Formation and Reactions of TM Complexes

What have we done so far?

1. What is the structure of these compounds?
    (Coordination Number, Geometry, Isomerization)

2. What holds these complexes together and how do we study them?
    (CFT d-orbital splitting, electronic spectroscopy, MO theory)

But….you can't study them if you can't get them…..

How are they made?

Where do we start?

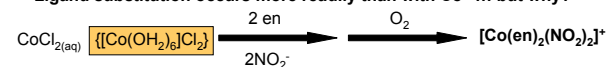How about with a Co and Pt complex? **$[Co(en)_2(NO_2)_2]^+$,** and **cis/trans platin.**

This is an interesting case:

We start with a Co^{2+} salt….**what is the oxidation state of Co in the product?**

Why do we use the Co^{2+}?

Ligand substitution occurs more readily than with Co^{3+}… but why?

$$CoCl_{2(aq)} \quad \boxed{\{[Co(OH_2)_6]Cl_2\}} \xrightarrow[2NO_2^-]{2\ en} \xrightarrow{O_2} [Co(en)_2(NO_2)_2]^+$$

If we change our starting material we can control stereochemistry…. but why?

$$[PtCl_4]^{2-} + 2NH_3 \longrightarrow \textit{cis}\text{-}PtCl_2(NH_3)_2$$

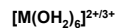$$[Pt(NH_3)_4]^{2+} + 2Cl^- \longrightarrow \textit{trans}\text{-}PtCl_2(NH_3)_2$$

Why do these reactions occur the way they do?
We are going to look at influencing factors and mechanisms.

Stable vs. Unstable
Inert vs. Labile

When TM ions are dissolved in water the ions form aqua complexes.

UV-Vis, NMR indicate a six-coordinate octahedral species for 1st row TMs.

$$[M(OH_2)_6]^{2+/3+}$$

(neutron diffraction of these species was first reported in 1984)

Given that the ions are not "free" in solution, formation of TM complexes involves the replacement (substitution) of one ligand with another.

$$[M(OH_2)_6]^{2+/3+} + nL \longleftrightarrow [ML_n]^{x+}$$

That these reactions occur in aqueous solution is VERY important to numerous disciplines including Inorganic Chemistry, Biochemistry, Analytical Chemistry, Environmental Chemistry and other applications.
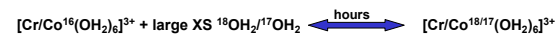

TM Aqua Complexes

An IMPORTANT point about TM-aqua complexes.

The amount of time (residence time) the H_2O ligands spends attached to the TM can vary significantly from metal to metal.

$[Cr(OH_2)_6]^{3+}$ and $[Co(OH_2)_6]^{3+}$ fail to exchange with $^{18}OH_2/^{17}OH_2$ after several hours.

$$[Cr/Co^{16}(OH_2)_6]^{3+} + \text{large XS } ^{18}OH_2/^{17}OH_2 \xrightarrow{\text{hours}} [Cr/Co^{18/17}(OH_2)_6]^{3+}$$

Most other TMs exchange water rapidly.

What does this tell us about formation of TM complexes and what we need to consider?

1. **Thermodynamics**: When examining thermodynamics of a reaction we are entirely interested in the start and finish of a reaction. What is the extent of reaction? Where does the equilibrium lie? **How do we investigate this?** **ΔG°**

2. **Kinetics:** How fast does a reaction reach equilibrium? This relates directly to the mechanism.

Look at the reaction coordinate diagram…
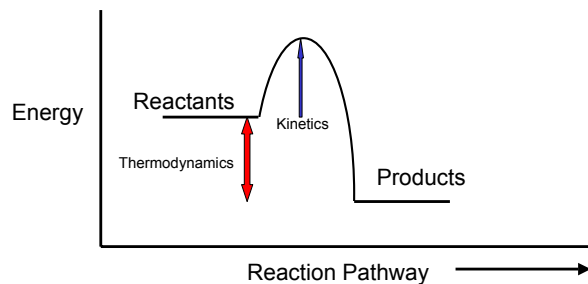
Kinetics vs. Thermodynamics

We use terms to describe the Thermodynamic and Kinetic aspects of reactivity.

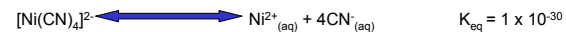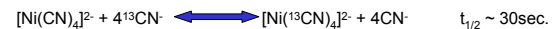**Thermodynamic. <u>Stable</u> or <u>Unstable</u>**

Kinetic. <u>Inert</u> or <u>Labile</u>

An inert compound is not "inert" in the usual sense that no reaction will occur. Rather, the reaction takes place slower than for labile compounds.
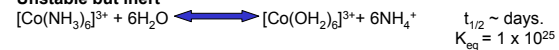
There is <u>NO</u> connection between Thermodynamic Stability/Instability of a complex and its Lability/Inertness toward substitution.

