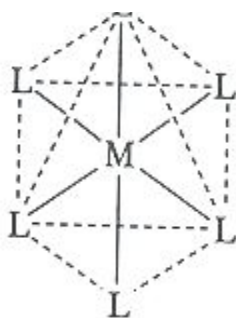


Coordination Number Six

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

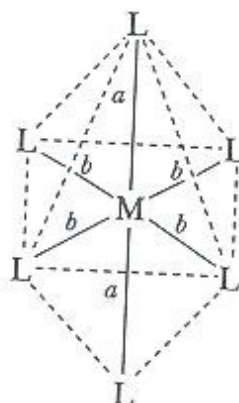
1. Regular Octahedron

all distances
are EQUIVALENT

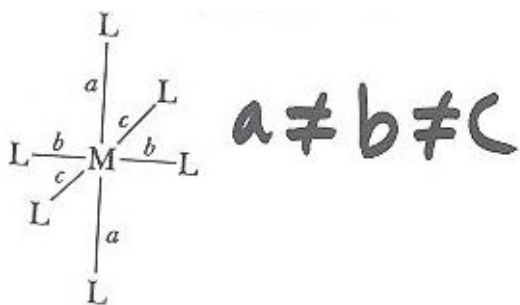


2. Distorted Octahedron (axial distortion)

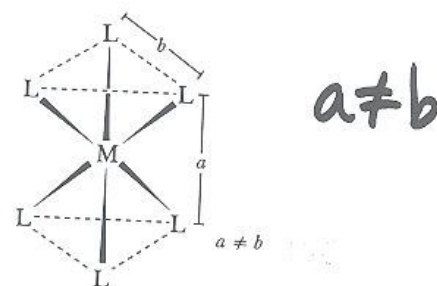
$a \neq b$



3. Distorted Octahedron (Rhombic distortion)



4. Distorted Octahedron (trigonal distortion)



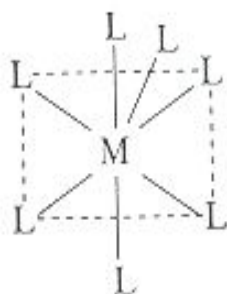


The last example, trigonal prismatic is not as stable as the regular octahedron, because L-L distances are not maximized in the trigonally distorted geometry. This is a rare geometry for ML_6 complexes

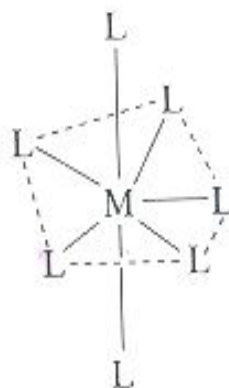
Higher Coordination numbers

Seven

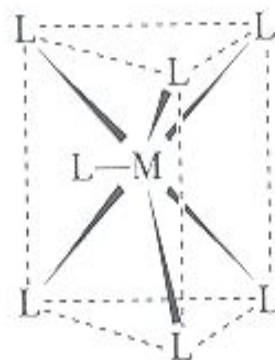
Pentagonal
bipyramid



Octahedron
+ an
extra
ligand



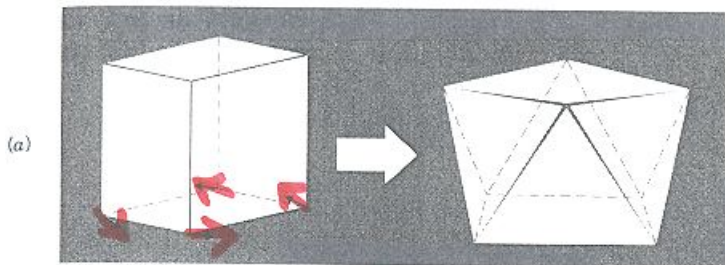
Trigonal
prism
+ an
extra
ligand



Eight

1. Cube →

2. square antiprism
twist one face

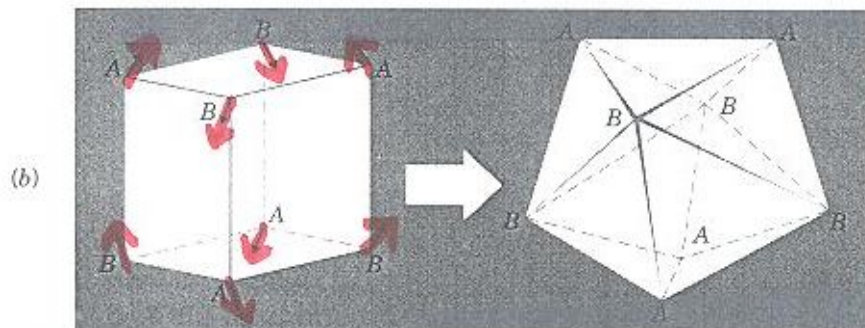


rotate the corners of
once face until it is 45°
out of phase



1. Cube →

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

2 di	bis
3 Tri	tris
4 Tetra	tetrakis
4 Penta	pentakis
6 Hexa	hexakis

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”

<u>ate</u> → ato	acet <u>ate</u>	→ acet <u>ato</u>
<u>ide</u> → ido	nitri <u>de</u>	→ nitri <u>do</u>
<u>ite</u> → ito	sulf <u>ite</u>	→ sulf <u>ito</u>

