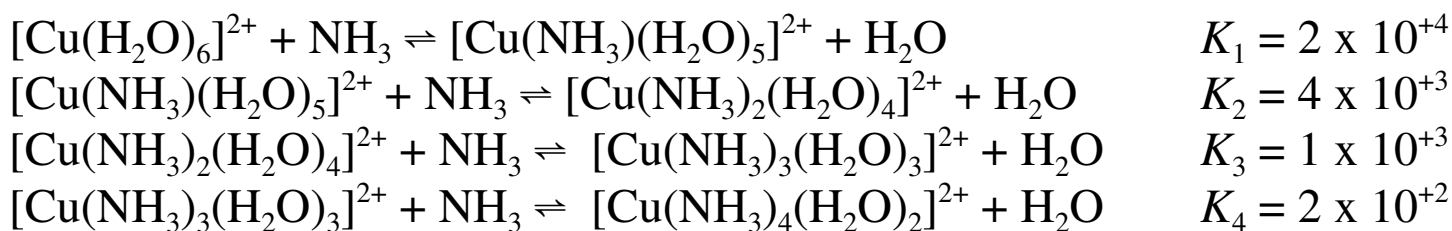


Consecutive Stability Constants in Solution

- 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, \dots, K_n associated with addition of each ligand are called *consecutive stability constants*.



- Successive stability constants decline through the series, such that $K_1 > K_2 > \dots > K_n$.
 - 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.

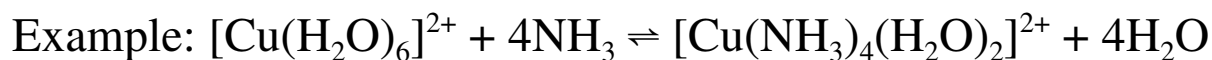
✓ Statistical factors appear to be the main cause of the trend.

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*.



$$\beta_4 = (2 \times 10^4)(4 \times 10^3)(1 \times 10^3)(2 \times 10^2) = 1.6 \times 10^{16}$$

☛ $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ 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: $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ 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

¹H. 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

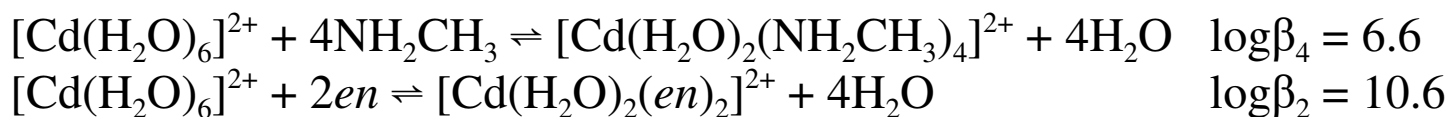
$$\Delta G = -RT \ln \beta_n = \Delta H - T\Delta S$$

- 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.

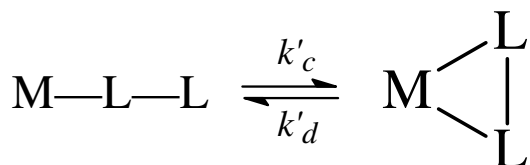
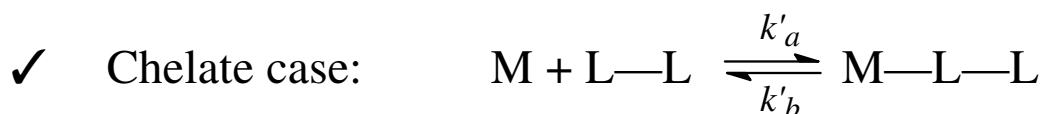
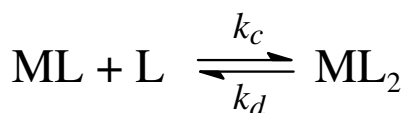
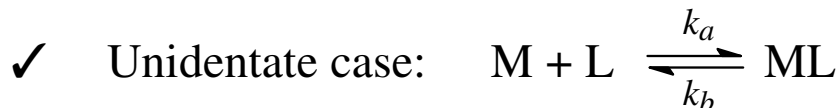
Example: $[\text{Cd}(\text{NH}_2\text{CH}_3)_4]^{2+}$ vs. $[\text{Cd}(\text{en})_2]^{2+}$



