CHEMISTRY 112 LECTURE

EXAM III

Transition Metals and Coordination Compounds

Chapter 24 pages 1046-1049,1052-1071

Background:
The colors associated with compounds provide insights into their structure and bonding. Transition metals display some of the most vibrant colors, this is due to their bonding Transition metals are capable of forming highly colorized ”complex ions”, $[Fe(H_2O)_6]^{3+}$, for example. These compounds are called **Coordination compounds.**

PART I COORDINATION COMPOUNDS

A. Tools- Coordinate Covalent Bonds

B. Ligands
(Chelating Agents/Complexing Agents)

1. Lewis bases/ e^- donor
2. uni, bi, tri, and polydentates
3. charged and neutral
4. Examples:
   NH_3, CO, CN^-, H_2O, Cl, NO^{2-}, EDTA, $C_2O_4^{2-}$

*__Note:__ you need to remember that *en*(ethylenediamine) and $C_2O_4^{2-}$ are bidentates. And EDTA is a tetradentate (polydentate)

a. Unidentates

b. Bidentates

c. Polydentates

B. Ligands, continued
(Chelating Agents/Complexing Agents)

5. Oxidation state of the metal

$[Cu(NH_3)_4]^{2+}$

$[Co(NH_3)_5Cl](NO_3)_2$

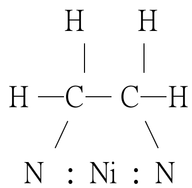
$[Cr(H_2O)_4Cl_2]$□ Cr(III)

$[Fe(en)_2Cl]$ Fe(III)

6. Coordination Number

The number of atoms attached to the metal is <u>coordination number</u> of the metal.

Ligand	Coordination #
[I:Hg:I]⁻ with Ï below Hg	
$[Ni(CO)_4]^{2+}$	
$[Co(CN)_4]^{3-}$	
$[Co(NH_3)_6]^{3+}$	



(Bidentate!)

C. Nomenclature

1 In naming salts, the cation is written before the anion

2 Within a complex ion, the ligands are named before the metal ion

3 Ligands are listed in alphabetical order

4 Prefixes that give the number of ligands are not considered in determining the alphabetical order

5 The names of anionic ligands end in the letter “o”

6 Neutral ligands generally have the molecule name
Exceptions are water and ammonia

7 A Greek prefix (di,tri,tetra, penta, and hexa) is used to indicate the number of each ligand.

8 If the complex is an anion, its name ends in -ate

9 The oxidation number of the metal is given in parentheses

10 Some metals which are part of the anion complex will use the latin name with -ate as an ending

11 When the name of the ligand has a prefix, use: bis(2), tris (3), tetrakis (4) to give the number of ligands in the compound

Cation Name	Latin Name	Anion Name
Copper Cuprum	Cuprate	
Gold	Aurum	Aurate
Iron	Ferrum	Ferrate
Lead	Plumbum	Plumbate
Silver	Argentum	Argentate
Tin	Stannum	Stannate

Anion Name	Ligand Name
Bromide, Br^-	Bromo
Carbonate, CO_3^{2-}	Carbonato
Chloride, Cl^-	Chloro
Cyanide, CN^-	Cyano
Fluoride, F^-	Fluoro
Hydroxide, OH^-	Hydroxo
*Oxalate, $C_2O_4^{2-}$	Oxalato *A bidentate!*
Oxide, O^{2-}	Oxo
Sulfate, SO_4^{2-}	Sulfato

* You need to remember that *Oxalate, $C_2O_4^{2-}$ and *Ethylenediammine,en are bidentates with 2 binding sites to the metal ion.