CH_3CO_2^- acetato

N_3^- nitrido

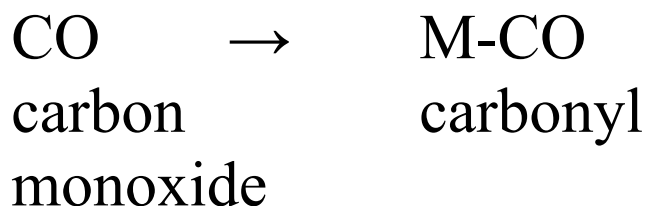
SO_3^{2-} sulfito

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

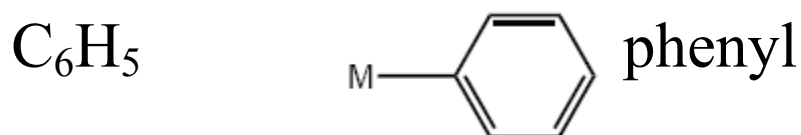
NH_3	→	M-NH_3
ammonia		ammine

H_2O	→	M-OH_2
water		aqua

NO	→	M-NO
nitrogen monoxide		nitrosyl



(c) organic groups (keep same name)



(d) metal suffix

- (i) if compound is neutral or cationic $[\text{RuL}_6]^{3+}$
no suffix ruthenium → ruthenium
- (ii) if compound is anionic, then metal name is
changed to ate ending
 $[\text{RuL}_6]^{3-}$ 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)

4

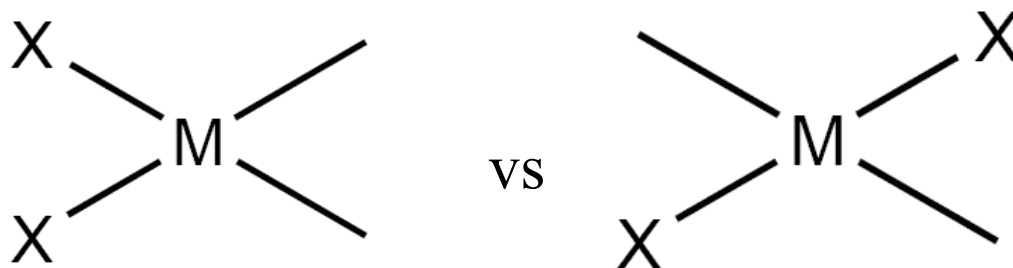
Metal oxidation state is written in parentheses in Roman numerals at the end

5

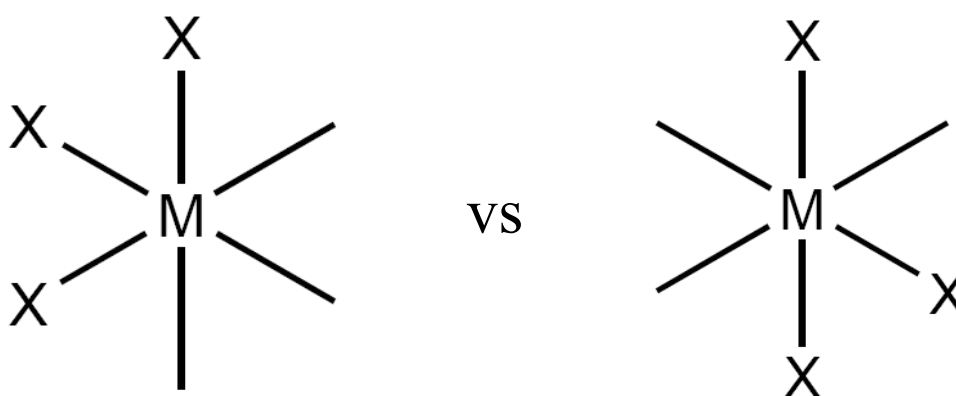
Special Characters and abbreviations

(a) Geometrical isomers

cis, trans arrangements for two types of X ligands

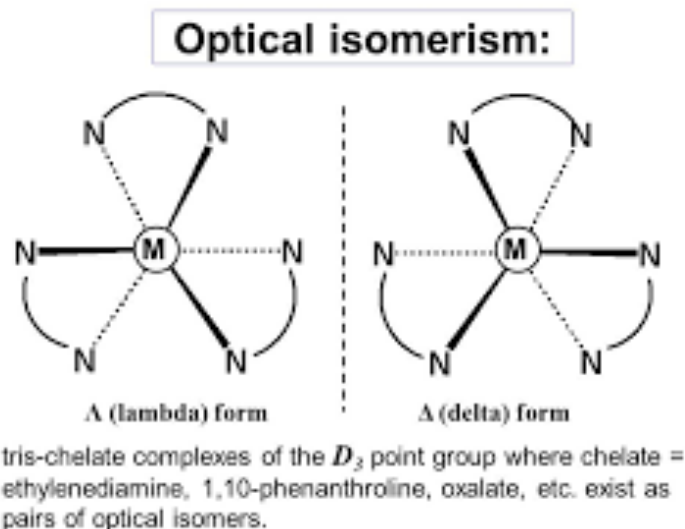


fac, mer arrangements for three types of X ligands



(b) optical isomers

use symbols Δ and Λ



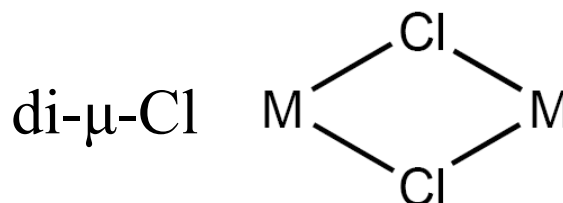
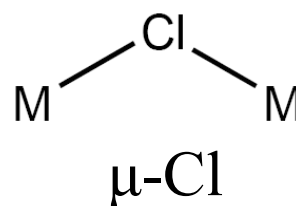
(c) bridging ligands

