Inorganic Chemistry with Doc M.
Fall Semester, 2012
Day 21. Transition Metals Complexes V: Reaction Mechanisms

Name(s):	Element:

Topics:

1. Substitution reactions: dissociative v. associative
2. Factors affecting reaction mechanisms
3. Stereochemistry of Reactions
4. Pseudorotation
5. The Chelate Effect
6. Trans Effect

A. Background/review

By definition, reaction mechanisms are part of the realm of kinetics. Reactions can be fast or slow. There may be two or more steps so an intermediate is involved. (a) Sketch the reaction profile for a 1-step reaction mechanism and (b) for a two-step mechanism. In both cases, make your reactions slightly exothermic. In (b), make the first step the rate-determining step.

(a)	(b)

B. Substitution reactions mechanisms: octahedral complexes

1. Octahedral complexes substitute ligands, one at a time:

$$ML_6^{+/-n} + L' \rightarrow ML_5L'^{+/-n} + L.$$

In class, you saw this reaction when I tossed some aqueous ammonia into a solutions of $[Co(H_2O)_6]Cl_2$, $[Cu(H_2O)_6]Cl_2$, and $[Ni(H_2O)_6]Cl_2$. Write the substitution reaction that took place in each case, assuming that only one ammonia was added per metal complex ion.

2. How did that ammonia come to substitute a water ligand? Did the water ligand leave first or did it leave after the ammonia ligand became attached? Or… did it leave in some other arrangement somehow — like an S_{N2} in organic chemistry? To explore these possibilities one at a time, we need to sketch out what must be happening.

a. Dissociative mechanism. In the first suggested reaction mechanism, where the water ligand leaves and then the ammonia ligand comes in to the vacated position, we have an intermediate that is 5-coordinate (square pyramidal). Sketch the reaction profile for the reaction in the box and include 3-D sketches of the molecules and intermediates positioned near where they relate to the reaction profile. This mechanism is called ***dissociative*** because the rate-determining step is the loss of water ligand.

1. What is the reaction mechanism, step-by-step?

2. The first step of the reaction mechanism is the rate-determining step. What is the rate law?

b. Associative mechanism. The second suggested mechanism is called ***associative*** in which the ammonia coordinates to the metal and then the water ligand leaves. This is also a two-step mechanism involving a 7-coordinate intermediate. Make another reaction profile sketch like you did in (a) above, adding molecular sketches to the drawing. This mechanism is called ***associative*** because the rate-determining step is the addition of new ligand (the first step.)

1. What is the reaction mechanism, step-by-step?

2. What is the rate law?

C. Factors affecting reaction mechanisms

1. Let's analyze each of the two rate-determining reaction steps in terms of the enthalpy and entropy changes associated with getting to the top of the energy hill for the slow step. Complete this table thinking in terms of bond making and breaking.

	ΔH^{act}	ΔS^{act}
Associative mechanism, A	> 0 < 0	> 0 < 0
Dissociative mechanism, D	> 0 < 0	> 0 < 0

2. Still thinking in terms of the slow step for each of these mechanisms (A vs. D), what role would steric considerations play in deciding which pathway may be favored?

3. When organic chemists aren't busy waving their hands about steric considerations, they are waving their hands about electronic considerations. We've already seen how an increase in the oxidation state on the metal makes the metal-ligand interaction stronger (stronger bond energy.) An increase in the oxidation state on the metal would indeed favor one mechanism over the other. How is each step of each mechanism (A and D) affected by increasing the oxidation state?

4. CFSE Considerations. Another way to look at the electronic environment and how the rate is affected is to focus on the d-electron configurations and the CFSE for each reactant and intermediate. For example, octahedral Cr^{+3} complexes are known to be slow to undergo substitution reactions. We know the CFSE for Cr^{+3} (d^3) is $-1.2D_o$, which is relatively large. This is the value we need to compare to the CFSE for the 5-coordinate square pyramid intermediate and then again to a 7-coordinate intermediate. The table given on Day 17, page 8 ("The Energy Levels of *d* Orbitals in Crystal Fields of Different Symmetries") allows one to make these calculations. All of the common geometries are included in the table and all the values have been reported in units of Δ_o.

a. Calculate the CFSE for d^3 in a square pyramidal geometry. Is this more or less stable than it was for the octahedron?

b. Repeat the calculation for d^3 in a 7-coordinate geometry. (Note: although only the pentagonal bipyramid is listed, the other 7-coordinate geometries are not much different.) Is this more or less stable than it was for the octahedron?

c. This provides some evidence for why octahedral d^3 complexes are kinetically slow to react when compared with other d-configurations. Always keep in mind, there are greater forces at work here, too, including those listed earlier.

