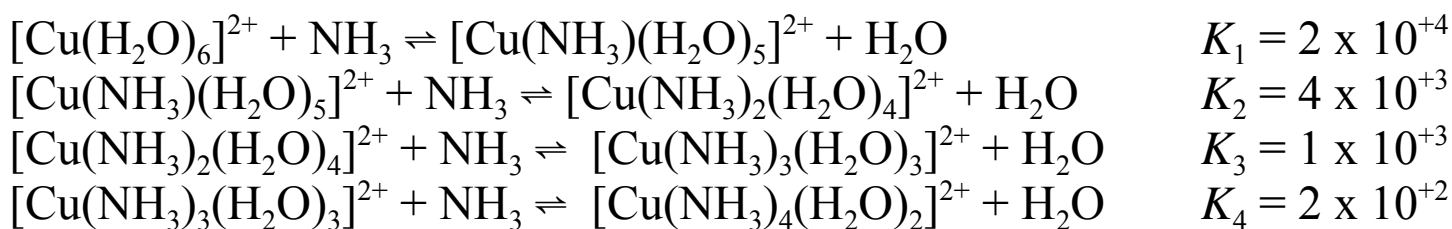# Consecutive Stability Constants in Solution

● In aqueous solution, formation of a complex generally proceeds by steps involving displacement of water molecules in the first hydration sphere.

● Equilibrium constants K_1, K_2, ..., K_n associated with addition of each ligand are called *consecutive stability constants*.

$$[Cu(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(H_2O)_5]^{2+} + H_2O \qquad K_1 = 2 \text{ x } 10^{+4}$$
$$[Cu(NH_3)(H_2O)_5]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + H_2O \qquad K_2 = 4 \text{ x } 10^{+3}$$
$$[Cu(NH_3)_2(H_2O)_4]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3(H_2O)_3]^{2+} + H_2O \qquad K_3 = 1 \text{ x } 10^{+3}$$
$$[Cu(NH_3)_3(H_2O)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + H_2O \qquad K_4 = 2 \text{ x } 10^{+2}$$

● Successive stability constants decline through the series, such that $K_1 > K_2 > ... > K_n$.
  • In the first step there are six sites for NH_3 substitution, but in the reverse step there is only one site for H_2O substitution; $K_1 \propto 6/1$.
  • In the second step there are five sites for NH_3 substitution, but in the reverse step there are two sites for H_2O substitution; $K_2 \propto 5/2$.
  • By similar reasoning we predict $K_3 \propto 4/3$ and $K_4 \propto 3/4$.

Ratio	Predicted	Observed
K_1/K_2	(6/1)/(5/2) = 2.40	5
K_2/K_3	(5/2)/(4/3) = 1.87	4
K_3/K_4	(4/3)/(3/4) = 1.78	5

☞ Agreement between predicted and observed ratios is remarkably good, considering that predictions are based only on statistical factors.
 ✓ Statistical factors appear to be the main cause of the trend.

Cumulative Stability Constant

● The product of consecutive stability constants is the *cumulative stability constant, β_n*.

$$\beta_n = \prod_{i=1}^{n} K_i$$

- When the overall equilibrium lies to the right the product complex is said to be *stable*.
- When the overall equilibrium lies to the left the product complex is said to be *unstable*.

Example: $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$
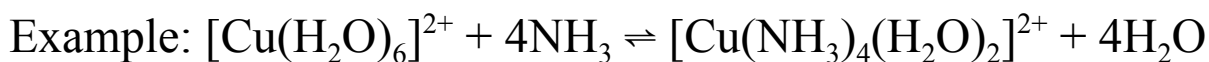
$$\beta_4 = (2 \times 10^{+4})(4 \times 10^{+3})(1 \times 10^{+3})(2 \times 10^{+2}) = 1.6 \times 10^{+16}$$

☞ $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is a very stable complex.

Stable/Unstable and Labile/Inert

- "Stable" and "unstable" refer to the thermodynamics of complex formation (e.g., K, β).

- "Labile" and "inert" refer to the kinetics of complex formation.

- A complex whose formation equilibria are established rapidly is *labile*.

- A complex whose formation equilibria are established slowly is *inert*.

Example: $[Cu(NH_3)_4(H_2O)_2]^{2+}$ has a large β_4 and its equilibria are established rapidly; therefore, the complex is stable and labile.

☞   As a "rule of thumb", if the half-life of a complex in a substitution reaction is less than one minute, it is labile.[1]

---

[1]H. Taube, *Chem. Rev.*, **1952**, *50*, 69.

