Kinetics & Mechanism of Substitution
Reactions in Non-aqueous Solvents:
Substitution in trans-Dibromo-bis-(ethylendiamine)cobalt(III) Bromide &
cis-Dichloro-bis(ethylendiamine)-
cobalt(III) Chloride by Organic Bases
in Aquo-organic Solvents

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Substitution in trans-[Co(en)₂Br₂]⁺ and cis-[Co(en)₂Cl₂]⁺ with
benzylamine, butylamine, cyclohexylamine, diethylamine and
piperidine in methanol, dimethylformamide and mixed solvent
media has been investigated. The observations have been explained
on the basis of catalysis by CH₂O⁻ ion and an
amido complex (conjugate base), we were interested
in finding out the effect of introducing a better leaving group such as
Br⁻ than the Cl⁻ ion in the complex and (ii) to study the rate trends when the geometry of the complex
substrate was altered. This prompted us to undertake
the title investigation.

We had earlier reported¹ the results of our studies on
the substitution of a chloride in trans-[Co(en)₂Cl₂]⁺ by organic bases in methanol medium. The reaction
rates depended upon the pKₐs of the bases and were
explained on the basis of an Sn1 CB mechanism (conjugate base) has been proposed. Both the complexes react faster
than the trans-dichloro complex. The higher rates in the case of the
dibromo complex are due to the facile cleavage of the Co–Br bond.
The higher rate in the case of the cis-complex is due to ion pairing,
which results in a higher equilibrium concentration of the reactive
amido complex.

In methanol medium, all kinetic studies were made under second
order conditions with [complex] = 5 × 10⁻⁴ M and
[base] = 2.5 to 4.2 × 10⁻⁴ M for trans-[Co(en)₂Br₂]⁺ and
[complex] = 5 × 10⁻⁴ M and [base] = 1.7 to 3.4
× 10⁻⁴ M for cis-[Co(en)₂Cl₂]⁺. In the range of concentrations studied, the rates increased with increase in [base]. Further, the rate constants
increased with the pKₐs of the bases. Activation
parameters were evaluated on the basis of studies at
four temperatures in the range 10-25°C for trans-
[Co(en)₂Br₂]⁺ and 15-30°C for cis-[Co(en)₂Cl₂]⁺. (The reaction is too rapid beyond 25°C for making rate
measurements with the trans-complex). These are
presented in Table 1 along with the rate constants.

(a) In methanol medium, the reaction mixtures at various intervals of time, using
an Elico CM 88 conductivity bridge. Reaction
mixtures were taken in an air-tight conductivity cell
with bright platinum foil electrodes. The rate
constants were evaluated as described earlier.¹ ² ³ ⁴ For runs where [complex] > [base], the second-order rate
constants (k₂) and pseudo first-order rate constants
were evaluated as described earlier.

(b) In dimethylformamide medium, rate studies
with the stronger of the five bases, viz. diethylamine
and piperidine in the temperature range, 20-35°C were
done under pseudo-first order conditions with
[complex] = 7.5 × 10⁻⁴ M and [base] = 2 to 10.0
× 10⁻⁴ M for trans-[Co(en)₂Br₂]⁺ and [complex] = 7
× 10⁻⁴ M and [base] = 2.0-2.82 × 10⁻² M for the cis-
Table 1—Second Order Rate Constants and Activation Parameters for Substitution of Bases in trans-[Co(en)2Br2]+ and cis-[Co(en)2Cl2]+ in Methanol and Dimethylformamide