For example:
Stable …but labile

$[Ni(CN)_4]^{2-} + 4^{13}CN^- \rightleftharpoons [Ni(^{13}CN)_4]^{2-} + 4CN^-$ $t_{1/2} \sim 30sec.$

$[Ni(CN)_4]^{2-} \rightleftharpoons Ni^{2+}_{(aq)} + 4CN^-_{(aq)}$ $K_{eq} = 1 \times 10^{-30}$

Unstable but inert
$[Co(NH_3)_6]^{3+} + 6H_2O \rightleftharpoons [Co(OH_2)_6]^{3+} + 6NH_4^+$ $t_{1/2} \sim days.$
    $K_{eq} = 1 \times 10^{25}$

Conclusions from these examples.

Stable complexes have a large POSITIVE ΔG^o_{RXN} for ligand substitution and Inert complexes have a large POSITIVE $\Delta G^{\ddagger}$ (activation).

Stability and Coordination Complexes ($[ML_n]^{x+}$)

Typically expressed in terms of an overall formation or stability constant.
(This is K_{st} on the Chemistry Data sheet you receive with exams)

$$[M]^{x+} + nL \Longleftrightarrow [ML_n]^{x+} \qquad K_{st} = \frac{[ML_n]^{x+}}{[M^{x+}_{(aq)}][L]^n}$$

BUT, this does not occur in one fell swoop!!
Water molecules do not just all fly off and are immediately replaced by nL ligands.

$$[M]^{x+}_{(aq)} + L \Longleftrightarrow [ML]^{x+} \qquad K_1$$

$$[ML_{(n-1)}]^{x+} + L \Longleftrightarrow [ML_n]^{x+} \qquad K_n$$

K_s are the stepwise formation constants and provide insight into the solution species present as a function of [L].

Stepwise formation constants

These formation constants provide valuable information given that different species may have VERY DIFFERENT properties…including environmental impact. Such information provides selective isolation of metal ions from solution through reaction with ligands.

For formation of divalent alkaline earth and 3d M^{2+} TM ions the **Irving-Williams Series** holds true.

Ba<Sr<Ca<Mg<Mn<Fe<Co<Ni<Cu>Zn

What is contributing to this trend?

1. Charge to radius ratio.
2. CFSE (beyond Mn^{2+})
   Jahn-Teller Distortion
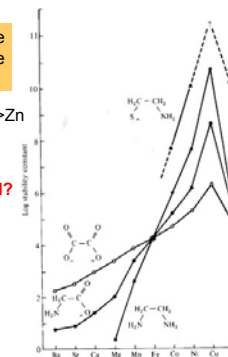3. Hard-Soft Acids/Bases

See R-C p 450-451.

Fig. 9.5 The Irving-Williams effect: The stability increases in the series Ba-Cu, decreases with Zn. [From Sigel, H.; McCormick, D. B. *Acc. Chem. Res.* 1970, 3, 201. Reproduced with permission.]

The Pearson LA/LB "Hard"/"Soft" Approach

Hard Lewis Bases: high EN, low polarizability, hard to oxidize: O, N, F⁻ donors (Cl⁻ is borderline).
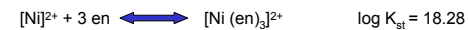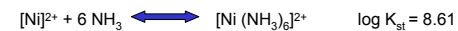
Soft Lewis Bases: low EN, highly polarizable, easy to oxidize: S, P, I⁻, Br⁻, R⁻, H⁻ donors.

Hard Lewis Acids: small, highly charged (high ox. State): H^+, alkali metal (M^+) and alkaline earth (M^{2+}) cations, Al^{3+}, Cr^{3+}, BF_3.

Soft Lewis Acids: large, low oxidation state: Cu^+, Ag^+, Au^+, Tl^+, Hg^{2+}, Pd^{2+}, Pt^{2+}, BH_3

In this model, hard acids "like" hard bases and soft acids "like" soft bases.

Chelate Effect

$[Ni]^{2+} + 6\ NH_3 \longleftrightarrow [Ni\ (NH_3)_6]^{2+}$ log K_{st} = 8.61

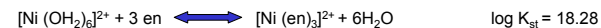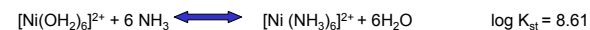$[Ni]^{2+} + 3\ en \longleftrightarrow [Ni\ (en)_3]^{2+}$ log K_{st} = 18.28

Both ligands have a N-donor, yet the en complex is 10 orders of magnitude more stable than the NH_3.

This is a general effect that a complex with one (or more) 5 or 5-membered rings has a greatly enhanced stability relative to the similar complex lacking rings.

Why is this happening? What's missing from our equation?

$[Ni(OH_2)_6]^{2+} + 6\ NH_3 \longleftrightarrow [Ni\ (NH_3)_6]^{2+} + 6H_2O$ log K_{st} = 8.61

$[Ni\ (OH_2)_6]^{2+} + 3\ en \longleftrightarrow [Ni\ (en)_3]^{2+} + 6H_2O$ log K_{st} = 18.28

In the GAS PHASE there is no difference in K_{st}

Reactions of Coordination Complexes

The reactions of Coordination Complexes may be divided into three classes:

i) Substitution at the metal center
ii) Reactions of the coordinated ligands
iii) Oxidation and Reduction reactions at the metal center.

