

Coordination Chemistry

course by Prof. Saurav Chatterjee

- Werner's coordination theory
- Chelate Effect (Metal-EDTA complexes)
- Monodentate, bidentate, polydentate Ligand
- Crystal Field Theory-CFSE calculation, Octahedral, tetrahedral splitting

Books:

J. D. Lee, Concise Inorganic Chemistry, 5th edition, Blackwell Publishing

J. E. Huheey, E. A. Keiter and R. L. Keiter, Inorganic Chemistry, Principles of structure and reactivity, Harper Collins

F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley Interscience, New York

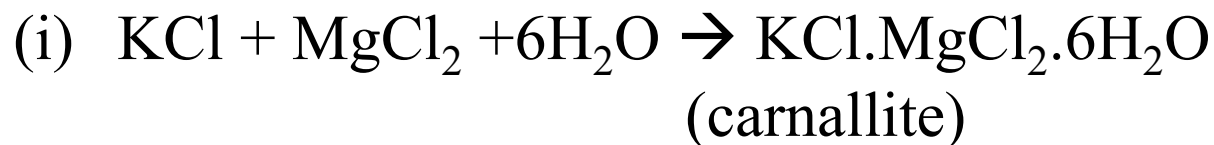
ADDITION COMPOUNDS

When stoichiometric amounts of two or more stable compounds join together two types of addition compounds are formed.

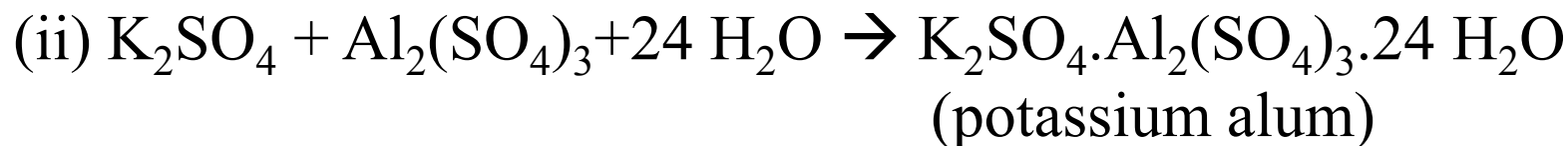
(i) Double salts

(ii) Coordination Compounds

Double Salts: lose their identity in solution

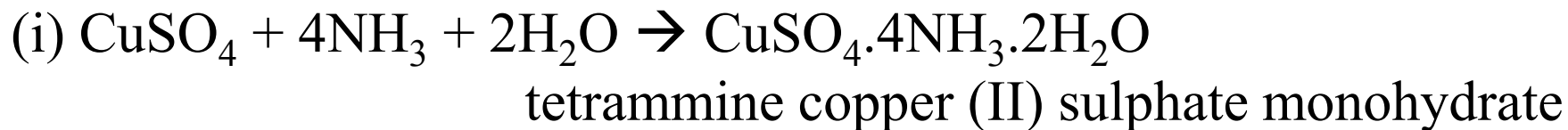


In solution: K^+ , Mg^{2+} and Cl^-



In solution: K^+ , Al^{3+} and SO_4^{2-}

Coordination Compounds: retain their identity in solution



Exists as $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4]^{2+}$ in aqueous solⁿ: **(Deep Blue)**

Cu^{+2} exists as $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ in aqueous solⁿ and in hydrated crystalline salts **(Pale Blue)**



$\text{K}_4[\text{Fe}(\text{CN})_6]$: Potassium ferrocyanide

$[\text{Fe}(\text{CN})_6]^{4-}$ is stable in solution.

Transition metal ions, in particular, form many stable coordination complexes

Main-group Elements		Transition Metals										Main-group Elements					
H																	
Li	Be															H	He
Na	Mg											B	C	N	O	F	Ne
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Al	Si	P	S	Cl	Ar
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Ga	Ge	As	Se	Br	Kr
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	In	Sn	Sb	Te	I	Xe
Fr	Ra	Ac	Rf	Ha	106	107	108	109				Tl	Pb	Bi	Po	At	Rn

Lanthanides

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Actinides

Transition elements: inner incomplete d- or f-sub-shell

Electrons from both inner d or f-sub-shell and outer s sub-shell can be involved in compound formation

Group 12: d^{10} configuration → not typical TM element

Element	Partial Orbital Diagram									
	4s	3d					4p			
Sc	↑↓	↑								
Ti	↑↓	↑	↑							
V	↑↓	↑	↑	↑						
Cr	↑	↑	↑	↑	↑					
Mn	↑↓	↑	↑	↑	↑	↑				
Fe	↑↓	↑↓	↑	↑	↑	↑				
Co	↑↓	↑↓	↑↓	↑	↑	↑				
Ni	↑↓	↑↓	↑↓	↑↓	↑	↑				
Cu	↑	↑↓	↑↓	↑↓	↑↓	↑↓				
Zn	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓				

TM elements: Variable valence

Sc			+3				
Ti	+1	+2	+3	+4			
V	+1	+2	+3	+4	+5		
Cr	+1	+2	+3	+4	+5	+6	
Mn	+1	+2	+3	+4	+5	+6	+7
Fe	+1	+2	+3	+4	+5	+6	
Co	+1	+2	+3	+4	+5		
Ni	+1	+2	+3	+4			
Cu	+1	+2	+3				
Zn		+2					

Werner's Coordination Theory-1893

Alfred Werner : father of the structure of coordination complexes



The Nobel Prize in Chemistry 1913

"in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry"

- First attempt to explain the bonding in coordination complexes.
- **Suggested the theory before the electron was discovered (1896) and before the electronic theory of valency.**
- Complexes must have been a complete mystery without any knowledge of bonding and structure.

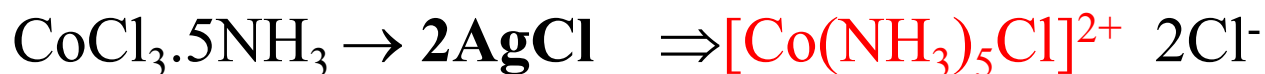
Without any modern analytical tools as IR, NMR, X-ray, all his studies were made using simple reaction chemistry

Werner was able to explain the nature of bonding in complexes, and he concluded that in complexes the metal shows two different sorts of valency

Why does a stable salt like CoCl_3 react with a varying number of stable molecules such as NH_3 to give several new compounds?

$\text{CoCl}_3 \cdot 6\text{NH}_3$	orange-yellow
$\text{CoCl}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$	red
$\text{CoCl}_3 \cdot 5\text{NH}_3$	purple
$\text{CoCl}_3 \cdot 4\text{NH}_3$	green

Treatment with excess AgNO_3



Werner explained these observations by suggesting that transition metals, such as the Co, have a primary valency and a secondary valency.

Primary valency:

- ❖ Non-directional
- ❖ Equivalent to the number of charges on the complex ion
- ❖ Applicable to simple salts and complex ions

Example: $\text{CoCl}_2 \rightarrow \text{Primary Valency} = 2$

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \rightarrow \text{Primary Valency} = 3$

Secondary valency:

- ❖ Directional
- ❖ Equals to the numbers of ligands coordinated to the metal
- ❖ Also called coordination number

For $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ Primary Valency = 3; Secondary Valency = 6

$\text{CoCl}_3 \cdot 6\text{NH}_3$	$[\text{Co}(\text{NH}_3)_6]^{3+}[\text{Cl}^-]_3$	orange-yellow
$\text{CoCl}_3 \cdot 5\text{NH}_3 \cdot \text{H}_2\text{O}$	$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}[\text{Cl}^-]_3$	red
$\text{CoCl}_3 \cdot 5\text{NH}_3$	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}[\text{Cl}^-]_2$	purple
$\text{CoCl}_3 \cdot 4\text{NH}_3$	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+[\text{Cl}^-]$	green

- The cobalt ion is coordinated to a total of **six ligands** in each complex, which satisfies the *secondary valency* of this ion.
- Some of the Cl^- ions are free to dissociate when the complex dissolves in water → satisfy the *primary valency*
- Others are bound to the Co^{3+} ion and does not dissociate → satisfy the *secondary valency*
- Secondary valencies are directional therefore a complex ion has a particular shape.
- Werner deduced the shape of many complexes by synthesizing the possible isomers
- He mostly came across complexes with coordination numbers 6 and 4
- Coordination number: **6 (Octahedral, planar hexagonal, trigonal prism)**
:4 (Square planar, tetrahedral)

Coordination Complex

Species where transition metal ion is surrounded by a certain number of *ligands* (ligare is Latin, to bind)

Metal-Ligand bond: Coordinate covalent bond

Metal-Ligand Bond is formed between a Lewis acid and a Lewis base

Transition metal ion: *empty orbitals*: Lewis acid

Ligands: *electrons rich*: Lewis bases

One of the most relevant principles in this consideration is the hard-soft interaction principle: *Hard acids prefer hard bases*
Soft acids prefer soft bases

Hard Lewis Acids: Metal ions having high charge and small size

Soft Lewis Acids: Metal ions having low charge and large size

Hard Lewis Bases: N and O donors (NH_3 , RNH_2 , H_2O , ROH etc.) and F^- , Cl^-

Soft Lewis Bases: H^- , CN^- , I^- , CO , SCN^- etc.

