Reactions of Coordination Compounds

The chemistry of coordination compounds has some additional features compare to simple organic / inorganic compounds, due to complexity in geometries and possibilities for rearrangement. The metal atoms posses more variability in their reactions, and different factors influence the course of reactions. Reactions of coordination complexes can be conveniently divided into:

1. **substitution reactions at the metal center**, 
2. **oxidation-reduction reactions**, and 
3. **reactions of the ligands that do not change the attachments to the metal center**.

Reactions that include more elaborate rearrangements of ligand structures are more often observed in organometallic compounds.

Substitution Reactions at The Metal Center

**LABILE vs INERT**

In terms of kinetic → **labile** is when the compounds reacts rapidly or fast (less than a minute), while **inert or robust** is when the compounds reacts slowly or slow (more than a minute)

**STABLE vs UNSTABLE**

In terms of thermodynamics → **stable** is when the reaction has a large equilibrium constant for formation, **unstable** is when the reaction has a small equilibrium constant for formation

Lability are influenced by:

1. **d electron configuration of metal ion**

   - **Slow Reactions (Inert)**
     - $d^3$, low-spin $d^4$, $d^5$, and $d^6$
     - Strong-field $d^8$ (square planar)
   
   - **Intermediate**
   
   - **Weak-field $d^8$**

   - **Fast Reactions (Labile)**
     - $d^1$, $d^2$, high-spin $d^4$, $d^5$, and $d^6$
     - $d^7$, $d^9$, $d^{10}$

Why are some configurations inert and some are labile?

<table>
<thead>
<tr>
<th>Changes In Crystal Field Stabilization Energies$^*$</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$d^n$</td>
<td>CFSE $M_{4a}$ (oct)</td>
<td>CFSE $M_{4a}$ (ap)</td>
<td>ΔCFSE</td>
</tr>
<tr>
<td>$d^1$</td>
<td>0.40</td>
<td>0.46</td>
<td>+0.06</td>
</tr>
<tr>
<td>$d^2$</td>
<td>0.80</td>
<td>0.91</td>
<td>+0.11</td>
</tr>
<tr>
<td>$d^3$</td>
<td>1.20</td>
<td>1.00</td>
<td>−0.20</td>
</tr>
</tbody>
</table>

$^*$The CFSEs (in units of $\Delta \epsilon$) for octahedral (oct) and square pyramidal (ap) fields are shown followed by the change in CFSE for the process $M_{4a}$ (octahedral) → $M_{4a}$ (square pyramidal). $\Delta \epsilon$ indicates a gain in CFSE during the process, and $\Delta \epsilon$ indicates a loss in CFSE.
2. Size of central atom
The smaller the central atom (other factors, i.e. charge of central atom, being equal), the more tightly the ligands are held and the more inert the complex is. Example:
Lability of $[\text{Mg(H}_2\text{O)}_6]^{2+} < [\text{Ca(H}_2\text{O)}_6]^{2+} < [\text{Sr(H}_2\text{O)}_6]^{2+}$.

3. Charge of central atom
The higher the charge (other factors, i.e. ligand, being equal), the more inert the complex. Example:
Lability of $[\text{Na(H}_2\text{O)}_6]^{+} > [\text{Mg(H}_2\text{O)}_6]^{2+} > [\text{Al(H}_2\text{O)}_6]^{3+}$.

Substitution Mechanisms

**Intimate mechanisms**
- **Dissociative** ($D$) ➔ the departing ligand leaves and an intermediate with a lower coordination number ($\text{ML}_5$) is formed.
- **Associative** ($A$) ➔ the incoming ligand adds to the complex and an intermediate with an increased coordination number ($\text{ML}_5\text{XY}$) is formed.

**Stoichiometric mechanisms**
- **Dissociative Interchange** ($I_d$) ➔ the degree of assistance is small and the reaction is primarily dissociative.
- **Associative Interchange** ($I_a$) ➔ the incoming ligand begins forming a bond to the central atom before the departing ligand bond is weakened appreciably.