Stability Constants and Thermodynamic State Functions

● The stability constant for a complex is related to ΔG, ΔH, and ΔS of its formation by
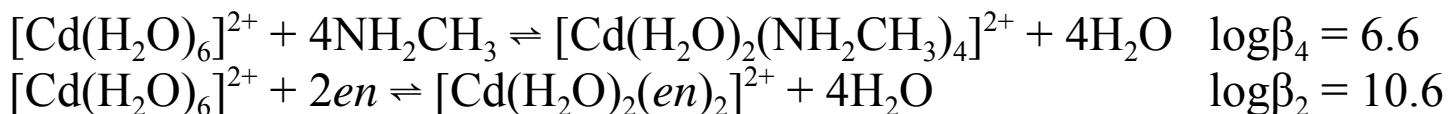$$\Delta G = -RT \ln\beta_n = \Delta H - T\Delta S$$

● The larger β_n is, the more negative (favorable) ΔG will be.

● Entropy plays an important role.
  • The more positive ΔS is, the more negative ΔG will be, and the greater β_n will be.
  • Entropy is largely responsible for the greater stability constants observed for chelates, compared to complexes of unidentate ligands with the same metal ion.

Chelate Effect - Entropy Factors

- The *chelate effect* is the name given to the general observation that chelate complexes have higher stability constants compared to similar unidentate ligand complexes.
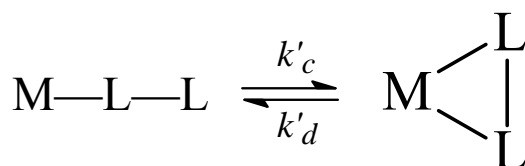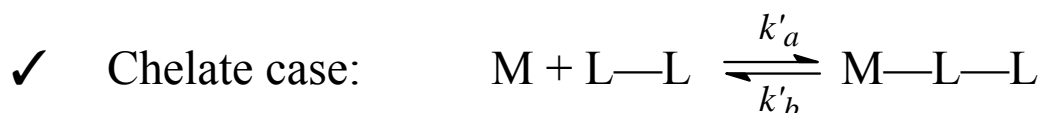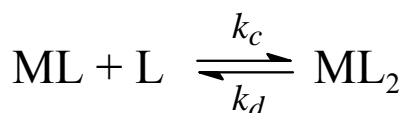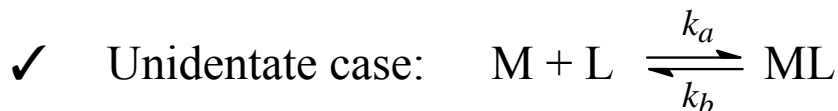
Example: $[Cd(NH_2CH_3)_4]^{2+}$ vs. $[Cd(en)_2]^{2+}$

$[Cd(H_2O)_6]^{2+} + 4NH_2CH_3 \rightleftharpoons [Cd(H_2O)_2(NH_2CH_3)_4]^{2+} + 4H_2O$ $\log\beta_4 = 6.6$
$[Cd(H_2O)_6]^{2+} + 2en \rightleftharpoons [Cd(H_2O)_2(en)_2]^{2+} + 4H_2O$ $\log\beta_2 = 10.6$

- ✓ For both, ΔH should be about the same, because the enthalpy change is due mainly to the change in bond strengths between Cd–O and Cd–N, so the difference in β values must be due principally to entropy differences.
- ✓ For $[Cd(NH_2CH_3)_4]^{2+}$, the reaction equation has equal numbers of particles on both sides (5), so $\Delta S \approx 0$.
- ✓ For $[Cd(en)_2]^{2+}$, there are three (3) particles on the left and five (5) on the right, so $\Delta S > 0$.
- ✓ The greater positive entropy change for formation of the chelate complex results in a more negative ΔG and a larger β value.

- ☞ In general, chelates have an entropy advantage over similar unidentate ligands.

Chelate Effect - Kinetic Factors

● We can make a mechanistic argument for the chelate effect by comparing the following idealized mechanisms and the associated rate constants for each step.

✓ Unidentate case: $M + L \underset{k_b}{\overset{k_a}{\rightleftharpoons}} ML$

$ML + L \underset{k_d}{\overset{k_c}{\rightleftharpoons}} ML_2$

✓ Chelate case: $M + L{-}L \underset{k'_b}{\overset{k'_a}{\rightleftharpoons}} M{-}L{-}L$

$M{-}L{-}L \underset{k'_d}{\overset{k'_c}{\rightleftharpoons}} M\begin{smallmatrix} L \\ | \\ L \end{smallmatrix}$

✓ For the first step in each case we can predict $k_a \approx k'_a$ and $k_b \approx k'_b$.

✓ But for the second steps
   $k_c < k'_c$ random vs. directed second substitution
   $k_d \geq k'_d$ chelate bond breaking same or harder

✓ Stability constants are defined in terms of the rate constants as

$$\beta_{uni} = \frac{k_a k_c}{k_b k_d} \qquad\qquad \beta_{chel} = \frac{k'_a k'_c}{k'_b k'_d}$$

✓ From the relationships among the k values, $\beta_{uni} < \beta_{chel}$.

☞ In general, chelates have a kinetic advantage over comparable unidentate ligands.

Labile vs. Inert

● Stable/unstable are thermodynamic terms, and labile/inert are kinetic terms, which can be applied in all possible combinations to various complexes.