- use prefix μ

“mu”

- if two of the same kind

di- μ



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

$M-\text{ONO}^-$ nitrite

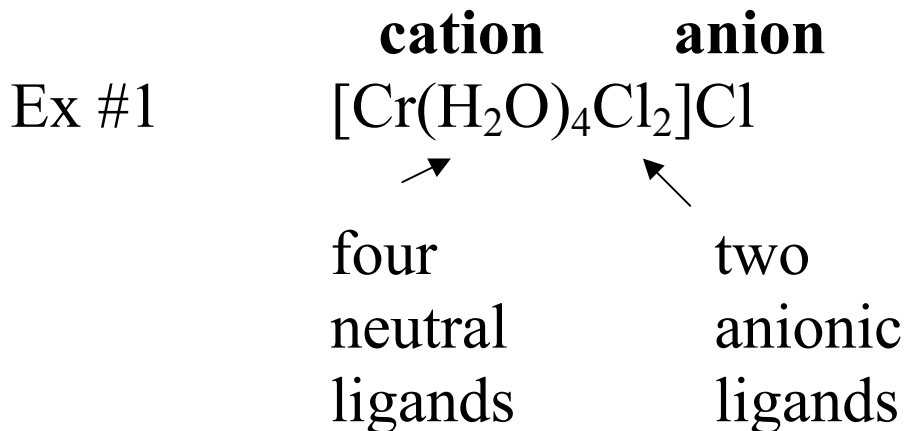
(a) H_2O (hydrate)

Water can be in a formula like this $\text{MCl}_6 \cdot n\text{H}_2\text{O}$

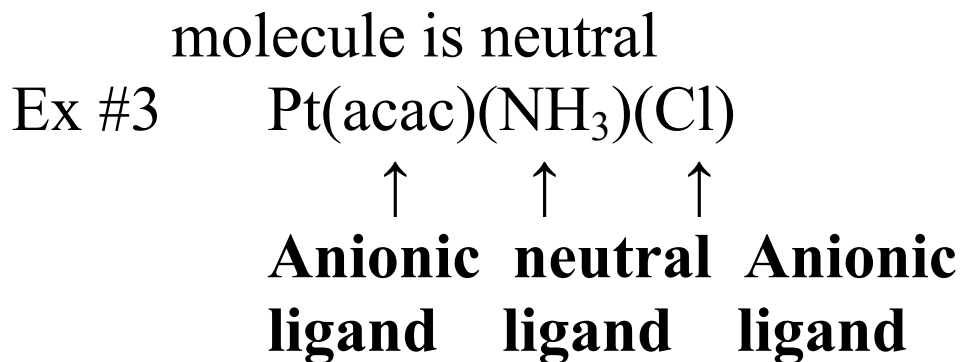
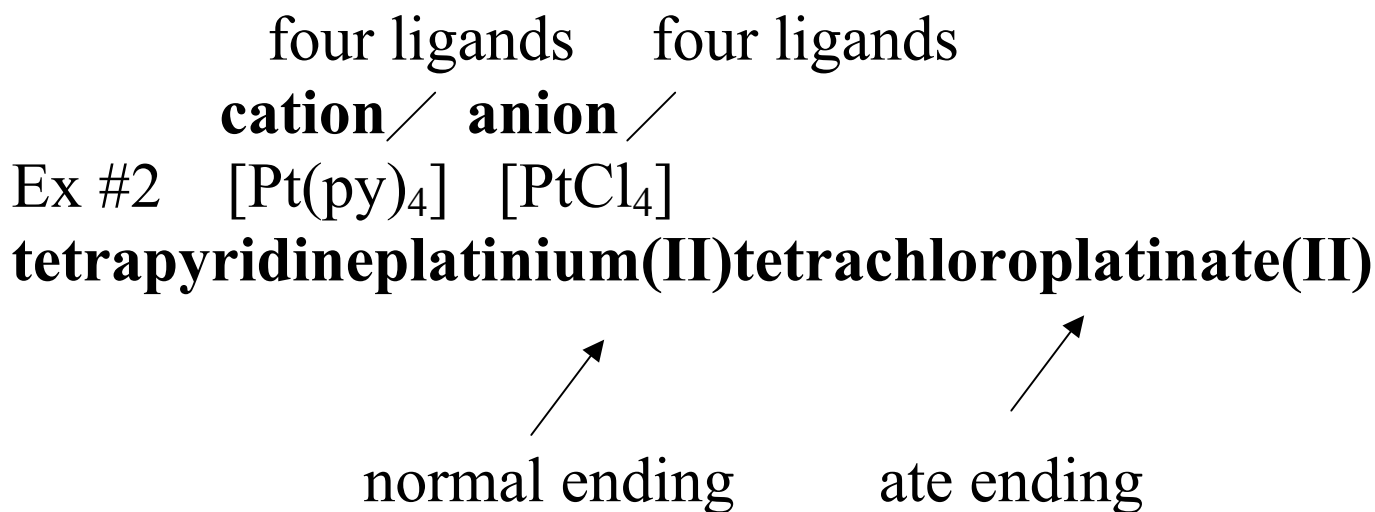
(Number of water molecules of hydration)

- H_2O monohydrate
- $2\text{H}_2\text{O}$ dihydrate etc.

