Crystal Field Theory

CFT takes an electrostatic approach to the interaction of ligands (as negative point charges) and to the central metal ions.

Shriver and Atkins: Inorg. Chem., 4thEd.

Rajakumar. A

Topic-II: 2019

Limitation of VB theory

Limitations: (1) Does not explain why some complexes are colored and others are not; (2) Does not explain the temp. dependence of the magnetic properties.

Follow up CFT

- **1929 Hans Bethe** - Developed **Crystal Field Theory (CFT)** and then
- **1932 J. H. Van Vleck** – Used CFT to interpret properties of transition metal complexes

Crystal Field Theory

- Charge of Central metal ion

- Size of the Metal ion and

- Strength of the approaching negative charge of the ligand

Octahedral Field

•If rather than a spherical field, discrete point charges (ligands) are allowed to interact with the metal, the degeneracy of the d orbitals is removed (or, better said, lifted). The splitting of d orbital energies and its consequences are at the heart of crystal field theory.
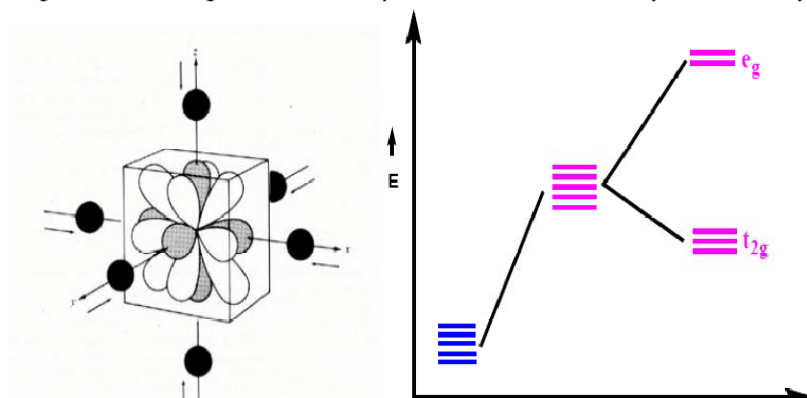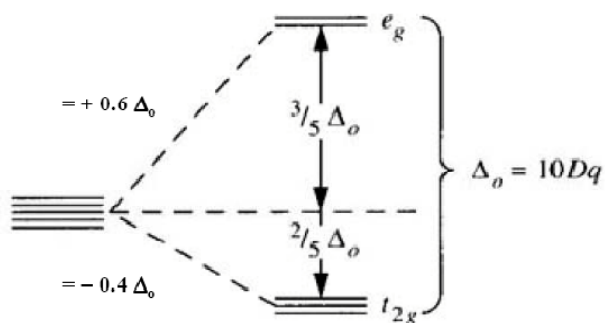

•Not all d orbitals will interact to the same extent with the six point charges located on the +x, -x, +y, -y, +z and -z axes respectively.
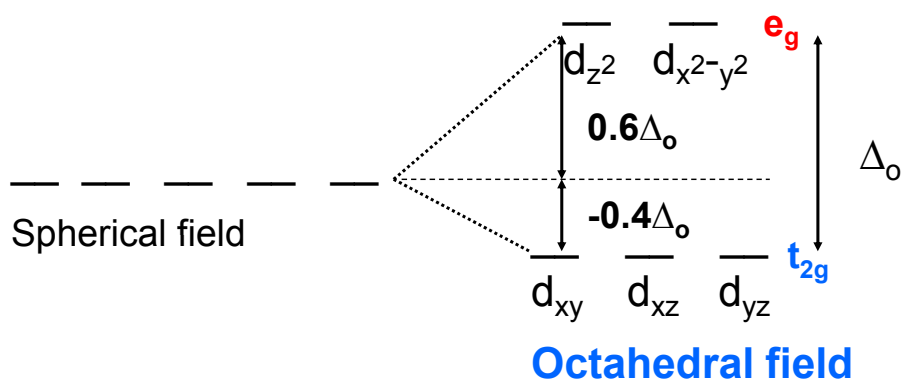
In Octahedral Field

d_{z^2}

$d_{x^2-y^2}$

d_{yz}

d_{xz}

d_{xy}
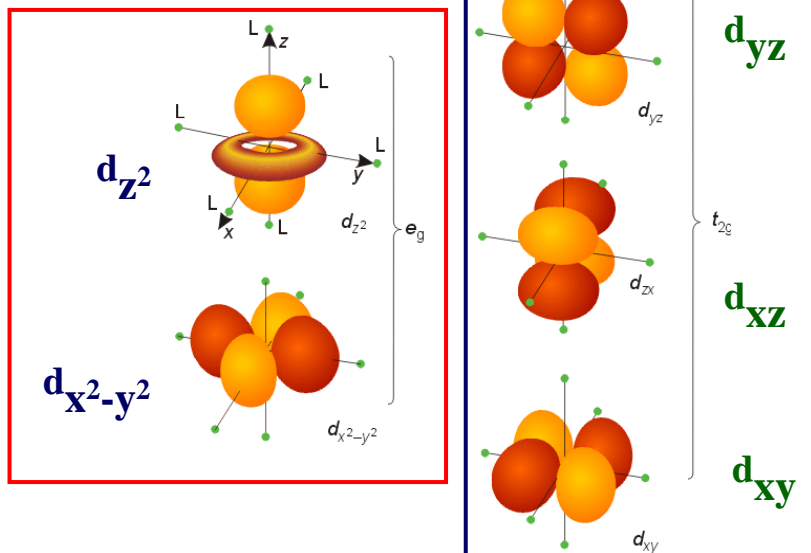
CFT-Octahedral Complexes

•For the Oh point group, the x^2-y^2, z^2 orbitals belong to the E_g irreducible representation and xy, xz, yz belong to the T_{2g} representation.

•The extent to which these two sets of orbitals are split is denoted by Δ_o or alternatively 10Dq. As the **baricenter** must be conserved on going from a spherical field to an octahedral field, the t_{2g} set must be stabilized as much as the e_g set is destabilized.