- ✓ 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 $[\text{Cd}(\text{NH}_2\text{CH}_3)_4]^{2+}$, the reaction equation has equal numbers of particles on both sides (5), so $\Delta S \approx 0$.
 - ✓ For $[\text{Cd}(\text{en})_2]^{2+}$, 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.



- ✓ 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

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

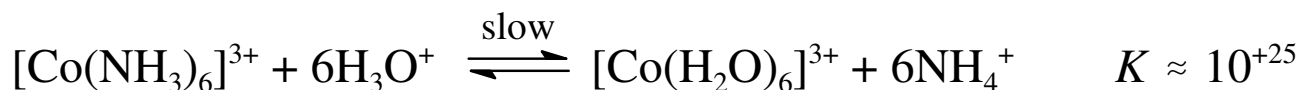
- ✓ From the relationships among the k values, $\beta_{\text{uni}} < \beta_{\text{chel}}$.

- ☛ 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.

- ✓ $[\text{Co}(\text{NH}_3)_6]^{3+}$ is unstable with respect to aquation but inert.



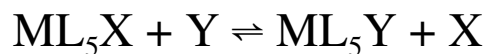
- ✓ $[\text{Ni}(\text{CN})_4]^{2-}$ is stable with respect to exchange with labeled CN^- but labile because the equilibrium is established quickly.



- 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 $\text{CFSE} = -(6/5)\Delta_o$ and low-spin d^6 has $\text{CFSE} = -(12/5)\Delta_o + 3P$.
- $d^7 - d^{10}$, 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.

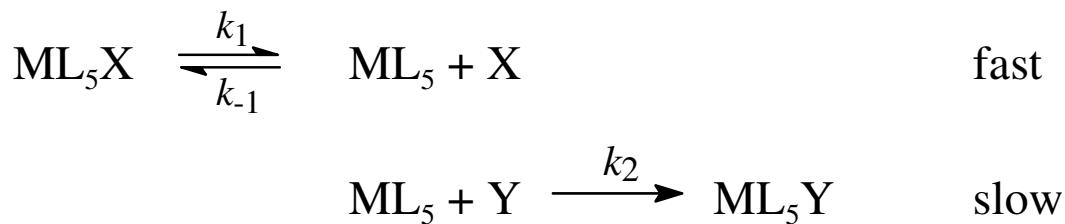
Substitution Mechanisms

- Ligand substitutions follow the general stoichiometry



- 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



$$\text{Rate} = k_2[\text{ML}_5][\text{Y}]$$

- 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 [ML₅], we can write

$$\frac{d[\text{ML}_5]}{dt} = 0 = k_1[\text{ML}_5\text{X}] - k_{-1}[\text{ML}_5][\text{X}] - k_2[\text{ML}_5][\text{Y}]$$

- Solving for [ML₅], we have

$$[\text{ML}_5] = \frac{k_1[\text{ML}_5\text{X}]}{k_{-1}[\text{X}] + k_2[\text{Y}]}$$

- Substituting into $\text{Rate} = k_2[\text{ML}_5][\text{Y}]$ gives

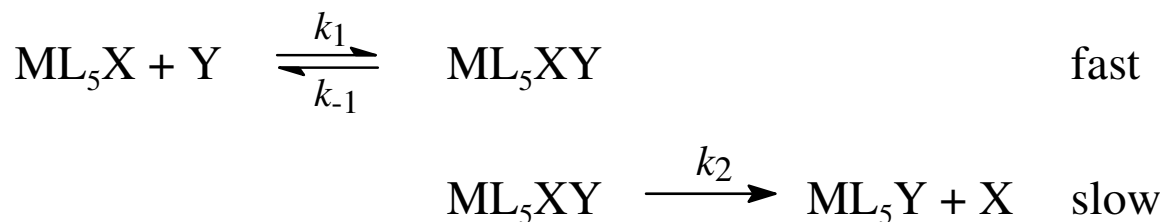
$$\text{Rate} = \frac{k_1 k_2 [\text{ML}_5\text{X}][\text{Y}]}{k_{-1}[\text{X}] + k_2[\text{Y}]}$$