Many reactions are described by $I$, or $I_d$ mechanisms rather than by $A$ or $D$ when the kinetic evidence points to association or dissociation but detection of intermediates is not possible.

Exercise
1. Explain why the reactivity of $\text{AlF}_6^{3-}$, $\text{SiF}_6^{2-}$, $\text{PF}_6^{-}$, and $\text{SF}_6$ with base are decrease respectively!
2. $[\text{M(H}_2\text{O)}_6]^{n+} + \text{H}_2\text{O} \rightleftharpoons [\text{M(H}_2\text{O)}_6]^{n+} + \text{H}_2\text{O}$

<table>
<thead>
<tr>
<th>$\text{M(III)}$</th>
<th>$d^n$</th>
<th>$V$ (per second)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cr(III)}$</td>
<td>$d^3$</td>
<td>$7 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\text{Fe(III)}$</td>
<td>$d^5$</td>
<td>$3 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Explain this data, why?
**Forms intermediate ML₅X**

- No intermediate, but activated complexes ML₅X --- Y or ML₅Y --- X

**Intermediate can be isolated**

- Activated complexes cannot be isolated

**Forms intermediate ML₆Y**

**Intermediate can be isolated**

**Dissociation**

In a dissociative (D) reaction, loss of a ligand to form an intermediate with a lower coordination number is followed by addition of a new ligand to the intermediate:

\[
\begin{align*}
ML₅X & \xrightarrow{k₁} ML₅ + X \\
ML₅ + Y & \xrightarrow{k₂} ML₅Y \\
\frac{d[ML₅Y]}{dt} & = \frac{k₂k₁[ML₅][Y]}{k_{-1}[X] + k₂[Y]}
\end{align*}
\]

**Interchange**

In an interchange (I) reaction, a rapid equilibrium between the incoming ligand and the 6-coordinate reactant forms an ion pair or loosely bonded molecular combination. This species, which is not described as having an increased coordination number and is not directly detectable, then reacts to form the product and release the initial ligand.

\[
\begin{align*}
ML₅X + Y & \xrightarrow{k₁} ML₅X-Y \\
ML₅X-Y & \xrightarrow{k₂} ML₅Y + X
\end{align*}
\]

**Association**

In an associative reaction, the first step, forming an intermediate with an increased coordination number, is the rate-determining step. It is followed by a faster reaction in which the leaving ligand is lost:

\[
\begin{align*}
ML₅X + Y & \xrightarrow{k₁} ML₅XY \\
ML₅XY & \xrightarrow{k₂} ML₅Y + X
\end{align*}
\]

**Dissociation**

\[
\begin{align*}
\frac{d[ML₅Y]}{dt} & = \frac{k₁k₂[ML₅X][Y]}{k_{-1} + k₂[Y]}
\end{align*}
\]

**Interchange**

\[
\begin{align*}
\frac{d[ML₅X]}{dt} & = \frac{k₂k₁[ML₅][Y]}{k_{-1}[X] + k₂[Y]}
\end{align*}
\]

**Association**

\[
\begin{align*}
\frac{d[ML₅XY]}{dt} & = \frac{k₁k₂[ML₅X][Y]}{k_{-1} + k₂[Y]}
\end{align*}
\]

**Dissociation**

\[
\begin{align*}
\frac{d[ML₅Y]}{dt} & = \frac{k₁k₂[ML₅X][Y]}{k_{-1} + k₂[Y]}
\end{align*}
\]

**Interchange**

\[
\begin{align*}
\frac{d[ML₅X]}{dt} & = \frac{k₂k₁[ML₅][Y]}{k_{-1}[X] + k₂[Y]}
\end{align*}
\]

**Association**

\[
\begin{align*}
\frac{d[ML₅XY]}{dt} & = \frac{k₁k₂[ML₅X][Y]}{k_{-1} + k₂[Y]}
\end{align*}
\]
The evidence for dissociative mechanisms can be grouped as follows:

1. The rate of reaction changes only slightly with changes in the incoming ligand.
   In many cases, aquation (substitution by water) and anation (substitution by an anion) rates are comparable. If dissociation is the rate-determining reaction, the entering group should have no effect at all on the reaction rate. Although there is no specific criterion for this, changes in rate constant of less than a factor of 10 are generally considered to be insignificant for this purpose.

