

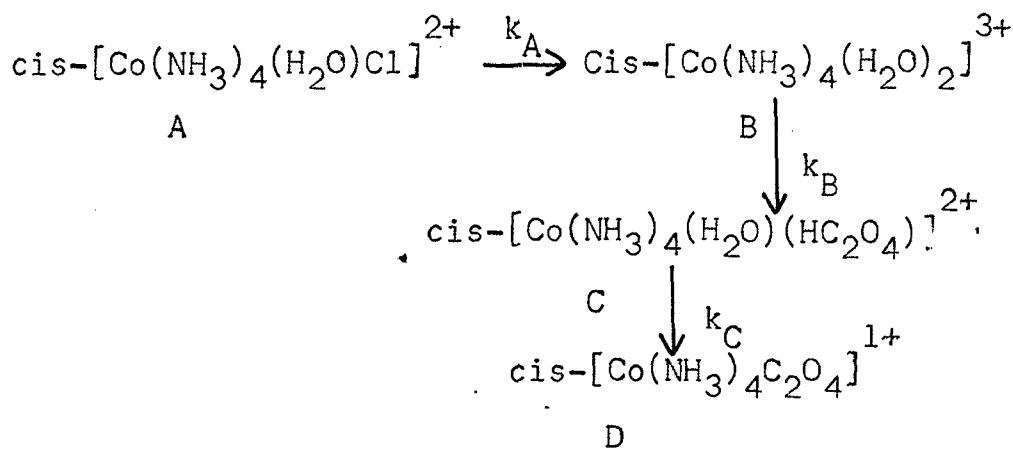
S U M M A R Y

During last three decades considerable amount of work has been done on the kinetics and mechanism of substitution reactions of inorganic complexes. In these studies, too much importance was given on the values of the pseudo-first order rate constants determined under various conditions and little has been done to elucidate the total mechanism of most reactions. Survey of literature shows that a small amount of work has been done on substitution of aquo ligands of cis-aquo-chlorotetrammine cobalt(III) and of cis-diaquotetrammine cobalt(III) ions by other ligands. In this context the present thesis offers some results of interest in substitution of chloro- and aquo-ligands in cis-aquo-chlorotetrammine cobalt(III) ion by oxalate and substitution of aquo-ligands in cis-diaquotetrammine cobalt(III) by oxalate, malonate and glycine.

The thesis consists of three chapters. Chapter-I deals with the Kinetics and Mechanism of the Reaction of cis-aquo-chloro- and cis-diaquo-tetrammine cobalt(III) ions with ammonium oxalate. This chapter has been however subdivided into three parts. Part-I deals with study of the hydrolysis of A [cis-aquo-chlorotetrammine cobalt(III) ion] in an aqueous solution (i) in absence of oxalate and (ii) in presence of excess ammonium oxalate (pseudo first order condition at

pH 4.0 and at 35°C. The study indicates that the rates of release of chloride from A in presence of ammonium oxalate and in absence of it are identical, ($k_A = 1.3 \times 10^{-3} \text{ sec}^{-1}$). However, the final product of the reaction of A with ammonium oxalate solution was found to be the ring closed $[\text{Co}(\text{NH}_3)_4 \text{C}_2\text{O}_4]^{1+}$ ion. It was therefore concluded that B, i.e. $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ ion, which was the product of hydrolysis of A, subsequently reacted with ammonium oxalate to form the above ring closed compound.