$= +0.6\,\Delta_o$

$\frac{3}{5}\Delta_o$

$\Delta_o = 10Dq$

$\frac{2}{5}\Delta_o$

$= -0.4\,\Delta_o$

e_g

t_{2g}

5

3

d-Orbital Splitting Oh

$$d_{z^2} \quad d_{x^2-y^2} \qquad \mathbf{e_g}$$

Spherical field

$$0.6\Delta_o$$

$$\Delta_o$$

$$-0.4\Delta_o$$

$$d_{xy} \quad d_{xz} \quad d_{yz} \qquad \mathbf{t_{2g}}$$

Octahedral field

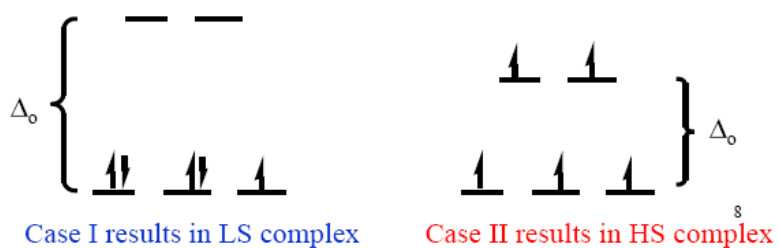# For an octahedral complex, CFSE

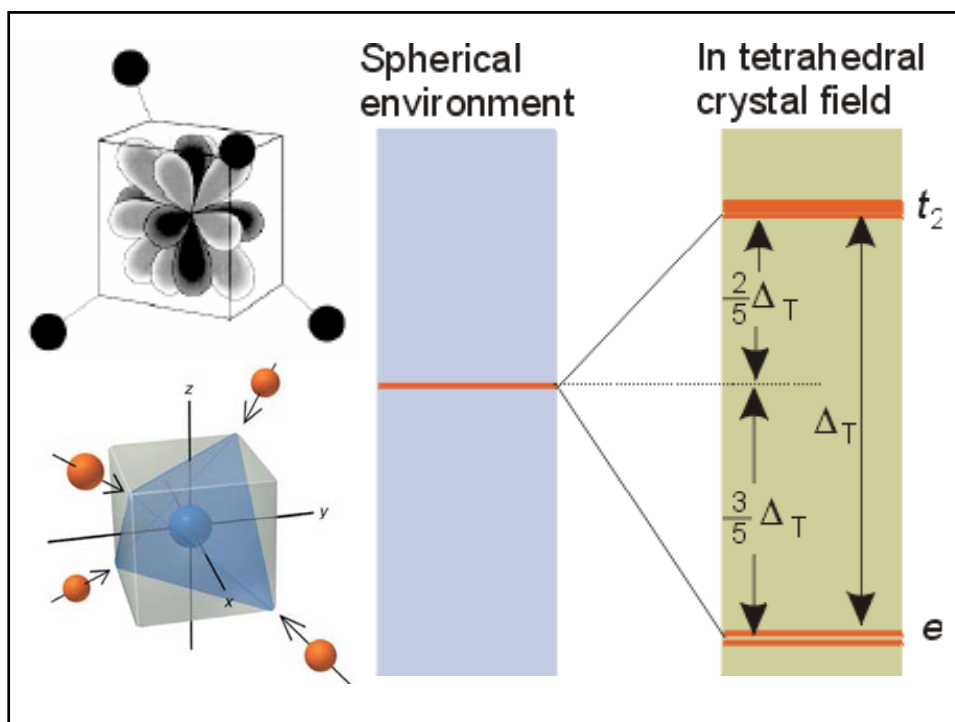$$= -0.4 \times n(t_{2g}) + 0.6 \times n(e_g) \, \Delta_o$$

Where, $n(t_{2g})$ and $n(e_g)$ are the no. of electrons occupying the respective levels

If CFSE is very large, pairing occurs (i.e. CFSE > P)
If CFSE is rather small, no pairing occurs (i.e P > CFSE)

d^5 system

Δ_o

Case I results in LS complex

Δ_o

Case II results in HS complex

8

Spherical environment	In tetrahedral crystal field

t_2

$\frac{2}{5}\Delta_T$

Δ_T

$\frac{3}{5}\Delta_T$

e

Are the Δ_{td} and Δ_{oh} comparable

$\Delta_{td} = 4/9\ \Delta_{oh}$

Reasons?

➢ Only 4 ligands in the td, hence, field is 2/3 of Oh.

➢ Direction of ligand approach in td does not coincide with the d-orbitals, which reduces the field by a factor 2/3.
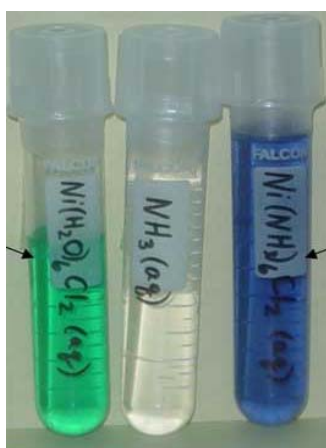
Therefore, Δ_t is roughly 2/3 x 2/3 = **4/9 of Δo**

Δ_o is dependent on:

- *Nature of the ligands*
- *The charge on the metal ion*
- *Whether the metal is a 3d, 4d, or 5d elemen*

Ligands which cause a small splitting are *Weak field ligands* (CFSE in the range 7000 - 30000 cm^{-1}) and those cause a large splitting are *Strong field ligands* (CFSE typically > 30000 cm^{-1})

Colour and d-Orbital Splitting

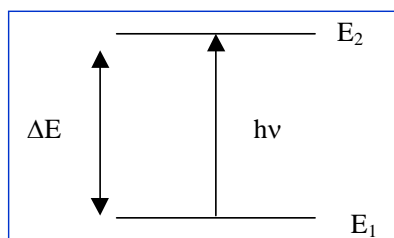Splitting due to the nature of the ligand can be obs. & measured by **Spectrophotometer.**

Smaller Δ_o = **green**
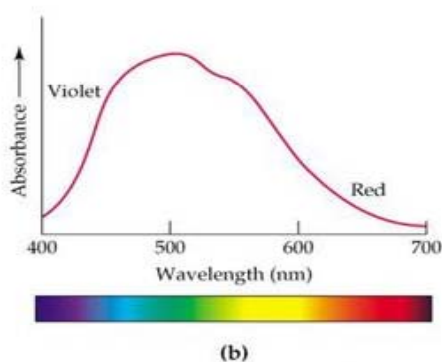
Larger gaps = shift to **yellow**

Origin of Colour

The origin of the color of the transition metal compounds

$$\Delta E = E_2 - E_1 = h\nu$$

Ligands influence Δ_O, therefore the colour

The optical absorption spectrum of $[Ti(H_2O)_6]^{3+}$

Absorbance

Violet

Red

400   500   600   700

Wavelength (nm)

(b)

494 nm = 20,300 cm^{-1}

Assigned transition:

$$e_g \longrightarrow t_{2g}$$

This corresponds to the energy gap

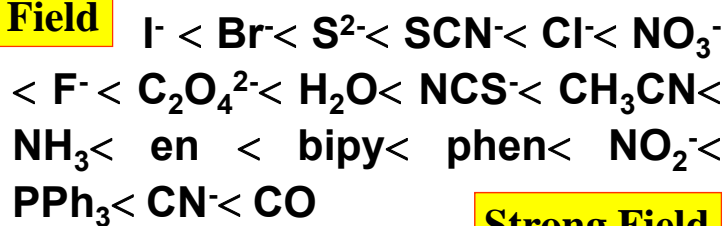$$\Delta_O = 243 \text{ kJ mol}^{-1}$$

Spectrochemical Series
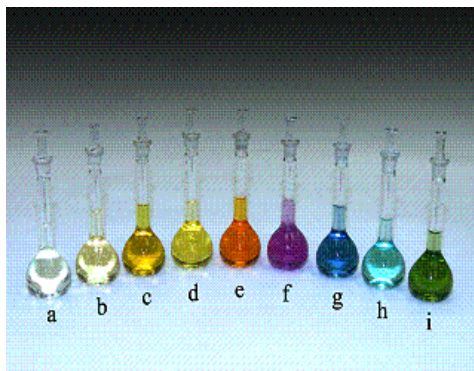
Complexes of cobalt(III) show shift in color due to the variation of ligand.
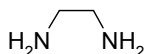
(a) CN^-, (b) NO_2^-, (c) phen, (d) en, (e) NH_3,
(f) gly, (g) H_2O, (h) ox^{2-}, and (i) CO_3^{2-}.

