<table>
<thead>
<tr>
<th>Ligand substitution reactions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand substitution in square-planar complexes</td>
<td></td>
</tr>
<tr>
<td>Ligand substitution in octahedral complexes</td>
<td></td>
</tr>
<tr>
<td>Redox reactions</td>
<td></td>
</tr>
<tr>
<td>Photochemical reactions</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 12 Coordination Chemistry IV: Reaction and Mechanisms

<table>
<thead>
<tr>
<th>Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-1 History and Principles</td>
</tr>
<tr>
<td>12-2 Substitution Reactions</td>
</tr>
<tr>
<td>12-3 Kinetic Consequences of Reaction Pathways</td>
</tr>
<tr>
<td>12-4 Experimental Evidence in Octahedral substitution</td>
</tr>
<tr>
<td>12-5 Stereochemistry of Reactions</td>
</tr>
<tr>
<td>12-6 Substitution Reactions of Square-Planar Complexes</td>
</tr>
<tr>
<td>12-7 The trans Effect</td>
</tr>
<tr>
<td>12-8 Oxidation-Reduction Reactions</td>
</tr>
<tr>
<td>12-9 Reactions of Coordinated Ligand</td>
</tr>
</tbody>
</table>

http://en.wikipedia.org/wiki/Expedia
Chapter 12 Coordination Chemistry IV: Reaction and Mechanisms

Share some characteristics with reactions of other molecules.

**Have some additional features** because the molecules have more complex (geometries, rearrangement, metal atom etc.)

Substitution
Oxidation-Reduction
Reactions of Coordinated Ligand
The unification of reaction theory is still a goal of chemists.

*The ability to predict products and choose appropriate reaction condition to obtain the desired products is still a matter of art as well as science.*

Understand the electronic structure of the compounds and their interactions.
the pass between the reactants and products is always the lowest energy pathway and must be the same regardless of the direction of the reaction – the principle of microscopic reversibility.
A number of parameters can be obtained from kinetic experiments.

Order, rate constant – the power of the reactant concentration, the speed of reaction.

T – free energy, enthalpy and entropy of activation.
P – volume of activation
12-2 Substitution Reactions; Inert and Labile compounds

**Substitution or replacement**

\[
[Cu(H_2O)_6]^{2+} + 4 NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4 H_2O
\]
blue

\[
[Fe(H_2O)_6]^{3+} + SCN^- \rightleftharpoons [Fe(H_2O)_5(SCN)]^{2+} + H_2O
\]
very pale violet

\[
[Fe(H_2O)_5(OH)]^{2+} + H^+ \rightarrow [Fe(H_2O)_6]^{3+}
\]
yellow
colorless (very pale violet)

\[
[Fe(H_2O)_6]^{3+} + Cl^- \rightarrow [Fe(H_2O)_5(Cl)]^{2+} + H_2O
\]
yellow

\[
[Fe(H_2O)_5(Cl)]^{2+} + PO_4^{3-} \rightarrow Fe(H_2O)_5(PO_4) + Cl^- \\
\text{colorless}
\]

\[
Fe(H_2O)_5(PO_4) + SCN^- \rightarrow [Fe(H_2O)_5(SCN)]^{2+} + PO_4^{3-} \\
\text{red}
\]

\[
[Fe(H_2O)_5(SCN)]^{2+} + F^- \rightarrow [Fe(H_2O)_5(F)]^{2+} + SCN^-
\]
colorless

Compounds such as these that react rapidly are called **labile**.

Inert or robust
12-2 Substitution Reactions; Inert and Labile compounds

**labile, inert vs stable, unstable**

**kinetic terms**

**thermodynamic terms**

Stable but labile

Unstable but inert

Inert compounds are easy to study
Labile compound → How?

General rules

Relationship with LFSA

<table>
<thead>
<tr>
<th>Slow Reactions (Inert)</th>
<th>Intermediate</th>
<th>Fast Reactions (Labile)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^3$, low-spin $d^4$, $d^5$, and $d^6$</td>
<td>Weak-field $d^8$</td>
<td>$d^1$, $d^2$, high-spin $d^4$, $d^5$, and $d^6$</td>
</tr>
<tr>
<td>Strong-field $d^8$ (square planar)</td>
<td></td>
<td>$d^7$, $d^9$, $d^{10}$</td>
</tr>
</tbody>
</table>
### 12-2 Substitution Reactions; Mechanisms of Substitution