2. Decreasing negative charge or increasing positive charge on the reactant complex decreases the rate of substitution. Larger electrostatic attraction between the positive metal ion and the negative ligand should slow the dissociation.

3. Steric crowding on the reactant complex increases the rate of ligand dissociation. When ligands on the reactant are crowded, loss of one of the ligands is made easier. On the other hand, if the reaction has an A or I mechanism, steric crowding interferes with the incoming ligand and slows the reaction.

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, although interpretation of these parameters is difficult. Another activation parameter now being measured by experiments at increased pressure is the volume of activation, the change in volume on forming the activated complex. Dissociative mechanisms generally result in positive values for $A_{\text{vmax}}$, because one species splits into two, and associative mechanisms result in negative $A_{\text{vmax}}$ values because two species combine into one, with a presumed volume smaller than the total for the reactants. However, caution is needed in interpreting volume effects because solvation effects, particularly for highly charged ions, may be larger than the difference expected for the reaction otherwise.

Determining the D or A Mechanisms

1. Entering Ligand ($Y_{\text{in}}$), by varying the $Y_{\text{in}}$:
   - If $K_{\text{obs}}$ also varied significantly $\Rightarrow$ A
   - If $K_{\text{obs}}$ does not varied significantly $\Rightarrow$ D

Example:
Anation or water exchange of $[\text{Co(NH}_3)_5(\text{H}_2\text{O})]^3+$ at 45°C

<table>
<thead>
<tr>
<th>$Y$</th>
<th>$K_{\text{obs}}$ (1/dec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>$100 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\text{N}_3^-$</td>
<td>$100 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>$24 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\text{Cl}^-$</td>
<td>$21 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\text{NCS}^-$</td>
<td>$16 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
2. Leaving Ligand ($X^-$), by varying the $X^-$:
   If $K_{obs}$ also varied significantly $\rightarrow$ D
   If $K_{obs}$ does not varied significantly $\rightarrow$ A

Example:
Aquation of $[\text{Co(NH}_3)_2(X)]^{n+}$ at 25 C

<table>
<thead>
<tr>
<th>$X^-$</th>
<th>$K_{obs}$ (1/detik)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OP(OCH$_3$)$_3$</td>
<td>$2.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>$2.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>I$^-$</td>
<td>$8.3 \times 10^{-6}$</td>
</tr>
<tr>
<td>F$^-$</td>
<td>$8.6 \times 10^{-8}$</td>
</tr>
<tr>
<td>N$_2^+$</td>
<td>$2.1 \times 10^{-9}$</td>
</tr>
<tr>
<td>NCS$^-$</td>
<td>$5.0 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

D or A ???

3. Sterical of the Ligand,
by increasing the sterical effect:
D $\rightarrow$ If $K_{obs}$ increased
A $\rightarrow$ If $K_{obs}$ decreased

Example: Aquation of trans-$[\text{Co(N-N)}_2\text{Cl}_2]^+$

<table>
<thead>
<tr>
<th>N-N</th>
<th>$K_{obs}$ [1/detik]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$CH$_2$CH$_2$NH$_2$</td>
<td>$3.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>NH$_2$CH$_2$CHNH$_2$</td>
<td>$6.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>$6.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>NH$_2$N-C-NH$_2$</td>
<td>spontan (cepat sekali)</td>
</tr>
<tr>
<td>CH$_3$CH$_3$</td>
<td></td>
</tr>
</tbody>
</table>

Substitution Reaction of Square Planar Complexes

The products of substitution reactions of square planar complexes [platinum(II) complexes are the primary examples] have the same configuration as the reactants, with direct replacement of the departing ligand by the new ligand.

The rates vary enormously and different compounds can be formed, depending both on the entering and the leaving ligands.