- If product formation is fast ($k_2 \gg k_{-1}$), or if the system has very large [Y] ($\gg [\text{X}]$), then rate becomes first-order in [ML₅X]; i.e.,

$$\text{Rate} \approx k_1[\text{ML}_5\text{X}]$$

- Thus, the S_N1 mechanism is first-order in [ML₅X].

Association Mechanism (A) – S_N2



$$\text{Rate} = k_2[\text{ML}_5\text{XY}]$$

- Applying a steady-state approximation for [ML₅XY] we have

$$\frac{d[\text{ML}_5\text{XY}]}{dt} = 0 = k_1[\text{ML}_5\text{X}][\text{Y}] - k_{-1}[\text{ML}_5\text{XY}] - k_2[\text{ML}_5\text{XY}]$$

- Solving for [ML₅XY] we obtain

$$[\text{ML}_5\text{XY}] = \frac{k_1[\text{ML}_5\text{X}][\text{Y}]}{k_{-1} + k_2}$$

- Substituting into $\text{Rate} = k_2[\text{ML}_5\text{XY}]$ gives

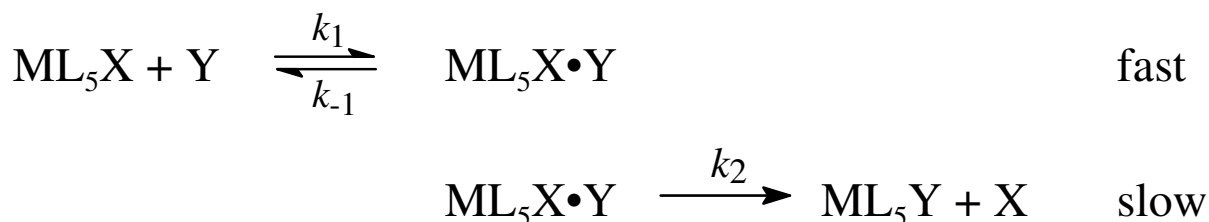
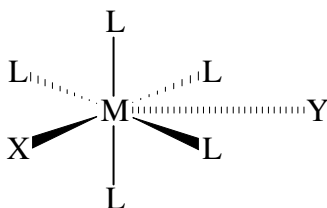
$$\text{Rate} = \frac{k_1 k_2 [\text{ML}_5\text{X}][\text{Y}]}{k_{-1} + k_2} = k[\text{ML}_5\text{X}][\text{Y}]$$

where $k = k_1 k_2 / (k_{-1} + k_2)$.

- Thus, the S_N2 mechanism is second-order overall; i.e., first-order in [ML₅X] 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.



- Assuming high $[Y] \approx [Y]_0$, it can be shown² that the rate is given by

$$Rate \approx \frac{k_2 K_1 [M]_0 [Y]_0}{1 + K_1 [Y]_0}$$

where $[M]_0 = [ML_5X]_0 + [ML_5X \cdot Y]$ and $[Y]_0$ are initial concentrations, and $K_1 = k_1/k_{-1}$.

- At high $[Y]$ and $K_1[Y]_0 \gg 1$, the rate is first-order in $[M]_0 \approx [ML_5X]$.
- At lower $[Y]$ the rate is second order.

²Miessler & Tarr, 4th ed., section 12.3.2, p. 448.