#### TABLE 12-1
Classification of Substitution Mechanisms

<table>
<thead>
<tr>
<th>Intimate Mechanism</th>
<th>Dissociative 5-Coordinate Transition State for Octahedral Reactant</th>
<th>Associative 7-Coordinate Transition State for Octahedral Reactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociative activation</td>
<td>$D$</td>
<td>$L_d$</td>
</tr>
<tr>
<td>Associative activation</td>
<td>$L_a$</td>
<td>$A$</td>
</tr>
</tbody>
</table>

**Alternative Labels**

- $S_{N1}^{\text{lim}}$ (limiting first-order nucleophilic substitution)
- $S_{N2}^{\text{lim}}$ (limiting second-order nucleophilic substitution)

#### Diagrams

1. **Free energy vs. Extent of reaction**
   - MX + Y (M + X + Y)
   - MY + X

2. **Free energy vs. Extent of reaction**
   - MX + Y (MXY)
   - MY + X
The kinetic raw and other experimental evidence to find out the mechanism of a reaction.

**Dissociation**

\[
\begin{align*}
ML_5X & \xrightleftharpoons[k_{-1}]{k_1} ML_5 + X \\
ML_5 + Y & \xrightarrow{k_2} ML_5Y
\end{align*}
\]

**The steady-state hypothesis:**
1. A very small concentration of a intermediate
2. The rates of the formation and reaction of the intermediate must be equal.

\[
\frac{d[ML_5]}{dt} = k_1[ML_5X] - k_{-1}[ML_5][X] - k_2[ML_5][Y] = 0
\]
12-3 Kinetic Consequences of Reaction Pathways; Dissociation (D)

ML₅X ⇌ \frac{k_1}{k_{-1}} ML₅ + X

ML₅ + Y \xrightarrow{k_2} ML₅Y

**Solving for \([ML₅]\)**

\[ [ML₅] = \frac{k_1[ML₅X]}{k_{-1}[X] + k_2[Y]} \]

**The rate raw for the formation of the product**

\[ \frac{d[ML₅Y]}{dt} = k_6[ML₅][Y] \quad \Rightarrow \quad \frac{d[ML₅Y]}{dt} = \frac{k_2k_1[ML₅X][Y]}{k_{-1}[X] + k_2[Y]} \]
A rapid equilibrium between the incoming ligand and the 6-coordinate reactant forms an ion pair or loosely bonded molecular combination.

When $k_2 \ll k_{-1}$

The steady-state hypothesis
If \([Y]\) is large enough compared with \([ML_5X] \rightarrow\)

Unstable transition species may be large enough to significantly change the concentration of the \(ML_5X\), but not that of \(Y\).

\[
[M]_0 = [ML_5X] + [ML_5X \cdot Y] \quad \text{and} \quad [Y]_0 \approx [Y]
\]

\[
\frac{d[ML_5X \cdot Y]}{dt} = k_1[ML_5X][Y] - k_{-1}[ML_5X \cdot Y] - k_2[ML_5X \cdot Y] = 0
\]

\[
k_1([M]_0 - [ML_5X \cdot Y])[Y]_0 - k_{-1}[ML_5X \cdot Y] - k_2[ML_5X \cdot Y] = 0
\]

\[
\frac{d[ML_5Y]}{dt} = k_2[ML_5X \cdot Y] = \frac{k_2K_1[M]_0[Y]_0}{1 + K_1[Y]_0 + \left(k_2/k_{-1}\right)} \approx \frac{k_2K_1[M]_0[Y]_0}{1 + K_1[Y]_0}
\]
12-3 Kinetic Consequences of Reaction Pathways; Interchange (I)

Two variations on the interchange mechanism are $I_d$ (dissociative interchange) and $I_a$ (associative interchange). The difference between them is in the degree of bond formation in the first step of the mechanism. If bonding between the incoming ligand and the metal is more important, it is an $I_a$ mechanism. If breaking the bond between the leaving ligand and the metal is more important, it is an $I_d$ mechanism. The distinction between them is subtle, and careful experimental design is required to determine which description fits a given reaction.

