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A comprehensive kinetic study on interaction of Co (II) with d-2, 2-(Ethylenediimino)-di- 1-butanol

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Abstract

Kinetics of complexation of Co(II) with d-2,2-(Ethylenediimino)-di-1-butanol has been investigated at 25, 30, 35 and 40± 0.05 °C in the pH range 6.04 -7.19 using Aminco Morrow Stopped Flow Spectrophotometer. The ionic strength was maintained at 0.1 M KNO_3. Kinetic results indicate that the ligand is not involved in the rate determining step which is, in fact, associated with the release of a water molecule from the shell of the metal ions prior to complexation with the ligand. The anionic form of d-2, 2-(Ethylenediimino)-di-1-butanol is more reactive and the protonated form interacts only to a small extent. The values of enthalpy of activation, entropy of activation corresponding to stepwise rate constants have been evaluated. The energy of the molecule and heat of formation were also calculated. A mechanism consistent with the kinetic data has been suggested.

Keywords: Complexation, Rate constant, Activation parameters, Energy of the molecule, Heat of formation

Introduction

d-2, 2-(Ethylenediimino)-di-1-butanol (ethambutol) is a synthetic compound and is used in the treatment of tuberculosis. Its antibacterial spectrum is limited to mycobacteria and only growing cells are affected by inhibiting mycobacterial RNA synthesis. Like EDTA, it is a good chelating agent [1-5]. Its prolonged administration affects the body copper, cobalt, iron and zinc reserves. So it is of interest to examine the effect of d-2, 2-(Ethylenediimino)-di-1-butanol on our plasma model. To understand these vital processes and steps of metal binding to the ligand, it was thought desirable to carry out a comprehensive kinetic study on the interaction of Co(II) with d-2, 2- (Ethylenediimino)-di-1-butanol. Therefore, the kinetics of complexation of metal ions Co(II) by d-2,2-(Ethylenediimino)-di-1-butanol would no doubt give important information regarding the types of interaction of these ions with d-2,2-(Ethylenediimino)-di-1-butanol and the clearance of d-2,2-(Ethylenediimino)-di-1-butanol in the form of metal – ligand complex through the animal body[6-7]. With the hope that these anomalies might have rational explanation and to understand the biological processes clearly, a comprehensive kinetic study has been undertaken on the reaction of Co(II) with d-2,2-(Ethylenediimino)-di-1-butanol.

Materials and Methods

d-2, 2-(Ethylenediimino)-di-1-butanol (Themis Chemicals), bromothymol blue (Loba) and $NaClO_4$ (Ferak) were used as such. Other chemicals used were of A.R. grade. The pH of ligand solution and metal ion solution was adjusted to same value using 2, 6-lutidine (Merck Schuchardt) and HCl. However, a slight change in pH value (~ 0.05 units) was observed after mixing of two solutions. The final pH was recorded from Radiometer pH meter, *pH* M26. pH's reported are those of reaction mixtures. The temperature of the system was maintained by immersion type thermostat (German NBE model). The kinetic runs were made on Aminco Morrow stopped flow spectrophotometer under pseudo first order conditions, i.e., [Co(II)] >>[d-2,2-(Ethylenediimino)- di-1-butanol] at 620nm by pH indicator method. This was desirable as very small changes in absorbance values were observed at 620nm in the absence of the indicator. Under the *pH* indicator method, nickel nitrate, 10^{-2}M, buffer 10^{-2}M Lutidine and, μ= 0.l M $NaClO_4$ was mixed with ligand solution containing indicator bromothymol blue ~ 10-5M.

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Blank experiments in which (i) indicator and ligand solutions and (ii) indicator and metal ion solutions were mixed showed no absorbance change to interfere with the results. The traces from the oscilloscope gave excellent first order plots, from which second order rate constants *(k_{obs})* were computed by the relation

k_{obs} = k'obs[M(II)] (i)

where k'obs is the pseudo first order rate constant.

