

TRANSITION METALS (The d Group Elements)

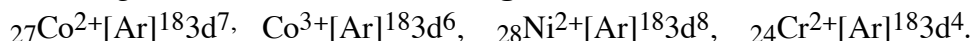
I. General.

A. Electronic Structure and Oxidation States.

1. Elements in groups 3 through 12.

a. <u>Group</u>	<u>1st Row Configuration</u>	<u>Valence Configuration</u>
3	$21\text{Sc}[\text{Ar}]183d^14s^2$	d^1s^2
4	$22\text{Ti}[\text{Ar}]183d^24s^2$	d^2s^2
5	$23\text{V}[\text{Ar}]183d^34s^2$	d^3s^2
6	$24\text{Cr}[\text{Ar}]183d^54s^1$	d^5s^1
7	$25\text{Mn}[\text{Ar}]183d^54s^2$	d^5s^2
8	$26\text{Fe}[\text{Ar}]183d^64s^2$	d^6s^2
9	$27\text{Co}[\text{Ar}]183d^74s^2$	d^7s^2
10	$28\text{Ni}[\text{Ar}]183d^84s^2$	d^8s^2
11	$29\text{Cu}[\text{Ar}]183d^{10}4s^1$	$d^{10}s^1$
12	$30\text{Zn}[\text{Ar}]183d^{10}4s^2$	$d^{10}s^2$

b. In forming cations, **lose s² before losing d electrons.**



c. As more d electrons become involved in bonding, variable valences are found. (exceptions are the groups 3 and 12 metals)

2. Consider some compounds of iron.

<u>Compound</u>	<u>Ox. State</u>	<u>Compound</u>	<u>Ox. State</u>
$\text{Fe}(\text{CO})_4^{2-}$	-II	Common	+ II
$\text{Fe}(\text{bipy})_3^-$	-I	Common	+ III
$\text{Fe}(\text{CO})_5$	0	FeO_4^{4-}	+ IV
$[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$	+I	FeO_4^{3-}	+ V
(NO ⁺)		FeO_4^{2-}	+ VI

The oxidation state of Fe can vary from - 2 to +6 depending on the complex.

3. The oxidation states of the transition metals are functions of the complex in which the metal is involved. These complexes are called **coordination compounds**, the chemistry of the transition metals is the chemistry of coordination compounds.

B. Coordination Compounds.

1. Lewis acid - base adducts in which the transition metal atom or ion acts as a Lewis acid.

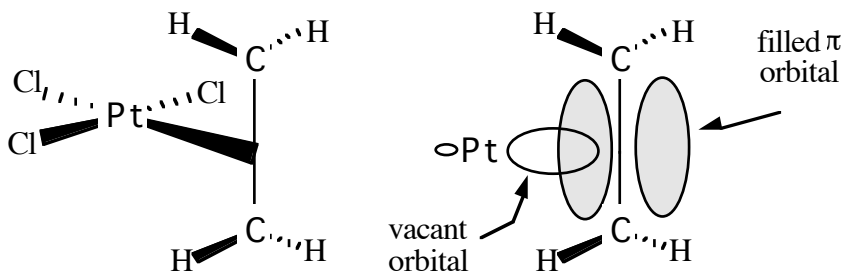
a. The Lewis bases are called **ligands**.

b. Most ligands are anions or neutral molecules. The only common cationic ligand is the nitrosyl group (NO⁺).

- c. **Coordination Number** = the number of σ bonds formed by the metal with the ligands.
2. In addition to σ bonds the metal and ligands can also participate in π bonding. There are two types of metal - ligand π bonding.
- a. π bonds formed by the overlap of filled ligand orbitals with vacant metal orbitals.
- 1) Ligands such as OH^- , O^{2-} and F^- can participate in forward π bonding.
 - 2) These should stabilize high oxidation state compounds. Note that the high oxidation states of Fe were found in the iron oxides.
- b. π bonds formed by the overlap of vacant ligand orbitals with filled metal orbitals. This type of π bonding is called **back π bonding**. Electron density transfer is in the opposite direction from that in σ bonding.
- 1) This is important in stabilizing low oxidation state complexes.
 - 2) Examples of ligands that can undergo back π bonding are: CO , NO^+ , PR_3 , olefins and polyolefins. Note in the table of Fe complexes the low oxidation state complexes were those with CO , NO^+ .

C. Ligands (Lewis bases)

1. Monodentate (most common).
- a. The Lewis base can form only one σ bond with a particular metal.
- b. In most cases the base site is a lone pair of electron in a hybridized orbital
 [NH_3 H_2O $\text{[C}\equiv\text{O]}$ Cl^- OH^- [PR_3 I^- F^- Br^-
- c. Olefins and polyolefins can use filled π molecular orbitals to form the primary σ bonds. Consider Zeise's salt $[\text{PtCl}_3\text{C}_2\text{H}_4]^-$. The structure has been determined and shows

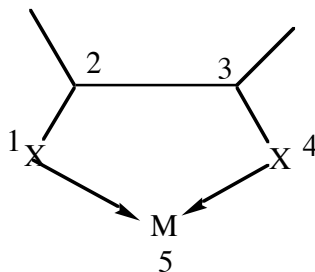


that the ethene molecule is perpendicular to the plane of the complex (see above). The coordinate covalent bond formed between the ethene and the metal is thought to arise from the overlap of a vacant metal orbital with the filled π olefin orbital.

2. Polydentates.
- a. Polyatomic molecules with several base sites; can form more than one σ bond with a particular metal.

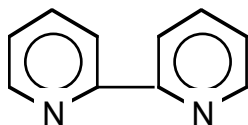
b. The majority of the polydentates have their base sites separated by two atoms so that they form five membered rings when coordinated to the metal.

1)

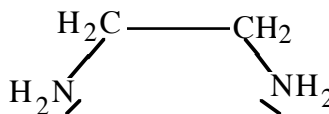


General form (X = base site)

2) Examples.

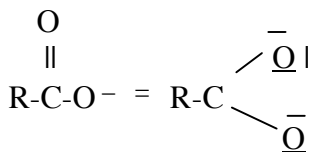
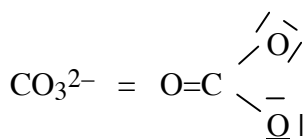


2,2'- bipyridine (bipy)



ethylene diamine (en)

c. Some form four membered rings. Examples are the oxyanions.



d. Note that six member and higher rings do not tend to form.

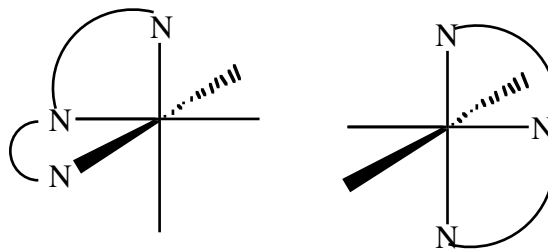
3. Classification of polydentates.

a. Bidentates. Form two σ bonds.

Examples: ethylene diamine; 2,2'- bipyridine, CO_3^{2-} .

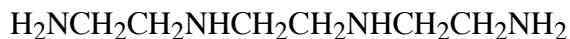
b. Tridentates. Form three σ bonds.

Example: $\text{H}_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ diethylene triamine (dien). This is a flexible ligand that can attach to give several geometries. Drawn below are two possible orientations of the ligand in an octahedral complex.



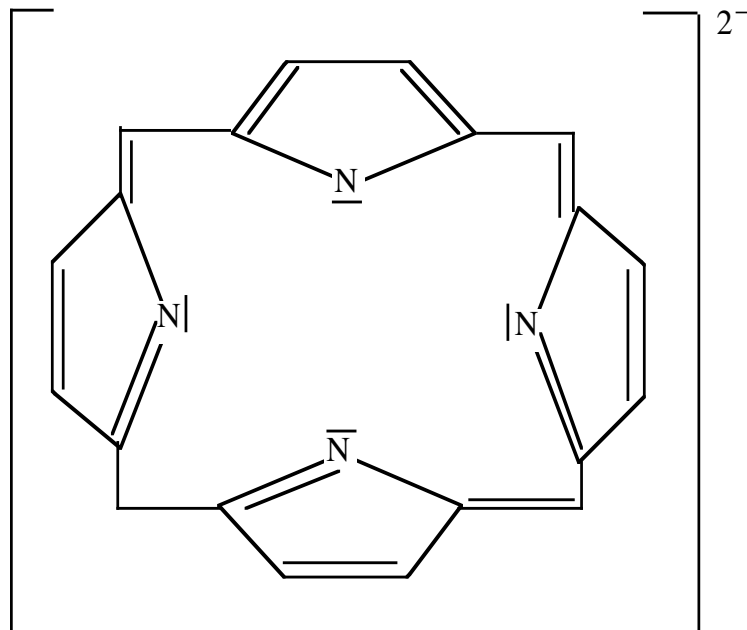
c. Tetradentates. Can form four σ bonds. Several general types.

1) Linear, flexible.



triethylene tetramine (trien)

2) Planar macrocyclic.



Porphyrin

The planar macrocyclic metalloporphyrin complexes are important biologically.

Examples: Hemoglobin, Cytochromes (Fe-porphyrins); Chlorophyll (Mg-porphyrin);

d. Can also have penta - and hexa - dentates. Most form series of five membered rings or are macrocyclic.