Molecule	Ligand Name
Ammonia, NH_3	Ammine
Carbon monoxide,CO	Carbonyl
Water	Aqua
*Ethylenediammine,en	Ethylenediammine *A bidentate!*

EXAMPLES:

$[Co(NH_3)_5Cl]Cl_2$ Pentaamminechlorocobalt(III) Chloride

$K_4[Fe(CN)_6]$ Potassium Hexacyanoferrate(II)

EXCERCISES

$[Co(NH_3)_4(H_2O)CN]Cl_2$

$Na_2[MoOCl_4]$

$Na[Al(OH)_4]$

$[Cr(H_2O)_4Cl_2]Cl$

$K_4[Ni(CN)_4]$

$[Co(en)_2F_2]$

Potassium amminepentachloroplatinate(IV)

Sodium hexabromoferrate(II)

Tetraamminedichlorocobalt(III)chloride

Practice

A. Name the following complex compounds of ions:

1. $[Al(H_2O)_6]Br_3$
2. $[Cr(NH_3)_6]Cl_3$
3. $K_3[FeF_6]$
4. $[Zn(OH)_4]^{-2}$
5. $[Co(H_2O)_4Cl_2]Cl$
6. $[Cu(NH_3)_4]^{+2}$
7. $K_2[SnCl_6]$
8. $[Pt(NH_3)_4Cl_2][PtCl_6]$

B. Write the formula for each of the following complex compounds or ions:

1. Hexaamminecobalt (III) chloride
2. Diamminetetrabromoplatinum (VI) bromide
3. Tetraaquacadmium (II) nitrate
4. Diamminesilver (I) ion
5. Sodium tetracyanocuprate (I)
6. Silver hexacyanoferrate(II)
7. Tertraammineoxalotonickel (II)

D. ISOMERISM IN COORDINATION COMPOUNDS

Isomers have the same chemical formula (chemical composition) but exhibit different properties due to different arrangements of atoms.

cis $[Pt(NH_3)_2]Cl_2$ is an orange isomer

trans $[Pt(NH_3)_2]Cl_2$ is a yellow isomer

Type I. Constitutional/Structural Isomers:

Different Sequences of Atoms

a. **Coordination Isomers** differ in that the ligands that are directly bonded to the metal, would be instead outside of the complex ion and be the counter ions.

(1)

(2)

b. **Linkage Isomers**

The binding site of the ligand is by a different atom on the ligand.

Structural/Constitutional Isomerism

Type 2 Stereoisomerism: Different Spatial Arrangements of Atoms

Compounds with the same sequence of atoms but different spatial arrangement of atoms

a. **Geometric Isomers/Diastereomers.**

The cis arrangement is where two ligands are on the same side of the metal atom and the trans arrangement is where the two ligands are across the metal atom from one another.

Stereoisomerism

1. Does $[Co(NH_3)_3(NO_2)_3]$ have geometric isomers?

<u>Stereoisomers</u> (continued)

b. **Fac - Mer Isomerism** occurs in a MA_3B_3 octahedral complex.
Example $Co(NH_3)_3Cl_3$

In the Fac Isomer, the 3 similar ligands are arranged at the 3 corners of a face of the octahedral. (Fac=Face)

In the Mer Isomer, the 3 similar ligands are arranged in an arc around the middle of the octahedron. (Mer = Meridian)

Stereoisomerism

Stereoisomers (continued)

C. Optical Isomers

Optical Isomers (enantiomers) are nonsuperimposable mirror images of one another.

1. only rotate
2. cannot flip

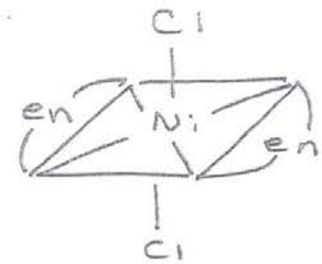
Stereoisomerism

Stereoisomers will have the same ordinary chemical and physical properties (i.e. color, density, formula weight, for example)

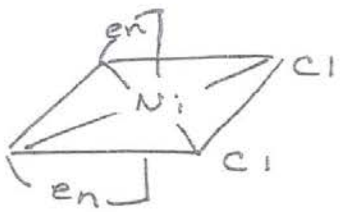
Optical Isomers are:

- Mirror Images
- Nonsuperimposable
- Enantiomers/optical isomers are optically active and will rotate a plane of light waves
- No plane of symmetry
- A Type of Stereoisomerism

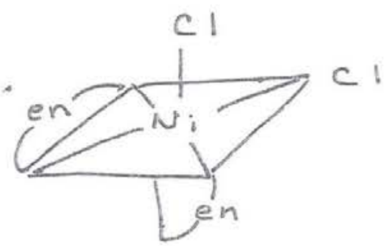
1.