✓ $[Co(NH_3)_6]^{3+}$ is <u>unstable</u> with respect to aquation but <u>inert</u>.

$$[Co(NH_3)_6]^{3+} + 6H_3O^+ \overset{slow}{\rightleftharpoons} [Co(H_2O)_6]^{3+} + 6NH_4^+ \qquad K \approx 10^{+25}$$
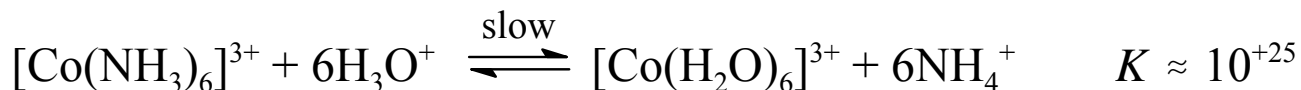
✓ $[Ni(CN)_4]^{2-}$ is <u>stable</u> with respect to exchange with labeled CN^- but <u>labile</u> because the equilibrium is established quickly.

$$[Ni(CN)_4]^{2-} + CN^{*-} \overset{fast}{\rightleftharpoons} [Ni(CN)_3CN^*]^{2-} + CN^- \qquad K \approx 10^{-22}$$

● Most first-row transition metal complexes are labile, but Cr^{3+} (d^3, $S = 3/2$) and low-spin Co^{3+} (d^6, $S = 0$) are usually inert.

● Inert octahedral complexes tend to be those with highest CFSE; viz., d^3, low-spin $d^4 - d^6$.
  • ML_6 complexes of both d^3 ($^4A_{2g}$) and low-spin d^6 ($^1A_{1g}$) are immune from Jahn-Teller distortions and therefore can be perfect O_h.
  • ML_6 d^3 has CFSE $= -(6/5)\Delta_o$ and low-spin d^6 has CFSE $= -(12/5)\Delta_o + 3P$.

● $d^7 - d^{10}$, with filling of e_g^* levels, are labile.
  • These configurations tend to have large Jahn-Teller distortions and/or low CFSEs.
  • d^7, d^9, and d^{10} cases are more labile than d^8.
  • d^8 has a $^3A_{2g}$ ground state, which is immune to Jahn-Teller distortion.
  • With strong-field ligands, d^8 may be square planar, often being inert.
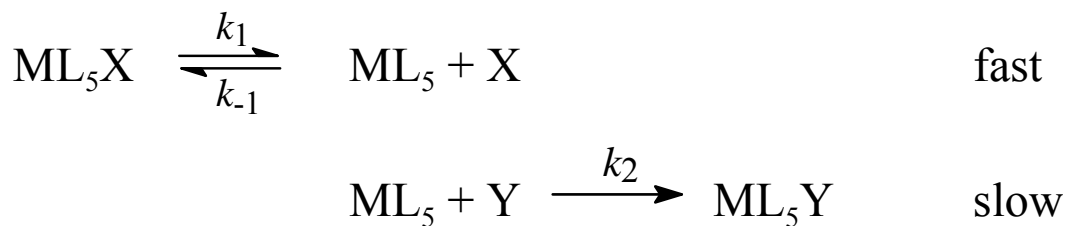
Substitution Mechanisms

- Ligand substitutions follow the general stoichiometry

$$ML_5X + Y \rightleftharpoons ML_5Y + X$$
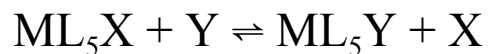
- Kinetic studies of the rates of such reactions provide data that suggest the detailed mechanisms by which substitution occurs.

- Two extreme models can be postulated:
  - ① dissociation (D)
  - ② association (A).

Dissociation Mechanism (D) – S_N1

$$ML_5X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5 + X \qquad\qquad \text{fast}$$

$$ML_5 + Y \xrightarrow{k_2} ML_5Y \qquad\qquad \text{slow}$$

$$Rate = k_2[ML_5][Y]$$

- The rate-determining step involves addition of Y to a CN5 intermediate formed by a rapid equilibrium in the first step.

- Assuming a steady state in $[ML_5]$, we can write

$$\frac{d[ML_5]}{dt} = 0 = k_1[ML_5X] - k_{-1}[ML_5][X] - k_2[ML_5][Y]$$

- Solving for $[ML_5]$, we have

$$[ML_5] = \frac{k_1[ML_5X]}{k_{-1}[X] + k_2[Y]}$$

- Substituting into $Rate = k_2[ML_5][Y]$ gives

$$Rate = \frac{k_1 k_2[ML_5X][Y]}{k_{-1}[X] + k_2[Y]}$$

- If product formation is fast ($k_2 \gg k_{-1}$), or if the system has very large [Y] ($\gg$[X]), then rate becomes first-order in $[ML_5X]$; i.e.,

$$Rate \approx k_1[ML_5X]$$

- Thus, the S_N1 mechanism is first-order in $[ML_5X]$.