Now, start practicing!



dichlorotetraaquachromium(III) chloride



acetylacetonatochloroammineplatinum(II)

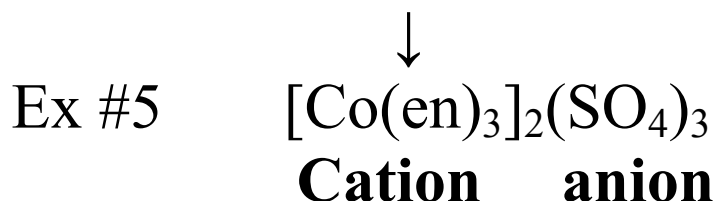
salt composed of a cation and n anion



potassium tetrachloroferrate(III)

(iron is not written as ironate!)

neutral ligand



Ratio of cation to anion is 2:1

two $[\text{Co}(\text{en})_3]^{2+}$ units

↓ three ethylenediamine (en) ligands

↓

bis{tris[ethylenediamine)cobalt(III)} sulfate

water



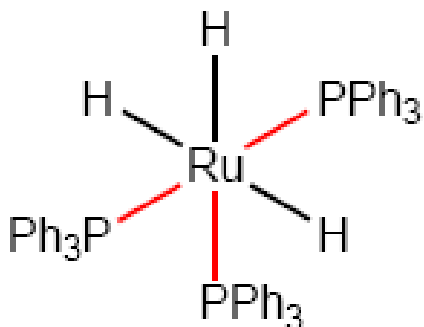
Ex #6 $[\text{Fe}(\text{H}_2\text{O})_6]\text{Br}_2$
 cation anion
hexaaquairon(II) bromide

neutral ligand anionic ligand

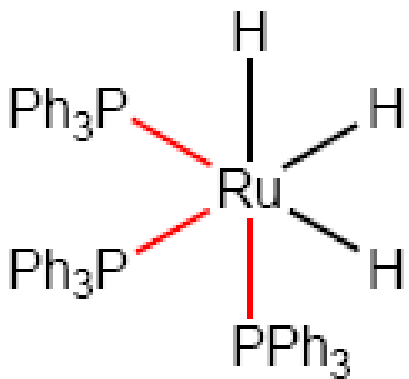
Ex #7 $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
 Cation Anions
chloropentaamminerhodium(III) chloride

Practice drawing the structure based on a formula

Mer-trihydrotris(triphenylphosphine)rhodium(III)

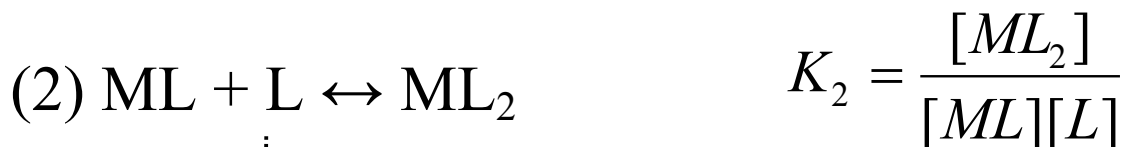


mer is 3 groups
around the perimeter

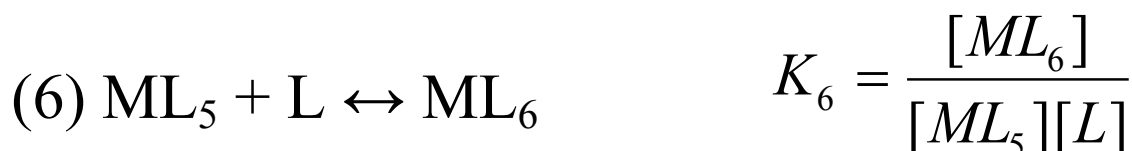
fac-trihydrotris(triphenylphosphine)rhodium(III)

Stability of Complexes in Solution

Stepwise formation of metal ligand complexes involve Equilibria



etc.,
until
last step ▼

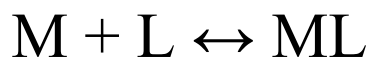


- Six equilibria are involved in the formation of ML_6 from M and 6L.
- Each K_i is a step-wise formation constant
- Concentration of [L] determines the relative concentrations of products

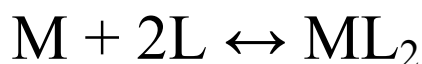
Overall (rather than stepwise)

Equilibrium Constants are:

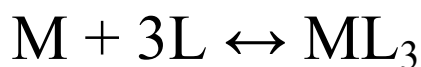
multiply
num. &
denom. by
this (really
just¹)



$$\beta_1 = \frac{[ML]}{[M][L]}$$



$$\beta_2 = \frac{[ML_2]}{[M][L]^2}$$



$$\beta_3 = \frac{[ML_3]}{[M][L]^3}$$



$$\beta_6 = \frac{[ML_6]}{[M][L]^6}$$

Take β_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: $\beta_K = K_1 \cdot K_2 \cdot K_3 \dots K_k$

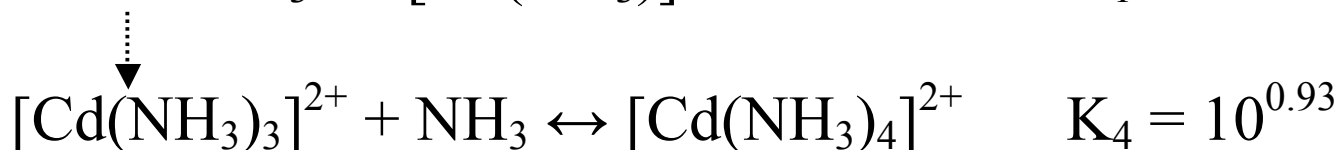
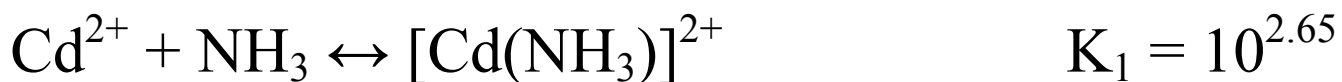
**overall formation
constants**