II. Nomenclature.

A. In any salt, name the cation first then the anion no matter which is complex.

B. Naming complex cations or neutral complexes.

1. Name the ligands first and indicate the number of times each ligand occurs.

a. Anionic Ligands.

1) If anion ends in **ide** drop the **ide** and add **o**.

Examples: Cl^- = chloro

Br^- = bromo

OH^- = hydroxo

I^- = iodo

CN^- = cyano

O^{2-} = oxo

2) Exception: NH_2^- = amido

3) If anion ends in **ate** or **ite**, drop the **e** and add **o**.

Examples: SO_4^{2-} = sulfato $\text{C}_2\text{O}_4^{2-}$ = oxolato
 SO_3^{2-} = sulfito NO_2^- = nitrito (if O bonded)
 CO_3^{2-} = carbonato NO_2^- = nitro (if N bonded)
 SCN^- = thiocyanato (if N bonded)
 SCN^- = isothiocyanato (if S bonded)

b. Neutral Ligands.

- 1) Use the name of the molecule without alteration.
- 2) Exceptions: H_2O = aquo CO = carbonyl
 NH_3 = ammine NO^+ = nitrosyl

c. Use prefixes to indicate the number of times a ligand occurs.

- 1) di = 2 tri = 3 tetra = 4 penta = 5 hexa = 6 etc.
- 2) For complex ligands that may have di- tri- etc. in their name, use the Greek prefixes and enclose the ligand name in parenthesis.
bis = 3 tris = 3 tetrakis = 4 pentakis = 5 etc.

d. Name ligands in alphabetical order.

2. After naming the ligands and indicating their numbers, give the name of the metal and write its oxidation state (charge) in Roman Numerals and enclosed in parenthesis.

B. Examples.

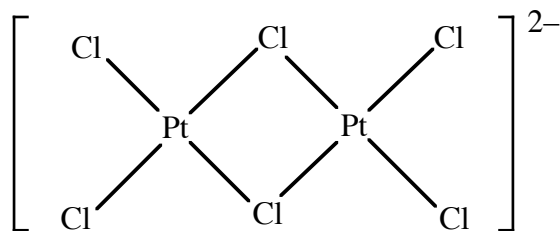
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ tetramminedichlorocobalt(III)
 $\text{Fe}(\text{CO})_5$ pentacarbonyliron(0)
 $[\text{Cr}(\text{en})_2\text{I}_2]^+$ bis(ethylenediamine)diiodochromium(III)
 $[\text{Pt}(\text{H}_2\text{O})_4](\text{NO}_3)_2$ tetraquoplatinum(II) nitrate

C. Anionic Complexes.

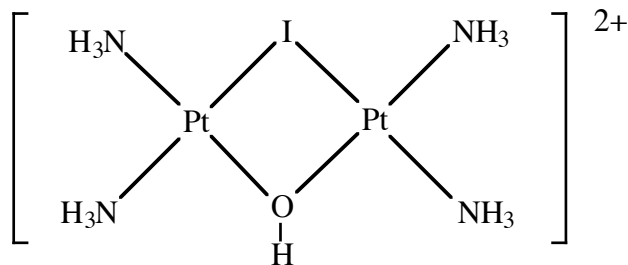
1. Name and number the ligands in the same way as for cationic complexes.
2. Drop the metallic ending of the metal (ium) and add **ate**.
3. Examples:
 $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ trioxolatoironate(III)
 $[\text{PtI}_4]^{2-}$ tetraiodoplatinate(II)
 $[\text{Co}(\text{CN})_5\text{OH}]^{3-}$ pentacyanohydroxocobaltate(III)

D. Bridged complexes.

1. Use μ (mu) to indicate a bridging group. μ should be repeated for each different bridging ligand.
2. Examples



dichloroplatinum(II)- μ -dichlorodichloroplatinate(II)



diammineplatinum(II)- μ -iodo- μ -hydroxo-diammineplatinum(II)

III. Isomerism in Coordination Compounds.

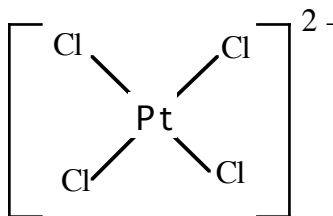
A. Coordination number = 4.

1. Tetrahedral complexes.

- Only isomerism possible is optical isomerism in complexes having four different ligands surrounding a metal.
- These are very difficult to resolve since most T_d complexes undergo very rapid ligand exchange (they are kinetically labile complexes).

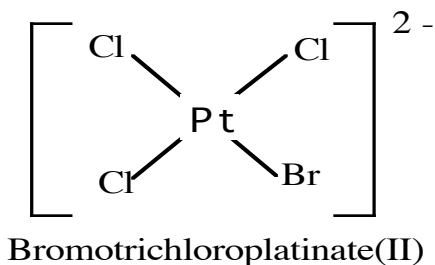
2. Square planar complexes.

- Consider $[\text{PtCl}_4]^{2-}$. This complex is square planar, all 4 Cl^- 's are equivalent. No isomers.



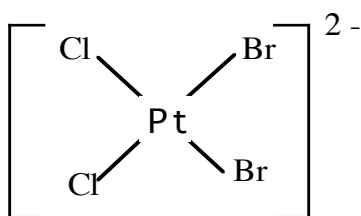
Tetrachloroplatinate(II)

- Consider $[\text{PtCl}_3\text{Br}]^{2-}$. Think of it being formed by replacing one Cl^- in $[\text{PtCl}_4]^{2-}$ with a Br^- . Since all Cl^- 's are equivalent, it does not matter which Cl^- is replaced. Therefore, only one structure, no isomers.

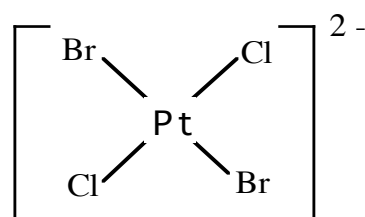


Now there are two different sets of Cl⁻ ions; the one opposite, or *trans* to the Br⁻, and the two next to, or *cis* to the Br⁻.

- c. Consider [PtCl₂Br₂]²⁻. Think of this complex as being derived from [PtCl₃Br]⁻ by replacing a Cl with a Br. Since there are two different sets of Cl⁻'s, there are two isomers of [PtCl₂Br₂]²⁻, designated as *cis* and *trans*.



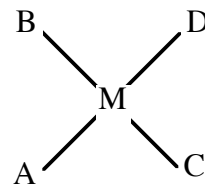
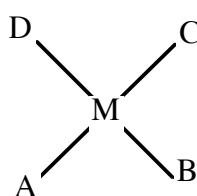
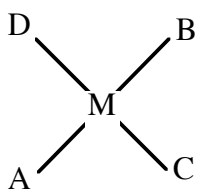
cis - dibromodichloroplatinate(II)



trans- dibromodichloroplatinate(II)

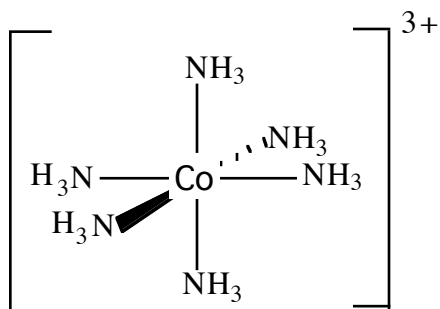
In the *cis* isomer the two like ligands are next to one another, while in the *trans* isomer they are opposite one another.

- d. Consider a square planar complex with four different ligands, [MABCD]. There are three different isomers. Note that the molecular plane is a mirror plane. Therefore, none of these isomers are optically active.



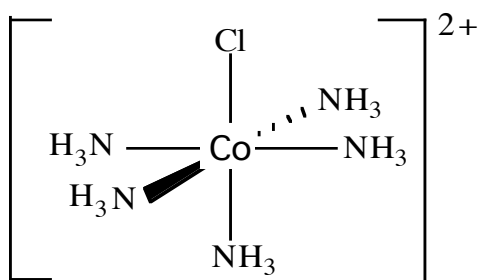
3. Octahedral Complexes.

- a. Consider [Co(NH₃)₆]³⁺. All six NH₃'s are equivalent. The molecule has octahedral symmetry. One structure, no isomers.



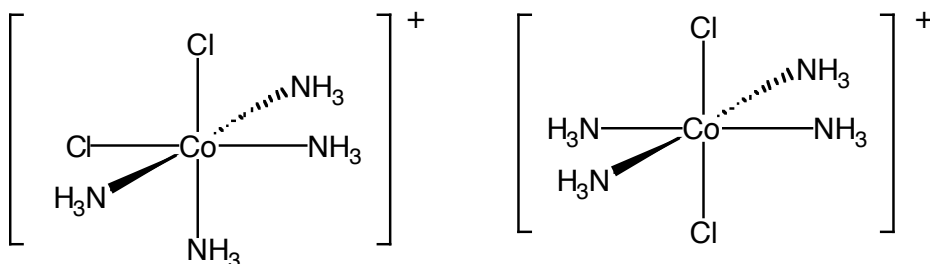
Hexamminecobalt(III)

- b. Consider $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$. One structure, no isomers. Note that there are now two different NH_3 's, the one *trans* to the Cl and the four *cis* to the Cl.



