constants ($logK_{app}$) on the pH for the axial ligation of trans-$[CH_3 CH_2CH_2 Co(en)_2H_2O]^{2+}$ by different ligands (L) at 25^0C in aqueous solution, ionic strength 1.0 M KCl.

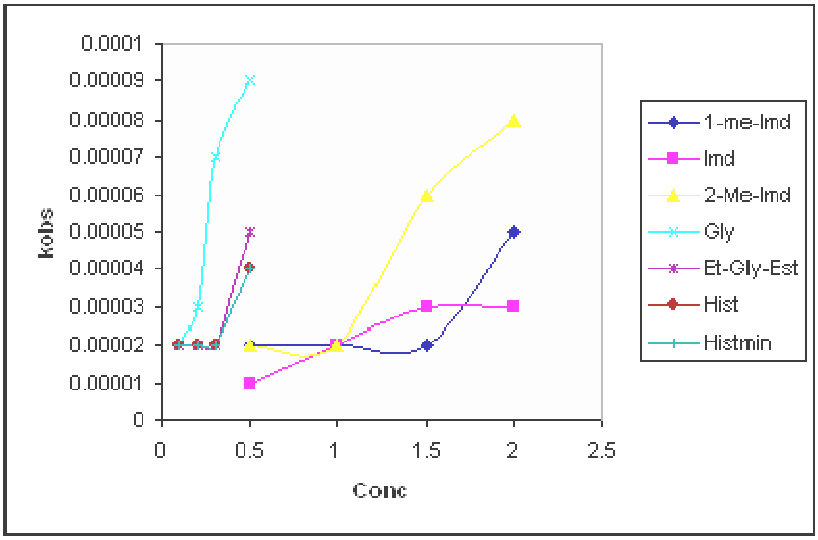

Fig 8: Dependence of the Rate Constants (k_{obs}) for the Axial Ligation of trans- $[CH_3CH_2CH_2Co(en)_2H_2O]^{2+}$ on the Concentration of different ligands (L) at 25^{0}C in aqueous solution, ionic strength 1.0 M KCl.

