Substitution Reactions of cis-Dichloro-bis(ethylenediamine)Cobalt(III) Chloride with Oxalate

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The substitution of chloride ions by oxalate in cis-dichloro-bis(ethylenediamine)cobalt(III) chloride proceeds in consecutive steps; in the first step one of the two chloride ions dissociates at a rate equal to that of acid hydrolysis giving a penta-coordinated intermediate which combines immediately with oxalate giving the relatively stable oxalatochloro intermediate. The subsequent chelation in the second step is a slow process controlled by dissociation of the remaining chloride ligand. The formation of an aquachloro intermediate is inconsistent with experimental results. The enthalpy and entropy of activation for the second step of the reaction have been evaluated by the Eyring equation.

BASOLO et al. have shown that substitution reactions of nitrochloro-bis(ethylenediamine)-cobalt(III) complex cation with azide, nitrite and thiocyanate ions proceed through intermediate formation of aquonitrato complex. Anation reactions of aquopentammine Co(III) complex with sulphate, chloride, thiocyanate and of diaquo-bis(ethylenediamine)Co(III) complex with oxalate attain a limiting rate at high ligand concentration and this limiting rate is about 20-25% of the rate of water exchange. This has been explained as due to the reaction proceeding through ion-pair formation which is assumed to be complete at high anion concentration and that water has a greater statistical advantage over the anion for capturing the penta-coordinated intermediate formed by dissociation of a water ligand. Nevertheless, there are instances such as anation reactions of hexaaquo chromium(III) ion with acetate, malonate, oxalate, citrate, etc., where the penta-coordinated intermediate is solely captured by the anion and the rate of anation is equal to the rate of water exchange. Such conflicting observations in different systems initiated us to make a detailed study of the substitution of chloride ions in cis-dichloro-bis(ethylenediamine)Co(III) complex by oxalate ion. In view of the presence of uncoordinated oxalate ion in the oxalato pentammine Co(III) cation and the conclusion of Brown and Harris that the reaction of hydroxo-bis(ethylenediamine)Co(III) ion with oxalate proceeds through the formation of oxalato-hydroxo-bis(ethylenediamine) intermediate, it was thought that the existence of an intermediate oxalatochloro-bis(ethylenediamine) species in the reaction of dichloro-bis(ethylenediamine)Co(III) ion with oxalate was also plausible.

Experimental Procedure

All reagents were of GR quality.

cis-[Coen 2 Cl 2 ]Cl. H 2 O was prepared by evaporating a neutral aqueous solution of the trans-isomer to dryness by the method of Werner (Found: Co, 19.6; N, 18.8; Cl, 35.6. Calc.: Co, 19.4; N, 18.5; Cl, 35.4%). cis-[Coen 2 ClH 5 O]SO 4 .1.5H 2 O was prepared by the method of Werner (Found: Co, 16.9; N, 16.0; Cl, 9.80. Calc.: Co, 16.6; N, 15.8; Cl, 10.0%). The final product [Coen 3 C 2 O 4 ]Cl has been isolated (Found: Co, 19.4; N, 18.7; Cl, 11.6. Calc.: Co, 19.5; N, 18.5; Cl, 11.7%). The ligand field bands of all the complexes were checked by Spectromom 201 spectrophotometer.

Substitution reactions — The reactions were followed in aqueous medium (pH 5-7) by two methods: (a) The chloride ion concentrations in thermostated reaction mixture were determined at chosen time intervals using a Ag-AgCl electrode (versus SCE). The oxalate concentrations were varied from 0.1 to 0.4 M, being at least ten times the concentration of the complex (pseudo first order condition). The pseudo first order rate constants were determined by the Guggenheim method on the basis of release of chloride ions at temperatures 26°, 30°, 35° and 40-5°C. (b) The oxalate, precipitated as calcium oxalate from the reaction mixture, was estimated at different time intervals by potassium permanganate and the pseudo first order rate constants for the formation of oxalate ion were determined by plotting log $V_o-V_m/(V_1-V_m)$ against time, where $V_o$, $V_1$ and $V_m$ are respectively the volumes of permanganate consumed at times 0, 1 and $m$.