Results and Discussion

The kinetics of complexation of Co(II) – d-2,2-(Ethylenediimino)-di-1-butanol was found to be of first order in cobalt ion, which was taken in large excess over ligand to ensure pseudo-first order conditions and complete formation of mono complex only [8-9]. As protonated form of the ligand predominates in the pH range 6-7(pK_{a2} = 9.49), the kinetic study of interaction has been made in the pH range 6.04 -7.19 at ionic strength 0.1M KNO_3 and at temperatures 25, 30, 35 and 40± 0.05 °C, under the condition [Co(II)] >> [d-2,2-(Ethylenediimino)-di-1-butanol]. Oscilloscope traces of voltage versus time were used to determine the values of pseudo-first order rate constants (k'obs), and these were further utilized to evaluate the values of second order rate constants (k_{obs}), using equation (i). These rate constants are tabulated in Table 1.

Table 1: First order and Second order rate constants for the complexations of Co (II) with d- 2,2- (Ethylenediimino)-di-1-butanol at different pH's and temperatures
I = 0.1 M KNO_3 [Co(II)] = 5.56 x 10-2 M
[Ethambutol] = 5.02 x 10-3 M

Temp. (± 0.05 °C)	**pH**	**k'obs x 10-1(s-1)**	**k_{obs} x 10^{-2} (M-1s-1)**	**Temp. (± 0.05 °C)**	**pH**	**k'obs x 10-1(s-1)**	**k_{obs} x 10^{-2} (M-1s-1)**
25	6.09	1.18	2.13	35	6.04	2.44	4.39
25	6.41	2.22	3.99	35	6.45	4.18	7.51
25	6.65	3.62	6.52	35	6.66	5.73	10.3
25	6.86	5.95	10.7	35	6.84	8.78	15.8
25	7.03	8.56	15.4	35	6.97	10.9	19.6
25	7.13	10.4	18.7	35	7.07	13.7	24.7
25	7.19	12	21.5	35	7.16	16.7	30
30	6.17	2.15	3.86	40	6.16	4.16	7.48
30	6.38	2.89	5.21	40	6.45	5.3	9.52
30	6.62	4.54	8.17	40	6.59	7.61	13.7
30	6.83	6.83	12.3	40	6.89	12	21.5
30	7	9.73	17.5	40	7.02	15.9	28.7
30	7.1	12.6	22.6	40	7.14	20.2	36.4
30	7.18	14.8	26.7				

The rate equation for Co(II) – d-2,2-(Ethylenediimino)-di-1-butanol interaction can be written as

Rate = -d/dt[Co(II)]
= -d/dt[d-2,2-(Ethylenediimino)-di-1-butanol]
= k_{obs} [d-2,2-(Ethylenediimino)-di-1-butanol] (ii)
= k'obs [d-2,2-(Ethylenediimino)-di-1-butanol] (iii)

Where k'obs= k_{obs} [Co(II)]

Dissociation equilibria of d-2,2-(Ethylenediimino)-di-1-butanol can be represented as

$$-O-N^+H_2-N^+H_2-O^- \overset{K_2}{\rightleftharpoons} {}^-O-NH-NH-O^- \qquad (iv)$$

From equation (iv), equation (iii) reduces to

Rate = k'obs {[-O-N+H2-N+H2-O-] + [-O-NH-NH-O-]} (iv')

Where -O-N+H2-N+H2-O- represent the protonated form and $^-$O-NH - NH-O- represents the deprotonated form of the ligand. The plots of $K_{obs}\{[H^+]^2 + K_1[H^+] + K_1K_2\} / K_1[H^+]$ versus $[H^+]^{-1}$ at 25, 30, 35 and 40±0.05 °C were found to be linear as shown below (Fig 1).