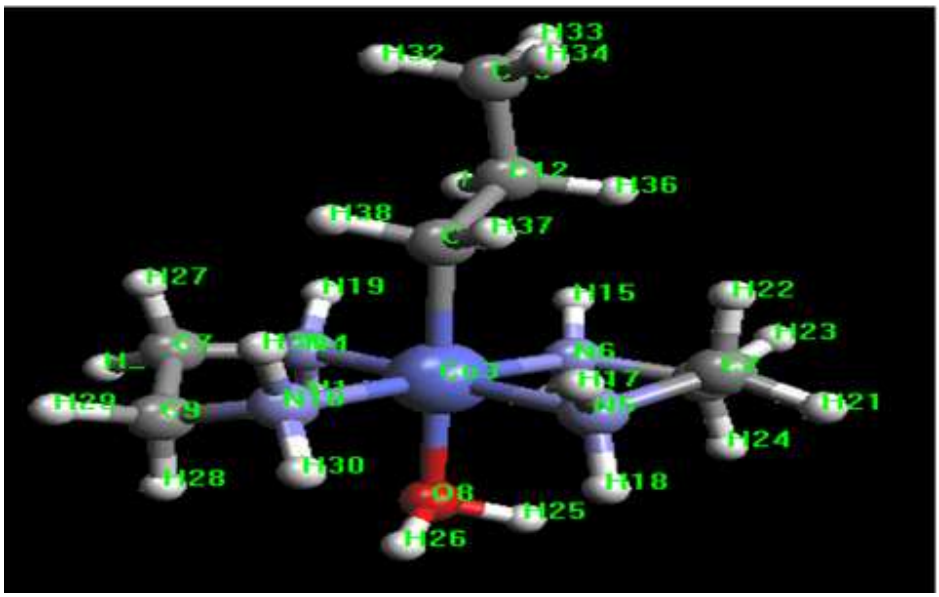

Fig. 9: Aqua bis (ethane -1,2-diamine) propyl Cobalt (III) complex

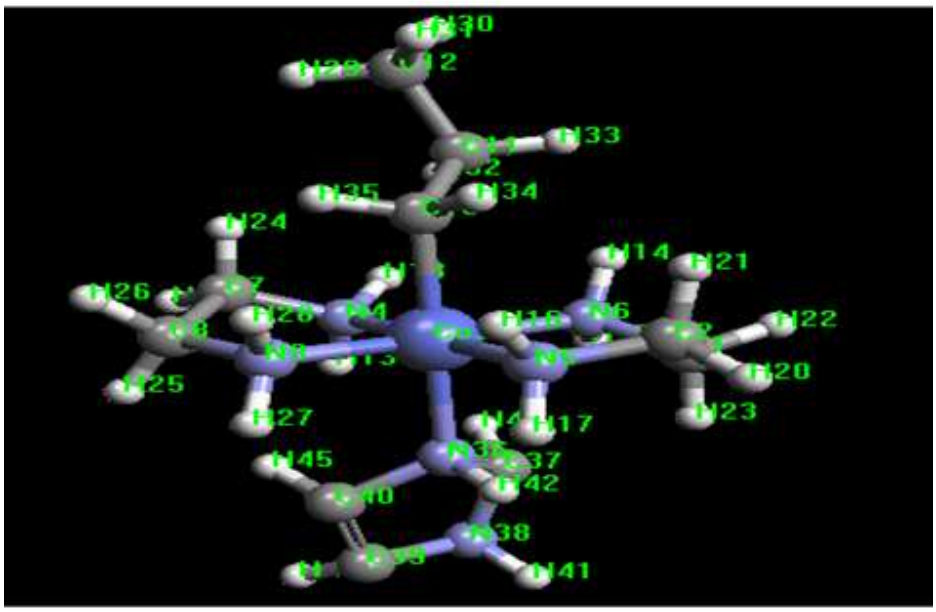

Fig 10: Imidazole (ethane – 1,2-diamine) propyl Coblat(III) Complex

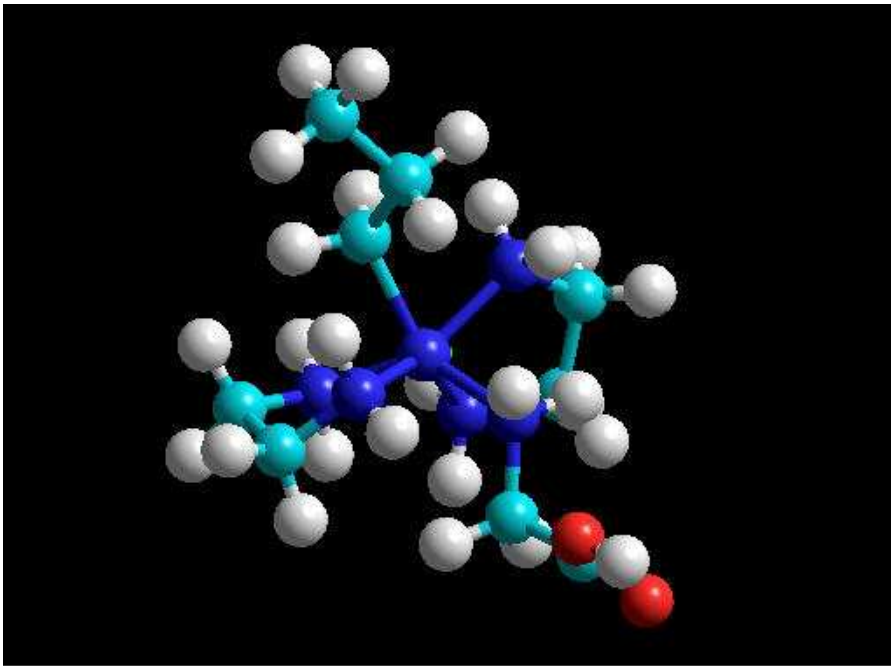

Fig 11: Glycine (ethane – 1,2-diamine) propyl Coblat(III) Complex

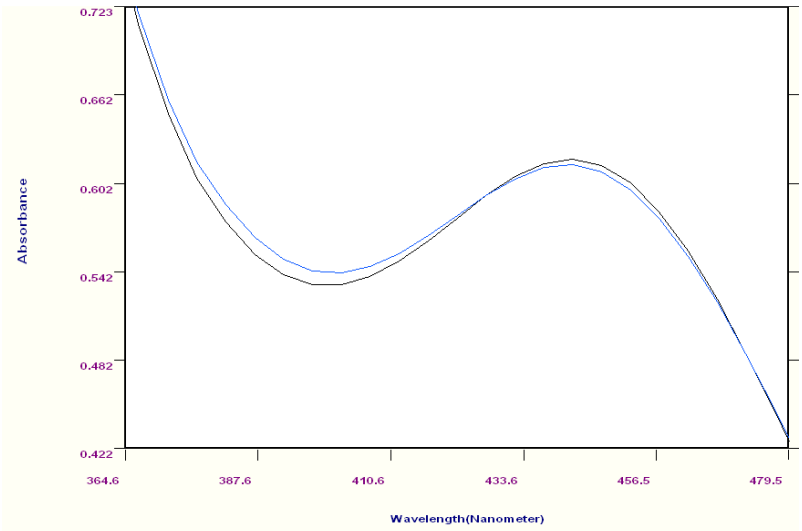

Fig - 12 U.V.Visible scan of DNA binding of $[CH_3\,CH_2CH_2\,Co(en)_2H_2O]^{2+}$

