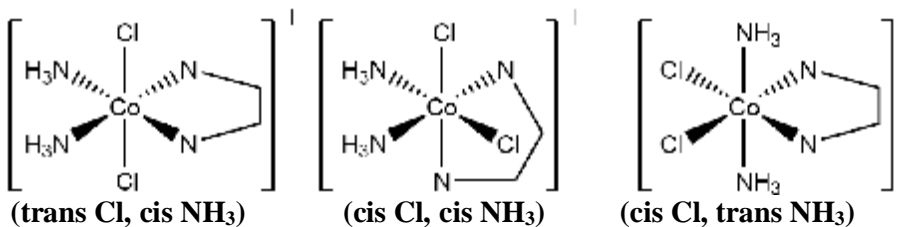
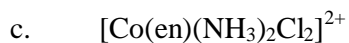
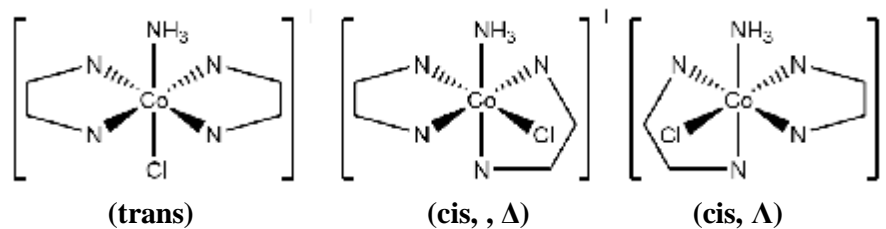
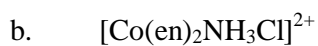
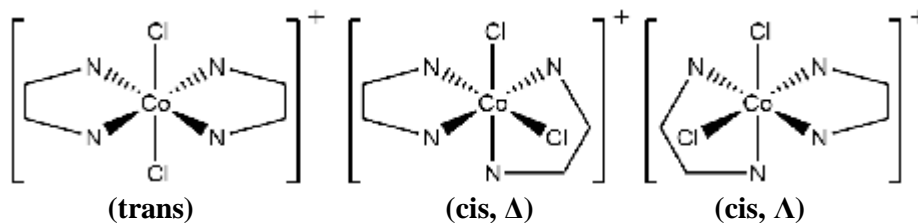
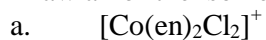


**HW 4**  
**CHEM 362**

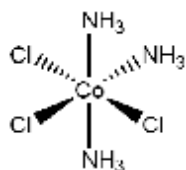
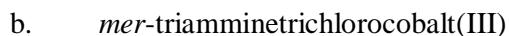
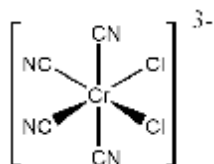
Available: Feb. 18, 2008

Due: Feb. 29, 2008

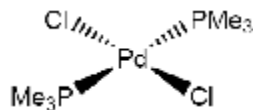
1. Draw all of the isomers, geometrical and optical for the following:



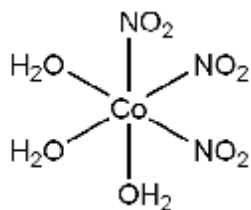
2. Draw the molecular structures of the following complexes:



- c. *trans*-dichlorobis(trimethylphosphine)palladium(II)



- d. *fac*-triaquatrin硝酸cobalt(III)



