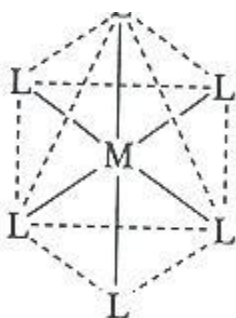


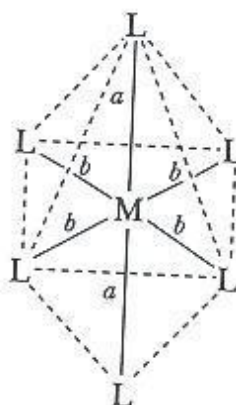
Coordination Number Six

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

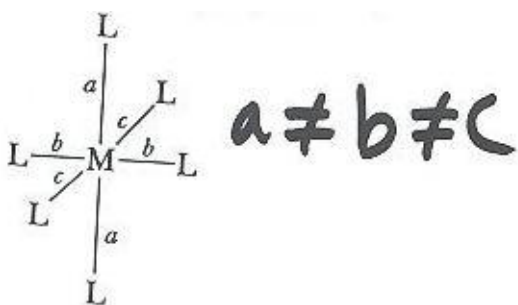
1. Regular octahedron
all distances
are EQUIVALENT



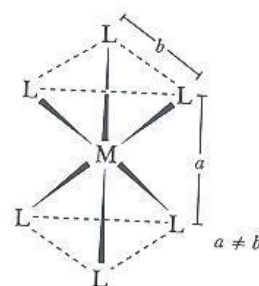
2. Distorted Octahedron
(axial distortion)
 $a \neq b$



3. Distorted Octahedron
(Rhombic distortion)



4. Distorted Octahedron
(trigonal distortion)
 $a \neq b$

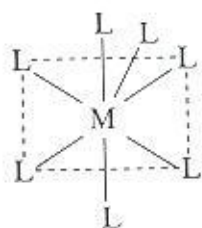


Trigonal prism is not as stable as the regular octahedron, because L-L distances are not maximized in the trigonally distorted geometry. This is a very rare geometry for ML_6 complexes

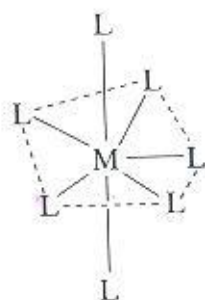
Higher Coordination numbers

Seven

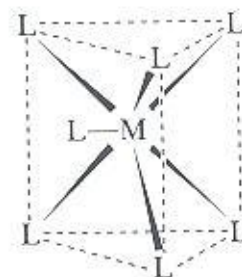
Pentagonal
bipyramid



Octahedron
+ an
extra
ligand



Trigonal
prism
+ an
extra
ligand



Eight

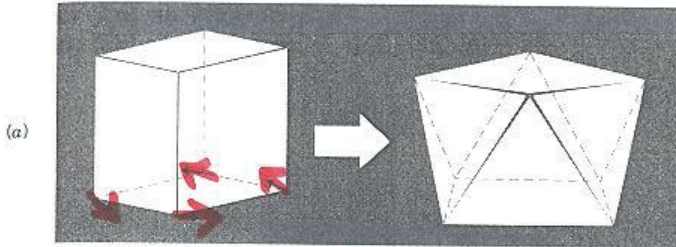
1.

Cube



2.

square antiprism
twist of face



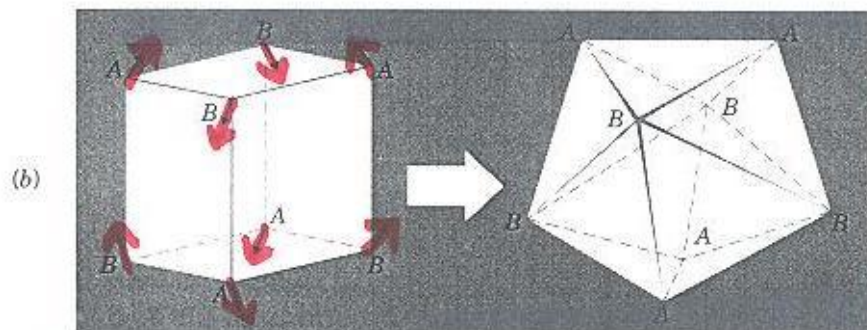
rotate the corners of once
face until it is 45° out of
phase



Cube



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 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

di	bis
Tri	tris
Tetra	tetrakis
Penta	pentakis
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	acetate	→ acetato
<u>ide</u> → ido	nitride	→ nitrido
<u>ite</u> → ito	sulfite	→ sulfito

CH_3CO_2^- acetato

N_3^- nitrido

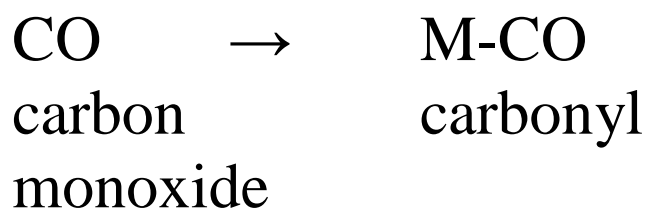
SO_3^{2-} sulfito

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

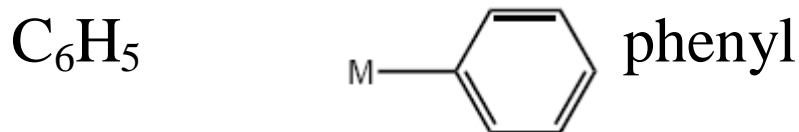
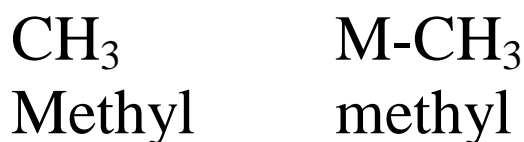
NH_3	→	M-NH_3
ammonia		ammine