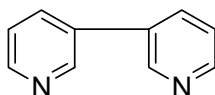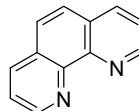**Spectrochemical Series: An order of ligand field strength based on experiment**

Weak Field $I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^-$
$< F^- < C_2O_4^{2-} < H_2O < NCS^- < CH_3CN <$
$NH_3 < en < bipy < phen < NO_2^- <$
$PPh_3 < CN^- < CO$ **Strong Field**

H_2N NH_2
Ethylenediamine (en)

2,2'-bipyridine (bipy)   1.10 - penanthroline (phen)

$[CrF_6]^{3-}$ $[Cr(H_2O)_6]^{3+}$ $[Cr(NH_3)_6]^{3+}$ $[Cr(CN)_6]^{3-}$

As Cr^{3+} goes from being attached to a weak field ligand to a strong field ligand, Δ increases and the color of the complex changes from green to yellow.
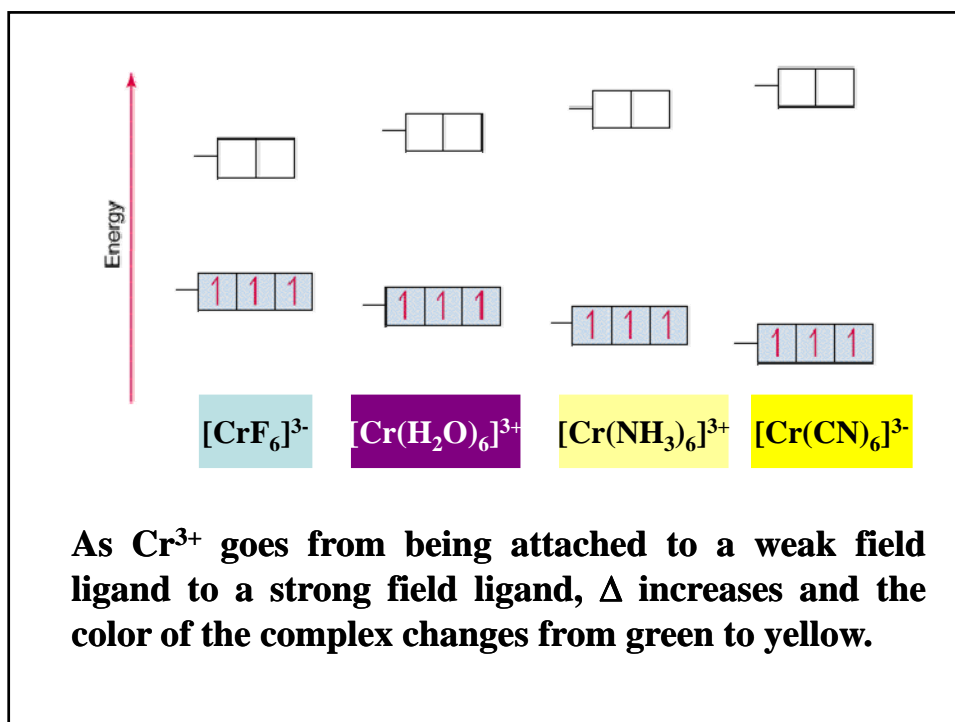
Colour

Origin of Color

Absorbed Color	λ (nm)	Observed Color	λ (nm)
Violet	400	Green-yellow	560
Blue	450	Yellow	600
Blue-green	490	Red	620
Yellow-green	570	Violet	410
Yellow	580	Dark blue	430
Orange	600	Blue	450
Red	650	Green	520

The Beer-Lambert Law

$$A = \log_{10}(I_0/I) = \varepsilon c l$$

where ε is the molar extinction coefficient (in L cm^{-1} mole^{-1}), c is concentration in mole L^{-1} and l is the path length in cm. A is known as 'Absorbance' and it is dimensionless.
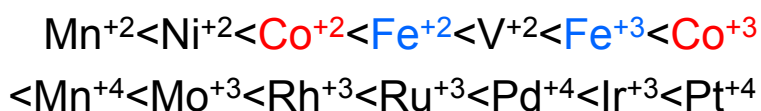
The Colors of Some Complexes of the Co^{3+} Ion

Complex Ion	Wavelength of Light absorbed (nm)	Color of Light absorbed	Color of Complex
$[CoF_6]^{-3}$	700	Red	Green
$[Co(C_2O_4)_3]^{3+}$	600, 420	Yellow, violet	Dark green
$[Co(H_2O)_6]^{3+}$	600, 400	Yellow, violet	Blue-green
$[Co(NH_3)_6]^{3+}$	475, 340	Blue, violet	Yellow-orange
$[Co(en)_3]^{3+}$	470, 340	Blue, ultraviolet	Yellow-orange
$[Co(CN)_6]^{3+}$	310	Ultraviolet	Pale Yellow

The complex with fluoride ion, $[CoF_6]^{3+}$, is high spin and has one absorption band. The other complexes are low spin and have two absorption bands. In all but one case, one of these absorptions is in the visible region of the spectrum. The wavelengths refer to the center of that absorption band.
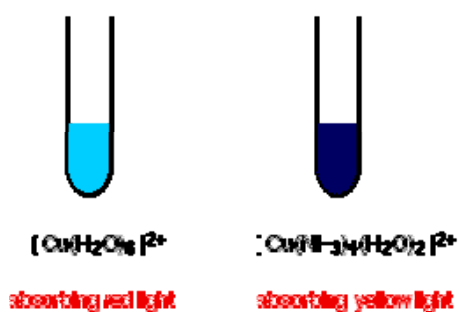
Ligand Field Strength Observations

1. Δ_o increases with increasing oxidation number on the metal.

   $Mn^{+2} < Ni^{+2} < Co^{+2} < Fe^{+2} < V^{+2} < Fe^{+3} < Co^{+3}$

   $< Mn^{+4} < Mo^{+3} < Rh^{+3} < Ru^{+3} < Pd^{+4} < Ir^{+3} < Pt^{+4}$
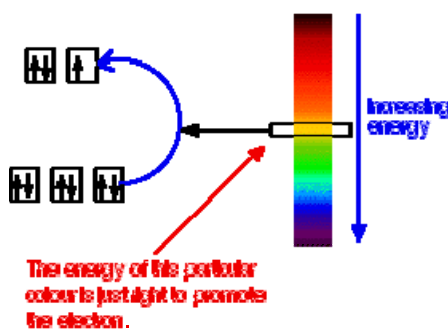
2. Δ_o increases with increases going down a group of metals.