For the purposes of our discussion we will confine our discussion to (i) for substitution reactions on **Octahedral** and **Square Planar** complexes.

We will only briefly discuss one specific reaction involving a coordinated ligand.

Rxns of Octahedral Complexes

Consider ML_5X : In this complex there are 5 inert ligands (L) and one labile ligand (X).

For our purposes we will consider the replacement of X with an incoming ligand Y.

$$ML_5X + Y \longrightarrow ML_5Y + X$$

How might this happen?

We need to look at the molecular components.

What elemental steps will result in this process….

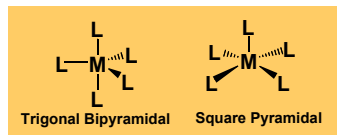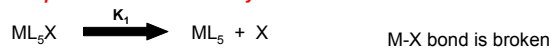In more technical terms: What is the mechanism of this reaction?

There are Two Extreme Cases

Dissociative Mechanism (D) Associative Mechanism (A)
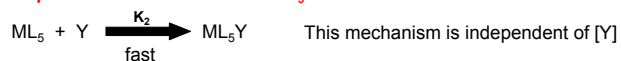
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Dissociative Mechanism

$$ML_5X + Y \longrightarrow ML_5Y + X$$

Step 1. Dissociation of X to yield a 5 coordinate intermediate.

$$ML_5X \xrightarrow{K_1} ML_5 + X$$

M-X bond is broken

Slow and *rate determining*

The rate of D is only depends on the conc. of ML_5X

Trigonal Bipyramidal   Square Pyramidal

Step 2. Coordination of Y to the ML_5 intermediate.

$$ML_5 + Y \xrightarrow[\text{fast}]{K_2} ML_5Y$$ This mechanism is independent of [Y]
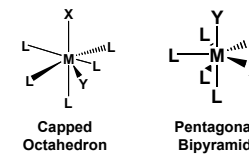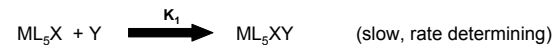
The rate law for this process is rate = $K_1[ML_5X]$ (the units of K_1 are sec^{-1})
If we find a reaction follows this rate law we conclude it is dissociative.

Associative Mechanism

$$ML_5X + Y \longrightarrow ML_5Y + X$$

Step 1. Collision of ML_5X with Y to yield a 7-coordinate intermediate. (slow)

$$ML_5X + Y \xrightarrow{K_1} ML_5XY$$ (slow, rate determining)

Capped
Octahedron

Pentagonal
Bipyramid

Step 2. Cleavage of the M-X bond. (fast)

$$ML_5XY \longrightarrow ML_5Y + X$$ (fast)

The rate law for this process is rate = $K_1[ML_5X][Y]$ (the units of K_1 are sec^{-1}Mole^{-1})
If we find a reaction follows this rate law we conclude it is associative.

Telling the difference…

By determining the rate law (uni- vs. bi- molecular) we can determine the mechanism of the reaction in question.

rate = $K_1[ML_5X]$ **or**   **rate = $K_1[ML_5X][Y]$**

This is achieved via monitoring the disappearance reactant(s) and the appearance of product(s) using spectroscopic methods and variations in reactant concentrations.

This is not always as simple as we see here….

We will discuss one complication.

Solvents and Water!!

Often experimental conditions "mask" the dependence upon [Y].

When a reaction is carried out in a solvent….the solvent is in HUGE excess and it is not necessarily "innocent" (it can take a role in the rxn)

What is the concentration of water?

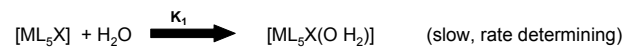Effectively constant at 55.5M.
Be sure you can determine this!!

Given the excess of water, its concentration remains seemingly constant. As a result, the influence of the water on the mechanism is "masked". This results in a pseudo-first order rate law.

Solvent and Associative Processes

$$ML_5X + Y \xrightarrow{H_2O} ML_5Y + X$$
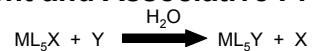
Step 1. Collision of ML_5X with Y or H_2O to yield a 7-coordinate intermediate.

Given the $[H_2O] >>>>[Y]$ it is much more likely that a collision with H_2O will occur.

$$[ML_5X] + H_2O \xrightarrow{K_1} [ML_5X(OH_2)] \quad \text{(slow, rate determining)}$$

Step 2. Cleavage of the M-X bond.

$$[ML_5X(OH_2)] \xrightarrow{K_2} [ML_5OH_2] + X \quad \text{(fast)}$$

Step 3 Formation of the M-Y bond.

$$[ML_5X(OH_2)] + Y \xrightarrow{K_3} [ML_5OH_2] + X \quad \text{(fast)}$$

Looking at the structures…
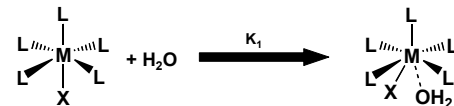
Rate Law

Rate = [overall rate] = $k_1[ML_5X][H_2O]$
= $\{k_1[H_2O]\}\,[ML_5X]$
= $K\,[ML_5X]$

Given the $[H_2O]$ is constant the rate appears to follow a pseudo-1st order rate law.