3. Give the proper name for each of the following compounds:

- a.  $[\text{Pt}(\text{py})_4][\text{PtCl}_4]$

**tetrapyridineplatinum(II) tetrachloroplatinate(II)**

- b.  $\text{Pt}(\text{acac})(\text{NH}_3)\text{Cl}$

**acetoacetonatochloroammineplatinum(II)**

- c.  $\text{Rh}(\text{NH}_3)_5\text{Cl}$

**chloropentaamminerhodium(I)**

- d.  $[\text{Pt}(\text{en})_2][\text{ClO}_4]_2$

**bis(ethylenediamine)platinum(II) perchlorate**

- e.  $\text{Na}_3[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$

**sodium hexacyanoferrate(III) dihydrate**

- f.  $\text{Na}_4[\text{Fe}(\text{CN})_6]$

**sodium hexacyanoferrate(II)**

- g.  $[\text{Co}(\text{H}_2\text{O})_6]\text{SO}_4$

**hexaaquacobalt(II) sulfate**

- h.  $[\text{Ni}(\text{phen})_3][\text{ClO}_4]_2$

**triphenanthroline nickel(II) perchlorate**

- i.  $\text{Ni}(\text{CO})_4$

**tetracarbonylnickel(0)**



**acetatobromochloroamminecobalt(III)**



**sodium hexachloropalladate(IV)**

4. For each coordination number from two to nine, mention the principal geometrical arrangement (or arrangements).

**C.N. = 2 → linear (note: not bent)**

**C.N. = 3 → trigonal planar, trigonal pyramidal**

**C.N. = 4 → tetrahedral, square planar**

**C.N. = 5 → trigonal bipyramidal, square pyramidal**

**C.N. = 6 → octahedral, trigonal prism**

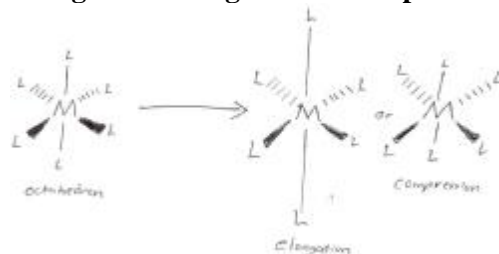
**C.N. = 7 → pentagonal bipyramidal, face capped trigonal prism**

**C.N. = 8 → square antiprism, dodecahedron**

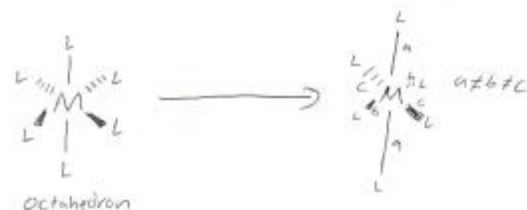
**C.N. = 9 → capped trigonal prism (all 3 faces)**

5. What is meant by tetragonal, rhombic and trigonal distortions of an octahedron?

**tetragonal – elongation or compression along the z-axis**



**rhombic – 3 distinct M-L distances arise**



**trigonal – compression or elongation along the axis containing two opposite faces**



6. Give one example of each of the following types of isomers:

**Note: There are many correct answers.**

- a. Ionization isomer



- b. Linkage isomer



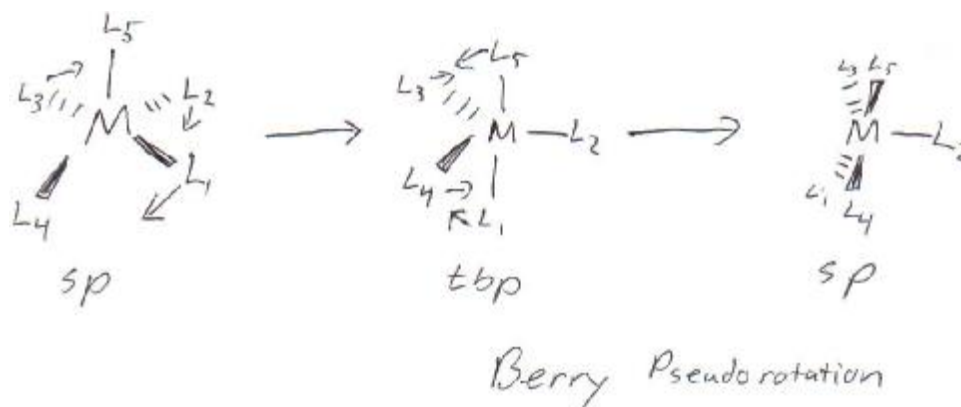
- c. Coordination isomer



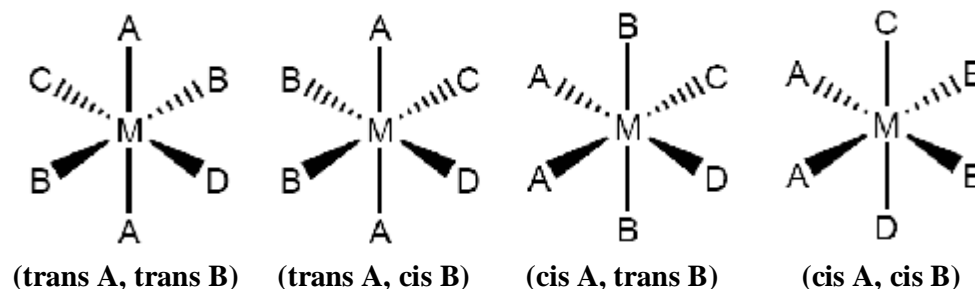
7. What is meant by the chelate effect? Give an example.

