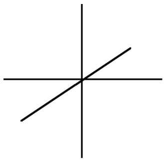
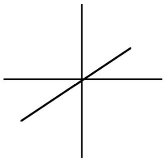
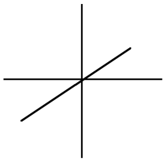
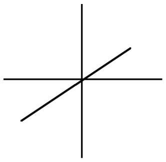
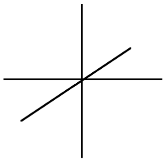
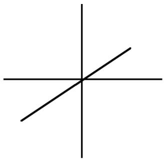
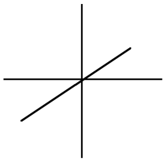
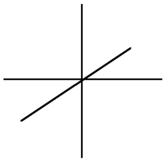
Inorganic Exam 3 **Name:**
Chm 451
1 December 2009

Instructions. Always show your work for full credit.

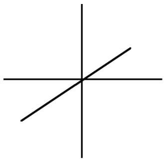
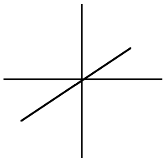
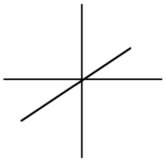
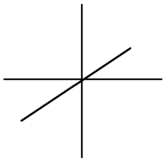
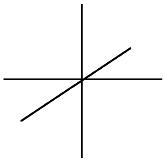
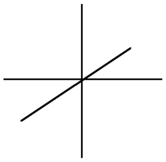
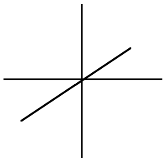
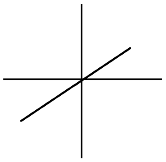
Chapter 9. Structures and Isomers

1a. (6 pts) Sketch all possible isomers of Co$(NH_3)_2(H_2O)_2Cl_2$. You may use A, B, and C to represent the ligands if you wish. I have provide more axes than you will actually need. (You may use models: The easiest way to make a model of an octahedron is to use toothpicks (labeled) and something to stick them in as a central metal. You might use a grape or a chunk of potato or a marshmallow.)

1b. (2 pts) Two of the isomers you drew above are enantiomeric. Circle them.

2. (5 pts) Sketch all possible isomers of Re(*dien*)Br_2Cl. *Dien* is the tridentate ligand $NH_2CH_2CH_2NHCH_2CH_2NH_2$. On your structures, sketch the dien as:  Again, I have provide more axes than you will actually need.

3. (6 pts) What is the oxidation state, coordination number and d-electron configuration of the metal ion in each of these compounds? Note: *en* = $NH_2CH_2CH_2NH_2$

	$[Cu(NH_3)_4]SO_4$	$K_4[Mn(CN)_6]$	$Cr(H_2O)_3BrClI$	$[Co(en)_2(CN)_2]NO_3$
Oxid. State:				
Coord. Number:				
d-electron config				

Chapter 10. Bonding

4. (5 pts) Only one member of each pair actually is known. Circle your choice for the most likely to exist.

a. $[Ti(NH_3)_4]^{+2}$ or $[Zn(NH_3)_4]^{+2}$

b. low spin $FeCl_6^{-3}$ or low spin $RuCl_6^{-3}$

c. diamagnetic $Co(CN)_6^{-3}$ or paramagnetic $Co(CN)_6^{-3}$

d. $[Ni(NH_3)_6]^{+2}$ or $[Ni(PPh_3)_6]^{+2}$ Ph = phenyl, C_6H_5-

e. square planar $[Pd(NH_3)_4]^{+2}$ or square planar $[Cu(NH_3)_4]^{+2}$

5. (5 pts) Predict the number of unpaired electrons in each of the following situations:

a tetrahedral d^6 ion	
an octahedral low-spin d^6 ion	
an octahedral high-spin d^6 ion	
$[Co(H_2O)_6](ClO_4)_2$	
$K_3[Fe(CN)_6]$	