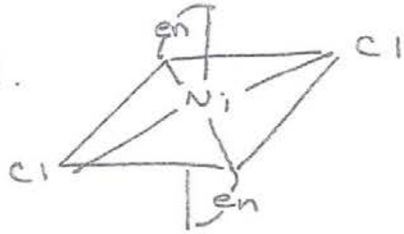
2.



3.



4.



E. Valence Bond Theory (VBT) of Complexes

Valence Bond Theory is the first theory to explain the electronic properties of complex ions.

1. Octahedral Complexes-metal coordination number = 6

Problems:

$Cr(NH_3)_6^{3+}$ (in $[Cr(NH_3)_6]Cl_3$)

Number of ligands around the central atom______________

Geometry

Magnetic Properties

Energy diagram

$Fe(H_2O)_6^{2+}$ (in $[Fe(H_2O)_6]Br_2$)

Number of ligands around the central atom______________

Geometry

Magnetic Properties

Energy diagram

Octahedral Complexes, cont'd

$Fe(CN)_6^{4-}$ (in $K_4[Fe(CN)_6]$)

Number of ligands around the central atom______________

Geometry

Magnetic Properties

Energy diagram

$Co(H_2O)_6^{2+}$ (in $[Co(H_2O)_6]Cl_3$)

Number of ligands around the central atom______________

Geometry

Magnetic Properties

Energy diagram

$Co(CN)_6^{3-}$ (in $[Co(CN)_6]Br_3$)

Number of ligands around the central atom______________

Geometry

Magnetic Properties

Energy diagram

$Cr(H_2O)_6^{3+}$ (in $[Cr(H_2O)_6]Cl_3$)

Number of ligands around the central atom______________

Geometry

Magnetic Properties

Energy diagram

$[Co(en)_3]^{3+}$

Number of ligands around the central atom______________

Geometry

Magnetic Properties

Energy diagram

2. Square Planar Complexes - d^8 metals/Coordination number = 4

Problems:

$Ni(CN)_4^{2-}$

Lewis electron dot structure

Number of ligands around the central atom______________

Geometry

Magnetic Properties

Energy diagram

$AuCl_4^-$

Lewis electron dot structure

Number of ligands around the central atom______________

Geometry

Magnetic Properties: Diamagnetic

Energy diagram

$Au(C_2O_4)_2^-$

Lewis electron dot structure

Number of ligands around the central atom______________

Geometry

Magnetic Properties: Consider $C_2O_4^{2-}$ as a strong field ligand

Energy diagram

3. Tetrahedral Complexes - Coordination number = 4

Problems:

$Ni(NH_3)_4^{2+}$

Lewis electron dot structure

Number of ligands around the central atom______________

Geometry

Magnetic Properties: paramagnetic

Energy diagram

$Cd(CN)_4^{-2}$

Lewis electron dot structure

Number of ligands around the central atom______________

Geometry

Magnetic Properties:

Energy diagram

Octahedral, Square Planar, and Tetrahedral Complexes
Problems:

$Co[(NH_3)_5H_2O]^{3+}$

Number of ligands around the central atom______________

Magnetic Properties

Energy diagram

Geometry

$FeCl_4^-$

Number of ligands around the central atom______________

Magnetic Properties

Energy diagram

Geometry

Octahedral, Square Planar, and tetrahedral Complexes, cont'd

$PdCl_4^{-2}$

Number of ligands around the central atom______________

Magnetic Properties: Diamagnetic

Energy diagram

Geometry

$ZnCl_4^{2-}$

Number of ligands around the central atom______________

Magnetic Properties:

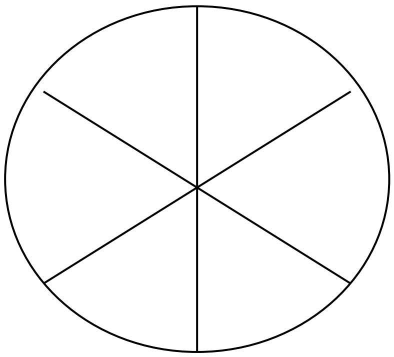
Energy diagram

Geometry

F. Crystal Field Theory (CFT)

Crystal Field Theory is a model that considers how ligands affect the electronic energy of the d orbitals. This theory best explains the color and magnetism of complex ions.

