

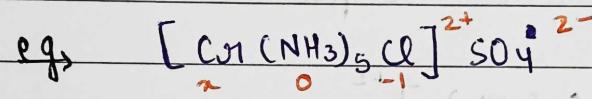
# Co-ordination Chemistry

OR

## Complex Compounds

Complex compounds are composed of

(a) Complex cation + simple anion



$$x + 0 + (-1) = 2$$

$$x = 3$$

[ ]  
↓

is called a co-ordination sphere

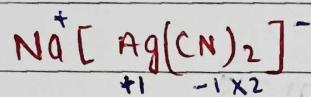
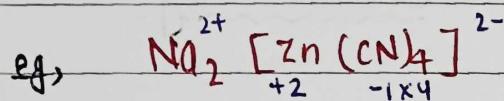
or co-ordination entity. It

is not going to dissociate.

e.g. For example, in above case the complex will not give any characteristic test of radicals present in them.

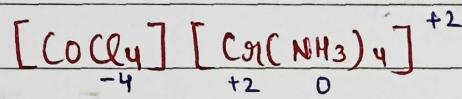
Because of this complex ion, comp<sup>n</sup> can retain its own properties even in aqueous state.

(b) simple cation and complex anion



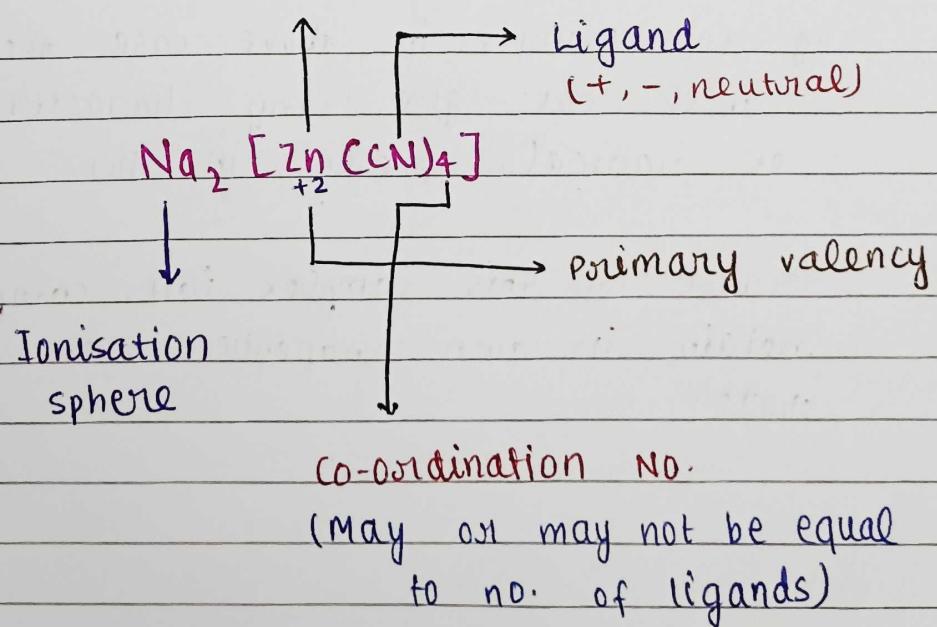
The above can give characteristic test of sodium only.

(c) complex cation and complex anion.

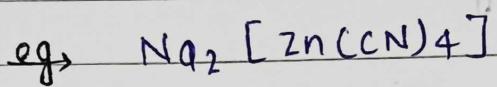


\* Representation of a complex compn:-

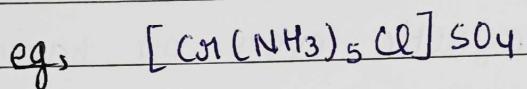
~~Representation of a complex compound~~  
Central Metal Ion (CMI)



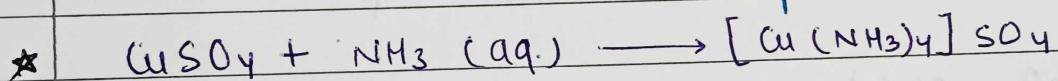
Homooleptic:- when all ligands are same in a co-ordination sphere.



Heteroleptic:- when all ligands present in a co-ordination sphere is not same.



→ Do not give characteristic test of Cu.



co-ordination No.      possible geometry.

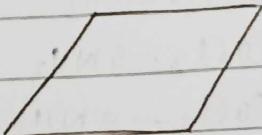
$d\text{sp}^2 \rightarrow$  square planar

4                           $\text{sp}^3 \rightarrow$  tetrahedral

$\text{d}^3\text{s} \rightarrow$  tetrahedral

6                           $\text{sp}^3\text{d}^2$  - Octahedral

$\text{d}^2\text{sp}^3$  - Octahedral



# Theories Associated with co-ordination compounds

## 1. Werner's Theory

In 1893 (before discovery of  $e^-$ )

## 2. Valence Bond Theory

"Hybrid", arrangement

Comp<sup>n</sup> was diamagnetic even on having unpaired  $e^-$

can't explain characteristic of comp<sup>n</sup>.