Copper(II) Solution

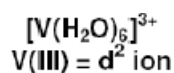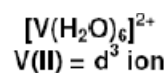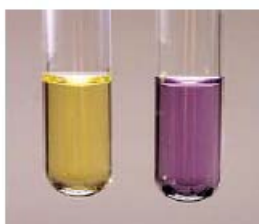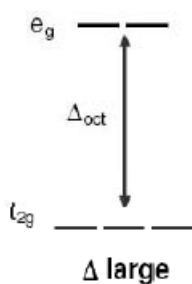- If you add an excess of ammonia solution to hexaaquacopper(II) ions in solution

$[Cu(H_2O)_6]^{2+}$ $[Cu(NH_3)_4(H_2O)_2]^{2+}$

absorbing red light   absorbing yellow light

Absorbing in….

Increasing energy

The energy of this particular colour is just right to promote the electron.

Color and CFT

$[V(H_2O)_6]^{3+}$
V(III) = d^2 ion

$[V(H_2O)_6]^{2+}$
V(II) = d^3 ion

violet light absorbed
complex appears yellow

yellow light absorbed
complex appears violet

Δ large

Δ small
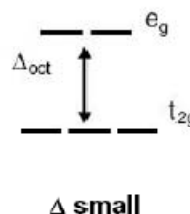
Colourless?

- For example, although scandium is a member of the d block, its ion (Sc^{3+}) hasn't got any d electrons left to move around.

- In the zinc case, the 3d level is completely full - there aren't any gaps to promote an electron in to. Zinc complexes are also colourless.
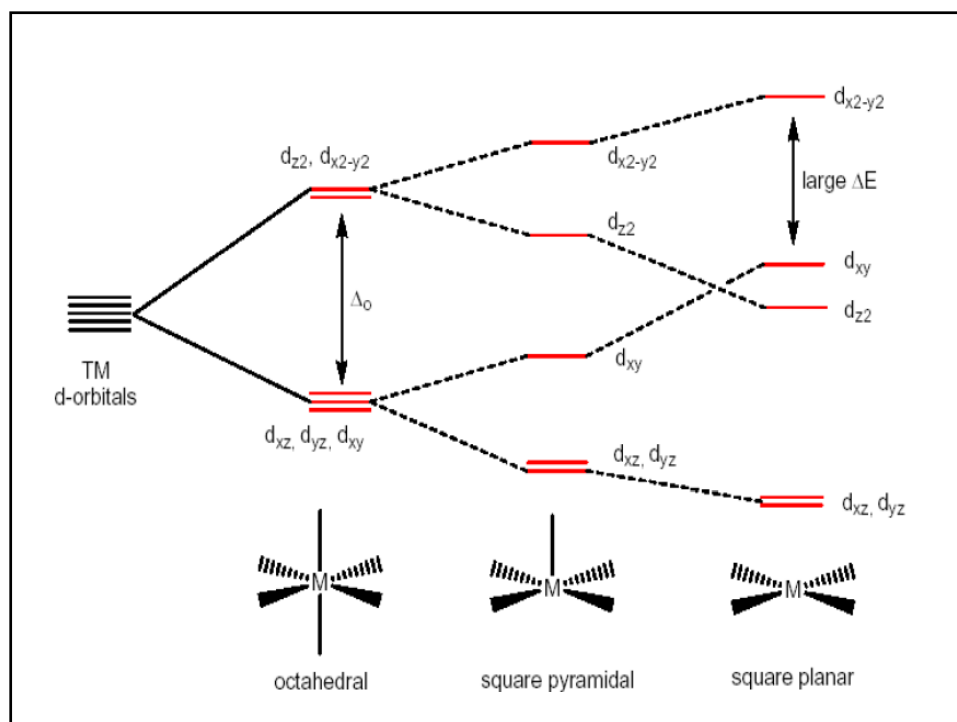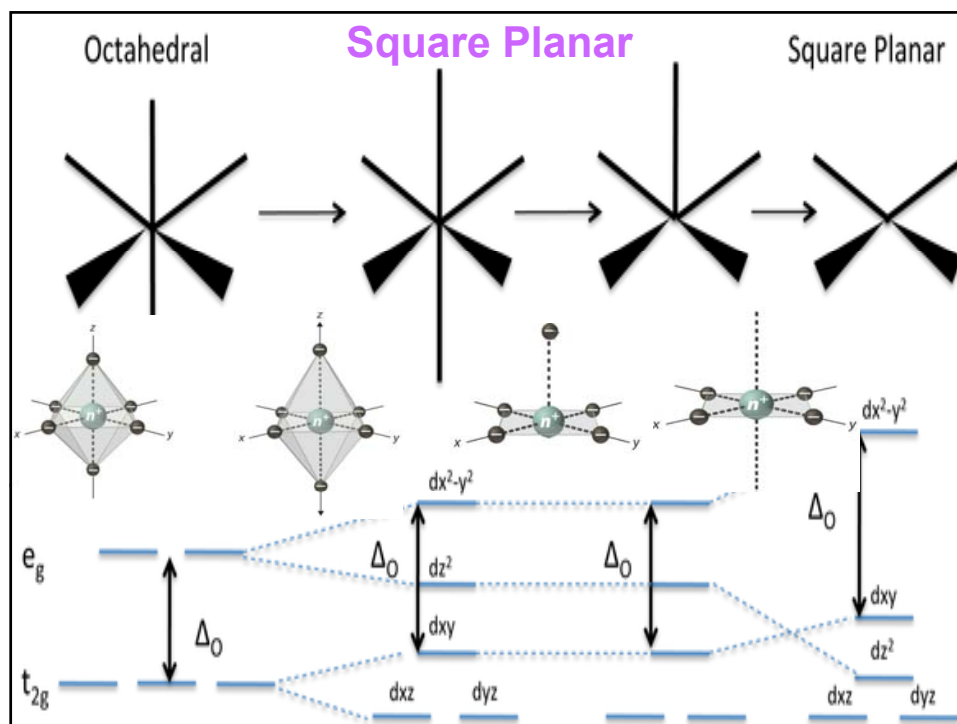
Distortion in Octahedral Systems

Distortion in Octahedral Systems

- **Distortion from ideal Octahedral Environments, causes different orb. Energy levels.**