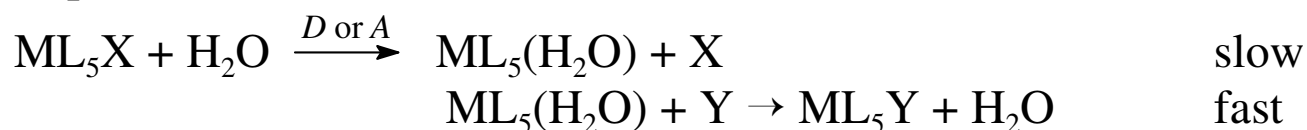
Variations on I

- 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.
- If the rates of a series of comparable substitution reactions are most sensitive to the identity of X, the leaving ligand, then the mechanism is more probably I_d .
- If the rates of a series of comparable substitution reactions are most sensitive to the identity of Y, the attacking ligand, then the mechanism is more probably I_a .

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.

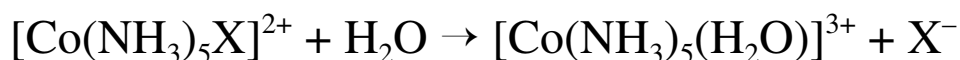


- If *D*, $\text{Rate} = k[\text{ML}_5\text{X}]$.
- If *A*, $\text{Rate} = k[\text{ML}_5\text{X}][\text{H}_2\text{O}]$, but with solvent water $[\text{H}_2\text{O}]$ is constant and $\text{Rate} = k'[\text{ML}_5\text{X}]$.

☞ 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 $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ is second order with a first-order dependence in $[\text{OH}^-]$.
 - Although this might suggest A , that appears unlikely.

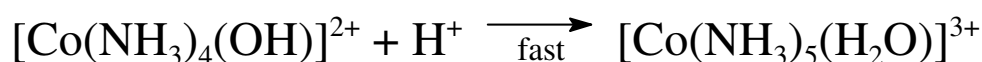
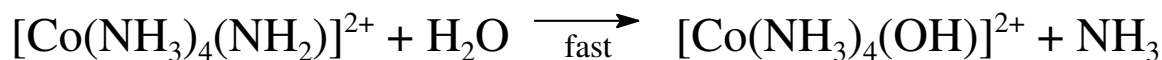
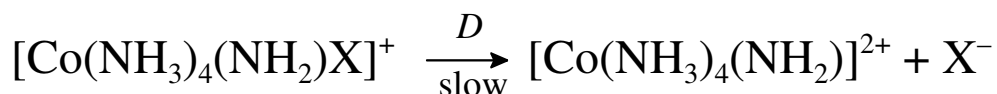
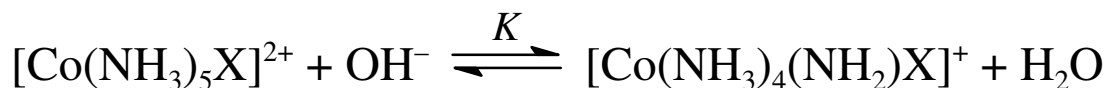


$$\text{Rate} = k_1 [\text{Co}(\text{NH}_3)_5\text{X}^{2+}] + k_2 [\text{Co}(\text{NH}_3)_5\text{X}^{2+}][\text{OH}^-]$$

- If $k_2 \gg k_1$ the rate is approximately $\text{Rate} \approx k_2 [\text{Co}(\text{NH}_3)_5\text{X}]^{2+}[\text{OH}^-]$.
- From the second-order kinetics, this appears to be A , but it is more likely an alternative mechanism called $\text{S}_{\text{N}}1\text{CB}$, where "CB" stands for "conjugate base."

S_N1CB Mechanism

- The postulated S_N1CB mechanism involves the following steps:



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

$$\text{Rate} = k [\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{X}^+]$$

- But

$$K = \frac{[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{X}^+]}{[\text{Co}(\text{NH}_3)_5\text{X}^{2+}][\text{OH}^-]}$$

(No [H₂O] because water is solvent.)