Results

For the reaction,

cis-[Coen 3 Cl 2 ] 2+ + C 2 O 4 2- \rightleftharpoons [Coen 2 C 2 O 4 ] 2+ + 2 Cl 2

in presence of excess oxalate, the Guggenheim plot based on the change of concentration of chloride ions...
RAY & SIDDHANTA: cis-DICHLORO-BIS(ETHYLENEDIAMINE)Co(II) CHLORIDE

**EXPERIMENTAL POINTS**

![Graph showing Guggenheim plots.](image)

**EXPERIMENTAL POINTS**

![Graph showing plots of log(V_0 - V) versus time.](image)

The Guggenheim plot is theoretical in consecutive steps with k_1 = 4.97 x 10^{-2} min^{-1} and k_2 = 1.55 x 10^{-2} min^{-1} at 35°C with conc. of complex = 0.0072 M; experimental points are obtained at 35°C with conc. of oxalate = 0.011 M and that of complex = 0.0072 M.

**Table 1** — Observed Rate Constant k_{act} for the Release of Both Chloride Ions from cis-[Co(CH_3Cl)_2]Cl Obtained by Guggenheim Method at Different Temperatures and Oxalate Concentrations

<table>
<thead>
<tr>
<th>(Complex)</th>
<th>(Oxalate)</th>
<th>10^4 x k_{act}</th>
<th>10^3 x k_{act}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(M)</td>
<td>(M)</td>
<td>(min^{-1})</td>
<td>(min^{-1})</td>
</tr>
<tr>
<td>0.0087</td>
<td>0.1</td>
<td>0.90</td>
<td>1.79</td>
</tr>
<tr>
<td>0.0098</td>
<td>0.2</td>
<td>0.92</td>
<td></td>
</tr>
<tr>
<td>0.0103</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 2** — Rate Constants for the Release of Chloride Ions from cis-[Coen(H_2O)Cl]^{+}

<table>
<thead>
<tr>
<th>(Complex) = 0.01 M; temp., 35°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Oxalate]</td>
</tr>
<tr>
<td>(M)</td>
</tr>
<tr>
<td>0.1</td>
</tr>
<tr>
<td>0.2</td>
</tr>
<tr>
<td>0.3</td>
</tr>
<tr>
<td>0.4</td>
</tr>
</tbody>
</table>

**Table 3** — Rate Constants for the Entrance of Oxalate

<table>
<thead>
<tr>
<th>(Temp., 35°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Complex]</td>
</tr>
<tr>
<td>[Oxalate]</td>
</tr>
<tr>
<td>(M)</td>
</tr>
<tr>
<td>cis-[CoenC_2H_4]^{+}</td>
</tr>
<tr>
<td>cis-[Coen(H_2O)Cl]^{+}</td>
</tr>
</tbody>
</table>

*Acid hydrolysis*.

- Limiting rate constant.

The values of k_{act} at different temperatures and oxalate concentrations are given in Table 1. The rate constants for aquation, k_1 (aquation), of cis-dichloro complex at pH 1 are also included in Table 1 for comparison.

The rates of release of chloride ions from and of the entrance of oxalate in the cis-aquo-chloro complex in the presence of excess oxalate have also been measured at 35°C and the pseudo first order rate constants for different oxalate concentrations are given in Tables 2 and 3 respectively. The plots of log(V_0 - V) versus time (Fig. 2) are slightly curved at the beginning but become virtually straight lines after the initial stages of the reactions are over. The rate constants obtained from the limiting slopes, i.e. the straight line portions, are given in Table 3.
Discussion

It was found that unlike simple acid hydrolysis reactions both the chloride ions are liberated in the reaction and that the Guggenheim plots based on the release of chloride ions are initially curved (Fig. 1); the plot of log \((V_o - V)/V_t - V\) versus time also shows an initial curvature (Fig. 2). Furthermore, the values of \(k_{in}\) are lower than the rate constants of acid hydrolysis at each temperature. From these observations it appears that the release of two chloride ions possibly occur in consecutive steps. Since the rate constants (Table 1) are practically independent of ligand concentration, the reaction depends only on the concentration of the complex ion and hence proceeds by dissociation mechanism.

Mechanism of the reaction — On the basis of the results obtained, three possibilities may be considered:

(i) Oxalate ion capture by the pentacoordinated intermediate.

\[
\begin{align*}
[\text{Coen}_{2}Cl_2]^{+} \rightarrow & [\text{Coen}_{2}Cl]^{+}Cl^{-}\quad \text{(A)} \\
[\text{Coen}_{2}Cl]^{+} \rightarrow & [\text{Coen}_{2}Cl(H_2O)]^{+}Cl^{-}\quad \text{(B)} \\
[\text{Coen}_{2}Cl(H_2O)]^{+} \rightarrow & [\text{Coen}_{2}Cl(H_2O)]^{+}Cl^{-}\quad \text{(C)} 
\end{align*}
\]