- **When we pull away one ligand (along z- axis); then ultimate removal gives 5-coord. Square Pyramidal. This partly removes unfav. Interaction in Z-direction.**
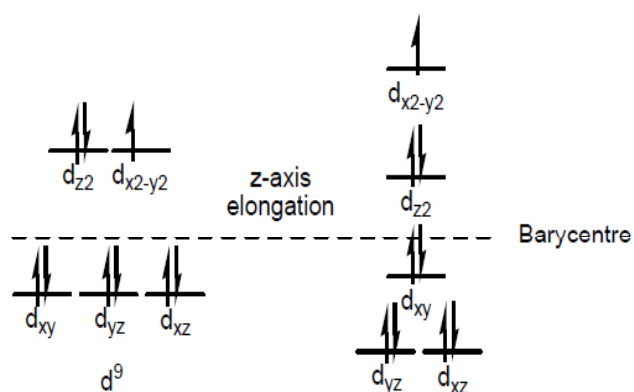
  All oribtal with z-component (dz^2, dxz and dyz) will <u>fall-in</u> energy.
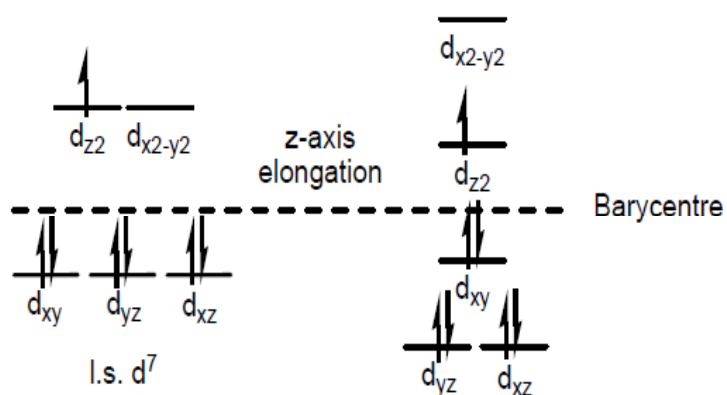 **The other orbitals (non z-components) will <u>go-up</u> in energy.**

Jahn-Teller Effect

d^9 system

d^7 system (low spin)

d^4 system (high spin)

- d_{z2} d_{x2-y2}

z-axis elongation

d_{x2-y2}

d_{z2}

Barycentre

d_{xy} d_{yz} d_{xz}

h.s. d^4

d_{xy}

d_{yz} d_{xz}
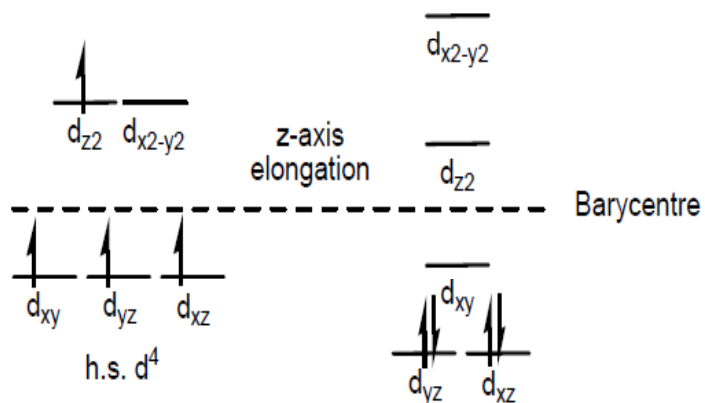
H.W. 1. Identify the J.T. Distortion for Low Spin Complexes

d^6 d^7 d^8 d^9 d^{10}

d^1 d^2 d^3 d^4 d^5
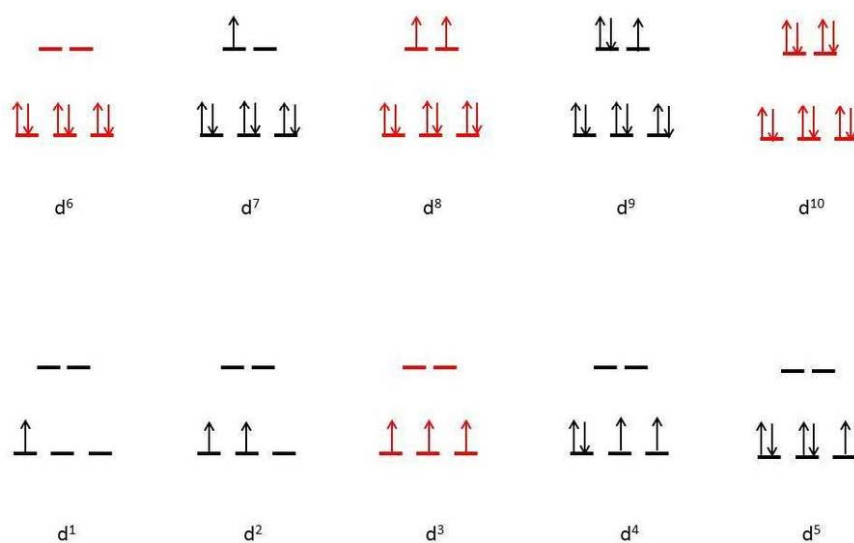
H.W. 2. Identify the J.T. Distortion for High Spin Complexes

⇅ ↑   ⇅ ↑   ↑ ↑   ⇅ ↑   ⇅ ⇅

⇅ ↑ ↑   ⇅ ⇅ ↑   ⇅ ⇅ ⇅   ⇅ ⇅ ⇅   ⇅ ⇅ ⇅

d^6 d^7 d^8 d^9 d^{10}

— —   — —   — —   ↑ _   ↑ ↑

↑ _ _   ↑ ↑ _   ↑ ↑ ↑   ↑ ↑ ↑   ↑ ↑ ↑

d^1 d^2 d^3 d^4 d^5
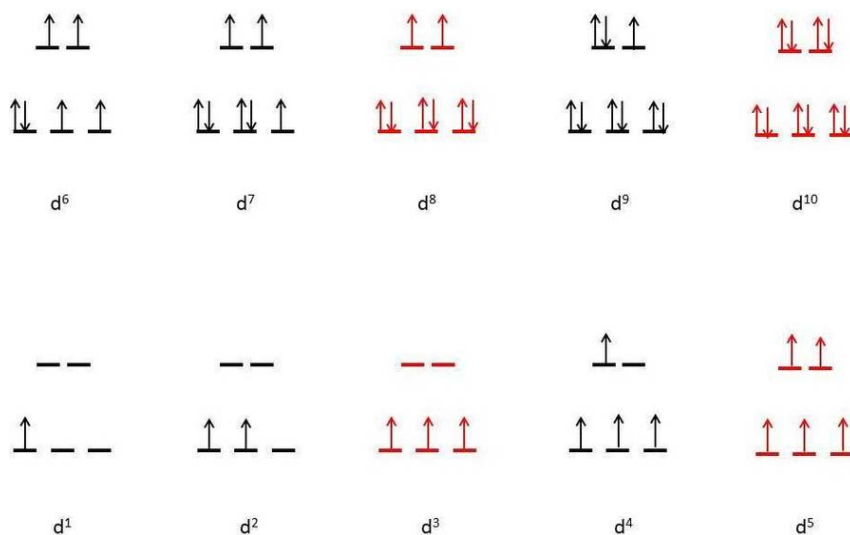
Magnetism

Each electron has a magnetic moment owing to its:

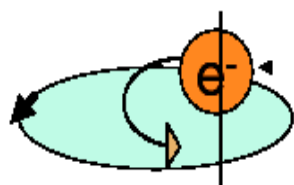spin angular momentum   orbital angular momentum