Now repeat the CFSE calculations for d^4, a configuration known to be kinetically fast with respect to ligand substitution:

Octahedral d^4	square pyramidal d^4	pentagonal bipyramidal d^4

5. Octahedral complexes with the configuration d^3 are kinetically slow to substitute and is thus called ***inert*** or ***kinetically inert***. The opposite of inert is ***labile***. These are kinetic terms. Do not confuse them with the thermodynamic terms ***stable*** and ***unstable***. What do these terms mean? Use ΔH, etc in your explanation.

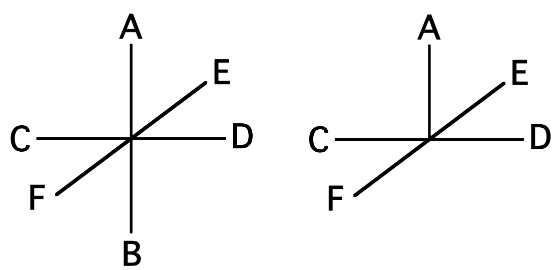
6. Associative routes are less common than dissociative routes for octahedral complexes, but that is not generally true with smaller coordination numbers. Propose a mechanism whereby coordinated water molecules exchange in $Cu(H_2O)_5^{+2}$(aq). For clarity, label the water molecules “A,” “B,” etc.

7. A third mechanism, something akin to the S_{N2} mechanism of organic chemistry is the interchange mechanism, I. The I mechanism covers a gamut between A and D. I mechanisms can be more A than D or more D than A in character. These are dubbed I_a and I_d, respectively.

D. Stereochemistry of Reactions

Dissociative mechanisms lead to five-coordinate complexes which can maintain a square pyramid geometry in the intermediate form (and frequently does so if the incoming ligand enters quickly or the intermediate can be stabilized by the solvent (water is a good ligand – and other solvents, such as acetonitrile, or anything with a Lewis base pair of electrons that are available – even the lone pair on chlorine in methylene chloride, for example. By numbers alone, there are plenty of solvent “ligands” always nearby.) Nonetheless, in some cases no ligand enters the coordination sphere and the five-coordinate complex can rearrange via a trigonal bipyramid. If this occurs, loss of stereochemistry also occurs.

1. Consider the octahedral complex labeled as shown at left:



2. Suppose the “B” ligand leaves in the first step of a dissociative mechanism. If the square-pyramidal geometry is maintained until a new ligand comes in, the product will have the same stereochemistry as the reactant (C and D trans to each other, etc.). If, however, the site remains vacant for too long, Ligands C and D or Ligands E and F can bend downward to create a trigonal bipyramidal geometry. Sketch these two possibilities in the space above to the right of the other sketches.

3. The relationship between the square pyramid and the trigonal bipyramid is one of an equilibrium. Now draw the three possible ways in which each of the trigonal bipyramids that you drew above can return to the square pyramid:

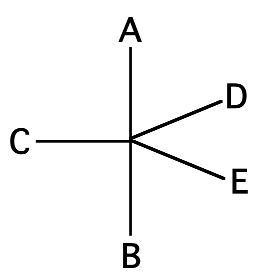
4. Would there be any advantage from a CFSE standpoint for either a d^3 or d^4 square pyramidal complex to shift and become a trigonal bipyramidal complex?

trigonal bipyramidal d^3	trigonal bipyramidal d^4
Comparison to square pyramidal:	Comparison to square pyramidal:

E. Pseudorotation in trigonal bipyramid complexes

Related to the above discussion, compounds that are known to be trigonal bipyramidal often undergo an exchange between axial and equatorial positions. One notices this in slow time-frame spectroscopic studies such as NMR (measuring things on the microsecond time frame). For example, the F-19 NMR (works just like proton) of a trigonal bipyramidal MF_5 complex would show only one type of F at normal temperatures, but two types (axial and equatorial) at very low temperatures.