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

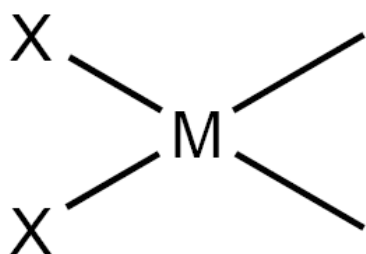
Metal oxidation state is written in parentheses in Roman numerals at the end

5

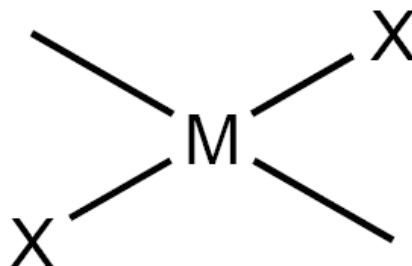
Special Characters and abbreviations

(a) Geometrical isomers

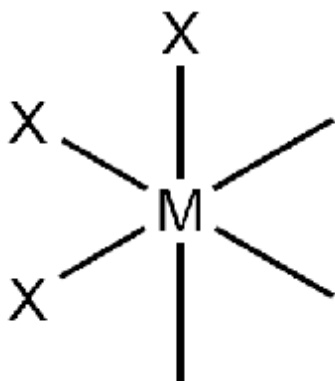
cis, trans



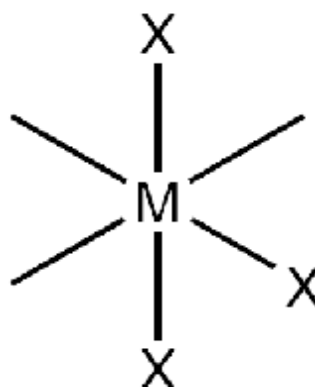
vs



fac, mer



vs



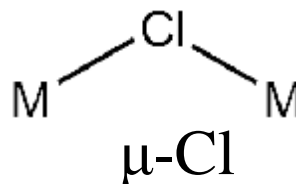
(b) optical isomers

use symbols Δ and Λ

(c) bridging ligands

- use prefix μ

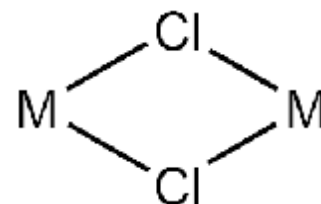
“mu”



- if two of the same kind

di- μ

di- μ -Cl



M-NO₂⁻ nitro

M-ONO⁻ nitrite

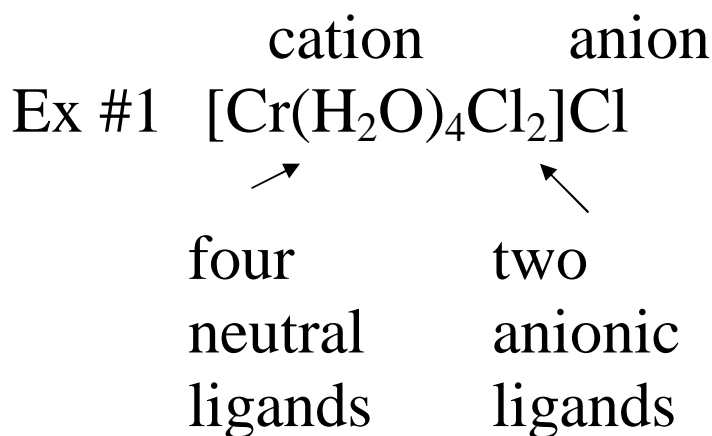
(a) H₂O (hydrate)