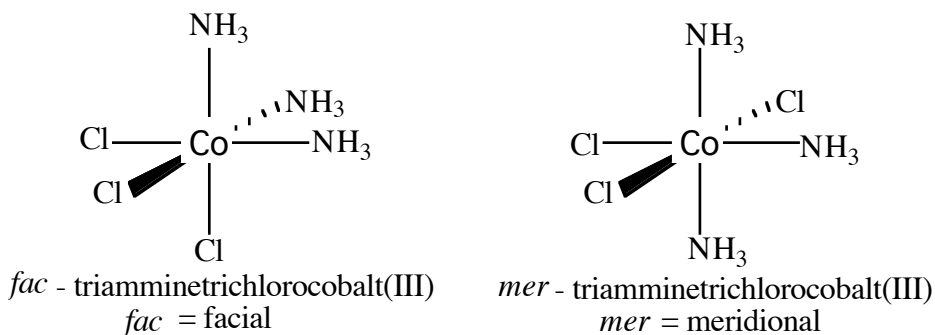
Pentamminechlorocobalt(III)

- c. Consider $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$. There are two isomers, *cis* and *trans*.

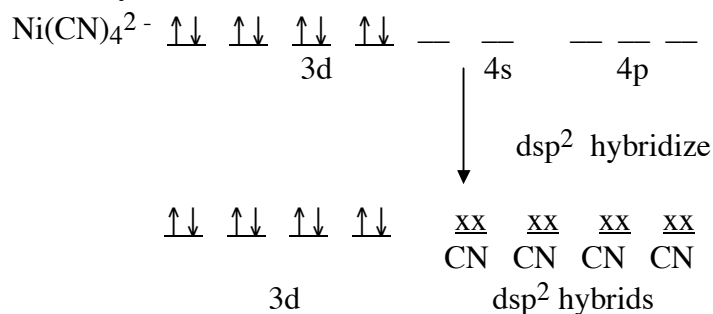


cis-tetramminedichlorocobalt(III) *trans*-tetramminedichlorocobalt(III)

- d. Consider $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$. There are two isomers, the facial (*fac*) and the meridional (*mer*) isomers.

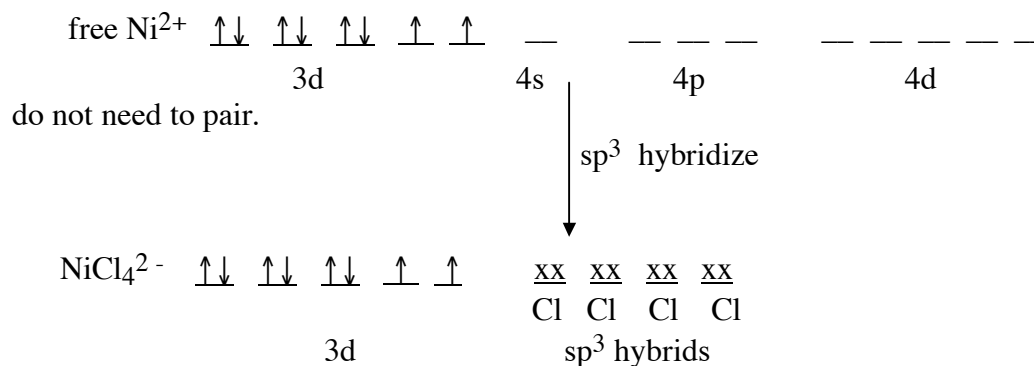


spin pair and hybridize.



Note that Ni(CN)_4^{2-} is diamagnetic. All square planar d^8 systems are diamagnetic.

2. Tetrahedral Complexes. Consider NiCl_4^{2-} [tetrachloronickelate(II)]



Note that NiCl_4^{2-} is paramagnetic. All tetrahedral d^8 complexes are paramagnetic.

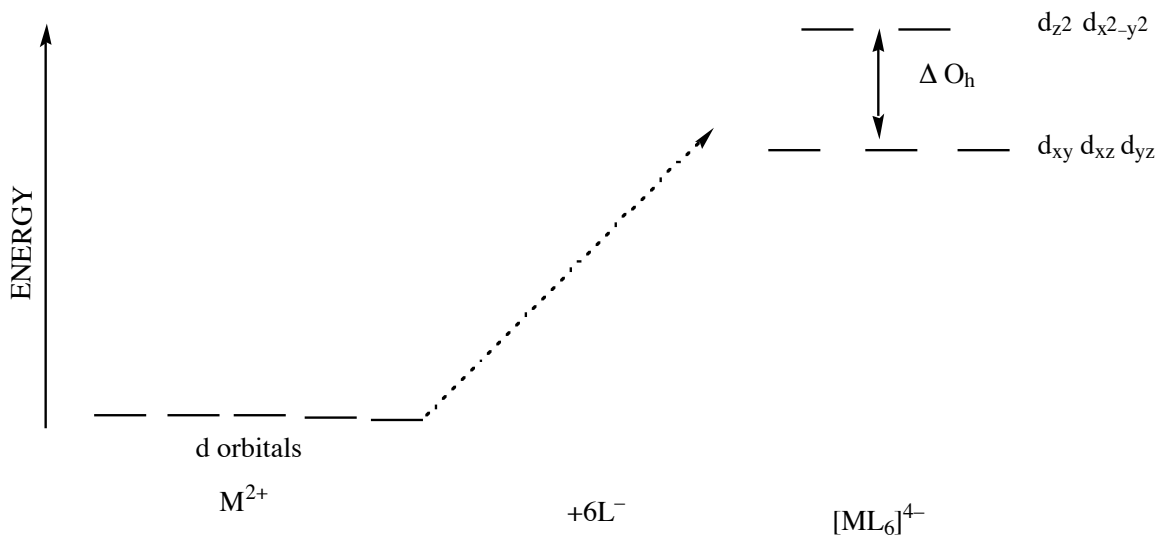
II. Crystal Field Theory(CFT).

A. CFT considers the effects that the ligands will have on the energies of the d orbitals in a complex.

1. Assume that the complex is held together by electrostatic interactions between the metal cation and the anionic or dipolar ligands.
2. Because we neglect the effects of covalent interactions, CFT is useful only in rationalizing the differences in properties of a series of compounds.
3. Review the orientations of d orbitals.

B. Octahedral Complexes.

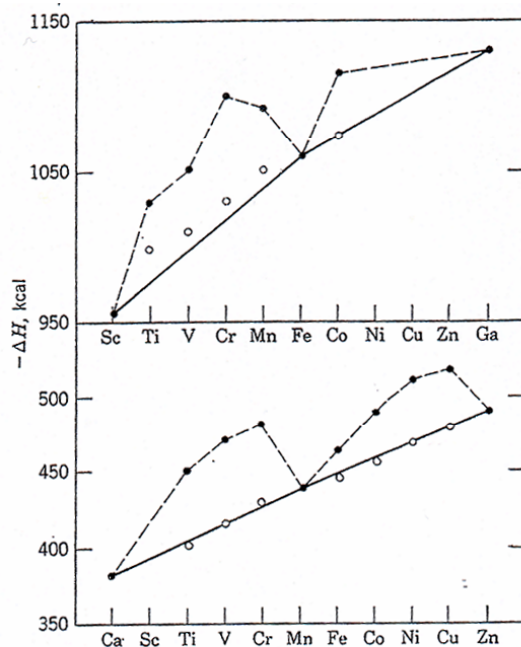
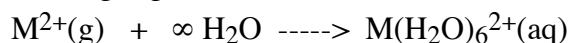
1. Consider the effect of 6 L^- ligands on the energies of the d orbitals of an M^{2+} ion in an octahedral complex.



2. The energies of all the d orbitals increase and the degeneracy of the d orbitals is lifted.
 - a. The $d_{x^2-y^2}$ and the d_{z^2} orbitals are higher in energy. Their lobes of maximum probability point directly towards the ligands. These two orbitals are called the e_g orbitals.
 - b. The d_{xy} , d_{xz} , and d_{yz} are lower in energy. Their lobes of maximum probability point away from the ligands. These orbitals are called the t_{2g} orbitals.
 - c. The difference in energy between the e_g and the t_{2g} orbitals (Δ_{O_h}) is called the **crystal field splitting energy**.
3. Δ_{O_h} is expressed in terms of an energy parameter called $10Dq$. Relative to the average energy of the d orbitals, each e_g orbital has an energy of $+6Dq$ and each t_{2g} orbital has an energy of $-4Dq$.
 - a. Preferential occupation of the lower energy t_{2g} orbitals will tend to stabilize the complex. This stabilization is called the **crystal field stabilization energy** (CFSE) and is expressed in terms of Dq .
 - b. Two tendencies.
 - 1) Half-fill with spins parallel before pairing in a single orbital.
 - 2) Preferentially fill the t_{2g} orbital before the e_g orbitals.
 - 3) d^1 to d^3 half fill t_{2g} with spins parallel.
 - 4) d^4 to d^7 two choices
 - half fill e_g before pairing in the t_{2g} - high spin complexes.
 - completely fill t_{2g} before filling the e_g - low spin complexes.
 - 5) d^8 to d^{10} only one possibility, complete the filling of the e_g .