Part-II deals with the study of the reaction, cis-diaquo-tetraammine cobalt(III) i.e. B \longrightarrow cis-oxalato-tetraammine cobalt(III) i.e. D and of the reaction cis-aquo-chlorotetraammine cobalt(III) i.e. A \longrightarrow cis-oxalatotetraammine cobalt(III) i.e. D in aqueous solution using excess of ammonium oxalate at pH 4.0 and at 35°C. Our studies indicate that the reaction B \longrightarrow D is a part of the reaction series A \longrightarrow D and D is formed from B through an intermediate C. The stoichiometric mechanism has been found to be as follows :



k_A , k_B and k_C being the respective rate constants.

$$\left. \begin{aligned} k_A &= 1.3 \times 10^{-3} \text{ sec}^{-1} \\ k_B &= 1.3 \times 10^{-3} \text{ sec}^{-1} \\ k_C &= 3.3 \times 10^{-4} \text{ sec}^{-1} \end{aligned} \right\} \text{ at } 35^\circ\text{C and at pH 4.0}$$

The value of k_A has been already obtained from our study in Part-I. The values of k_B and k_C were obtained by adopting the following procedure.

Reaction mixtures of A with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and of B with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ using large excess of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in solution were studied spectrophotometrically with $\lambda = 500 \text{ nm}$ and $\lambda = 528 \text{ nm}$ at 35°C and at pH 4.0. The plot of $\log \frac{d_\alpha - d_0}{d_\alpha - d_t}$ vs t in for both reactions ($\text{A} \rightarrow \text{D}$ and $\text{B} \rightarrow \text{D}$) were curved lines, starting with a near zero slope, but the slopes increased in both cases with time finally attaining the same limiting value so as observed from the fact that final portions of the curves in both plots were straight lines parallel to each other. From this result we concluded that the last steps of each of the reaction series $\text{A} \rightarrow \text{D}$ and $\text{B} \rightarrow \text{D}$ were **identical** proceeding from the same intermediate C; we proved that intermediate C was $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{HC}_2\text{O}_4)]^{2+}$ ion and in fact we succeeded in isolating the double complex salt $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{HC}_2\text{O}_4)] [\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{ClO}_4)_5$ from a mixture of B and oxalic acid at pH 1.0. The series $\text{B} \rightarrow \text{C} \rightarrow \text{D}$ is therefore a part of the reaction series $\text{A} \rightarrow \text{B} \rightarrow \text{D}$.

For both reactions $A \rightarrow D$ and $B \rightarrow D$, the final straight line portions of the $\log \frac{d_\alpha - d_0}{d_\alpha - d_t}$ vs t plots began from a point of time when all A and B in the first reaction and all B in the second reaction were practically exhausted and the reaction with oxalate proceeded from intermediate C alone. The same limiting slope of the final straight lines in the two above plots, therefore gives the value of the rate constant k_C for the last step $C \rightarrow D$ of the reaction series.

Using the same [B] but different $[(NH_4)_2C_2O_4]$ values at $35^\circ C$ and at pH 4.0, we found that the curves obtained by plotting $\log \frac{d_\alpha - d_0}{d_\alpha - d_t}$ vs t for all concentrations of $[(NH_4)_2C_2O_4]$ coincided with each other; this definitely indicated that both the steps $B \rightarrow C$ and $C \rightarrow D$ in the reaction series $B \rightarrow C \rightarrow D$ were oxalate independent and the rate constants k_B and k_C were of the first order with respect to B and C respectively.

Since the value of k_C was known from the limiting slopes of the final straight line portions of $\log \frac{d_\alpha - d_0}{d_\alpha - d_t}$ vs t plots, we could evaluate k_B by a trial and error method using the value of k_C obtained as above and also the two step first order consecutive reaction equation (1) for the first order reaction series $B \rightarrow C \rightarrow D$.

$$\frac{D_t}{B_0} = 1 + \frac{1}{k_B - k_C} (k_C \cdot e^{-k_B t} - k_B \cdot e^{-k_C t}) \dots (1)$$