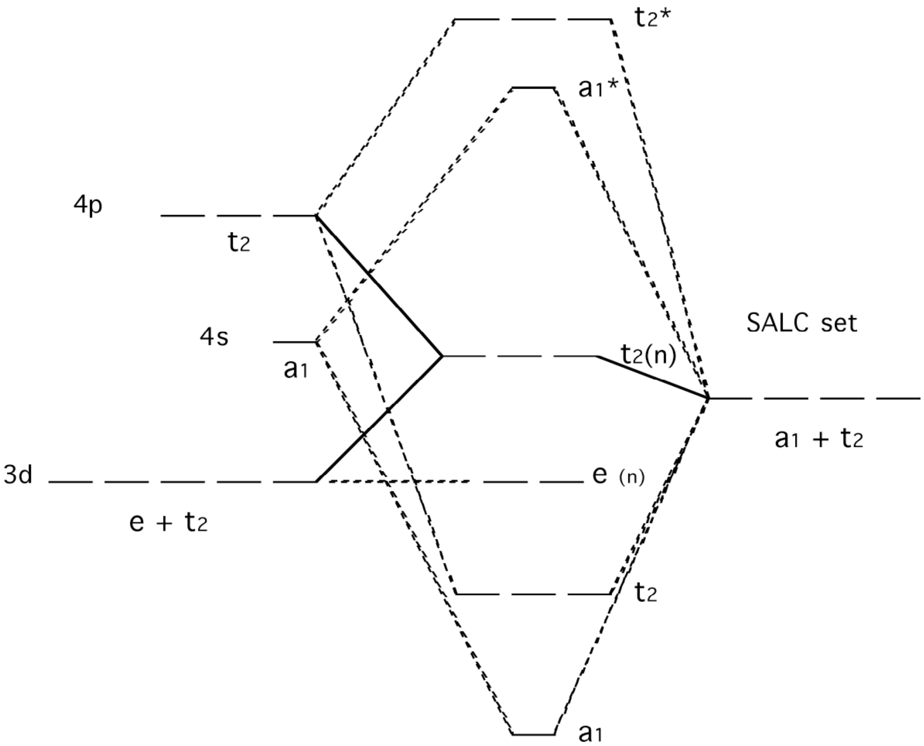
6a. (5 pts) Predict the crystal field splitting pattern for a square planar compound. Label the orbitals.

6b. (2 pts) Populate the above diagram for $[Pt(NH_3)_4]SO_4$, given that the compound is diamagnetic.

7. (5 pts) Sketch the crystal field splitting pattern for a metal ion in an octahedral field. Label Δ_{oct}. Populate the diagram for high-spin d^4. Repeat with another drawing of the splitting pattern, but alter Δ_{oct} so that one would predict low-spin. Populate the diagram for d^4, low-spin.

8. The T_d character table and MO diagram for σ-only bonding for a tetrahedral complex such as $FeCl_4^-$ are both given below. Answer the questions that follow about this MO diagram.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(x^2 - y^2, z^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xz, yz, xy)



8a. (2 pts) Populate the MO diagram for the complex $FeCl_4^-$.

8b. (2 pts) Draw a box around the region that corresponds to the splitting predicted by crystal field theory.

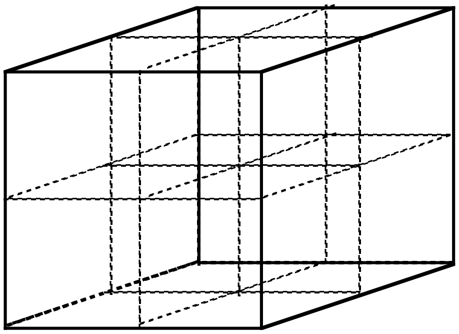
8c. (2 pts) How many unpaired electrons are there in the complex?

8d. (2 pts) Why are there three sets of triply degenerate t_2 molecular orbitals?