Kinetics and Stereochemistry of Square Planar Substitutions

Square-planar substitution reactions frequently show two term rate laws, of the form:

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

where:
[Y] is concentration of the incoming ligand

Both pathways (both terms in the rate law) are considered to be associative, in spite of the difference in order.
The $k_2$ term easily fits an associative mechanism in which the incoming ligand $Y$ and the reacting complex form a 5-coordinate transition state.

The accepted explanation for the $k_2$ term is a solvent-assisted reaction, with solvent replacing $X$ on the complex through a similar 5-coordinate transition state, and then itself being replaced by $Y$.

The second step of this mechanism is presumed to be faster than the first, and the concentration of solvent is large and unchanging, so the overall rate law for this path is first order in complex.

It is generally accepted that reactions of square-planar compounds are associative, although there is doubt about the degree of association, and they are classified as $I_\alpha$.

This same general description will fit whether
- the incoming ligand bonds strongly to Pt before the departing ligand bond is weakened appreciably ($I_\sigma$) or
- the departing ligand bond is weakened considerably before the incoming ligand forms its bond ($I_{d\sigma}$).

This mechanism explains naturally the effect of the incoming ligand. A strong Lewis base is likely to react readily, but the hard-soft nature of the base has an even larger effect. Pt(II) is generally a soft acid, so soft ligands react more readily with it. The order of ligand reactivity depends somewhat on the other ligands on the Pt, but the order for the reaction:

$$\text{trans-PtL}_2\text{Cl}_2 + Y \to \text{trans-PtL}_2\text{ClY} + \text{Cl}^-$$

for different $Y$ in methanol was found to be as follows:

$$PR_3 > CN^- > SCN^- > Br^- > N_3^- > NO_2^- > py > NH_2 = Cl^- > CH_3OH$$
Reactants with ligands other than chloride as T is found in a similar order, with some shuffling of the center of the list. The ratio of the rate constants for the extremes in the list is very large, with $k(\text{PPh}_3)/k(\text{CH}_3\text{OH}) = 9 \times 10^8$. Because T and Y have similar positions in the transition state, it is reasonable for them to have similar effects on the rate, and they do.

By the same argument, the leaving group X should also have a significant influence on the rate, and it does. The order of ligands is nearly the reverse of that given above, with hard ligands such as Cl$^-$, NH$_3$, and NO$_3^-$ leaving quickly, while soft ligands with considerable π bonding such as CN$^-$ and NO$_2^-$ leave reluctantly.

Good leaving groups (those that leave easily) show little discrimination between entering groups. Apparently, the ease of breaking the Pt — X bond takes precedence over the formation of the Pt — Y bond.

On the other hand, for complexes with less reactive leaving groups, the other ligands have a significant role; the softer PEt$_3$ and AsEt$_3$ ligands show a large selective effect when compared with the harder dien or en ligands.

$$[\text{Pt}(\text{dien})X]^- + \text{py} \rightarrow [\text{Pt}(\text{dien})(\text{py})]^{2+} + X^-$$

The rate increases by a factor of $10^5$ with H$_2$O as compared with X = CN$^-$ or NO$_2^-$ as the leaving group. The bond-strengthening effect of the metal-to-ligand π bonding reduces the reactivity of these ligands significantly.

In addition, π bonding to the leaving group uses the same orbitals as those bonding to the entering group in the trigonal plane.

These two effects result in the slow displacement of metal-to-ligand-π bonding ligands when compared with ligands with only σ bonding or ligand-to-metal π bonding.

The Trans Effect

In 1926, Chernyaev introduced the concept of the trans effect in platinum chemistry.

In reactions of square-planar Pt(II) compounds, ligands trans to chloride are more easily replaced than those trans to ligands such as ammonia; chloride is said to have a stronger trans effect than ammonia.

When coupled with the fact that chloride itself is more easily replaced than ammonia, this trans effect allows the formation of isomeric Pt compounds.
In reaction (a), after the first ammonia is replaced, the second replacement is trans to the first $\text{Cl}^-$.
In reaction (b), the second replacement is trans to $\text{Cl}^-$ (replacement of ammonia in the second reaction is possible, but then the reactant and product are identical).