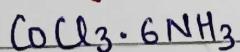
## 3. Crystal Field Theory

Most acceptable Theory.

### Werner's Theory.

To explain the bonding in complex compounds, the first imaginary theory was proposed by Werner in 1893 (before the discovery of  $e^-$ )

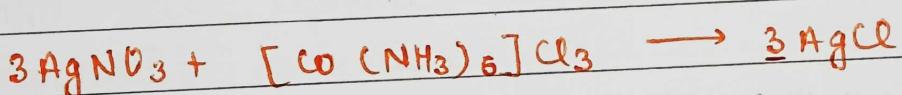
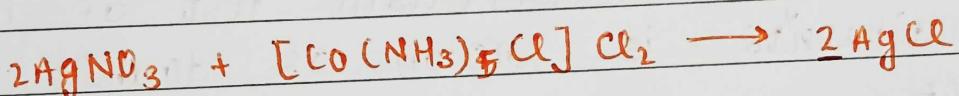
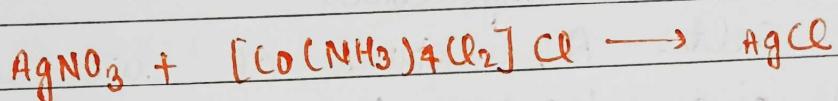
He reacted  $\text{CoCl}_3$  with reagents like  $\text{NH}_3$  to get series of comp<sup>n</sup>



} with different properties  
like colour, geometry  
and chemical nature.

	$C^+ : A^-$	Colour
$[Co(NH_3)_6]Cl_3$	1:3	Yellow
$[Co(NH_3)_5Cl]Cl_2$	1:2	Purple
$[Co(NH_3)_4Cl_2]Cl$	1:1	Green

He knew about the no. of Cl outside the bracket by reacting the complex with  $AgNO_3$ .



The main postulates are:

- (i) In co-ordination compn metals show two types of linkages (valences) - primary and secondary.
- (ii) The primary valence are normally ionisable and are satisfied by negative ions.
- (iii) The secondary valences are non-ionisable satisfied by neutral molecule or negative ions. [Secondary valence = Co-ordination No.]
- (iv) Metals have characteristics spatial arrangements corresponding to different coordination numbers.

Co-ordination polyhedra:- Spatial arrangement of ions/groups bounded by secondary linkage.

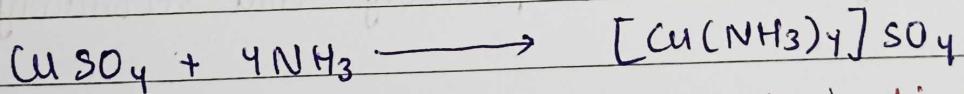
### Ligands

Those radical ions or molecules which can donate  $\text{lp}$  to form complex units or co-ordinate bonds are called ligands.

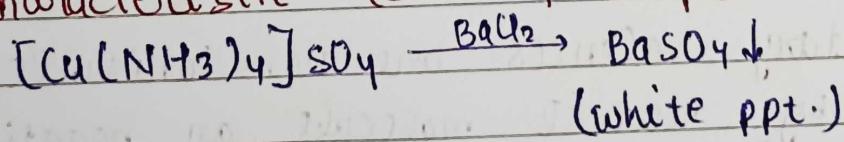
crystallised

Double salt:- A mixture of two salts which give characteristic test of its constituents is known as double salt.

Complex salt:- A crystallised mixture of two salts which do not give characteristic test of its constituents is known as complex salt.

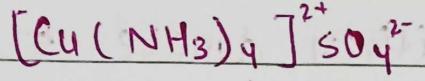


In this compn,  $\text{SO}_4^{2-}$  is in ionisation sphere. So, the above product can give characteristic test of sulphate ion.



~~HSO<sub>4</sub>~~

→ Primary valency



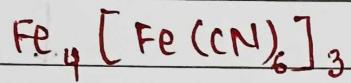
↳ Secondary valency

(May or may not equal  
to no. of ligands)

\* \*

Ferric Ferro cyanide

Prussian Blue

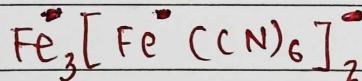


(colour is due to  
complex ion)

\*

Ferro Ferric cyanide

Turmsbull Blue



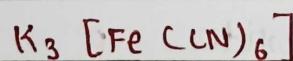
\*

Potassium Ferro cyanide



\*

Potassium Ferric cyanide



## Ligands

↳ is ligands either donate e<sup>-</sup> pair or gain e<sup>-</sup> pair.