8e. (2 pts) Add the label Δ_t.

8f. (2 pts) What are the non-bonding orbitals labeled 'e (n)'?

8g. (2 pts) Recall that a tetrahedron can be represented as alternating corners of a cube. Use the template below, sketch the a_1 bonding molecular orbital.

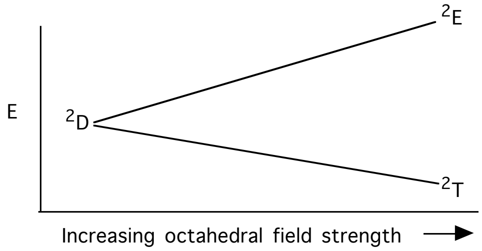


Chapter 11. Electronic Spectra

8h. (2 pts) Are d-d electronic transitions spin-allowed for tetrahedral $FeCl_4^-$?

8i. (2 pts) What is the ground state free ion (no tetrahedral field) term symbol for Fe^{+3}?

9. (4 pts) Another complex ion similar to $FeCl_4^-$ is $FeCl_4^{-2}$. The sketch below is for a d^1 configuration split in an octahedral field. Create a similar diagram for the d-electrons in $FeCl_4^{-2}$, including a sketch of a typical microstate for each of the situations.



10. The familiar purple permanganate ion, MnO_4^- is an example of a tetrahedral complex ion. It is easily reduced to MnO_4^{-2}, which is also tetrahedral.

10a. (3 pts) The complex MnO_4^{-2} is d^1 tetrahedral. The Tanabe-Sugano The Tanabe-Sugano diagram for d^1 is not given at the end of the exam. What would you expect it to look like? Sketch it here.

10b. (3 pts) How many absorbance bands would you expect to see?

10c. (2 pts) The complex MnO_4^{-2} is a very pretty green. Given that there is only one absorbance band in the visible region, what is the approximate wavelength of the absorbance band?

Circle one: 400 nm 500 nm 600 nm 700 nm

11. In class we learned that some d configurations give rise to three spin-allowed d-d transitions. The octahedral d^3 complex is an example of such a configuration. In the case of d^3, the spectrum is fairly easy to interpret, because one of the bands corresponds directly to Δ_o.

11a. (3 pts) Suppose an octahedral Mo^{+3} complex exhibits three bands at 12000 cm^{-1}, 17500 cm^{-1}, and 28000 cm^{-1}. Which of these is Δ_o?

11b. (2 pts) What is the transition that corresponds to υ_1? Format of answer must be like: $^2E \rightarrow {}^2D$

11c. (2 pts) What makes obtaining Δ_o for an octahedral d^2 complex more difficult that doing so for a d^3 complex?

11d. (2 pts) What other octahedral high spin d-configuration would be similar to d^3 in terms of having three absorbance bands, one of which is directly related to Δ_o.

12. (2 pts) How many spin-allowed d-d absorbance bands are expected for an octahedral high-spin d^7 complex?

13. (3 pts) Jahn-Teller distortions are not expected for all d electron configurations. Which of these configurations, all in octahedral crystal fields, would not be expected to exhibit a Jahn-Teller distortion? Circle all that apply.

d^0 d^1 d^2 d^3 d^4 hs d^4 ls d^5 hs d^5 ls

d^6 hs d^6 ls d^7 hs d^7 ls d^8 d^9 d^{10}

Chapter 12. Reactions and mechanisms

14. Octahedral Cr^{+2} complexes are d^4 and can be either high-spin or low-spin. The complex $[Cr(H_2O)_6]^{+2}$ is high-spin and readily undergoes substitution. Low-spin $[Cr(CN)_6]^{-4}$ is inert to substitution.

a. (4 pts) Determine the CFSE for both complexes (you can ignore the pairing energy)