The first steps in reactions (c) through (f) are the possible replacements, with nearly equal probabilities for replacement of $\text{NH}_3$ or py in any position. The second steps of (c) through (f) depend on the trans effect of $\text{Cl}^-$. Both steps of (g) and (h) depend on the greater lability of $\text{Cl}^-$. By using reactions such as these, it is possible to prepare specific isomers with different ligands.

Chernyaev and coworkers did much of this, preparing a wide variety of compounds and establishing the order of trans effect ligands:

$\text{CN}^- \approx \text{CO} \approx \text{C}_2\text{H}_3 > \text{PH}_3 > \text{SH}_2 > \text{NO}_2^- > I^- > \text{Br}^- > \text{Cl}^- > \text{NH}_3 \approx \text{py} > \text{OH}^- > \text{H}_2\text{O}$

Sigma-bonding effects

Two factors dominate the explanations of the trans effect, weakening of the Pt — X bond and stabilization of the presumed 5-coordinate transition state. The energy relationships are given in figure below, with the activation energy the difference between the reactant ground state and the first transition state.

(a) Poor trans effect, low ground state, high transition state.
(b) $\sigma$-Bonding effect, higher ground state (trans influence).
(c) $\pi$-Bonding effect, lower transition state (trans effect).
The Pt—X bond is influenced by the Pt—T bond, because both use the Pt $p(x)$, and $d(x^2-y^2)$ orbitals. When the Pt—T $\sigma$-bond is strong, it uses a larger part of these orbitals and leaves less for the Pt—X bond. As a result, the Pt—X bond is weaker and its ground state ($\sigma$-bonding orbital) is higher in energy, leading to a smaller activation energy for the breaking of this bond [figure b].

This ground state effect is sometimes called the trans influence and applies primarily to the leaving group. It is a thermodynamic effect, contributing to the overall kinetic result by changing the reactant ground state.

Pi-bonding effects

The additional factor needed is $\pi$ bonding in the Pt—T bond. When the T ligand forms a strong $\pi$-acceptor bond with Pt, charge is removed from Pt and the entrance of another ligand to form a 5-coordinate species is more likely. In addition to the charge effect, the $d(x^2-y^2)$ orbital, which is involved in $\sigma$ bonding in the square-planar geometry, and both the $d_{xz}$ and $d_{yz}$ orbitals can contribute to $\pi$ bonding in the trigonal-bipyramidal transition state.

Here, the effect on the ground state of the reactant is small, but the energy of the transition state is lowered, again reducing the activation energy [figure c]. The order of $\pi$-acceptor ability of the ligands is:

$$C_2H_4 \approx CO \approx CN^- > NO_2^- > SCN^- > I^- > Br^- > Cl^- > NH_3 > OH^-$$

This part of the explanation predicts the order for the trans effect based on the relative $\sigma$-donor properties of the ligands:

$$H^+ > PR_3 > SCN^- > I^- = CH_3^- = CO = CN^- > Br^- > Cl^- > NH_3 > OH^-$$

The order given here is not quite correct for the trans effect, particularly for CO and CN$^-$, which have strong trans effects.

The expanded overall trans effect list is then the result of the combination of the two effects:

$$CO \approx CN^- \approx C_2H_4 > PR_3 \approx H^+ \approx NO > CH_3^- \approx SC(NH_2)_2 > C_6H_5^- > NO_2^- \approx SCN^- \approx I^- > Br^- > Cl^- > py, NH_3 \approx RH_2 > OH^- > H_2O$$

Ligands highest in the series are strong $\pi$ acceptors, followed by strong $\sigma$-donors.

Ligands at the low end of the series have neither strong $\sigma$-donor nor $\pi$-acceptor abilities.