To determine if the process follows A or D mechanism we need to do other exps.

ML$_6$ Preferred Mechanism

Octahedral complexes tend to favor a *D* mechanism through a 5 -coordinate intermediate.

$$[M(OH_2)_6]^{X+} + {}^{17}OH_2 \longleftrightarrow [M(OH_2)_5 {}^{17}(OH_2)]^{X+}$$

We already discussed that the residence time of H_2O varies a lot. 1×10^{10} s^{-1} to 1×10^{-8}s^{-1}

M^{X+}	K$_1$ (s^{-1})
Cs$^+$	5×10^9
Li$^+$	5×10^8
Ba^{2+}	2×10^9
Be^{2+}	2×10^2

As the charge/radius ratio increases the rate of water exchange decreases.

What obs. of M^{2+} and M$^+$ can be made?

Charge/Radius Ratio

Given the M-OH$_2$ bond strength increases as the charge/radius ratio increases, data are consistent with a mechanism where the intermediate was obtained from the cleavage of the M-OH$_2$ bond and a new M-*OH$_2$ bond is formed quickly.

This is Characteristic of a Dissociative Mechanism

Exceptions to the charge/ratio rule exist:

Ni^{2+}(0.83Å), Cr^{2+}(0.94Å), Cu^{2+}(0.87Å) very similar size

Ni^{2+}(K$_1$= 1×10^4s^{-1}), Cr^{2+}/Cu^{2+}(K$_1$= 1×10^9s^{-1}) very different rates.

Some inert TM ions that exchange H$_2$O very slowly:

Cr^{3+}, LS Co^{3+} and sqr. planar Pt^{2+}

The inert nature of these complexes made it possible for Werner to work out his theory.

Inert/Labile d-electron configurations

Generally, INERT *oct.* complexes have large CFSE*, specifically

d^3, and L.S. d^4-d^6

Other compounds tend to be labile.

(dividing line labile vs. inert is t1/2 of 1 min. at 25ºC)

	Inert Complexes	Labile Complexes
Octahedral	d3 and LS d^4, d^5, d^6	$d^1, d^2, d^7, d^8, d^9, d^{10}$ HS d^4, d^5, d^6
Sqr. Planar	d^8 Pt^{2+}	Ni^{2+}

Pd^{2+}
(intermediate)

This summary applies best for 3d TMs.

If you consider 4d and 5d metals it is found that these metals have greater CFSE and achieve sigma bonds with better overlap than 3d metals.Hence, such systems tend to be inert on the above time scale.

Why look at water exchange?

The study of simple water exchange reactions is important and valuable given the rate at which $M(OH_2)_6^{X+}$ aqua ions combine with other ligands (L) to form other complexes…..

Shows little or no dependence on L

Rates for each metal ion are practically the same as the rate of exchange for H_2O on the same metal ion.

We can use exchange reactions to provide insight into other substitution reactions.

Anation Reactions

$$[M(OH_2)_6]^{X+} + X^- \longrightarrow [M(OH_2)_5 X]^{(X-1)+} + H_2O$$

This type of reaction is important as its behavior indicates not only how new complexes are formed but also where coordinated water is replaced by X^-.

$$[L_5M(OH_2)]^{X+} + X^- \longrightarrow [L_5M X]^{(X-1)+} + H_2O$$

Generally two observations can be drawn:

1. For a given aqua ion, the rate of anation show little dependence on the nature of L.

2. The rate constant for anation of a given aqua complex is almost the same as for H_2O exchange.

These are consistent with a dissociative mechanism…..WHY?

Why look at water exchange?
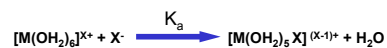
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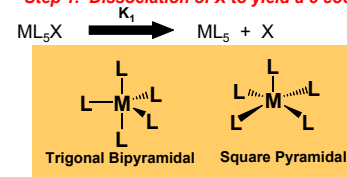
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Which Mechanism

$$ML_5X + Y^- \longrightarrow [ML_5Y]^- + X$$

Step 1. Dissociation of X to yield a 5 coordinate intermediate.

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Slow and *rate determining*

The rate of D is only depends on the conc. of ML_5X

Trigonal Bipyramidal   Square Pyramidal

OR

Step 1. Collision of ML_5X with Y to yield a 7-coordinate intermediate. (slow)

$$ML_5X + Y^- \xrightarrow{K_1} [ML_5XY]^- \qquad \text{(slow, rate determining)}$$

Capped Octahedron   Pentagonal Bipyramid
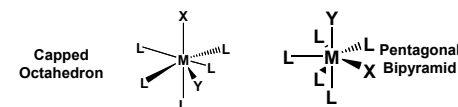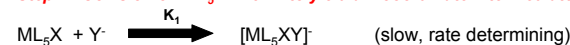
Aquation Reactions

Complexes present in solution are susceptible to aquation or hydrolysis.

This means their ligands can be replaced with water (the opposite of the anation reactions).