Orbital motion of e generates current and magnetic field

Spin motion of e about its own Axis also generates a magnetic field

- **The magnetic moment μ of a complex with total spin quantum number S is:**
- **$\mu = 2\{S(S+1)\}^{1/2} \, \mu_B$ (μ_B is the Bohr magneton)**
- **$\mu_B = eh/4\pi m_e = 9.274 \times 10^{-24}$ J T^{-1}**

- **Since each unpaired electron has a spin ½,**
- **S = (½)n, where n = no. of unpaired electrons**

- **$\mu = \{n(n+2)\}^{1/2} \, \mu_B$**

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n = no. of unpaired electrons
$\mu = \{n(n+2)\}^{1/2} \, \mu_B$

Ion	n	S	μ/μ_B Calculated	Experimental
Ti^{3+}	1	1/2	1.73	1.7 – 1.8
V^{3+}	2	1	2.83	2.7 – 2.9
Cr^{3+}	3	3/2	3.87	3.8
Mn^{3+}	4	2	4.90	4.8 – 4.9
Fe^{3+}	5	5/2	5.92	5.3

Similar Calculation can be done for Low-spin Complex

- **In d^4, d^5, d^6, and d^7 Oh complexes, magnetic measurements can very easily predict weak versus strong field.**
- **Tetrahedral complexes: only H.S. complexes,**
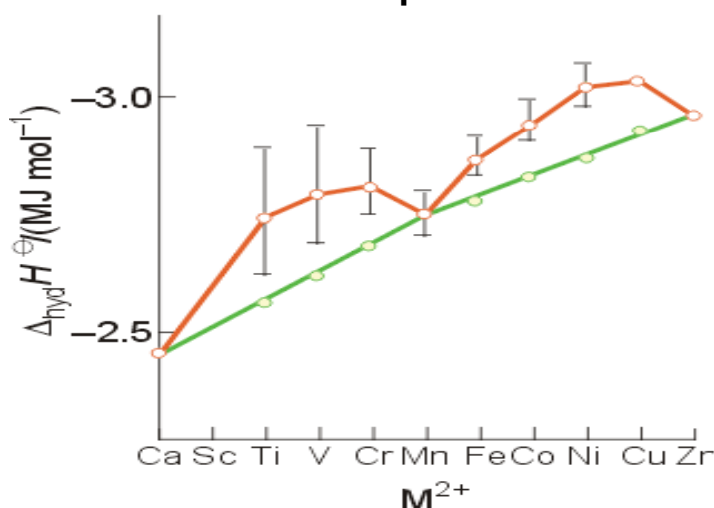- **for $\Delta_t \ll \Delta_O$.**

Limitations of CFT

Considers Ligand as Point charge/dipole only
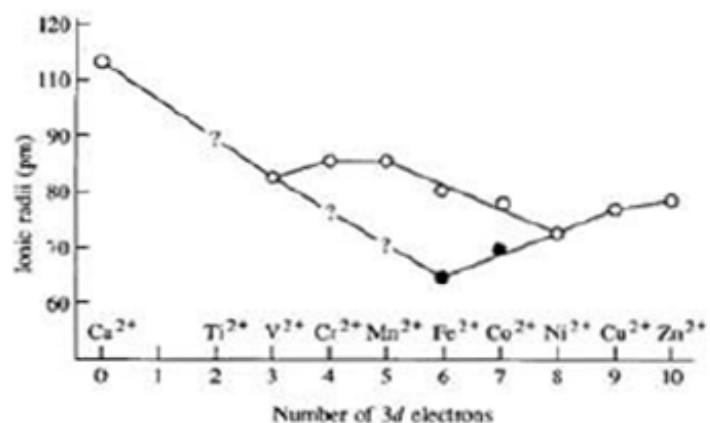**Does not take into account of the overlap of ligand and metal orbitals**

Consequence

e.g. Fails to explain why CO is stronger ligand than CN$^-$ in complexes having metal in low oxidation state

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H. W. 1: Explain the enthalpy of hydration of transition metal ions from the given graphical report.

H.W. 2: In case of strong field ligand (CN⁻) ionic radii of M²⁺

Chelate Effect?

Complexes: Have **metal** ion (can be zero oxidation state) bonded to number of molecules/ions (i.e. **ligands**).

Lewis acid = metal = center of coordination

Lewis base = ligand = molecules/ions covalently bonded to metal in complex

The term ligand (ligare [Latin], to bind) was first used by Alfred Stock in 1916 in relation to silicon chemistry. The first use of the term in a British journal was by H. Irving and R.J.P. Williams in *Nature*, 1948, 162, 746.

For a fascinating review on 'ligand' in chemistry - *Polyhedron*, 2, 1983, 1-7.

Teeth of a ligand (teeth → dent)

- **Ligands**
  - **classified according to the number of donor atoms**
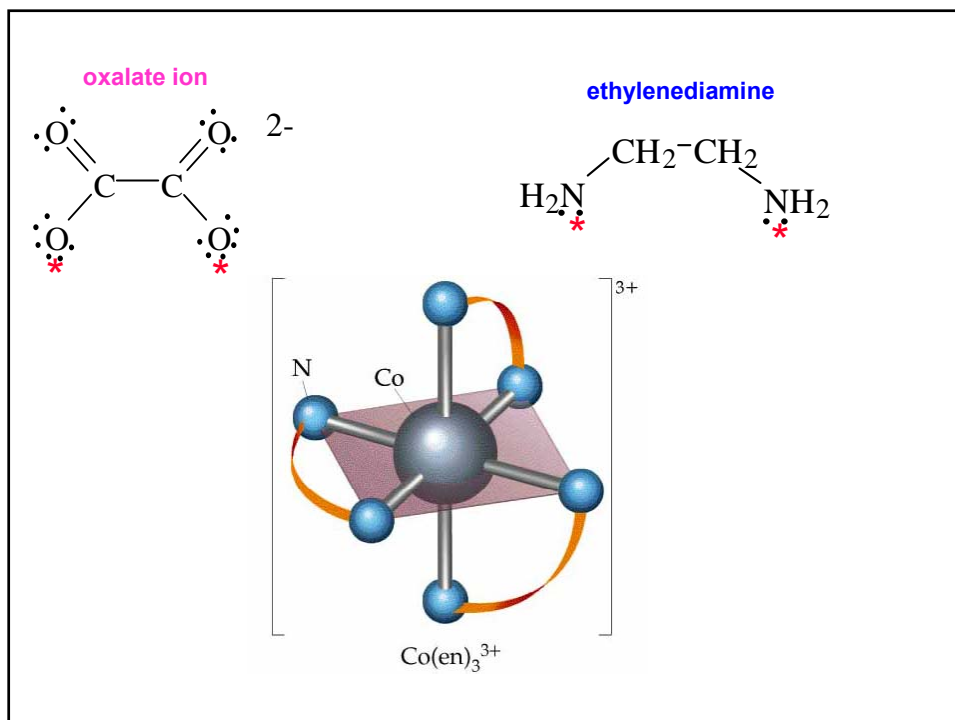 - **Examples**
    - monodentate = 1
    - bidentate = 2
    - tetradentate = 4
    - hexadentate = 6
    - polydentate = 2 or more donor atoms

    chelating agents

monodentate, bidentate, tridentate etc. where the concept of teeth (dent) is introduced, hence the idea of bite angle etc.