Water can be in a formula like this MCl₆·nH₂O

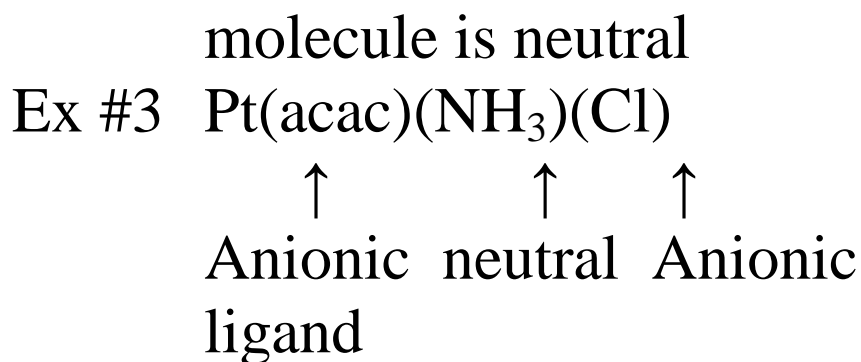
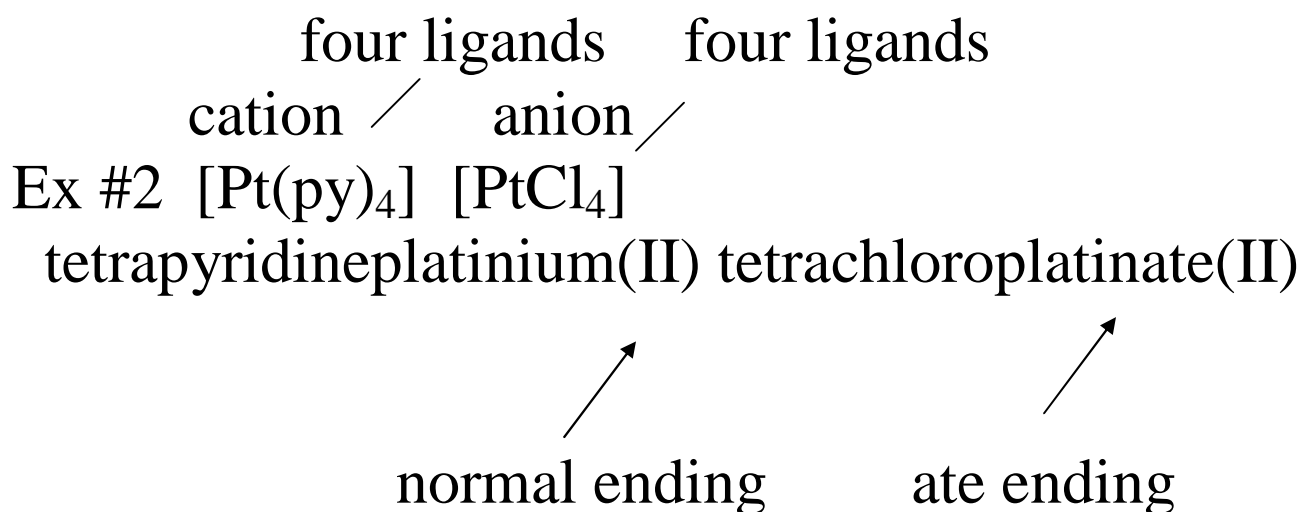
(Number of water molecules of hydration)

- H₂O monohydrate
- 2H₂O dihydrate etc.

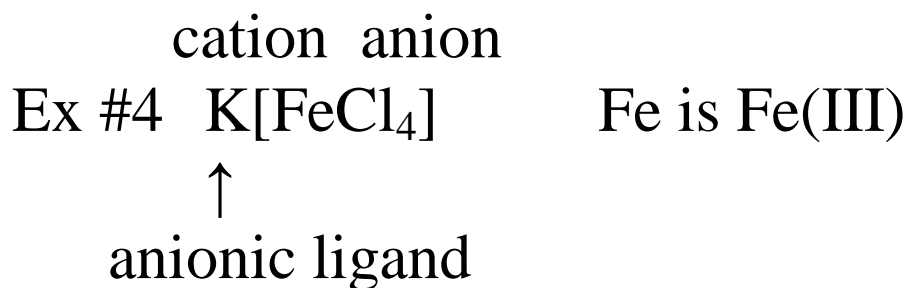
Now, start practicing!



dichlorotetraaquachromium(III) chloride

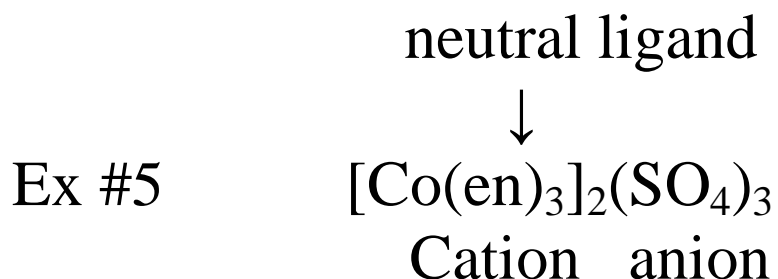


acetylacetonatochloroammineplatinum(II)



potassium tetrachloroferrate(III)

(iron is not written as ironate!)