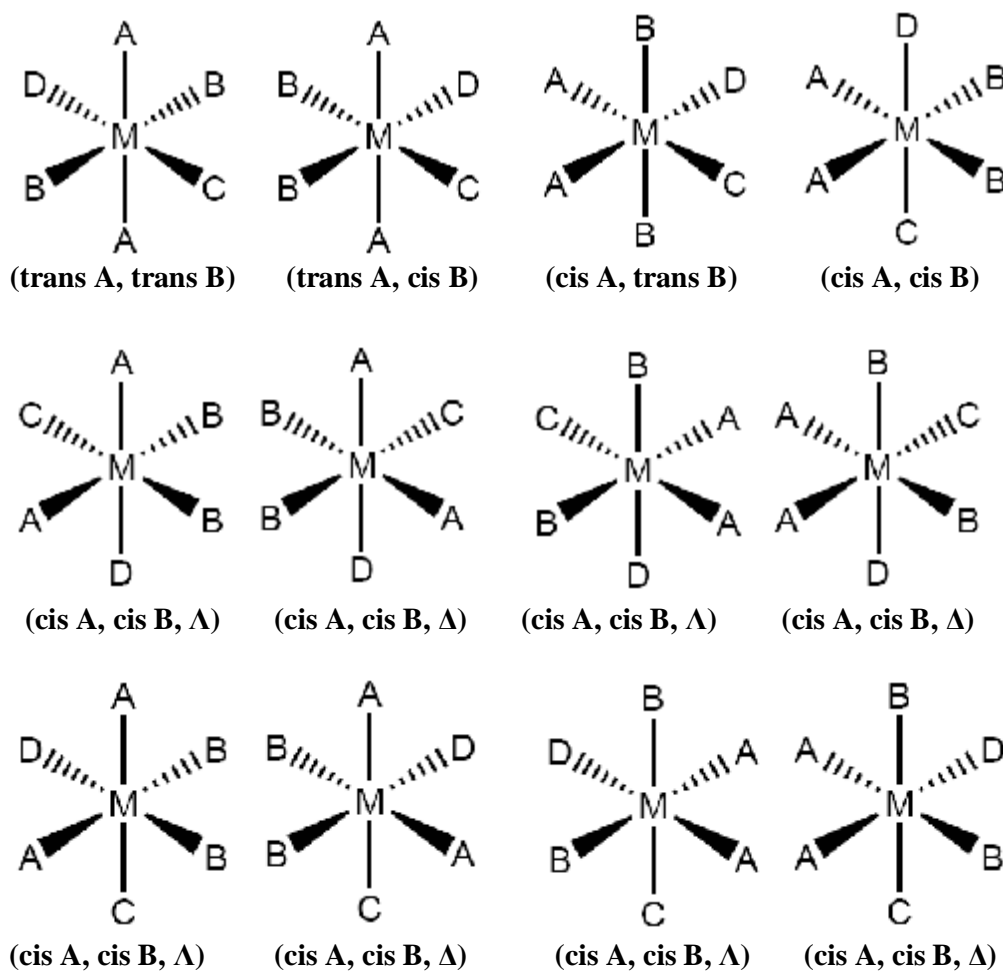
The chelate effect is characterized by the dramatic stability of compounds containing bi-(or higher)dentate ligands which form 5 or 6 membered rings with the metal. This effect is manifested in the much higher formation constants for chelate complexes versus monodentate complexes of similar type (ex.  $\text{NH}_3$  versus ethylenediamine). This stabilization arises primarily from entropic considerations. (recall in class we discussed the formation of  $[\text{Ni}(\text{en})_3]^{2+}$  and  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  from  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ ). An example of the chelate effect is the stability of  $[\text{Ni}(\text{en})_3]^{2+}$  versus  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  because the number of molecules involved in the reactant and product side of the reaction favors the formation of  $[\text{Ni}(\text{en})_3]^{2+}$ .

8. Show with drawings how axial-equatorial exchange in a square pyramidal (sp) complex  $\text{AB}_5$  could occur through a trigonal bipyramidal (tbp) intermediate.