As we discussed earlier, even when other ligands are involved, very few reactions proceed without solvent intervention. This complicates the determination of kinetic behavior.

For inert Co(III) complexes it has been found that hydrolysis depends greatly on the pH of the solution.

Acid Hydrolysis of $[Co(NH_3)_5X]^{2+}$

$[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(OH_2)]^{3+} + X^-$

rate = $k_a[Co(NH_3)_5X^{2+}]$ (k_a = acid hydrolysis rate constant, s^{-1})

From the rate law, what mechanism would you predict?

Evidence for the D mechanism:
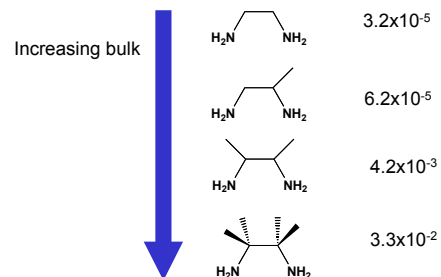
The rate of aquation follows the bond strength of the Co-X bond; as the bond energy decreases the rate increases.

	X =	K_a =	
BE_{Co-X} ↓	F^-		$9 \times 10^{-8} s^{-1}$
(HSAB theory)	Cl^-		$2 \times 10^{-6} s^{-1}$
	Br^-		$6 \times 10^{-6} s^{-1}$
	I^-		$8 \times 10^{-6} s^{-1}$

Given K_a is a thermodynamic quantity a larger value means greater stability for $[Co(NH_3)_5(X/L)]^{2+}$ and *implies* a stronger bond energy. It is clear that as the Co-X bond energy increases, the (or the k_a for anation increases) K_a for aquation/hydrolysis decreases.

Steric Acceleration of Aquation

As the size of the bidentate ligand in trans-$[Co(N-N)_2Cl_2]^+$ increases, the rate of aquation increases. This is consistent with a dissociatve mechanism as **STERIC CROWDING** weakens the Co-Cl bond.

Increasing bulk

H_2N NH_2 $3.2x10^{-5}$

H_2N NH_2 $6.2x10^{-5}$

H_2N NH_2 $4.2x10^{-3}$

H_2N NH_2 $3.3x10^{-2}$

Charge Effects

A stronger Co-Cl bond in $[Co(NH_3)_5Cl]^{2+}$ results in slower aquation.

$[Co(NH_3)_5Cl]^{2+}$ $[Co(NH_3)_5Cl_2]^+$

$6.7x10^{-6}$ $1.8x10^{-3}$

Base Hydrolysis

$[Co(NH_3)_5X]^{2+} + {}^-OH \longrightarrow [Co(NH_3)_5(OH)]^{2+} + X^-$

rate $= k_b[Co(NH_3)_5X^{2+}][OH^-]$ (k_b = base hydrolysis rate constant, $s^{-1}M^{-1}$)

In basic solution, the product of the reaction is the hydroxo complex.

It is found that for this compound k_b is 10^3-10^6 larger than expected.

In fact Co^{3+} complexes are labile toward substitution and decompose to give hydroxides and hydrous metal oxides.

Whys is this reaction so fast?

What does the rate law tell us?

rate $= k_b[Co(NH_3)_5X^{2+}][OH^-]$

BUT......?

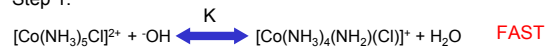There are many anomalous observations to the contrary:

1. OH^- is unique in accelerating the hydrolysis (I^-, and CN^- don't)

2. When NH_3 is replaced by NR_3 the rate decreases and the magnitude of K_b is normal.

3. In basic D_2O (^-OD), H exchanges quickly for D.

These observations suggest a *conjugate base mechanism*.

Specifically, $S_{N1}CB$.

$S_{N1}CB$

Step 1.

$[Co(NH_3)_5Cl]^{2+} + {}^-OH$ $\xrightarrow{\ \ K\ \ }$ $[Co(NH_3)_4(NH_2)(Cl)]^+ + H_2O$ **FAST**
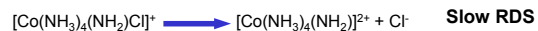
Rapid reversible ionization of the complex.
OH⁻ acts as a base and deprotonates the NH$_2$-H to give NH$_2^-$ (amido)

THIS IS NOT A RAPID SUBSTITUTION STEP
THIS IS NOT THE RDS

THIS EXPLAINS H/D EXCHANGE

Step 2.

$[Co(NH_3)_4(NH_2)Cl]^+$ $\longrightarrow$ $[Co(NH_3)_4(NH_2)]^{2+} + Cl^-$ **Slow RDS**

Rate determining step is the loss of Cl- from the amido complex.

(What does the bonding look like?)

This is a dissociative process.
Since the formation of the amido complex is dependent on [⁻OH], the second order rate Law can be understood.

The RDS is very rapid because the amido group is a strong π-donor, it promotes the elimination of Cl⁻ and the extra l.p. stabilizes the intermediate.

There is also a charge reduction which weakens the Co-Cl bond.