Association Mechanism (*A*) – S$_N$2

$$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5XY \qquad\qquad \text{fast}$$

$$ML_5XY \xrightarrow{k_2} ML_5Y + X \quad \text{slow}$$
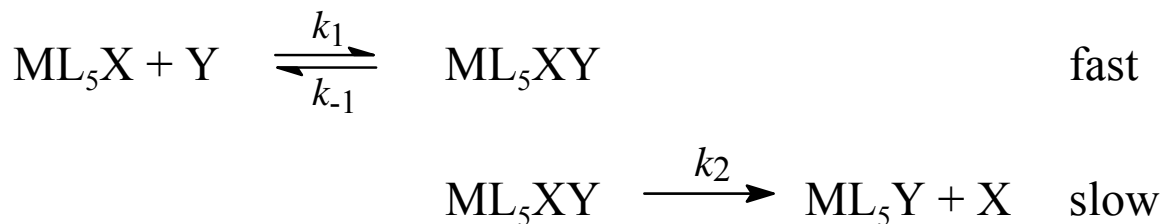
$$Rate = k_2[ML_5XY]$$

● Applying a steady-state approximation for $[ML_5XY]$ we have

$$\frac{d[ML_5XY]}{dt} = 0 = k_1[ML_5X][Y] - k_{-1}[ML_5XY] - k_2[ML_5XY]$$

● Solving for $[ML_5XY]$ we obtain

$$[ML_5XY] = \frac{k_1[ML_5X][Y]}{k_{-1} + k_2}$$

● Substituting into $Rate = k_2[ML_5XY]$ gives

$$Rate = \frac{k_1k_2[ML_5X][Y]}{k_{-1} + k_2} = k[ML_5X][Y]$$

where $k = k_1k_2/(k_{-1} + k_2)$.

● Thus, the S$_N$2 mechanism is second-order overall; i.e., first-order in $[ML_5X]$ and first-order in $[Y]$.

Interchange Mechanism (*I*)

- It is too simplistic to assume that a first-order rate law implies D (S_N1) and a second-order rate law implies A (S_N2).
  - Most substitution reactions probably involve a mechanism that is intermediate between these extremes, a mechanism called *interchange* (*I*).

- In an interchange mechanism the intermediate involves an association between the original ML_5X complex and the attacking Y ligand.
  - The Y ligand remains outside the coordination sphere of ML_5X, unlike the S_N2 mechanism, so the intermediate is not seven coordinate.

$$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5X{\cdot}Y \qquad \text{fast}$$

$$ML_5X{\cdot}Y \xrightarrow{k_2} ML_5Y + X \qquad \text{slow}$$
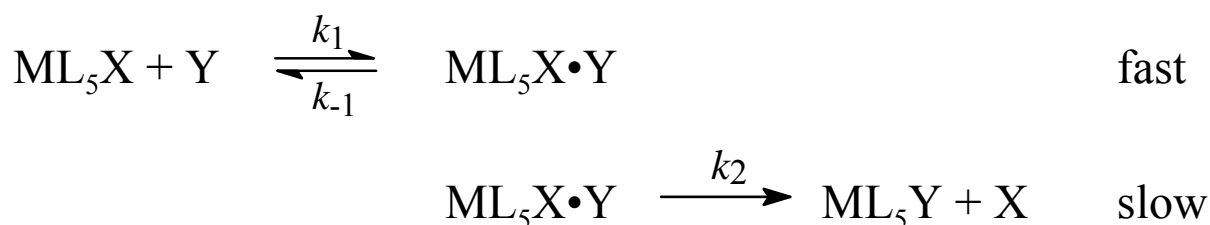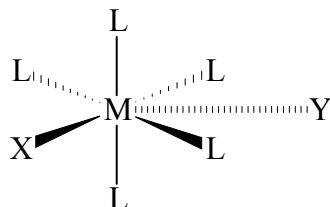
- It can be shown[2] that the rate is given by
$$Rate = \frac{k[ML_5X]_o[Y]}{1 + k'[Y]_o}$$
  where $[ML_5X]_o$ and $[Y]_o$ are initial concentrations.
  - At high $[Y]$, $[Y] \approx [Y]_o$ and $k_1'[Y]_o \gg 1$, and the rate is first-order in $[ML_5X]$.
  - At lower $[Y]$ the rate is second order.

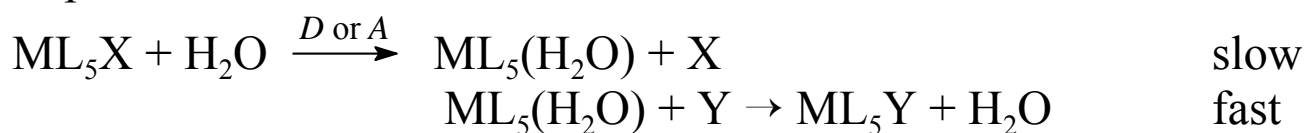[2]Miessler & Tarr, 3rd ed., p. 418.

Variations on *I*

- Two minor variations on the *I* mechanism are I_d (dissociative interchange) and I_a (associative interchange) interchange.