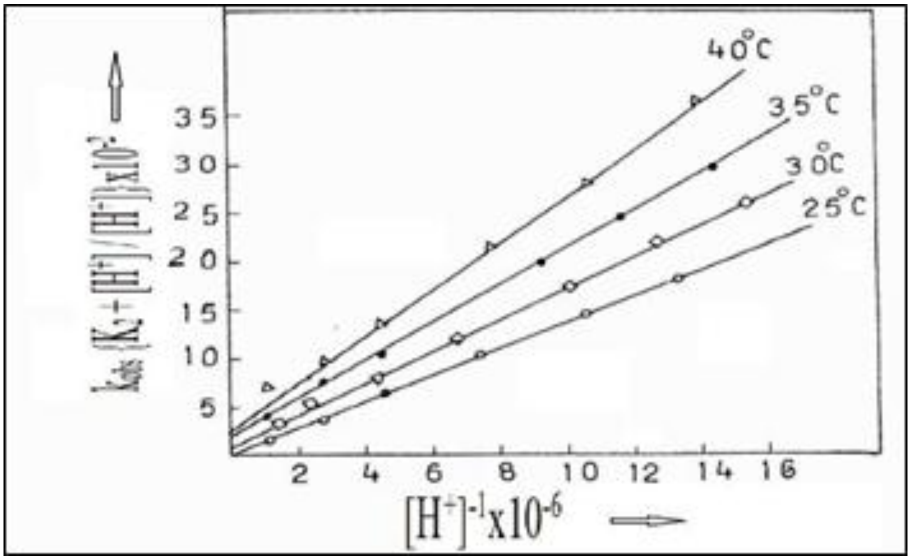
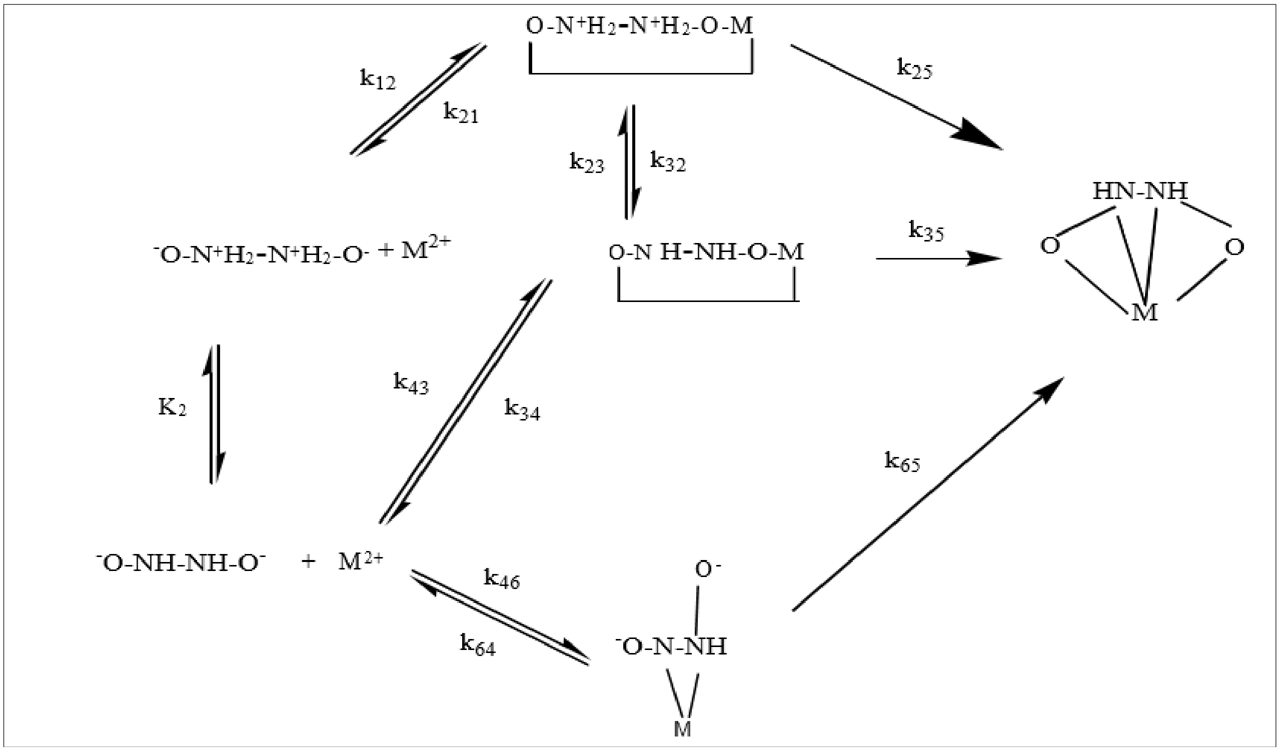