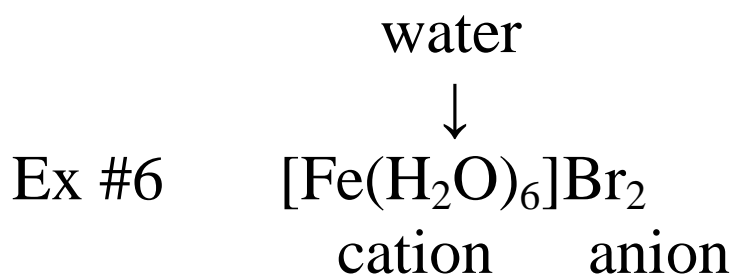


Ratio of cation to anion is 2:3

three ethylenediamine (en) ligands

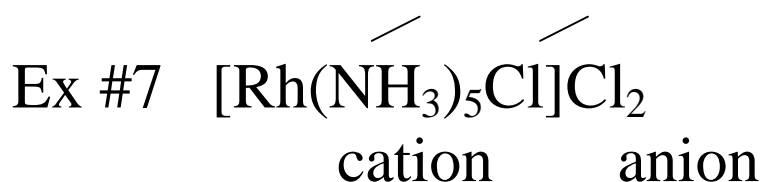
↓

tris(ethylenediamine)cobalt(III) sulfate



hexaaquairon(II) bromide

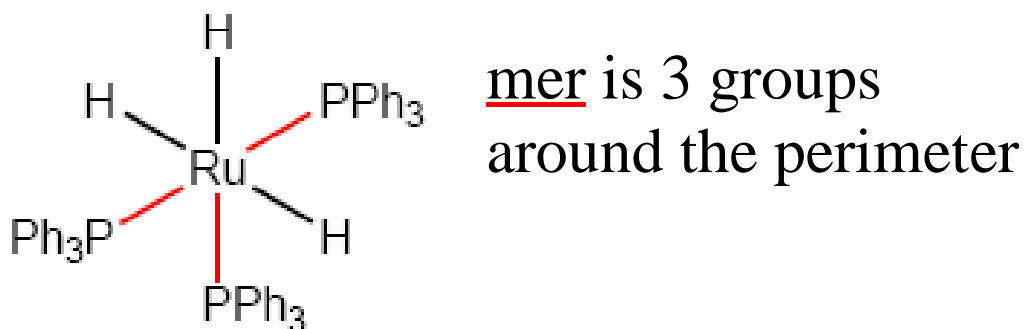
neutral anion



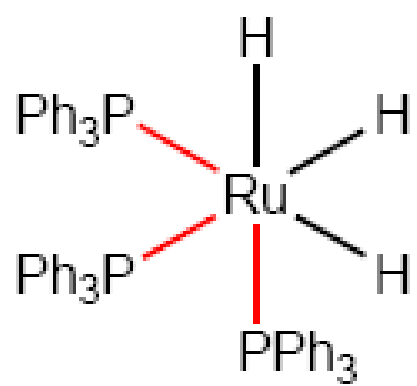
chloropentaamminerhodium(III) chloride

Practice drawing the structure based on a formula

mer-trihydrotris(triphenylphosphine)rhodium(III)

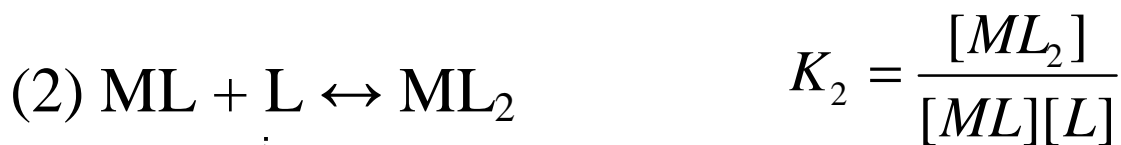


fac-trihydrotris(triphenylphosphine)rhodium(III)



Stability of Complexes in Solution

Stepwise formation of metal ligand complexes involve Equilibria



- 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:



Take β_3 for example:

$$b_3 = \frac{[ML_3]}{[M][L]^3} \cdot \frac{[ML][ML_2]}{[ML][ML_2]}$$

rearrange...

$$b_3 = \frac{[ML]}{[M][L]} \cdot \frac{[ML_2]}{[ML][L]} \cdot \frac{[ML_3]}{[ML_2][L]}$$

multiply
num. &
denom. by
this (really
just 1)

Then $\beta_3 = K_1 \cdot K_2 \cdot K_3$

or the product of all three step-wise

Equilibrium Constants

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

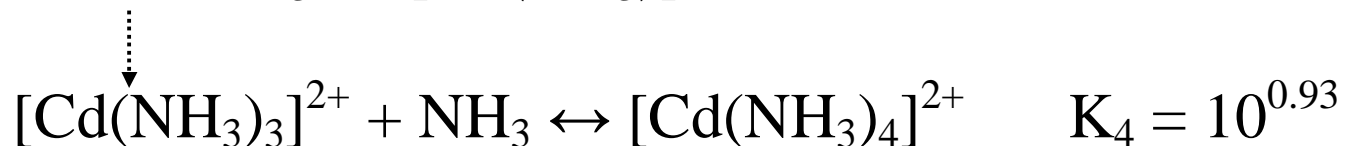
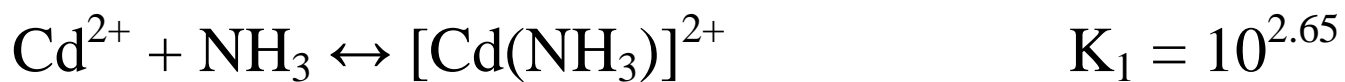
overall formation
constants

stepwise formation
constants

Usually K_i decreases with each subsequent step.

As ligand is added to the metal ion M^{n+} , 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 progresses with greater n values, there are more ligands to 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.

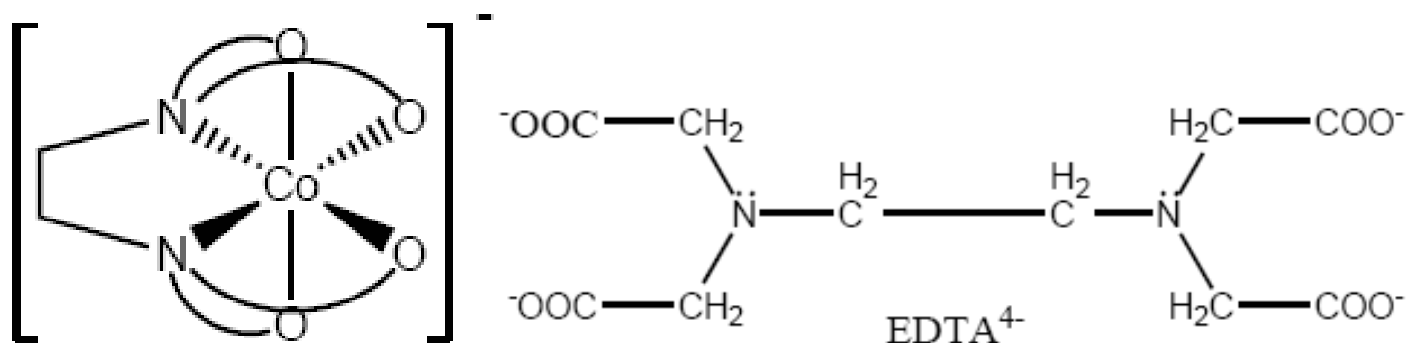


↑
formation of $[\text{Cd}(\text{NH}_3)_4]^{2+}$ illustrates

the drop in equilibrium constant with added L groups.