- If breaking the M–X bond is more important, the mechanism is I_d.

- If bond formation between ML_5X and Y is significant, the mechanism is I_a.

- Difference between I_d and I_a is subtle and does not necessarily correspond to whether the observed rate law is first or second order.

Substitution Reactions in Solvent Water

● Many substitution reactions occurring in solvent water may have first-order kinetics regardless of whether their initial steps are primarily D or A.

• For example, this occurs if aquation is a precursor rate determining step.

$$ML_5X + H_2O \xrightarrow{D \text{ or } A} ML_5(H_2O) + X \qquad\qquad \text{slow}$$
$$ML_5(H_2O) + Y \rightarrow ML_5Y + H_2O \qquad \text{fast}$$

• If D, $Rate = k[ML_5X]$.

• If A, $Rate = k[ML_5X][H_2O]$, but with solvent water $[H_2O]$ is constant and $Rate = k'[ML_5X]$.

☞   Both mechanisms lead to apparent first-order kinetics in solvent water.

Factors Favoring D or I_d

● For most octahedral complexes, steric factors inhibit formation of a CN7 intermediate, which suggests a dissociative mechanism (D or I_d) is more plausible.
  - Even cases showing second-order kinetics may not be A for this reason.

● For example, aquation of the ammine-halide complexes $[Co(NH_3)_5X]^{2+}$ is second order with a first-order dependence in $[OH^-]$.
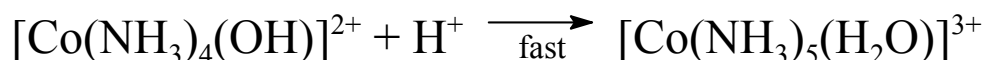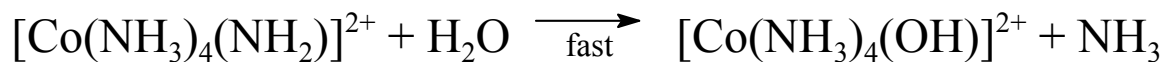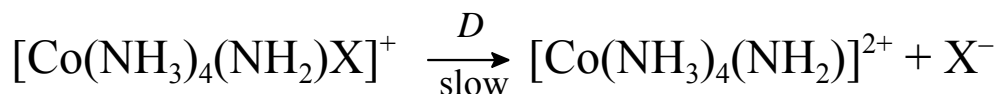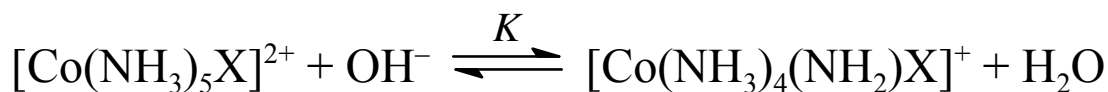 - Although this might suggest A, that appears unlikely.

$$[Co(NH_3)_5X]^{2+} + H_2O \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + X^-$$
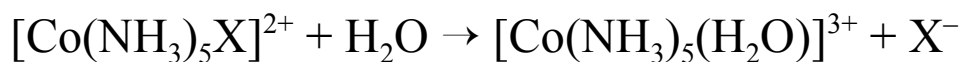
$$Rate = k_1\,[Co(NH_3)_5X^{2+}] + k_2\,[Co(NH_3)_5X^{2+}][OH^-]$$

  - If $k_2 \gg k_1$ the rate is approximately $Rate \approx k_2\,[Co(NH_3)_5X]^{2+}[OH^-]$.

  - From the second-order kinetics, this appears to be A, but it is more likely an alternative mechanism called S_N1CB, where "CB" stands for "conjugate base."

S_N1CB Mechanism

● The postulated S_N1CB mechanism involves the following steps:

$$[Co(NH_3)_5X]^{2+} + OH^- \overset{K}{\rightleftharpoons} [Co(NH_3)_4(NH_2)X]^+ + H_2O$$

$$[Co(NH_3)_4(NH_2)X]^+ \xrightarrow[\text{slow}]{D} [Co(NH_3)_4(NH_2)]^{2+} + X^-$$

$$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_4(OH)]^{2+} + NH_3$$

$$[Co(NH_3)_4(OH)]^{2+} + H^+ \xrightarrow{\text{fast}} [Co(NH_3)_5(H_2O)]^{3+}$$

● The second step, which is rate determining, is D (S_N1), for which

$$Rate = k \, [Co(NH_3)_4(NH_2)X^+]$$

• But

$$K = \frac{[Co(NH_3)_4(NH_2)X^+]}{[Co(NH_3)_5X^{2+}][OH^-]}$$

(No $[H_2O]$ because water is solvent.)
• Solving K gives

$$[Co(NH_3)_4(NH_2)X^+] = K \, [Co(NH_3)_5X^{2+}][OH^-]$$

• Substituting into the expression for $Rate$ gives

$$Rate = kK \, [Co(NH_3)_5X^{2+}][OH^-]$$

☞   This is the same as the observed rate
$$Rate = k_1 \, [Co(NH_3)_5X^{2+}] + k_2 \, [Co(NH_3)_5X^{2+}][OH^-]$$
when $k_2 \gg k_1$; i.e.,
$$Rate = k_2 \, [Co(NH_3)_5X^{2+}][OH^-]$$

● Although steric factors favor D-type mechanisms for octahedral complexes, square planar ML_4 complexes are not so inhibited.
• For square planar ML_4 complexes, an associative (A) mechanism, in which a CN5 intermediate is formed, is plausible.