1. Starting with the assigned trigonal bipyramid shown here, sketch the three square pyramidal complexes in which this structure is in equilibrium.



2. Now each of these three square pyramidal geometries can revert back to the trigonal bipyramid in two different ways. Show them here.

This distribution of products represents just one cycle of trigonal bipyramidal-to-square planar-to-trigonal bipyramidal. Looking over all six resulting products, what fraction of the ligand locations in the products are axial or equatorial?

	A	B	C	D	E
Axial					
Equatorial					
Total	1	1	1	1	1

If the fraction in axial positions for all five ligands is 2/5 and equatorial is 3/5, then only this one cycle is necessary to completely average the five positions. Is this the case?

If it is not, how many cycles would be necessary to get the job done? Hint: you may want to think in terms of the least common multiple.

F. The Chelate Effect.

1. The chelate effect is easy to understand in terms of entropy. For example, consider the two similar substitution reactions in aqueous solution:

$Cu(H_2O)_6^{+2} + 2\ NH_3 \rightarrow Cu(H_2O)_4(NH_3)_2^{+2} + 2\ H_2O$ $\Delta H = -46$ kJ/mol $\Delta S = -8.4$ J/mol K

$Cu(H_2O)_6^{+2} + en \rightarrow Cu(H_2O)_4(en)^{+2} + 2\ H_2O$ $\Delta H = -54$ kJ/mol $\Delta S = +23$ J/mol K

Predict the signs for ΔH and ΔS for these reactions:

$Cu(NH_3)_6^{+2} + en \rightarrow Cu(NH_3)_4(en)^{+2} + 2\ H_2O$ ΔH = ΔS =

$Cu(NH_3)_6^{+2} + 3\ en \rightarrow Cu(en)_3^{+2} + 6\ H_2O$ ΔH = ΔS =

$Cu(en)_3^{+2} + 2\ dien^* \rightarrow Cu(dien)_2^{+2} + 3\ en$ ΔH = ΔS =

*Recall dien is $NH_2CH_2CH_2NHCH_2CH_2NH_2$

2. Another aspect of a chelate ligand's ability to form stable compounds can be seen when we think of trying to substitute a bidentate ligand with two monodentate ligands. When one leg of a chelate

dissociates, the other end still holds the chelate in the neighborhood and significantly increases the chances that the loose end with re-associate. Sketch this "drama and action" here:

G. The Trans Effect (Substitution Reactions of Square Planar Complexes).

Substitution reactions for square planar complexes follow associative pathways. The ligands strongly influence which ligand will leave during the dissociation part of the mechanism (the downhill part of the reaction profile). The trans effect is a story of greed and cunning. Any particular ligand shares most of its overlap with the metal's orbital with the ligand trans to it. This is true for p- and d-orbitals and is quite easy to see with the p-orbitals. A ligand shares p-orbital overlap with the ligand across from it but none with the ligands cis to it. The d-orbitals are similar — and we are mostly concerned with the e_g orbitals as the t_{2g} are non-bonding as we have seen (unless we have pi-back bonding). If a ligand is forming a strong bond with the metal, the result is that the ligand trans to the strongly bonded ligand has its bonding to the metal weakened. The weakened metal-ligand bond is more likely to undergo substitution reactions.

