Coordination Number Six

Octahedral is a very important geometry. It is the starting point for the shapes of most transition metal complexes.

1. Regular Octahedron
   all distances
   are EQUIVALENT

2. Distorted Octahedron
   (axial distortion)
   \( a \neq b \)

3. Distorted Octahedron
   (Rhombic distortion)

4. Distorted Octahedron
   (trigonal distortion)
The last example, trigonal prismatic is not as stable as the regular octahedron, because L-L distances are not maximized in the trigonally distorted geometry. This is a rare geometry for ML₆ complexes

**Higher Coordination numbers**

**Seven**

- Pentagonal bipyramid
- Octahedron + an extra ligand
- Trigonal prism + an extra ligand
Eight

1. Cube $\rightarrow$ 2. square antiprism
twist one face

rotate the corners of
once face until it is $45^\circ$
out of phase

1. Cube $\rightarrow$ 2. dodecahedron
pull corners away
from each other

(Grab opposite ends & pull up & down)
Nomenclature of Coordination Complexes

Follow IUPAC rules very specific

Examples
1. mer–trichlorotris(triphenylphosphine)rhodium(I)
2. potassium tetrabromocuprate (II)
3. trans–dichlorotetraaquachromium (II) chloride

key aspects of these names
1. prefix cis, trans, mer, fac

1 define

2. Which ligands come first in a mixed – ligand complex

3. Which type of prefix bi, bis, tri, tris, tetra, tetrakis etc.,
4. oxidation state of the metal

5. Special issues such as

- Optical isomers
- Bridging vs. non-bridging
- Endings for ligands
  "ite" "ide" "ate" "o"
- Special names for ligands
- Charge on the compound

**Book gives 11 rules**

**Distill them down**

1. No spaces in name except if it is a salt, put a space between cation and anion, and the cation is first.
Name is organized according to:

Anionic Ligands/Neutral Ligands/Cationic Ligands/Metal Name/Oxidation state of Metal

Within these categories we must establish rules of:

- (a) alphabetical order
- (b) prefixes and suffixes for ligands
- (c) suffix or not for the metal

2 Prefixes and Suffixes

Prefixes

<table>
<thead>
<tr>
<th>Number</th>
<th>Prefix</th>
<th>Suffix</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>di</td>
<td>bis</td>
</tr>
<tr>
<td>3</td>
<td>Tri</td>
<td>tris</td>
</tr>
<tr>
<td>4</td>
<td>Tetra</td>
<td>tetrakis</td>
</tr>
<tr>
<td>4</td>
<td>Penta</td>
<td>pentakis</td>
</tr>
<tr>
<td>6</td>
<td>Hexa</td>
<td>hexakis</td>
</tr>
</tbody>
</table>

use di, tri etc., unless the ligand name already has one of these as part of it’s name then use bis, tris etc.
Suffixes
(a) anionic ligands end in “o”

- \text{ate} \rightarrow \text{ato} \quad \text{acetate} \quad \rightarrow \text{acetato}
- \text{id} \rightarrow \text{ido} \quad \text{nitride} \quad \rightarrow \text{nitrido}
- \text{ite} \rightarrow \text{ito} \quad \text{sulfite} \quad \rightarrow \text{sulfito}

\begin{align*}
\text{CH}_3\text{CO}_2^- & \quad \text{acetato} \\
\text{N}_3^- & \quad \text{nitrido} \\
\text{SO}_3^2 & \quad \text{sulfito}
\end{align*}

(b) neutral ligands are the same as molecule name with a few exceptions:

- \text{NH}_3 \quad \rightarrow \quad \text{M-NH}_3 \\
  \text{ammonia} \quad \text{ammine}

- \text{H}_2\text{O} \quad \rightarrow \quad \text{M-OH}_2 \\
  \text{water} \quad \text{aqua}

- \text{NO} \quad \rightarrow \quad \text{M-NO} \\
  \text{nitrogen} \quad \text{nitrosyl}

\text{monoxide}
CO → M-CO
  carbon         carbonyl
  monoxide

(c) organic groups (keep same name)

CH₃        M-CH₃
Methyl     methyl

C₆H₅      phenyl

(d) metal suffix

(i) if compound is neutral or cationic [RuL₆]³⁺
  no suffix ruthenium → ruthenium

(ii) if compound is anionic, then metal name is
  changed to ate ending
  [RuL₆]³⁻ ruthenium → ruthenate

[3] Within each category of ligand, alphabetize the
ligands within each group if more than one type is
present (anions first, neutral second, cationic third)
(NOTE: don’t count bi, tri etc., in alphabetizing)
Metal oxidation state is written in parentheses in Roman numerals at the end.