Trans Effect

- Substitution of square planar complexes, such as $PtLX_3$, leads to a mixture of *trans* and *cis* isomers.

$$L-\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{Pt}}-X \quad + \ Y^- \quad \left\{ \begin{array}{c} L-\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{Pt}}-Y \\ \\ L-\underset{\underset{Y}{|}}{\overset{\overset{X}{|}}{Pt}}-X \end{array} \right. \quad + \ X^-$$
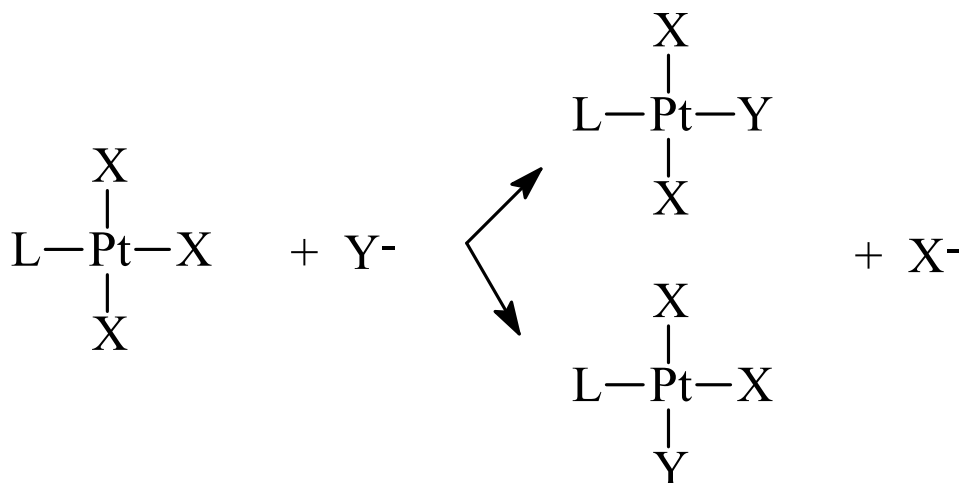
- The rate law is

$$Rate = k_1[PtLX_3] + k_2[PtLX_3][Y^-] \qquad k_2 > k_1$$

  - Suggests two paths, where the first term may be pseudo-first-order due to excess solvent acting as an attacking group.

- The ratio of *trans* and *cis* isomers is found to vary with the ability of L to act as a *trans*-directing ligand.

- The increasing order of *trans*-directing ability is
$$H_2O < OH^- < py \approx NH_3 < Cl^- < Br^- < I^- < NO_2^- < PR_3 \approx SH_2$$
$$<< CO \approx C_2H_4 \approx CN^-$$

- The effect is kinetic rather than thermodynamic.

- Two factors are cited to explain the effect:
  - ① Weakening of the Pt–X bond *trans* to the directing ligand;
  - ② Stabilization of the presumed CN5 intermediate.

M-X Bond Weakening

- For ligands at the left of the series, weakening of the *trans* Pt–X bond may be most important.

- The *trans*-directing ligand polarizes the metal ion, inducing a slight repulsion for the leaving ligand in the *trans* position.

$$\mathrm{X}$$

$$\boxed{L \ominus}\ \widehat{\delta^+\ Pt\ \delta-}\ \boxed{\delta-X\ \delta+}$$

$$\mathrm{X}$$

weakened by induced repulsion
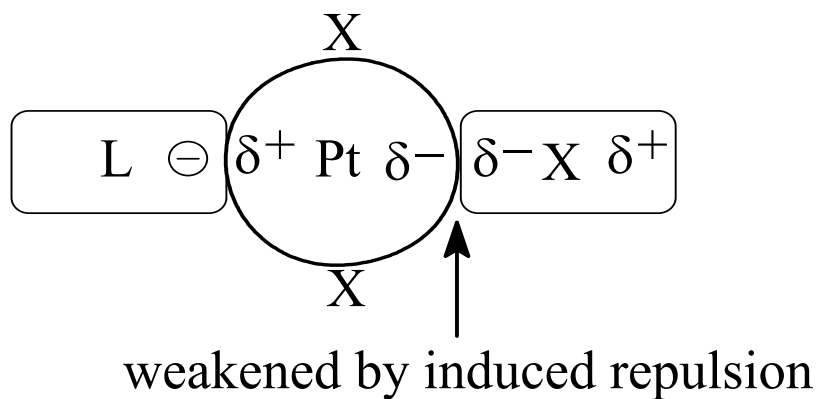
- The more polarizable the L ligand, the better *trans*-director it is; e.g., $I^- > Br^- > Cl^-$.