Carbonyl ligand (CO) is the only ligand which can donate as well as gain

Classification based on charge

Negatively charged Ligands

Cl<sup>-</sup> → Chlorido

I<sup>-</sup> → Iodo

F<sup>-</sup> → Fluorido

CN<sup>-</sup> → Cyanido

OH<sup>-</sup> → Hydroxo

SH<sup>-</sup> → Mercapto

C<sub>2</sub>O<sub>4</sub><sup>2-</sup> (ox) → Oxalato

Neutral ligands

Positively charged ligands

NO<sub>2</sub><sup>+</sup> → Nitronium

NO<sup>+</sup> → Nitrosonium

NH<sub>2</sub>-NH<sub>3</sub><sup>+</sup> → Hydrozonium

CO<sub>3</sub><sup>2-</sup> → Carbonato

SO<sub>4</sub><sup>2-</sup> → Sulphato

NO<sub>3</sub><sup>-</sup> → ~~Nitrito~~ Nitrato

NO<sub>2</sub><sup>-</sup> → Nitro

ONO<sup>-</sup> → Nitrito

SCN<sup>-</sup> → Thiocyanato (S)

~~Thiocyanato~~ Thiocyanato (N)

CNO<sup>-</sup> → Cyanato (C)

NCO<sup>-</sup> → Cyanato (N)

O<sub>2</sub><sup>2-</sup> → Oxido

O<sub>2</sub><sup>2-</sup> → peroxido

O<sub>2</sub><sup>-</sup> → superoxido

NH<sub>2</sub><sup>-</sup> → Amido

NH<sup>2-</sup> → Imido

N<sup>3-</sup> → Nitrido

N<sub>3</sub><sup>-</sup> → Azido

H<sup>-</sup> → Hydrido

SO<sub>3</sub><sup>2-</sup> → Sulphito

PO<sub>4</sub><sup>3-</sup> → Phosphato

## Neutral ligands

$H_2O \rightarrow$  Aqua

$NH_3 \rightarrow$  Amine

$CO \rightarrow$  Carbonyl

$NO \rightarrow$  Nitrosyl

$NS \rightarrow$  Thio nitrosyl

$CS \rightarrow$  Thio carbonyl

$PH_3 \rightarrow$  Phosphine

$P(Ph)_3 \rightarrow$  Tri-phenyl phosphine  $\rightarrow$  Monodentate

$NH_2-NH_2 \rightarrow$  Hydrazine

$NH_2-CH_2-CH_2-NH_2 \rightarrow$  (en)  $\rightarrow$  Ethylene diamine

- \*  $NH_4^+ \rightarrow$  Ammonium  $\rightarrow$  Neither donate nor accept d.p.  
 $PH_4^+ \rightarrow$  Phosphonium  $\rightarrow$  can accept d.p.

- \* Classification based on dentisity

↓  
Donation tendency / ability of  
a ligand is called its dentisity.

Monodentate

Polydentate

Bidentate

Tridentate

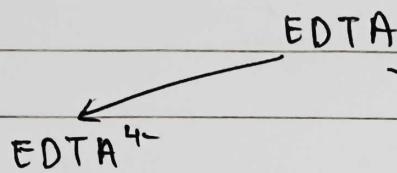
Tetridentate

Pentadentate

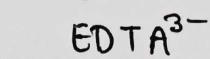
Hexadentate

$[CrI_3 + F \rightarrow$  dentate]

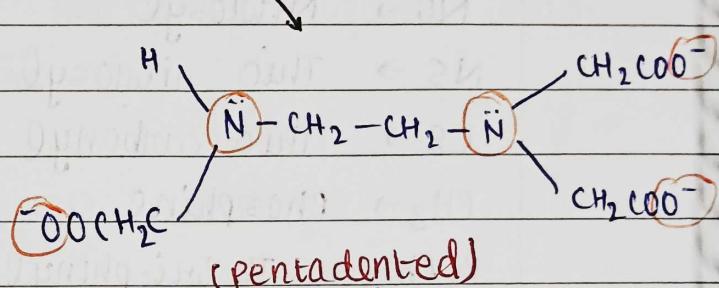
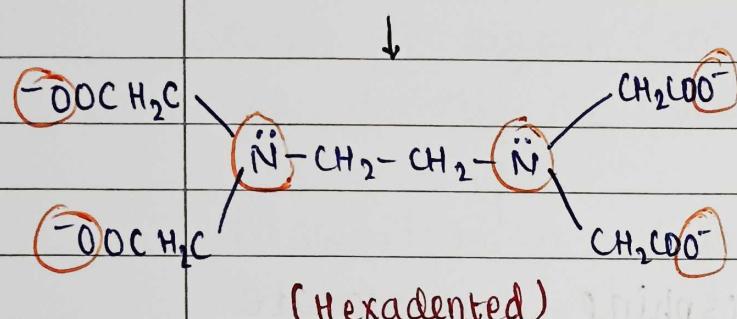
$[CrI_3 + H \rightarrow$  dentate]