Special Characters and abbreviations

(a) Geometrical isomers
- cis, trans arrangements for two types of X ligands

\[
\begin{array}{c}
\text{cis} \\
\text{trans}
\end{array}
\]

- fac, mer arrangements for three types of X ligands

\[
\begin{array}{c}
\text{fac} \\
\text{mer}
\end{array}
\]
(b) optical isomers
   use symbols $\Delta$ and $\Lambda$

(c) bridging ligands
   - use prefix $\mu$
     "mu"
   - if two of the same kind
     di-$\mu$

M-$\text{NO}_2^-$ nitro
M-$\text{ONO}^-\text{ nitrite}$

(a) $\text{H}_2\text{O}$ (hydrate)
   Water can be in a formula like this $\text{MCl}_6\cdot\text{nH}_2\text{O}$
   (Number of water molecules of hydration)
   - $\text{H}_2\text{O}$ monohydrate
   - $2\text{H}_2\text{O}$ dihydrate etc.
Now, start practicing!

cation anion

Ex #1 \([\text{Cr(H}_2\text{O)}_4\text{Cl}_2]\text{Cl}\)

four two
neutral anionic
ligands ligands

dichlorotetraaquachromium(III) chloride

four ligands four ligands
cation/ anion/

Ex #2 \([\text{Pt(py)}_4]\ [\text{PtCl}_4]\)
tetrapyridineplatinium(II)tetrachloroplatinate(II)

normal ending ate ending

molecule is neutral

Ex #3 \(\text{Pt(acac)(NH}_3)(\text{Cl})\)

↑ ↑ ↑
Anionic neutral Anionic
ligand ligand ligand

acetylacetonatochloroammineplatinum(II)
salt composed of a cation and n anion

Ex #4 \[ \text{K[FeCl}_4\text{]} \] Fe is Fe(III) called ferrous

\[ \text{anionic ligand} \]

potassium tetrachloroferrate(III)

(iron is not written as ironate!)

\[ \text{neutral ligand} \]

Ex #5 \[ \text{[Co(en)}_3\text{]}_2\text{(SO}_4\text{)}_3 \]

Cation anion

Ratio of cation to anion is 2:1
two \([\text{Co(en)}_3\text{]}^{2+}\) units
three ethylenediamine (en) ligands
\[ \text{bis\{tris[ethylenediamine)cobalt(III)}\text{\}} \text{ sulfate} \]
Ex #6 \[\text{[Fe(H}_2\text{O)}_6]\text{Br}_2\]
\text{cation anion}
\text{hexaaquairon(II) bromide}

\begin{align*}
\text{neutral ligand} & \quad \text{anionic ligand} \\
\end{align*}

Ex #7 \[\text{[Rh(NH}_3)_5\text{Cl]}\text{Cl}_2\]
\text{Cation Anions}
\text{chloropentaamminerhodium(III) chloride}

Practice drawing the structure based on a formula

Mer-trihydrotris(triphenylphosphine)rhodium(III)

\begin{align*}
\text{mer is 3 groups} & \quad \text{around the perimeter}
\end{align*}
fac-trihydrotris(triphenylphosphine)rhomdium(III)
Stability of Complexes in Solution

Stepwise formation of metal ligand complexes involve Equilibria

(1) \[ M + L \leftrightarrow ML \]

\[ K_1 = \frac{[ML]}{[M][L]} \]

(2) \[ ML + L \leftrightarrow ML_2 \]

etc.,

until

last step \[ \downarrow \]

(6) \[ ML_5 + L \leftrightarrow ML_6 \]

\[ K_6 = \frac{[ML_6]}{[ML_5][L]} \]

- Six equilibria are involved in the formation of \( ML_6 \) from \( M \) and \( 6L \).