π-Acceptor Ligands

● The strongest *trans*-directors are good π-acceptor ligands; e.g., CO, C_2H_4, CN^-.

● Assuming an *A* (S_N2) mechanism, substitution involves a trigonal bipyramidal transition state.

● The *trans* intermediate (activated complex) is more favorable for π-acceptor ligands, because it permits π-delocalization in the trigonal plane.
  • Stabilizing the reaction intermediate lowers the activation energy, E_a, for the reaction.
  • In the *cis* intermediate, L lies above the trigonal plane, which decreases its ability to stabilize the activated complex through π delocalization.
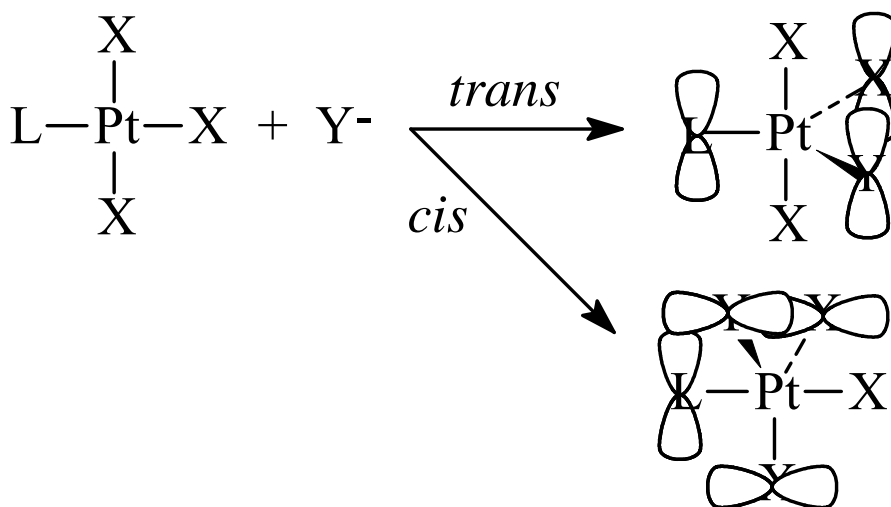
Synthetic Use of the Trans Effect

● The synthetic utility of the *trans* effect can be illustrated by the selective production of *cis* or *trans* $Pt(NH_3)_2Cl_2$, using the greater *trans*-directing ability of Cl^- relative to NH_3.

✓ To make *cis*-$Pt(NH_3)_2Cl_2$, start with $[PtCl_4]^{2-}$:
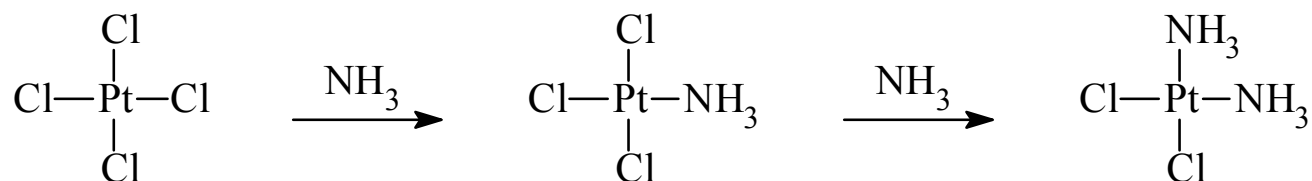
☞ In the second step, the greater *trans*-directing ability of Cl^- causes preferential substitution of NH_3 in the *trans* position to one of the existing Cl^- ligands, resulting in the *cis* isomer.

✓ To make *trans*-$Pt(NH_3)_2Cl_2$, start with $[Pt(NH_3)_4]^{2+}$:
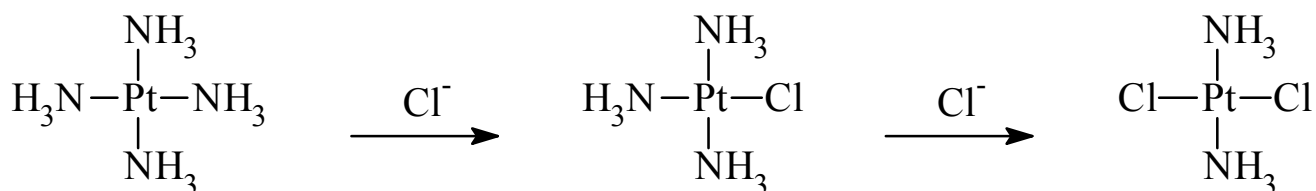
☞ In the second step, the greater *trans*-directing ability of Cl^- causes preferential substitution of Cl^- in the *trans* position to the first Cl^-, resulting in the *trans* isomer.

Electron Transfer Reactions
Outer Sphere Mechanism

● Transition-metal complexes can engage in redox reactions with one another, primarily by one of two mechanisms: *outer-sphere* and *inner-sphere*.