At low $[Y]$

\[
\text{Rate} = \frac{k[M][Y]}{[X] + k'[Y]}
\]

At high $[Y]$

\[
\text{Rate} = \frac{k[M]_0[Y]_0}{1 + k'[Y]_0}
\]

Rate = $k[M]_0[Y]_0$ or $k[M]_0[Y]_0/[X]$

Second order

Rate = $(k/k')[M]_0$

First order
12-3 Kinetic Consequences of Reaction Pathways; Association (A)

**Association**

\[
\begin{align*}
    ML_5X + Y & \xrightleftharpoons[k_-]{k_1} ML_5XY \\
    ML_5XY & \xrightarrow[k_2]{\text{}} ML_5Y + X
\end{align*}
\]

**The steady-state hypothesis**

\[
\frac{d[ML_5Y]}{dt} = \frac{k_1 k_2 [ML_5X][Y]}{k_- + k_2} = k[ML_5X][Y]
\]

As with the dissociative mechanism, there are very few clear examples of associative mechanism in which the intermediate is detectable. Most reaction fit better between the two extremes.
From six coordination (octahedral)  
To five coordination (square pyramidal or trigonal-bipyramidal)  
The change in LFSE between these two.

**Ligand field activation energy (LFAE)**

<table>
<thead>
<tr>
<th>System</th>
<th>Octahedral LFSE</th>
<th>Square pyramidal LFSE</th>
<th>LFAE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^0$</td>
<td>-12</td>
<td>-10</td>
<td>2</td>
</tr>
<tr>
<td>$d^1$</td>
<td>-12</td>
<td>-10</td>
<td>2</td>
</tr>
<tr>
<td>$d^2$</td>
<td>-12</td>
<td>-10</td>
<td>2</td>
</tr>
<tr>
<td>$d^3$</td>
<td>-12</td>
<td>-10</td>
<td>2</td>
</tr>
<tr>
<td>$d^4$</td>
<td>-12</td>
<td>-10</td>
<td>2</td>
</tr>
<tr>
<td>$d^5$</td>
<td>-12</td>
<td>-10</td>
<td>2</td>
</tr>
<tr>
<td>$d^6$</td>
<td>-12</td>
<td>-10</td>
<td>2</td>
</tr>
<tr>
<td>$d^7$</td>
<td>-12</td>
<td>-10</td>
<td>2</td>
</tr>
<tr>
<td>$d^8$</td>
<td>-12</td>
<td>-10</td>
<td>2</td>
</tr>
<tr>
<td>$d^9$</td>
<td>-12</td>
<td>-10</td>
<td>2</td>
</tr>
<tr>
<td>$d^{10}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

LFAE calculated for trigonal-bipyramidal transition states are generally the same or larger than those for square-pyramidal.

Provide estimates of the energy necessary to form the transition state.
Thermodynamic favorable ($\Delta H$) vs reaction rate ($E_A$)

$$k = A e^{-\frac{E_a}{RT}} \quad \text{or} \quad \ln k = \ln A - \frac{E_a}{RT}$$

Enthalpy, entropy, activation energy
12-4 Experimental evidence in Octahedral substitution; Dissociation

**Stabilization energy for water exchange**

The results are similar to those of the thermodynamic case of enthalpy of hydration.
Other metal ion facts that affect reaction rates

1. Oxidation state of the central ion
   Higher oxidation states have ??? ligand exchange rates

\[
[\text{AlF}_6]^{3-} > [\text{SiF}_6]^{2-} > [\text{PF}_6]^{-} > \text{SF}_6
\]
\[
3^+ \quad 4^+ \quad 5^+ \quad 6^+
\]

\[
[\text{Na(H}_2\text{O)}_n]^+ > [\text{Mg(H}_2\text{O)}_n]^{2+} > [\text{Al(H}_2\text{O)}_6]^{3+}
\]
\[
1^+ \quad 2^+ \quad 3^+
\]

2. Ionic radius
   Smaller ions have ??? ligand exchange rates

\[
[\text{Sr(H}_2\text{O)}_6]^{2+} > [\text{Ca(H}_2\text{O)}_6]^{2+} > [\text{Mg(H}_2\text{O)}_6]^{2+}
\]
\[
112 \text{ pm} \quad 99 \text{ pm} \quad 66 \text{ pm}
\]

Higher electronic attraction
1. The rate of reaction changes only slightly with changes in the incoming ligand. (rate constant of less than a factor of 10)

2. Decreasing negative charge or increasing positive charge on the reactant compound decreases the rate of substitution.

3. Steric crowding on the reactant complex increases the rate of ligand dissociation.

4. The rate of reaction correlates with the metal-ligand bond strength of the leaving group, in a linear free energy relationship (LFER).