MONODENTATE					
Formula[a]	Name as Ligand[b]	Formula[a]	Name as Ligand[b]	Formula[a]	Name as Ligand[b]
Neutral Molecules					
NH_3	Ammine	NO	Nitrosyl	H_2O	Aqua
CH_3NH_2	Methylamine	CO	Carbonyl	C_5H_5N	Pyridine
Anions					
F^-	Fluoro	OH^-	Hydroxo	NCS^-	Thiocyanato-*N*
Cl^-	Chloro	NO_2^-	Nitrito-*N*	SCN^-	Thiocyanato-*S*
Br^-	Bromo	ONO^-	Nitrito-*O*	OSO_3^{2-}	Sulfato
I^-	Iodo	CN^-	Cyano	SSO_3^{2-}	Thiosulfato

POLYDENTATE		
Name of Ligand[b]	Abbreviation	Formula[a]
Ethylenediamine	en	$H_2NCH_2CH_2NH_2$
Oxalato	ox	$[OOCCOO]^{2-}$
Ethylenediaminetetraacetato	EDTA	$[(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2]^{4-}$

oxalate ion

ethylenediamine

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

Coordination Equilibria & Chelate effect

"The adjective chelate, derived from the great claw or chela (chely - Greek) of the lobster, is suggested for the groups which function as two units and fasten to the central atom so as to produce heterocyclic rings."
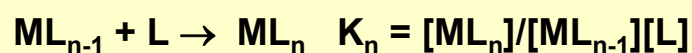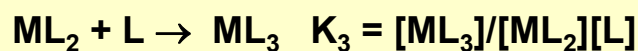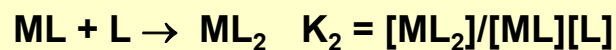
J. Chem. Soc., **1920**, *117*, **1456**

The chelate effect or chelation is one of the most important ligand effects in transition metal coordination chemistry.

Coordination Equilibria & Chelate effect

$$[Fe(H_2O)_6]^{3+} + NCS^- \rightarrow [Fe(H_2O)_5(NCS)]^{2+} + H_2O$$

$$K_f = [Fe(H_2O)_5(NCS)]^{2+} / [Fe(H_2O)_6]^{3+}[NCS^-]$$

Equilibrium constant $K_f \Rightarrow$ formation constant

$$M + L \rightarrow ML \quad K_1 = [ML]/[M][L]$$

$$ML + L \rightarrow ML_2 \quad K_2 = [ML_2]/[ML][L]$$

$$ML_2 + L \rightarrow ML_3 \quad K_3 = [ML_3]/[ML_2][L]$$

$$ML_{n-1} + L \rightarrow ML_n \quad K_n = [ML_n]/[ML_{n-1}][L]$$

Coordination Equilibria and Chelate effect

- K_1, K_2…. $\Rightarrow$ **Stepwise formation constant.**
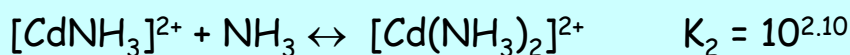- **To calculate concentration of the final product, use overall formation constant β_n:**
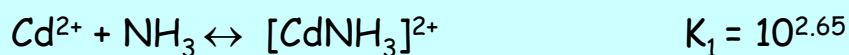
$$\beta_n = [ML_n]/[M][L]^n$$

$$= K_1 \times K_2 \times K_3 \times \dots \times K_n$$

$\Delta G^\ominus = -RT\ln(\beta)$
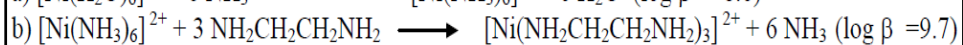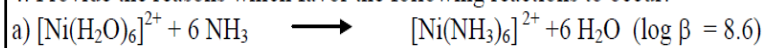$\Delta G^\ominus = -2.303\ RT\log_{10}(\beta)$
$\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$
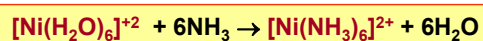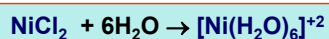

Example: $[Cd(NH_3)_4]^{2+}$

$Cd^{2+} + NH_3 \leftrightarrow [CdNH_3]^{2+}$	$K_1 = 10^{2.65}$
$[CdNH_3]^{2+} + NH_3 \leftrightarrow [Cd(NH_3)_2]^{2+}$	$K_2 = 10^{2.10}$
$[Cd(NH_3)_2]^{2+} + NH_3 \leftrightarrow [Cd(NH_3)_3]^{2+}$	$K_3 = 10^{1.44}$
$[Cd(NH_3)_3]^{2+} + NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+}$	$K_4 = 10^{0.93}$

Overall: $Cd^{2+} + 4\ NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+}$

$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$
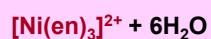$= 10^{(2.65 + 2.10 + 1.44 + 0.93)} = 10^{7.12}$

4. Provide the reasons which favor the following reactions to occur:

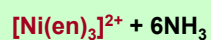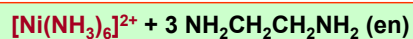a) $[Ni(H_2O)_6]^{2+} + 6\ NH_3 \longrightarrow [Ni(NH_3)_6]^{2+} + 6\ H_2O$ (log β = 8.6)

b) $[Ni(NH_3)_6]^{2+} + 3\ NH_2CH_2CH_2NH_2 \longrightarrow [Ni(NH_2CH_2CH_2NH_2)_3]^{2+} + 6\ NH_3$ (log β =9.7)

What are the implications of the following results?

$NiCl_2 + 6H_2O \rightarrow [Ni(H_2O)_6]^{+2}$	
$[Ni(H_2O)_6]^{+2} + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$	log β = 8.6
$[Ni(H_2O)_6]^{+2} + 3\ NH_2CH_2CH_2NH_2$ (en) $\downarrow$ $[Ni(en)_3]^{2+} + 6H_2O$	log β = 18.3
$[Ni(NH_3)_6]^{2+} + 3\ NH_2CH_2CH_2NH_2$ (en) $\downarrow$ $[Ni(en)_3]^{2+} + 6NH_3$	log β = 9.7

Complex Formation: Major Factors

$$[Ni(H_2O)_6] + 6NH_3$$
$$\rightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$$

➢ NH$_3$ is a **stronger (better) ligand** than H$_2$O

➢ Δ_O NH$_3$ > Δ_O H$_2$O

➢ $[Ni(NH_3)_6]^{2+}$ is more stable

➢ $\Delta G = \Delta H - T\Delta S$ (ΔH -ve, $\Delta S \approx 0$)

➢ ΔG for the reaction is negative

Chelate Formation: Major Factors

$$[Ni(NH_3)_6]^{2+} + 3\ NH_2CH_2CH_2NH_2\ (en)$$

$$\downarrow$$

$$[Ni(en)_3]^{2+} + 6NH_3$$

➢ **en and NH$_3$ have similar N-donor environment**
➢ **but en is bidentate and *chelating* ligand**
➢ **rxn proceeds towards right, ΔG negative**
➢ **$\Delta G = \Delta H - T\Delta S$ (ΔH -ve, ΔS ++ve)**

