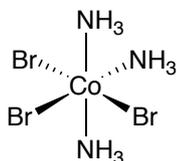


HW 5
CHEM 362

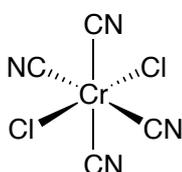
Due: October 22, 2019

1. Draw the molecular structures of the following complexes

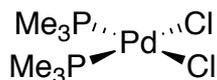
a. *mer*-triamminetribromocobalt(III)



b. *trans*-dichlorotetracyanochromate(III)



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



2. For each of the following compounds

- Give the proper name
- Give the coordination number of the central metal atom.
- Give the principle geometric arrangement(s) for the above coordination number
Hint: Be mindful of oxidation states!

- Pt(acac)(NH₃)Br
- Co(NH₃)₅Cl
- [Pt(phen)₂][PF₆]₂
- K₃[Fe(CN)₆] · 2H₂O
- Na₄[Fe(CN)₆]
- [Ni(en)₃][ClO₄]₂
- Ni(CO)₄

- Pt(acac)(NH₃)Br
 - acetoacetatobromoammineplatinum(II)
 - CN=4
 - Tetrahedral or square planar
- Co(NH₃)₅Cl
 - chloropentaamminecobalt(I)
 - CN=6
 - Octahedral or trigonal prism.

- iii. $[\text{Pt}(\text{phen})_2][\text{PF}_6]_2$
 - a. **bisphenanthrolineplatinum(II) hexafluorophosphate**
 - b. **CN=4**
 - c. **Tetrahedral or square planar**
- iv. $\text{K}_3[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$
 - a. **potassium hexacyanoferrate(III) dehydrate**
 - b. **CN=6**
 - c. **Octahedral or trigonal prism**
- v. $\text{Na}_4[\text{Fe}(\text{CN})_6]$
 - a. **sodium hexacyanoferrate(II)**
 - b. **CN=6**
 - c. **Octahedral or trigonal prism**
- vi. $[\text{Ni}(\text{en})_3][\text{ClO}_4]_2$
 - a. **tris(ethylenediamine)nickel(II) perchlorate**
 - b. **CN=6**
 - c. **Octahedral or trigonal prism**
- vii. $\text{Ni}(\text{CO})_4$
 - a. **Nickel tetracarbonyl**
 - b. **CN=4**
 - c. **Tetrahedral or square planar**

3. Give an example **not from the notes** of each of the following types of isomers
There are many correct answers

a. Ionization isomer



b. Linkage isomer



c. Coordination isomer



4. For each of the following ligands

a. Classify as sigma donor, pi donor or pi acceptor

b. Draw the structure and give the common abbreviation (if there is one)

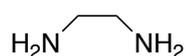
i. CO

pi acceptor



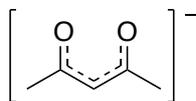
ii. Ethylenediamine

sigma donor
(en)



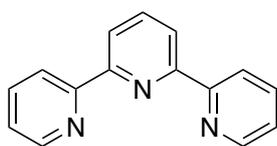
iii. Acetylacetonate

**pi donor
(acac)**



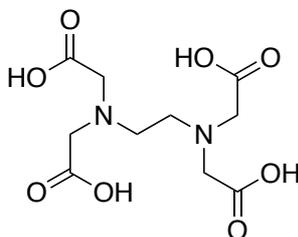
iv. Terpyridine

**Sigma donor
(tpy)
also pi acceptor**



v. ethylenediaminetetraacetic acid

pi donor through O (and also sigma donor)



vi. ammonia

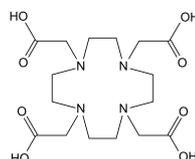
sigma donor



5. Why does K_i decrease with each subsequent step of a metal ligand complex formation equilibria?

As ligand is added to the metal ion M, ML forms first, then when more ligand is added, $[ML_2]$ rises sharply & $[ML]$ drops. With more added L, $[ML_2]$ drops and $[ML_3]$ rises etc., etc., Since the ligand addition to form a new complex is always reversible, an ML_n reaction progresses with greater n values and there are more ligands to dissociate (fall back off) and fewer places to put the new ligands in the coordination sphere, so it is expected that step- wise K_i 's would drop