$S_{N1}CB$

Step 3

$[Co(NH_3)_4(NH_2)]^{2+} + H_2O$ $\longrightarrow$ $[Co(NH_3)_5(OH)]^{2+}$ **FAST**

The overall rate law:

$$rate = K[Co(NH_3)_4(NH_2)Cl^+]$$

$$= k_2K[Co(NH_3)_5X^{2+}][OH^-]$$

If $k_b = k_2K$ then

Agreement with Exp.

$$rate = k_b[Co(NH_3)_5X^{2+}][OH^-]$$

Reactions of Coordinated Ligands

It is also possible to carry out reactions where ligand exchange does not involve cleaving the M-L bond. Rather, bonds within the ligands are broken and reformed.

This is seen in the aquation of a carbonato complex in acid solution.

$$[Co(NH_3)_5(OCO_2)]^+ + 2H_3O^+ \longrightarrow [Co(NH_3)_5(OH_2)]^{3+} + 2H_2O + CO_2$$

This is a rapid reaction, something out of character for inert Co^{3+} complexes.

Why?

From experiment with labeled water, there is no label incorporated into the Co coordination sphere.
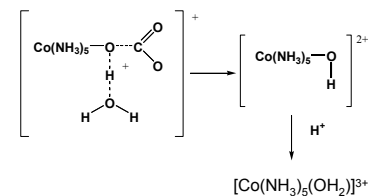
$$[Co(NH_3)_5(OCO_2)]^+ + 2H_3{}^*O^+ \longrightarrow [Co(NH_3)_5(OH_2)]^{3+} + 2H_2{}^*O + CO_2$$

What is happening?

What's happening?

The most likely path for this reaction involves proton attack on the oxygen of the CO_3^{2-} bonded to the Co.

This attack is followed by the elimination of CO2 and protonation of the hydroxo complex.

THIS IS NOT A SIMPLE SUBSTITUTION OF CO_3^{2-} BY H_2O.

$$[Co(NH_3)_5(OH_2)]^{3+}$$

Reactions of 4-Coordinate SP Complexes

Complexes with d^8 electron configurations are usually 4-coordinate and have sqr. planar geometry.

Pt(II), Pd(II), Ni(II) (sometimes tetrahedral, often 6-coordinate, octahedral)
Ir(I), Rh(I), Co(I), Au(III)

Pt(II) has been studied a lot. Its complexes are stable, easy to synthesize and undergo ligand exchange reactions at rates slow enough to allow easy monitoring.

Other d^8 systems react much faster (10^5-10^7x) and the data on these systems is limited.

Current knowledge of SP substitution reactions stems from studies in the 1960s and 70s.

Wacker process. Industrial conversion of ethylene to acetaldehyde.

$$H_2C{=\!=}CH_2 \ + \ 1/2 \ O_2 \xrightarrow{\ PdCl_2/CuCl_2\ } \overset{\displaystyle O}{\underset{H_3C}{\big\Vert}}\!\!-\!H$$

BUT……?

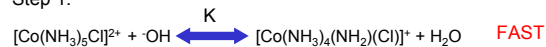There are many anomalous observations to the contrary:

1. OH^- is unique in accelerating the hydrolysis (I^-, and CN^- don't)

2. When NH_3 is replaced by NR_3 the rate decreases and the magnitude of K_b is normal.

3. In basic D_2O (^-OD), H exchanges quickly for D.

> These observations suggest a *conjugate base mechanism*.
>
> **Specifically, $S_{N1}CB$.**

$S_{N1}CB$

Step 1.

$$[Co(NH_3)_5Cl]^{2+} + {}^-OH \quad \overset{K}{\longleftrightarrow} \quad [Co(NH_3)_4(NH_2)(Cl)]^+ + H_2O \qquad \text{FAST}$$
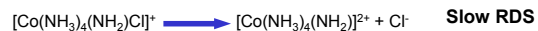
Rapid reversible ionization of the complex.
OH$^-$ acts as a base and deprotonates the NH$_2$-H to give NH$_2^-$ (amido)

THIS IS NOT A RAPID SUBSTITUTION STEP
THIS IS NOT THE RDS

THIS EXPLAINS H/D EXCHANGE

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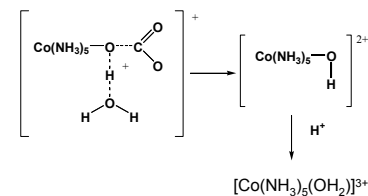
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Cis-platin

This is an anti cancer drug which binds to the DNA of cancer cells.

The reversible aquation assists in the transfer of the drug from blood to the tumor where water and Cl- are replaced by the DNA.
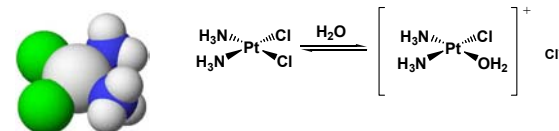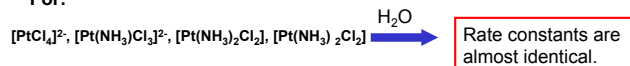
Mechanistic Considerations

It is easier to understand mechanisms with 4-coordinate systems than with 6-coordinate octahedral systems as it is expected that S.P. 4-coordinate complexes will be more likely to react via an associative mechanism.