There is a series of ligand tough guys called the trans-director series. It includes, in part:

$$CN^- > I^- > Br^- > Cl^- > NH_3 > py > OH^- > H_2O$$

Most of this chemistry has been done on square planar Pt^{+2} complexes. Complete the reactions, sketching out the complexes as you go:

$Pt(NH_3)_4^{+2} + Cl^- \rightarrow$ [A] and then: $[A] + Cl^- \rightarrow$

$PtCl_4^{-2} + NH_3 \rightarrow$ [B] and then: $[B] + NH_3 \rightarrow$

Review for the ACS final exam

1. Which species is most likely to add a ligand (increasing its coordination number by one) to its coordination sphere?
   (a) $[Ni(P(C_2H_5)_3)_4]SO_4$
   (b) $[Cr(H_2O)_6]SO_4$
   (c) $(NH_4)_2[ZnCl_4]$
   (d) $K_3[Fe(CN)_6]$
   (e) $[Fe(NH_3)_5]^{+2}$

2. The complex L-M(dppe)$_3]^{+n}$ forms a racemic mixture with the D enantiomer when warmed gently. Which of these is the most plausible explanation?
   (a) One dppe ligand completely dissociates and then reattaches in a random arrangement.
   (b) One or more d-electrons become excited and lead to loss of chirality.
   (c) Two dppe ligands simultaneously partially dissociates and then reattach in the opposite configuration.
   (d) The complex goes through a trigonal prismatic intermediate by rotation along the C_3 axis.
   (e) None of these.

3. Given the *trans*-director series, predict the product of these reaction of $Pt(Cl)_3(I)^{-2}$ with two equivalents of NH_3.

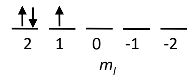
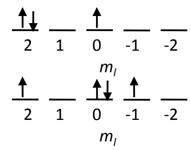
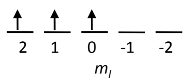
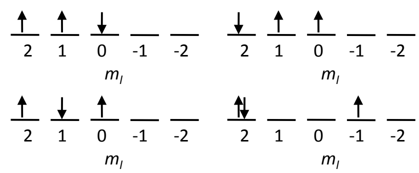
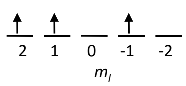
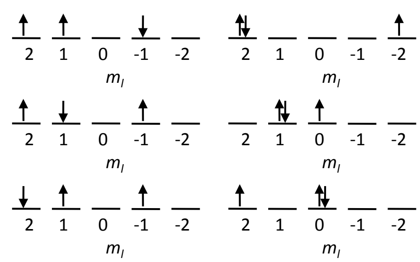
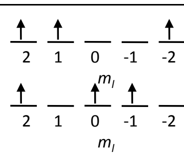
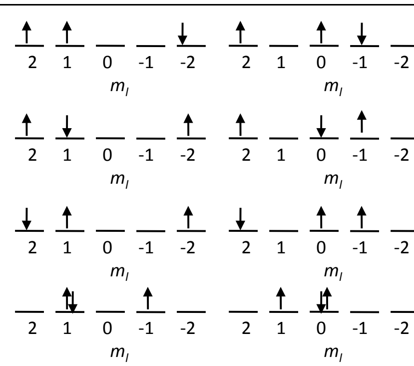
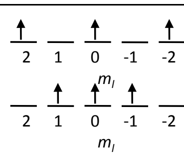
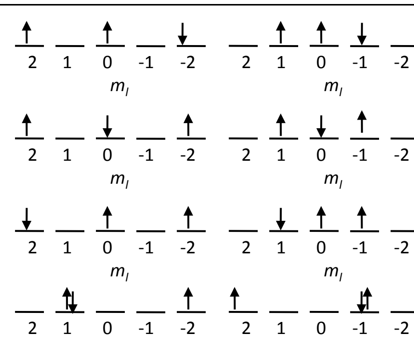
   trans series: $I^- > Br^- > Cl^- > NH_3 > H_2O$

   (a) *cis*-$Pt(NH_3)_2(I)(Cl)$
   (b) *trans*-$Pt(NH_3)_2(I)(Cl)$
   (c) *cis*-$Pt(NH_3)_2(Cl)_2$
   (d) *trans*-$Pt(NH_3)_2(Cl)_2$
   (e) *trans* -$Pt(NH_3)(I)(Cl)_2$

Answers: E, D, A

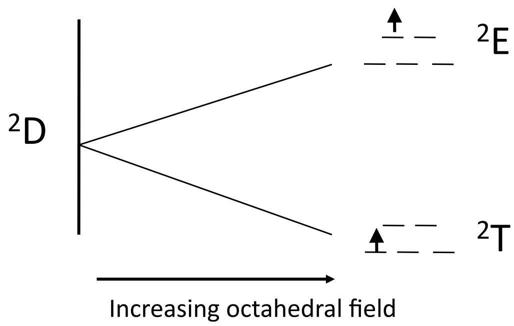
Answers to Day 20.