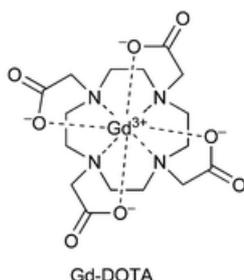
6. Gadolinium-Based Contrast Agents (GBCA) are intravenous drugs used in diagnostic imaging procedures to enhance the quality of magnetic resonance imaging (MRI) or magnetic resonance angiography (MRA). Gadolinium as a free ion and gadolinium complexes with low denticity ligands are known to be highly toxic. However, compounds such as Gd(DOTA) are generally non-toxic and can be used for such imaging purposes. The chemical structure of the DOTA ligand is shown below



- a. What is the denticity of the DOTA ligand? Draw how you think this ligand would bind to a gadolinium ion.

8 if only one O coordinates
12 if all CH₃COO⁻ act bidentate

Any drawing that shows all nitrogen and oxygen atoms forming coordination bonds with the Gd atom is sufficient.



This is how it actually bonds, from the literature.

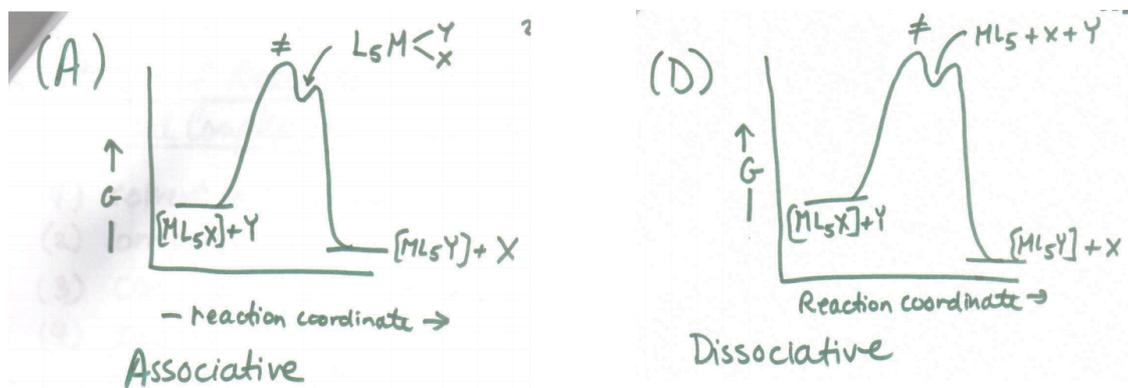
- b. What are the thermodynamic considerations that make this complex more stable than a complex with a comparable coordination number but low denticity ligands?

ENTROPY

- c. What is the name of the effect that you described in part b)

Chelate effect

7. The two main types of substitution reactions for coordination complexes are Associate and Dissociative. Draw the reaction coordinate diagram for each *and be sure to include all relevant labels*. What is the difference between these two types of reactions? How does the reaction rate give insight regarding the type of reaction?



Associative: new ligand binds to metal, forming 7-coordinate intermediate (in the case of octahedral substitution), before the original ligand leaves. A is a bimolecular process, and can be considered analogous to an S_N2 type of reaction.

Dissociative: the original ligand leaves, resulting in a 5-coordinate intermediate (in the case of octahedral substitution), and then new ligand then attacks. This is a unimolecular process, and can be considered analogous to an S_N1 type of reaction.

If the reaction rate is not affected by addition of the ligand, then it is dissociative. If addition of the ligand increases the reaction rate, then it is associative.

8. Compare and contrast the general trends for substitution reactions of octahedral and square planar complexes regarding:
- 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.

- 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

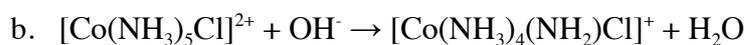
In octahedral complexes, steric bulk on the ligands will decrease the favorability of reactions that occur by an associative pathway.

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.

9. Describe in words each of the following reactions. What type of reaction is occurring?



Water exchange in the hexaaquanickel(II) ion



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



Aquation reaction of *cis*-Pt(PEt₃)₂(CN)(Cl)