Fig 1: Variation of k_{obs} $\{K_2 + [H^+] / [H^+]$ versus $[H^+]^{-1}$ for Co(II) - d-2,2- (Ethylenediimino)-di-1-butanol interaction at different temperatures

Of the various plausible schemes, the following scheme 1 for complexation of Co(II) with d-2,2- (Ethylenediimino)-di-1-butanol, which could explain linearity of the curves was suggested:



Scheme 1

The rate of the reaction can be written as

$$\text{Rate} = k_{25}[\underbrace{O\text{-}N^+H_2\text{-}N^+H_2\text{-}O\text{-}Co}] + k35[\underbrace{O\text{-}NH\text{-}NH\text{-}O\text{-}Co}] + k65\ [\text{-}O\text{-}\underset{\overset{|}{Co}}{NH}\text{-}NH\text{-}O\text{-}] \quad (v)$$

Steady state approximation for species

$\underline{[O\text{-}NH\text{-}NH\text{-}O\text{-}Co]}$ and $[^{-}O\text{-}NH\text{-}\underset{Co}{N}H\text{-}O^{-}]$ can be written as

$$\frac{d}{dt}[\,\underline{[O\text{-}N^{+}H_2\text{-}N^{+}H_2\text{-}O\text{-}Co]} = k_{12}[Co(II)][^{-}O\text{-}N^{+}H_2\text{-}N^{+}H_2\text{-}O^{-}] + k_{32}[H^{+}]^2\underline{[O\text{-}NH\text{-}NH\text{-}O\text{-}Co]}$$

$$- (k_{21}+k_{23}+k_{25})\underline{[O\text{-}N^{+}H_2\text{-}N^{+}H_2\text{-}O\text{-}Co]} = 0 \qquad \text{(vi)}$$

$$\frac{d}{dt}\underline{[O\text{-}NH\text{-}NH\text{-}O\text{-}Co]} = k_{43}[Co(II)][^{-}O\text{-}NH\text{-}NH\text{-}O^{-}] + k_{23}\underline{[O\text{-}N^{+}H_2\text{-}N^{+}H_2\text{-}O\text{-}Co]}$$

$$- k_{32}\underline{[O\text{-}NH\text{-}NH\text{-}O\text{-}Co]}[H^{+}]^2 - k_{34}\underline{[O\text{-}NH\text{-}NH\text{-}O\text{-}Co]}$$

$$- k_{35}\underline{[O\text{-}NH\text{-}NH\text{-}O\text{-}Co]} = 0 \qquad \text{(vi')}$$

$$\frac{d}{dt}[[^{-}O\text{-}NH\text{-}\underset{Co}{N}H\text{-}O^{-}] = k46[Co(II)][^{-}O\text{-}NH\text{-}NH\text{-}O^{-}] - (k65 + k64)[^{-}O\text{-}\underset{Co}{N}H\text{-}NH\text{-}O^{-}] = 0 \qquad \text{(vii)}$$

Assuming the two proton equilibria to be very fast, i.e.

$k_{23}/k_{32} = \underline{[O\text{-}NH\text{-}NH\text{-}O\text{-}Co]}[H^{+}]^2 / \underline{[O\text{-}N^{+}H_2\text{-}N^{+}H_2\text{-}O\text{-}Co]} = 1/K_2$

$K2 = [^{-}O\text{-}NH\text{-}NH\text{-}O^{-}][H^{+}]^2 / [^{-}O\text{-}N^{+}H2\text{-}N^{+}H_2\text{-}O^{-}]$ (viii)

