Transition Elements and Complexes

Only responsible for topics covered in class

Structure of complex compounds

Central **metal cation surrounded by ligands** (anions or molecules)

- Ligand is bonded to metal through an electron pair
- Ligands act like Lewis bases by donating an electron pair
- Ligands bond in first coordination sphere [does not dissociate in water]

Coordination number - the number of atoms bonded directly to metal
Shapes and coordination numbers shown below
Octahedral most important

![Diagram of coordination compounds](image)

- **Square Planar (4)**
- **Linear (2)**
- **Tetrahedral (4)**
- **Octahedral (6)**

Examples of metals that could be in center of each of these (see below):

<table>
<thead>
<tr>
<th>Pt - center</th>
<th>Ag – center</th>
<th>Cd – center</th>
<th>Co – center</th>
</tr>
</thead>
</table>

Examples of ammonia molecules acting as ligands for each of above complexes

Ammonia can donate pair of electrons :NH₃ toward metal to bond

\[
[Ag\,(NH₃)₂]^+
\]
\[
[Pt\,(NH₃)₄]^{2+}
\]
\[
[Cd\,(NH₃)₄]^{2+}
\]
\[
[Co\,(NH₃)₆]^{3+}
\]
Pair of electrons on ligand donate to metal

http://www.chemguide.co.uk/inorganic/complexions/whatis.html

Can be bonded through ion or molecule

The active lone pair (in red) forms coordinate bonds with metal ions.

Charge of complex can be positive or negative and is the sum of parts

Most stable complexes metal ions that are transition elements or Group 3 (IIIA) or Group 4 (IVA) metals.
  1) high positive charge
  2) small ionic radius

<table>
<thead>
<tr>
<th>Complex</th>
<th>Charge of Complex</th>
<th># of species in H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pt (NH₃)₆ Cl₄]</td>
<td>+4</td>
<td>5</td>
</tr>
<tr>
<td>[Pt (NH₃)₅ Cl] Cl₃</td>
<td>+3</td>
<td>4</td>
</tr>
<tr>
<td>[Pt (NH₃)₄ Cl₂] Cl₂</td>
<td>+2</td>
<td>3</td>
</tr>
<tr>
<td>[Pt (NH₃)₃ Cl₃] Cl</td>
<td>+1</td>
<td>2</td>
</tr>
<tr>
<td>[Pt (NH₃)₂ Cl₄]</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>K[Pt (NH₃) Cl₅]</td>
<td>-1</td>
<td>2</td>
</tr>
<tr>
<td>K₂[Pt Cl₆]</td>
<td>-2</td>
<td>3</td>
</tr>
</tbody>
</table>

Examples  [Pt (NH₃)₆ Cl₄] dissolves to [Pt(NH₃)₆]⁴⁺ and 4 Cl⁻  
          K₂[Pt Cl₆]  dissolves to 2 K⁺ and [Pt Cl₆]²⁻

The potassium and chlorine atoms not coordinated (outside of the [ ]) will dissociate in water. Platinum is 4⁺ charge

The ammonia molecules and chlorine ions coordinated (inside of the [ ]) will NOT dissociate in water.
Types of Ligands
Unidentate – one bond
Bidentate – two bonds  Ligand may form more than one bond with a metal

http://www.bgsu.edu/departments/chem/faculty/endres/ch128/Calcium.htm (1)
http://www.chemguide.co.uk/inorganic/complexions/whatis.html (2)

Multidentate ligands
Multidentate ligands can coordinate 2, 3, 4, 5, or 6 positions

Ethylenediaminetetraacetate (EDTA)

http://www.progressivegardens.com/growers_guide/plantnut.html

Can wrap around metal and bond at six positions in octahedral complex

EDTA used to bind to Hg to treat heavy metal poisoning, prevent atoms from binding in body
Porphyran and Hemoglobin – example of multidentate ligand

Men on average 5,200,000,000 5.2 billion red blood cells per cm$^3$ of blood
Woman about 4.6 billion RBCs
RBCs are 40 to 45% of blood
Each red blood cell contains several hundred thousand hemoglobin molecules


Porphyran- molecule can bind four nitrogen atoms with metal – quadridentate

Hemoglobin contains Fe$^{2+}$ that binds to oxygen
Hemoglobin picks up O$_2$ in lungs and releases in body tissue
Hemoglobin + O$_2$ $\rightleftharpoons$ oxyhemoglobin + H$_2$O
Fe octahedral ligand: 4 to ring, 1 to protein, and 1 to O$_2$ or water

Images below from varied websites
Fe octahedral ligand: 4 to ring, 1 to protein, and 1 to O₂ or water
Sickle Cell Anemia change in an amino acid sequence in protein changes behavior of hemoglobin and can change shape and behavior of red blood cells

“People with this disorder have atypical hemoglobin molecules called hemoglobin S, which can distort red blood cells into a sickle, or crescent, shape.”