The value of D_t/B_0 at any time t was found spectrophotometrically using the equation (2)

$$\frac{D_t}{B_0} = \frac{d_t - d_0}{d_\alpha - d_t} \dots \quad (2)$$

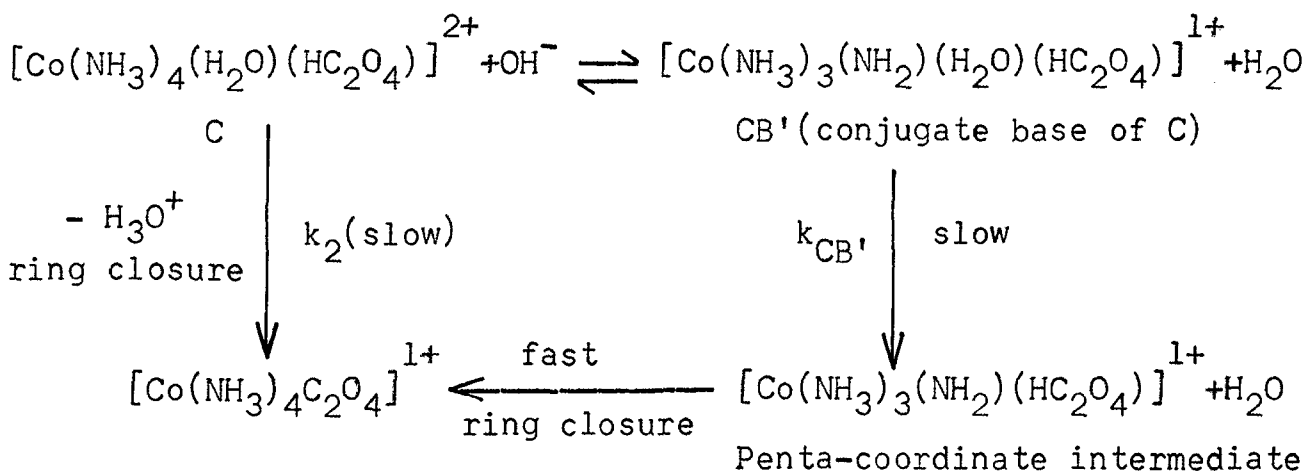
The reaction scheme $A \xrightarrow{k_A} B \xrightarrow{k_B} C \xrightarrow{k_C} D$ was further confirmed by calculating out the values of D_t at different time t by a new method of calculation, using the values of k_A , k_B and k_C obtained above. These calculated D_t values at different times t were compared with experimental D_t values at the corresponding times t found by using equation (2). The agreement between calculated and experimental values of D_t for each time t was good enough to justify the Reaction Scheme proposed.

In Part III, studies were made on the anation reaction $B \rightarrow C$ and on the ring closure reaction $C \rightarrow D$, in order to decipher the detailed mechanism of both reactions. In the reaction $B \rightarrow C$, the rate constant k_B was found to increase with the increase in pH for a reaction mixture of $0.005 \text{ mol dm}^{-3}$ of B and 0.05 mol dm^{-3} of $(\text{NH}_4)_2\text{C}_2\text{O}_4$ at 35°C .

In a solution of 0.05 mol dm^{-3} of $(\text{NH}_4)_2\text{C}_2\text{O}_4$, it was found by using the Henderson equation and the values of the first and second acid dissociation constants K_1 and K_2 of oxalic acid, that $[\text{H}_2\text{C}_2\text{O}_4]$ was small, but $[\text{HC}_2\text{O}_4^-]$ was very

reaction also has been shown to follow two parallel paths, one being pH independent SN^1 path and other being an SN^1CB path represented by the following reaction scheme