5. Activation energies and entropies are consistent with dissociation. (volume of activation $\Delta V_{\text{act}}$; positive or negative?)
12-4 Experimental evidence in Octahedral substitution; Linear Free Energy Relationship (LFER)

Many kinetic effects can be related to thermodynamic effects by a LFER

The bond strength of a metal-ligand bond (a thermodynamic function) vs the dissociation rate of that ligand (a kinetic function). The equilibrium constant (thermodynamic) vs the rate constant: has to be linear relationship.

\[
\ln k = \ln A - \frac{E_a}{RT} \quad \text{and} \quad \ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}
\]

\(E_a\) vs \(\Delta H^\circ\)

In molecular bonding term, a stronger bond between the metal and the leaving group results in a larger activation energy.

\[\text{[Co(NH}_3\text{)}_5X]^2+ + \text{H}_2\text{O} \rightarrow \text{[Co(NH}_3\text{)}_5(\text{H}_2\text{O})]^3+ + \text{X}^-\]
Many kinetic effects can be related to thermodynamic effects by a LFER.

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\]
Many kinetic effects can be related to thermodynamic effects by a LFER.

The bond strength of a metal-ligand bond (a thermodynamic function) vs the dissociation rate of that ligand (a kinetic function).

The equilibrium constant (thermodynamic) vs the rate constant: has to be linear relationship.

$E_a$ vs $\Delta H^\circ$

In molecular bonding term, a stronger bond between the metal and the leaving group results in a larger activation energy.
For the first-order region (large [Y]); The rate constant are all relatively close to that for water exchange → dissociative mechanism

For the second-order region

\[ \text{Ni} - \text{OH}_2 + \text{L} \rightleftharpoons \text{Ni} - \text{OH}_2 \cdot \text{L} \]

\[ \text{Ni} - \text{OH}_2 \cdot \text{L} \rightarrow \text{Ni} - \text{L} + \text{H}_2\text{O} \]
**Much less common**

### TABLE 12-5
**Effects of Entering Group and cis-Ligands on Rates**

<table>
<thead>
<tr>
<th>Entering Ligand</th>
<th>([\text{Cr(H}_2\text{O)}_6]^{3+}) Rate Constants for Anation</th>
<th>([\text{Cr(NH}_3)_2\text{H}_2\text{O}]^{3+}) Rate Constants for Anation</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCS(^-)</td>
<td>180 (10^{-8} \text{ M}^{-1} \text{ s}^{-1})</td>
<td>4.2 (10^{-4} \text{ M}^{-1} \text{ s}^{-1})</td>
</tr>
<tr>
<td>NO(_3^-)</td>
<td>73 (10^{-8} \text{ M}^{-1} \text{ s}^{-1})</td>
<td>—</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>2.9 (10^{-8} \text{ M}^{-1} \text{ s}^{-1})</td>
<td>—</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>1.1 (10^{-8} \text{ M}^{-1} \text{ s}^{-1})</td>
<td>0.7 (10^{-4} \text{ M}^{-1} \text{ s}^{-1})</td>
</tr>
<tr>
<td>I(^-)</td>
<td>0.08 (10^{-8} \text{ M}^{-1} \text{ s}^{-1})</td>
<td>—</td>
</tr>
<tr>
<td>CF(_3)COO(^-)</td>
<td>—</td>
<td>1.4 (10^{-4} \text{ M}^{-1} \text{ s}^{-1})</td>
</tr>
</tbody>
</table>

\(l_a\) \hspace{1cm} \(l_d\)
12-4 Experimental evidence in Octahedral substitution; Associative Mechanism

Much less common

Why?
Experimental evidence in Octahedral substitution

The Conjugate Base Mechanism

\[
[\text{Co(NH}_3\text{)}_5\text{X}]^{2+} + \text{OH}^- \rightleftharpoons [\text{Co(NH}_3\text{)}_4(\text{NH}_2)\text{X}]^{2+} + \text{H}_2\text{O} \quad \text{(equilibrium)} \quad (1)
\]
\[
[\text{Co(NH}_3\text{)}_4(\text{NH}_2)\text{X}]^{2+} \rightarrow [\text{Co(NH}_3\text{)}_4(\text{NH}_2)]^{2+} + \text{X}^- \quad \text{(slow)} \quad (2)
\]
\[
[\text{Co(NH}_3\text{)}_4(\text{NH}_2)]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Co(NH}_3\text{)}_5(\text{OH})]^{2+} \quad \text{(fast)} \quad (3)
\]

Overall,
\[
[\text{Co(NH}_3\text{)}_5\text{X}]^{2+} + \text{OH}^- \rightarrow [\text{Co(NH}_3\text{)}_5(\text{OH})]^{2+} + \text{X}^-
\]

The ligand \textbf{trans} to the amido or hydroxo group is frequently the one lost.