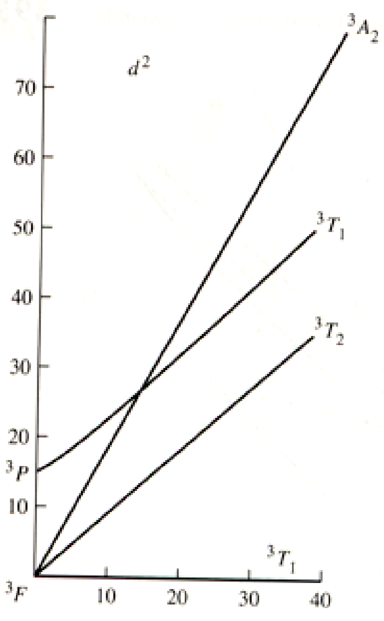
b. (3 pts) Why is the low-spin complex kinetically slow to substitute, while ligand substitution for the high-spin complex is kinetically fast?

15. The neutral complex *fac*-$Co(NH_3)_3(Cl)_3$ undergoes substitution with cyanide to yield $Co(NH_3)_3(Cl)_2CN$. The reaction proceeds by a dissociative mechanism.

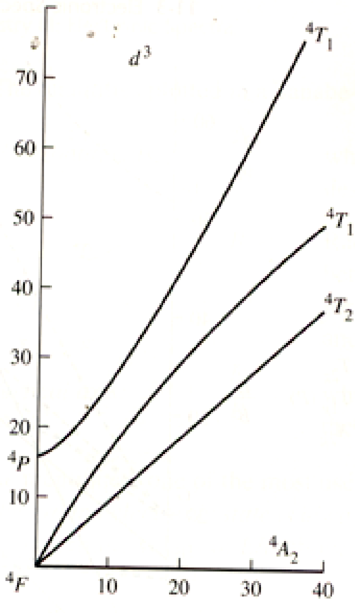
a. (2 pts) Write the two steps of the reaction mechanism.

b. (3 pts) After the first step, ligand scrambling is a possibility. What sort of products would we expect to find if ligand scrambling is faster (or slower) than the addition of cyanide?

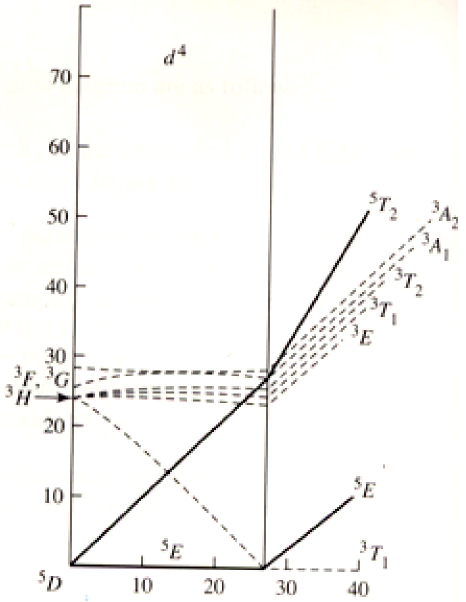
c. (3 pts) Ligand exchange (substitution) is also possible in square planar complexes. The trans series which in part is $CN^- > Cl^- > NH_3$, Starting with cis-$Pt(NH_3)_2(Cl)_2$, what product is expected if we added one equivalent of cyanide? Be specific — designate *cis* or *trans* and the product — or sketch the structure. What product is expected if we added a second equivalent of cyanide? Again, be specific.