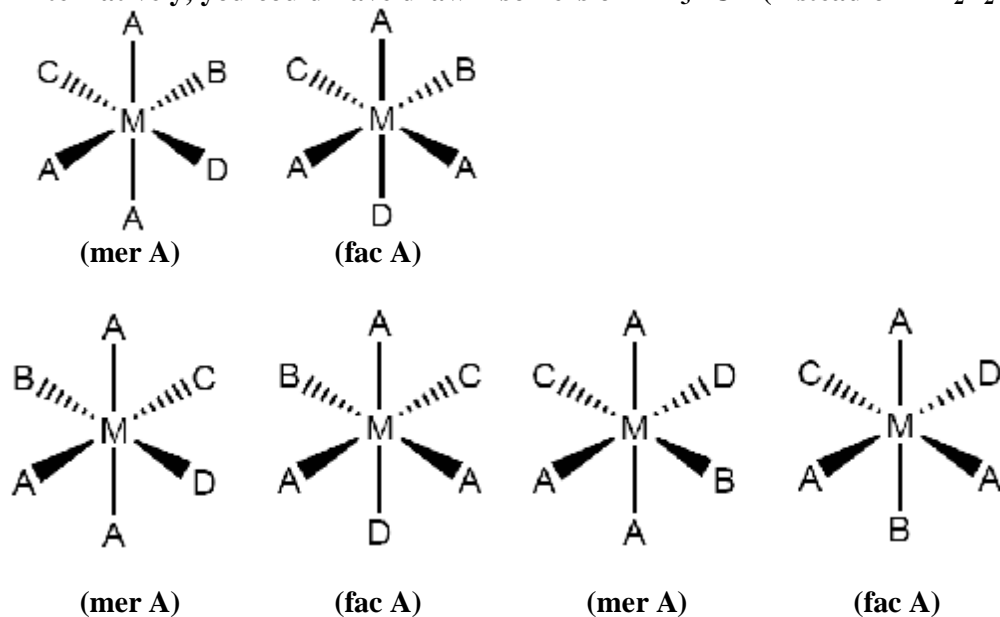
9. Draw all the possible isomers for an octahedral complex having four different monodentate ligands. Indicate optical isomers.





Note: Δ and Λ are assigned arbitrarily in these drawings

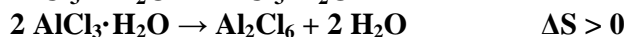
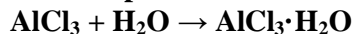
Alternatively, you could have drawn isomers of MA<sub>3</sub>BCD (instead of MA<sub>2</sub>B<sub>2</sub>CD)



10. Why do you think that species such as  $\text{AlCl}_3$ ,  $[\text{CuCl}_3]^-$  and  $\text{Pt}(\text{NH}_3)_2\text{Cl}^+$  are not actually three-coordinate mononuclear complexes but rather dinuclear compounds?

**These species form solvates in solution, and giving up solvent molecules to form dimers in entropically favorable (in that sense its similar to the chelate effect).**

**for example:**

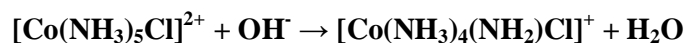


11. Write the chemical reactions for:

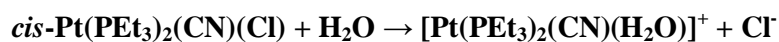
- a. Water exchange in the hexaaquanickel(II) ion



- b. Base hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$

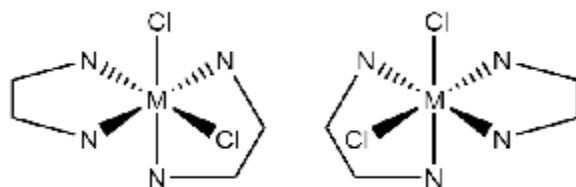


- c.  $\text{cis-Pt}(\text{PEt}_3)_2(\text{CN})(\text{Cl}) + \text{H}_2\text{O}$

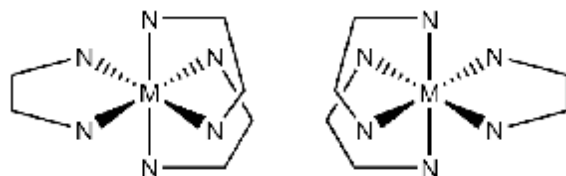


12. Show with drawings, the enantiomorphs of

- a.  $\text{M}(\text{en})_2\text{Cl}_2$



- b.  $\text{M}(\text{en})_3$



13. Contrast the general trends for substitution reactions of (1) octahedral and (2) square planar complexes regarding:
- a. Leaving group effects

**For octahedral complexes, better leaving groups will make dissociative pathways more favorable than associative. By the same token, poorer leaving groups will favor the associative.**