Additional evidence

1. Base catalyzed exchange of hydrogen from the amine groups takes place under the same conditions.
2. The \textit{isotope ratio} \((^{18}\text{O}/^{16}\text{O})\) in the product in \(^{18}\text{O}\)-enriched water is the same as that in the water regardless of the leaving group. (no associative)
3. \(\text{RNH}_2\) compounds react fast than \(\text{NH}_3\). (help to form 5-coordinate)
4. A plot of \(\text{InK}_{\text{OH}}\) versus \(\text{InK}_{\text{OH}}\) is linear.
5. When \textit{substituted amines} used (no protons), the reaction is very slow or nonexistent.
The reaction in (a) is $10^4$ times faster than that in (b).
The increased energy needed to remove the first bound atom and the probability of a reversal of this first step

*The ligand must bend and rotate to move the free amine group away from the metal.*

The concentration of the intermediate is low and the first dissociation can readily reverse

This kinetic chelate effect reduces the rates of aquation reactions by factors from 20 to $10^5$. 
A common assumption is that reactions with **dissociative mechanisms** are more likely to result in **random isomerization or racemization** and associative mechanisms are more likely to result in single-product reactions; however, the evidence is much less clear-cut.

The higher concentration of ion pairs $[\text{Co(en)}_2\text{Cl}_2]^+ \cdot \text{OH}^-$
Temperature dependence

In the substitution of ammonia for both chlorides in [Co(en)$_2$Cl$_2$]$^+$

At low T: there is inversion of configuration
At high T: there is retention
Small fraction of trans

No complete explanation of these reactions

In some cases, a preferred orientation of the other ligands may dictate the product.

the $\alpha$ form of trien complexes is more stable than the $\beta$ form
12-5 Stereochemistry of Reactions; Substitution in \textit{trans} complexes

Dissociation mechanism and stereochemical change; three different pathways

Axial B requires \textit{more arrangement} of the ligands and \textit{larger stretch for the LL} ring in the equatorial plane.

A change from \textit{trans} to \textit{cis} is two thirds for a trigonal-bipyramidal intermediate.


### TABLE 12-8

Stereochmistry of Acid Aquation

\[
[\text{Co(en)}_2\text{LX}]^{n+} + \text{H}_2\text{O} \rightarrow [\text{Co(en)}_2\text{LH}_2\text{O}]^{(1+n)+} + \text{X}^{-}
\]

<table>
<thead>
<tr>
<th>cis-L</th>
<th>X</th>
<th>% cis Product</th>
<th>trans-L</th>
<th>X</th>
<th>% cis Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH(^-)</td>
<td>Cl(^-)</td>
<td>100</td>
<td>OH(^-)</td>
<td>Cl(^-)</td>
<td>75</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>Br(^-)</td>
<td>100</td>
<td>OH(^-)</td>
<td>Br(^-)</td>
<td>73</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>Cl(^-)</td>
<td>100</td>
<td>Br(^-)</td>
<td>Cl(^-)</td>
<td>35</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>Br(^-)</td>
<td>100</td>
<td>Cl(^-)</td>
<td>Br(^-)</td>
<td>20</td>
</tr>
<tr>
<td>N(_3)(^-)</td>
<td>Cl(^-)</td>
<td>100</td>
<td>N(_3)(^-)</td>
<td>Cl(^-)</td>
<td>50–70</td>
</tr>
<tr>
<td>NCS(^-)</td>
<td>Cl(^-)</td>
<td>100</td>
<td>NCS(^-)</td>
<td>Cl(^-)</td>
<td>0</td>
</tr>
<tr>
<td>NCS(^-)</td>
<td>Br(^-)</td>
<td>100</td>
<td>NH(_3)</td>
<td>Cl(^-)</td>
<td>0</td>
</tr>
<tr>
<td>NO(_2)(^-)</td>
<td>Cl(^-)</td>
<td>100</td>
<td>NO(_2)(^-)</td>
<td>Cl(^-)</td>
<td>0</td>
</tr>
</tbody>
</table>


### TABLE 12-9

Stereochmistry of Base Substitution

\[
[\text{Co(en)}_2\text{LX}]^{n+} + \text{OH}^{-} \rightarrow [\text{Co(en)}_2\text{LOH}]^{n+} + \text{X}^{-}
\]