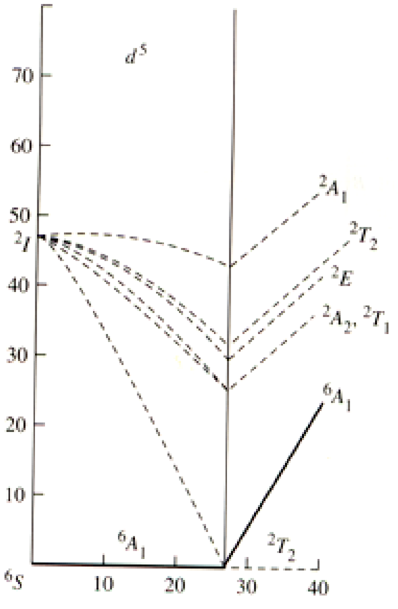
d^2
$^3A_2$
$^3T_1$
$^3T_2$
^3P
^3F
$^3T_1$
70
60
50
40
30
20
10
10
20
30
40



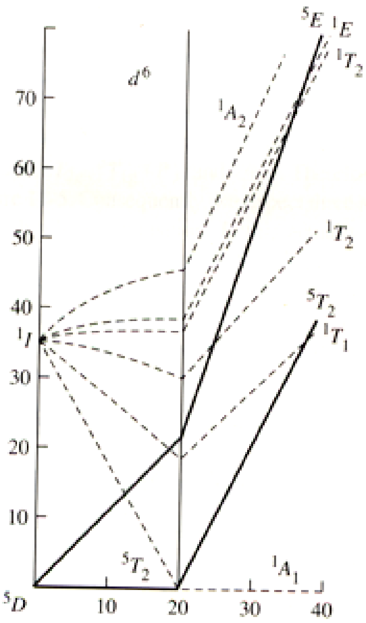
d^3
$^4T_1$
$^4T_1$
$^4T_2$
^4P
^4F
$^4A_2$
70
60
50
40
30
20
10
10
20
30
40



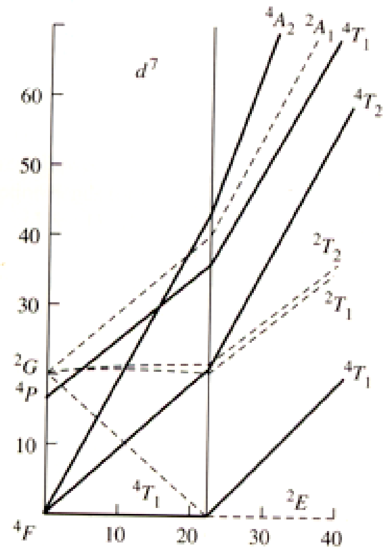
d^4
$^5T_2$
$^3A_2$
$^3A_1$
$^3T_2$
$^3T_1$
^3E
^3F, ^3G
^3H
^5E
^5E
$^3T_1$
^5D
70
60
50
40
30
20
10
10
20
30
40



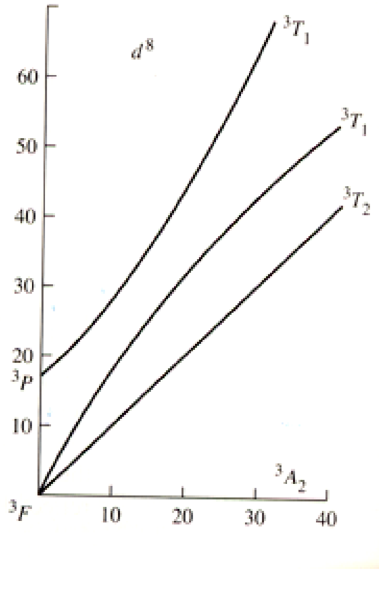
d^5
$^2A_1$
$^2T_2$
^2E
$^2A_2$, $^2T_1$
$^6A_1$
^2I
$^6A_1$
$^2T_2$
^6S
70
60
50
40
30
20
10
10
20
30
40