Substituting the value of $O\text{-}N^{+}H_2\text{-}N^{+}H_2\text{-}O\text{-}Co$ from the above equation (viii) in equation (v), we get

$$Rate = \{k_{25}k_{32}[H^{+}] / (k_{23} + k_{35})\}\ \underline{[O\text{-}NH\text{-}NH\text{-}O\text{-}Co]} + k_{65}[^{-}O\text{-}NH\text{-}NH\text{-}\underset{O^{-}}{Co}] \qquad \text{(xi)}$$

Similarly substituting the value of $\underline{O\text{-}N^{+}H_2\text{-}N^{+}H_2\text{-}O\text{-}Co}$ from equation (viii) in equation (vi) and (vi'), and adding, we get:

$$\underline{[O\text{-}NH\text{-}NH\text{-}O\text{-}Co]} = \frac{k_{43}[Co(II)][^{-}O\text{-}NH\text{-}NH\text{-}O^{-}] + k_{12}[Co(II)]\underline{[O\text{-}N^{+}H_2\text{-}N^{+}H_2\text{-}O\text{-}Co]}}{k_{43} + k_{35} - (k_{21} + k_{45})K'_2[H^{+}]} \qquad \text{(x)}$$

Equation (vii) is rearranged to get

$$[\underline{O\text{-}NH\text{-}\underset{Co}{N}}H\text{-}O^{-}] = k_{46}[Co(II)][^{-}O\text{-}NH\text{-}NH\text{-}O^{-}] / (k65 + k64) \qquad \text{(xi)}$$

Substituting (x) and (xi) in equation (ix), we obtain

$$Rate = \frac{\{k_{25}k_{32}[H^{+}] / k_{23} + k_{35}\}\ k_{12}[Co(II)][^{-}O\text{-}N^{+}H_2\text{-}N^{+}H_2\text{-}O\text{-}Co] + k_{43}[Ni(II)][^{-}O\text{-}NH\text{-}NH\text{-}O^{-}]}{k_{43} + k_{35} - (k_{21} + k_{25})K'_2[H^{+}]}$$

$$+ \frac{k_{65}k_{46}[Co(II)][^{-}O\text{-}NH\text{-}NH\text{-}O^{-}]}{(k_{46} + k_{65})} \qquad \text{(xii)}$$

The value of [-O-NH-NH-O-] from equation (viii) is substituted in equation (xii) to give equation (xiii)

$$+ \frac{k_{65}\, k_{46}\, K_2\, [\mathrm{Co(II)}]\, [^-\mathrm{O\text{-}N^+H_2\text{-}N^+H_2\text{-}O\text{-}Co}]}{(k_{46} + k_{65})[H^+]} \qquad \text{(xiii)}$$

Now combining equation (iv’) and (viii), we get:

$$\text{Rate} = \frac{k_{obs}\, (K_2 + [H^+])\, [\mathrm{Co(II)}]\, [^-\mathrm{O\text{-}N^+H_2\text{-}N^+H_2\text{-}O\text{-}Co}]}{[H^+]} \qquad \text{(xiv)}$$

$$k_{obs} \frac{(K_2 + [H^+])}{[H^+]} = \frac{k_{65}\, k_{46}\, K_2}{k_{46} + k_{65}\, [H^+]} + \{k_{45}\, K'_2\, [H^+] + k_{35}\} \text{ x } \{\frac{k_{12} + k_{43}\, K_2 / [H^+]}{k_{34} + k_{35} - (k_{21} + k_{45})\, K'_2[H^+]}\} \qquad \text{(xv)}$$

If the reaction goes to completion we can very well assume that $k_{35} >> k_{34}$ and $k_{65} >> k_{64}$, $k_{25}\ k_{12}\ K'2[H^+] << k_{35}k_{43}K_2/[H^+]$, Equation (xv), therefore, reduces to

$$K_{obs} \frac{(K_2 + [H^+])}{[H^+]} = k_{12} \quad + \{\frac{(k_{43} + k_{46})\, K_2}{[H^+]}\} \qquad \text{(xvi)}$$

From equation (xvi) it is obvious that a plot of $k_{obs} \frac{(K_2 + [H^+])}{[H^+]}$ versus $[H^+]^{-1}$ should be linear. The plots at different temperatures are shown in Fig 1. In the absence of Scheme 1, it was difficult to predict that the rate constants corresponding to which of the two steps (k43 or k46) is larger. From Scheme 1, it is evident that k43 is larger than k46, due to strong electrostatic attraction between negatively charged oxygen and positively charged cobalt ions.