Q. What are formation constants useful for?

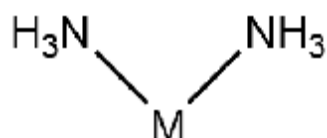
A. Separation of ions in the presence of each other
Ex. EDTA^{2-} selectively pulls Co^{2+} out of water in the presence of more highly charged cations such as Th^{4+}



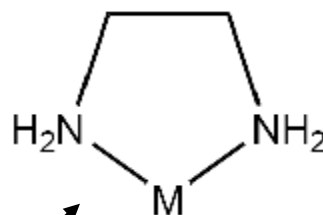
The hexadentate ligand “wraps itself” around the Co^{2+} center. EDTA^{2-} has less affinity for the 4+ cations

EDTA^{2-} brings up another important stability issue, namely the “Chelate Effect”

:NH_3 versus



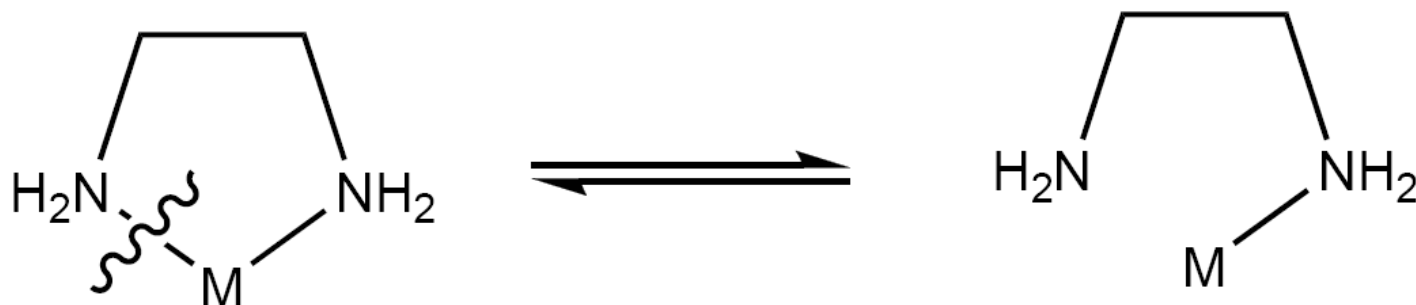
versus



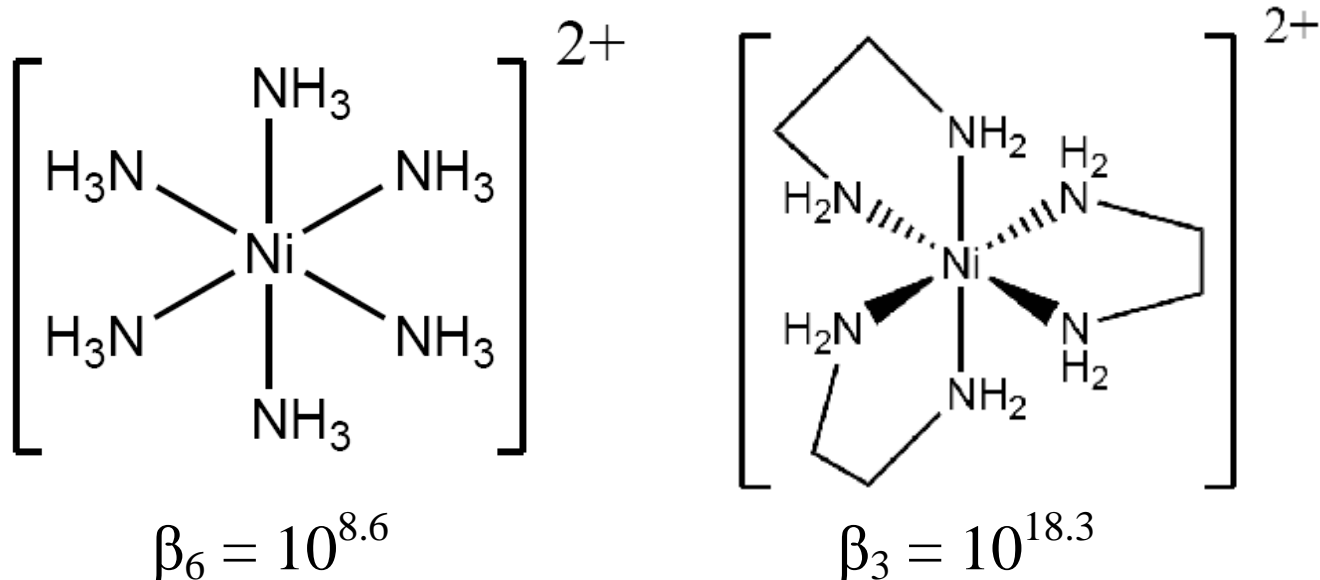
the five-membered ring
formed here is much more
stable than the independent
 NH_2 groups

Why?