**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.,

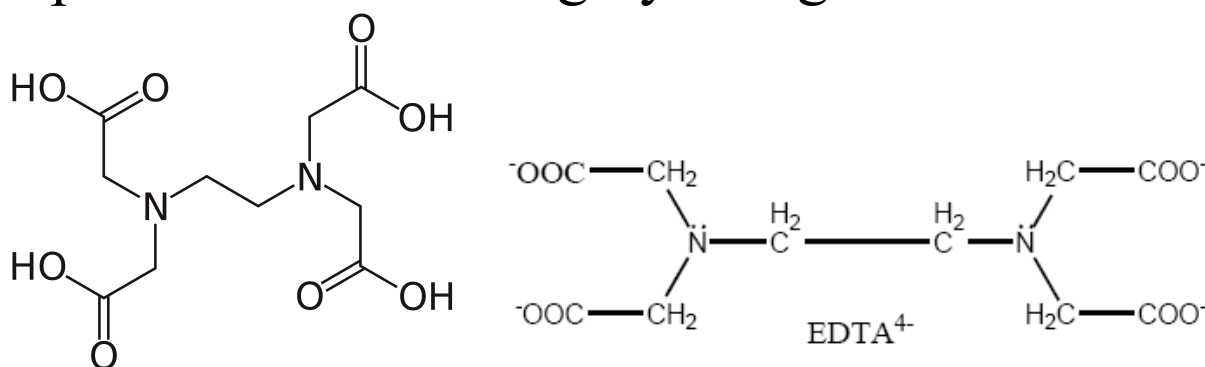
Since the ligand addition to form a new complex is always reversible, an ML_n reaction progresses with greater n values and there are more ligands to dissociate (fall back off) and fewer places to put the new ligands in the coordination sphere, so it is expected that step-wise K_i 's would drop.



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

Q. What are formation constants useful for?

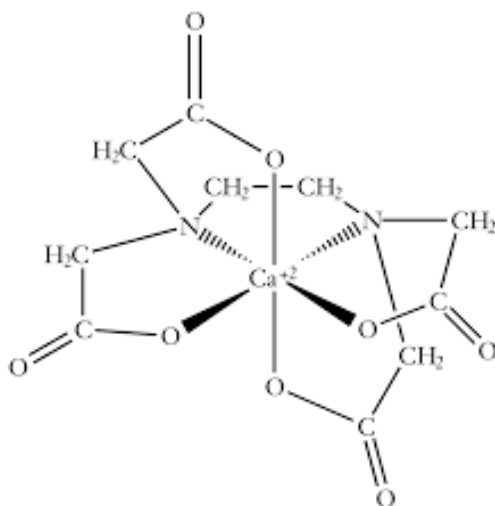
A. Separation of ions in the presence of each other
Ex. EDTA^{2-} selectively pulls M^{2+} out of water in the presence of more highly charged cations



.....
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 five-membered ring

much more
independent



The hexadentate ligand “wraps itself” around the M^{2+} center.

EDTA binding brings up another important stability issue, namely the **Chelate Effect**

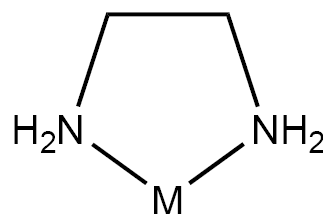
$:\text{NH}_3$
ammonia

versus



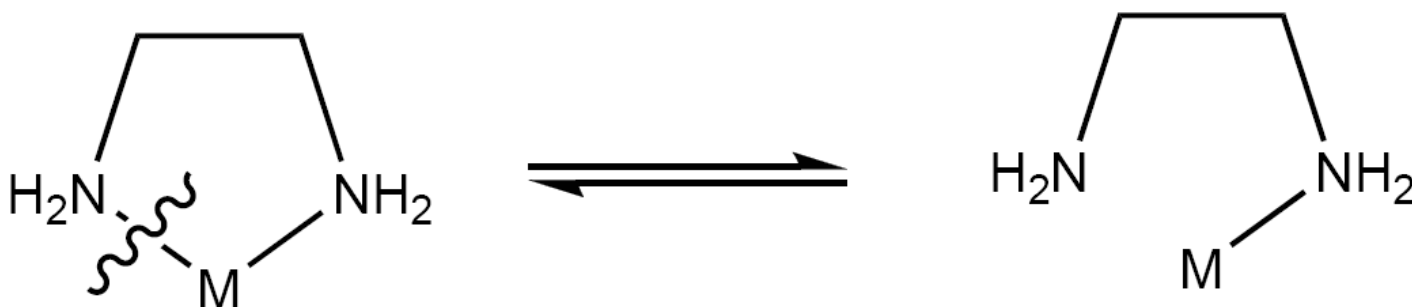
$\text{H}_3\text{N} \quad \text{NH}_3$
M
ethylenediamine (en)