(Mechanism i)

(ii) Intermediate aquation step [Chloride substitution mechanism in nitrochloro-bis(ethylenediamine)Co(III) complex by azide, nitrite, thioconate ions through intermediate formation of aquonitrocomplex has been postulated by Basolo et al.\(^2\)].

\[
[\text{Coen}_{2}Cl_2]^{+} \rightarrow [\text{Coen}_{2}Cl]+Cl^{-}\quad \text{(A)} \\
[\text{Coen}_{2}Cl]+Cl^{-} \rightarrow [\text{Coen}_{2}Cl(H_2O)]^{+}\quad \text{(B)} \\
[\text{Coen}_{2}Cl(H_2O)]^{+} +Cl^{-} \rightarrow [\text{Coen}_{2}Cl(H_2O)]^{+}Cl^{-}\quad \text{(C)}
\]

(Mechanism ii)

(iii) Competitive capture of oxalate and water by the pentacoordinated intermediate [combination of steps (i) and (ii)].

\[
[\text{Coen}_{2}Cl_2]^{+} \rightarrow [\text{Coen}_{2}Cl]+Cl^{-}\quad \text{(A)} \\
[\text{Coen}_{2}Cl]+Cl^{-} \rightarrow [\text{Coen}_{2}Cl(H_2O)]^{+}\quad \text{(B)} \\
[\text{Coen}_{2}Cl(H_2O)]^{+} \rightarrow [\text{Coen}_{2}Cl(H_2O)]^{+}Cl^{-}\quad \text{(C)}
\]

(Mechanism iii)

For mechanisms (i) and (ii) \(k_1\) is the rate constant for the dissociation of the first chloride ion and it must be equal to the rate constant for acid hydrolysis, i.e. \(4.97 \times 10^{-2}\) min\(^{-1}\) at 35\(^\circ\) (Table 1). The limiting rate constant for the entrance of oxalate into the coordination sphere of the complex obtained by oxalate estimation method is \(1.55 \times 10^{-2}\) min\(^{-1}\) at 35\(^\circ\) (Table 3), much less than the rate of dissociation of the first chloride ion. This suggests that this limiting rate constant corresponds to the second slow step of the consecutive reaction when the first slow step is virtually complete. Therefore, \(k_2\) should be equal to \(1.55 \times 10^{-2}\) min\(^{-1}\) at 35\(^\circ\) for the mechanisms (i) and (ii). (It has been assumed that calcium chloride can precipitate single linked oxalate ion from oxalatechloro complex immediately.) Using these values of \(k_1\) and \(k_2\) theoretical Guggenheim plots based on decrease of concentration of oxalate can be calculated as follows:

The concentration of chloride ions at different times obtained on the basis of mechanisms (i) and (ii) are given by

\[
C_t = A_0 + A_1(1-e^{-k_1t}) + C_i = A_0(2-e^{-k_2t}) + C_i \quad \text{(1)}
\]

where, concentration of chloride ion at zero time = initial concentration of complex \([\text{Coen}_{2}Cl_2]Cl = A_0\), \(C_i\) and \(C_t\) are respectively the concentrations of oxalato complex and chloride ion at time \(t\).

For consecutive reactions as in (i) and (ii):

\[
C_t = A_0 \left[1 + \frac{1}{k_1-k_2} (k_2e^{-k_2t} - k_1e^{-k_1t})\right] \quad \text{(2)}
\]

The values of \(C_t\) for different arbitrary values of time were computed from Eq. (2) using \(k_1 = 4.97 \times 10^{-2}\) min\(^{-1}\) and \(k_2 = 1.55 \times 10^{-2}\) min\(^{-1}\) and \(A_0 = 0.02\). With these computed values of \(C_t\), log \((V_o - V)/V_t - V\) versus time curve was drawn. Fig. 2 shows that the experimental points fit nicely with this theoretical curve, giving support to the assumption of consecutive reaction mechanism with \(k_1 = 4.97 \times 10^{-2}\) min\(^{-1}\) and \(k_2 = 1.55 \times 10^{-2}\) min\(^{-1}\).

Combining Eqs. (1) and (2) we get,

\[
C_t = A_0 \left[1 + \frac{1}{k_1-k_2} (k_2e^{-k_2t} - k_1e^{-k_1t})\right] \quad \text{(3)}
\]

Theoretical Guggenheim plot for the release of chloride ion can be computed from Eq. (3) using the values of \(k_1\) and \(k_2\) given above. Experimental points are found to fit well with this theoretical Guggenheim curve (Fig. 1) lending further support in favour of consecutive reaction mechanism involving two slow steps.