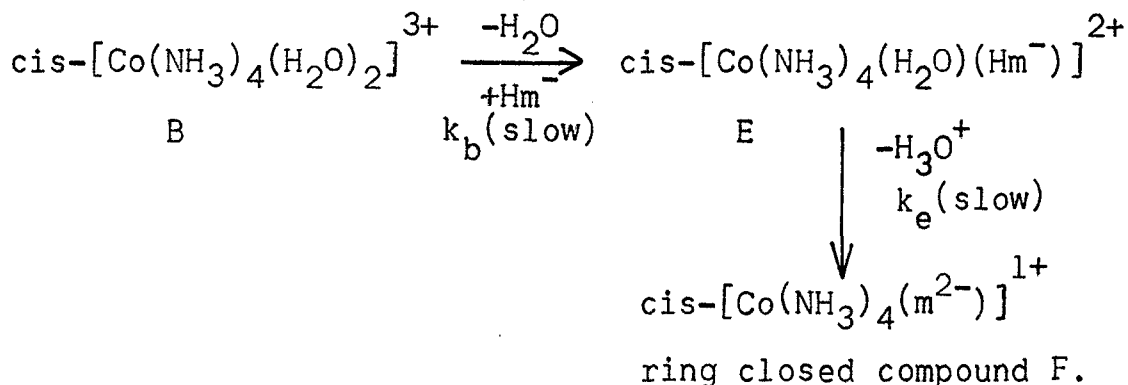
Reaction Scheme



k_2 is the hydrogen ion independent rate constant and $k_{\text{CB}'}$ is the rate constant for the SN^1CB path [k_2 at $35^\circ\text{C} = 8.0 \times 10^{-5} \text{ sec}^{-1}$].

Chapter-II deals with the kinetics and mechanism of reaction between diaquo-tetrammine Co(III) ion and malonic acid. It is shown that the stoichiometric mechanism of the reaction B [cis-diaquotetrammine cobalt(III)] \rightarrow F [ring closed cis-malonatotetrammine cobalt(III)] at a certain pH consists of two consecutive first order steps involving the formation

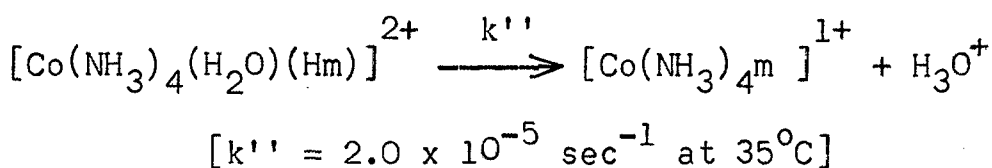
of the intermediate E [cis-Co(NH₃)₄(H₂O)(CH₂ $\begin{array}{l} \nearrow \text{COOH} \\ \searrow \text{COO} \end{array}$)]²⁺ e.g.



The same method as used in the case of the reaction between $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ and $[(\text{NH}_4)_2\text{C}_2\text{O}_4]$, was used in this case too. k_e was determined from the limiting slope of the plot of $\log \frac{d_\alpha - d_0}{d_\alpha - d_t}$ vs t and k_b , by the trial and error method following the same procedure as adopted for the reaction between B and $(\text{NH}_4)_2\text{C}_2\text{O}_4$. The rate constant k_b and k_e were both found to be pH dependent. The pH dependence of these constants explained by adopting an ion-pair-cum- SN^1CB mechanism. [For values of k_b and k_e at different pH values and at 35°C , see Table-4, page- 129].