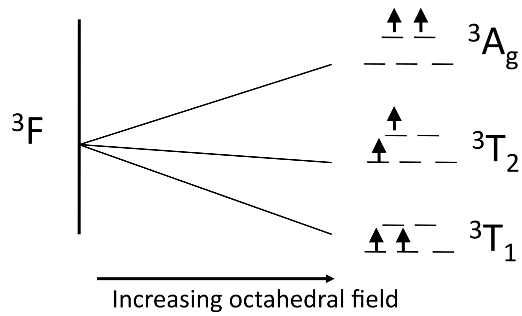
1. Use the method of microstates to determine the term symbols for d^3.

	M_S	
M_L	**+3/2**	**+1/2**
5	none	
4	none	
3		
2		
1		
0		

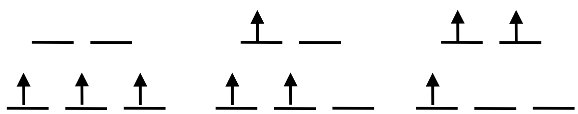
2. Term symbols for the d^3 free ion. ^4F, ^4P, ^2H, ^2F, two doublet ^2D and two doublet ^2P

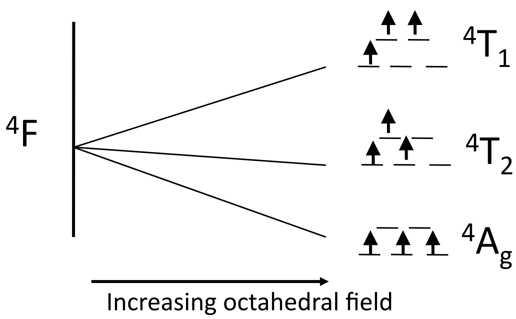
3. Review from previous worksheet: the d^1 and d^2 ions in an octahedral field.





4. The d^3 ion in an octahedral field.





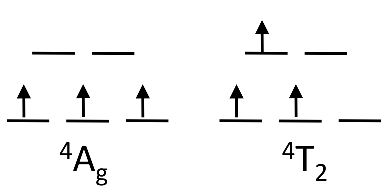
Estimate values for the three spin-allowed transitions expected and the first one corresponds to Δ_o:

$^4A \rightarrow {}^4T_2$ ω_1 = 17000 cm^{-1} or about 590 nm = Δ_o

$^4A \rightarrow {}^4T_1(F)$ ω_2 = 24000 cm^{-1}

$^4A \rightarrow {}^4T_1(P)$ ω_3 = cannot estimate

5. The transition $^4T_2 \rightarrow {}^4T_1(F)$ also represents Δ_o:



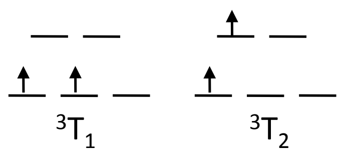
6. Use Jorgenson's relationship to estimate Δ_o.= 17.4 x 1.00 x 1000 cm^{-1} = 17400 cm^{-1}

7. $\Delta_o = \omega_1$

8. 17400 cm^{-1} corresponds to λ = 575 nm, so it absorbs in the orange and should appear blue-green.