To reverse the reaction of $\text{M} + \text{en}$ is more difficult
than for $\text{M}_n + 2\text{NH}_3$. 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 10¹⁰ times more stable!

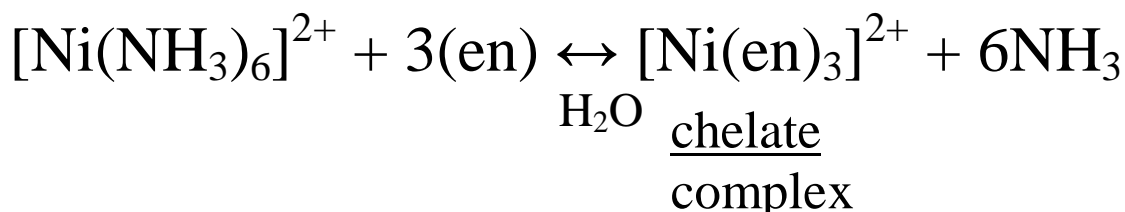
Q. Why? The bonds are very similar!

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

$$\Delta G^\circ = RT \ln K = \Delta H^\circ - T \Delta S^\circ$$

recall

in the [Ni(NH₃)₆]²⁺ vs [Ni(en)₃]²⁺ case, we can perform a reaction and determine K.



$$K = 10^{9.7}$$

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

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

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

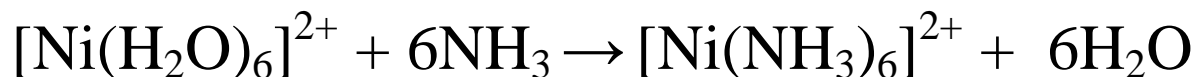
Then $-T\Delta S = -55 \text{ kJ/mol}$

Note, both enthalpy and entropy considerations favor the chelate complex, but the entropy effect is much more important

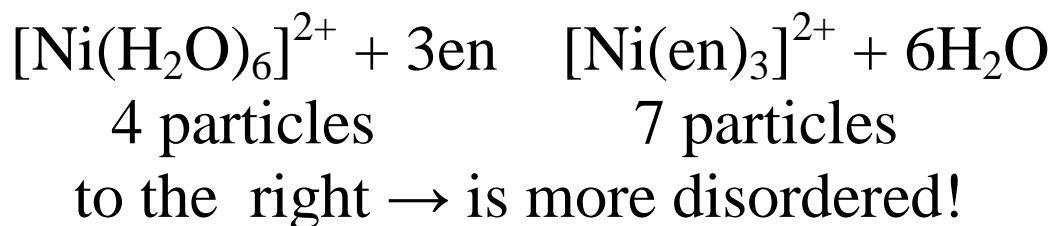
Bottom line:

The Chelate Effect is Essentially an Entropic Effect.

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



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



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

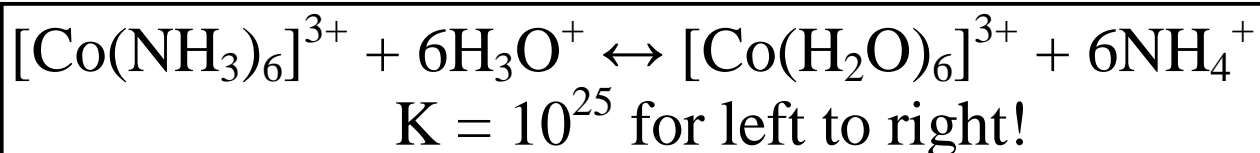
2. Inert – refers to the lack of ability of a coordination complex to lose one or more of its ligands with others in solution

*” labile vs inert” is not the same as
“unstable vs stable.”

Stability refers to the tendency of a species to exist.
è Thermodynamic issue.

Labile vs. 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 “inertness” of the compound. The reaction is very slow.

Working definition of inert and labile

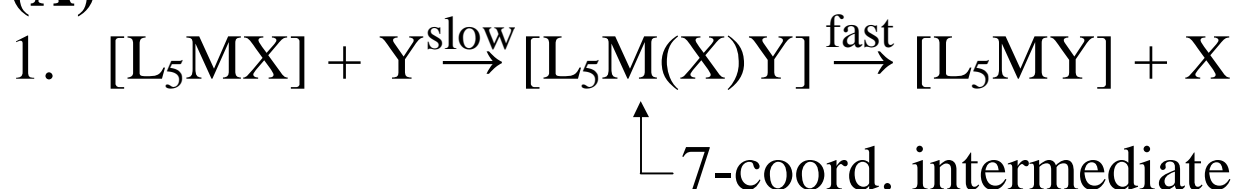
labile reactions <1 minute half-life (over in time of mixing)

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

Two Types of Ligand Substitution:

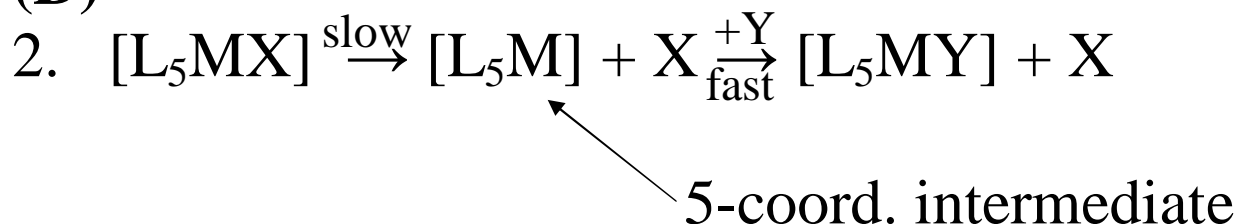
1. Associative (A) (addition-elimination)
2. Dissociative (D)