Ethylenediamine  
Tetra Acetato

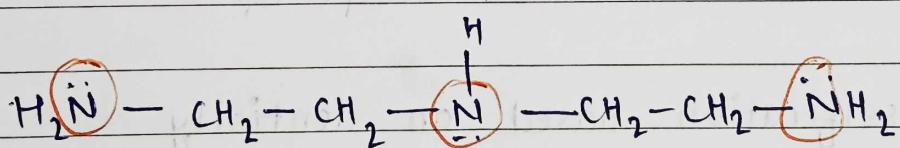


Ethylenediamine  
Tri Acetato



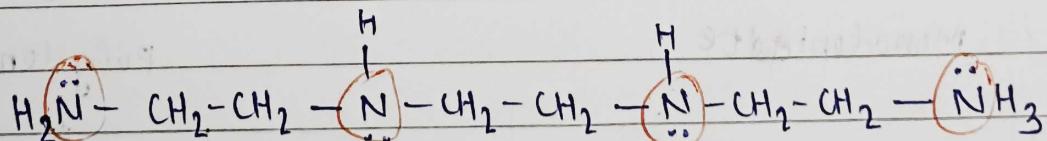
[  $\textcircled{\text{O}}$  → Donating Unit ]

e.g. Diethylenetriamine (dien)



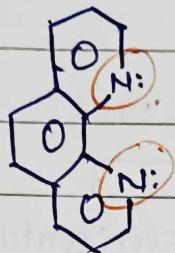
(Tridentate)

e.g. Triethylenetetra-amine (trien)

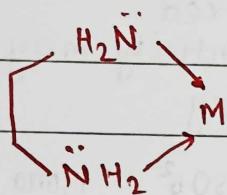


(Tetradeятate)

e.g. Phenanthroline



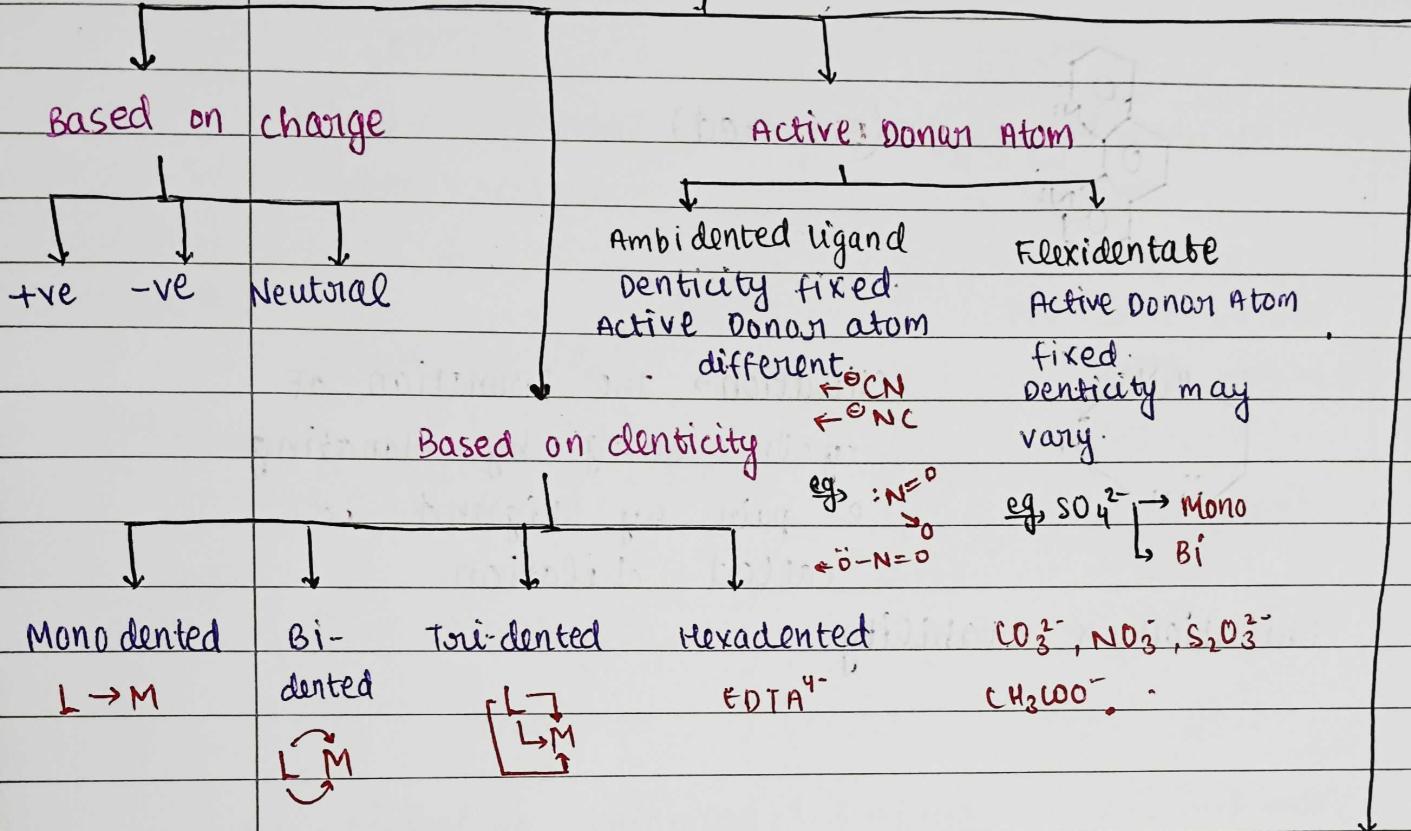
(Bidentate)