e.	WEAK FIELD					STRONG FIELD						
	t _{2g}			e _g		CFSE (Dq)	t _{2g}			e _g		CFSE (Dq)
d ¹	↑	—	—	—	—		- 4	↑	—	—	—	
d ²	↑	↑	—	—	—	- 8	↑	↑	—	—	—	- 8
d ³	↑	↑	↑	—	—	- 12	↑	↑	↑	—	—	- 12
d ⁴	↑	↑	↑	↑	—	- 6	↑↓	↑	↑	—	—	- 16
d ⁵	↑	↑	↑	↑	↑	0	↑↓	↑↓	↑	—	—	- 20
d ⁶	↑↓	↑	↑	↑	↑	- 4	↑↓	↑↓	↑↓	—	—	- 24
d ⁷	↑↓	↑↓	↑	↑	↑	- 8	↑↓	↑↓	↑↓	↑	—	- 18
d ⁸	↑↓	↑↓	↑↓	↑	↑	- 12	↑↓	↑↓	↑↓	↑	↑	- 12
d ⁹	↑↓	↑↓	↑↓	↑↓	↑	- 6	↑↓	↑↓	↑↓	↑↓	↑	- 6
d ¹⁰	↑↓	↑↓	↑↓	↑↓	↑↓	0	↑↓	↑↓	↑↓	↑↓	↑↓	0

f. Experimental evidence for crystal field stabilization. Consider the heats of hydration ΔH_{hyd} of the high spin first row M^{2+} ions. That is, ΔH for the process

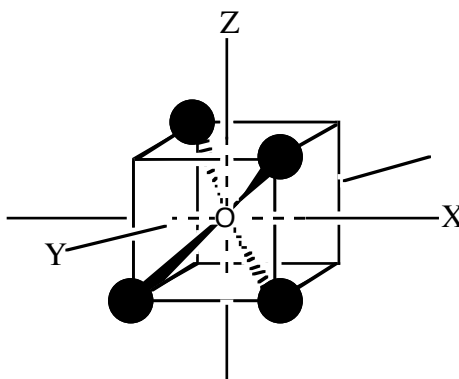


The uncorrected (dotted line) and crystal field corrected (solid line) hydration energies of the divalent (lower) and trivalent (upper) ions of the first transition series. (After O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).)

C. Other fields.

1. Tetrahedral Fields.

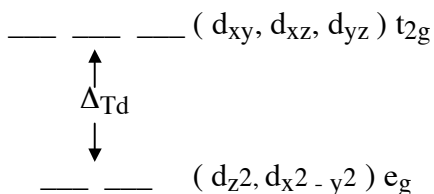
a. Tetrahedral symmetry is a form of cubic symmetry.



The four groups at alternate corners of the cube tetrahedrally coordinate a particle at the center of the cube. If the central particle is a transition metal and the ones on the corners ligands, the metal's d_{xy} , d_{xz} and d_{yx} orbitals will be closer to the ligands than will the d_{z^2} and the $d_{x^2 - y^2}$ orbitals.

- b. The e_g orbitals will be the low energy orbitals and the t_{2g} orbitals will be the high energy ones. Since none of the orbitals point directly towards the ligands, the crystal field splitting energy is smaller than in octahedral complexes $\Delta_{Td} = 4/9\Delta_{Oh}$.

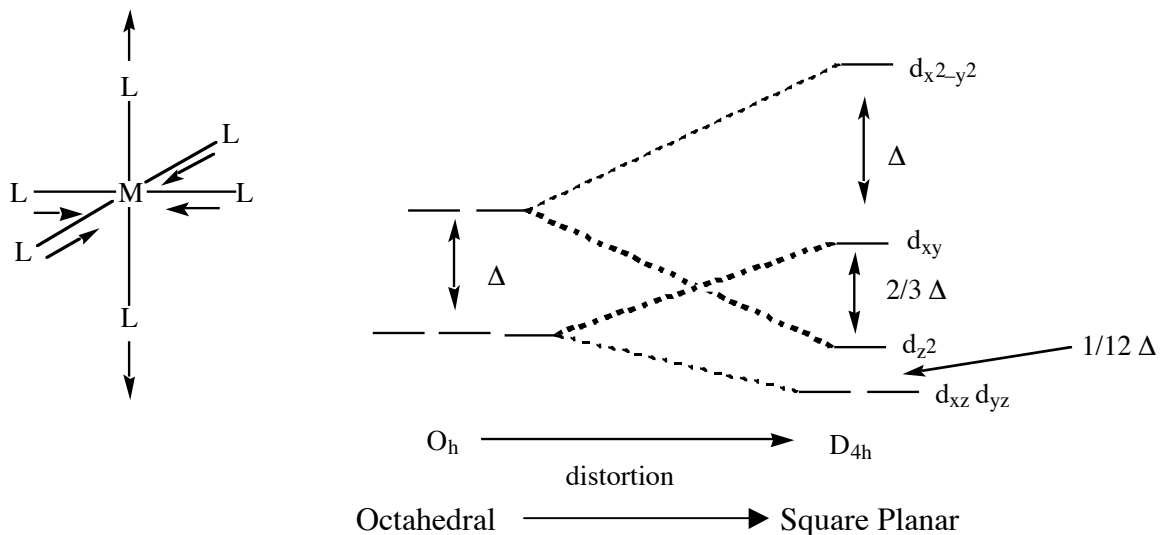
- c. Splitting diagram.



Each t_{2g} orbital is destabilized by an amount $2/5\Delta_{Td}$ and each e_g orbital is stabilized by $3/5\Delta_{Td}$

2. Square Planar Complexes.

- a. Think of a square planar complex as resulting from the distortion of an octahedral complex by moving the ligands on the Z axis away from the metal. Since this lowers ligand - ligand repulsion, the ligands in the XY plane will move in a little. This distortion will effect the energy of the d orbitals in the following way.



b. In some cases the d_{z^2} orbital falls below the d_{xz} and d_{yz} orbitals.

3. Trigonal bipyramid.

- Can only obtain a qualitative picture of relative orbital energies. Assume that the equatorial plane is the xy plane.
- The ordering of the orbitals is
 - d_{z^2} highest. 2 ligands are on the z axis.
 - d_{xy} and $d_{x^2-y^2}$ are next.
 - d_{xz} and d_{yz} are next.
- The largest energy difference is between the d_{z^2} and the d_{xy} , $d_{x^2-y^2}$ ($\approx 8Dq$), the other energy gap is much smaller ($\approx 2Dq$)

D. Trends in Δ .

1. General considerations regarding Δ .

- Δ 's are of the order of about 40 to 210 kJ / mol.
Bond energies are of the order of 1200 to 6000 kJ / mol. Therefore, Δ 's are only about 2 to 10% of bond energy.
- Cannot account for the general stability of a complex (ΔH_f°), but you may be able to account for the differences in the ΔH_f° 's of a series of compounds.
- Experimentally Δ is obtained from the visible / U.V. spectra of complexes and is many times expressed in cm^{-1} ($= 1 / \lambda$ in cm). This is a convenient spectroscopic energy unit.

$$1000 \text{ cm}^{-1} = 12.1 \text{ kJ / mol}$$

- Δ 's for complexes of transition metals in the same period, with the same charge, and having the same ligands are of similar magnitudes.

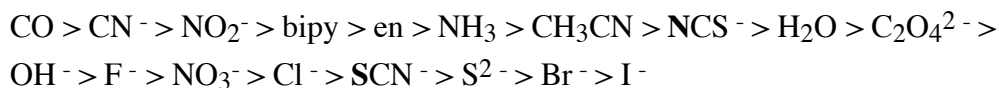
Example:

Δ 's for the high spin $M(\text{H}_2\text{O})_6^{2+}$ of the first row metals range from a low of 7500 cm^{-1} for $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ to a high of $14,000 \text{ cm}^{-1}$ for $\text{Cr}(\text{H}_2\text{O})_6^{2+}$.

3. Δ increases as you go down a group. Increase is from 30 to 50% per period.

<u>complex</u>	<u>Δ</u>
$\text{Co}(\text{NH}_3)_6^{3+}$	$23,000 \text{ cm}^{-1}$
$\text{Rh}(\text{NH}_3)_6^{3+}$	$34,000 \text{ cm}^{-1}$
$\text{Ir}(\text{NH}_3)_6^{3+}$	$41,000 \text{ cm}^{-1}$

4. For octahedral complexes in their normal oxidation states, the ligands arranged in order decreasing Δ are:



a. Those ligands with large Δ 's.

- 1) Are good back π bonders (CO, CN^- , NO_2^- etc.)
- 2) Are good σ bonders. (H^- , NH_3 , CH_3^-)

b. In general $\text{N} > \text{O}$.

c. Δ is not related to charge; it is an empirical series obtained spectroscopically.

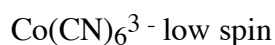
5. Δ increases as the charge on the metal increases. Increase is of from 40 to 80% in going from +2 to +3 salts.

E. Predictions using Crystal Field Theory.

1. Spin pairing of complexes.

a. Octahedral complexes.

- 1) High spin / low spin complexes found for d^4 through d^7 .
- 2) First row complexes will have low spin complexes with ligands giving large Δ 's (CN^-) and high spin with ligands giving small Δ 's (F^-)



3) In the second and third row, only low spin complexes are found.

b. Tetrahedral complexes. High spin only.

c. Square planar complexes.