The trans effect can be very large; rates may differ as much as $10^6$ between complexes with strong trans effect ligands and those with weak trans effect ligands.
Explanations for the trans-effect (in summary)

- **trans-Influence** = ground state effect where the strong T—Pt sigma bond using the px and d(x²−y²) orbitals prevents the trans leaving group Pt—X bond from being strong.
  - The weak bond makes Pt—X has a high energy ground state
  - The Eₐ required to get X to leave is small
  - Does not quite give the correct trans-effect ligand ordering

- **Strong π-acceptors remove e⁻ from Pt making association with Y more likely**
  - This interaction from T—Pt lowers the energy of the 5-coord. intermediate
  - Eₐ is lowered and the Pt—X bond is more easily broken
  - d(x²−y²), dₓz, and dᵧz can all π-bond in the trigonal bipyramidal transition state

Exercise

![Diagram of Pt(II) complex](image)

60 minutes assignments!!

1) Explain by definition in brief, the three different reactions that commonly occurred in coordination compounds! (25 points)

2) Explain the role of HSAB principle of leaving (Y) and incoming ligands (X) toward the rate of substitution reaction in Pt(II) complexes! (20 points)

3) Identity which of the following complexes is more labile and explain the data! (15 points each)
   a. Cr(H₂O)₆²⁺ vs Cr(CN)₆⁴⁻ (Ar Cr = 24)
   b. Fe(H₂O)₆²⁺ vs Fe(CN)₆⁴⁻ (Ar Fe = 26)

4) There are two isomers of [PtCl₂(NH₃)₂], which is A and B. When A is treated with thiourea (tu), [Pt(tu)₂]⁺² is formed. When B is treated with thiourea (tu), [Pt(NH₃)₂(tu)]⁺² is formed. Identity the isomers (A and B) and explain the data! (25 points)
**Oxidation – Reduction Reactions**

**Basic of redox reactions**
- Oxidation = loss of electrons; metal ion becomes more positively charged
- Reduction = gain of electrons; metal ion becomes less positively charged
- Countless biological and industrial processes use metal ions to carry out redox reactions. Examples include Photosynthesis, destruction of toxins, etc...

**There are two mechanisms:**
- **Outer Sphere Electron Transfer Mechanism**
  - electron transfer with no change of coordination sphere
- **Inner Sphere Electron Transfer Mechanism**
  - tunneling of an electron through a bridging ligand

**Tunneling**
- Moving through an energy barrier (the ligands) that is normally too high to allow the electron to pass through. This is a quantum mechanical process having to do with the wave nature of e-. Ligands with p or π orbitals good for bonding more easily allow tunnelling (CN⁻, F⁻) than those that do not (NH₃).

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>[Cr(bipy)]³⁺</th>
<th>[Ru(NH₃)₆]³⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(NH₃)₆]³⁺</td>
<td>6.9 x 10⁻²</td>
<td>1.1 x 10⁻²</td>
</tr>
<tr>
<td>[Co(NH₃)₆(NH₄)⁺]²⁺</td>
<td>1.8 x 10⁻¹</td>
<td></td>
</tr>
<tr>
<td>[Co(NH₃)₆(OH)]²⁺</td>
<td>3 x 10⁻¹</td>
<td>4 x 10⁻²</td>
</tr>
<tr>
<td>[Co(NH₃)₆(NO₃)]⁺</td>
<td>5 x 10⁻¹</td>
<td>3.4 x 10⁻¹</td>
</tr>
<tr>
<td>[Co(NH₃)₆(H₂O)]²⁻</td>
<td>8 x 10⁻¹</td>
<td>2.6 x 10⁻²</td>
</tr>
<tr>
<td>[Co(NH₃)₆Cl]²⁻</td>
<td>5 x 10⁻¹</td>
<td>1.6 x 10⁻²</td>
</tr>
<tr>
<td>[Co(NH₃)₆Br]²⁻</td>
<td></td>
<td>6.7 x 10⁻¹</td>
</tr>
</tbody>
</table>

The rates of reaction depend on the ability of the electron to “tunnel” through the ligands from one metal to the other.