Chelation  $\rightarrow$  The formation of cyclic ring by donating  $e^-$  pair by ligand is called chelation.

Chelation  $\propto$  stability.

## Ligand Classification



### On the basis of bonding

All ligands are Lewis base  
 i.e.,  $e^-$  pair donor.

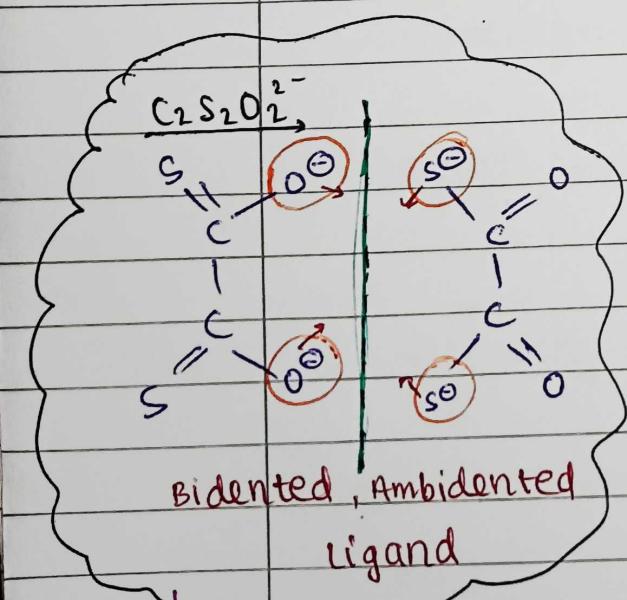
Classical ligands

$\sigma$ -ligands  
 $\pi$ -ligands

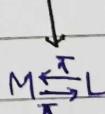
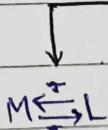
$\text{M} \leftarrow \text{L}$  ligands

Non-classical ligands

$\pi$ -ligands  
 (Acceptor ligands)  
 (synergic bonds)



Dithiooxalato



## Ligands on the basis of bonding

Classical ligands

$\sigma$  ligands

or

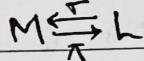
$M \leftarrow L$  ligands

Non-classical ligands

$\pi$  ligands

$\pi$ -acceptor ligands

(synergic bonds)

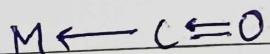


$\text{NO}_3^+$

$\text{CO}$ ,  $\text{CN}^-$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_5\text{H}_5^-$  can make  $\pi$  bond.

Effects of Synergic bond:-

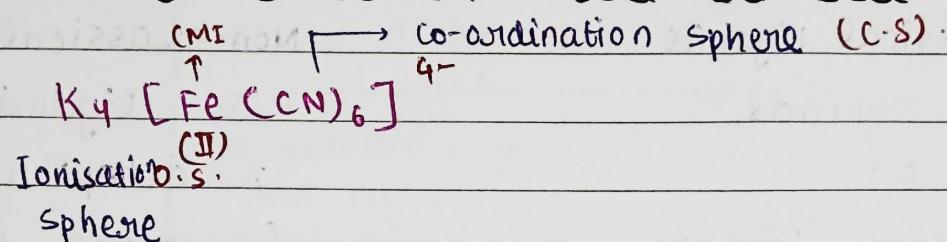
due to synergic bond, metal attract donor atom towards itself. Thus, bond length b/w the two atom of ligand increases and bond order decreases.



due to attraction by metal co bond length increases and bond ~~order~~ width decreases.