The values of k12 and (k43 +k46) were calculated from linear plots of log k versus 1/T and those of entropies and enthalpies of activation corresponding to k12 and (k43 +k46) were calculated from linear plot of log k /T versus 1/T (Fig 2 and 3). These values are reported in Table 2 &3.

Table 2: Values of k_{12} and (k_{43} + k_{46}) for the complexation of Co(II) with d-2,2-(Ethylenediimino)-di-1- butanol

Temp.(± 0.05 °C)	k12 (M-1s-1)	(k_{43} + k_{46})x10^{-5}($M^{-1}s^{-1}$)
25	--	3.42
30	0.75	4.18
35	2.0	5.19
40	2.5	7.85

Table 3: Values of activation parameters corresponding to (k_{43} + k_{46}) and k_{12} for the complexation of Co(II) with d-2,2-(Ethylenediimino)-di-1-butanol

	(k_{43} + k_{46})	k_{12}
ΔH#(kJmol-1)	47.8 ± 2.6	103 ± 3.0
ΔE#(kJmol-1)	31.9 ± 1.4	144 ± 3.6
ΔS#(JK-1mol-1)	-67.8 ± 3.6	105 ± 4.9

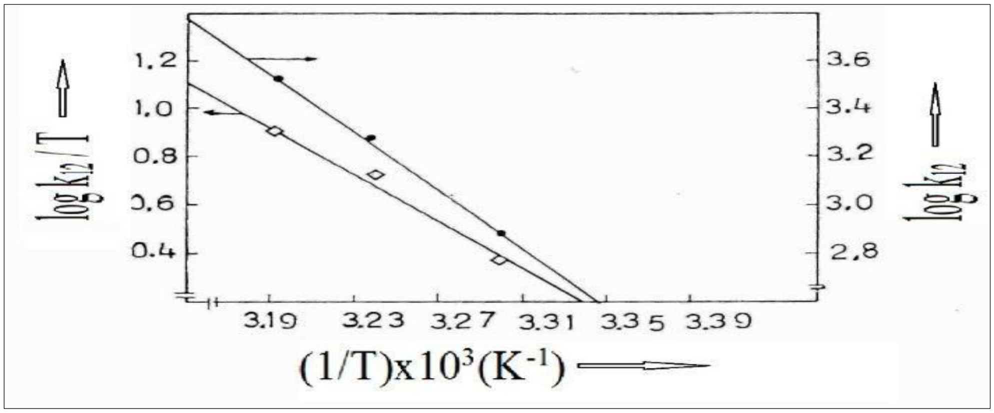


Fig 2: Plots of log k_{12} and log k_{12} / T versus (1/T) for the interaction of Co(II)- d-2,2- (Ethylenediimino)-di-1-butanol