1. Color



Observed color	Absorbed color	E

2. The Energy Split of d Orbitals in an Octahedral Field of Ligands

Crystal field splitting is the energy difference between the 2 sets of d orbitals on the central metal atom, arising from the interaction of the orbitals with the electric field of the ligands

Problem: Calculate the crystal field splitting energy if a complex ion absorbed a light where: $\lambda = 589$ nm

3. Strong and Weak Field Ligands

Strong Field Ligands

Weak Field Ligands

$I^- < Cl^- < F^- < OH^- < H_2O < SCN^-\ NH_3 < en\ ,\ NO_2^- < CN^- < CO$

Weaker field Ligands ⟶ Stronger Field Ligands

Smaller Δ ⟶ Larger Δ

Longer λ ⟶ Shorter λ

4. Transition Metal Complex Colors

The Color of Transition Metal complexes are due to the energy difference between the d orbital energy split between the eg and t2g orbitals.

CFT and VBT

5. High Spin and Low Spin Complexes

	Weak field ligands: $E_{pairing} > \Delta$	Strong field ligands: $E_{pairing} < \Delta$
d_2		
d_3		
d_4		
d_5		
d_6		
d_7		
d_8		
d_9		
d_{10}		

6. Magnetic Properities

The crystal field splitting energy affects the d-orbital occupancy and the magnetic properties (paramagnetic/diamagnetic) of the complex.

7. Why is Zn^{2+} colorless?

8. Tetrahedral and Square Planar Complexes:
   Ex. $Ni(NH_3)_4^{2+}$ vs $Ni(CN)_4^{2-}$

CFT PROBLEMS

1. $[Co(NO_2)_4(H_2O)_2]^{1-}$ & $[Co(NO_2)_4(NH_3)_2]^{1-}$
   a. Draw the CF splitting diagram
   b. Match the following observed colors to the correct complex: Green & Red
   c. Explain your answers
2. $[Co(OH)_6]^{4-}$ & $[Co(en)_3]^{2+}$
   a. Which complex is high spin? Low spin?
   b. Magnetism= Paramagnetic or Diamagnetic?
   c. Explain your answers
3. Give the VBTenergy diagam for:
   a. $[Cu(NH_3)_2 (NO) (Cl)]^{+}$
   b. $[Co(C_2O_4)_2I_2]^{2-}$ (high spin)
   c. $[Fe(CO)_2(en)_2]^{2+}$
4. $[NiX_6]^{3+}$ = yellow

   $[Ni(CN)_6]^{3-}$ = Orange

   $[NiI_6]^{3-}$ = Blue
   a. Is 'X' CO, NH_3, or NO_2
   b. Explain
5. If $[Ni(NH_3)_6]^{3+}$ is a blue colored complex, what color would you predict $[Ni(en)_3]^{3+}$ to be? Explain
6. $[FeCl_6]^{4-}$
   a. Draw the CF splitting diagram
   b. Is this complex high or low spin? Why
   c. Draw the VBT energy diagram
7. $[Ni(CO)_2(CN)_2]^{1+}$
   a. Draw the VBT energy diagram
   b. Draw all possible isomers. Label them.

PART II COMPLEX ION EQUILIBRIA
Chapter 16 pages 755-759
I. EQUILIBRIUM REVIEW

A. BACKGROUND

Consider the following reversible reaction:

$$a\,A \; + \; b\,B \; \leftrightarrows \; c\,C \; + \; d\,D$$

1. The forward reaction (→) and reverse (←) reactions are occurring simultaneously.

2. The rate for the forward reaction is equal to the rate of the reverse reaction and a dynamic equilibrium is achieved.

3. The ratio of the concentration of the products to reactants is constant.

B. THE EQUILIBRIUM CONSTANT - Types of K's

For

Gases	Kc & Kp
Acids	Ka
Bases	Kb
Solubility	Ksp
Ionization of water	Kw
General	Keq

C. Meaning of K

1. If K > 1, equilibrium favors the products
2. If K < 1 equilibrium favors the reactants
3. If K = 1, neither is favored