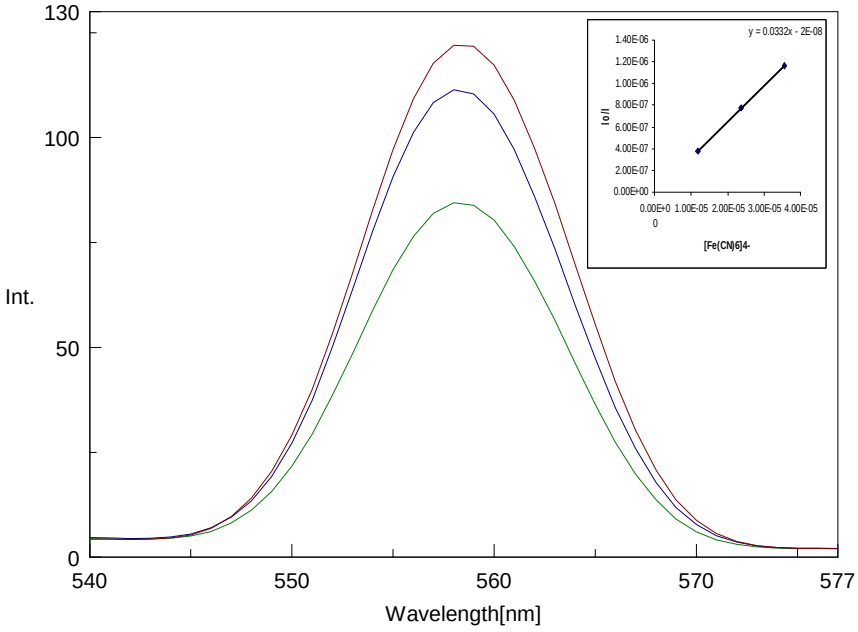

Fig -13:Fluorescente emisión spectra of complex$[CH_3\,CH_2CH_2\,Co(en)_2H_2O]^{2+}$ in aqueous buffer.

Tris 5mM, NaCl 50mM, pH 7.0) in the presence of CT DNA, [Co] = 20μM, [DNA] / [Co] 0,5,10,15,20 (The arrow shows the intensity changes upon increasing concentration. Inset: Plots of relative integrated emission intensity vs [DNA] / [Co].

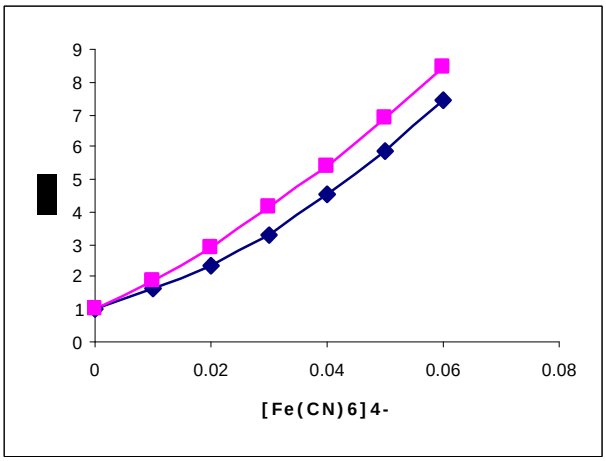

Fig 14 :Emission quenching curves of $[CH_3CH_2CH_2Co(en)_2H_2O]^{2+}$in the absence ofof DNA (upper) and presence of DNA (lower)

CONCLUSION

The ligand substitution reactions were studied by different ligands on *trans*-aquo bis(ethylenediamine)Propyl cobalt(III) andfollowthe basicity order

1-MeIMD>IMD>2-MeIMD>glycine>glycine ethyl ester.

The binding and kinetic constants varied with the incoming nucleophile suggesting that the nucleophile is taking part in the transition state. Thus, Id mechanism is suggested. The DNA binding studies suggests that the complex binds with CTDNA.

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