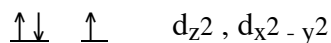
- 1) d^1 to d^3 all high spin.
- 2) d^4 to d^8 could have high spin or low spin.
- 3) Essentially all square planar d^7 and d^8 complexes are low spin.
- 4) Ligands that have large Δ 's favor square planar geometries in d^8 systems.

All Pt(II), Pd(II), Au(III), Rh(I), and Ir(I) complexes are diamagnetic, low spin square planar complexes.

2. Distortions.

a. Have assumed that complexes had perfect octahedral or tetrahedral geometry. Is that always the most stable configuration ?

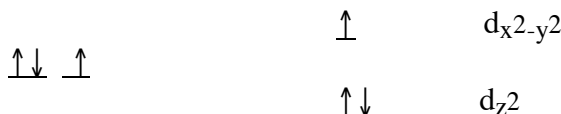
1) Consider an O_h Cu^{2+} (d^9) complex



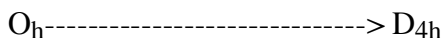
2) Have an asymmetric electron distribution in the e_g orbitals, that is $(d_{z^2})^2, (d_{x^2-y^2})^1$

How does this effect the geometry ?

3) If the configuration is $(d_{z^2})^2, (d_{x^2-y^2})^1$, there will be less shielding of the nuclear charge in the xy plane and more shielding along the z axis. This unequal shielding will cause the four ligands in the xy plane to be drawn in closer to the metal than the two ligands on the z axis. Therefore there should be a distortion from O_h symmetry to D_{4h} symmetry. Since two electrons are stabilized while only one is destabilized, such a distortion will tend to stabilize the complex.



distortion



The distortion due to an asymmetric electron distribution is called Jahn-Teller distortion.

b. Highly distorted complexes. Those that have asymmetric e_g electron distribution.

1) High spin: d^4, d^9 .

2) Low spin: d^7

c. Slightly distorted complexes. Have a symmetric e_g and an asymmetric t_{2g} electron distribution.

1) High spin: d^1, d^2, d^6 and d^7

2) Low spin: d^4, d^5 .

d. No distortion. Have symmetric e_g and t_{2g} electron distributions.

1) High spin: d^3, d^5

2) Low spin: d^6, d^{10}

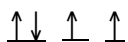
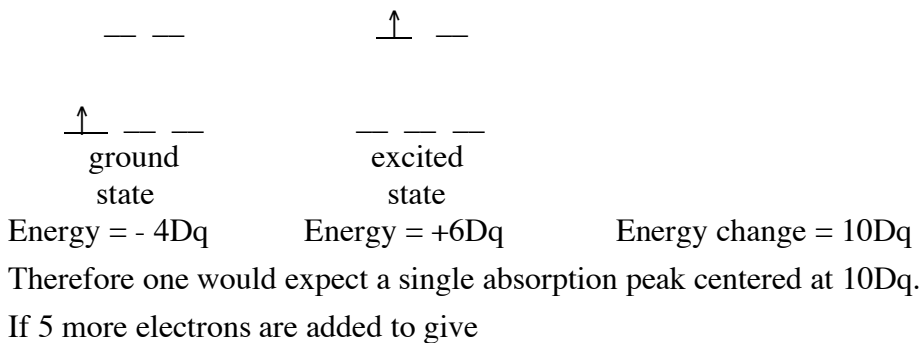
e. Tetrahedral complexes are not distorted.

3. Spectra of complexes.

a. Except for $d^0(Sc^{3+})$ and $d^{10}(Zn^{2+})$ complexes, transition metal complexes are colored. Color is due to electron is low energy d orbitals absorbing photons and going to higher energy orbitals (color not absorbed is the color seen).

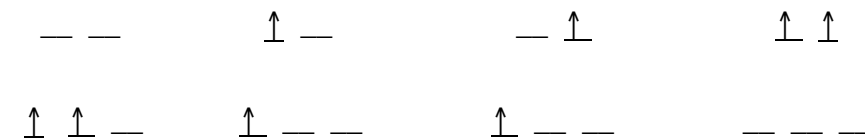
b. High spin octahedral complexes.

1) High spin d^1 and d^6 complexes.



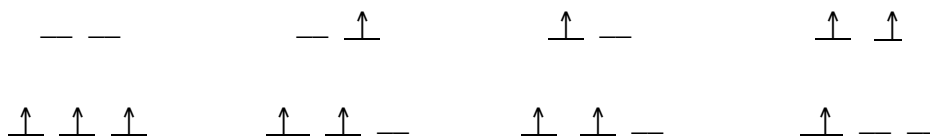
the possibilities are the same as with one electron. Therefore, high spin d^6 complexes also have a single peak centered at an energy of $10Dq$

2) High spin d^2 and d^7 octahedral complexes.



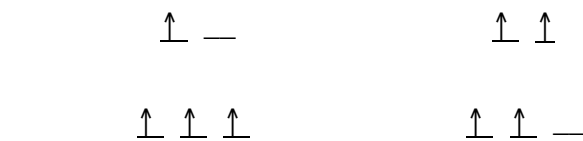
Three transitions.

3) High spin d^3 and d^8 octahedral complexes.



Three transitions.

4) High spin d^4 and d^9 octahedral complexes.



One transition (energy = $10 Dq$)

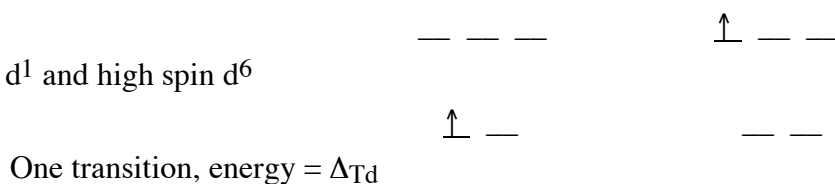
5) High spin d^5 octahedral complexes.



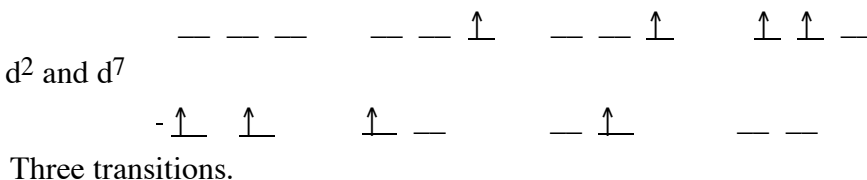
No spin allowed transitions. These complexes are essentially colorless.

c. Tetrahedral complexes.

1) d^1 and high spin d^6



2) d^2 and d^7



3) Others are done in the same way. **YOU DO THESE FOR PRACTISE.**

III. Molecular Orbital Theory.

A. Approach.

1. Construct the MO's of the complex by taking a linear combination of ligand orbitals and metal atomic orbitals.

a. The metal can use its $(n-1)d$, ns , and np atomic orbitals.

b. There are two types of ligand orbitals that can be used.

σ orbitals

- lobes point directly towards the metal.
- filled with electrons. They are the lone pair electron orbitals on the ligand.
- only one such orbital for each ligand.

π orbitals

- lobes are perpendicular to the metal - ligand internuclear line.
- could be either vacant or filled.
- can be several such orbitals for each ligand.

c. There can be both σ and π MO's involving the metal and the ligands. Will treat them separately.

2. For σ molecular orbitals.

a. The total number of σ ligand orbitals is equal to the coordination number (CN) of the metal.

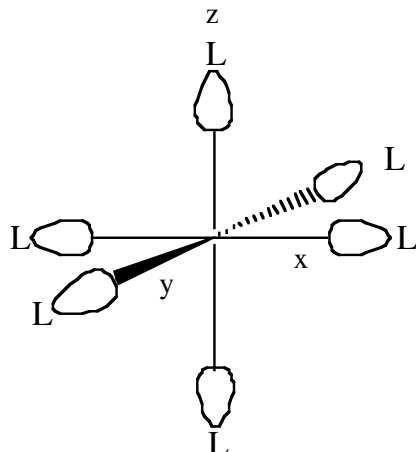
CN = 4 have 4 ligand σ orbitals.

CN = 6 have 6 ligand σ orbitals.