Ligands (ligare is Latin, to bind)

Classified according to the number of donor atoms

Monodentate: one bond to metal ion

Bidentate: two bonds to metal ion

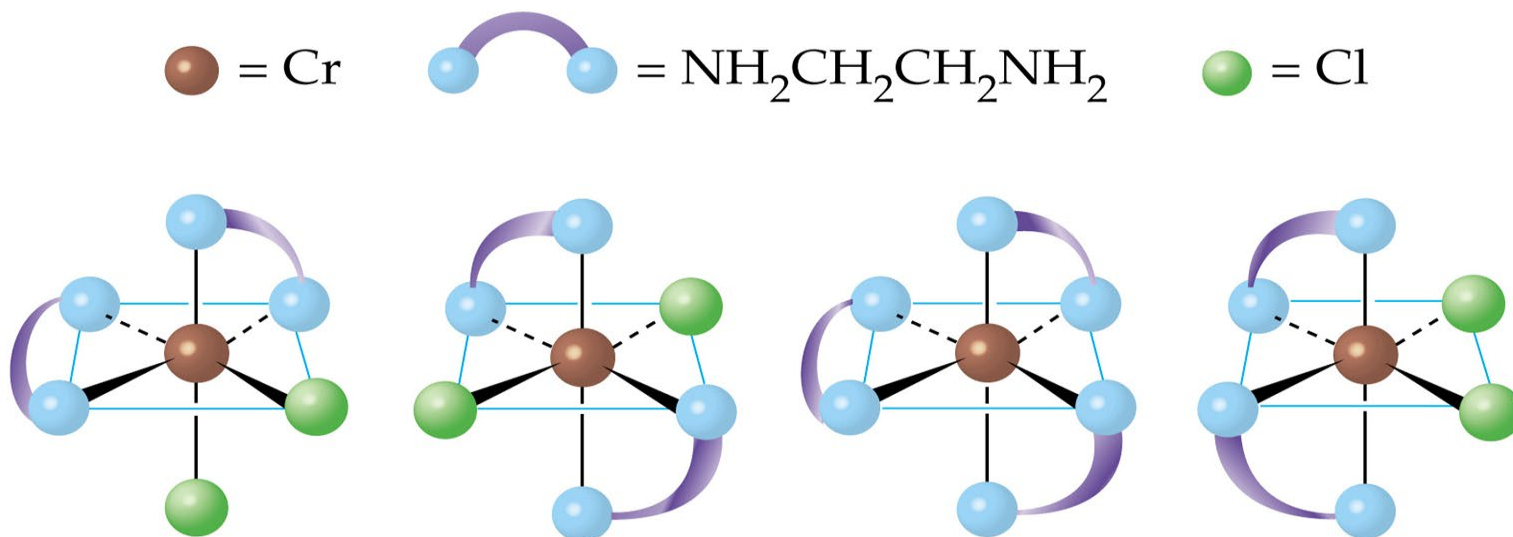
Latin: “dent” → tooth

Polydentate: more than two bonds to a metal ion possible

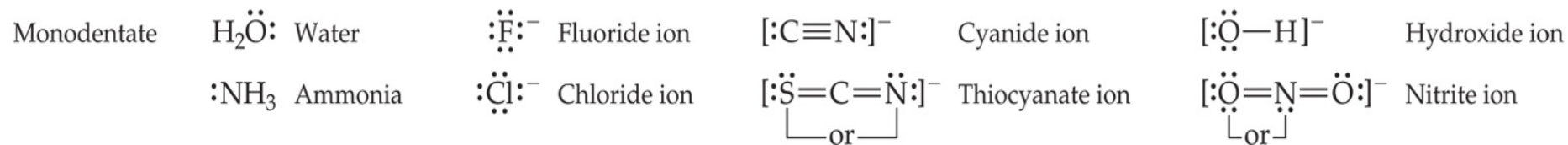
Chelate (crab like): Greek *chelos*: “crab”

When more than one atom of the ligand is bonded to the central metal atom, ring structures are formed.

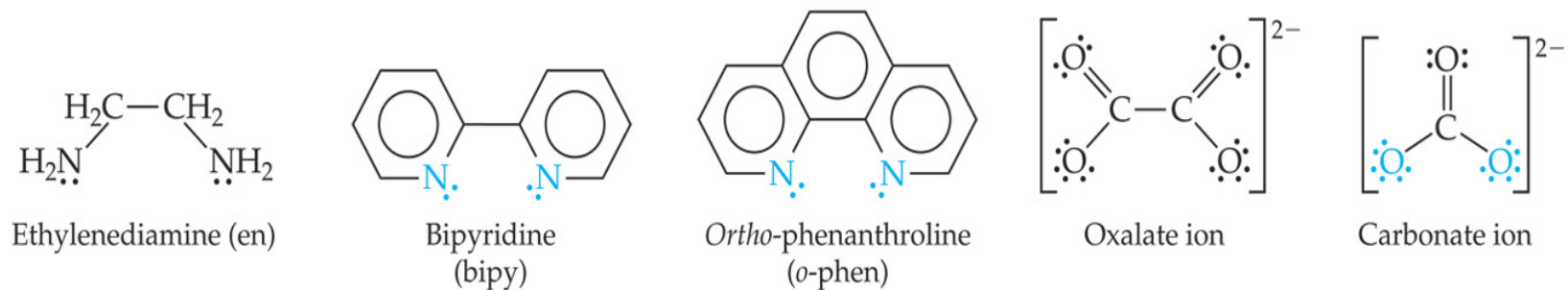
Such ring structures are called chelates.



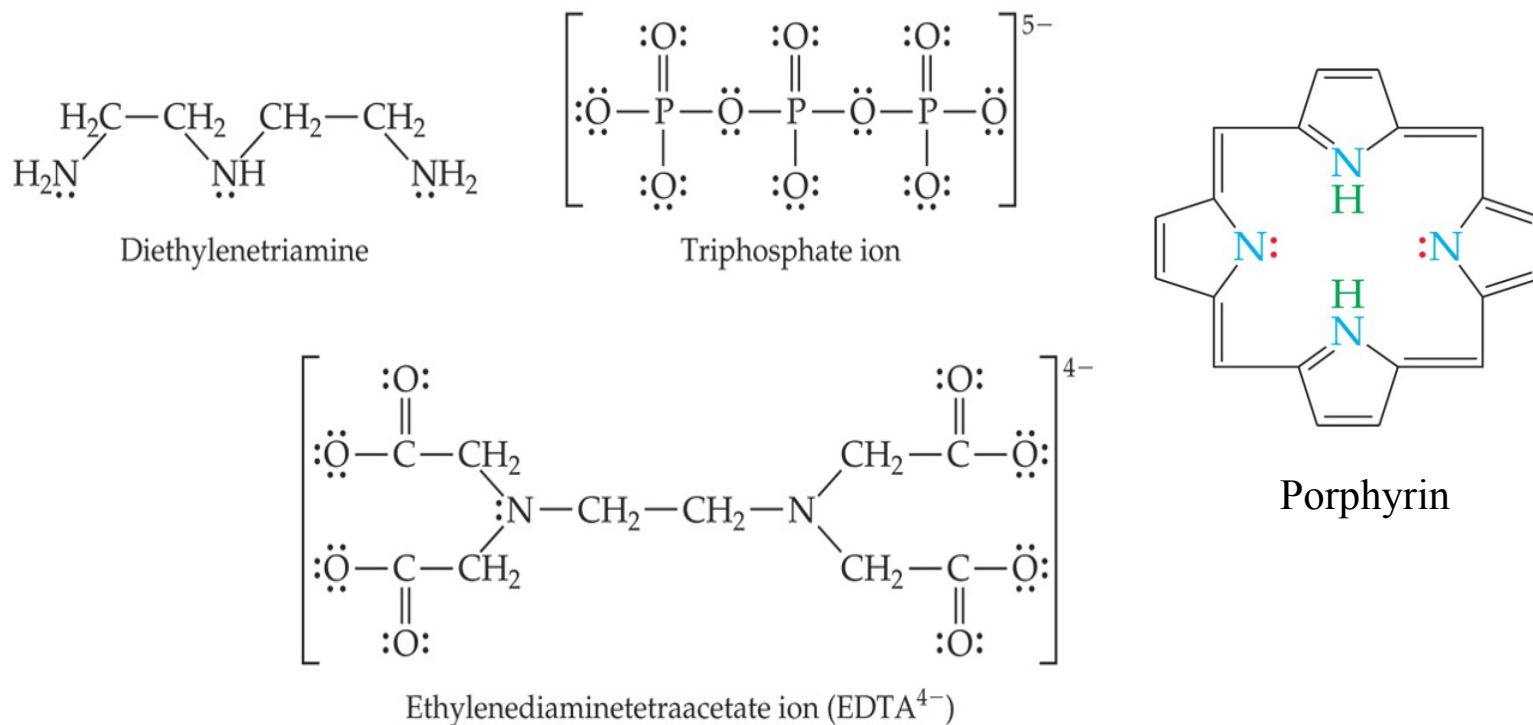
Ligand Type Examples



Bidentate



Polydentate

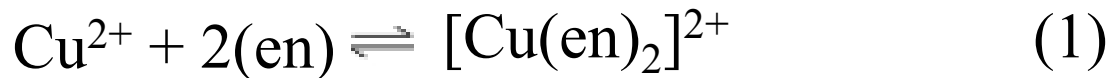


Chelate Effect

Stability of Chelates

Chelate = Claw (Greek)

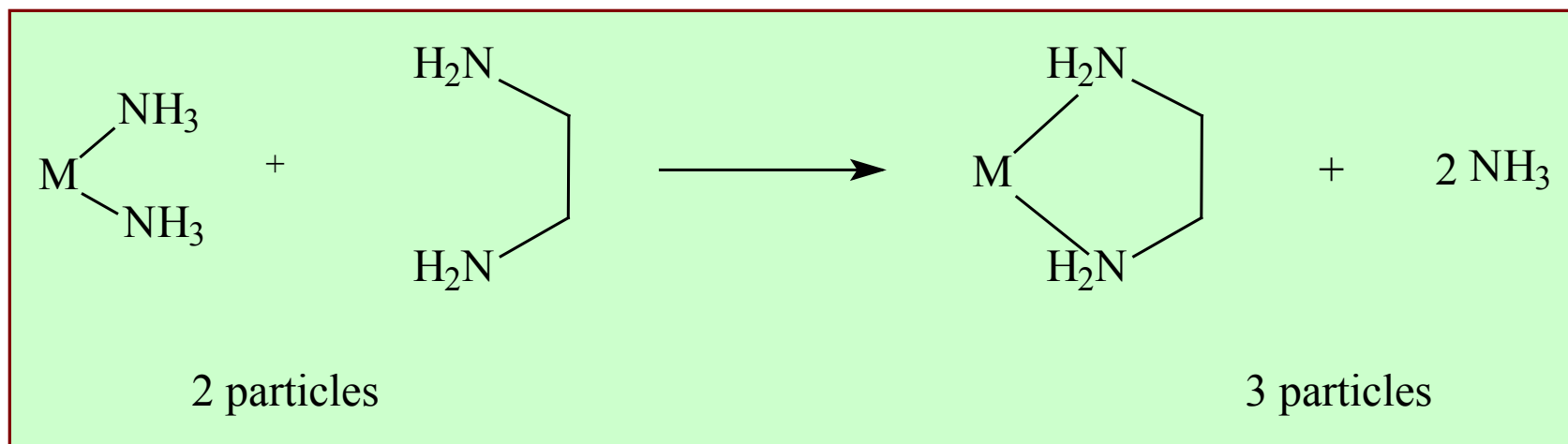
The chelates are more stable than similar complexes with unidentate ligands



Equilibrium	ΔG	$\Delta H / \text{kJ mol}^{-1}$	$T\Delta S / \text{kJ mol}^{-1}$
1	-60.67	-56.48	4.19
2	-37.40	-57.30	-19.9

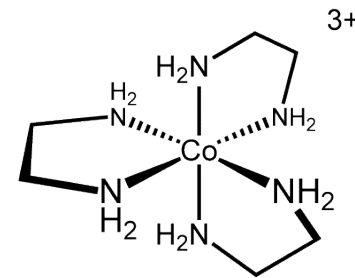
Higher stability of chelates is due to

- i) More no. of bonds have to be simultaneously broken to detach the ligand
- ii) Entropy factor



Chelate Effect

Other factors:



- More the rings are formed more will be the stability
(n dentate ligand: n-1 rings)
- Among the ring structures five and six membered rings are more stable
- For smaller and larger ring sizes the steric factors dominate; rings are strained
- Alternate single and double bonds gives further stability; conjugation brings delocalisation of electrons

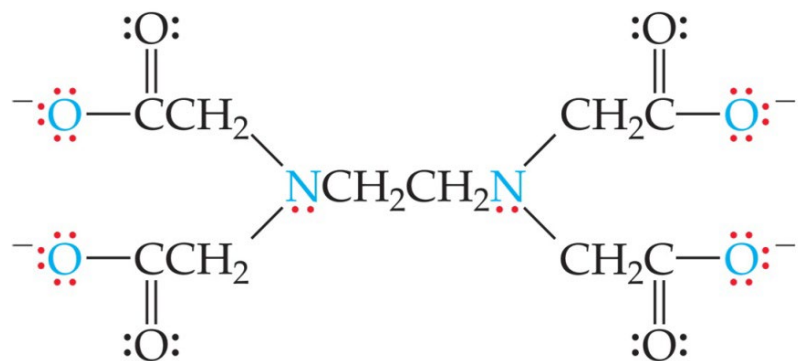
Chelation and Bite Angle:

- **Geometry of complexes can be limited by the “bite angle” of a chelating ligand**
 - The carbon chain or other backbone of a chelate ligand restricts the angle spanned by the bonding atoms
 - This can distort or drive a complex geometry into a particular shape
 - i.e. conversion from octahedral to trigonal prism

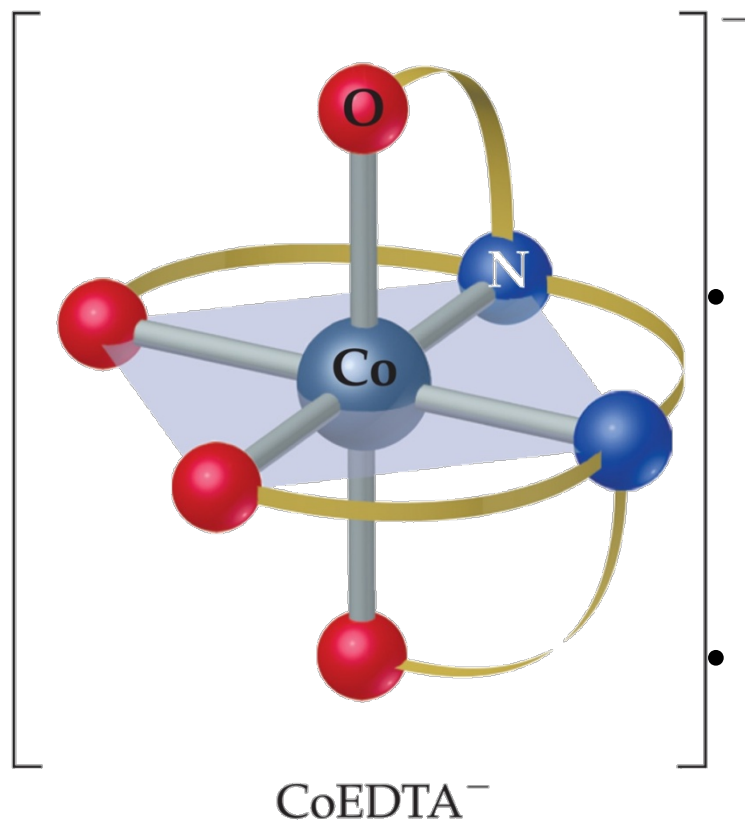
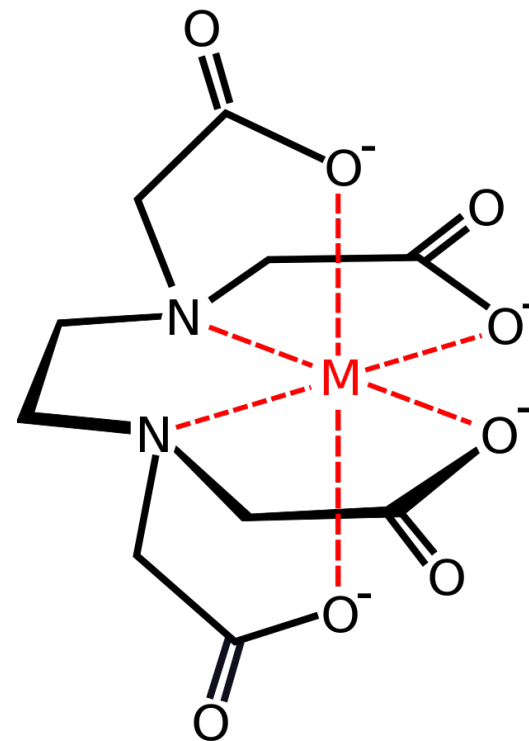
Application of Chelating agents:

- Used to remove unwanted metal ions in water
- Selective removal of Hg^{2+} and Pb^{2+} from body when poisoned
- Prevents blood clots
- Solubilizing iron in plant fertilizer
- Body contains several chelating agents adrenaline, citric acid, cortisone etc.
- Biologically important chelates:
 - Haemoglobin (Fe), Chlorophyll (Mg), Vitamine B12 (Co),
 - Cytochrome oxidase enzyme (Fe, Cu)

One very important chelating agent is **ethylenediaminetetracetate [EDTA]⁴⁻**



[EDTA]⁴⁻



[CoEDTA]⁻

- EDTA occupies 6 coordination sites, for example [CoEDTA]⁻ is an octahedral Co³⁺ complex.
- Both N atoms (blue) and O atoms (red) coordinate to the metal.

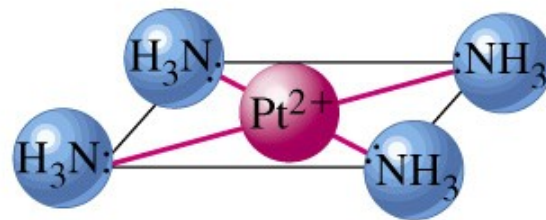
EDTA is used

- To tie up Ca^{+2} in bathroom cleaners and shower sprays
- To prevent blood clots
- To remove heavy metals from body when poisoned
- To solubilize iron in plant fertilizers
- To remove the iron taste from mayonnaise arising from its preparation in iron vats
- As an external or internal medicine
 - Cr^{2+} , Ni^{2+} etc. cause dermatitis (skin disease): removed by EDTA cream.
 - Cu^{2+} , Ni^{2+} excess present in the body can be removed by EDTA ingestion.

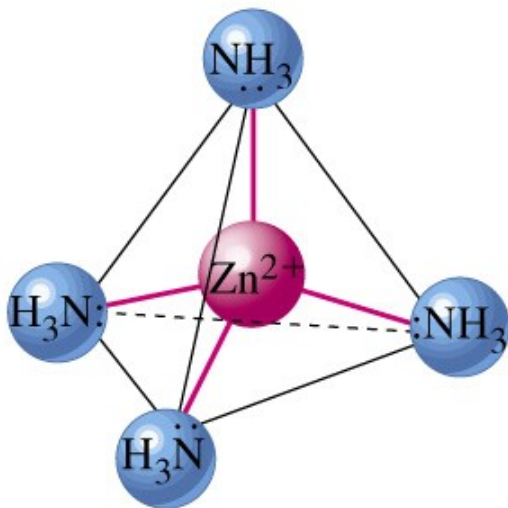
Geometry of coordination complex



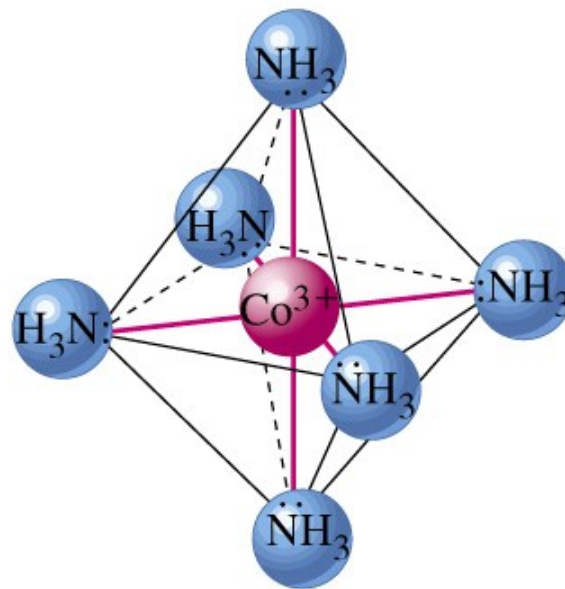
Linear



Square planar



Tetrahedral



Octahedral

1. Calculate the charge on the transition-metal ion in the following Complexes.



2. The type of hybridization and shape of the molecule in ClF_3 are respectively

i) sp^3 , pyramidal ii) sp^2 , trigonal planer iii) dsp^3 , trigonal bipyramidal iv) sp^3d , T-shaped

3. Draw the structure and identify the coordination sites of the following ligands:

(a) NN'- Diethyldithiocarbamate ion

(b) 8-Hydroxyquinoline (Oxine)

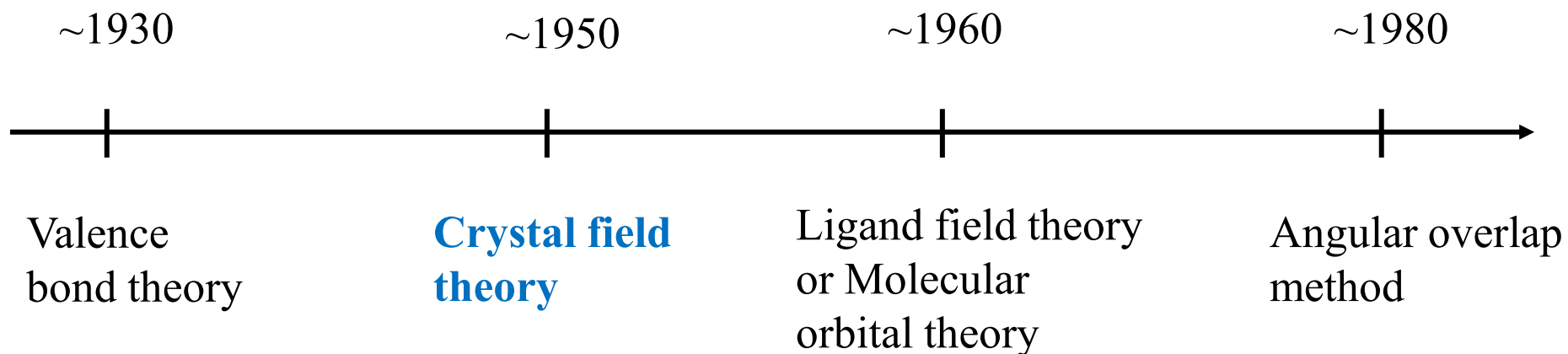
Ans:1(a) $\text{Na}_2\text{Co}(\text{SCN})_4$ +2
(b) $\text{Ni}(\text{NH}_3)_6(\text{NO}_3)_2$ +2
(c) K_2PtCl_6 +4

Ans:2 sp^3d , T-shaped

Bonding in coordination compounds



To explain nature of bonding in coordination compounds, several theories developed.



Crystal Field Theory



It was proposed by Hans Bethe and further developed by Van Vleck.

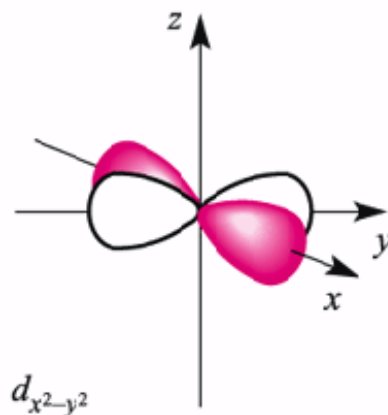
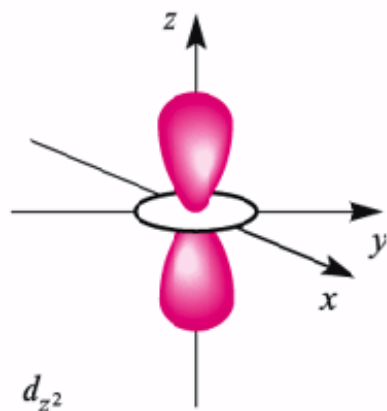
CFT-Assumptions

- The interaction between the metal ion and the ligands are purely electrostatic (ionic).
- The ligands are regarded as point charges or dipoles.
- CFT does not allow ligand electrons to enter metal orbital. Thus the metal and ligand do not share their electrons.
- Electrons on the metal are under repulsive from those on ligands.

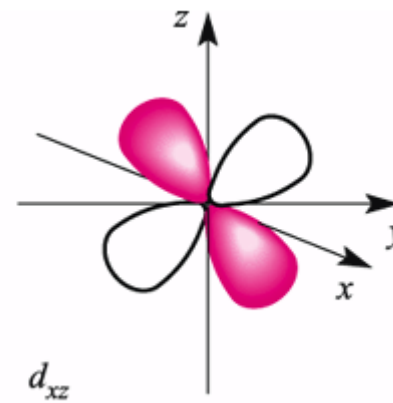
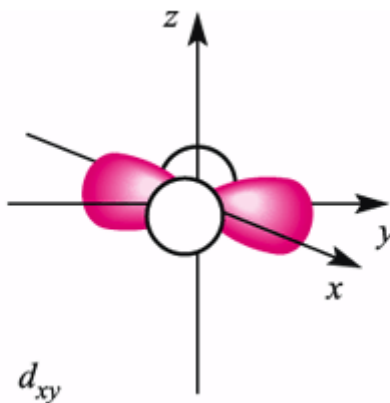
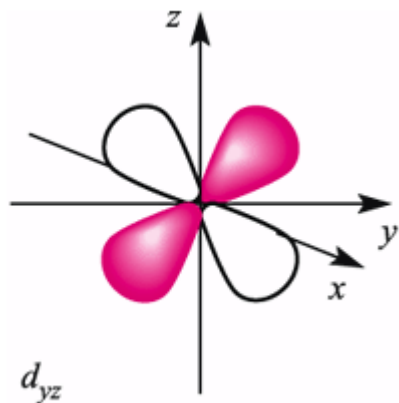
Crystal Field Theory



In order to understand the interaction of crystal or ligand field with valence orbitals (d-orbitals) of transition metal in complexes, it is necessary to understand the geometrical relationship of d-orbitals in different geometry of ligands.



along the axis



In between axis

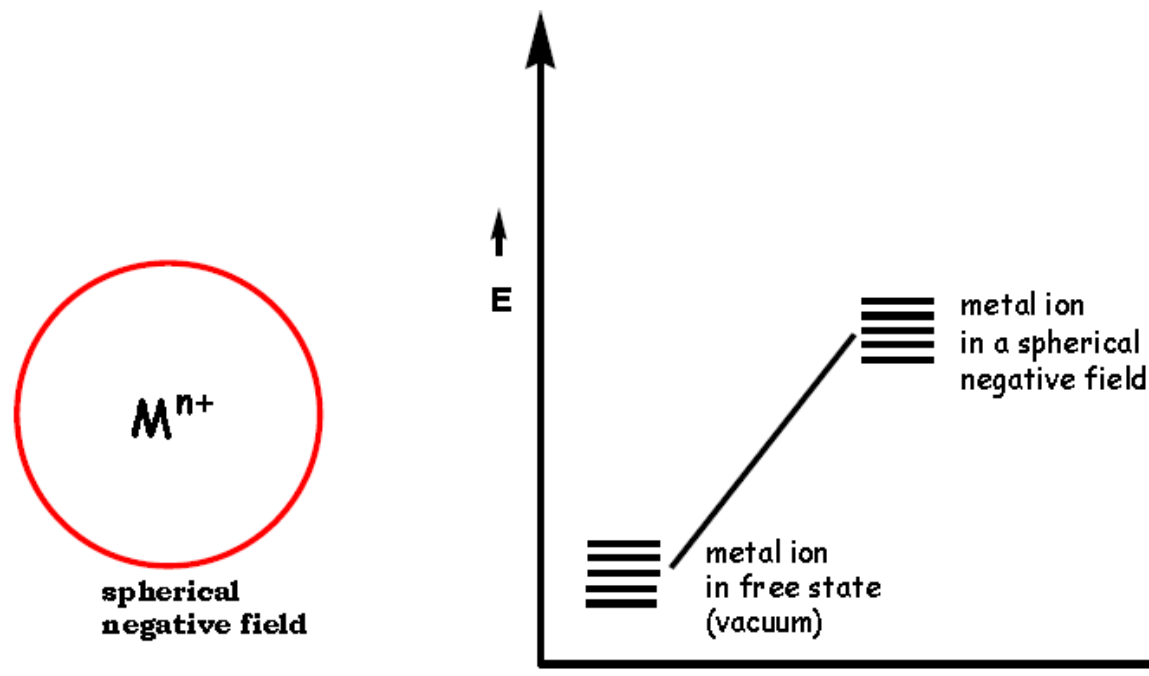
Pink color = positive sign; white = negative sign

Spherical symmetric field



Five d-orbitals of an isolated gaseous transition metal ion are degenerate.

If a spherical symmetric field of negative charges is placed around the metal, these orbitals remain degenerate, but all of them raised in energy as a result of repulsion between the negative charge on the ligand and electron(s) in d-orbital.



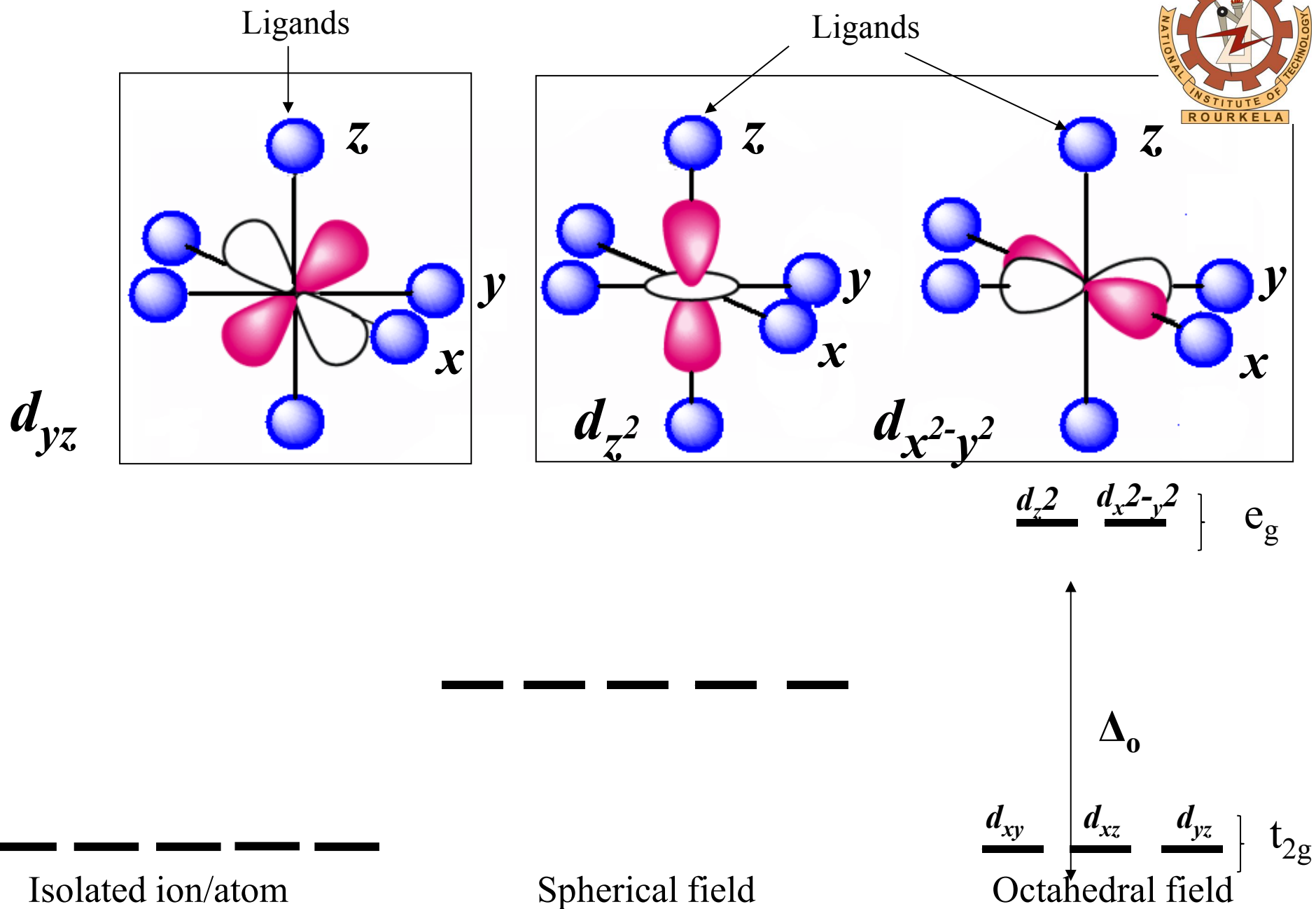
Crystal field effect in octahedral symmetry



Q. How the six d-electrons are filled in the d-orbitals of Co^{3+} ion in presence of six NH_3 ligands in $[\text{Co}(\text{NH}_3)_6]^{3+}$?

Energy level diagram of d-orbitals in presence of ligands in octahedral geometry

- If we have an electron in each d-orbital, then how much repulsion each d-orbital feels, by ligands in octahedral geometry (octahedral field), decide its relative energy.
- If the d-orbital feels more repulsion, then its energy will be higher.
- Since $d_{x^2-y^2}$ and d_{z^2} orbitals directed along axial directions and the ligands come along the axial directions, so these orbitals feel more repulsion and hence have higher energy.
- d_{xy} , d_{xz} , d_{yz} orbitals directed in between axes and the ligands come along the axial directions, so these orbitals feel less repulsion and hence have lower energy.

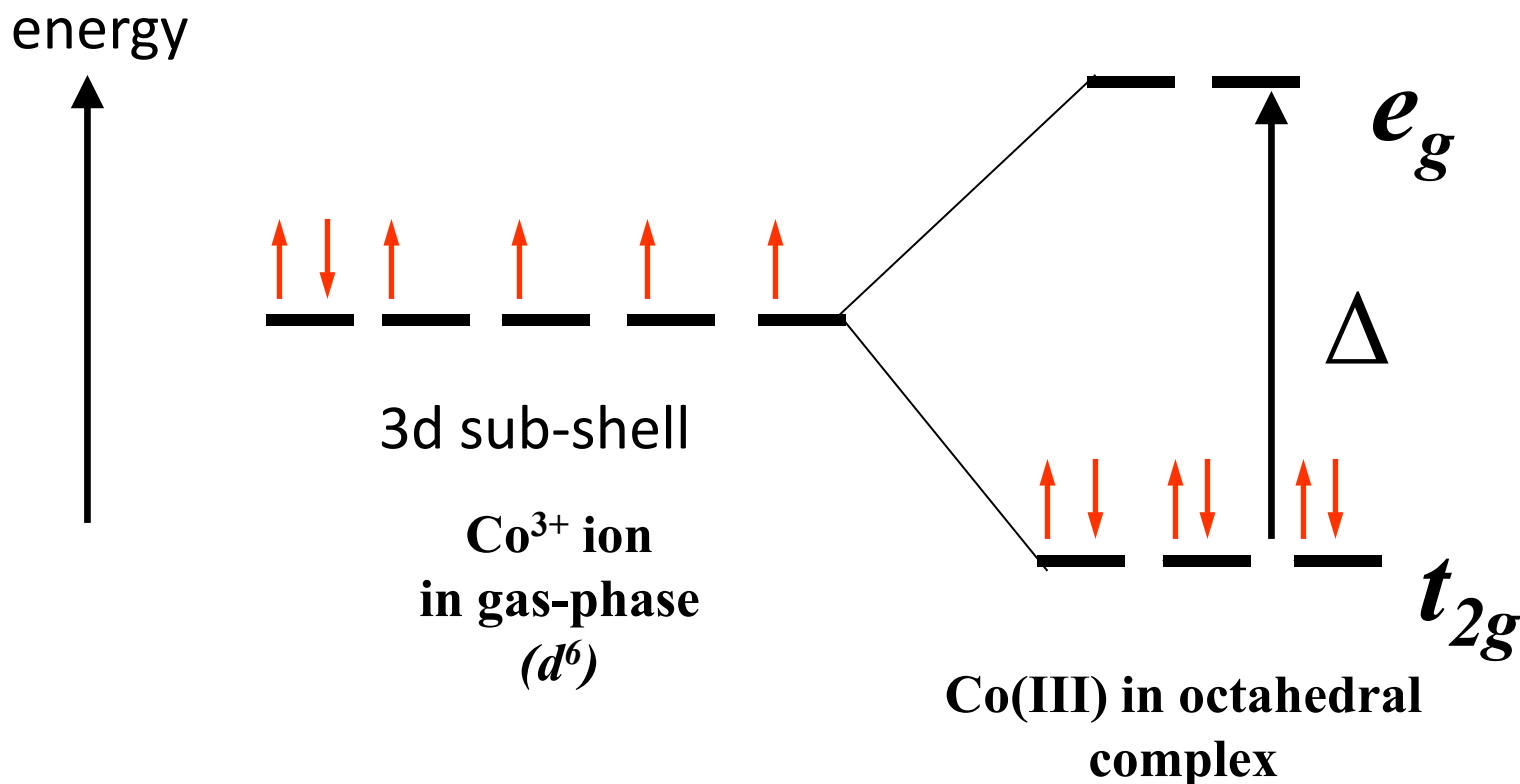


Crystal field effect in octahedral symmetry



In presence of ligands in octahedral geometry, the d-orbitals split into two sets, e_g and t_{2g} . The energy difference between e_g and t_{2g} set of orbitals is the crystal field splitting energy (Δ_o).

d-electrons filling in $[\text{Co}(\text{NH}_3)_6]^{3+}$



Crystal field effect in tetrahedral symmetry

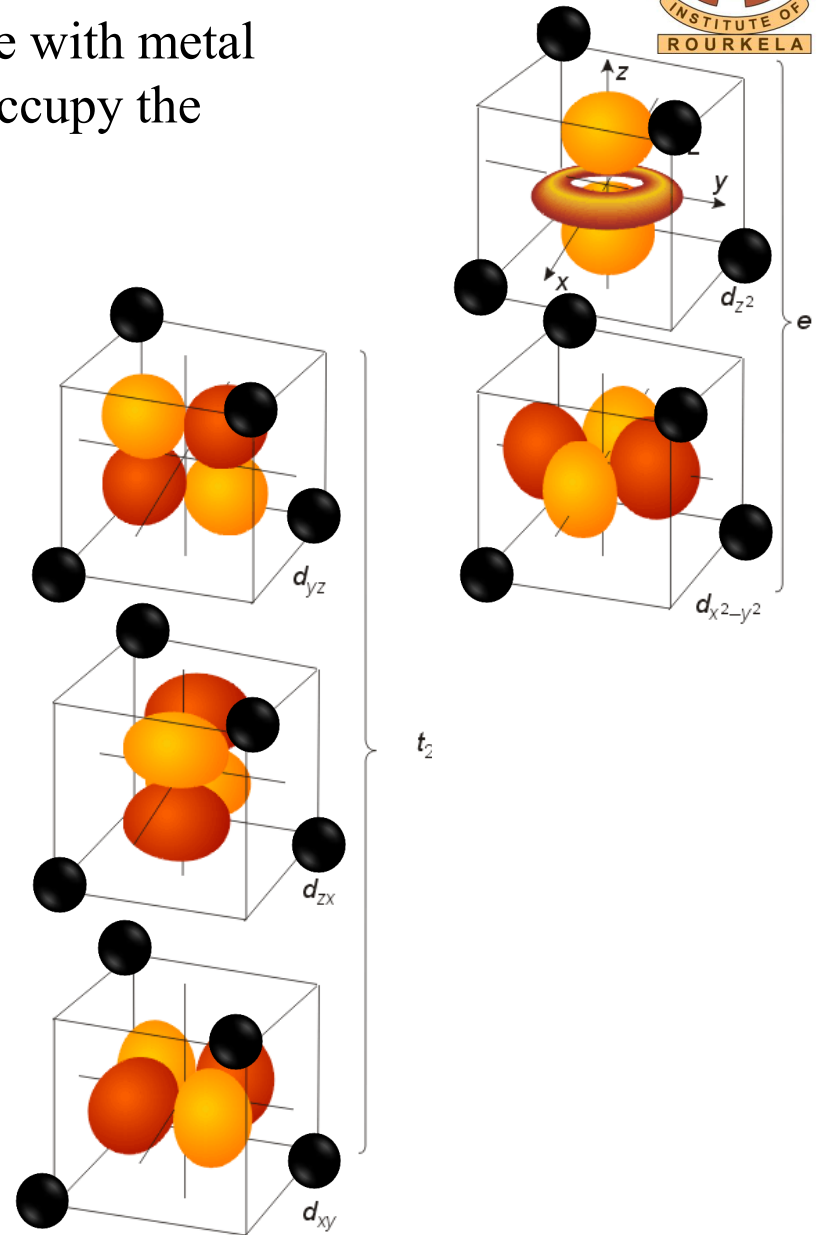


➤ Imagine a tetrahedral molecule inside a cube with metal ions in the center of the cube. The ligands occupy the four alternate corners of the cube.

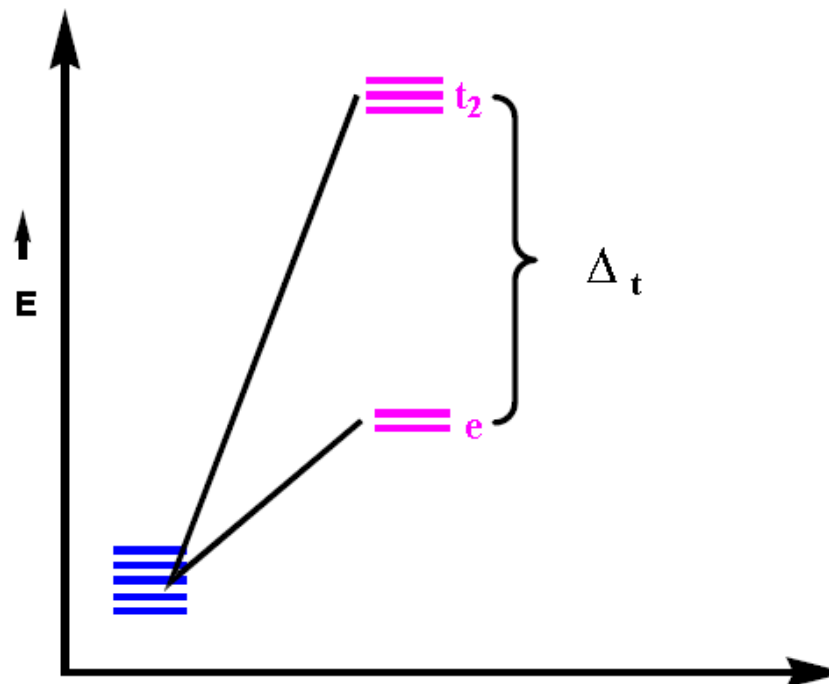
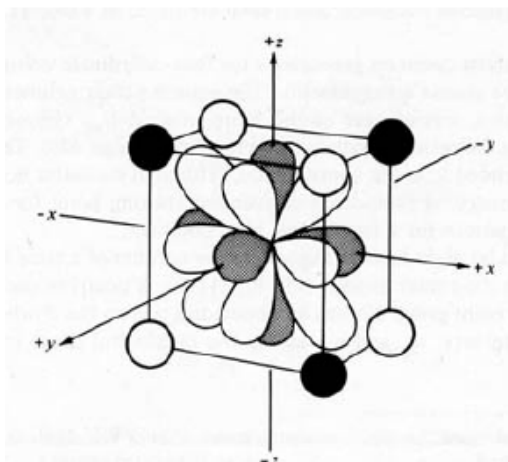
➤ The two e-orbitals (d_{z^2} and $d_{x^2-y^2}$) point to the center of the face of the cube. The three t_2 -orbitals point to the center of edges of the cube.

➤ Therefore the t_2 -orbitals are nearer to the ligands than e-orbitals.

➤ Hence t_2 -orbitals have higher energy compared to e-orbitals.



Tetrahedral Field



$$\Delta_t < \Delta_o$$

$$\Delta_t = \frac{4}{9} \Delta_o$$

Factors affecting the magnitude of Δ



Number of factors that affect the extent to which d-orbitals split by surround ligands:

1. Oxidation state of the metal ion

The magnitude of Δ increases with increasing oxidation state on the central metal ion.

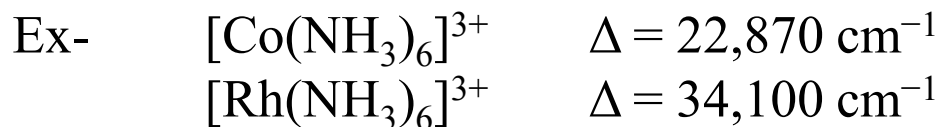
Complex	Δ (cm ⁻¹)
$[\text{CrF}_6]^{2-}$	22,000
$[\text{CrF}_6]^{3-}$	15,060
$[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$	28,600
$[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$	19,800



Factors affecting the magnitude of Δ

2. Nature of metal ion

The magnitude of Δ increases from 3d to 4d and to 5d transition elements.

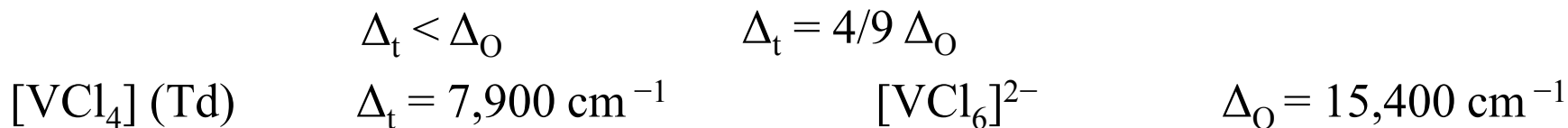


The pairing energy decreases as we go from 3d to 4d and to 5d transition elements.



3. Number and geometry of ligands

If there are more number of ligands then there is larger splitting of d-orbitals.



4. Effect of type of ligand

Different ligands split the d-orbitals of the metal atom/ion to different extent.