- Each \( K_i \) is a step-wise formation constant

- Concentration of \([L] \) determines the relative concentrations of products
Overall (rather than stepwise) Equilibrium Constants are:

\[ M + L \leftrightarrow ML \quad \beta_1 = \frac{[ML]}{[M][L]} \]

\[ M + 2L \leftrightarrow ML_2 \quad \beta_2 = \frac{[ML_2]}{[M][L]^2} \]

\[ M + 3L \leftrightarrow ML_3 \quad \beta_3 = \frac{[ML_3]}{[M][L]^3} \]

\[ M + 6L \leftrightarrow ML_6 \quad \beta_6 = \frac{[ML_6]}{[M][L]^6} \]

Take \( \beta_3 \) for example:

\[ \beta_3 = \frac{[ML_3]}{[M][L]^3} \cdot \frac{[ML][ML_2]}{[ML][ML_2]} \]

rearrange...

\[ \beta_3 = \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \frac{[ML_3]}{[ML_2][L]} \]
Then $\beta_3 = K_1 \cdot K_2 \cdot K_3$

or the product of all three step-wise reactions

**Equilibrium Constants**

in general: $\beta_K = K_1 \cdot K_2 \cdot K_3 \ldots K_k$

| overall formation constants | stepwise formation constants |

Usually $K_i$ decreases with each subsequent step.

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.
\[
\text{Cd}^{2+} + \text{NH}_3 \leftrightarrow [\text{Cd(NH}_3)]^{2+} \quad K_1 = 10^{2.65}
\]

\[
[Cd(NH_3)_3]^{2+} + \text{NH}_3 \leftrightarrow [Cd(NH_3)_4]^{2+} \quad K_4 = 10^{0.93}
\]

formation of \([\text{Cd(NH}_3)_4]^{2+}\) illustrates the decrease in equilibrium constant with added L groups.

**Q.** What are formation constants useful for?

**A.** Separation of ions in the presence of each other

Ex. EDTA\(^2-\) selectively pulls \(M^{2+}\) out of water in the presence of more highly charged cations

EDTA is an aminopolycarboxylic acid and a colorless, water-soluble solid. Its conjugate base is ethylenediaminetetraacetate. It is widely used to dissolve limescale (which is mostly CaCO\(_3\)). Its usefulness arises because of its role as a hexadentate ("six-toothed") ligand and chelating agent, i.e., its ability to sequester metal ions such as Ca\(^{2+}\) and Fe\(^{3+}\). After being bound by EDTA into a metal complex, metal ions remain in solution but exhibit diminished reactivity. EDTA is produced as several salts, notably disodium EDTA, calcium disodium EDTA, and tetrasodium EDTA.
The hexadentate ligand “wraps itself” around the $M^{2+}$ center. EDTA binding brings up another important stability issue, namely the **Chelate Effect**

$:\text{NH}_3 \quad \text{versus} \quad \text{NH}_2\text{NH}_2$

$\text{H}_3\text{N} \quad \text{NH}_3 \quad \text{versus} \quad \text{NH}_2\text{NH}_2$

ethylenediamine (en)

.... Why?
To reverse the reaction of M + en is more difficult than for M+2NH$_3$. If one of the NH$_2$ groups “falls off” there is still another bond to hold it onto the metal easy to reverse “partial dissociation”

\[
\beta_6 = 10^{8.6} \quad \beta_3 = 10^{18.3}
\]

………… [Ni(en)$_3$]$^{2+}$ is $10^{10}$ times more stable!

Q. Why? The bonds are very similar!
A. $\Delta G^\circ$ is affected by enthalpic and entropic contributions.
\[ \Delta G^\circ = RT \ln K = \Delta H^\circ - T \Delta S^\circ \]

..... recall

in the \([\text{Ni(NH}_3\text{)}_6]^2+\) vs \([\text{Ni(en)}_3]^2+\) case, we can perform a reaction and determine \(K\).

\[
[\text{Ni(NH}_3\text{)}_6]^2+ + 3(\text{en}) \leftrightarrow [\text{Ni(en)}_3]^2+ + 6\text{NH}_3
\]

\[
K = 10^{9.7}
\]

\[
\Delta G^\circ = -RT \ln K
= -67 \text{ kJ/mol}
\]

\[
\Delta H^\circ = -T \Delta S^\circ = -67 \text{ kJ/mol}
\]

If we know that \(\Delta H^\circ\) is: \(\Delta H^\circ = -12 \text{ kJ/mol}\)
Then \(-T \Delta S = -55 \text{ kJ/mol}\)

Note, both enthalpy and entropy considerations favor the \textit{chelate complex}, but the entropy effect is much more important
**Bottom line:**
The **Chelate Effect** is Essentially an Entropic Effect.