- Solving *K* gives

$$[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{X}^+] = K [\text{Co}(\text{NH}_3)_5\text{X}^{2+}][\text{OH}^-]$$

- Substituting into the expression for *Rate* gives

$$\text{Rate} = kK [\text{Co}(\text{NH}_3)_5\text{X}^{2+}][\text{OH}^-]$$

☞ This is the same as the observed rate

$$\text{Rate} = k_1 [\text{Co}(\text{NH}_3)_5\text{X}^{2+}] + k_2 [\text{Co}(\text{NH}_3)_5\text{X}^{2+}][\text{OH}^-]$$

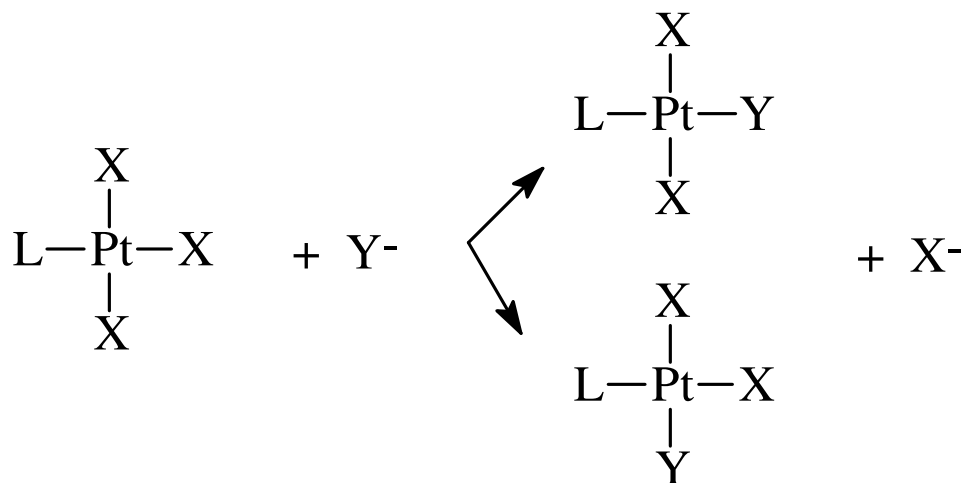
when $k_2 \gg k_1$; i.e.,

$$\text{Rate} = k_2 [\text{Co}(\text{NH}_3)_5\text{X}^{2+}][\text{OH}^-]$$

- Although steric factors favor *D*-type mechanisms for octahedral complexes, square planar ML₄ complexes are not so inhibited.
 - For square planar ML₄ 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.



- The rate law is

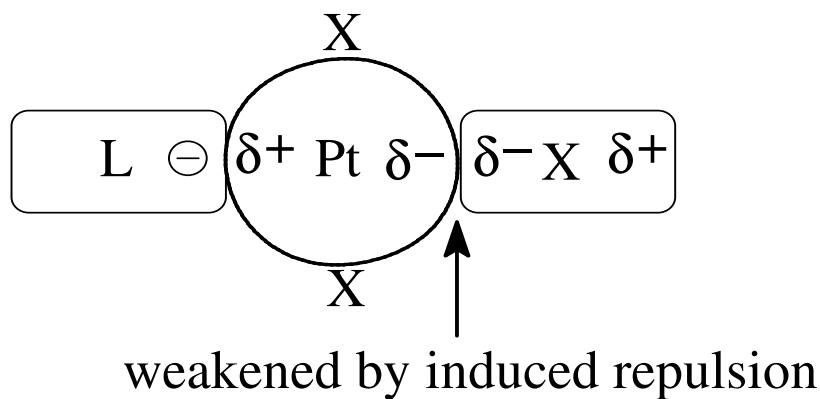
$$\text{Rate} = k_1[\text{PtLX}_3] + k_2[\text{PtLX}_3][\text{Y}^-] \quad k_2 > k_1$$