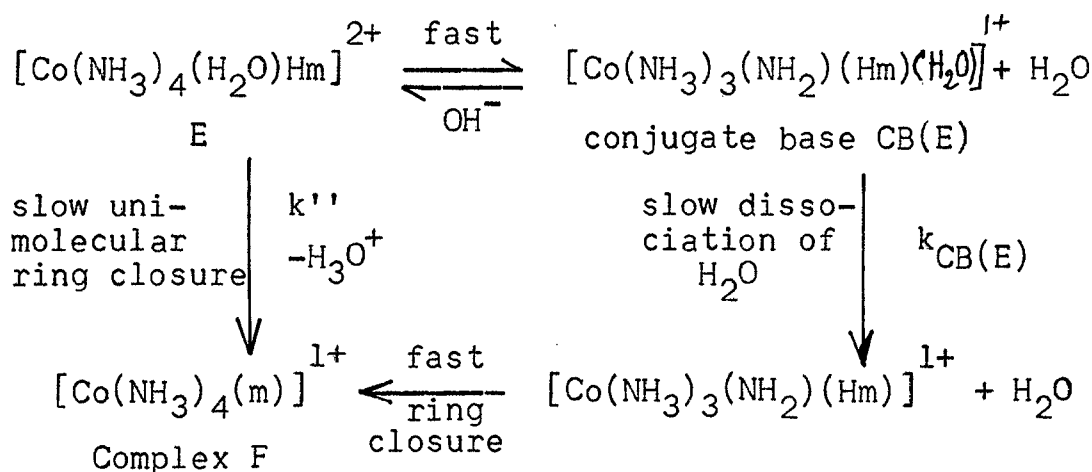
Malonic acid is a weaker acid than oxalic acid and hence in a 0.10 mol dm^{-3} solution of malonic acid at the pH range of our study (pH = 4.0 to 3.0), the concentration of the ion m^{2-} ($= \text{C}_3\text{H}_2\text{O}_4^{2-}$) was negligible, but Hm^- ($\text{C}_3\text{H}_3\text{O}_4^{1-}$) was predominant and that of the molecule H_2m^0 ($= \text{C}_3\text{H}_4\text{O}_4$) was comparatively large. But since [malonic acid] was present in large excess over [B], we could prove that the entire of B in the solution was present in form of two ion-pairs only namely $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+} \cdot \text{H}_2\text{m}^0$ and $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+} \cdot \text{Hm}^-$.

Both ion-pairs were shown to form the same intermediate E through two parallel paths - one SN^1CB path (rate constant = $2.89 \times 10^{-2} \text{sec}^{-1}$ at 35°C) and another pH independent simple SN^1 interchange path (rate constant = $2.0 \times 10^{-4} \text{sec}^{-1}$ at 35°C). The ring closure reaction $E \rightarrow F$ also follows two parallel paths one pH independent simple unimolecular in ring closure path



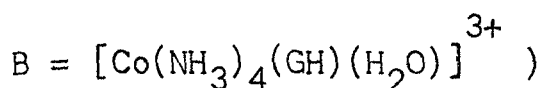
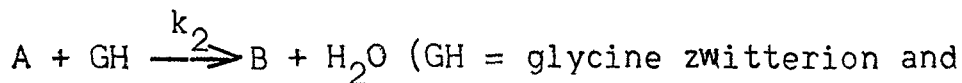
and another SN^1CB path. The complete reaction $E \rightarrow F$ has been depicted in the following reaction scheme.

Reaction Scheme



In Chapter-III, the kinetics and mechanism of the reaction between $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ ion (depicted as A) and glycine have been studied; this reaction has not been so far studied from the mechanistic point of view.

It has been found by varying [glycine] but keeping [A] const. at 35°C and pH 4.0 that the rate constant k_2 of the reaction



is one of the second order ($k_2 = 2.4 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$) at 35°C and at pH 4.0).

The rate of the reaction was found to increase with the increase of pH at 35°C. Two reaction paths - path-I and path-II were found to be consistent with experimental results of the pH variation experiments. In path-I, the conjugate base of A undergoes a bimolecular reaction with GH in the slowest step [SN^2CB (complex) mechanism]; in path-II, G^- the conjugate base of the ligand GH, reacts bimolecularly with A in the slowest step [SN^2CB (ligand) mechanism]. It has also been shown the rates by path-I and path-II are equal to each other and the conclusion, that the total reaction proceeds in two parallel paths - path-I and path-II at exactly equal rates was drawn, half of A being converted to B by path-I and other half by path-II. From the experiments done at pH 4.0 but at different temperatures, the variation of k_2 values with temperature was determined and the activation parameters ΔH^\ddagger and ΔS^\ddagger were found out to be $109.89 \text{ KJ mol}^{-1}$ and $59.64 \text{ JK mol}^{-1}$ respectively from the slope and the intercept of $\log k_2$ vs $1/T$ plot.