## Nomenclature of Complex compounds

Case I: When ionisation sphere on LHS.



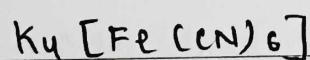
Way to Write Name:-

Ionisation sphere + No. of ligands + Ligand + CMI + o.s. of CMI  
Element

↓  
Its Latin  
name is  
taken  
and [ends  
with ate]

There is small space  
left b/w name of I-S  
and C.S. and no space  
b/w name of C-S.

only when  
C-S. is  
-vely  
charged.



Potassium hexacyanidoferrate (II)

↓                          ↓  
Name of                no gap in  
I-S.                    name of C-S.

(None, Di, Tri,  
Tetra, etc are  
not used)

Small gap  
b/w I-S.  
and C-S.

## Rules of Naming:-

1. Cationic part is always written before anionic part.
2. No. of ligand is always listed before CMI.
3. No space is left b/w the names of the species placed in same co-ordination entity.
4. In case of multiple ligands, alphabetical order should be followed.

↓

Alphabet of name of ligand.

e.g., Tetra amine    Di chloro  
    ↓ written first.

5. When a number is in the name of ligand, then for number of ligand:

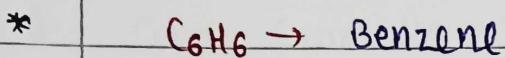
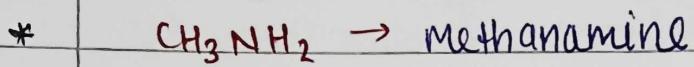
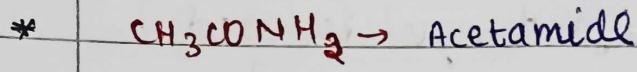
2 → bis

3 → triis

4 → tetrakis

e.g., (en)<sub>2</sub> → bis ethylene di amine

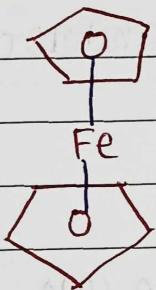
6. When a vowel comes in the name of ligand at end, it is not removed, nor hyphen is used.



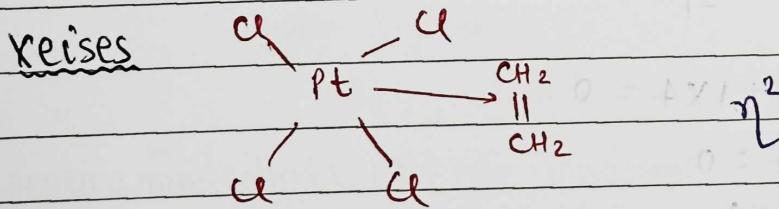
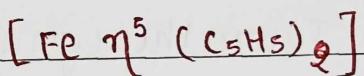
7. For  $n$  donor ligands, the prefix like  $\eta^x$  is to be used where  $n$  is ~~no.~~<sup>No. of</sup>  $\pi$  bond.  $x$  is hepticity.

~~In case~~

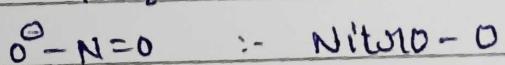
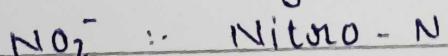
Ferrocene.



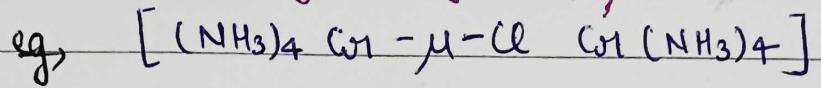
Fe makes 5  $\pi$  bonds with one ring hence, it is written as:



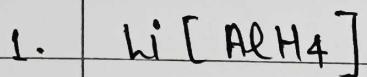
8. In case of ambident ligand



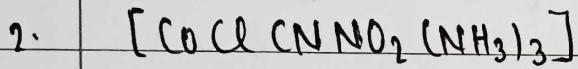
In case of bridge ligand,  $\mu$  is used.