- 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

$$\begin{array}{c}
 \text{H}_2\text{O} < \text{OH}^- < \text{py} \approx \text{NH}_3 < \text{Cl}^- < \text{Br}^- < \text{I}^- < \text{NO}_2^- < \text{PR}_3 \approx \text{SH}_2 \\
 << \text{CO} \approx \text{C}_2\text{H}_4 \approx \text{CN}^-
 \end{array}$$
- The effect is kinetic rather than thermodynamic.
- Two factors are cited to explain the effect:
 - ① Weakening of the $\text{Pt}-\text{X}$ bond *trans* to the directing ligand;
 - ② Stabilization of the presumed $\text{CN}5$ intermediate.

M-X Bond Weakening

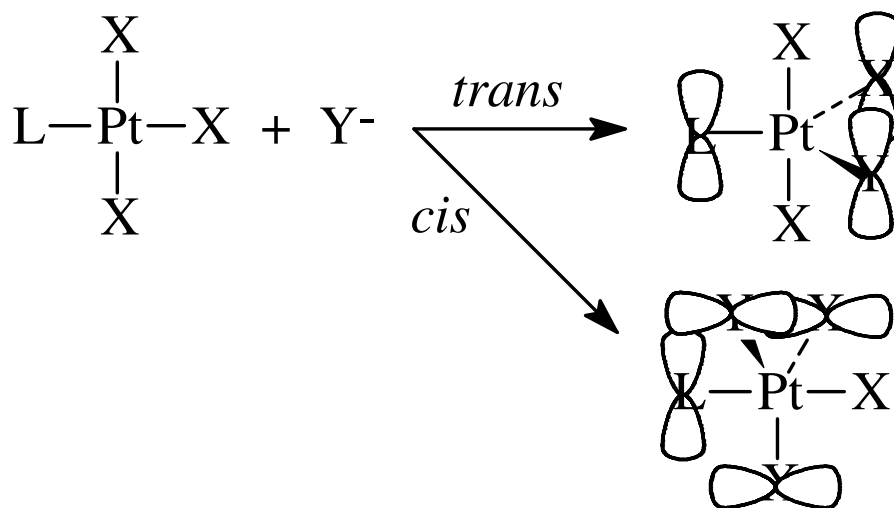
- For ligands at the left of the series, weakening of the *trans* Pt–X bond may be most important.
- The *trans*-directing ligand polarizes the metal ion, inducing a slight repulsion for the leaving ligand in the *trans* position.



- The more polarizable the L ligand, the better *trans*-director it is; e.g., $\text{I}^- > \text{Br}^- > \text{Cl}^-$.

π -Acceptor Ligands

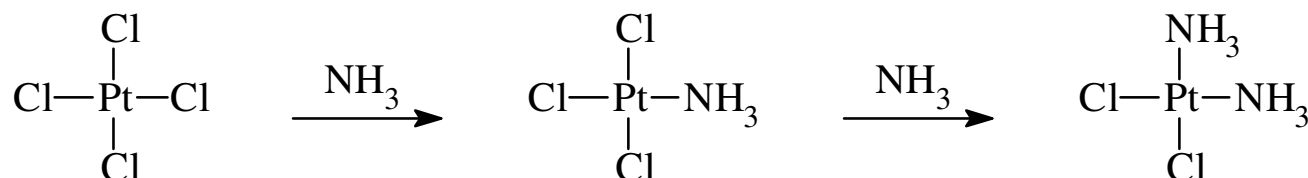
- The strongest *trans*-directors are good π -acceptor ligands; e.g., CO, C₂H₄, CN⁻.
- Assuming an A (S_N2) mechanism, substitution involves a trigonal bipyramidal transition state.
- The *trans* intermediate (activated complex) is more favorable for π -acceptor ligands, because it permits π -delocalization 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