<table>
<thead>
<tr>
<th>cis-L</th>
<th>X</th>
<th>(\Delta)</th>
<th>Racemic(^a)</th>
<th>(\Lambda)</th>
<th>trans-L</th>
<th>X</th>
<th>% cis Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH(^-)</td>
<td>Cl(^-)</td>
<td>61</td>
<td>96</td>
<td>36</td>
<td>OH(^-)</td>
<td>Cl(^-)</td>
<td>94</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>Br(^-)</td>
<td>21</td>
<td>16</td>
<td>5</td>
<td>OH(^-)</td>
<td>Br(^-)</td>
<td>90</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>Cl(^-)</td>
<td>21</td>
<td>30</td>
<td>5</td>
<td>Cl(^-)</td>
<td>Cl(^-)</td>
<td>5</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>Br(^-)</td>
<td>40</td>
<td>51</td>
<td>13</td>
<td>Cl(^-)</td>
<td>Cl(^-)</td>
<td>13</td>
</tr>
<tr>
<td>N(_3)(^-)</td>
<td>Cl(^-)</td>
<td>56</td>
<td>24</td>
<td>76</td>
<td>N(_3)(^-)</td>
<td>Cl(^-)</td>
<td>76</td>
</tr>
<tr>
<td>NCS(^-)</td>
<td>Cl(^-)</td>
<td>59</td>
<td>26</td>
<td>81</td>
<td>NCS(^-)</td>
<td>Br(^-)</td>
<td>81</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>Cl(^-)</td>
<td>60</td>
<td>24</td>
<td>76</td>
<td>NH(_3)</td>
<td>Cl(^-)</td>
<td>76</td>
</tr>
<tr>
<td>NO(_2)(^-)</td>
<td>Cl(^-)</td>
<td>46</td>
<td>20</td>
<td>6</td>
<td>NO(_2)(^-)</td>
<td>Cl(^-)</td>
<td>6</td>
</tr>
</tbody>
</table>
12-5 Stereochemistry of Reactions; Substitution in \textit{trans} complexes

**Effect of the leaving ligand \( X \).**

<table>
<thead>
<tr>
<th>( X )</th>
<th>cis ( \rightarrow ) trans</th>
<th>trans ( \rightarrow ) cis</th>
<th>Racemization</th>
<th>( \text{H}_2\text{O} ) Exchange</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{OH}^- )</td>
<td>200</td>
<td>300</td>
<td>—</td>
<td>160</td>
</tr>
<tr>
<td>( \text{Br}^- )</td>
<td>5.4</td>
<td>16.1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>( \text{Cl}^- )</td>
<td>2.4</td>
<td>7.2</td>
<td>2.4</td>
<td>—</td>
</tr>
<tr>
<td>( \text{N}_3^- )</td>
<td>2.5</td>
<td>7.4</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>( \text{NCS}^- )</td>
<td>0.0014</td>
<td>0.071</td>
<td>0.022</td>
<td>0.13</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} )</td>
<td>0.012</td>
<td>0.68</td>
<td>( \sim 0.015 )</td>
<td>1.0</td>
</tr>
<tr>
<td>( \text{NH}_3 )</td>
<td>(&lt; 0.0001 )</td>
<td>0.002</td>
<td>0.003</td>
<td>0.10</td>
</tr>
<tr>
<td>( \text{NO}_2^- )</td>
<td>0.012</td>
<td>0.005</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

three different pathways

As a general rule, *cis* reactants retain their *cis* configuration, but *trans* reactants are more likely to give a mixture of *cis* and *trans* products.
12-5 Stereochemistry of Reactions

; Isomerization of Chelate Rings

FIGURE 12.10 Twist Mechanisms for Isomerization of $M(LL)_3$ and $[Co(trien)Cl_2]^+$ Complexes.

(a) Trigonal twist. The front triangular face rotates with respect to the back triangular face.
(b) Twist with perpendicular rings. The back ring remains stationary as the front two rings rotate clockwise.
(c) Twist with parallel rings. The back ring remains stationary as the front two rings rotate counterclockwise.
(d) $[Co(trien)Cl_2]^+$ $\alpha-\beta$ isomerization. The connected rings limit this isomerization to a clockwise trigonal twist of the front triangular face.

Which one?
12-6 Substitution Reactions of Square-Planar Complexes

Square-planar substitution reactions frequently show two-term rate laws.

\[
\text{Rate} = k_1[C\text{plx}] + k_2[C\text{plx}][Y]
\]

(a) Direct substitution by Y.

(b) Solvent-assisted substitution.