➢ **rxn proceeds due to entropy gain**
➢ **ΔS ++ve is the major factor in chelate effect.**

H. W. 1:

$Cd^{2+} + 4\ NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+}$ $Cd^{2+} + 4\ MeNH_2 \leftrightarrow [Cd(MeNH_2)_4]^{2+}$

$Cd^{2+} + 2\ en \leftrightarrow [Cd(en)_2]^{2+}$

Ligands	log β
4 NH_3	7.44
4 $MeNH_2$	6.52
2 en	10.62

Chelate Effect : Data & understanding

NH_3 complexes				en complexes				Chelate effect		
	ΔG	ΔH	ΔS		ΔG	ΔH	ΔS	ΔΔG	ΔΔH	ΔΔS
$[Ni(NH_3)_2(H_2O)_4]^{2+}$	-29.0	-33	-12	$[Ni(en)(H_2O)_4]^{2+}$	-41.9	-38	17	-12.9	-5	29
$[Ni(NH_3)_4(H_2O)_2]^{2+}$	-46.3	-65	-63	$[Ni(en)_2(H_2O)_2]^{2+}$	-77.2	-77	12	-30.9	-11	74
$[Ni(NH_3)_6]^{2+}$	-74.2	-92	-58	$[Ni(en)_3]^{2+}$	-111.8	-107	29	-50.0	-17	121

H.W. 2: How can you justify the chelate formation is linked with entropy Gain?

Reaction of ammonia and en with Cu^{2+}

$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Cu(NH_3)_2(H_2O)_2]^{2+} + 2 H_2O$

Log β_2 = 7.7

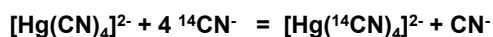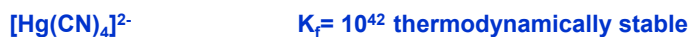$[Cu(H_2O)_6]^{2+} + en \rightarrow [Cu(en)(H_2O)_4]^{2+} + 2 H_2O$

Log K_1 = 10.6

Kinetic stability   Inert and labile complexes

The term inert and labile are relative

"A good rule of thumb is that those <u>complexes that react completely within 1 min at 25º</u> should be considered labile and those that take longer should be considered inert."

Thermodynamically stable complexes can be labile or inert

$[Hg(CN)_4]^{2-}$ $K_f = 10^{42}$ **thermodynamically stable**

$[Hg(CN)_4]^{2-} + 4\ ^{14}CN^- = [Hg(^{14}CN)_4]^{2-} + CN^-$
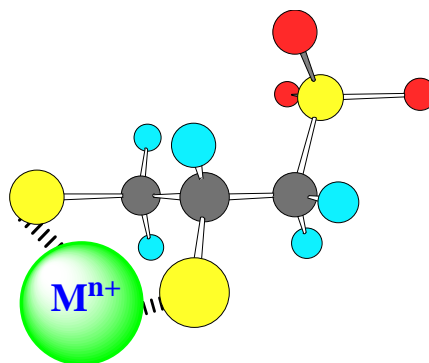
Very fast reaction   **Labile**
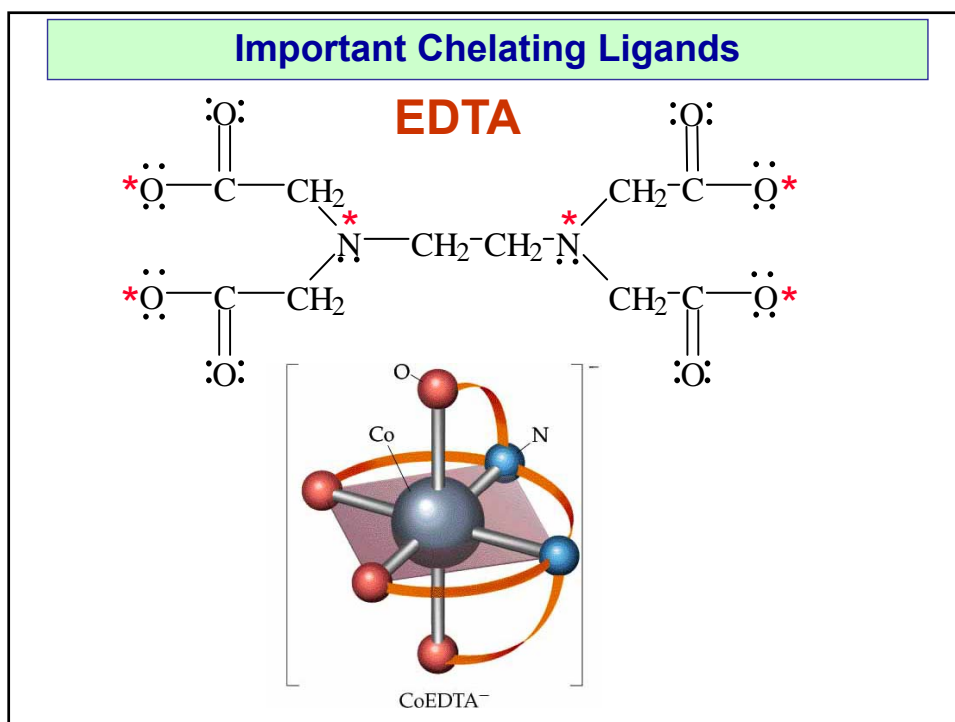
Chelating agents:

(1) Used to remove unwanted metal ions in water.

(2) Selective removal of Hg^{2+} and Pb^{2+} from body when poisoned.

(3) Prevent blood clots.

(4) Solubilize iron in plant fertilizer.

Important Chelating Ligands

2,3-dimercapto-1-propanesulfonic acid sodium (DMPS)

M^{n+}

DMPS is a effective chelator with two groups thiols - for mercury, lead, tin, arsenic, silver and cadmium.

SH   O

HO   OH

O   SH

(*R,S*)-2,3-dimercaptosuccinic acid

As, Cu, Pb, Hg

SH

CH₃ — C — CH — COOH

CH₃   NH₂

D-Penicillamine

Zn
As
Hg
Au
Pb

SH

HS   OH

M^+ →

M   S   OH
          S

Dimercaprol

As
Hg
Au
Pb

Important Chelating Ligands

EDTA

:O: :O:

O — C — CH₂   CH₂ — C — O

N — CH₂ — CH₂ — N

O — C — CH₂   CH₂ — C — O

:O: :O:

O

Co   N

CoEDTA⁻

EDTA: another view

Ca^{2+}

Anticoagulant

$$+n-4$$
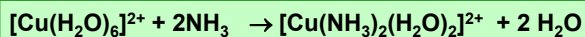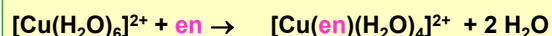
M^{n+}