As regards mechanism (iii) we have taken the same values of \(k_1\) and \(k_2\). The rate constant for the reaction between aquochloro complex and oxalate ion has been found by us to be \(1.12 \times 10^{-2}\) min\(^{-1}\) (Table 3). The value of \(k_2/k_1\) is chosen arbitrarily to be 1/3, since in anation reactions usually the limiting rate of anation at high ligand concentration is 20-25% of the water exchange rate thus providing the possibility that pentacoordinated intermediate preferentially captures water. Theoretical logarithmic plots for the decrease of oxalate are drawn from calculated values of \(C_t\) given by

\[
C_t = A_0 - A_i - B_i = A_0 - A_i e^{k_1t} - B_i (e^{-k_2t} - e^{-k_1t}) \quad \text{(4)}
\]
where
\[ B' = \frac{2A}{h} \frac{k_1}{h_1 - h_2} (e^{+h_1} - e^{+h_2}) \]

This theoretical plot shown in Fig. 2 does not match with the experimentally obtained curve, thus excluding mechanism (iii).

The consecutive reaction in mechanism (ii) requiring the formation of aquochloro intermediate, \( B' \), can be excluded on the following grounds:

(i) If the aquochloro species is formed as an intermediate then it will be the cis-isomer, since aquation of cis-dichloro species occurs with retention of configuration\(^5\). The rate of release of chloride ions from cis-aquochloro complex in 0.1M oxalate at the same \( \rho \)H (5.7) at which the dichloro complex was studied is \( 3.3\times10^{-2} \) min\(^{-1} \) at 35\(^\circ\)C (Table 2). This should be equal to \( k_2 \) if mechanism (ii) is valid. With this value of \( k_2 \) the Guggenheim plot on the basis of release of chloride ions from cis-dichloro complex obtained using Eq. (3) does not fit with the experimental points.

(ii) The data of Table 3 show that the rate constant for the release of chloride ion from cis-aquochloro complex increases with increasing concentration of oxalate, but the rate for the substitution of both chloride ions in cis-dichloro complex is independent of concentration of oxalate. This is contrary to the formation of aquochloro intermediate.

(iii) The rate of entrance of oxalate into the coordination sphere of aquochloro complex is \( 1.12 \times 10^{-2} \) min\(^{-1} \) at 35\(^\circ\)C (Table 3). With this value of \( k_2 \) a logarithmic plot for the decrease of oxalate concentration calculated using Eq. (2) has been drawn in Fig. 2; the resulting curve does not fit with the experimental one, thereby contradicting mechanism (ii).

The values of \( k_2 \) at other temperatures have been calculated in the following ways: For consecutive reaction as in mechanism (i), \( \log t_0/t_0' \), where \( t_2 \) and \( t_0 \) are respectively the times required for \( x \)-fraction and \( y \)-fraction of the reaction (based on release of chloride ions) to occur, is a function\(^6\) of the ratio \( k_1/k_2 \). Thus a plot of \( \log t_{50\%}/t_{50\%} \) versus \( k_1/k_2 \) can be drawn, \( t_{50\%} \) and \( t_{50\%} \) being respectively the times required for 70% and 35% of the reaction. From this curve the ratio \( k_1/k_2 \) has been determined from measured values of \( t_{50\%} \) and \( t_{50\%} \). Taking \( k_1 \) to be equal to the rate constant for the acid hydrolysis, \( k_2 \) can be determined at the respective temperatures studied. These values are given in Table 4. In the second method, the time for 50% reaction on the basis of release of two chloride ions was determined and the value of \( k_2 \) determined by trial and error method using the Eq. (5)\(^8\)

\[ \delta = 2 - \frac{k_1 - 2k_2}{k_1} e^{-h_1} - \frac{k_1}{k_2} e^{-h_2} \quad \ldots(5) \]

where \( \delta \) is a reaction parameter defined by \( \delta = (B + 2C)/A \), i.e. (chloride ion released at a given instant)/\( A \); for 50% reaction \( \delta = 1 \), \( t \) = time for 50% chloride release and \( k_1 \) is rate constant of acid hydrolysis. The values of \( k_2 \) thus obtained are shown in Table 4. The mean values of \( k_2 \) obtained by these two methods are also included in Table 4 and the activation parameters were calculated from the Arrhenius plot (Fig. 3). The activation parameters for acid hydrolysis reactions are also incorporated for comparison.