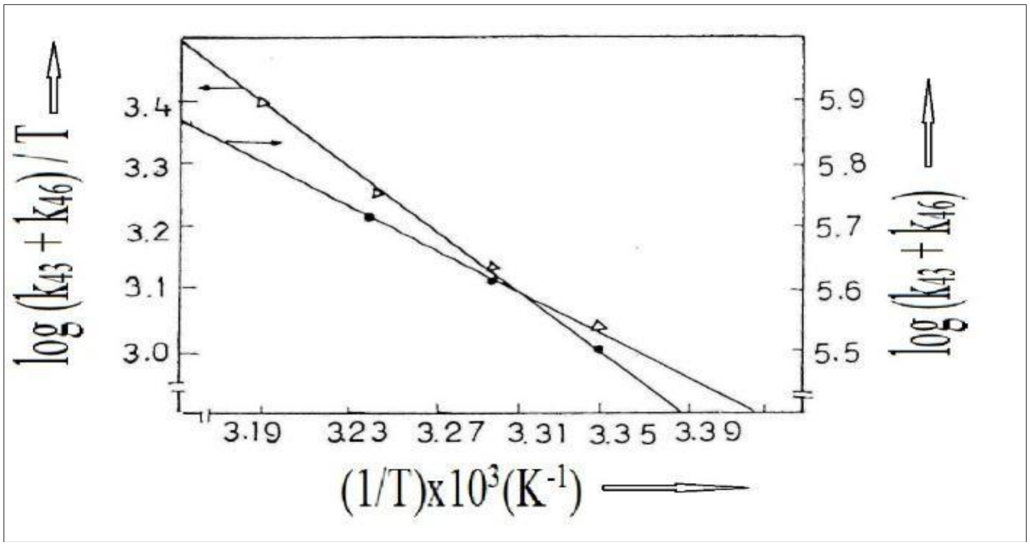
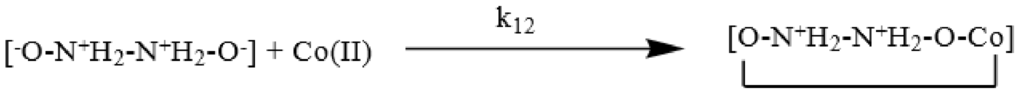


Fig 3: Plots of log (k_{43} + k_{46}) and log (k_{43} + k_{46}) / T versus (1/T) for the interaction of Co(II) - d- 2,2-(Ethylenediimino)-di-1-butanol

Mechanism

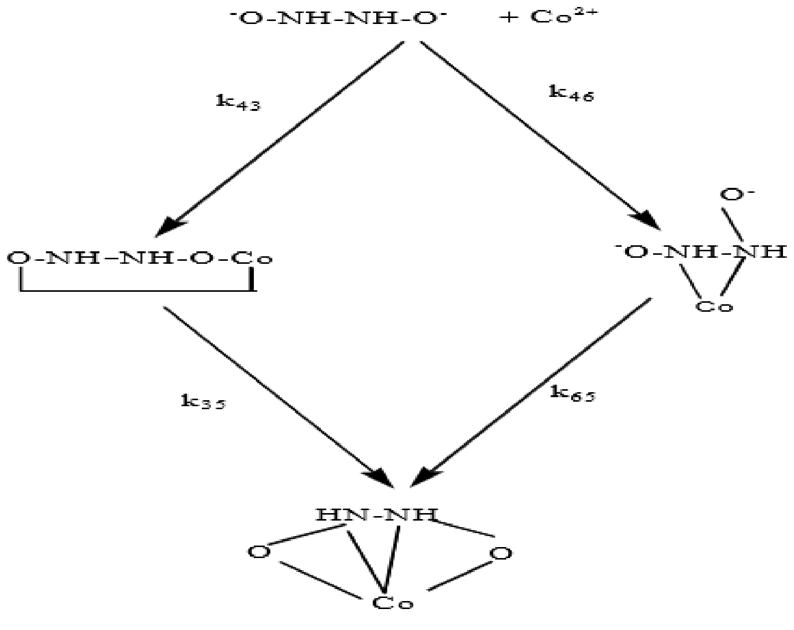
The zwitterionic form of d-2,2-(Ethylenediimino)-di-1-butanol reacts with Co(II) via k_{12} path as shown below:



$$[^{-}O\text{-}N^{+}H_2\text{-}N^{+}H_2\text{-}O^{-}] + Co(II) \xrightarrow{k_{12}} [O\text{-}N^{+}H_2\text{-}N^{+}H_2\text{-}O\text{-}Co]$$

The value of k_{12} at 25 °C was found to be zero (Table 2) confirming that zwitterionic form of ligand is unreactive with cobalt at this temperature.