**For square planar complexes, the associative pathway is already favored by the open coordination sites on the metal, so one would not expect the leaving group to effect the mechanism very much.**

**In both cases, the better the leaving group the more likely the reaction will proceed.**

- b. Charge effects

**In both octahedral and square planar complexes the loss of a negatively charged ligand from a compound with a positive charge will be less likely than from a neutral or negatively charged compound. Likewise the loss of a positively charged ligand from a positively charged compound will be favorable but less likely from a negatively charged compound.**

- c. Steric effects

**In octahedral complexes, steric bulk on the ligands will decrease the favorability of reactions that occur by an associative pathway.**

**In square planar complexes, which strongly favor associative pathways, steric bulk will decrease the overall reactivity for the same reason as in the octahedral complex. It will be harder for an attacking ligand to bind with the metal.**

14. Summarize the types of data that indicate a predominantly dissociative mechanism for substitution reactions of octahedral complexes.

**Addition of the ligand has no effect upon the rate of the reaction.**

15. Summarize the types of data that indicate a predominantly associative mechanism for substitution reactions of octahedral complexes.

**Addition of the ligand increases the rate of the reaction.**

16. For  $[\text{PtX}_4]^{2-}$  compounds, both ligand exchange and thermodynamic stability increase in the order



Explain why these observations are not inconsistent with each other.

**Ligand exchange is governed by kinetics, it refers to the lability of a given ligand. The thermodynamic stability refers to the strength of a given ligand metal bond. The observations are not inconsistent because they refer to two separate properties of the ligand.**

17. What do each of the following abbreviations stand for?

a. tbp

**trigonal bipyramid**

b. fac

**facial**

c. mer

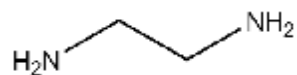
**meridional**

d. bpy

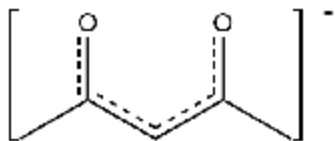
**2,2'-bipyridine**

18. Draw structures of the following ligands:

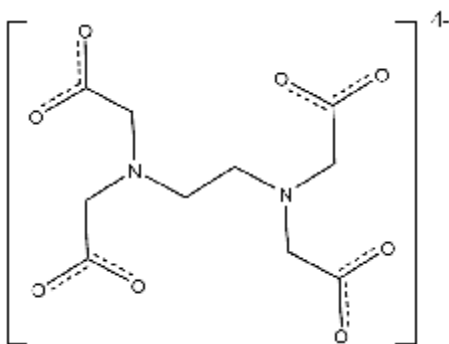
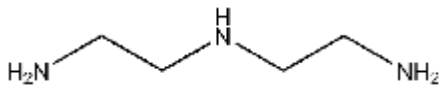
a. ethylenediamine (en)



b. acetylacetonate (acac)



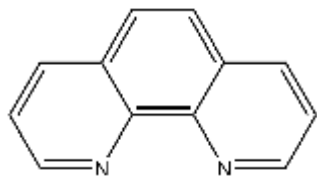
c. diethylenetriamine (EDTA)



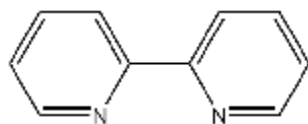
**Either structure is acceptable because the diethylenetriamine (trien) is not ethylenediamminetetraacetate (EDTA)**



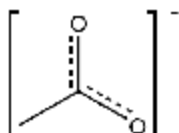
d. 1,10-phenanthroline



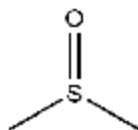
e. 2,2'-bipyridine



f. acetate ion



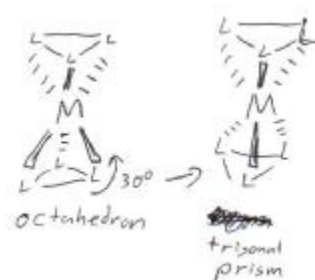
g. dimethylsulfoxide (DMSO)



19. Draw the six-coordinate  $ML_6$  complex as an octahedron and as a trigonal prism

a. What is the relationship between the two structures?

**A  $30^\circ$  twist of the parallel trigonal faces.**



b. Why is the octahedral geometry more favored than the trigonal prism?

**Octahedral geometry is less sterically crowded than the trigonal prism which has 3 of its ligands eclipsing the other 3.**

- c. Show how the number of geometrical isomers differ for the octahedron and the trigonal prism geometry for  $M(\text{bpy})_2\text{Cl}_2$ .