versus

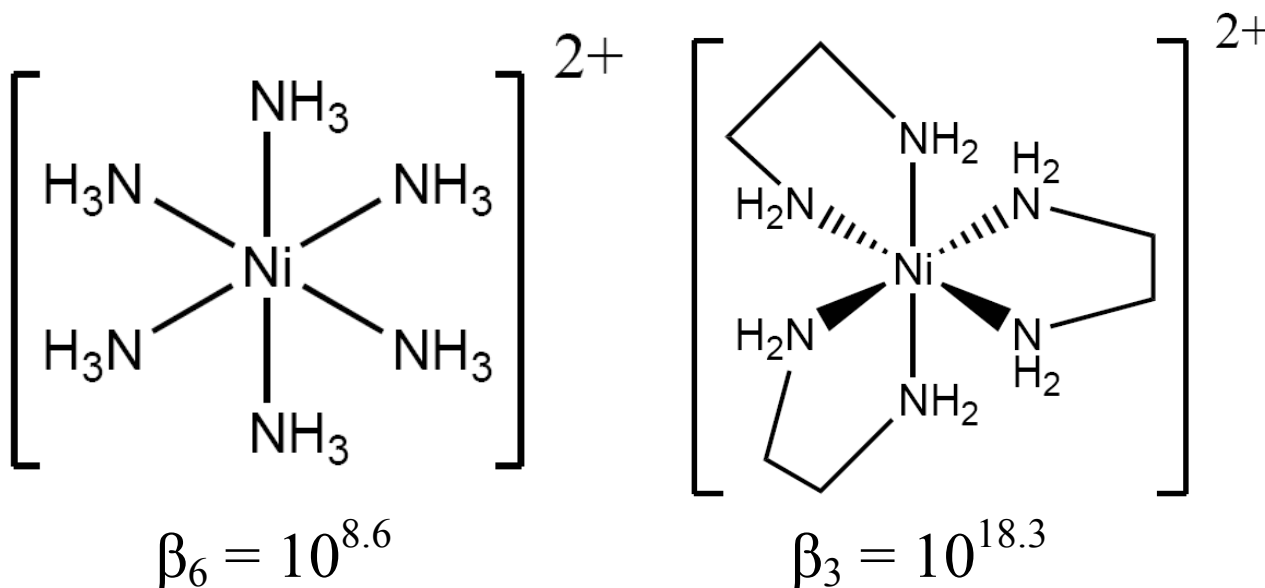


.... Why?

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”



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

Q. Why? The bonds are very similar!

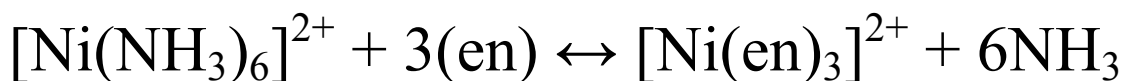
A. ΔG° is affected by enthalpic and entropic contributions.

$$\Delta G^\circ = RT \ln K_{\text{H}_2\text{O complex}}^{\text{chelate}} = \Delta H^\circ - T\Delta S^\circ$$

..... recall



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



$$\begin{aligned} K &= 10^{9.7} \\ \Delta G^\circ &= -RT \ln K \\ &= -67 \text{ kJ/mol} \end{aligned}$$

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

If we know that ΔH° is: $\Delta H^\circ = -12 \text{ kJ/mol}$

Then $-T\Delta S = -55 \text{ kJ/mol}$

Note, both enthalpy and entropy considerations favor the 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.



The number of “particles” hasn’t changed from Reactant to products (7 in both cases)

BUT....



4 particles

7 particles

The reaction is entropically driven to the right
→ 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

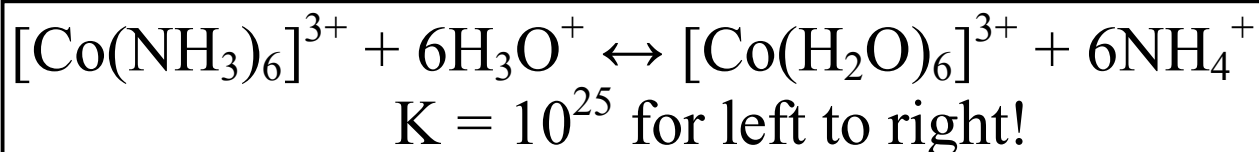
1. Labile – ligands that are easily substituted
Lability – refers to the ability of a coordination complex to lose one or more of its ligands with others in solution

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

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



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

Working definition of inert and labile

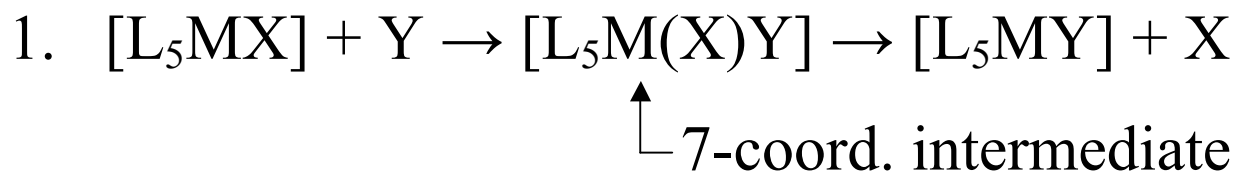
labile reactions <1 minute half-life (over in time of mixing)

inert reactions >1 minute half-life (can easily be studied by conventional means)

Two Types of Ligand Substitution:

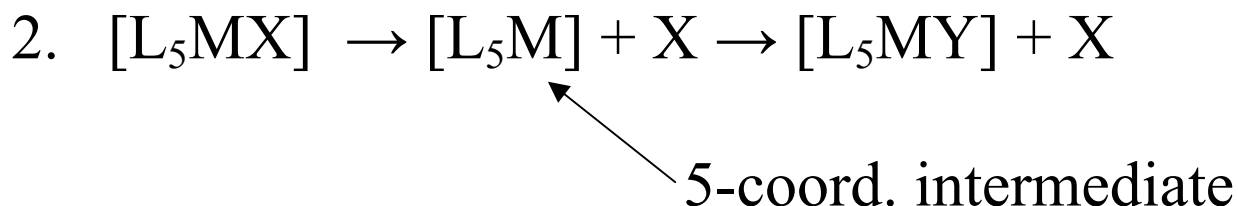
1. Associative (A) (addition-elimination)
2. Dissociative (D)