The reaction of deprotonated form of d-2,2-(Ethylenediimino)-di-1-butanol with Co(II) can be represented as:



Scheme 2

As can be seen from table 2 that deprotonated form will react faster with Co(II) as compared to zwitterionic form. This fact is further confirmed by activation parameter values (Table3). Energy of activation corresponding to k_{12} path is very high compared to (k_{43}+ k_{46}) path and entropy which has negative value, supports a reaction is occurring between two oppositely charged ions for (k_{43}+ k_{46}) step.

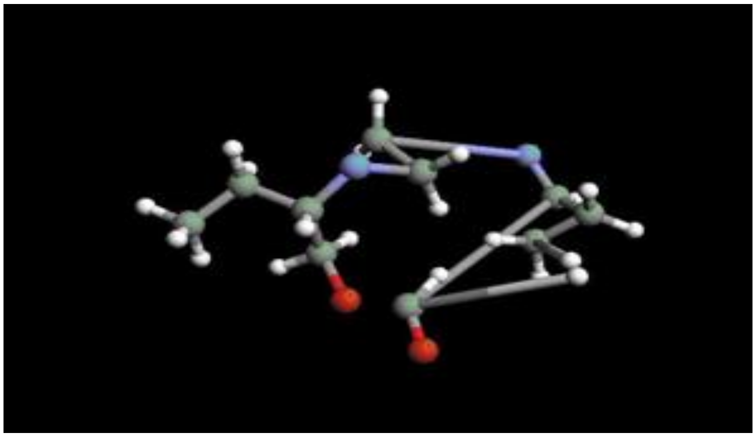


Fig 4: Deprotonated form of d-2,2-(Ethylenediimino)-di-1-butanol Final Geometry Energy = -55357.0379 kcal/mol Heat of Formation = 31.7745 kcal/mol

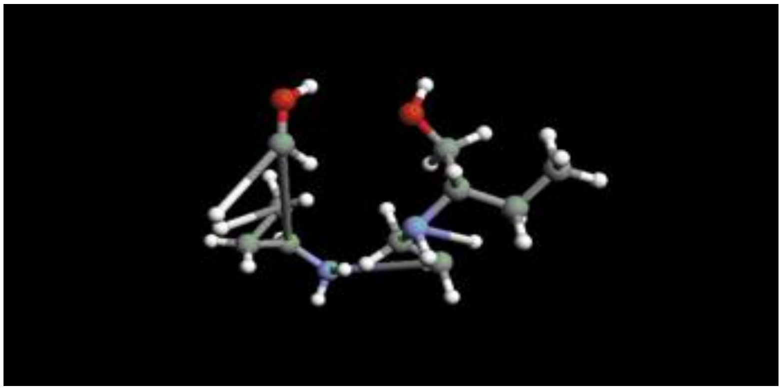


Fig 5: Protonated form of d-2,2-(Ethylenediimino)-di-1-butanol Final Geometry Energy = -57558.0705 kcal/mol Heat of Formation = -47.8176 kcal/mol

The deprotonated form react with Co(II) in two ways (i) Ring formation via nitrogen and (ii) Ring formation via oxygen. It is evident from Table 3 that deprotonated form will react more rapidly with Co(II) as compared to the zwitterionic form. Due to strong electrostatic interaction between the positive charge of Co(II) and negative charge on the oxygen of d-2,2-(Ethylenediimino)-di-1- butanol, it is inferred that k_{43} is greater than k_{46}. The value of activation parameters corresponding to (k_{43} +k_{46}) further confirm that the deprotonated form is more reactive than the zwitterionic form of the ligand. This mechanism is further confirmed by the values of energy of activation and entropy of activation. The positive value of entropy of activation corresponding to k_{12} step suggests that the reaction is occurring between ions having similar type of charges. The high negative value of entropy of activation is suggestive of associative mechanism being observed. This mechanism is further confirmed from the molecular modelling method in which the energy as well as the heat of formation of the zwitterionic form and protonated form has been calculated [10-14]. Values of energies of the protonated and deprotonated form as well as heat of formation were calculated after optimizing the geometry of the molecules. These values are given along with the Fig 4 and 5. It has been found that the deprotonated form is more reactive than the protonated form.

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