In fact many d^8 systems do react via an S_N2 type mechanism.

For:

$[PtCl_4]^{2-}$, $[Pt(NH_3)Cl_3]^{2-}$, $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_2Cl_2]$ $\xrightarrow{H_2O}$ | Rate constants are almost identical.

This is most readily explained via an associative mechanism.

The General Reaction Pathway

$$[Pt(L)_3X] + Y \longrightarrow [Pt(L)_3Y] + X$$

(L = non-labile ligand, X = L.G., Y = entering ligand)

Rate law. **Rate= $k_1[PtL_3X] + k_2[PtL_3X][Y]$**
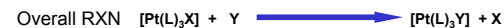
What does this tell you?
How does this differ from every other rate law you have seen?

It indicates that the reaction proceeds via two independent pathways.

The first term…. $k_1[PtL_3X]$ This occurs only when the solvent is a Lewis Base and a potential ligand.

It is believed that this is a two step process involving X being slowing replaced by solvent. The solvent is in turn replaced readily by Y.

$$[Pt(L)_3X] + S \longrightarrow [Pt(L)_3S] + X \quad \text{slow, RDS}$$

$$[Pt(L)_3S] + Y \longrightarrow [Pt(L)_3Y] + S \quad \text{fast}$$

Overall RXN $[Pt(L)_3X] + Y \longrightarrow [Pt(L)_3Y] + X$

The General Reaction Pathway

Solvent Intervention. **Does this look familiar?**

Didn't we say this was an associative mechanism?

Often experimental conditions "mask" the dependence upon [Y].

When a reaction is carried out in a solvent….the solvent is in HUGE
excess and it is not necessarily "innocent" (it can take a role in the rxn)

Effectively constant at 55.5M.
**Be sure you can determine
this!!**

Given the excess of water, its concentration remains seemingly constant.
As a result, the influence of the water on the mechanism is "masked". This
results in a **pseudo-first order rate law**.

Rate Law

$$\text{Rate} = [\text{overall rate}] = k_1[\text{Complex}][H_2O]$$
$$= \{k_1[H_2O]\} [\text{complex}]$$
$$= K [\text{complex}]$$

$[Pt(L)_3X] + S \longrightarrow [Pt(L)_3S] + X \quad \text{slow, RDS}$

The first term…. $k_1[PtL_3X]$

The General Reaction Pathway

The Second Step

$$k_2[PtL_3X][Y]$$

$F^-, H_2O < Cl^- < NH_3 < py < Br^- < I^- < SCN < CN^- < PR_3$
increasing k_2 ⟶
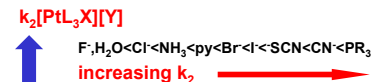
Strongly dependent upon Y.

This sequence is the "Nucleophilicity Sequence" for Pt(II).

**Generally, Pt(II) prefers soft, polarizable ligands. Recall it is
a soft Lewis acid (large, low valent metal ion See HSAB)**

What does this tell you about the mechanism?

Step 1. Collision of PtL$_3$X with Y to yield a 5-coordinate intermediate. (slow)

$PtL_3X + Y \xrightarrow{k_2} PtL_3XY \quad$ (slow, rate determining)

The General Reaction Pathway

The leaving group should also influence the rate…and k_2.

It is noted that the order of ligands is nearly the reverse of the Nu Series.

Hard ligands (NO_3^-, H_2O) leaving easily and quickly.
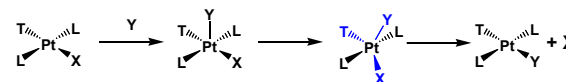**Soft ligands (CN^-, ^-SCN) leaving reluctantly.**

$F^-, H_2O < Cl^- < NH_3 < py < Br^- < I^- < ^-SCN < CN^- < PR_3$

k_{obs} (s^{-1}M^{-1})	X$^-$
1.9×10^{-3}	H_2O
3.5×10^{-5}	Cl^-
1.7×10^{-8}	CN^-

Stereochemistry

In the majority of reactions, substitution at the Pt(II) center proceeds with retention of the stereochemistry.

This means that the incoming Y replaces the outgoing X.

1. The entering Y approaches from one side of the plane.

2. Formation of a tbp intermediate via a sp (**TYX** are in the eq plane, **Ls** are in the axial positions). This maintains the trans position of the two L ligands and elimination of X gives the new product with the same stereochemistry.
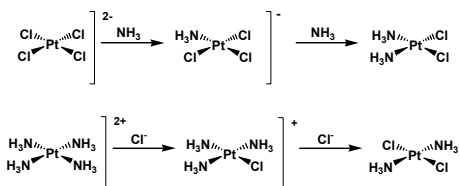
trans- effect.

This observation is particularly true for Pt(II) complexes.
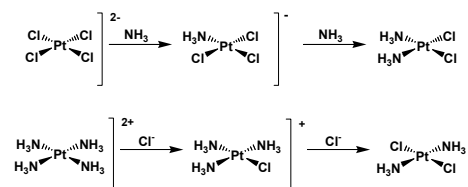
The ligand trans to the "leaving" ligand
can alter the rate of exchange by orders
of magnitude.