**Example: Co(NH₃)₆³⁺ + Cr(bipy)²⁺ → Co(NH₃)₆²⁺ + Cr(bipy)³⁺**

**Outer Sphere Electron Transfer Mechanism**
- The rates of reaction depend on the ability of the electron to “tunnel” through the ligands from one metal to the other.

**The ligands do not change in Outer Sphere electron transfer, but the M—L bond distances do**
- High Oxidation ➔ short bond distance
- Low Oxidation ➔ longer bond distance

The stronger the ligand field, the less favored reduction is (or more favored oxidation is), because more energy is gained by losing high energy eg* electrons (NH₃ > H₂O).

**Redox Reactions**

- **Co(NH₃)₆³⁺ + e⁻ ➔ Co(NH₃)₆²⁺**  \( E^0 = +0.108 \text{ V} \)
- **Co(H₂O)₆³⁺ + e⁻ ➔ Co(H₂O)₆²⁺**  \( E^0 = +1.108 \text{ V} \)
Inner Sphere Electron Transfer Mechanism

- Substitution links the reactants
- e⁻-transfer
- Separation of products

\[
\text{Co(III) oxidant} \quad \text{Cr(II) reductant} \quad \text{Co(III)} \quad \text{Cr(II)} \\
[\text{Co(NH}_3\text{)}_6\text{Cl}]^{2+} + [\text{Cr(H}_2\text{O)}_6]^{3+} \rightarrow ([\text{NH}_3\text{]}_6\text{Co(Cl)}\text{Cr(H}_2\text{O)}_6]^{3+} + \text{H}_2\text{O} \\
([\text{NH}_3\text{]}_6\text{Co(Cl)}\text{Cr(H}_2\text{O)}_6]^{3+} \rightarrow ([\text{NH}_3\text{]}_6\text{Co(Cl)}\text{Cr(H}_2\text{O)}_6]^{3+} \\
([\text{NH}_3\text{]}_6\text{Co(Cl)}\text{Cr(H}_2\text{O)}_6]^{3+} + \text{H}_2\text{O} \rightarrow ([\text{NH}_3\text{]}_6\text{Co(H}_2\text{O)}_6]^{2+} + ([\text{Cr(H}_2\text{O)}_6]^{3+}
\]

This reaction could be followed by ion exchange and UV-Vis.

Choosing Mechanisms

1. Very inert metal ions substitute too slowly to allow bridging, i.e. [Ru(NH\textsubscript{3})\textsubscript{6}]\textsuperscript{3+}
2. Ligands that are able to bridge are required for the inner sphere mechanism
3. Most metals can undergo both types of reactions, inner-sphere is more likely if the metal is very labile (Cr\textsuperscript{2+})
4. Comparison with experimental data of known reactions helps decide
5. Reducible ligands speed up inner sphere reactions

Reactions of Ligands

Organic Chemistry often does reactions on complexed ligands

- Example: Friedel-Crafts Electrophilic Substitution

\[
\text{RCH}_2\text{CH}_2\text{X} \rightarrow \text{RCH}_2\text{CH}_3 \quad \text{RCH}_2\text{CH}_3 \rightarrow \text{RCH}_2\text{CH}_2\text{X} \quad \text{RCH}_2\text{CH}_3 \rightarrow \text{RCH}_3 \\
\]

- The Lewis Acid nature of the metal ion creates positively charged carbon atoms to react with aromatic rings
Organic and Biological Hydrolysis Reactions

• Hydrolysis = breaking of C—O or C—N bonds in carboxylic acids and amides (proteins) or the P—O bond in phosphate esters (DNA)

• Coordination of the reacting biopolymer to the metal activates the bond to be cleaved by the Lewis Acid nature of the metal ion

• The reaction can proceed with either bound or free OH- in basic conditions

Template Reactions

• Template: organizes an assembly of atoms, with respect to one or more geometric loci to achieve a particular linking of atoms

   Anchor = organizing entity around which the template complex takes shape, due to geometric requirements. This is often a metal ion.

   Turn = Flexible entity in need of geometric organization before the desired linking can occur

Metal complexes make good templates because many metal ions have strict geometric requirements, and they can often be removed easily after the reaction.