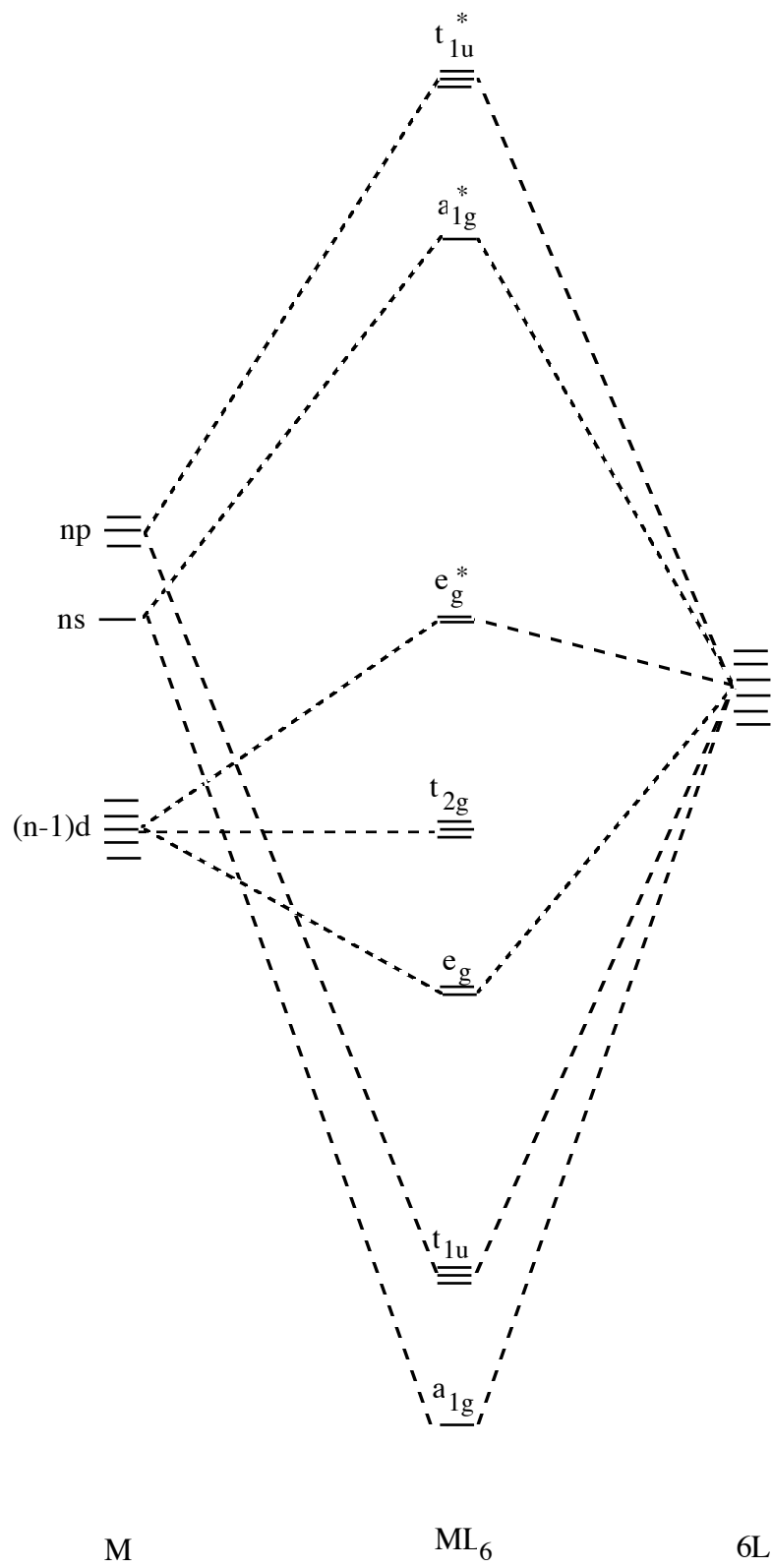
b. Certain of the metal orbitals will have the correct symmetry to interact with these ligand orbitals to form σ MO's.

B. σ bonded octahedral complexes.

1. The σ ligand orbitals are sketched below on the metal Cartesian axes.



2. On the metal, the following atomic orbitals will have σ symmetry and can interact with the ligand σ orbitals: $(n-1)d_{z^2}$, $(n-1)d_{x^2-y^2}$, ns , np_x , np_y , np_z .
 - a. The $(n-1)d_{xy}$, $(n-1)d_{xz}$, $(n-1)d_{yz}$ orbitals have π symmetry with respect to the metal-ligand bond axes and will not interact with the σ ligand orbitals.
 - b. Can construct the σ MO's by taking a pair-wise linear combination of one of the σ metal orbitals and a matching linear combination of the ligand orbitals. Since there are 6 σ metal orbitals, these linear combinations will yield 6 bonding σ MO's and 6 antibonding σ MO's. The correlation diagram is shown below.
- 3 The labelling of the orbitals is as follows.
 - a. The np_x , np_y , and np_z metal orbitals all have the same energies as do the ligand σ orbitals. Therefore their resulting MO's will have the same energies. This will result in three-fold degenerate sets of MO's, labelled t_{1u} (bonding) and t_{1u}^* (antibonding). The label **t** indicates a three-fold degenerate state.
 - b. The $(n-1)d_{z^2}$ and the $(n-1)d_{x^2-y^2}$ metal orbitals have the same energies and will yield a doubly degenerate set of bonding MO's (two MO's of equal energy) and a doubly degenerate set of antibonding MO's. The MO's are labelled e_g and e_g^* .
 - c. The ns metal orbital will give nondegenerate bonding and antibonding MO's (a_{1g} and a_{1g}^*).
 - d. The $(n-1)d_{xy}$, $(n-1)d_{xz}$, $(n-1)d_{yz}$ orbitals do not interact, they will form a three-fold degenerate nonbonding set of orbitals labelled t_{2g}



4. Filling of the MO's.

a. Number of electrons

12 electrons from the ligands+ the number of metal d electrons (assuming no ns electrons)

b. The 12 "ligand" electrons will fill the first 6 bonding MO's up through the e_g set. ($a_{1g}^2 t_{1u}^6 e_g^4$).

c. The transition metal d electrons will be distributed between a nonbonded t_{2g} set and a higher energy e_g^* set. This is exactly the result obtained from the Crystal Field Theory. Δ must now be redefined.

Δ = difference in energy between the nonbonding t_{2g} orbitals (d_{xy} , d_{xz} , d_{yz}) and the antibonding e_g^* orbitals (formed from the d_{z^2} and $d_{x^2-y^2}$).

d. All the generalizations about Δ given in Crystal Field Theory are applicable to MO Theory.

C. Other Geometries.

1. Tetrahedral Complexes.

a. The metal orbitals that can be used are the ns,np, (n-1) d_{xy} , d_{xz} , d_{yz} . The (n-1) d_{z^2} and (n-1) $d_{x^2-y^2}$ orbitals are nonbonding.

b. The MO correlation diagram shows 4 low energy bonding MO's that are filled with 8 electrons (the "ligands electrons").

c. The metal d electrons will be distributed between a nonbonding doubly degenerate e_g set and a higher energy triply degenerate t_{2g}^* antibonding set of MO's. This is the same result as given by Crystal Field Theory.

2. Square planar complexes show the same distribution of metal d electrons as given by Crystal Field Theory.

D. π Bonding in Octahedral Complexes.

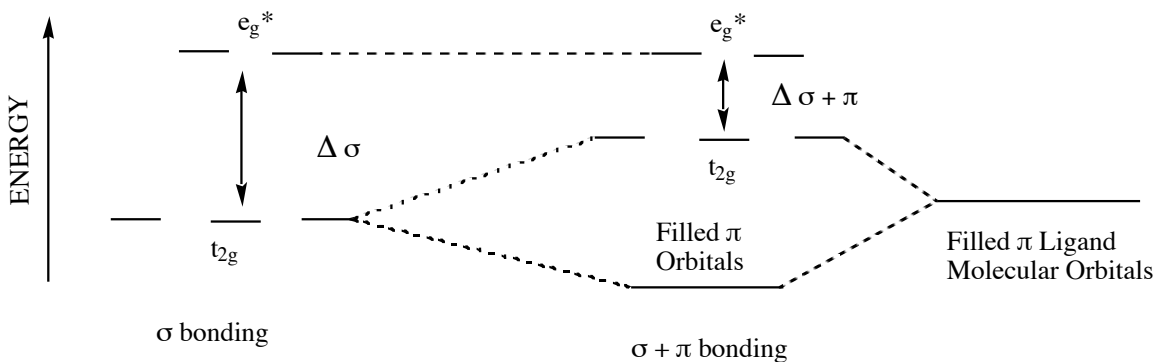
1. Ligands with low energy filled π orbitals.

a. Can overlap with the t_{2g} (d_{xy} , d_{xz} , d_{yz}) metal orbitals (these orbitals were nonbonding in σ complexes). therefore the π MO's can be formed by taking a linear combination of the π ligand orbitals and the t_{2g} metal orbitals

b. In general the ligand π orbitals will be lower in energy than the t_{2g} orbitals.

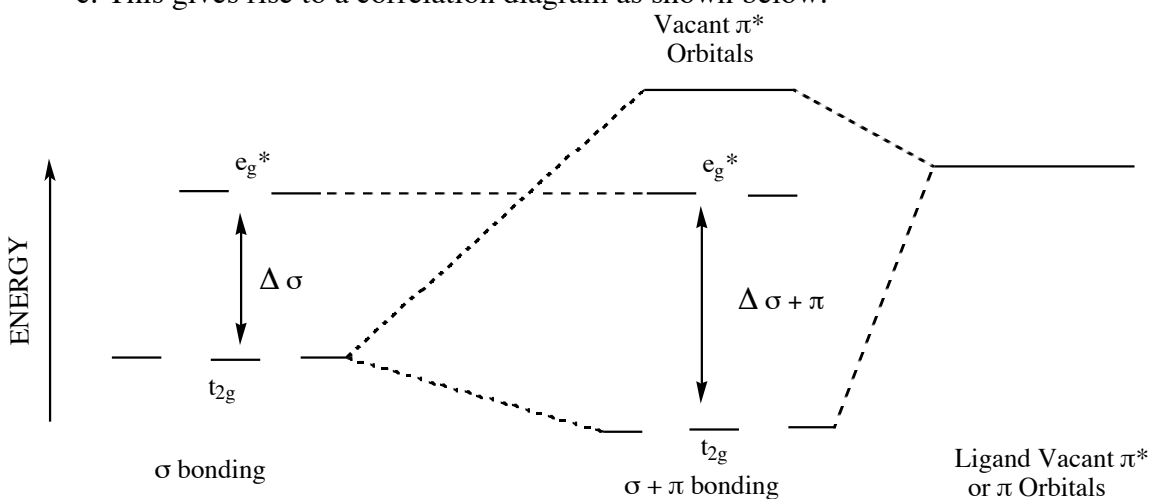
Therefore the low energy bonding orbitals will be similar to the original ligand orbitals, while the high energy orbitals will resemble the metal orbitals.

c. This will give a correlation diagram as shown below



will occupy the bonding π MO's, and the metal t_{2g} electrons, which are assigned to the higher energy π^* MO's.