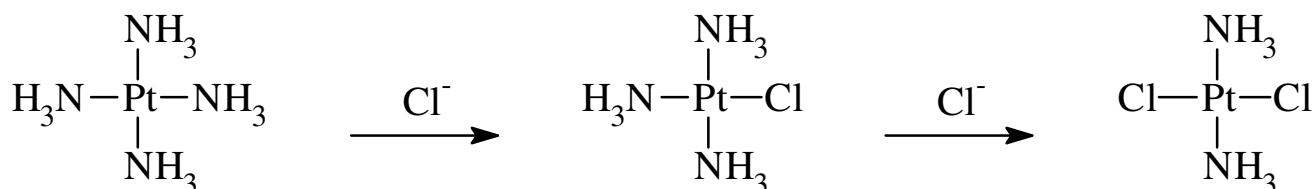
- The synthetic utility of the *trans* effect can be illustrated by the selective production of *cis* or *trans* $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, using the greater *trans*-directing ability of Cl^- relative to NH_3 .

✓ To make *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, start with $[\text{PtCl}_4]^{2-}$:



☞ 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*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$, start with $[\text{Pt}(\text{NH}_3)_4]^{2+}$:

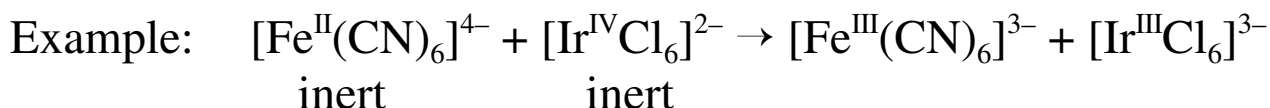


☞ In the second step, the greater *trans*-directing ability of Cl^- causes preferential substitution of Cl^- in the *trans* position to the first Cl^- , resulting in the *trans* isomer.

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.



- 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.,
$$\begin{array}{ccc} \text{Co}^{2+} (t_{2g}^5 e_g^2) & \rightarrow & \text{Co}^{3+} (t_{2g}^6) + e^- \\ \text{high-spin} & & \text{low-spin} \\ \text{long M–L} & & \text{shorter M–L} \end{array}$$
 - 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

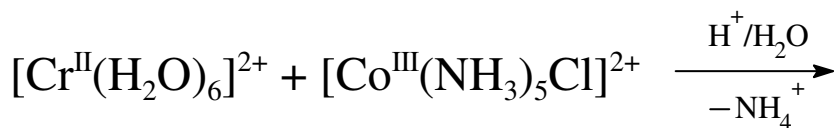
³F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley, NY, 1980, p. 1206.

Electron Transfer Reactions

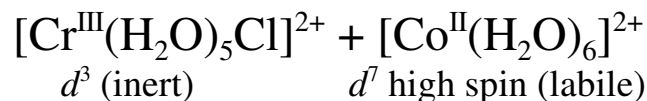
Inner Sphere Mechanism

- *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.

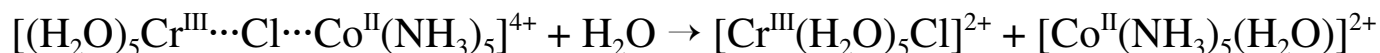
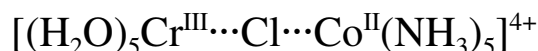
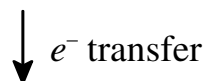
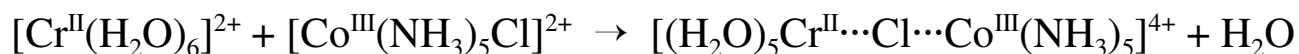
Example of Inner Sphere Redox



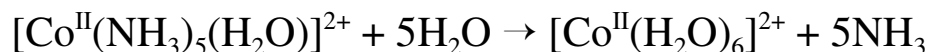
d^4 high spin (labile) d^6 low spin (inert)



Mechanism:



Co(II) complexes are labile, so $[\text{Co}^{\text{II}}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$ undergoes rapid aquation:



✓ 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.