**Figure 12-11** The Interchange Mechanism in Square-Planar Reactions.
Pt(II) is a soft acid, so soft ligand react more readily
The order of ligands is nearly the reverse. The bond-strength effect of the metal-to-ligand \( \pi \) bonding → ??
Each of the parameters $s$ and $\eta_{Pt}$ may change by a factor of 3 from fast reactions to slow reactions, allowing for an overall ratio of $10^6$ in the rates.
12-7 The *Trans* Effect

It is possible to prepare specific isomers different ligands

The order of *trans* effect

\[ \text{CN}^- \sim \text{CO} \sim \text{C}_2\text{H}_4 > \text{PH}_3 \sim \text{SH}_2 > \text{NO}_2^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{NH}_3 \sim \text{py} > \text{OH}^- > \text{H}_2\text{O} \]
12-7 The **Trans Effect**

; explanations of the *trans* effect

**Sigma-bond effects**

Two factors

Weakening of the Pt-X bond

Stabilization of the presumed 5-coordinate transition state

**σ-donor properties only**
12-7 The *Trans* Effect; explanations of the *trans* effect

**Pi-bond effects**

Stabilization of the presumed 5-coordinate transition state

Strong \( \pi \)-acceptor bond \( \rightarrow \) charge is removed from Pt \( \rightarrow \) the entrance of another ligand to form a 5-coordinate species

\[ E_a \]

\[ C_2H_4 \sim CO > CN^- > NO_2^- > SCN^- > I^- > Br^- > Cl^- > NH_3 > OH^- \]

\[ \pi \text{-acceptor properties only} \]

**Overall trans effect**

\[ CO \sim CN^- \sim C_2H_4 \sim PR_3 \sim H^- \sim CH_3^- \sim SC(NH_2)_2 \sim C_6H_5^- \sim \]

\[ NO_2^- \sim SCN^- \sim I^- \sim Br^- \sim Cl^- \sim py, NH_3 \sim OH^- \sim H_2O \]
12-8 Oxidation-Reduction Reactions; inner- and outer-sphere reactions

Inner-sphere reaction; two molecules may be connected by a common ligand
Outer-sphere reaction; two separate molecules

The rates show very large differences; depend on the ability of the electrons to tunnel through the ligands
Ligands with \( \pi \) or \( p \) electrons or orbitals that can be used in bonding provide good pathways for tunneling.
12-8 Oxidation-Reduction Reactions; inner- and outer-sphere reactions

Change on electron transfer → change in bond distance
A higher ox. # leads to ___ bond
Form high spin Co(II)
To low spin Co(III)
$e_g$ orbitals are antibonding
Removal electrons from these orbitals → more stable compound and shorter bond distances, large LFSE.

**Inner-sphere reaction**

$$[\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+} + [\text{Cr(H}_2\text{O)}_6]^{2+} \rightarrow [(\text{NH}_3)_5\text{Co(Cl)}\text{Cr(H}_2\text{O)}_5]^{4+} + \text{H}_2\text{O} \quad (1)$$

Co(III) oxidant Cr(II) reductant Co(III) Cr(II)

Electron transfer

$$[(\text{NH}_3)_5\text{Co(Cl)}\text{Cr(H}_2\text{O)}_5]^{4+} \rightarrow [(\text{NH}_3)_5\text{Co(Cl)}\text{Cr(H}_2\text{O)}_5]^{4+} \quad (2)$$

Co(III) Cr(II)

Association and separation

$$[(\text{NH}_3)_5\text{Co(Cl)}\text{Cr(H}_2\text{O)}_5]^{4+} + \text{H}_2\text{O} \rightarrow [(\text{NH}_3)_5\text{Co(H}_2\text{O)}_2]^{2+} + [(\text{Cl})\text{Cr(H}_2\text{O)}_5]^{2+} \quad (3)$$
12-8 Oxidation-Reduction Reactions

; inner- and outer-sphere reactions

**Labile**
- But the parallels in the rate constants of the two species

**Inert**
- Not allow formation of bridging species

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>[Co(NH$_3$)$_5$(NH$_3$)$_3$]$_3^+$</th>
<th>[Co(NH$_3$)$_5$I$_3$]$_2^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(NH$_3$)$_5$(NH$_3$)]$_3^+$</td>
<td>$6.9 \times 10^2$</td>
<td>$1.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>[Co(NH$_3$)$_5$(F)]$_2^+$</td>
<td>$1.8 \times 10^3$</td>
<td></td>
</tr>
<tr>
<td>[Co(NH$_3$)$_5$(OH)]$_2^+$</td>
<td>$3 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>[Co(NH$_3$)$_5$(NO$_3$)]$_2^+$</td>
<td>$3.4 \times 10^1$</td>
<td></td>
</tr>
<tr>
<td>[Co(NH$_3$)$_5$(H$_2$O)]$_3^+$</td>
<td>$5 \times 10^4$</td>
<td></td>
</tr>
<tr>
<td>[Co(NH$_3$)$_5$(Cl)]$_2^+$</td>
<td>$8 \times 10^5$</td>
<td>$2.6 \times 10^2$</td>
</tr>
<tr>
<td>[Co(NH$_3$)$_5$(Br)]$_2^+$</td>
<td>$5 \times 10^6$</td>
<td>$1.6 \times 10^3$</td>
</tr>
<tr>
<td>[Co(NH$_3$)$_5$(I)]$_2^+$</td>
<td>$6.7 \times 10^3$</td>
<td>$6.7 \times 10^3$</td>
</tr>
</tbody>
</table>
12-8 Oxidation-Reduction Reactions; inner- and outer-sphere reactions