In order to understand this: the Ni reaction must be examined in more detail.

\[
[Ni(H_2O)_6]^{2+} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O
\]
The number of “particles’ hasn’t changed from Reactant to products (7 in both cases)

**BUT…**

\[
[Ni(H_2O)_6]^{2+} + 3en \rightarrow [Ni(en)_3]^{2+} + 6H_2O
\]
4 particles \quad 7 particles

The reaction is entropically driven to the right \(\rightarrow\) is more disordered!
Reactivity Patterns of Coordination Compounds

Covers a very large number of issues in transition metal chemistry.

Main ones to be highlighted in this course:

- Substitution
- Electron – Transfer
- Isomerization

*The correlation of these reactions with electronic and molecular structure is the essence of much of inorganic chemistry.

Octahedral Complexes

Substitution chemistry

1. Labile – ligands that are easily substituted

   Lability – refers to the ability of a coordination complex to lose one or more of it’s ligands with others in solution
2. **Inert** – refers to the lack of ability of a coordination complex to lose one or more of its ligands with others in solution.

* “Labile versus Inert” is not the same as ……“Unstable versus Stable.”

**Stability refers to the tendency of a species to exist which is a Thermodynamic issue whereas Labile versus Inert is a Kinetic Issue**

\[\text{[Co(NH}_3\text{)}_6\text{]}^{3+} \text{ is not a very “stable” compound thermodynamically judging by:} \]

\[\text{[Co(NH}_3\text{)}_6\text{]}^{3+} + 6\text{H}_3\text{O}^+ \leftrightarrow \text{[Co(H}_2\text{O)}_6\text{]}^{3+} + 6\text{NH}_4^+ \]

\[K = 10^{25} \text{ for left to right!} \]

But the reaction takes months because of the “inertness” of the compound. The reaction is very slow.

**Working definition of inert and labile**

labile reactions <1 minute half-life (over in time of mixing)

inert reactions >1 minute half-life (can easily be studied by conventional means)
Two Types of Ligand Substitution:

1. Associative (A) (addition-elimination)
2. Dissociative (D)

(A)

1. \([L_5MX] + Y \rightarrow [L_5M(X)Y] \rightarrow [L_5MY] + X\)

\[7\text{-coord. intermediate}\]

Y directly binds before X leaves

(D)

2. \([L_5MX] \rightarrow [L_5M] + X \rightarrow [L_5MY] + X\)

\[5\text{-coord. intermediate}\]

In both cases, the first step, which is slow, is rate-determining.

(A) is bimolecular process
(D) is unimolecular process
(A) & (D) are just extremes of what can really happen

**Associative** may not involve a “real” 7-coordinate intermediate. Some “degree” of bond-breaking to X and bond-making to Y is happening in the intermediate (or transition state complex)

**Dissociative**, likewise, may also have most of the M-X bond broken (but not all) before the near M-Y bond forms.

Real life is rarely simple!
(D) Dissociative

(ID) Interchange - Dissociative
(A) 

\[ \text{reaction coordinate} \rightarrow \text{Associative} \]

\[ \begin{align*} 
&[\text{ML}_5\text{X}] + Y \\
&\rightarrow
\\
&[\text{ML}_5\text{Y}] + X 
\end{align*} \]

(I_A) Interchange - Associative

\[ \begin{align*} 
&\text{reaction coordinate} \\
&\rightarrow
\\
&[\text{ML}_5\text{X}] + Y \\
&\rightarrow
\\
&[\text{ML}_5\text{Y}] + X 
\end{align*} \]
Types of Reactions in Octahedral Metal Complex Substitution Chemistry

(1) Solvent interactions
(2) ion-pair formation
(3) conjugate-base formation
(4) anation reactions
(5) aquation reactions
   acid, base hydrolysis
(6) ligand assisted reactions

Square-Planar Substitution Reactions

(1) charge effects
(2) steric effects
(3) entering ligand effects
(4) stereochemistry