(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

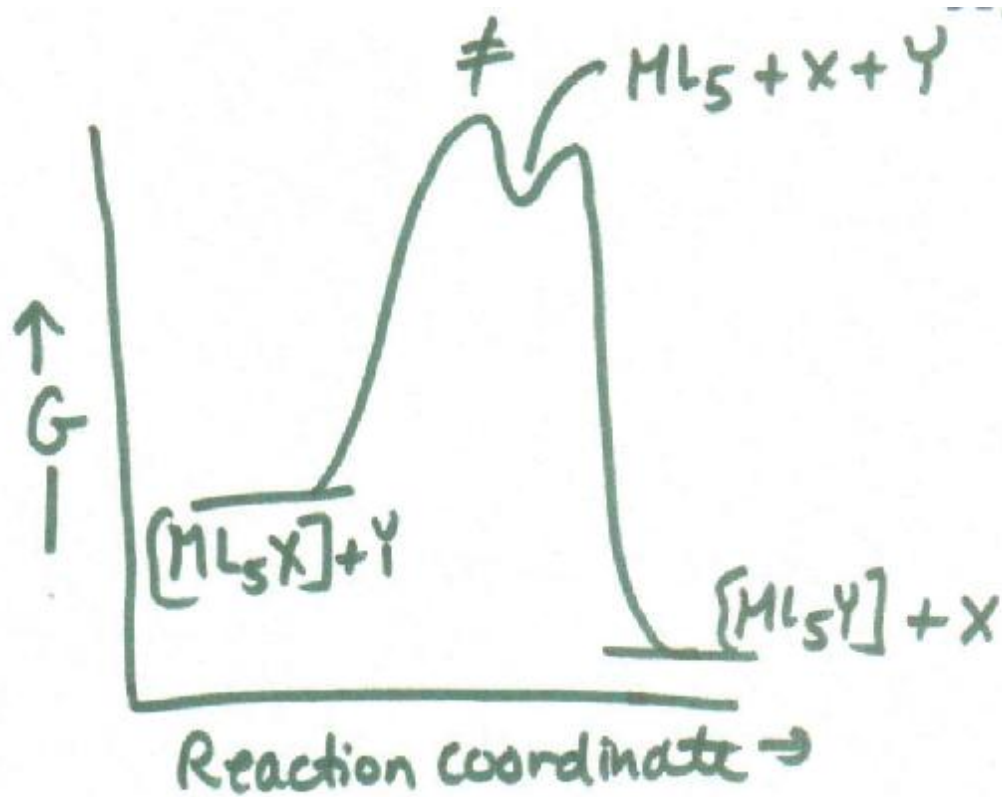
(A) & (D) are just extremes of what can really happen

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)

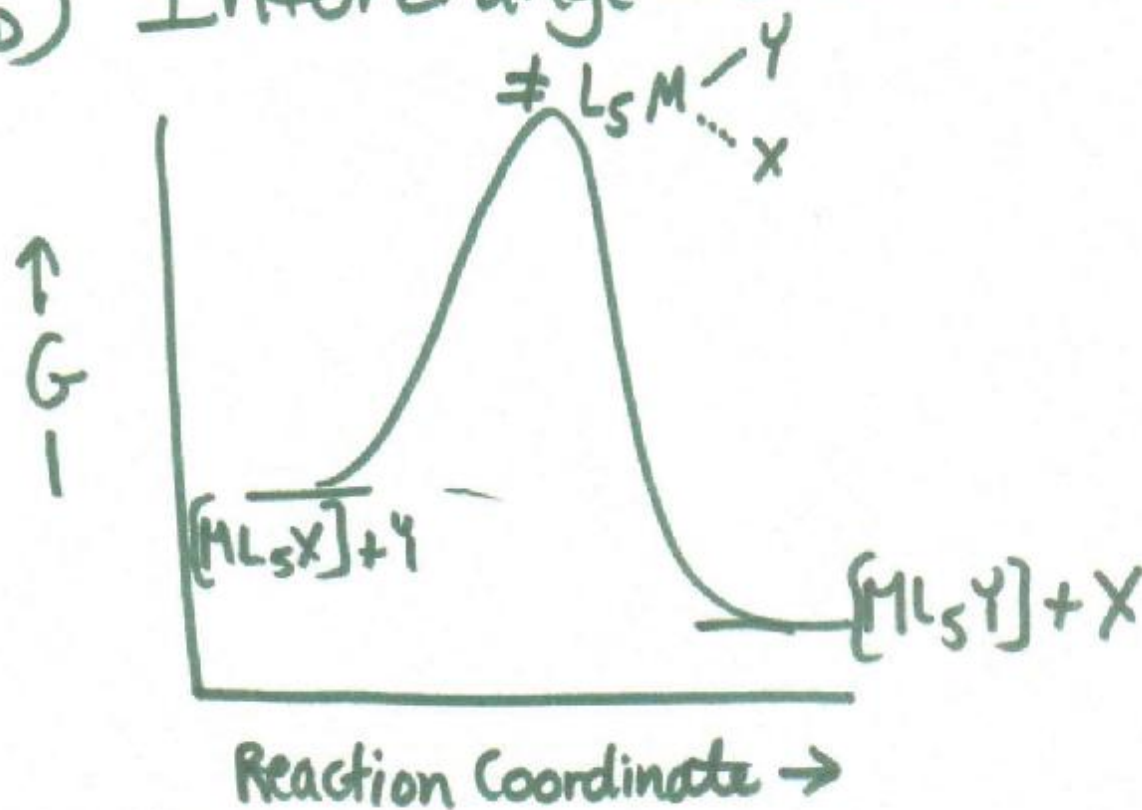
Dissociative, likewise, may also have most of the M-X bond broken (but not all) before the near M-Y bond forms.