D. Equilibrium constant

For the reaction, aA + bB ⇆ cC + dD , The equilibrium constant, **K**, has the form:

$$K = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

II. SOLUBILITY PRODUCT CONSTANTS, Ksp

A. Meaning

B. **Solubility, s - {Molar solubility}**

1. AgCl

2. Ag_2S

C. **Solubility Limit -**

Point where precipitation begins

D. **Solubility Calculations**

Calculate the solubility of AgCl

IV. COMPLEX FORMATION

Complex Ion	K_f
$Ag(CN)_2^-$	3.0×10^{20}
$Fe(CN)_6^{4-}$	3.0×10^{35}
$Fe(CN)_6^{3-}$	4.0×10^{43}
$Hg(CN)_4^{2-}$	9.3×10^{38}
$Zn(CN)_4^{2-}$	4.2×10^{19}
AlF_6^{3-}	4×10^{19}
CdI_4^{2-}	1×10^{6}
$Ag(NH_3)_2^+$	1.7×10^{7}
$Cu(NH_3)_4^{2+}$	5.6×10^{11}
$Zn(NH_3)_4^{2+}$	7.8×10^{8}
$Al(OH)_4^-$	3×10^{33}
$Be(OH)_4^{2-}$	4×10^{18}
$Co(OH)_4^{2-}$	5×10^{9}
$Ni(OH)_4^{2-}$	2×10^{28}
$Pb(OH)_3^-$	8×10^{13}
$Sn(OH)_3^-$	3×10^{25}
$Zn(OH)_4^{2-}$	3×10^{15}
$Ag(S_2O_3)_2^{3-}$	4.7×10^{13}

The formation constant (stability constant), K_f, of a complex ion is the equilibrium constant for the formation of the complex ion.

The dissociation constant (instability), K_{inst} is the reciprocal of K_f

A. **Stepwise-formation constants are symbolized by K_i.**

$$Ni^{2+} + CN^- \rightleftarrows Ni(CN)^+ \quad K_1 = \frac{[Ni(CN)^+]}{[Ni^+][CN^-]}$$

$$Ni(CN)^+ + CN^- \rightleftarrows Ni(CN)_2 \quad K_2 = \frac{[Ni(CN)_2]}{[Ni(CN)^+][CN^-]}$$

$$Ni(CN)_2 + CN^- \rightleftarrows Ni(CN)_3^- \quad K_3 = \frac{[Ni(CN)_3^-]}{[Ni(CN)_2][CN^-]}$$

$$Ni(CN)_3^- + CN^- \rightleftarrows Ni(CN)_4^{2-} \quad K_4 = \frac{[Ni(CN)_4^{2-}]}{[Ni(CN)_3^-][CN^-]}$$

B. **Overall Constant**

$$Ni^+ + 4\ CN^- \rightleftarrows Ni(CN)_4^{2-} \quad K_f = K_1K_2K_3K_4 = \frac{[Ni(CN)_4^{2-}]}{[Ni^+][CN^-]^4}$$

PROBLEMS

1. What is the concentration of Ag^+ in solution when a 0.010 M solution of silver nitrate is made 0.50 M in aqueous ammonia?

2. Calculate the concentration of Fe^{3+} when 0.050 mole of Iron (III) nitrate is mixed with 1.00 liter of 1.50 M sodium cyanide solution

3. What is the Co (II) concentration when 3.00 g of $CoCl_2$ is added to 1.00 liter of 0.80 M NaOH?

4. What is the concentration of Cu (II) when 0.66 g of copper (II) sulfate is dissolved in 2.00 L of a 3.00 M aqueous ammonia solution?

5. 50.0 mL of 0.10 M zinc bromide is mixed with 50.0 mL of 2.00 M NaOH. What is the concentration of Zn^{2+}?

6. Calculate the concentration of Cd^{2+} in a solution prepared by dissolving 0.010 mol of $Cd(NO_3)_2$ in a liter of solution containing 2.00 M NH_3.

Complex Ions and the solubility of precipitates.

A ligand will increase the solubility some ionic compounds by forming a water soluble complex ion with the metal:

Problems:

1. What is the molar solubility of AgCl in 0.10 M NH_3?

2. Calculate the molar solubility of AgBr in 1.0 M NaCN.

3. Calculate the number of grams of zinc hydroxide that will dissolve in 2.00 M NaOH.