- e. The net effect is to stabilize the complex, but decrease Δ . Ligands such as OH^- and F^- are such ligands and give small Δ 's.
2. Ligands with vacant high energy π orbitals.
 - a. π MO's can be formed by combining the ligand orbitals with the metal t_{2g} orbitals.
 - b. Since the ligand orbitals will, in general, have higher energies than the metal orbitals, the resulting low energy π MO's will resemble the t_{2g} orbitals, and the high energy π^* MO's will resemble the ligand orbitals.
 - c. This gives rise to a correlation diagram as shown below.

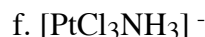
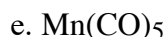
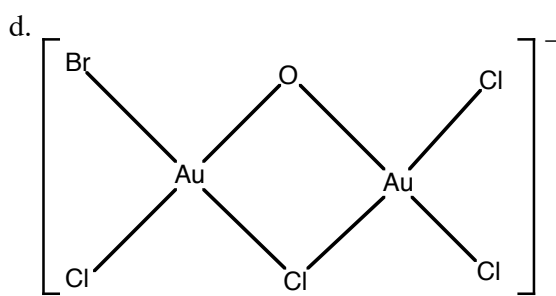
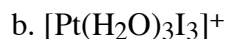
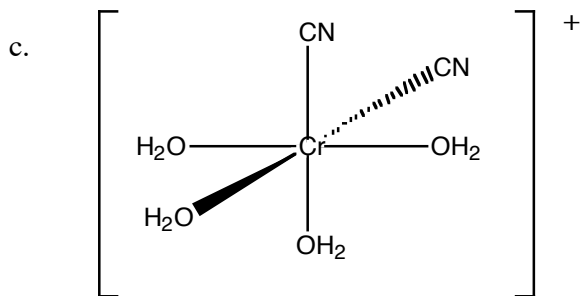
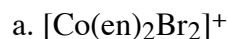


- d. Since the ligand orbitals were vacant, the only π electrons will be those that occupied the metal t_{2g} orbitals.
- e. The interaction will lead to an increase in Δ . Therefore, ligands such as PH_3 and the olefins will produce large Δ 's.
3. There are many ligands that have both filled and empty π orbitals, and both types of interactions will take place. Whether Δ is increased or decreased will depend on the relative importances of the interactions.
 - a. In complexes such as CO and CN^- back π bonding predominates and large Δ 's result.

b. For ligands such as Cl^- and Br^- , forward π bonding is more important and these ligands yield small Δ 's.

CHEMISTRY 1304
TRANSITION METALS

- Write electron configurations for the following: Zn^{2+} ; Fe^{2+} ; Fe^{3+} ; Cu^+ ; Co^{3+} ; Mn^{3+} .
- Give the number of unpaired electrons in each of the ions in question 1.
- Name the following.



- Write formulas for the following, show structures when necessary.
 - Bis*-(bipyridine)dichlorocobalt(III)
 - trans*-tetraaquodicyanochromium(III)
 - Potassium hexachloroplatinate(IV)
 - Sodium tetraoxomanganate(VII)
 - diammineplatinum(II) μ -bromo- μ -chlorodithiocyanatoplatinum(II)
- Draw all the isomers for the following and name each isomer. Indicate which isomers are optically active.
 - $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$
 - $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2\text{I}_2]$
 - $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$
 - $[\text{RuBr}_2\text{I}(\text{CN})(\text{H}_2\text{O})]^{2-}$
- Account for the following observations.
 - Although $\text{NH}_2\text{-CH-CH}_2\text{-NH}_2$ has three base sites it functions as a bidentate ligand.

$$\begin{array}{c} | \\ \text{NH}_2 \end{array}$$
 - The complex $\text{Co}(\text{CN})_6^{3-}$ is diamagnetic while CoF_6^{3-} is paramagnetic.
 - There are no low spin tetrahedral complexes.
 - $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ is paramagnetic with five unpaired electrons while $\text{Re}(\text{H}_2\text{O})_6^{2+}$ has only one unpaired electron.
 - The complex $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is a perfect octahedron while $\text{Fe}(\text{CN})_6^{3-}$ is distorted.
 - There are two isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ but $[\text{Ni}(\text{NH}_3)_2\text{Cl}_2]$ does not have any isomers.
 - The $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ is a good bridging ligand but it is not a bidentate.
 - The compound $\text{Ni}(\text{CO})_4$ is known but $\text{Ni}(\text{NH}_3)_4$ has never been prepared.

7. Give the number of spectral peaks for each of the following: $\text{Ni}(\text{H}_2\text{O})_6^{2+}$; $\text{V}(\text{H}_2\text{O})_6^{2+}$; $\text{Cu}(\text{H}_2\text{O})_6^{2+}$.
8. Arrange the following in order of increasing Jahn-Teller distortion: $\text{Cu}(\text{H}_2\text{O})_6^{2+}$; $\text{Ni}(\text{H}_2\text{O})_6^{2+}$; $\text{Co}(\text{H}_2\text{O})_6^{2+}$.
9. It is known that the tetrahedral complexes of Ni(II) are paramagnetic while its square planar complexes are diamagnetic. Account for this using both valence bond and crystal field theories.
10. $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is essentially colorless while $\text{Fe}(\text{CN})_6^{3-}$ is highly colored. Explain.
11. How many absorption peaks will be found in the spectrum of each of the following: PtCl_4^{2-} (D_{4h}); CoCl_4^{2-} (T_d); $\text{Ni}(\text{H}_2\text{O})_6^{2+}$?
12. For the ligands PH_3 , NH_3 , and H_2O the value of Δ increases in the order $\text{H}_2\text{O} < \text{NH}_3 < \text{PH}_3$. Explain.
13. The complex $\text{Ti}(\text{NH}_3)_6^{3+}$ absorbs at a lower wavelength than does $\text{Ti}(\text{H}_2\text{O})_6^{3+}$. Explain.
14. The complex $\text{Mn}(\text{CN})_6^{4-}$ is less paramagnetic than is $\text{Mn}(\text{H}_2\text{O})_6^{2+}$. Explain.
15. Which ligand will have the larger Δ , NO^+ or OH^- ? Justify your choice.
16. CoCl_4^{2-} has three unpaired electrons while PtCl_4^{2-} is diamagnetic. Explain.
17. Arrange the following ligands in order of increasing Δ and justify your arrangement. NH_3 , NF_3 , and NCl_3 .

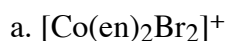
CHEMISTRY 1304
TRANSITION METALS

(answers)

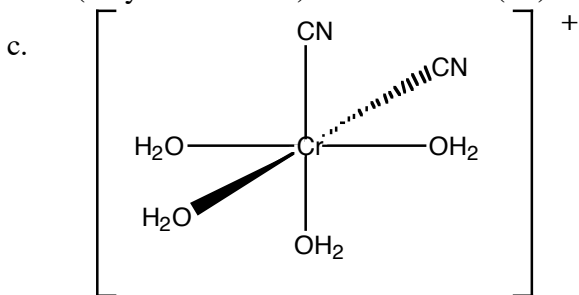
- Write electron configurations for the following: Zn^{2+} ; Fe^{2+} ; Fe^{3+} ; Cu^+ ; Co^{3+} ; Mn^{3+} .
- Give the number of unpaired electrons in each of the ions in question 1.

	<u>Electron Configuration</u>	<u>No. of unpaired electrons</u>
Zn^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$	0
Fe^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$	4
Fe^{3+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$	5
Cu^+	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$	0
Mn^{3+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^4$	4

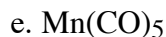
- Name the following.