(A)



Y directly binds before X leaves

(D)



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

(A) is bimolecular process

(D) is unimolecular process

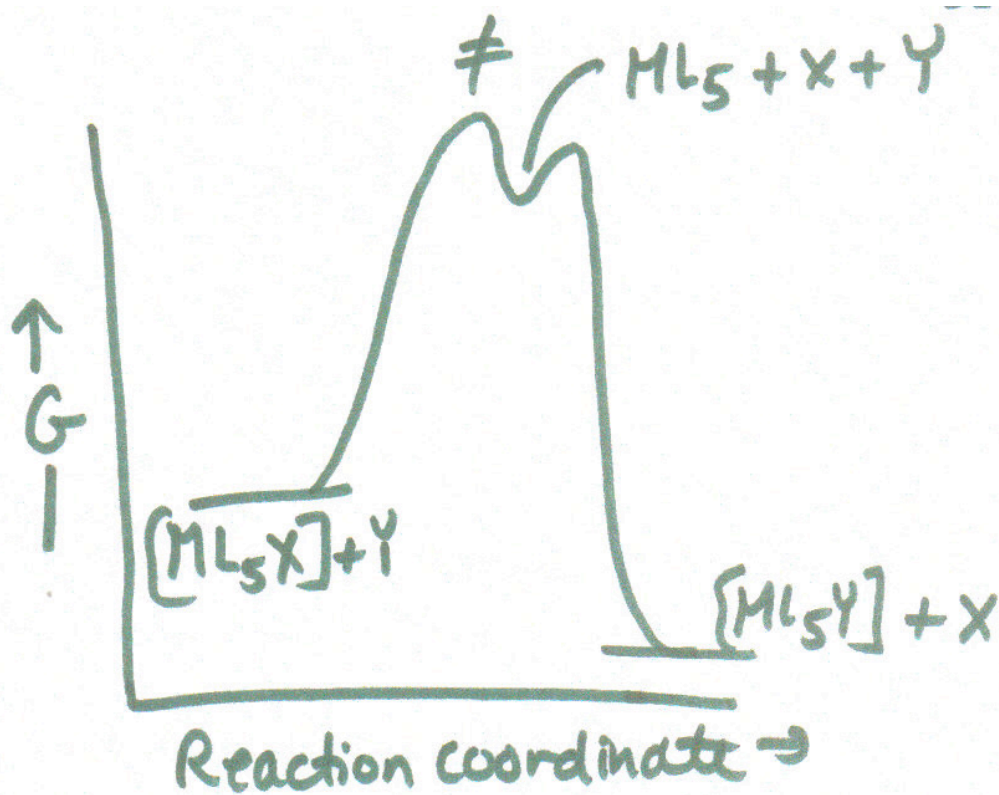
(A) & (D) are just extremes of what can really happen

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)

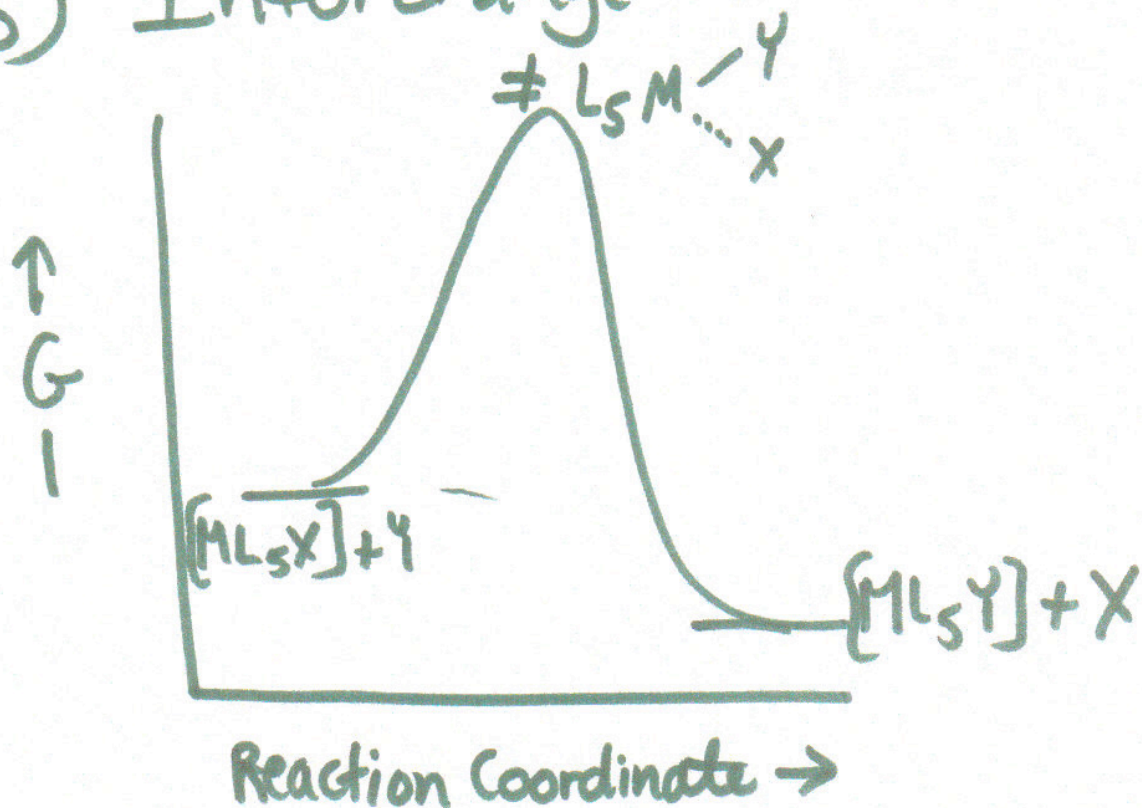
Dissociative, likewise, may also have most of the M-X bond broken (but not all) before the near M-Y bond forms.