The rich Pt deposits in Russia saw the development of many intensive studies into Pt coordination chemistry. The first stereospecific ligand displacement reactions were discovered.

In 1926 Chernyaev introduced the trans effect.

$$[Cl_4Pt]^{2-} \xrightarrow{NH_3} [PtCl_3(NH_3)]^{-} \xrightarrow{NH_3} PtCl_2(NH_3)_2$$

$$[Pt(NH_3)_4]^{2+} \xrightarrow{Cl^-} [PtCl(NH_3)_3]^{+} \xrightarrow{Cl^-} PtCl_2(NH_3)_2$$

---

trans-effect

$$[Cl_4Pt]^{2-} \xrightarrow{NH_3} [PtCl_3(NH_3)]^{-} \xrightarrow{NH_3} PtCl_2(NH_3)_2$$

$$[Pt(NH_3)_4]^{2+} \xrightarrow{Cl^-} [PtCl(NH_3)_3]^{+} \xrightarrow{Cl^-} PtCl_2(NH_3)_2$$

How do we understand this?

Step 1. Simple displacement….all the groups on the starting material are the same. Only one compound forms.

Step 2. Two products can form BUT only one does. Note that in each case the observed isomer arises from the substitution of a ligand trans to to a Cl.

trans-effect

The trans-effect is defined:

"The ability of a ligand to promote rapid substitution of a ligand trans to itself."

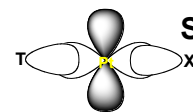**Is this a <mark>kinetic</mark> or thermodynamic phenomenon?**
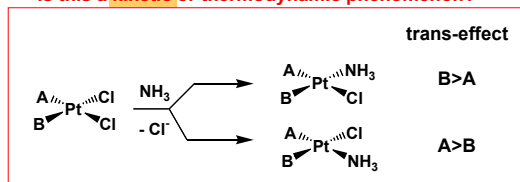
trans-effect

B>A

A>B

The general order of ligand trans-effect is

H_2O, OH^-<NH_3,py<Cl^-<Br^-<I^-<SCN, NO_2^-<C_6H_5<CH_3^-,SR_2<H^-,PR_3<$H_2C=CH_2$,CN^-,CO

Things to think about…

This is a kinetic effect, it depends on activation energies, stabilities of ground state and transition state is relevant.
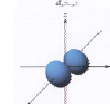

Sigma Bonding Effect

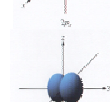How can the Pt-T bond weaken the trans Pt-X bond?

**Molecular orbital calculations hold the answer.**
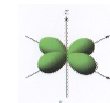
Both the Pt-X and Pt-T bonds involve the d_{x2-y2} and p_x (p_y) orbitals to form sigma bonds.

In the case of a VERY STRONG Pt-σ-bond, there is good overlap between the ligand orbitals and these Pt orbitals.

THIS IS A FANCY WAY TO SAY THAT THE ORBITALS ARE USED UP BY THE STRONG BOND and there is less of the Pt orbitals available for other bonding.
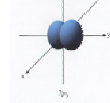
Given the weaker Pt-X bond, its ground state (σ-bonding orbital) is higher energy…….
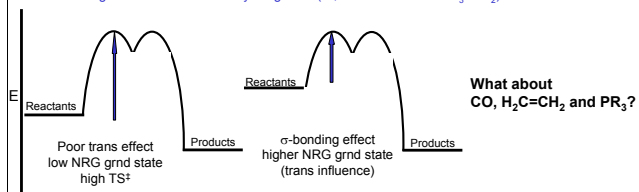
Pt-X Bond and Activation Energy

Given the weaker Pt-X bond, its ground state (σ-bonding orbital) is higher energy leading to a lower activation energy.

This is a thermodynamic effect and influences the kinetics of the reaction by changing the G.S..
The trans-ligand is labilized in an associative mechanism.
influence of ligands follows the σ-ability of ligands. (H⁻,R⁻>>⁻SCN>I⁻>Cl⁻>NH$_3$>OH$_2$)

E

Reactants

Reactants

Products

Products

Poor trans effect
low NRG grnd state
high TS‡

σ-bonding effect
higher NRG grnd state
(trans influence)

What about CO, H$_2$C=CH$_2$ and PR$_3$?

Summary of trans effect

1. The highest trans effect is seen for strong π-acceptors followed by strong σ-donors.
2. Ligands at the low end of the series have neither strong σ-donating abilities or π-accepting abilities. **This makes BOTH GS and TS important.**

Propose how to prepare cis-/trans-[Pt(NH$_3$)(NO$_2$)Cl$_2$]⁻.

Start with?

The general order of ligand trans-effect is

H$_2$O, OH⁻<NH$_3$,py<Cl⁻<Br⁻<I⁻<⁻SCN, NO$_2$⁻<C$_6$H$_5$<CH$_3$⁻,SR$_2$<H⁻,PR$_3$<H$_2$C=CH$_2$,CN⁻,CO