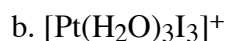
bis(ethylenediamine)dibromocobalt(III)



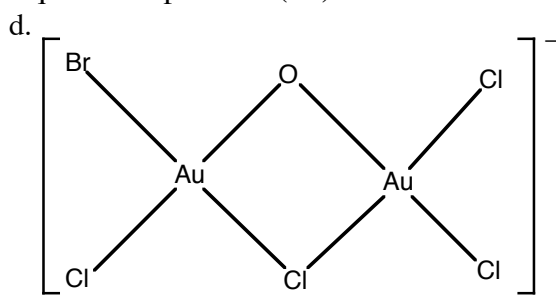
cis- tetraquodicyanochromium(III)
oxodichlorogold(III)



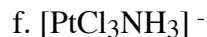
pentacarbonylmanganese(0)



triaquotriiodoplatinum(IV)

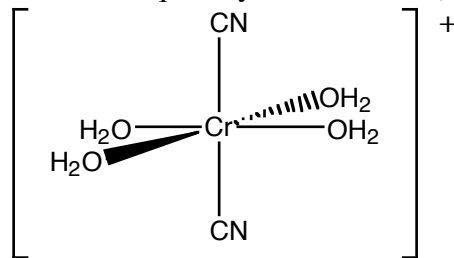
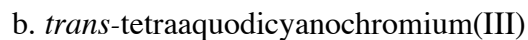
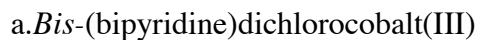


bromochlorogold(III)- μ -chloro- μ -
oxodichlorogold(III)

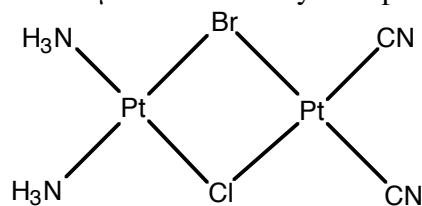


amminetrichloroplatinate(II)

- Write formulas for the following, show structures when necessary.

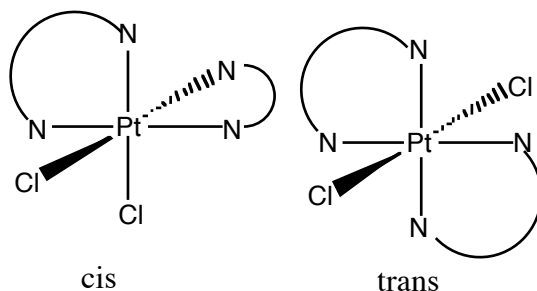


e. diammineplatinum(II) μ -bromo- μ -chlorodithiocyanatoplatinum(II)

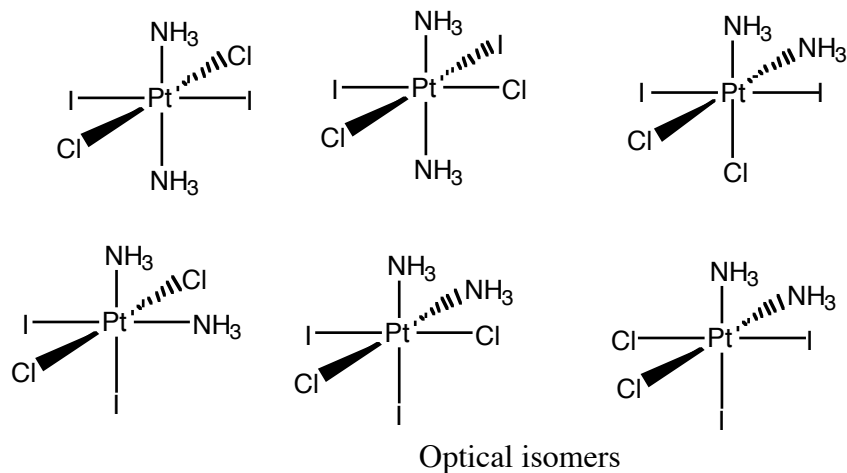


5. Draw all the isomers for the following and name each isomer. Indicate which isomers are optically active.

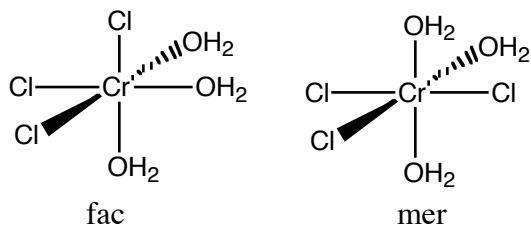
a. $[\text{Pt}(\text{en})_2\text{Cl}_2]^{2+}$



b. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2\text{I}_2]$

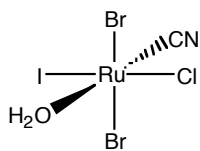


c. $[\text{Cr}(\text{H}_2\text{O})_3\text{Cl}_3]$

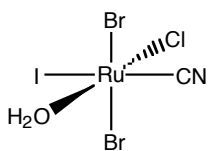


d. $[\text{RuBr}_2\text{ICl}(\text{CN})\text{H}_2\text{O}]^{2-}$

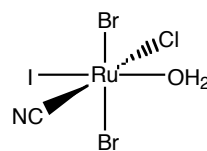
* = Optically active



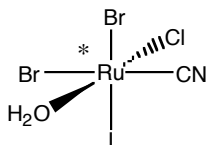
4-aquo-1,6-dibromo-3-chloro-2-cyano-5-iodoruthinium(III)



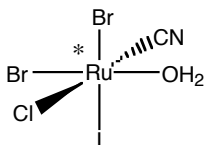
4-aquo-1,6-dibromo-2-chloro-3-cyano-5-iodoruthinium(III)



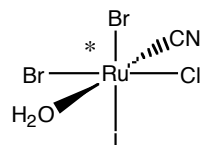
3-aquo-1,6-dibromo-2-chloro-4-cyano-5-iodoruthinium(III)



4-aquo-1,5-dibromo-2-chloro-3-cyano-6-iodoruthinium(III)



2-aquo-1,5-dibromo-4-chloro-2-cyano-6-iodoruthinium(III)



4-aquo-1,5-dibromo-3-chloro-2-cyano-6-iodoruthinium(III)

6. Account for the following observations. (**Hints only**)

a. Although $\text{NH}_2\text{-CH-CH}_2\text{-NH}_2$ has three base sites it functions as a bidentate ligand.



(**five vs four membered ring**)

b. The complex $\text{Co}(\text{CN})_6^{3-}$ is diamagnetic while CoF_6^{3-} is paramagnetic.

(**Δ for $\text{CN}^- > \Delta$ for F^-**)

c. There are no low spin tetrahedral complexes.

(**Δ vs pairing energy**)

d. $\text{Mn}(\text{H}_2\text{O})_6^{2+}$ is paramagnetic with five unpaired electrons while $\text{Re}(\text{H}_2\text{O})_6^{2+}$ has only one unpaired electron. (**Δ change in group**)

e. The complex $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is a perfect octahedron while $\text{Fe}(\text{CN})_6^{3-}$ is distorted.

(**$\text{Fe}(\text{CN})_6^{3-}$ has low spin asymmetric (t_{2g}^5) while high spin d^5 is symmetric**)

f. There are two isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ but $[\text{Ni}(\text{NH}_3)_3\text{Cl}_2]$ does not have any isomers. (**look at geometry**)

g. The $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ is a good bridging ligand but it is not a bidentate.

(**six-membered ring**)

h. The compound $\text{Ni}(\text{CO})_4$ is known but $\text{Ni}(\text{NH}_3)_4$ has never been prepared.

(**consider back π bonding**)

7. Give the number of spectral peaks for each of the following: $\text{Ni}(\text{H}_2\text{O})_6^{2+}$; $\text{V}(\text{H}_2\text{O})_6^{2+}$; $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. (see notes)

8. Arrange the following in order of increasing Jahn-Teller distortion: $\text{Cu}(\text{H}_2\text{O})_6^{2+}$; $\text{Ni}(\text{H}_2\text{O})_6^{2+}$; $\text{Co}(\text{H}_2\text{O})_6^{2+}$. (look at electron distribution)

9. It is known that the tetrahedral complexes of $\text{Ni}(\text{II})$ are paramagnetic while its square

planar complexes are diamagnetic. Account for this using both valence bond and crystal

field theories. (see notes)

10. $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ is essentially colorless while $\text{Fe}(\text{CN})_6^{3-}$ is highly colored. Explain.
(look at electron distribution)
11. How many absorptions peaks will be found in the spectrum of each of the following:
 PtCl_4^{2-} (D_{4h}) ; CoCl_4^{2-} (T_d) ; $\text{Ni}(\text{H}_2\text{O})_6^{2+}$? (see notes)
12. For the ligands PH_3 , NH_3 , and H_2O the value of Δ increases in the order
 $\text{H}_2\text{O} < \text{NH}_3 < \text{PH}_3$. Explain. (NH_3 good σ bonder, PH_3 good back π bonder)
13. The complex $\text{Ti}(\text{NH}_3)_6^{3+}$ absorbs at a lower wavelength than does $\text{Ti}(\text{H}_2\text{O})_6^{3+}$. Explain.
(look at Δ and charge)
14. The complex $\text{Mn}(\text{CN})_6^{4-}$ is less paramagnetic than is $\text{Mn}(\text{H}_2\text{O})_6^{2+}$. Explain.
(high spin vs low spin and Δ)
15. Which ligand will have the larger Δ , NO^+ or OH^- ? Justify your choice.
(consider back π bonding)
16. CoCl_4^{2-} has three unpaired electrons while PtCl_4^{2-} is diamagnetic. Explain. (T_d vs D_{4h})
17. Arrange the following ligands in order of increasing Δ and justify your arrangement.
 NH_3 , NF_3 , and NCl_3 . ($\text{NF}_3 < \text{NCl}_3 < \text{NH}_3$ --look at basicities)