<table>
<thead>
<tr>
<th>Base</th>
<th>$k_2$ (dm³ mol⁻¹ s⁻¹)</th>
<th>$\Delta H^\ddagger$ (kJ mol⁻¹)</th>
<th>$\Delta S^\ddagger$ (JK⁻ mol⁻¹)</th>
<th>$\Delta G^\ddagger$ (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>trans-[Co(en)2Br2]⁺</strong> in MeOH at 25°C</td>
<td></td>
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</tr>
<tr>
<td>Benzylamine</td>
<td>3.05 ± 0.02</td>
<td>97.2 ± 2.6</td>
<td>91 ± 3</td>
<td>72.7 ± 0.8</td>
</tr>
<tr>
<td>n-Butylamine</td>
<td>9.34 ± 0.02</td>
<td>112.4 ± 3.0</td>
<td>151 ± 4</td>
<td>67.5 ± 0.7</td>
</tr>
<tr>
<td>Cyclohexylamine</td>
<td>10.34 ± 0.08</td>
<td>108.4 ± 3.0</td>
<td>138 ± 4</td>
<td>67.2 ± 0.7</td>
</tr>
<tr>
<td>Diethylamine</td>
<td>11.27 ± 0.07</td>
<td>93.3 ± 2.4</td>
<td>88 ± 3</td>
<td>67.0 ± 0.8</td>
</tr>
<tr>
<td>Piperidine</td>
<td>12.20 ± 0.01</td>
<td>75.3 ± 2.4</td>
<td>29 ± 1</td>
<td>66.8 ± 0.7</td>
</tr>
<tr>
<td><strong>trans-[Co(en)2Br2]⁺</strong> in DMF at 30°C</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Diethylamine</td>
<td>3.81 ± 0.03 x 10⁻²</td>
<td>99.2 ± 3.0</td>
<td>55 ± 2</td>
<td>82.5 ± 0.8</td>
</tr>
<tr>
<td>Piperidine</td>
<td>5.70 ± 0.01 x 10⁻²</td>
<td>95.1 ± 3.0</td>
<td>45 ± 2</td>
<td>81.5 ± 0.8</td>
</tr>
<tr>
<td><strong>cis-[Co(en)2Cl2]⁺</strong> in MeOH at 30°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzylamine</td>
<td>2.72 ± 0.02</td>
<td>84.6 ± 2.0</td>
<td>43 ± 1</td>
<td>71.7 ± 0.7</td>
</tr>
<tr>
<td>n-Butylamine</td>
<td>7.65 ± 0.12</td>
<td>85.1 ± 2.2</td>
<td>53 ± 2</td>
<td>69.1 ± 0.7</td>
</tr>
<tr>
<td>Cyclohexylamine</td>
<td>8.28 ± 0.05</td>
<td>81.9 ± 1.7</td>
<td>43 ± 1</td>
<td>69.0 ± 0.8</td>
</tr>
<tr>
<td>Diethylamine</td>
<td>10.02 ± 0.03</td>
<td>82.5 ± 2.0</td>
<td>46 ± 2</td>
<td>68.5 ± 0.7</td>
</tr>
<tr>
<td>Piperidine</td>
<td>12.23 ± 0.05</td>
<td>88.4 ± 2.4</td>
<td>68 ± 3</td>
<td>68.0 ± 0.6</td>
</tr>
<tr>
<td><strong>cis-[Co(en)2Cl2]⁺</strong> in DMF at 30°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diethylamine</td>
<td>7.91 ± 0.09 x 10⁻²</td>
<td>91.3 ± 2.5</td>
<td>35 ± 1</td>
<td>80.6 ± 0.8</td>
</tr>
<tr>
<td>Piperidine</td>
<td>11.0 ± 0.1 x 10⁻²</td>
<td>88.3 ± 2.0</td>
<td>28 ± 1</td>
<td>80.0 ± 0.7</td>
</tr>
</tbody>
</table>

$k_2$ values in MeOH are the mean of three runs while in DMF they are mean of four runs.

The reactions were first order in [base] and second order overall. The second order rate constants $k_2 = k_1/[\text{base}]$ at 30°C along with the activation parameters are presented in Table 1. It can be seen that there is a considerable reduction in rate as compared to rates in MeOH medium.

(c) In mixed solvent medium, rate studies with four of the bases, viz. benzylamine, cyclohexylamine, diethylamine and piperidine were carried out under pseudo-first order conditions at 30°C, in MeOH-dimethylformamide mixtures (2 to 5% MeOH v/v) in the case of trans-bromo complex and 5-20% (v/v) MeOH in the case of cis-chloro complex. The complex concentration is maintained at $5 \times 10^{-4}$ M for both complexes, while the [base] = 0.5 to $4.0 \times 10^{-2}$ M in the case of $\text{trans-[Co(en)2Br2]⁺}$ and 0.2 to $4.2 \times 10^{-2}$ M, with the cis-chloro complex. The results are presented in Table 2. The rates for a given base increased with the percentage of MeOH in the medium. Further, in a given medium the rates increased (cf. Table 2) in the order: benzylamine < cyclohexylamine < diethylamine < piperidine, which happens to be the increasing order of base strengths.

The rates of substitution are found to depend on the nature of the base and the base strength. The significantly higher rates in the protic solvent may be due to the fact that equilibrium (1) exists in MeOH.

$$B + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{O}^- + BH^+ \quad \ldots \quad (1)$$

due to the fact that equilibrium (1) exists in MeOH.

The high positive entropies of activation suggest dissociative activation. Hence our conclusion based on our previous study is that the CH₃O⁻ ion generates an active amido complex [Co(C₂H₅N₂)₂Cl₂] in a fast equilibrium (X = Cl or Br).

This is followed by the dissociation of the amido complex in a slow step and the subsequent fast protonation of the complex ion and substitution of base. The equilibrium concentration of the amido complex determines the overall rate.

The significantly lower rates in the aprotic solvent diethylformamide and the gradual increase in rate with the increase in MeOH content in the mixed solvent support this mechanism. In dimethylformamide, the formation of amido complex is not
possible and catalytic assistance by CH$_3$O$^-$ is absent. In the mixtures, the concentration of catalyst increases with the increase in the percentage of methanol.

The rates of substitution in the complexes in this study are higher than those in trans-[Co(en)$_2$Cl$_2$]$^+$. Once the amido complex is generated, further reaction can proceed along the familiar steps of $S_{N}$1 $CB$ process. It is, therefore, understandable that the cis-dichloro complex reacts faster than the trans-dichloro complex.

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References