The Arrhenius parameters show that like the acid hydrolysis reactions the second step of the reaction

### Table 4 — Values of \( k_2 \) at Different Temperatures Obtained by the Time Ratio Method

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>[Complex] (M)</th>
<th>[Oxalate] (M)</th>
<th>( 10^4 \times k_2 ) (min(^{-1} ))</th>
<th>( t_{50%} ) (min)</th>
<th>( t_{70%} ) (min)</th>
<th>( 10^4 \times k_1 ) (min(^{-1} ))</th>
<th>( 10^4 \times k_2 ) (Eq. 5) (min(^{-1} ))</th>
<th>( 10^4 \times k_2 ) (average) (min(^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>0.0087</td>
<td>0.1</td>
<td>1.70</td>
<td>55</td>
<td>92</td>
<td>168</td>
<td>0.58</td>
<td>0.56</td>
</tr>
<tr>
<td>30</td>
<td>0.0083</td>
<td>0.1</td>
<td>2.76</td>
<td>33</td>
<td>56</td>
<td>101</td>
<td>0.91</td>
<td>0.94</td>
</tr>
<tr>
<td>35</td>
<td>0.0072</td>
<td>0.1</td>
<td>4.97</td>
<td>19</td>
<td>32</td>
<td>61</td>
<td>1.55</td>
<td>1.50</td>
</tr>
<tr>
<td>40</td>
<td>0.0105</td>
<td>0.1</td>
<td>9.30</td>
<td>10</td>
<td>16.5</td>
<td>37.5</td>
<td>2.98</td>
<td>3.20</td>
</tr>
</tbody>
</table>

\( \Delta H_2^\ddagger = 21.9 \) kcal/mole; \( \Delta S_2^\ddagger = -3.5 \) cal/deg.

\( \Delta H_2^\ddagger = 22.0 \) kcal/mole; \( \Delta S_2^\ddagger = -3.5 \) cal/deg.

\( \Delta H_2^\ddagger \) and \( \Delta S_2^\ddagger \) are the enthalpy and entropy of activation for the second step of the reaction and \( \Delta H_1^\ddagger \) and \( \Delta S_1^\ddagger \) are the corresponding values for acid hydrolysis reaction of the cis-dichloro complex.

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with oxalate involving ring closure appears to proceed by a dissociation mechanism, i.e. the Co-Cl bond breaks producing pentacoordinated intermediate and subsequently the free carboxylate group fills the vacated coordination position. Since $\Delta H^\circ_1$ and $\Delta H^\circ_2$ are very nearly the same, it seems that Co-Cl bond strength differs little in dichloro and oxalatochloro complexes though the overall charge on the latter (intermediate B) is zero. It, therefore, appears that the free carboxylate group in the singly linked oxalate ion in (B) does not affect appreciably the charge around the central metal ion which is at a distance. Indeed, groups like thio­cyanate, cyanide, azide and nitrite are known to deactivate other ligands due to the following possible resonance structures, whereby the electron density around the ligand atom bound to the metal ion decreases, causing an electron drift from metal to ligand:

\[
\begin{align*}
\text{M} & \quad \text{O} \quad \text{C} \quad \text{O} \\
& \quad \text{R} \quad \text{R}
\end{align*}
\]

This principle is illustrated by the very striking example\(^\text{10}\) that the highly negatively charged ion \(\text{trans-[Rh(C}_2\text{O}_4\text{)}\text{Cl}_2^-}\) undergoes acid hydrolysis at a slower rate than the positively charged ion \(\text{trans-[Rhen}_2\text{Cl}_2]\text{H}^+\). Thus it appears that the effective positive charge on the central metal ion may be even slightly greater in the intermediate (B) than in (A). Necessarily, the dissociation of chloride in (B) will be slow and the chelation is controlled by the dissociation of the remaining coordinated chloride ion.

The values of $\Delta S^\circ_1$ and $\Delta S^\circ_2$ have also been found to be nearly the same indicating the operation of similar electrostriction effects in the two dissociation steps concerned. The effective charge on the complex ion increases from +1 to +2 in the first case and from 0 to +1 in the second case in forming the pentacoordinated intermediate. Probably the increase of charge on the complex by +1 unit and the separation of chloride ion, being common in both steps, control the electrostriction in both steps and eventually the values of $\Delta S^\circ_1$ and $\Delta S^\circ_2$ become similar. This can be regarded as an additional support in favour of the dissociation controlled mechanism of ring closure.

Acknowledgement

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References

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