d^6
^5E
^1E
$^1T_2$
$^1A_2$
$^1T_2$
$^5T_2$
$^1T_1$
^1I
$^5T_2$
$^1A_1$
^5D
70
60
50
40
30
20
10
10
20
30
40



d^7
$^4A_2$
$^2A_1$
$^4T_1$
$^4T_2$
$^2T_2$
$^2T_1$
^2G
^4P
$^4T_1$
$^4T_1$
^2E
^4F
60
50
40
30
20
10
10
20
30
40



d^8
$^3T_1$
$^3T_1$
$^3T_2$
^3P
$^3A_2$
^3F
60
50
40
30
20
10
10
20
30
40

Answers

Chapter 9. Structures and Isomers

1a. There are six of them.
One is where the As are trans, Bs are trans and Cs are trans.
There are three similar ones:
one has the As are trans and the Bs and Cs are cis;
one has the Bs are trans and the As and Cs are cis;
and one has the Cs are trans and the As and Bs are cis.
The fifth one has all three types of ligands cis. (As cis, Bs cis and Cs cis). This last one is chiral.

1b. Two of the isomers you drew above are enantiomeric. Circle them.

2. There are actually six of them that are theoretically possible. (Recall our test to eliminate candidates for chirality: If there is an internal mirror plane or rotation axis (such as a C_2), it is not chiral.)

The dien theoretically can take the *fac* or *mer* positions. Starting with the *mer*:
The middle nitrogen can be *trans* to a Cl.
The middle nitrogen can be *trans* to a Br. (This arrangement is chiral due to the hydrogen on the middle nitrogen (looking down the middle N-to-Co-to-Br bond, the hydrogen on N can be directed on the same "side" as the other Br or on the same side as Cl.)

Dien in a fac arrangement:
The middle nitrogen can be trans to a Cl.
The middle nitrogen can be trans to a Br. This one is chiral.

3.

	$[Cu(NH_3)_4]SO_4$	$K_4[Mn(CN)_6]$	$Cr(H_2O)_3BrClI$	$[Co(\textit{en})_2(CN)_2]NO_3$
Oxid. State:	+2	+2	+3	+3
Coord. Number:	4	6	6	6
d-electron config	d^9	d^5	d^3	d^6

Chapter 10. Bonding

4.

a. $[Zn(NH_3)_4]^{+2}$

b. low spin $RuCl_6^{-3}$

c. diamagnetic $Co(CN)_6^{-3}$

d. $[Ni(NH_3)_6]^{+2}$

e. square planar $[Pd(NH_3)_4]^{+2}$

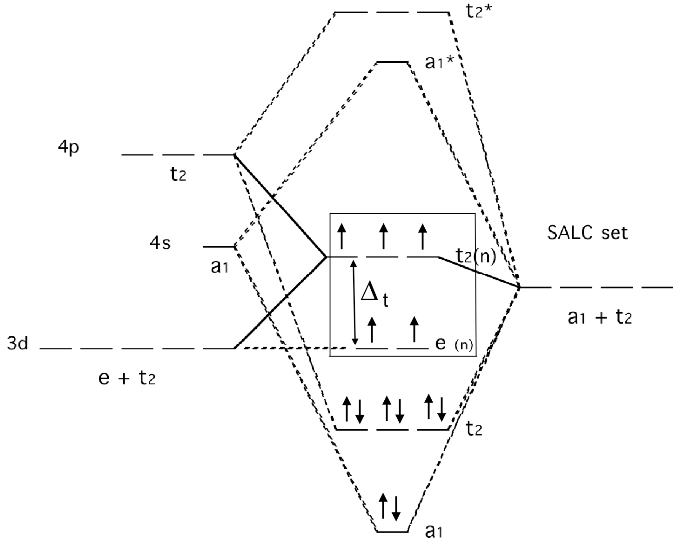
5. 4 upe, 0 upe, 4 upe, 3 upe, 1 upe

6a. I was looking for you to conclude that $d_{x^2-y^2}$ was the highest in energy. Next I was looking for you to conclude that d_{xz} and d_{yz} are degenerate in energy. The other two orbitals are not degenerate by inspection. (One interesting way to think about the square plane is to start with a John-Teller distortion (elongation) and then just keep going. In the limit that the z-axis ligands are removed and you have a square plane.)