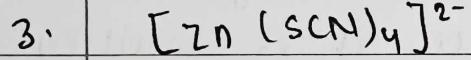
Q. Give IUPAC name



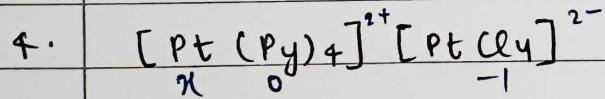
$\Rightarrow$  Lithium tetrahydridoaluminate (III)



$\Rightarrow$  Triaminechlorido cyanido nitro cobalt (III)



$\Rightarrow$  Tetra thio cyanato zincate (II)e



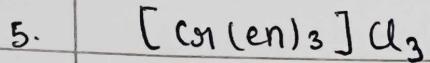
$$x + 0 \times 4 + x - 1 \times 4 = 0$$

$$x + x - 4 = 0$$

$$2x = 4$$

$$\boxed{x = +2}$$

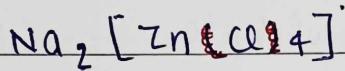
$\Rightarrow$  Tetra pyridine platinum (II) tetrachloridoplatinate (II)



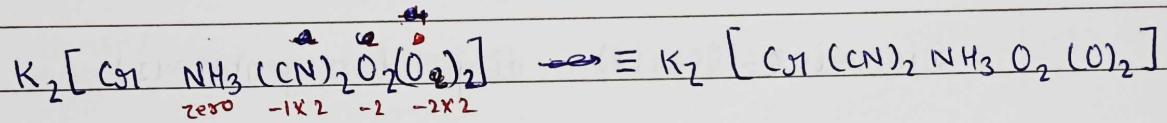
$\Rightarrow$  Tris(ethylene diamine)<sup>m</sup> chromium (III) chloride

Q. Give formula of:

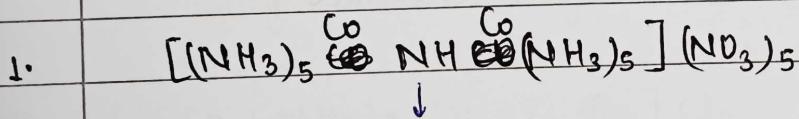
1. sodium tetrachlorido zincate (II)



2. Potassium aminedicyano dioxoperoxochromate (VI)

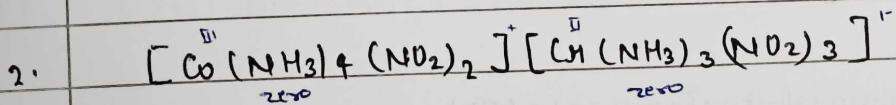


Q. 2. Iuvie name of:



Bridge ligand

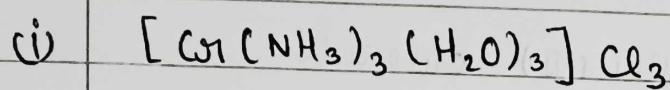
Pentaamminecobalt (III)- $\mu$ - imido pentaminecobalt (III) nitrate



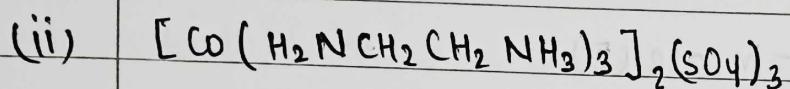
Tetraammine dinitro cobalt (III)

triaminetetrinitro chromate (IV)

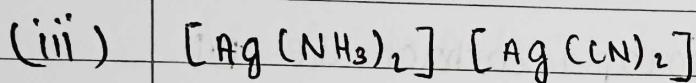
Q. Write IUPAC name of:



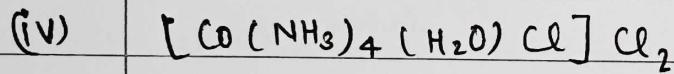
Triamminetriaquachromium (III) chloride



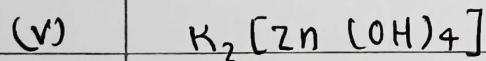
tris(ethylenediamine)cobalt (II) sulphate



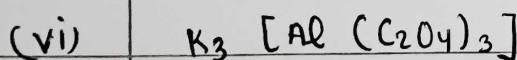
Diamminesilver (I) dicyanidoargentate (I)



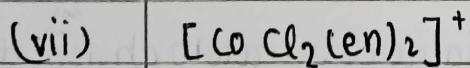
Tetraammineaquachloridocobalt (III) chloride



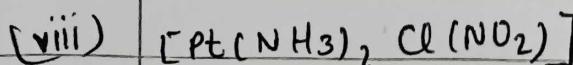
Potassium tetrahydroxozincate (II)



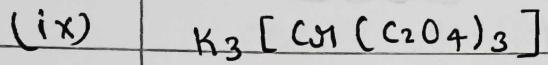
Potassium trioxalatoaluminate (III)



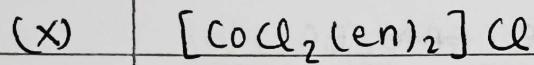
Dichlorido bis(ethylenediamine)cobalt (III)



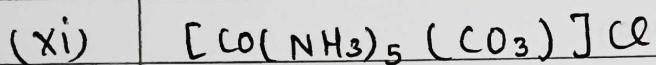
Diamminochloridonitro-N-platinum(II).