Real life is rarely simple!

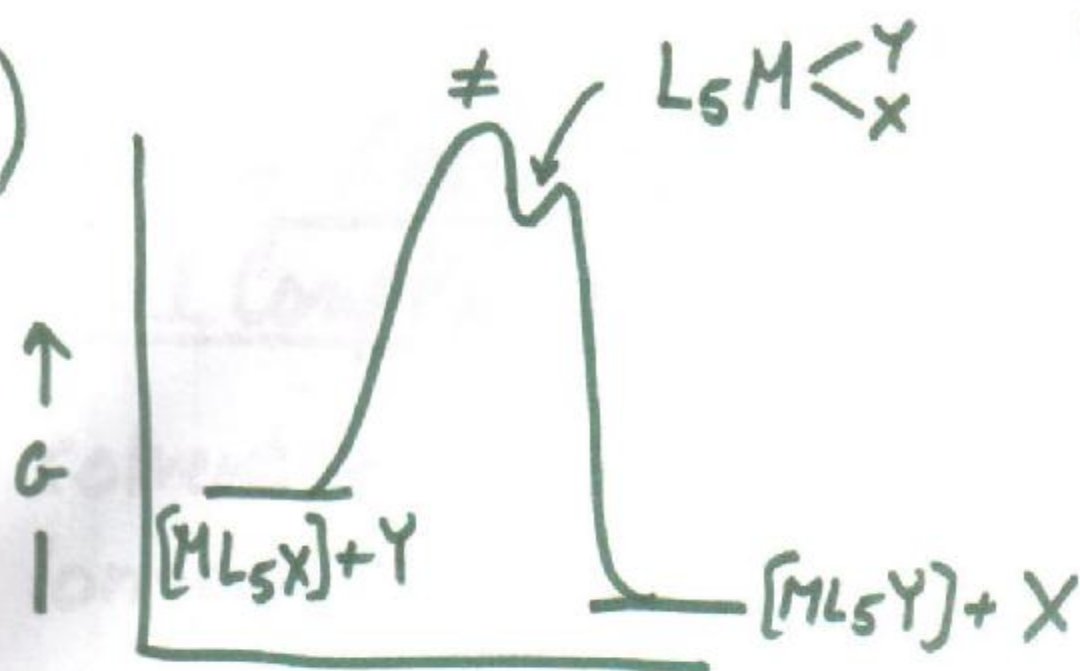
(D)



Dissociative

(I_D) Interchange - Dissociative

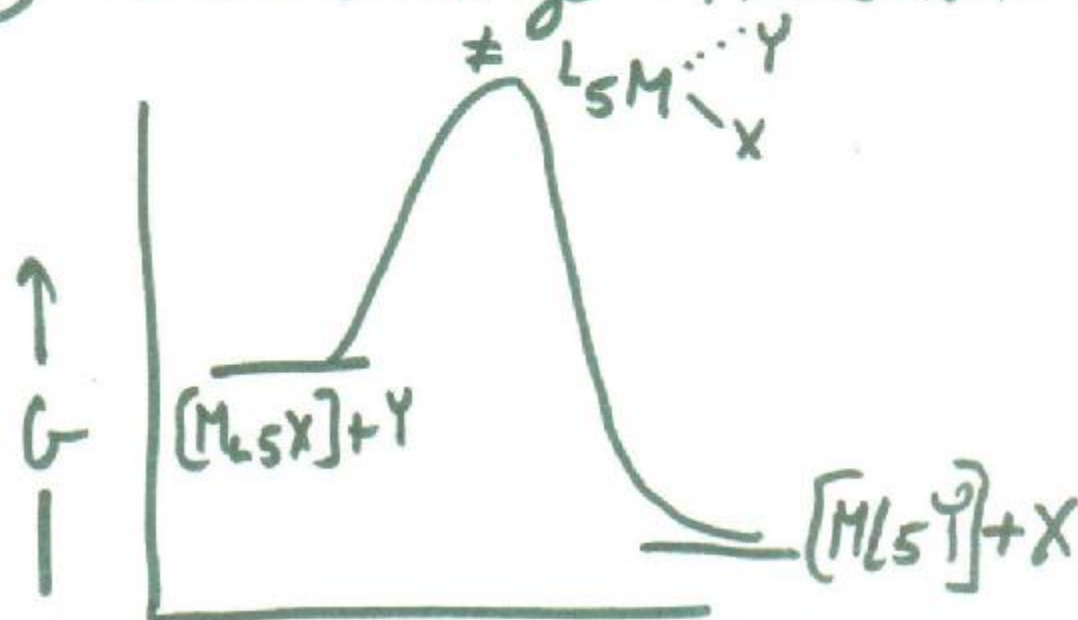
(A)



— 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