6b. Given that the compound is diamagnetic, all orbitals except the $d_{x^2-y^2}$ are filled.

7. I was looking for the familiar octahedral t_{2g} and e_g orbitals. There should be one electron in each of the t_{2g} orbitals and one in the e_g orbitals. I looked for Δ_{oct} to be labeled. For the low-spin configuration, I was looking for a convincingly larger Δ_{oct}. The four electrons would all be in the t_{2g} orbitals.

8.



8a and b. See diagram above

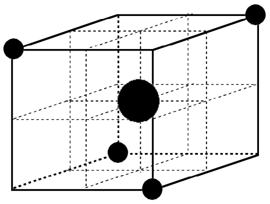
8c. five (tetrahedral complexes are always high spin due to the relatively small Δ_t)

8d. There are three sets of triply degenerate t_2 molecular orbitals: they are d_{xz}, d_{yz}, and d_{xy}.

8e. See diagram above.

8f. $d_{x^2-y^2}$ and d_{z^2}

8g.

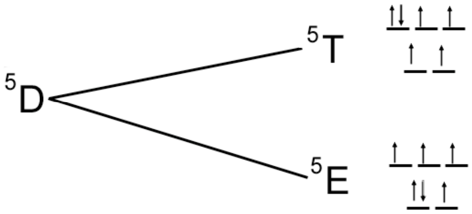


Chapter 11. Electronic Spectra

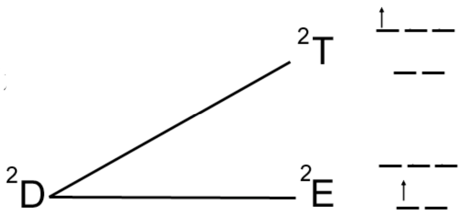
8h. No

8i. ^6S

9.



10a.



10b. one (also shoulder due to JT)

10c. 700 nm

11a. 12000 cm^{-1}

11b. $^4A \rightarrow {}^4T_2$

11c. None of the absorbances directly give Δ_o due to "mixing" between $T_1(F)$ and $T_1(P)$ states. The ground state is $T_1(F)$ which is distorted due to the mixing and cannot be used to determine Δ_o. We can use $^4T_1 \rightarrow {}^4A$ minus $^4T_1 \rightarrow {}^4T_2$ in order to calculate Δ_o. This corresponds to either $\upsilon_2 - \upsilon_1$ or $\upsilon_3 - \upsilon_1$, depending on the relative position of $^4T_1$ (P) and ^4A.

11d. d^8

12. three as per Tanabe-Sugano diagram

13. d^0 d^3 d^5 hs d^6 ls d^8 d^{10}

Chapter 12. Reactions and mechanisms

14a. d^4 high-spin: CFSE = $0.6\ \Delta_o$; d^4 low-spin: CFSE = $1.6\ \Delta_o$

b. The low-spin complex is lower in energy than the high-spin complex due to the CFSE calculated above. That means that E_{act} is larger for the low-spin complex making it kinetically slower than the high-spin complex.

15a. Step 1. *fac*-$Co(NH_3)_3(Cl)_3 \rightarrow$ *fac*-$Co(NH_3)_3(Cl)_2^+ + Cl^-$

Step 2. *fac*-$Co(NH_3)_3(Cl)_2^+ + CN^- \rightarrow$ *fac*-$Co(NH_3)_3(Cl)_2CN$

b. If no scrambling takes place, one isomer is expected for a product. If the intermediate, *fac*-$Co(NH_3)_3(Cl)_2^+$, rearranges before Step 2 can take place, more than one product, all isomers of $Co(NH_3)_3(Cl)_2CN$ is expected.

c. *cis*-$Pt(NH_3)(CN)(Cl)_2$, *trans*-$Pt(NH_3)(Cl)(CN)_2$,