B. Back to d^2 complexes.

(a) Why is Δ_o equal to $^3T_2(F) \rightarrow {}^3A_2$? Use microstates (like you did on previous page for d^3)



(b) Complete the transitions below by inspecting the Tanabe-Sugano diagram:

ω_1 = 17,800 cm^{-1} $\quad$ $^3T_1(F) \rightarrow {}^3T_2(F)$

ω_2 = 25,700 cm^{-1} $\quad$ $^3T_1(F) \rightarrow {}^3A_g(F)$ $\quad$ or $\quad$ $^3T_1(F) \rightarrow {}^3T_1(P)$

ω_3 = 38,000 cm^{-1} $\quad$ $^3T_1(F) \rightarrow {}^3T_1(P)$ $\quad$ or $\quad$ $^3T_1(F) \rightarrow {}^3A_g(F)$

2. Yes, there is more than one possibility: $\Delta_o = \omega_2 - \omega_1$ = 25,700 - 17,800 cm^{-1}= 7,900 cm^{-1} or

$\Delta_o = \omega_3 - \omega_1$ = 38,000 - 17,800 cm^{-1}= 20,200 cm^{-1}

C. Other d-configurations.

1. Determine the ground state free ion term symbols for $d^1 - d^{10}$:

	Ground State Term:
d^1	^2D
d^2	^3F
d^3	^4F
d^4	^5D
d^5	^6S

	Ground State Term:
d^6	^5D
d^7	^4F
d^8	^3F
d^9	^2D
d^{10}	^1S

2. $d^1 = d^9$, $d^2 = d^8$, $d^3 = d^7$, and $d^4 = d^6$.

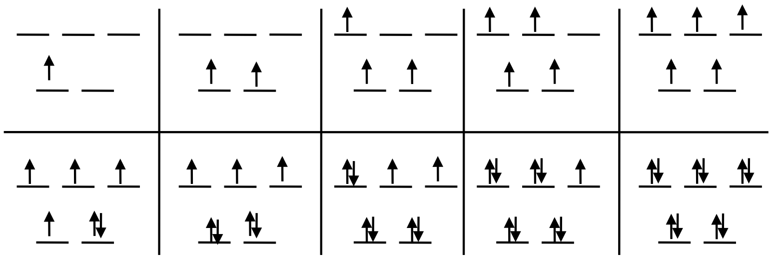
3.

	Ground state	First excited state	Second excited state	Comments:
d^1	^2T	^2E	N/A	
d^2	^3T	^3T	^3A	
d^3	^4A	^4T	^4T	
d^4	^5E	^5T	NA	
d^5	^6A	N/A	N/A	
d^6	^5T	^5E	N/A	Same as d^1
d^7	^4T	^4T	^4A	Same as d^2
d^8	^3A	^3T	^3T	Same as d^3
d^9	^2E	^2E	N/A	Same as d^4
d^{10}	^1A	N/A	N/A	Same as d^5

4.

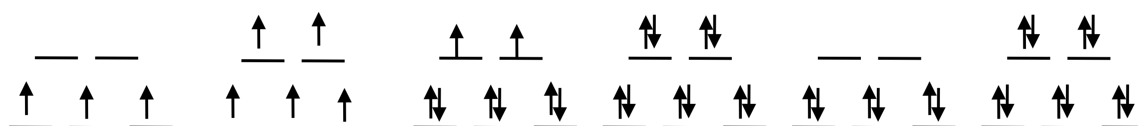
Oct d^1 and d^6	Oct d^2 and d^7	Oct d^3 and d^8	Oct d^4 and d^9	Oct d^5 and d^{10}
Tetr d^4 and d^9	Tetr d^3 and d^8	Tetr d^2 and d^7	Tetr d^1 and d^6	Tetr d^5 and d^{10}

D. Tetrahedral complexes

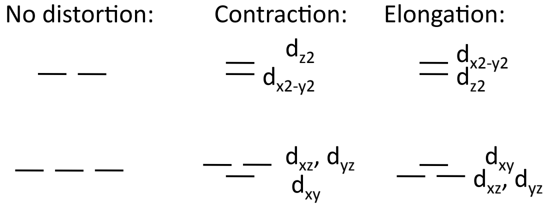


F. Jahn-Teller distortion.

1.



2.



No distortion: d^0, d^3, d^5(hs), d^6(ls), d^8, d^{10}

Contraction: d^1, d^4(ls), d^6(hs), d^9

Elongation: d^2, d^5(ls), d^7(hs)

Elongation or contraction: d^4(hs), d^7(ls)

G. Charge Transfer. One example of L→M CT: