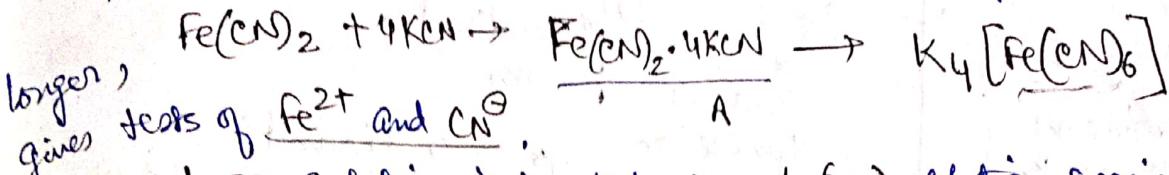


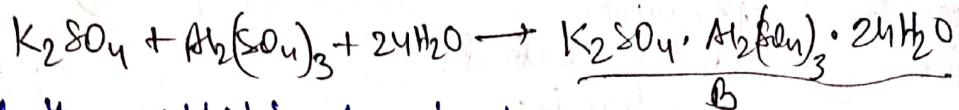
18/5/19

## Coordination Compounds

When  $\text{Fe}(\text{CN})_2$  solution is treated with  $\text{KCN}$  soln, species formed, no



When  $\text{K}_2\text{SO}_4$  solution is treated with  $\text{Al}_2(\text{SO}_4)_3$ , solution species formed gives tests of  $\text{K}^+$ ,  $\text{Al}^{3+}$  &  $\text{SO}_4^{2-}$ .



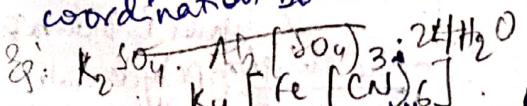
We call them addition compds. of

Type I : those which lose their identity in solution (complexes) as potassium ferricyanide (A)

Type II : those which retain their identity in solution (double salts) as alum (B).

### Coordination Compd.

1) A coordination compound contains a central metal atom or ion surrounded by no. of oppositely charged ions or neutral molecules. These ions or molecules are rebounded to the metal atom/ ion by a coordination bond.

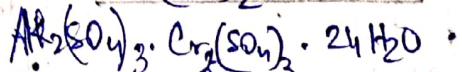
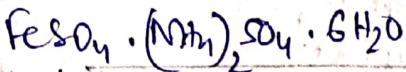
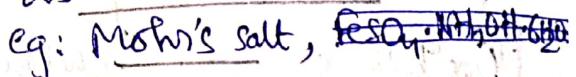


2) sum of the constituent ions or molecules lose their identity when dissolved in  $\text{H}_2\text{O}$  due to formation of complex ion. (They do not give test for all constituent ions.)

3) They exist in solids as well as in aqueous soln.

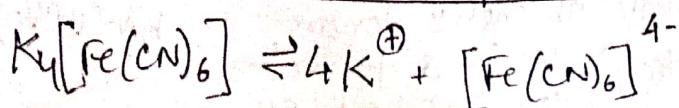
### Double Salt

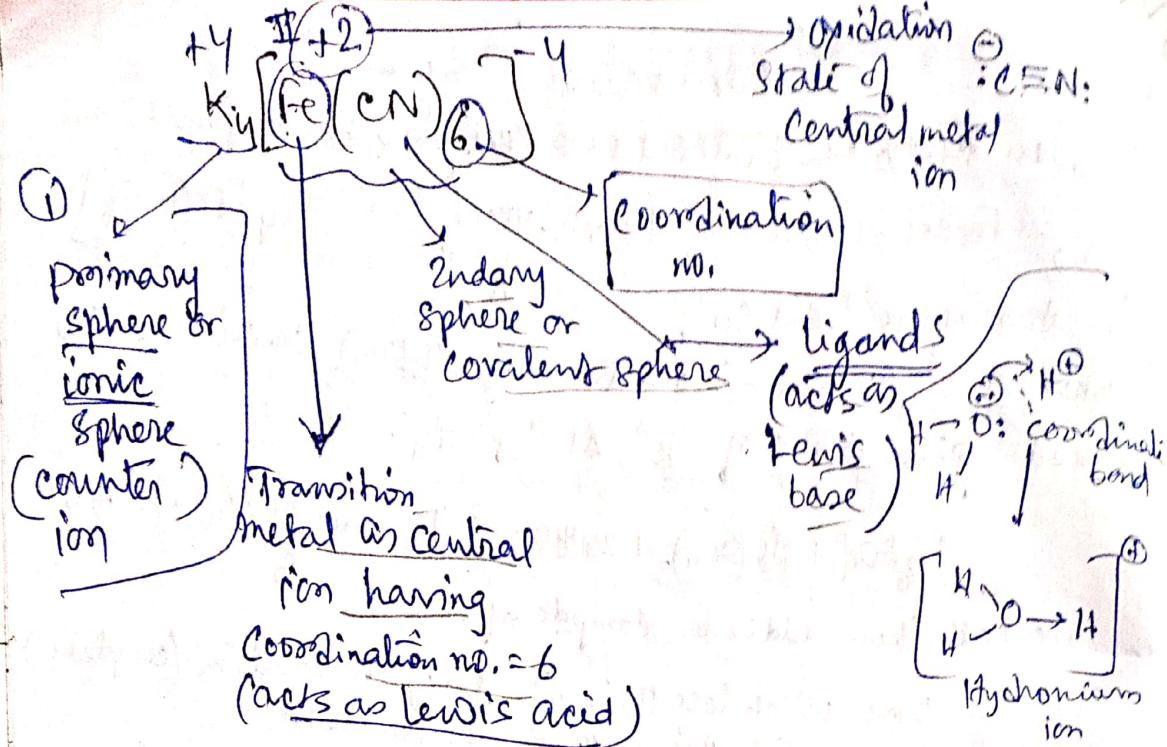
1) When two salts in stoichiometric ratio are crystallized together from their saturated solution, they are called as double salt.



2) They give test for all individual ions.

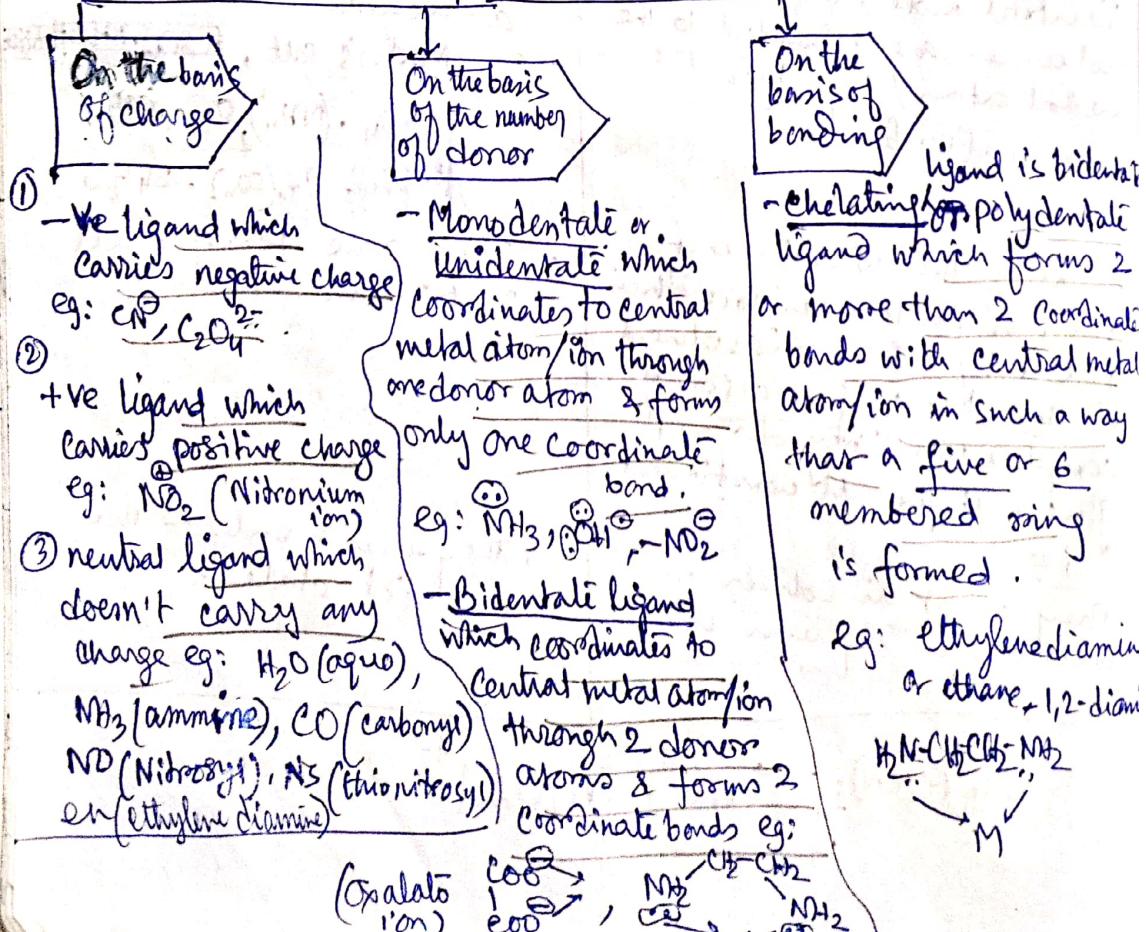
3) They exist only in the solid state.

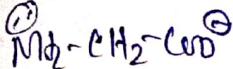
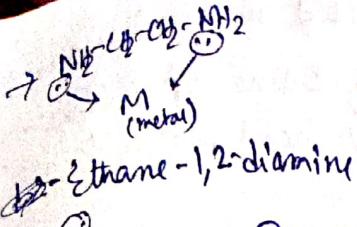




■ Most of the transition elements act as central metal atom/ion in coordination compd or complexes due to the fact that transition metals have incompletely filled d-orbital within them for which they can accommodate lone pair of electrons from the ligands.

### Types of ligands



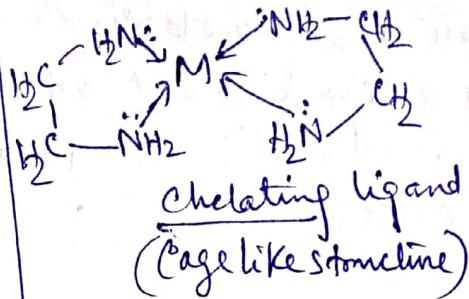
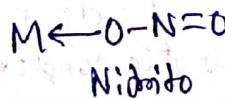
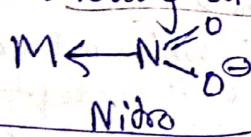


glycinate

- Chelating or polydentate ligand which coordinates to central metal atom through lone or more donor atoms & forms coordinate bonds.
- Some ligands can be

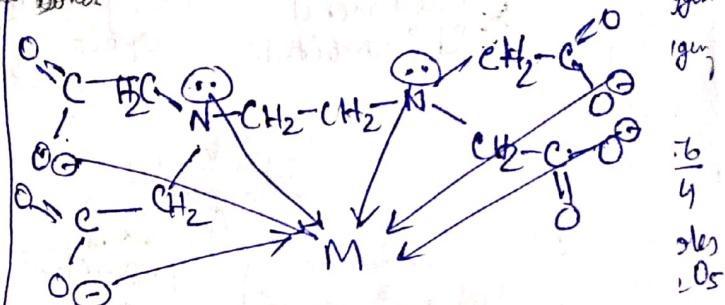
coordinated to the metal/metal ion, through either of the sides. They're called "ambidentate" ligands.

a) They're monodentate ligand containing more than one coordinating atoms.



One most important polydentate

ligand is EDTA (Ethylene diamine tetra acetate)

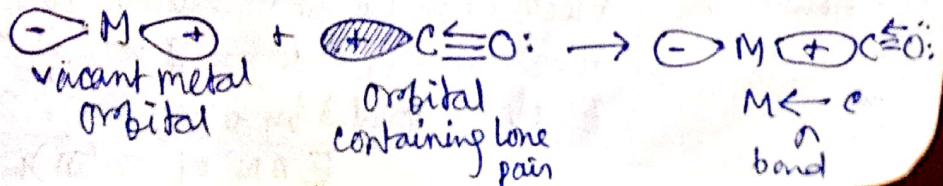


EDTA is a hexadentate ligand (a good chelating ligand)

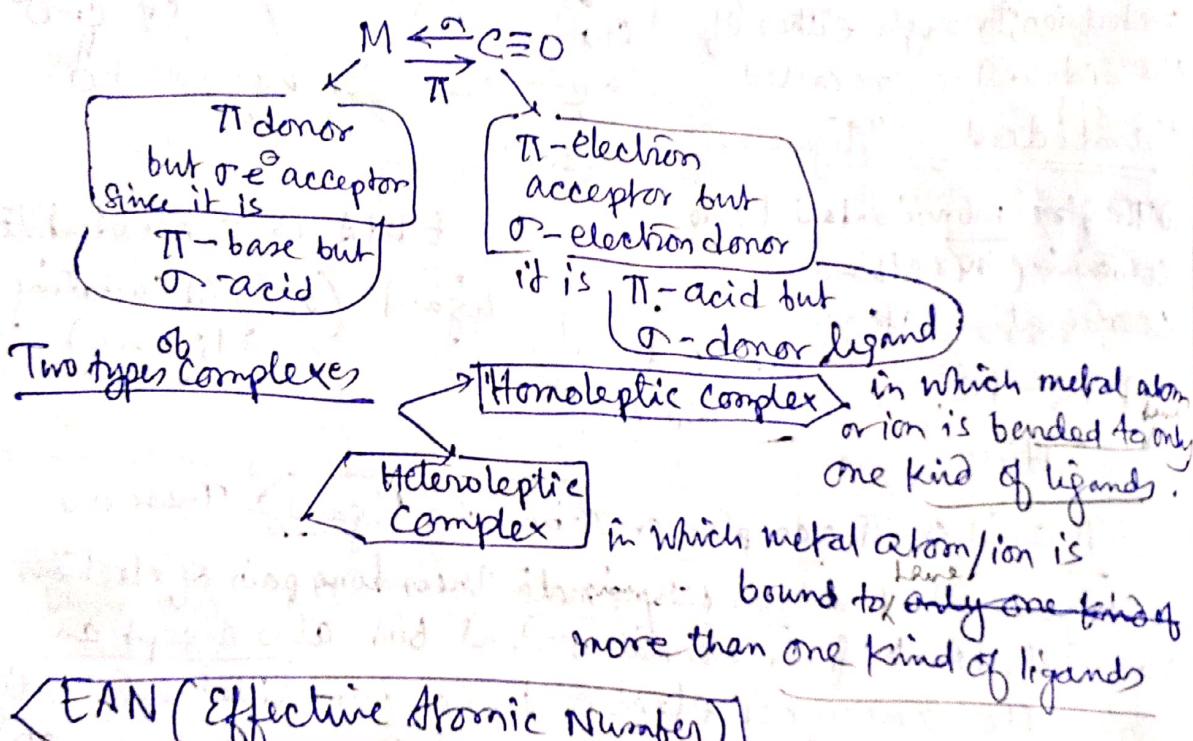
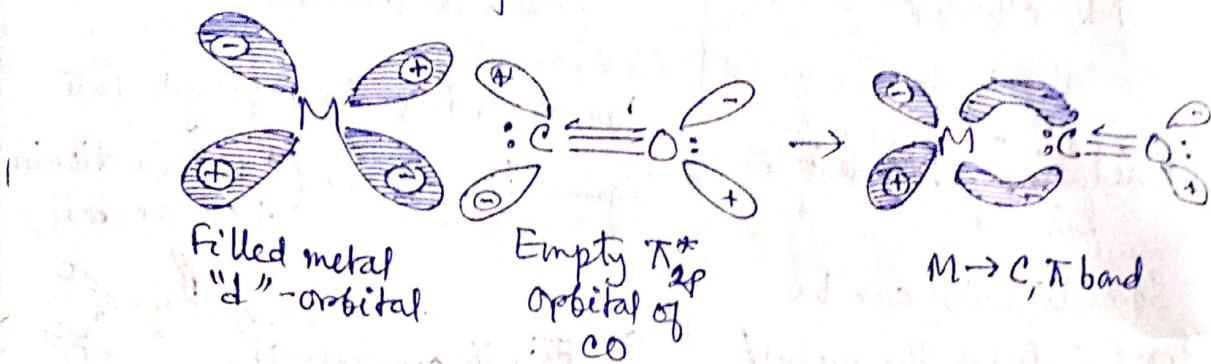
- $\pi$  acid or  $\pi$ -acceptor or  $\pi$ -bonding ligand. These are ligands which not only donate their lone pair of electrons to metal atom to form normal  $\sigma$  bond but also accept an appreciable amount of electron density from filled metal orbitals to their vacant  $\pi^*$  orbitals to form  $\pi$ -bonds, e.g.,  $\text{CO}$ ,  $\text{NO}$  etc.

↳ Bonding in metal carbonyls: Metal-Carbon bond in metal carbonyls possesses both  $\sigma$  and  $\pi$ -character. Its formation involves following steps :-

- There is an overlap of filled  $\pi_{2p_x}$  orbital of  $\text{C}\equiv\text{O}$  with suitable empty metal orbital resulting in the formation of Sigma bond.



- Then there is a  $\pi$ -overlap involving filled metal d-orbitals and empty antibonding  $\pi^*$  orbital of same CO. This results in formation of  $M \rightarrow C$   $\pi$  bond. This is also called back bonding.



### EAN (Effective Atomic Number)

It is defined as is the total number of electrons on the metal atom/ion after gaining electrons from the donor atoms of the ligands (Noble gas rule).

$$\text{EAN} = \text{Atomic no. of metal} - \text{Number of electrons lost in ion formation} + \text{No. of electrons gained from the donor atom of the ligand.}$$

As Example: EAN of Co(III) in  $[\text{Co}(\text{NH}_3)_6]^{3+}$  can be calculated as follows:

Electrons in Co atom = atomic no. of Co = 27 electrons

Electrons in  $\text{Co}^{3+}$  ion =  $(27 - 3) = 24$

Electrons donated by 6 ammonia =  $2 \times 6 = 12$

∴ EAN ( $= 36$ ) of  $\text{Co}(\text{III})$  is evidently equal to the atomic number of Krypton.

## Nomenclature of Coordination Compounds

### Rules for naming Coordination Compounds

- The cation is named first, then the anion.
- In naming the coordination sphere, ligands are named first in alphabetical order followed by metal atom and then oxidation state of metal by a roman numerical in parenthesis.
- Name of coordination compounds is started with a small letter and the complex part is written as one word.

### Naming of Ligands:

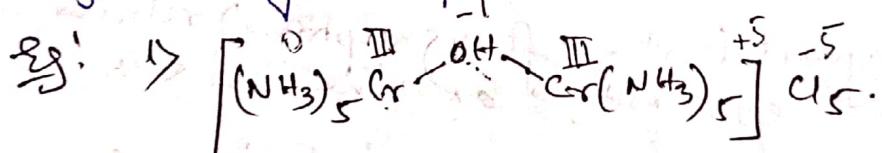
- Name of anionic ligands end in  $-O^-$  eg:  $\text{Cl}^-$ ; chloro or chloro.
- Neutral ligands (with a few exceptions) retain their names, eg:  $\text{NH}_3$ ; ammine,  $\text{H}_2\text{O}$ -aqua.
- Name of cationic ligands end in  $-ium$ ,  
eg:  $\text{NO}_2^+$ : Nitronium.  
 $\text{NO}^+$ : Nitrosonium.
- Certain ligands are represented by abbreviations in parenthesis instead of their complex structural formula. e.g; Ethylene diamine (en) / Ethan-1,2-diamine
- Ambidentate ligands are named by using different names of ligands or by placing the symbol of donor atom, eg!

- $\text{SCN}^-$ ; Thiocyanato- $S$  or Thiocyanato.
- $\text{NCS}^-$ ; Thiocyanato- $N$  or Thiocyanato.
- $\text{ONO}^-$ ; Nitrito- $O$ ) or Nitrito.
- $\text{NO}_2^-$ ; Nitrito- $N$ ) or Nitro.

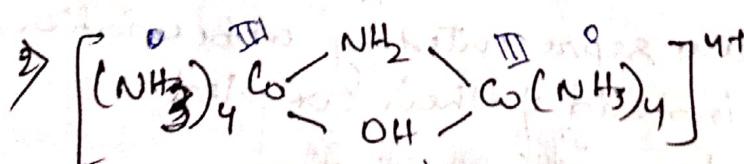
• The prefixes di-, tri-, tetra-, penta- & hexa- are used to indicate the number of each ligand. If the ligand name includes such a prefix, the ligand name should be placed in parenthesis and preceded by bis-(2), tris-(3), tetrakis-(4), pentaakis-(5), & hexakis-(6).

• When the coordination sphere is anionic, name of central metal ends in "-ate".

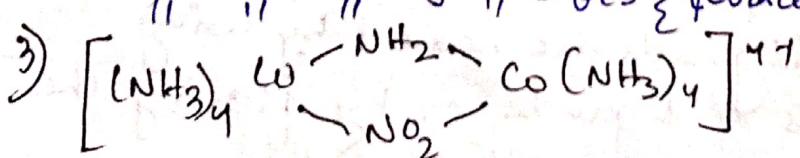
• Naming of the bridging ligands of the bridged polynuclear complexes: the complexes having two or more metal atoms are called as polynuclear complexes. In this complexes, the bridging group is indicated in the formula of the complex by separating it from the rest of the complex by hyphens and by adding the prefix  $\mu$ - before its name.



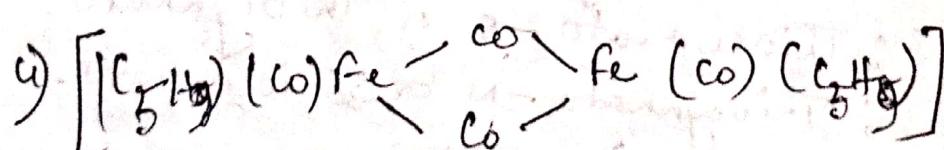
$\mu$ -hydroxo-bis{penta-ammine chromium (III)}  $\gamma$  chloride.



$\mu$ -amido. $\mu$ -hydroxo octa ammine dicobalt (II) ion.



$\mu$ -amido- $\mu$ -nitro octa ammine dicobalt (II) ion.



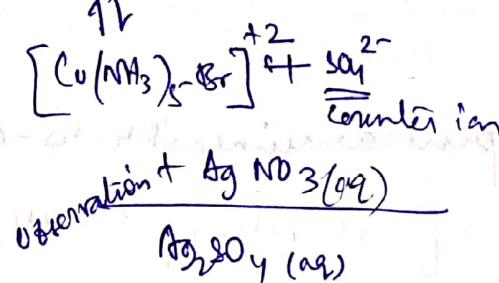
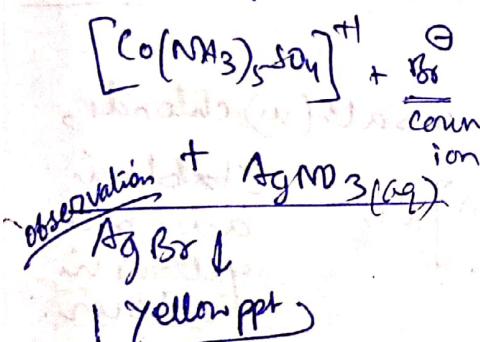
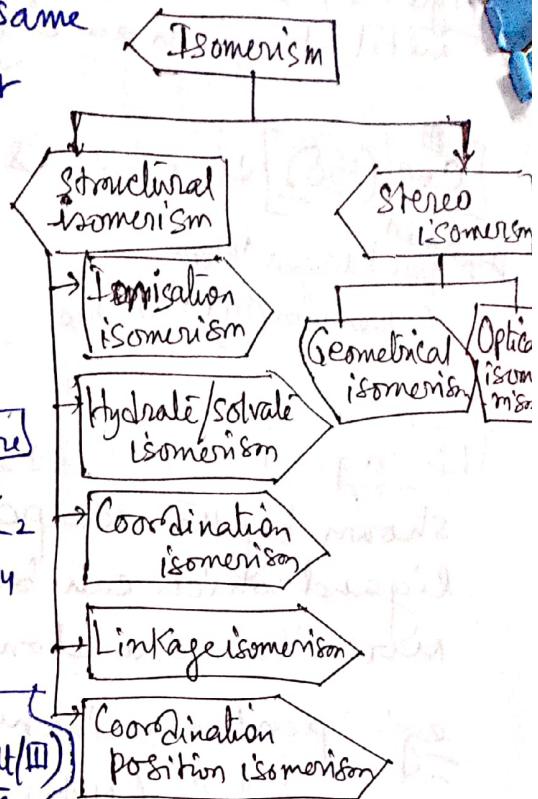
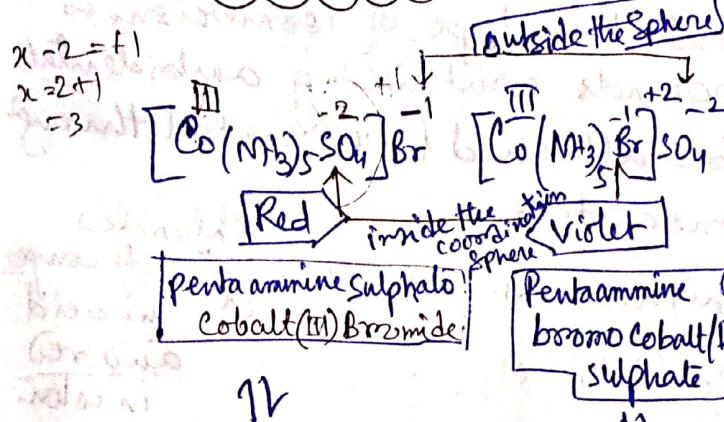
$\mu$ -carbonyl-bis(carbonyl cyclopentadienyl iron)

# Isomerism in Coordination Compounds

Isomers are the compds with the same molecular formula but different arrangements of atoms. They've different properties.

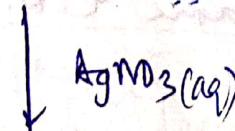
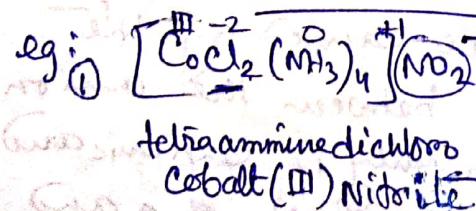
## Structural Isomerism

### Ionisation isomerism :-

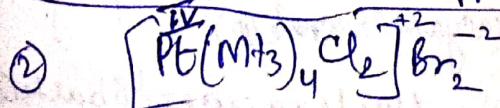


No such characteristic ppt appears

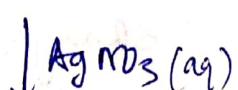
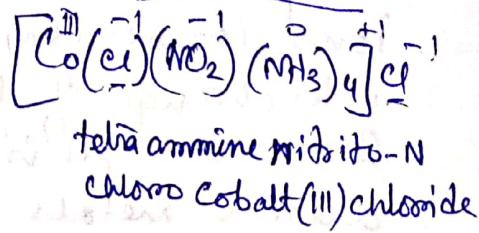
Compounds which give different ions in solution are called ionisation isomers. It occurs due to the exchange of ions between the coordination sphere & the counter ion.



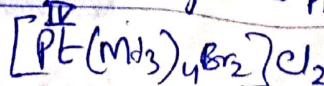
No such characteristic ppt.



tetraammine dichloroplatinum (IV) bromide

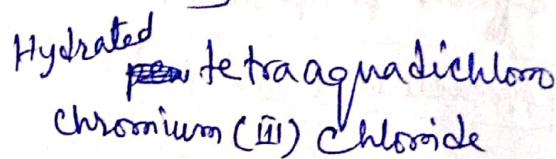
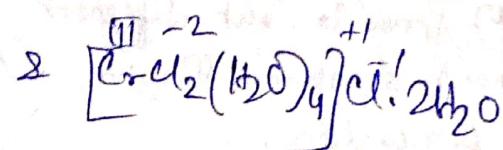
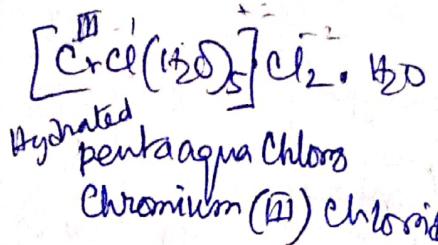


AgCl  $\downarrow$   
curdy white ppt



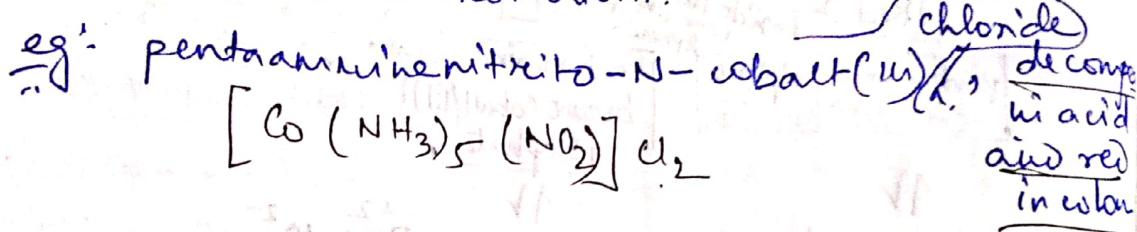
tetraamminedibromo Platinum(IV) chloride

Hydrate / Solvate isomerism  $\rightarrow$  Isomers which differ in the no. of water molecules attached to metal atom / ion as ligands are called hydrated isomers.

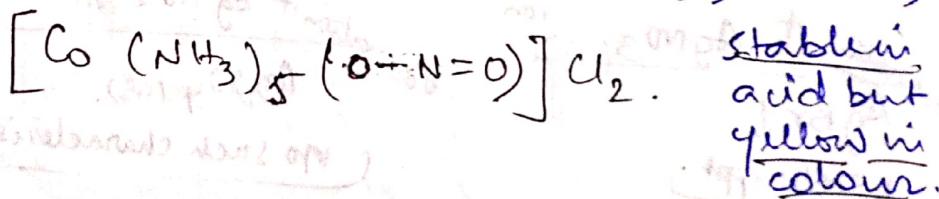


Linkage isomerism

This type of isomerism is shown by the compounds containing ambidentate ligand which can be attached to the metal through more than one donor atom.

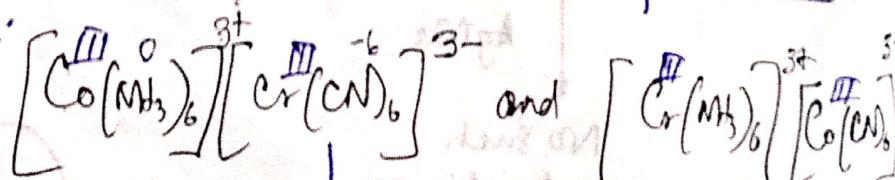


pentaamminenitrito-O-cobalt(III) chloride,



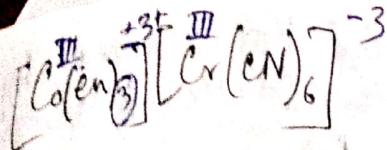
Coordination isomerism

When both the positive and negative ions are complex ions, isomerism may be caused by the interchange of ligands between the anion & cation. This arises only if cationic and anionic metals have same C.N. if a and charge.



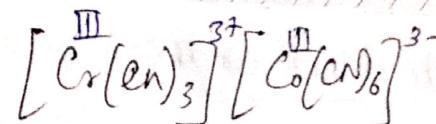
hexaammine Cobalt(III) hexacyano Chromate(II)

hexaammine chromium(III) hexacyanocobaltate(IV)



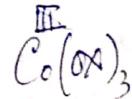
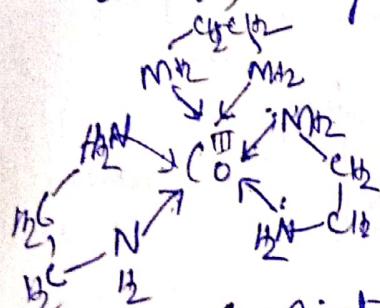
triethylenediamine

Cobalt(II) hexacyanochromate(III)



triethylenediamine chromium

(III) hexacyanocobaltate(II)



Stereoisomerism

Coordination compds having different positions & arrangements of ligands in space.

Geometrical isomerism

Arises in heteroleptic complexes due to different possible geometric arrangements of the ligands

Optical isomerism

Occurs when a complex is represented by two different structures which are non-superimposable mirror images of each other called enantiomers

Octahedral complex

Type -  $\text{Ma}_3\text{b}_3$

Facial or  
Fare

Meridional or mer

Type -  $\text{Ma}_3\text{b}_2$

cis

In square planar complex

Type -  $\text{Ma}_3\text{b}_3$

cis -  
a b  
a b  
M  
a b  
a b  
diam -  
a b  
a b  
M

Type -  $\text{Ma}_2\text{bc}$

cis -  
a b  
a c  
M  
a b  
a c  
diam -  
a b  
a c  
M

Type -  $\text{Mabed}$

a b  
c d  
M  
a b  
c d  
M

NB only cis-isomers of only octahedral complexes can exhibit such type of isomers. Type -

$\text{M}(\text{aa})_2\text{b}_2$

a b  
a b  
M  
a b  
a b  
M

$\text{M}(\text{aa})_3$

a b  
a b  
M  
a b  
a b  
M

$\text{M}(\text{aa})_2\text{b}_2\text{c}_2$

a b  
c d  
e f  
M  
a b  
c d  
e f  
M

Type of the complex

$\text{M}(\text{aa})_2\text{b}_2$  or  $\text{M}(\text{aa})_2\text{bc}$

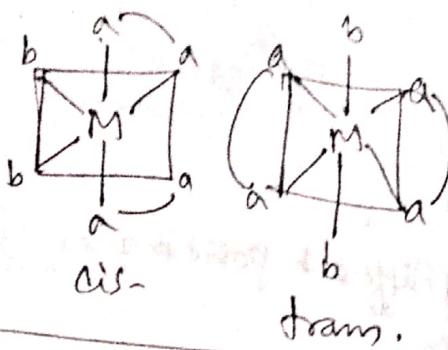
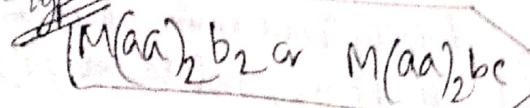
cis

trans

3 isomers may possible

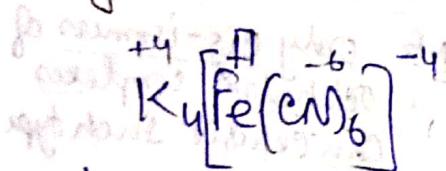
## Octahedral Complex

Type

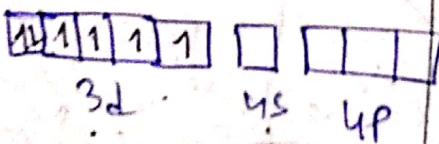
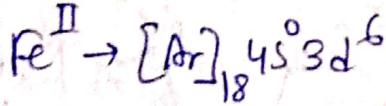
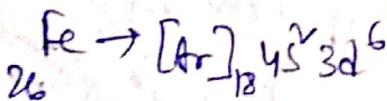


## VBT

Q1. Show the structure & hybridisation & magnetic behaviour of Potassium ferrocyanide



Potassium hexacyanoferrate(II)

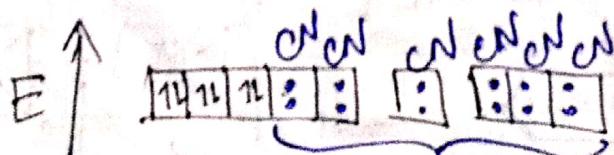


$\text{CN}^-$  is a strong field ligand i.e.

$$P < \text{CFSE} \rightarrow$$

CFSE (crystal field stabilisation energy)  
P (pairing energy)

inner orbital complex

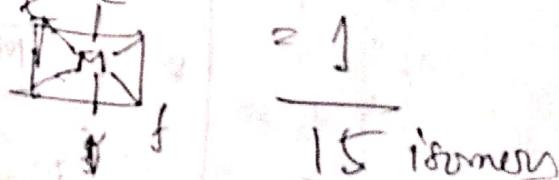
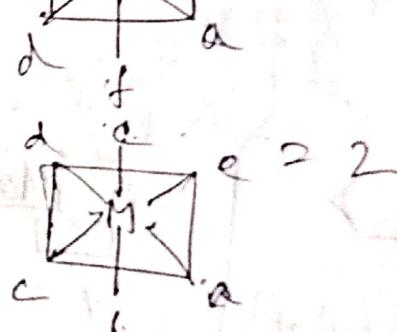
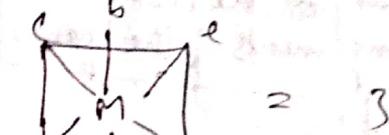
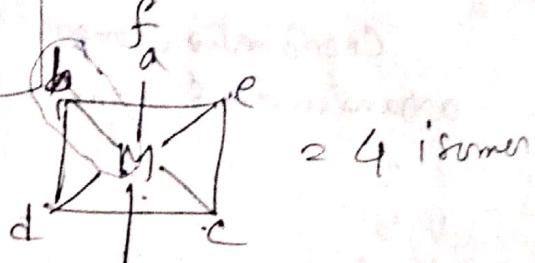
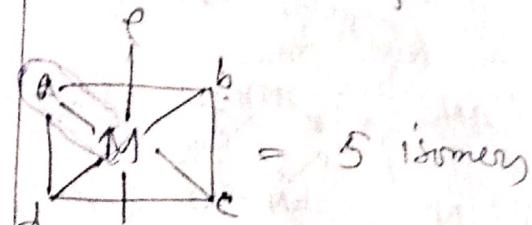


$d^2sp^3$  (octahedral shape)

all are paired electron  
since it is diamagnetic in nature

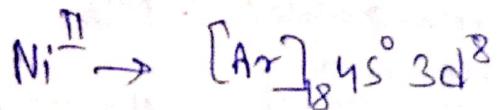
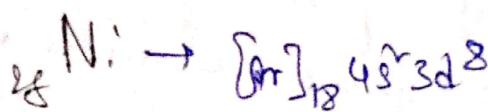
Find how many isomers are possible for the given complex.

Mabcdef



May possible.

Q2. What is the difference in the magnetic behaviour of  $[\text{NiCl}_4]^{2-}$  &  $[\text{Ni}(\text{CN})_4]^{2-}$



$$P > \text{CFSE}$$

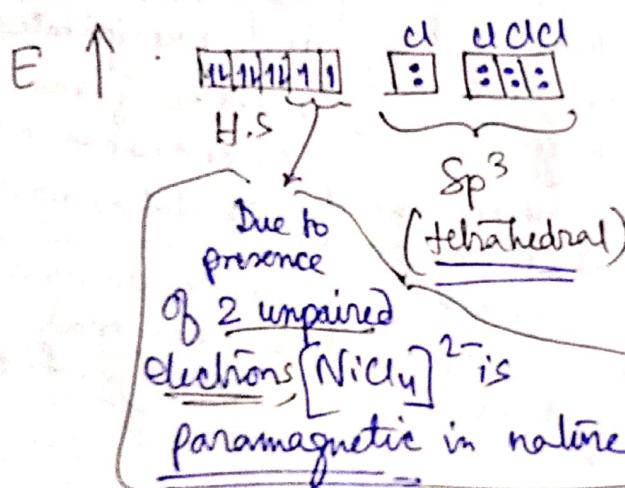
$\text{Cl}^-$  is a weak field ligand  $\rightarrow$  produces outer d-orbital or HS complex

While CN<sup>-</sup> is a strong field ligand

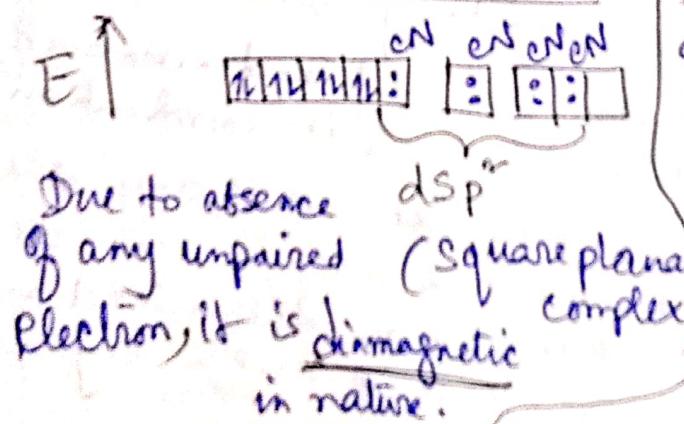
$\rightarrow$  produces inner d-orbital or LS-complex

$$P < \text{CFSE}$$

■ In case of  $[\text{NiCl}_4]^{2-}$  complex



■ In case of  $[\text{Ni}(\text{CN})_4]^{2-}$  complex



Limitations of VBT

- i) It involves a no. of assumptions.
- ii) It gives only the qualitative explanation for complexes.
- iii) It does not explain the detailed magnetic property of the complexes.
- iv) This theory does not explain the spectral properties of the coordination compounds.

- v) It does not explain the thermodynamic & kinetic stabilities of different coordination compounds.
- vi) It does not make exact predictions regarding the tetrahedral or square planar structures of four coordinate complexes.
- vii) It does not distinguish between the weak and strong field ligands.

Werner's Co-ordination Theory In 1892, Werner put forward his famous theory of coordination to explain the formation and structure of complex compounds.

The main postulates of Werner's theory are :-

- Metals possess two types of valencies viz. primary or principle or ionizable valency and secondary or directive or non-ionizable valency. Primary valency is represented by dotted lines (---).

- Primary valency corresponds to the oxidation state of the central metal atom / ion and it is satisfied by negative ions.

- Secondary valency represented by solid lines (—), corresponds to the coordination number of the central metal atom / ion and it is satisfied by neutral molecules or negative ions (ligand) is fixed for a metal.

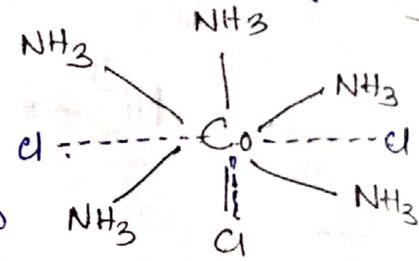
✓ Every metal atom tends to satisfy both its primary and secondary valencies.

✓ Every metal atom has a fixed number of secondary valencies, i.e., its coordination no.

✓ The secondary valencies are always directed towards fixed positions in space. The stereochemistry of a complex is determined by the arrangements of such ligands.

→ Compounds with central metal having coordination no. 6, show octahedral geometry. Compounds with central metal having coordination no. 4 shows either tetrahedral / square planar geometry.

→ Compounds with central metal having coordination no. 6, show octahedral geometry. Compounds with central metal having coordination no. 4 shows either tetrahedral / square planar geometry.



Structure of  $\text{Co}(\text{Cl}_6)^{3-}$

Complex Number of  $\text{Cl}^-$  ions precipitated =

Total no. of ions = 3.  
Co-ordination no. 6

Oxidation no. 3

✓ Every metal atom tends to satisfy both its primary and secondary valencies.

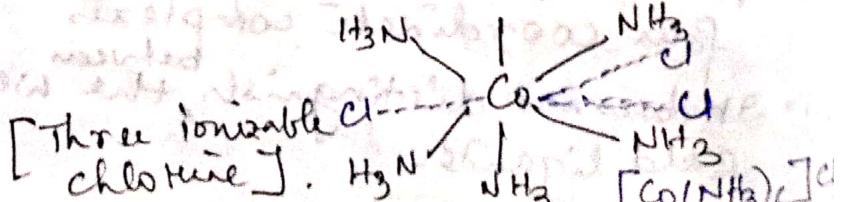
✓ Every metal atom has a fixed number of secondary valencies, i.e., its coordination no.

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→ Compounds with central metal having coordination no. 6, show octahedral geometry. Compounds with central metal having coordination no. 4 shows either tetrahedral / square planar geometry.



Coordination number	Type of hybridisation	Geometry	Examples
2	sp	Linear	$[\text{Ag}(\text{NH}_3)_2]^+$ , $[\text{Ag}(\text{CN})_2]$
3	$\text{sp}^2$	Trigonal planar	$[\text{AgI}_3]^-$
4	$\text{sp}^3$	Tetrahedral	$\text{Ni}(\text{CO})_4$ , $[\text{Ni}(\text{X}_4)]^{2-}$ , $[\text{ZnCl}_4]^{2-}$ , $[\text{CuX}_4]^{2-}$ where $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$
	$\text{dsp}^2$	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$ , $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , $[\text{Ni}(\text{NH}_3)_4]^{2+}$
5	$\text{d}\text{sp}^3$	Square pyramidal	$[\text{SbF}_5]^{2-}$
	$\text{sp}^3\text{d}$	Trigonal bipyramidal	$[\text{Fe}(\text{CO})_5]$ , $[\text{CnCl}_5]^{3-}$
6	$\text{d}^2\text{sp}^3$	Octahedral (Inner orbital)	$[\text{Cr}(\text{NH}_3)_6]^{3+}$ , $[\text{Fe}(\text{CN})_6]^{3-}$
	$\text{sp}^3\text{d}^2$	Octahedral (Outer orbital)	$[\text{FeF}_6]^{3-}$ , $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , $[\text{Ni}(\text{NH}_3)_6]^{2+}$

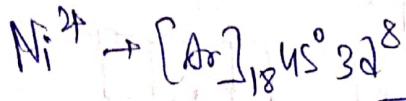
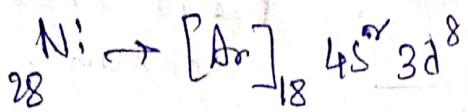
Inner orbital complexes

Outer orbital complexes

- Involves inner 'd' orbitals → Involves outer 'd' orbitals that is  $(n-1)d$  orbitals
- low spin complexes (L.S.) → High spin complexes (H.S.)
- Have less or no unpaired electrons → Have large no. of unpaired electrons.
- e.g.:  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ,  $[\text{Co}(\text{CN})_6]^{4-}$  e.g.:  $[\text{MnF}_6]^{3-}$ ,  $[\text{CoF}_6]^{3-}$

No.	Atom/ion coupled	Configuration.	Oxid. state	Hybridization Geometry.	No. unpaired electrons	Magnetic behavior					
1.	$\text{Ni}^{2+} (\text{d}^8)$ $[\text{NiCl}_6]^{2-}$	$\begin{array}{ccccccccc} 1v & 1v & 1v & 1v & 1v & \square & \square & \square \\ 3d & & & & & & & \\ & & & & & 4s & & \\ & & & & & & 4p & \end{array}$ $\begin{array}{ccccccccc} 1v & 1v & 1v & 1v & 1v & \square & \square & \square \\ 3d & & & & & & & \\ & & & & & 4s & \square & \\ & & & & & & 4p & \end{array}$	+2	$\text{sp}^3$ tetrahedral	2	Paramagnetic					
			+2		2	Paramagnetic					
2.	$[\text{Ni}(\text{CN})_4]^{2-}$	$\begin{array}{ccccccccc} 1v & 1v & 1v & 1v & 1v & \square & \square & \square \\ 3d & & & & & & & \\ & & & & & 4s & \square & \\ & & & & & & 4p & \end{array}$ <small>Rearrangement:</small> $\begin{array}{ccccccccc} 1v & 1v & 1v & 1v & 1v & \square & \square & \square \\ 3d & & & & & & & \\ & & & & & 4s & \square & \\ & & & & & & 4p & \end{array}$	+2	$\text{dsp}^2$ square planar	0	Diamagnetic					
	$[\text{Mn}^{2+} (\text{d}^5)]$ $[\text{Mn}(\text{CN})_6]^{4-}$	$\begin{array}{ccccccccc} 1v & 1v & 1v & 1v & 1v & \square & \square & \square \\ 3d & & & & & & & \\ & & & & & 4s & & \\ & & & & & & 4p & \end{array}$ $\begin{array}{ccccccccc} 1v & 1v & 1v & 1v & 1v & \square & \square & \square \\ 3d & & & & & & & \\ & & & & & 4s & \square & \\ & & & & & & 4p & \end{array}$	+2	$\text{d}^2\text{sp}^3$ (inner)	5	Paramagnetic					
	$[\text{Mn}(\text{Cl})_6]^{2-}$	$\begin{array}{ccccccccc} 1v & 1v & 1v & 1v & 1v & \square & \square & \square \\ 3d & & & & & & & \\ & & & & & 4s & \square & \\ & & & & & & 4p & \end{array}$ <small>Rearrangement:</small> $\begin{array}{ccccccccc} 1v & 1v & 1v & 1v & 1v & \square & \square & \square \\ 3d & & & & & & & \\ & & & & & 4s & \square & \\ & & & & & & 4p & \end{array}$	+2	$\text{sp}^3$ tetrahedral.	5	Paramagnetic					
3.	$\text{Cu}^{2+} (\text{d}^9)$ $[\text{CuCl}_4]^{2-}$	$\begin{array}{ccccccccc} 1v & 1v & 1v & 1v & 1v & \square & \square & \square \\ 3d & & & & & & & \\ & & & & & 4s & \square & \\ & & & & & & 4p & \end{array}$ $\begin{array}{ccccccccc} 1v & 1v & 1v & 1v & 1v & \square & \square & \square \\ 3d & & & & & & & \\ & & & & & 4s & \square & \\ & & & & & & 4p & \end{array}$	+2	$\text{sp}^3$ tetrahedral	4	paramagnetic					
			+2		1	paramagnetic					
4.	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	$\begin{array}{ccccccccc} 1v & 1v & 1v & 1v & 1v & \square & \square & \square \\ 3d & & & & & & & \\ & & & & & 4s & \square & \\ & & & & & & 4p & \end{array}$ <small>one 'e'</small> is shifted from 3d orbital to 4p orbital.	+2	$\text{dsp}^2$ square planar	1	paramagnetic					
	$\text{Fe}^{3+} (\text{d}^5)$	$\begin{array}{ccccccccc} 3d & & & & & 4s & & & 4p \\ 1v & 1v & 1v & 1v & 1v & \square & \square & \square & \end{array}$ $\begin{array}{ccccccccc} 3d & & & & & 4s & & & 4p \\ 1v & 1v & 1v & 1v & 1v & \square & \square & \square & \end{array}$	+3	$\text{d}^2\text{sp}^3$ (inner)	5	Paramagnetic					
5.	$[\text{Fe}(\text{CN})_6]^{3-}$	$\begin{array}{ccccccccc} 3d & & & & & 4s & & & 4p \\ 1v & 1v & 1v & 1v & 1v & \square & \square & \square & \end{array}$ <small>Rearrangement:</small> $\begin{array}{ccccccccc} 3d & & & & & 4s & & & 4p \\ 1v & 1v & 1v & 1v & 1v & \square & \square & \square & \end{array}$	+3	$\text{d}^2\text{sp}^3$ Octahedral	1	Paramagnetic					
	$\text{Fe}^{\circ} (\text{d}^6 \text{s}^2)$	$\begin{array}{ccccccccc} 3d & & & & & 4s & & & 4p \\ 1v & 1v & 1v & 1v & 1v & \square & \square & \square & \end{array}$	0	$\text{dsp}^3$ (inner) trigonal bipyramic	4	Paramagnetic					
6.	$[\text{Fe}(\text{CO})_5]$	$\begin{array}{ccccccccc} 3d & & & & & 4s & & & 4p \\ 1v & 1v & 1v & 1v & 1v & \square & \square & \square & \end{array}$ <small>Rearrangement:</small> $\begin{array}{ccccccccc} 3d & & & & & 4s & & & 4p \\ 1v & 1v & 1v & 1v & 1v & \square & \square & \square & \end{array}$	0	-d <sub>10</sub> dia	0	Diamagnet					
			0								
Gr III B		Gr IV B	Gr V B	Gr VI B	Gr VII B	Gr VIII B	Gr I B / Gr II				
4-th period (3d series)		$(\text{d}^1)$ Sc	$(\text{d}^2)$ Ti	$(\text{d}^3)$ V	$(\text{d}^5)$ Cr	$(\text{d}^5)$ Mn	$(\text{d}^6)$ Fe	$(\text{d}^7)$ Co	$(\text{d}^8)$ Ni	$(\text{d}^1)$ Cu	$(\text{d}^0)$ Zn

Q10 Using valence bond approach explain the shape & magnetic behaviour of  $[\text{Ni}(\text{NH}_3)_6]^{2+}$ . (Atomic no. of Ni = 28)

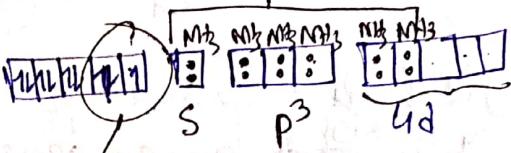


$\begin{array}{ c c c c }\hline \text{H} & \text{H} & \text{H} & \text{H} \\ \hline 1 & 1 & 1 & 1 \\ \hline\end{array}$	$\begin{array}{ c c c }\hline & & \\ \hline & & \\ \hline\end{array}$	$\begin{array}{ c c c }\hline & & \\ \hline & & \\ \hline\end{array}$	$\begin{array}{ c c c }\hline & & \\ \hline & & \\ \hline\end{array}$
3d <sup>8</sup>	4s	4p <sub>x</sub> 4p <sub>y</sub> 4p <sub>z</sub>	4d

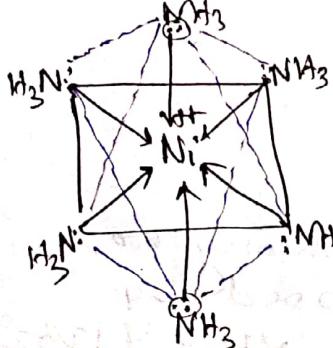
$\text{NH}_3$  is a neutral, strong field

ligand i.e. CFSE > P (Pairing energy)

sp<sup>3</sup>d<sup>2</sup> (outer d orbital complex)



Due to presence of unpaired electron in 3d orbital  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  will show its paramagnetism.

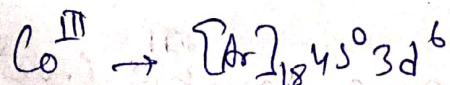


Shape is Octahedral geometry.

Model Testpaper - 12 Q4. Explain the following :-

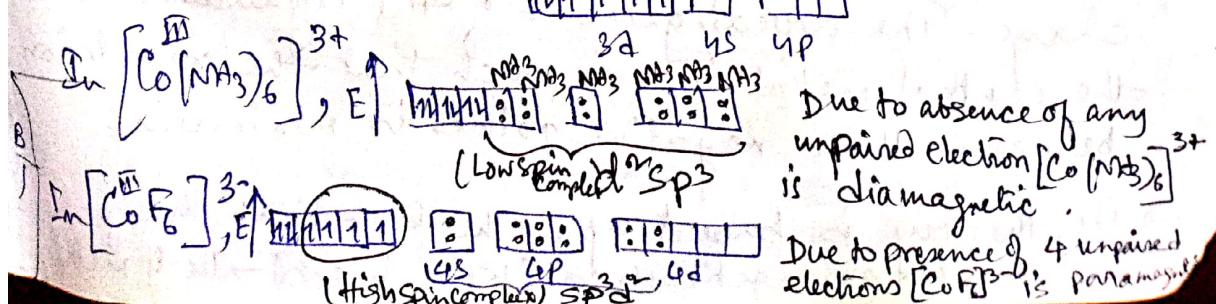
(i)  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is diamagnetic, whereas  $[\text{CoF}_6]^{3-}$  is paramagnetic.

(ii)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  is more paramagnetic than  $[\text{Fe}(\text{CN})_6]^{3-}$ .



$\text{NH}_3$  is a strong field ligand while fluoride ( $\text{F}^-$ ) ion is a weak field ligand

$\begin{array}{ c c c c }\hline \text{H} & \text{H} & \text{H} & \text{H} \\ \hline 1 & 1 & 1 & 1 \\ \hline\end{array}$	$\begin{array}{ c c c }\hline & & \\ \hline & & \\ \hline\end{array}$	$\begin{array}{ c c c }\hline & & \\ \hline & & \\ \hline\end{array}$	$\begin{array}{ c c c }\hline & & \\ \hline & & \\ \hline\end{array}$
3d	4s	4p	4d



Due to absence of any unpaired electron  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is diamagnetic.

Due to presence of 4 unpaired electrons  $[\text{CoF}_6]^{3-}$  is paramagnetic.

Fe -	1V	1	1	1	1	1	1V				
------	----	---	---	---	---	---	----	--	--	--	--

Fe <sup>3+</sup> -	3d	9s	4p.								
	1	1	1	1	1						

[Fe(CN) <sub>6</sub> ] <sup>3-</sup> -	3d	9s	4p.								
	1V	1V	1	1	1	1	1	1	1	1	1

(H <sub>2</sub> O) <sub>6</sub> Fe <sup>3+</sup> -	3d	9s	4p								
	1	1	1	1	1	1	1	1	1	1	1

[Fe(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> -	3d	9s	4p	4d							
	1	1	1	1	1	1	1	1	1	1	1

Octahedral Geometry.  $sp^3 d^2$ .

It is ~~highly~~ paramagnetic

It has high spin complex.

Octahedral Group

It is ~~highly~~ paramagnetic due to unpaired electrons.

Crystal field theory (CFT) This theory was developed by

Hans Bethe (1929) and John Van Vleck (1932) and gives a much more satisfactory explanation for the bonding and the properties of the complex. The main postulates are as follows:-

→ CFT considers that the bonding between a central metal ion and its ligand arises from purely electrostatic interaction. As these interactions are similar to those between the ions in a crystal that is why, it has been named as ~~as~~ Crystal Field Theory (CFT)

→ It treats each ligand as a point of (-ve) charge. The arrangement of the ligands around the central metal ion is such that the repulsion between these negative points is minimum.

→ The theory is based upon the fact that the degenerate (energetically alike) d-orbitals of metal

ions are spread evenly wise due to the concentration of point charges in specific positions. This is seen because the energy of the orbitals lying in the direction of point charges increases more in comparison to orbitals lying in between the point charges as the electrons in former case experience greater repulsion than in the latter case.

### \* Crystal field Splitting in Octahedral Complexes:

The octahedral arrangement of 6 ligands surrounding the central metal ion can be shown as: It is obvious from the figure that the ligands approach along Z axis. The two d-orbitals lying along the axis namely  $d_{x^2-y^2}$  and  $d_{z^2}$  will suffer more electrostatic repulsion and hence energy will be greater than the other three d-orbitals  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  which have their lobes lying in between the two axis. Thus, the degenerate set of d-orbitals split into two sets: e<sub>g</sub>: orbitals of higher energy including  $d_{x^2-y^2}$  &  $d_{z^2}$  & t<sub>2g</sub> orbitals of lower energy including  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ . The crystal field splitting is measured in terms of energy difference between two sets ( $t_{2g}$  and  $e_g$ ) is known as the Ligand field splitting Parameters (LFSE) can be symbolised as  $\Delta_0$ , where 0 is Octahedral.

- According to conservation of energy, the energies of the  $t_{2g}$  orbitals lie at  $-0.4\Delta_0$  and the  $e_g$  orbitals lie at  $+0.6\Delta_0$ , so the total energy is  $[3 \times (-0.4\Delta_0)] + [2 \times (+0.6\Delta_0)] = 0$ , the change in energy is generally measured in terms of a parameter  $D_q$ , which is called as  $\rightarrow$

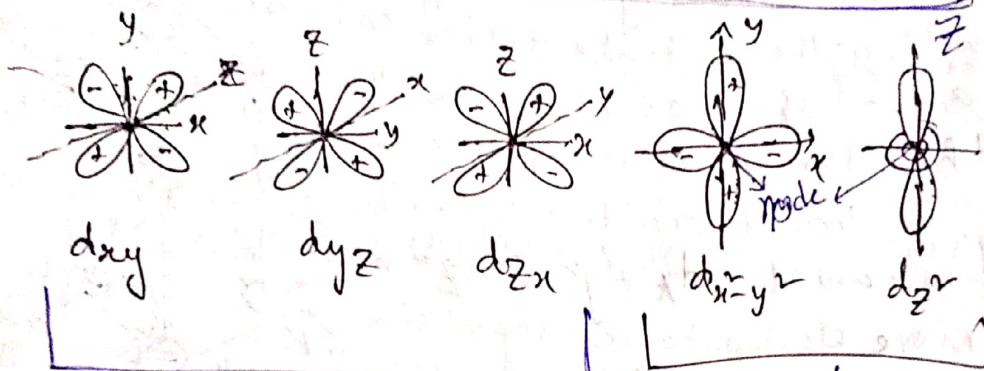
Crystal Field Splitting Energy (CFSE) or Crystal field Stabilisation Energy (CFSE). Since it stabilises d-orbitals by lowering their energy which results from their splitting into  $t_{2g}$  &  $e_g$  orbitals, since  $\Delta_0 = 10D_q$ .

$$\text{for } d^5 \quad \frac{t_{2g} e_g}{5+2}$$

$$\text{ion, } \text{CFSE} = [-0.4xp + 0.6xq] \Delta_0$$

$$= [-0.4xp + 0.6xq] \times 10D_q$$

$$\boxed{\text{CFSE} = (4p + 6q) Dq}$$

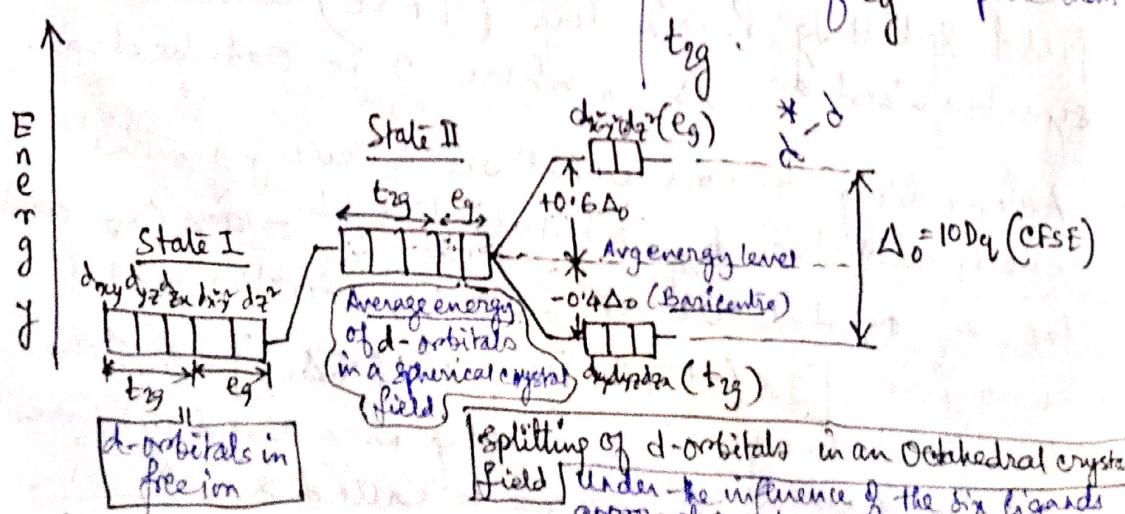


$t_{2g}$  (triplet set  
doubly filled  
gyrad)

Their lobes are oriented  
in between two axes, where  
repulsion is not so much  
effective.

$e_g$  (equatorial  
gyrad)

Their lobes  
orient along the  
axis since in Octahedral  
geometry the (-ve)-(-ve)  
repulsion in between the central  
metal ion & the approaching  
ligand will be maximum  
in case of  $e_g$  compare than  
 $t_{2g}$ .



Splitting of d-orbitals in an Octahedral crystal field under the influence of the six ligands approaching towards the central metal ion during the formation of an octahedral complex.

central metal ion has split into  $t_{2g}$ ,  $e_g$ ,  $t_{2g}$  and energy set & higher energy set.

- For complexes in a ligand field d-orbital occupancy depends on  $\Delta_0$  and pairing energy, P.

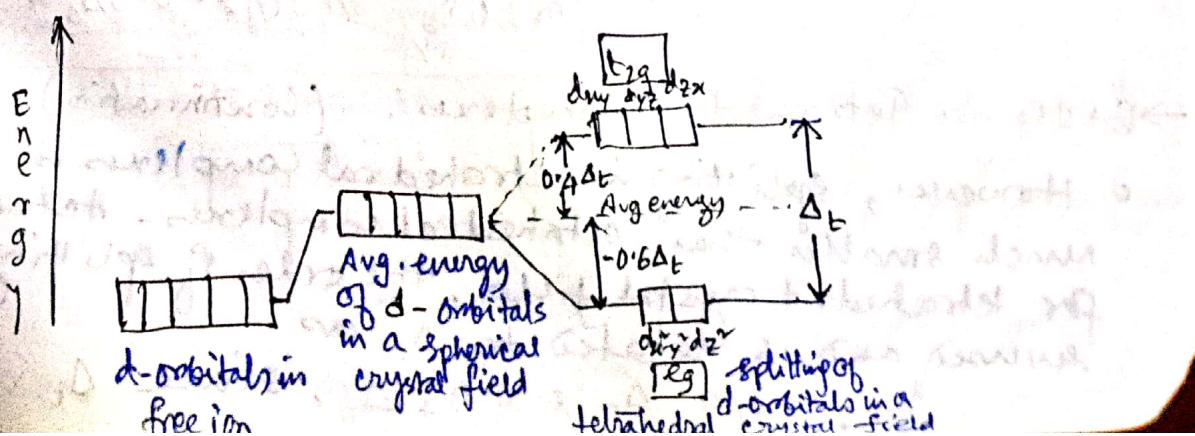
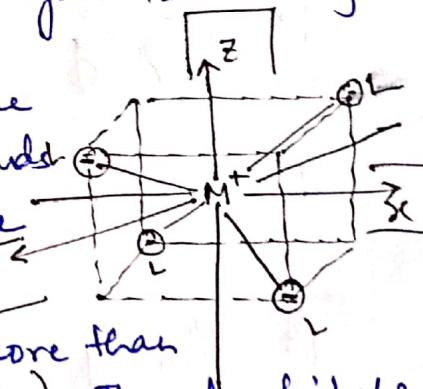
→ If  $\Delta_0 > P$  (i.e.,  $\Delta_0$  large, in presence of strong field ligand) → electrons pair up in lower energy d-subshell first → forms low spin complex (L.S.).

→ If  $\Delta_0 < P$  (i.e.,  $\Delta_0$  small, in presence of weak field ligand) → electrons spread out among all d-orbitals before pairing up → forms high spin complex (H.S.).

### Crystal field splitting in tetrahedral Complex

The tetrahedral arrangement of four ligands surrounding the metal ion can be shown as follows:-

It is obvious from the figure that none of the d-orbitals point exactly towards the ligand. As a result of this, the energy of three orbitals - ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ) increases much more than the other two d-orbitals - ( $d_{x^2-y^2}$ ,  $d_{z^2}$ ). The d-orbitals thus splits into two sets of orbitals,  $t_{2g}$  orbitals of higher energy and  $e_g$  orbitals of lower energy. Energy difference between these two sets of orbitals is represented by  $\Delta_t$ .



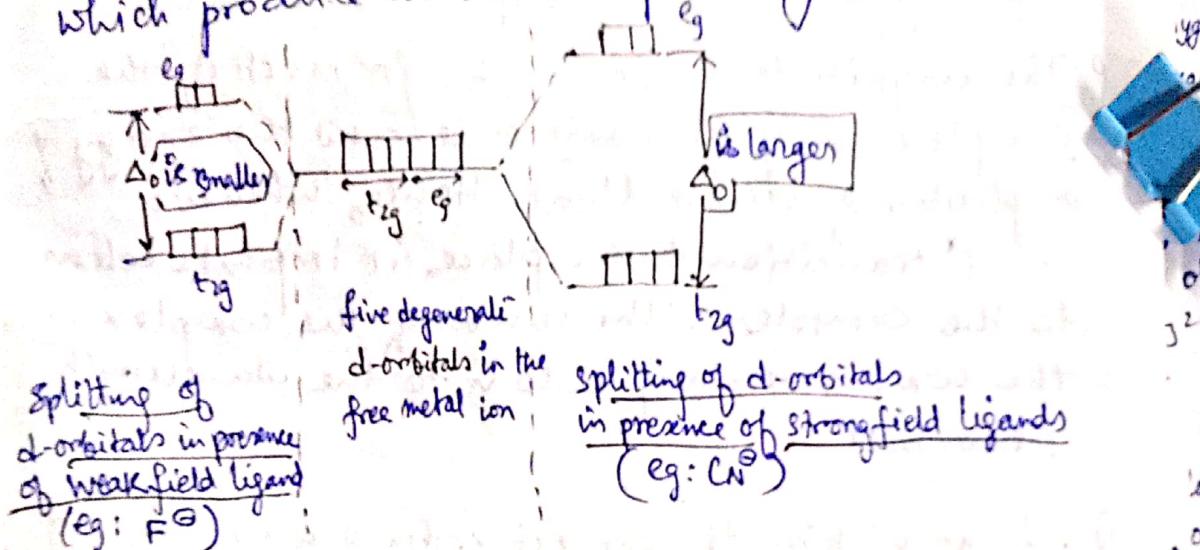
Metal-ion configuration (strong field ligand)	Low-spin state CFSE ( $\Delta_0 / D_q$ )	High spin state (weak field ligand)	CFSE ( $\Delta_0 / D_q$ )
d <sup>1</sup>	t <sub>2g</sub> <sup>1</sup> e <sub>g</sub> <sup>0</sup>	$0.4 \times 1 = -0.4 \Delta_0 \text{ or } -4 D_q$	t <sub>2g</sub> <sup>1</sup> e <sub>g</sub> <sup>0</sup> $-0.4 \times 1 = -0.4 \Delta_0 \text{ or } -4 D_q$
d <sup>2</sup>	t <sub>2g</sub> <sup>2</sup> e <sub>g</sub> <sup>0</sup>	$-0.4 \times 2 = -0.8 \Delta_0 \text{ or } -8 D_q$	t <sub>2g</sub> <sup>2</sup> e <sub>g</sub> <sup>0</sup> $-0.4 \times 2 = -0.8 \Delta_0 \text{ or } -8 D_q$
d <sup>3</sup>	t <sub>2g</sub> <sup>3</sup> e <sub>g</sub> <sup>0</sup>	$-0.4 \times 3 = -1.2 \Delta_0 \text{ or } -12 D_q$	t <sub>2g</sub> <sup>3</sup> e <sub>g</sub> <sup>0</sup> $-0.4 \times 3 = 1.2 \Delta_0 \text{ or } -12 D_q$
d <sup>4</sup>	t <sub>2g</sub> <sup>4</sup> e <sub>g</sub> <sup>0</sup>	$-0.4 \times 4 = -1.6 \Delta_0 \text{ or } -16 D_q$	t <sub>2g</sub> <sup>3</sup> e <sub>g</sub> <sup>1</sup> $-0.4 \times 3 + 2 \times 0.6 = 0.0 \Delta_0 \text{ or } 0 D_q$
d <sup>5</sup>	t <sub>2g</sub> <sup>5</sup> e <sub>g</sub> <sup>0</sup>	$-0.4 \times 5 = -2.0 \Delta_0 \text{ or } -20 D_q$	t <sub>2g</sub> <sup>3</sup> e <sub>g</sub> <sup>1</sup> $-0.4 \times 4 + 2 \times 0.6 = -0.4 \Delta_0 \text{ or } -4 D_q$
d <sup>6</sup>	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>0</sup>	$-0.4 \times 6 = -2.4 \Delta_0 \text{ or } -24 D_q$	t <sub>2g</sub> <sup>4</sup> e <sub>g</sub> <sup>2</sup> $-0.4 \times 4 + 2 \times 0.6 = -0.4 \Delta_0 \text{ or } -4 D_q$
d <sup>7</sup>	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>1</sup>	$-0.4 \times 6 + 0.6 = -1.8 \Delta_0 \text{ or } -18 D_q$	t <sub>2g</sub> <sup>5</sup> e <sub>g</sub> <sup>2</sup> $-0.4 \times 5 + 2 \times 0.6 = -0.8 \Delta_0 \text{ or } -8 D_q$
d <sup>8</sup>	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>2</sup>	$-0.4 \times 6 + 2 \times 0.6 = -1.2 \Delta_0 \text{ or } -12 D_q$	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>2</sup> $-0.4 \times 6 + 2 \times 0.6 = -1.2 \Delta_0 \text{ or } -12 D_q$
d <sup>9</sup>	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>3</sup>	$-0.4 \times 6 + 3 \times 0.6 = -0.6 \Delta_0 \text{ or } -6 D_q$	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>3</sup> $-0.4 \times 6 + 3 \times 0.6 = -0.6 \Delta_0 \text{ or } -6 D_q$
d <sup>10</sup>	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>4</sup>	$-0.4 \times 6 + 4 \times 0.6 = 0.0 \Delta_0 \text{ or } 0 D_q$	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>4</sup> $-0.4 \times 6 + 4 \times 0.6 = 0.0 \Delta_0 \text{ or } 0 D_q$

→ CFSE for Tetrahedral Complexes: (continuation)

- However, splitting in tetrahedral complexes is much smaller than octahedral complexes. Actually for tetrahedral crystal field, the order of splitting is reversed and is related to  $\Delta_t$  as  $\Delta_t = 4/9 \Delta_0 = 0.45 \Delta_0$ , since  $\Delta_t < \Delta_0$

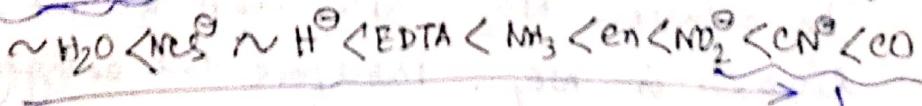
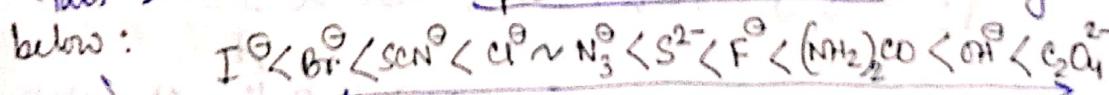
Therefore crystal field splitting favours the formation of ~~for~~ octahedral complexes.

- The crystal field splitting depends on the field produced by the ligand and charge of the metal ion. Some ligands are able to produce strong fields in which the splitting will be large whereas, other ligands produce weak fields which produce in small splitting of d-orbitals.



Thus stronger field ligands give larger value of  $\Delta_o$  and weaker field ligands yield a smaller value of  $\Delta_o$ .

- Ligands are arranged in the order of increasing field strength or increasing splitting power to cause d-orbitals splitting. This series is called Spectrochemical Series and is given below:



water  
field ligand

Stronger Field ligand

Stability of Coordination Compds depends on -

Charge on the central metal ion (i.e. oxidation state) - Greater the charge on central metal ion, more is the stability.

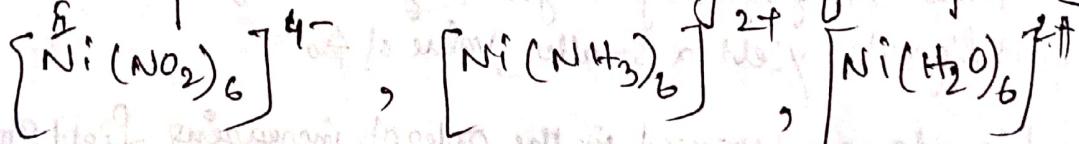
Basic nature of ligands - More the basic strength of ligands (Lewis base), more is the stability of complex.

Presence of chelate rings - Formation of chelate ring increases the stability of complex.

- Size of the metal ion ; Smaller the size of metal ion, more is the stability.
  - Electronegativity and polarising power of the central metal ion More is the electronegativity and polarising power of the central metal ion, more is the stability of the complex.
- Colour of coordination compounds :

- The magnitude of CFSE ( $\Delta_0$ ) for most of the complexes is of the same order and the energy of a photon of visible light. Hence, whenever d-d\* transition takes place, it imparts colour to the complex. The colour of the complex is the complementary colour to the wavelength absorbed.

Q. What will be the correct order of wavelength of absorption in the visible region of the following



Give reason for your answer.

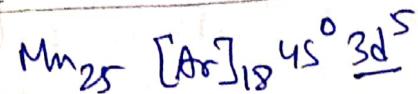
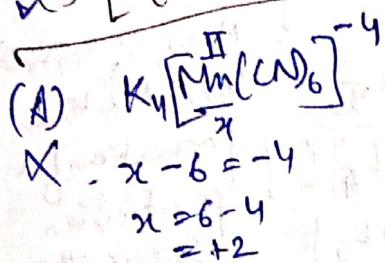
$$\Delta E = h\nu = h \cdot \frac{c}{\lambda}, \Delta E \propto \frac{1}{\lambda}$$

In between  $\text{NO}_2$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  the strongest ligand is  $\text{NO}_2$ . Therefore the energy gap is highest among all compounds. Hence, the wavelength is lowest among all compounds.

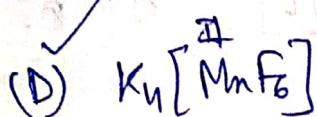
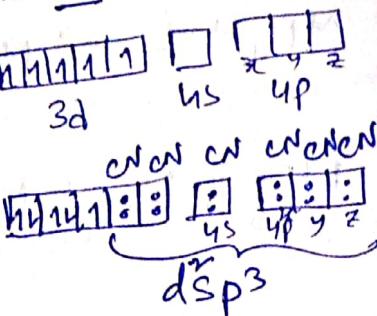
But,  $\text{H}_2\text{O}$  is the weakest ligand.

Hence,  $\text{H}_2\text{O}$  has the highest wavelength among all compounds.

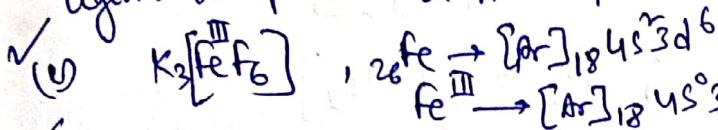
Q78. Compounds with spin-only magnetic moment are:  
 five unpaired electrons are: (A)  $K_4[Mn(CN)_6]$   
 (B)  $[Fe(H_2O)_6]^{+3}$  (C)  $K_3[FeF_6]$  (D)  $K_4[MnF_6]$



CN is a strong field ligand will produce a HS complex



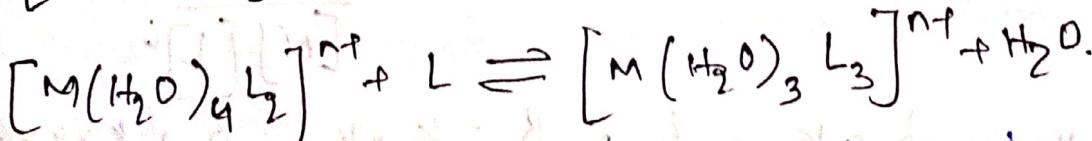
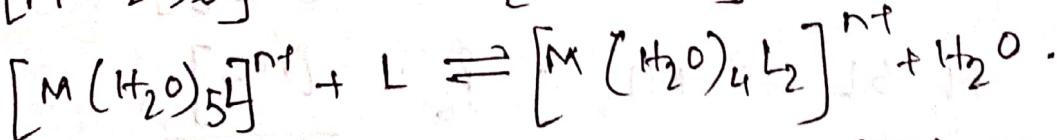
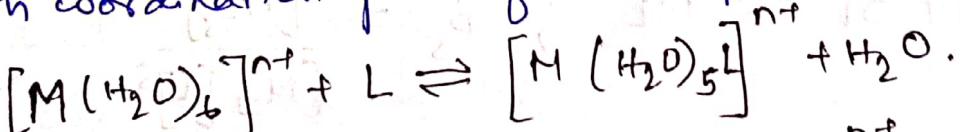
But here, Fluoride is a weak field ligand will produce a LS complex.



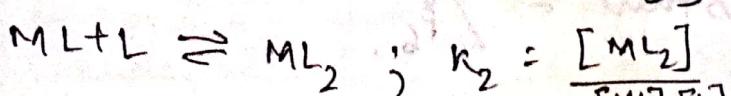
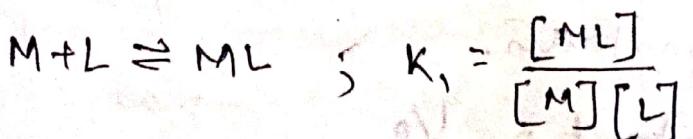
(B)

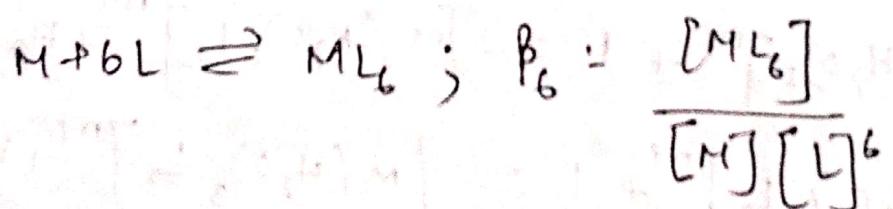
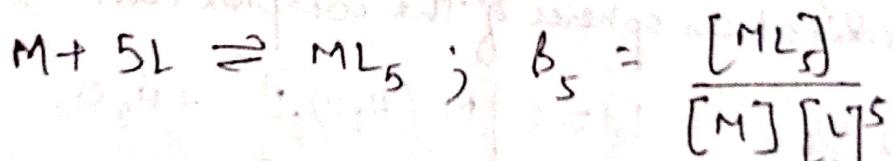
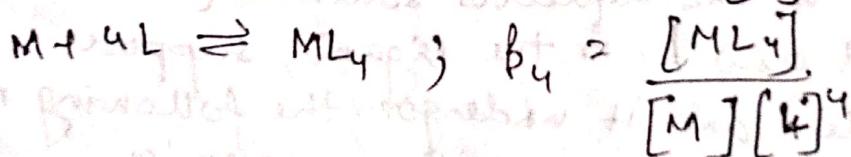
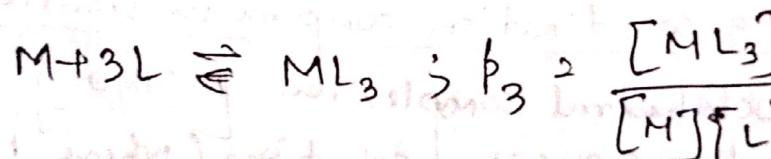
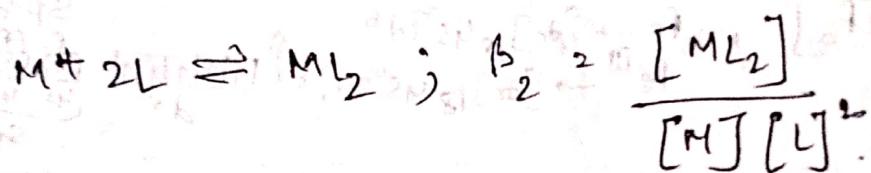
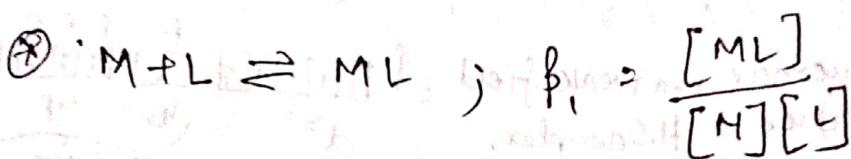
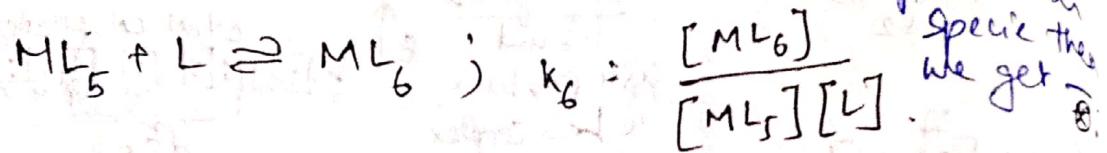
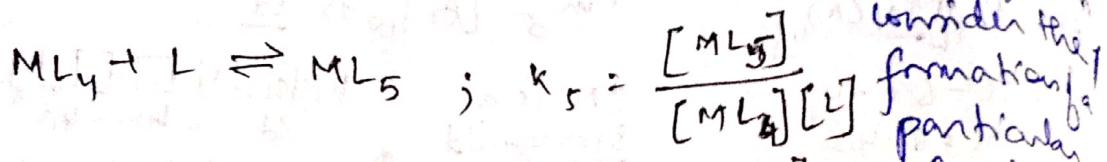
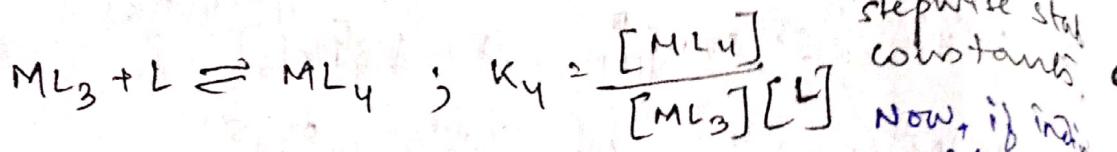
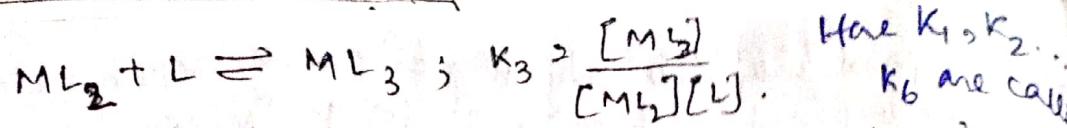
Stability of a coordination complex in solution:

Let take an octahedral complex ion  $[\text{M}(\text{H}_2\text{O})_6]^{n+}$  which is present in the aqueous solution (where M is the metal and L is the ligand, suppose M is unidentate) and it undergoes the following steps with coordination spheres of the complex ion.



Now as here the interaction is purely ionic in between the metal and the ligand. Therefore, we can rewrite the above reaction as —





Here,  $\beta_1 = k_1$ ;  $\beta_2 = k_1 \times k_2$ ;  $\beta_3 = k_1 \times k_2 \times k_3$   
and in the similar way,  $\beta_6 = k_1 \times k_2 \times k_3 \times k_4 \times k_5 \times k_6$ .

Here,  $\beta_1, \beta_2, \dots, \beta_6$  are called overall formation or stability constants.

Overall stability constant =  $1/\beta_6$ .

## Applications of Coordination Compounds

- Coordination compounds are of great importance in biological system.  
eg: Chlorophyll, haemoglobin, Vitamin B<sub>12</sub> etc.
- are coordinate compounds of Mg, Fe & Co respect.
- Coordination compounds are used for qualitative and quantitative analysis, extraction of metals, electroplating, photography & as dyes.
- cis-platin is used for cancer treatment.
- EDTA is often used for treatment of Lead poisoning.
- Coordination compounds are used as catalyst.

## Organometallics:

These are the compounds which contain one or more metal carbon bonds.

These are the compounds of metalloids like - B, Si, Ge etc. with organic group.

## Types of Organometallic Compounds:

Based on the nature of metal-carbon bond, They are classified into three types:-

\*  $\delta$ -bonded Organometallic Compounds: These are, formed by main group (s and p block) elements, non-metallic and metalloid elements and Zn, Cd, Hg through a normal two electron covalent bond.

Example:  $R-Mg-X$ ,  $(C_2H_5)_2Zn$  etc.

\*  $\pi$ -bonded organometallic compounds ( $\pi$ -complexes): These are formed mainly by transition elements.

Here, normal  $\delta$ -bond is formed through the  $\pi$ -cloud of electrons of the organic molecule.

Example: Leisi's salt,  $K[PtCl_3(\eta^2-C_2H_4)]$

ferrocene,  $[\text{Fe}(\eta^5-\text{C}_5\text{H}_5)_2]$  etc.

→  $\sigma$  and  $\pi$  bonded organometallic compound

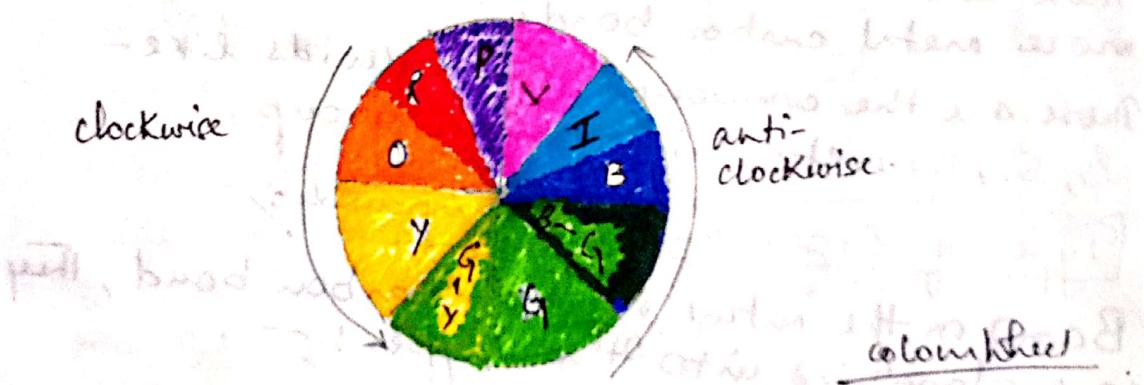
(Metal carbonyls): Transition metal

carbonyls constitute this class of organometallic. Examples are homoleptic carbonyls (compounds containing carbonyl ligands only)  $[\text{M}(\text{CO})_6]$  where,  $\text{M} = \text{V}, \text{Cr}, \text{Mo}, \text{W}$ .

Example:  $[\text{Fe}(\text{CO})_5]$ ;  $[\text{Ni}(\text{CO})_4]$ .

### Colour in Coordination Chemistry:

Sequence can be either clockwise or anti-clockwise



P - Purple; V - Violet; I - Indigo; B - Blue  
B - Blue-Green; G - Green; G - Y - Green  
Y - Yellow; O - Orange; R - Red

B>

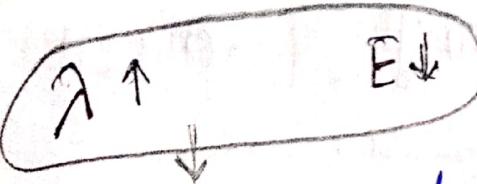
V I B G Y O R

E↓

S↓

Z↑

C)

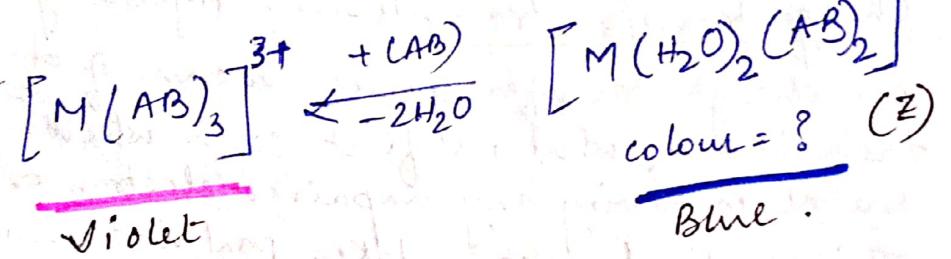
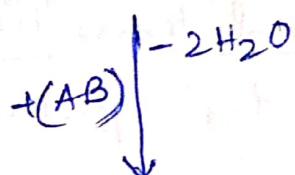
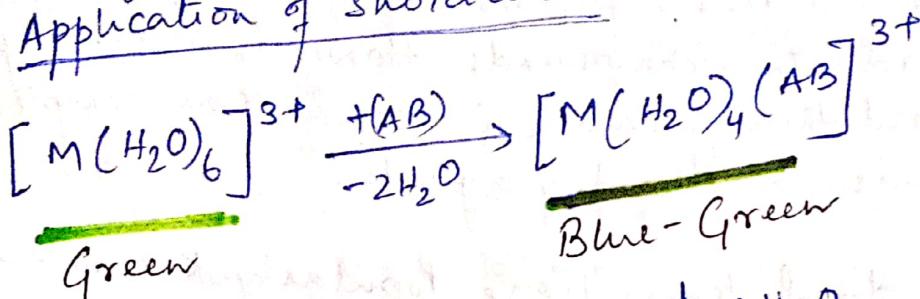


$\rightarrow \propto$  weak field ligand

$$E = h\nu$$

D)

### Application of Shortcut - 1

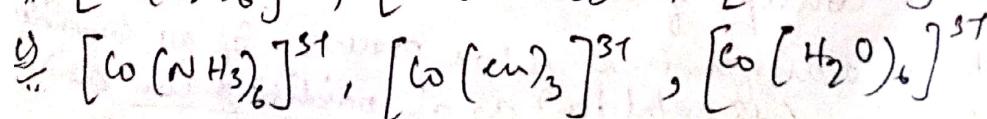
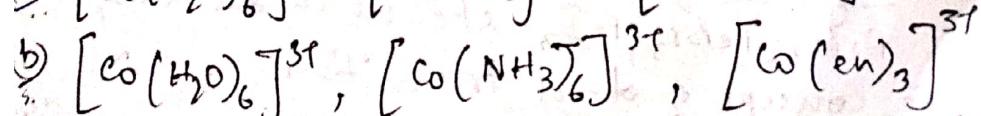
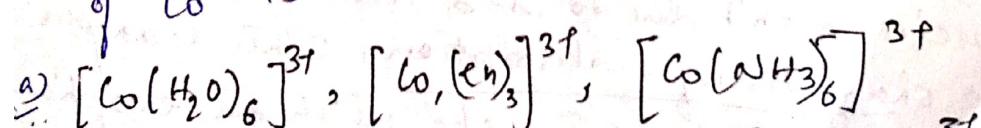


Q. What is the colour of  ${}^2?$

- (a) P (b) Y (c) B (d) Y-G.

→ As X is green, therefore if the colour wheel starts from green and visit to blue, then we get blue in between.

Correct increasing order of the wavelength of absorption in the visible region for the complexes of  $\text{Co}^{3+}$  is —



$\text{Cr}^{+3}$ ,  $\text{Co}^{+2}$ ,  $\text{Fe}^{+2}$

→  $\lambda$  is weak field ligand.

i.  $\text{H}_2\text{O}$  &  $\text{NH}_3$  (as far as ligand change)

ii. Bariumgite ( $\text{A}$ ) is  $\text{H}_2\text{O}$  &  $\text{NH}_3$  ion.

There are many factors responsible for colour coordination compounds. However, as per crystal field theory colour in coordination complexes arise due to two aspects:

1. d-d transition: Popularly known as d-d splitting or ligand free spectra.

2. Charge transfer transitions: Popularly known as charge transfer species. In case of d-d transitions, what we first see is whether the metal is having any unpaired electron or not. This unpaired electron takes part in transition. We have also seen the eg &  $t_{2g}$  splitting of d-orbitals. However colour due to d-d transition is not so simple as orgel diagrams, spin selection rule, dipole selection rule etc. needs to discuss to understand d-d transition completely.

On the other hand, there are certain  $\text{d}^0$  &  $\text{d}^{10}$  species like  $\text{K}_2\text{CrO}_4$ ,  $\text{KMnO}_4$ ,  $\text{AgI}_2$  which are intensely coloured. But definitely the colours of these species aren't due to d-d transition but due to charge transfer absorption. Other examples like  $\text{FeCl}_3$ ,  $\text{FeBr}_3$ ,  $\text{FeI}_3$  etc. which are exception for the concept of d-d transition.

Charge transfer is a redox process. (i.e. oxidation and reduction of metal ion as an oxidizing agent)

(like O<sub>2</sub>, I<sub>2</sub>, etc.) as reducing ion then an electron transfer takes place from X<sup>2-</sup> to the empty valence orbital of the oxidising ion. Now the major question is, what conditions will favour charge transfer absorption? Answer can be attributed to both oxidising as well as reducing ion differently.

For metal ion: Having high ionisation energy.

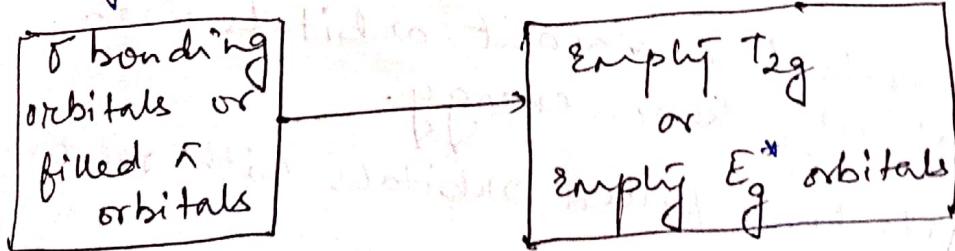
- Empty orbitals with lower energies.
- These two conditions will favour charge transfer from ligand. → metal.

For Ligand: lower electron affinity.

- Filled orbitals of relatively higher energy. It is an important point to remember that absorption of light is more probable because of charge transfer spectra than that of d-d transition. Hence charge transfer absorption always produces intense colour.

### Ligand To Metal Charge Transfer (LMCT)

Mostly octahedral and tetrahedral complexes undergo this type of charge transfer.



[ $t_{2g}$  and  $e_g$  rotations are slightly different in meaning than  $t_{2g}^*$  and  $E_g^*$ .]

HOMO  $\xrightarrow{\text{charge transfer}}$  LUMO  
(Highest Occupied Molecular Orbital)  $\xrightarrow{\text{transfer}}$  (Lowest Unoccupied Molecular Orbital)

Energy difference is quite low.

Here light is absorbed from the visible region or near UV region.

Example:

1 MnO<sub>4</sub><sup>-</sup> (Purple): Simple ligand - metal charge transfer takes place.

2 I<sup>0</sup> complexes: I<sup>0</sup> is an easily oxidisable species due to its large size. So in case of I<sup>0</sup> complexes, even if the metal ions aren't good oxidants, LMCT takes place. FeI<sub>3</sub> (intense black), P<sub>6</sub>I<sub>2</sub> (yellow), HgI<sub>2</sub> (red).

3 Examples for the transitions where charge transfer takes place from  $\delta$ -orbital of ligand to metal orbital include CdS (yellow), HgS (red), PbO (yellow) etc. In these transitions, ns, np or nd-orbitals of metal can participate.

### Metal To Ligand Charge Transfer (MLCT):

There are ~~the~~ two conditions —

- Ligands have vacant orbitals with relatively lower energy.
- Metals have filled orbitals with relatively higher energy.

MLCT is basically observed for octahedral complexes having — CO, py, bipy, O-phen etc. as ligands and SCN<sup>-</sup> too in some cases.

Eg)  $[Fe(SCN)_6]^{3-}$ ,  $[Fe(O-phen)_3]^{4+}$ ,  $[Fe(bipy)_3]$  etc.

## Metal To Metal charge transfer

It is very easy to understand as here the whole idea revolves around metal.

MMCT occurs in those cases where a metal ion exists in two different oxidation states - &

e.g. Prussian blue- $\text{Fe}_4^{2+} \left[ \text{Fe}^{3+} (\text{CN})_6 \right]_3$  etc.

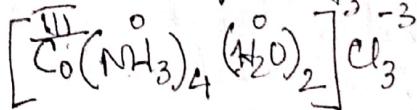
Q1. Which one of the following complexes shows optical isomerism? [2016 Main]

- (a) Cis  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  (c)  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$   
 (b) trans  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  (d)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

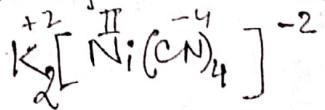
Q2. Which of the following complex species isn't expected

- (a)  $[\text{Co}(\text{en})_3]^{3+}$  (b)  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  to exhibit optical isomerism?  
 (c)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  (d)  $[\text{Co}(\text{en})(\text{NH}_3)\text{Cl}_2]^+$

① tetraammine diqua cobalt (III) chloride



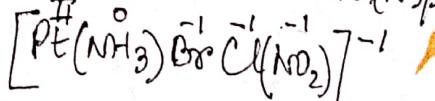
② potassium tetracyanidomanganese (II) lactate (IV)



③ Iron (II) hexacyanido ferrate (III)



④ Ammine bromido chlorido nitrito (N) platinum (II) platinato (I)



⑤ dichloridobis(ethan-1,2-diamine)platinum (IV) nitrate