Complex	Δ (cm ⁻¹)
$[\text{VCl}_6]^{3-}$	~12,000
$[\text{VF}_6]^{3-}$	~16,000
$[\text{V}(\text{Urea})_6]^{3+}$	~17,000
$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	~18,000
$[\text{V}(\text{CN})_6]^{3+}$	~23,000

Spectrochemical series:

Organization of ligands according to the magnitude of (Δ) crystal field splitting energy exerted.



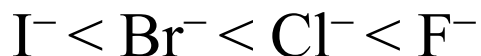
Increasing order of Δ

Weak field ligands: Ligands cause small splitting of d-orbitals.

Strong field ligands: Ligands cause larger splitting of d-orbitals.



Qualitative explanation:

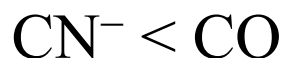


Smaller the ligand, the closer it comes to the metal ion, thus greater the repulsion.



F^- , OH^- can donate a pair of electrons from their p-orbital to d-orbital of metal forming a π bond. F^- , OH^- are π donor ligands but H_2O is not.

This reduces the charge on both ligand and metal resulting less repulsion on d-orbitals and hence less splitting.



Metal donate electrons to empty atomic orbital or low lying antibonding MO of ligand, resulting a π bond. PPh_3 , CN^- , CO are π acceptor ligands.

When a bond forms by donation of electron from metal to ligand, it is called as back bonding.

Combination of bonding and back bonding creates strong bonding in complexes containing PPh_3 , CN^- , CO ligands.

Crystal Field Stabilization Energy (CFSE)



Occupation of the

lower energy d-orbitals by electrons causes a stabilization of the complex.

higher energy d-orbitals causes a rise in energy of the complex.

In octahedral field

$$\text{CFSE} = [-0.4 n(t_{2g}) + 0.6 n(e_g)] \Delta_o$$

In tetrahedral field

$$\text{CFSE} = [-0.6 n(e) + 0.4 n(t_2)] \Delta_t$$

where $n(t_{2g})$ and $n(e_g)$ are the numbers of electrons in the t_{2g} and e_g levels respectively in octahedral complex.

And $n(t_2)$ and $n(e)$ are the numbers of electrons in the t_2 and e levels respectively in octahedral complex.

CFSE in octahedral field



d^1-d^3

If there are one to three valence electrons present in metal ion, the t_{2g} orbitals are filled in an octahedral geometry of ligands.

So the CFSE will be $-0.4\Delta_o$, $-0.8\Delta_o$ and $-1.2\Delta_o$ for d^1 , d^2 and d^3 electronic configuration, respectively.

— — e_g

— — — — —

d^4-d^7

— — — t_{2g}

Two possibilities.

The electron may enter the higher energy, e_g , level.

(High spin complexes, seen in weak field ligands.)

Or, it may pair up with another electron in one of the t_{2g} orbital.

Low spin complexes, observed in strong field ligands.

CFSE in octahedral field



d^4 - d^7

The actual configuration depends on the relative magnitude of Δ_o and P (pairing energy).

Pairing energy is the amount of energy needed to pair up d -electron.

For $\Delta_o < P$, the fourth electron enters one of the e_g orbital. **High spin complex**

For $\Delta_o > P$, the fourth electron pair up with one in t_{2g} orbital. **Low spin complex**

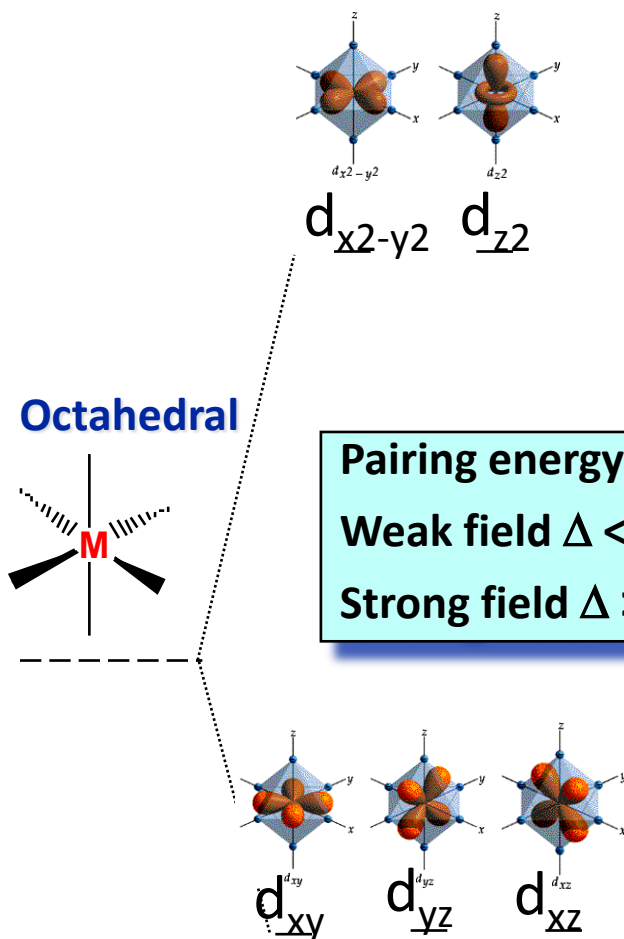
Weak field ligand \Rightarrow smaller $\Delta_o \Rightarrow$ High spin complex

strong field ligand \Rightarrow larger $\Delta_o \Rightarrow$ Low spin complex

Since $\Delta_t = 4/9 \Delta_o$, all the tetrahedral complexes are high spin complexes.

Q. Calculate the CFSE for d^5 , d^6 , d^7 metal ions in both high spin and low spin octahedral complex.

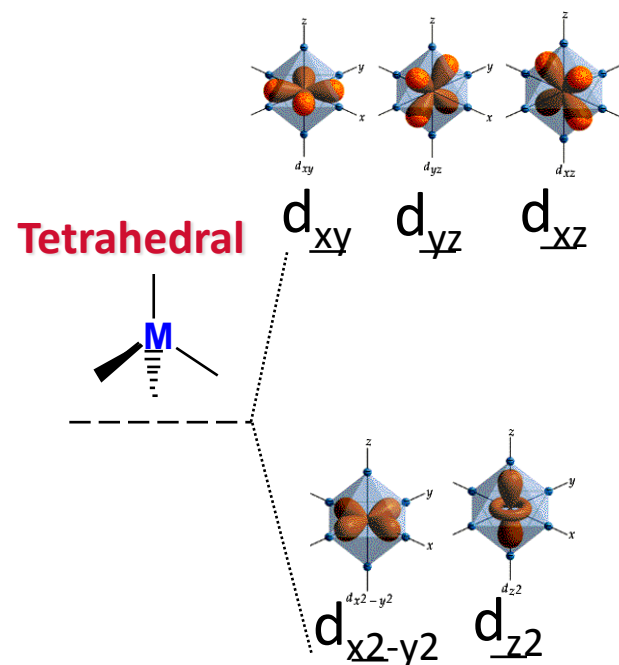
CF splitting for Octahedral, Tetrahedral Geometry



Pairing energy Vs. Δ

Weak field $\Delta < P$

Strong field $\Delta > P$



Small $\Delta \rightarrow$ High Spin



1. Among $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$, explain which forms low spin complex.

2. Determine the electronic configuration (in terms of $t_{2g}^m e_g^n$ or $e^m t_2^n$, as appropriate) and draw the d-orbital splitting energy diagram of the following complexes.

(a) $[\text{Fe}(\text{CN})_6]^{3-}$, (b) $[\text{Co}(\text{Br})_4]^{2-}$

Calculate the CFSE for each of these complexes.

4. $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is a strong oxidizing agent, but $[\text{Co}(\text{NH}_3)_6]^{3+}$ is stable in aqueous solution. Explain.

5. Predict the number of unpaired electrons for: (a) A tetrahedral d^6 ion, (b) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, (c) $[\text{MnO}_4]^-$

6. Among $[\text{Co}(\text{F})_6]^{3-}$ and $[\text{Rh}(\text{F})_6]^{3-}$, explain which forms low spin complex.

7. Calculate the CFSE of tetrahedral complex $[\text{Fe}(\text{Cl})_4]^{2-}$ in the unit of Δ_t and Δ_o .