● In an *outer-sphere reaction* the coordination spheres of the reacting complexes remain intact.
  • Outer-sphere reactions are extremely fast.
  • Redox occurs before ligand substitution can take place.

Example: $[Fe^{II}(CN)_6]^{4-} + [Ir^{IV}Cl_6]^{2-} \rightarrow [Fe^{III}(CN)_6]^{3-} + [Ir^{III}Cl_6]^{3-}$
                    inert   inert

● As the charge on the metal increases, the M–L bond distance decreases.
  • The effect is most pronounced when electrons are removed from an $e_g{}^*$ MO; e.g.,

$$Co^{2+}\ (t_{2g}{}^5 e_g{}^2) \rightarrow Co^{3+}\ (t_{2g}{}^6) + e^-$$
        high-spin   low-spin
        long M–L   shorter M–L

  • Electron loss from $e_g{}^*$ stabilizes the complex.

☞   The outer-sphere mechanism is certain to be the correct one when *both* species participating in the reaction undergo ligand-exchange reactions more slowly than they participate in the electron transfer process.[3]
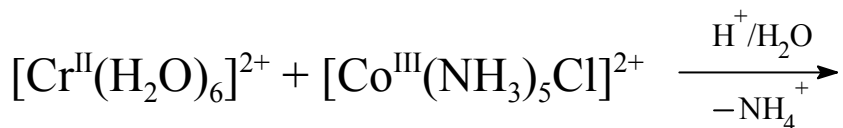
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[3]F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley, NY, 1980, p. 1206.
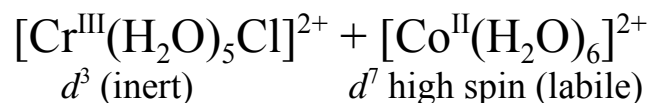
Electron Transfer Reactions
Inner Sphere Mechanism

● *Inner-sphere* mechanisms generally proceed in three steps:

① Substitution resulting in two complexes being linked through a bridging ligand.

② Electron transfer, sometimes with ligand transfer.

③ Separation of products.

● This is sometimes called a ligand-bridged mechanism, because of the formation of the bridged intermediate.

☞ Inner-sphere mechanism requires that one of the participating species have a ligand capable of functioning as a bridge.
   • For example, H_2O and NH_3 cannot function as bridging ligands, but Cl^- and CN^- can.
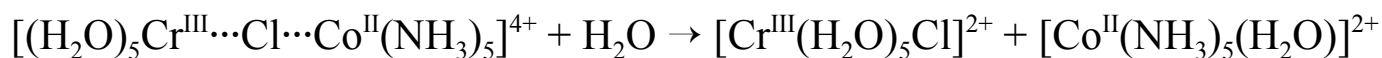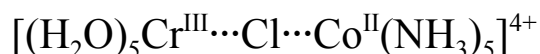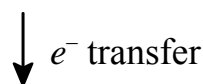
● Inner-sphere redox is slower than outer-sphere.

Example of Inner Sphere Redox

$$[Cr^{II}(H_2O)_6]^{2+} + [Co^{III}(NH_3)_5Cl]^{2+} \xrightarrow[-NH_4^+]{H^+/H_2O}$$

d^4 high spin (labile) d^6 low spin (inert)

$$[Cr^{III}(H_2O)_5Cl]^{2+} + [Co^{II}(H_2O)_6]^{2+}$$
$$d^3 \text{ (inert)} \qquad\qquad d^7 \text{ high spin (labile)}$$

Mechanism:

$$[Cr^{II}(H_2O)_6]^{2+} + [Co^{III}(NH_3)_5Cl]^{2+} \rightarrow [(H_2O)_5Cr^{II}\cdots Cl\cdots Co^{III}(NH_3)_5]^{4+} + H_2O$$

$$\downarrow e^- \text{ transfer}$$

$$[(H_2O)_5Cr^{III}\cdots Cl\cdots Co^{II}(NH_3)_5]^{4+}$$

$$[(H_2O)_5Cr^{III}\cdots Cl\cdots Co^{II}(NH_3)_5]^{4+} + H_2O \rightarrow [Cr^{III}(H_2O)_5Cl]^{2+} + [Co^{II}(NH_3)_5(H_2O)]^{2+}$$

Co(II) complexes are labile, so $[Co^{II}(NH_3)_5(H_2O)]^{2+}$ undergoes rapid aquation:

$$[Co^{II}(NH_3)_5(H_2O)]^{2+} + 5H_2O \rightarrow [Co^{II}(H_2O)_6]^{2+} + 5NH_3$$
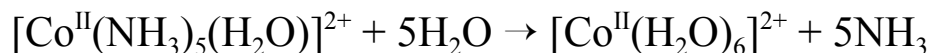
✓ This reaction cannot be explained as an outer-sphere mechanism followed by Cl⁻ substitution, because adding labeled Cl*⁻ to the solution yields no labeled product.
   • This is expected, because all Cr(III) complexes are inert to substitution.