**Inner-sphere mechanism**

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Rate Constant ( k (M^{-1} s^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(NH}_3\text{)}_5\text{(F)}]^{2+})</td>
<td>(1.8 \times 10^4)</td>
</tr>
<tr>
<td>([\text{Co(NH}_3\text{)}_5\text{(OH)}]^{2+})</td>
<td>(9.3 \times 10^3)</td>
</tr>
<tr>
<td>([\text{Co(NH}_3\text{)}_5\text{(NH}_3\text{)}]^{3+})</td>
<td>(8.0 \times 10^2)</td>
</tr>
<tr>
<td>([\text{Co(NH}_3\text{)}_5\text{(NCS)}]^{2+})</td>
<td>(1.1 \times 10^2)</td>
</tr>
<tr>
<td>([\text{Co(NH}_3\text{)}_5\text{(N}_3\text{)}]^{2+})</td>
<td>(1.6 \times 10^2)</td>
</tr>
<tr>
<td>([\text{Co(NH}_3\text{)}_5\text{(Cl)}]^{2+})</td>
<td>(5.5 \times 10^2)</td>
</tr>
</tbody>
</table>
12-8 Oxidation-Reduction Reactions; inner- and outer-sphere reactions

Inner-sphere mechanism;
Overall rate usually depends on the first two step (substitution and transfer of electron)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>$k_2 (M^{-1} s^{-1})$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_6$H$_5$C$\equiv$O$^{-}$</td>
<td>0.18</td>
<td>Benzoate is difficult to reduce</td>
</tr>
<tr>
<td>CH$_3$C$\equiv$O$^{-}$</td>
<td>0.30</td>
<td>Acetic acid is difficult to reduce</td>
</tr>
<tr>
<td>CH$_3$NC$_5$H$_4$C$\equiv$O$^{-}$</td>
<td>1.8</td>
<td>N-methyl-4-carboxyprpyidine is more reducible</td>
</tr>
<tr>
<td>O$=$CHC$\equiv$O$^{-}$</td>
<td>0.3</td>
<td>Glyoxylate is easy to reduce</td>
</tr>
<tr>
<td>HOCH$_2$C$\equiv$O$^{-}$</td>
<td>$7 \times 10^{-3}$</td>
<td>Glycolate is very easy to reduce</td>
</tr>
</tbody>
</table>
The rate for Co compounds with other bridging ligands is frequently as much as $10^5$ larger than the rate for corresponding Cr compounds.

Seems to depend more on the rate of electron transfer from Cr$^{2+}$ to the bridging ligand than electron transfer from Cr$^{2+}$ to metal low-spin Ru(III).
12-8 Oxidation-Reduction Reactions

- conditions for high and low oxidation number

The overall stability of complexes with different charges on the M;
- LFSE, bonding energy, redox properties, the hard and soft character

High oxidation # vs Low oxidation #

- MnO$_4^-$, CrO$_4^{2-}$, FeO$_4^{2-}$, AgF$_2$, RuF$_5$, PtF$_6$, OsF$_6$
- V(CO)$_6$, Cr(CO)$_6$, Fe(CO)$_5$
- I$^-$ vs Cl$^-$

- Soft ligand: cyanide
- Hard ligand: ammonia

Strong oxidizing agent
- Co(III) more stable
- LFSE
- High spin Co(II)
- Low spin Co(III)
The properties of ligand (organic compound) will be changed by coordinated to the metal.
The formation of the cyclic compound by coordination to a metal ion.
12-9 Reactions of Coordinated Ligands; template reactions

**Imine or Schiff base**

**Geometric:** formation of the complex brings the reactants into close proximity with the proper orientation for reaction

**Electronic:** complexation may change the electronic structure sufficiently to promote the reaction
Electrophilic Substitution on Acetylacetone