Real life is rarely simple!

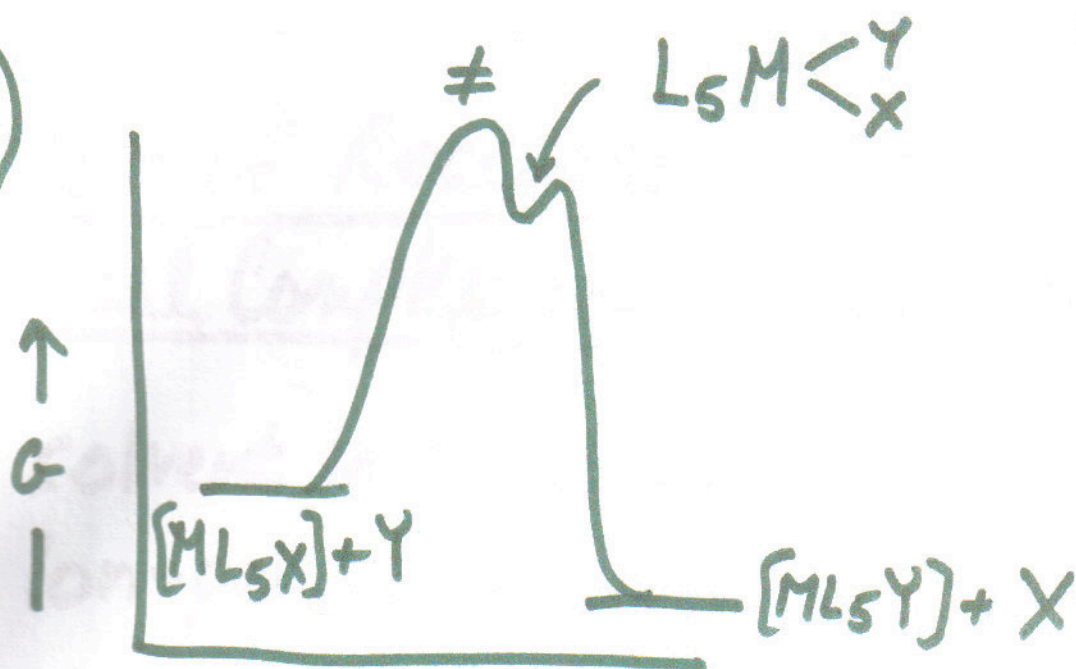
(D)



Dissociative

(I_D) Interchange - Dissociative

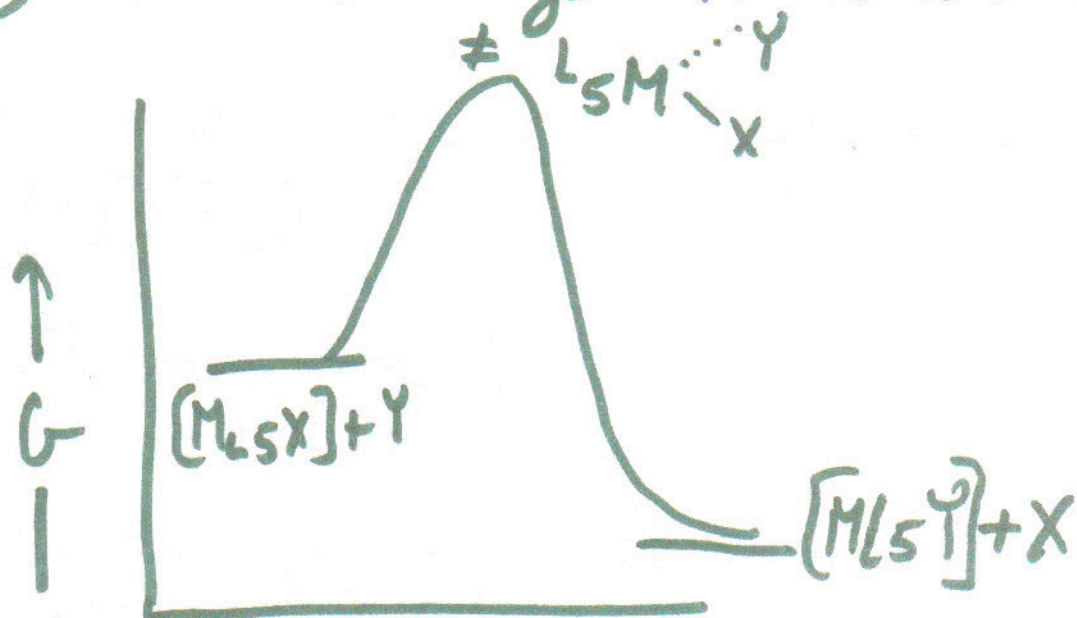
(A)



— reaction coordinate →

Associative

(I_A) Interchange - Associative



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