Why is Carbon Monoxide Poison?
Chlorophyll contains Mg$^{2+}$ held by porphyrin ring and is the green pigment of plants that acts as catalyst for conversion of 
\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_12\text{O}_6\text{(glucose)} + \text{O}_2 \]

Chlorophyll absorbs sunlight


Basic structure of ring
Porphyrin- with substituted groups on it
Thermodynamic or Kinetic Limits

Labile complexes rapidly undergo reactions in which ligands are replaced
Nonlabile or inert complexes will not exchange ligands or will do so only very slowly

Distinction between rate (how fast, kinetics) and extent of reaction (how far, thermodyn.)

\[ [\text{Co} (\text{NH}_3)_6]^{3+} + 6 \text{H}_2\text{O} \rightleftharpoons [\text{Co} (\text{H}_2\text{O})_6]^{3+} + 6 \text{NH}_4^+ \]
\[ K = 10^{-34} \text{ reactants favored} \]
Products not form  (say it is thermodynamically limited)

\[ [\text{Co} (\text{NH}_3)_6]^{3+} + 6 \text{H}_3\text{O}^+ \rightleftharpoons [\text{Co} (\text{H}_2\text{O})_6]^{3+} + 6 \text{NH}_4^+ \]
\[ K = 10^{22} \text{ products favored} \]
This second reaction is a very slow process - can take weeks in dilute acid to convert so it is practically inert  (say it is rate limited)

Other cases may be very rapid exchange of ligands
Extra Material below (will not cover)

Naming Transition Compounds - Simple Nomenclature

1. If naming a salt, name the cation first

2. Name the parts of a complex in alphabetical order including anions, neutral molecules, and metal ions

3. Anionic ligands given -o ending

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Naming</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH⁻</td>
<td>hydroxo</td>
</tr>
<tr>
<td>O₂⁻</td>
<td>oxo</td>
</tr>
<tr>
<td>S²⁻</td>
<td>thio</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>chloro</td>
</tr>
<tr>
<td>F⁻</td>
<td>fluoro</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>carbonato</td>
</tr>
<tr>
<td>CN⁻</td>
<td>cyano</td>
</tr>
<tr>
<td>CNO⁻</td>
<td>cyanato</td>
</tr>
<tr>
<td>C₂O₄²⁻</td>
<td>oxalate</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>nitrato</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>nitro</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>sulfato</td>
</tr>
</tbody>
</table>

4. Neutral ligands names not changed except:

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Naming</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>aqua</td>
</tr>
<tr>
<td>NH₃</td>
<td>ammine</td>
</tr>
<tr>
<td>CO</td>
<td>carbonyl</td>
</tr>
<tr>
<td>NO</td>
<td>nitrosyl</td>
</tr>
</tbody>
</table>

5. Number of ligands indicated by a prefix (di-, tri-, tetra-, penta-, hexa-)
   and for multidentate (bis-, tris-, tetrakis-)

6. Oxidation number of metal is given as a Roman numeral in parentheses

7. If complex is an anion then ending –ate is used but not changed for neutral or cation

The following examples illustrate further applications of the IUPAC guidelines:

Na₂[FeEDTA]                  Sodium ethylenediaminetetraacetato ferrate (II)
[Co (en)₃] Cl₃              Tris(ethylenediamine) cobalt (III) chloride
[Zn (NH₃)₄] (NO₃)₂          Tetraamminezinc nitrate
K[Ag (CN)₂]                 Potassium Dicyanosilver (I)
[Rh (NH₃)₅ Br] Br₂          Pentaamminebromorhodium (III) bromide
Bonding in complexes

Ligands donate a pair of electrons to form coordinate covalent bonds with the central metal ion

More involved theories deal with details of
- Electronic configuration
- Electronic energy levels
- Spatial location of orbitals
- Valence Bond theory
- Crystal Field theory
- Molecular Orbital theory

Be aware that d²sp³ (or sp³d²) hybrid orbitals on metal from empty orbitals form octahedral spatial orientation