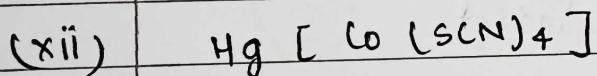
Potassium trioxalatochromate(III)



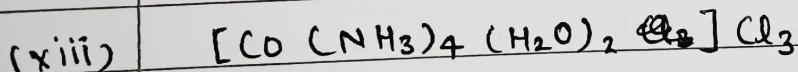
Dichlorido bis(ethylenediamine)cobalt(III) chloride



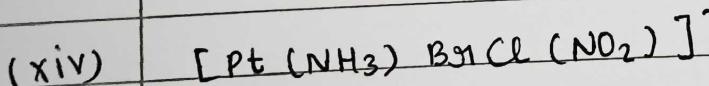
Penta<sup>ammine</sup>quacarbonatocobalt(III) chloride



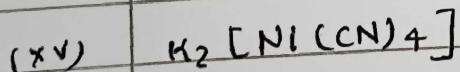
Mercury tetrathiocyanato-s-cobaltate(III)



Tetraamminediaqua cobalt(III) chloride



Amminebromidochloridonitroplatinate(II)



Potassium tetracyanidonickelate(II)

# EAN (Effective Atomic Number)

This is total number of  $e^-$  present on central atom in a complex.

Every comp" tries to achieve ~~EA~~ EC  
• similar to nearest noble gas.

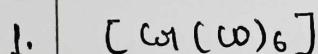
3d series  $\rightarrow$  36 (Kr)

4d series  $\rightarrow$  54 (Xe)

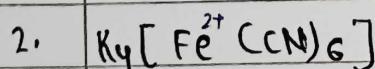
5d series  $\rightarrow$  ~~86~~ 86 (Rn)

$EAN = Z - O.S. + \text{no. of } e^- \text{ gained}$   
from ligands

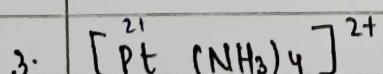
• Calculate EAN of:



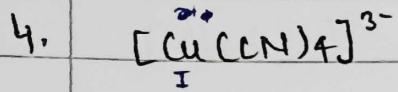
$$\begin{aligned}EAN &= 24 - 0 + 12 \\&= 36\end{aligned}$$



$$\begin{aligned}EAN &= 26 - 2 + 12 \\&= 36\end{aligned}$$



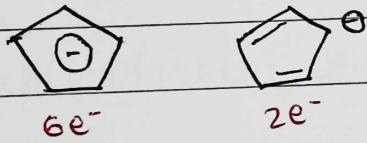
$$\begin{aligned}EAN &= 78 - 2 + 8 \\&= 84\end{aligned}$$



$$\begin{aligned}\text{EAN} &= 29 - 1 + 8 \\ &= 36\end{aligned}$$

Rules for EAN:

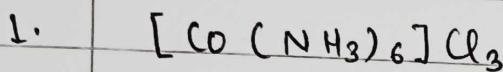
1. All donation of ligands are considered as two  $e^-$  but  $\text{NO}$  is considered as  $3e^-$  donor.
2. For  $\pi$ -donor, the no. of  $\pi e^-$  involved can be calculated by



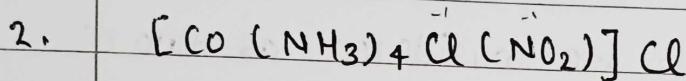
3. For some comp' like  $\text{Mn}(\text{O})_5 \equiv \text{Mn}_2(\text{O})_{10}$
- $$\begin{aligned}\text{EAN} &= 25 - 0 + 10 + 1 \rightarrow (\text{s-bond}) \\ &= 36\end{aligned}$$

## NCERT Questions

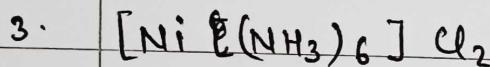
Q. Write IUPAC names of the following



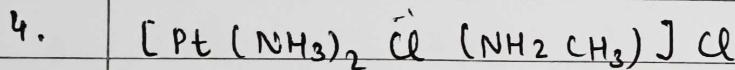
Hexaammincobalt (III) chloride



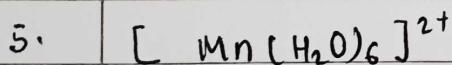
Tetraamminechloridonitrocobalt (III) chloride



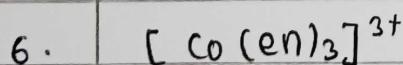
Hexaamminenickel (II) chloride



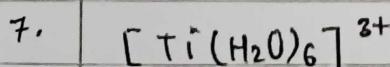
Diamminechloridomethanamineplatinum (II) chloride



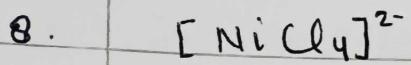
Hexaaquamanganese (II)



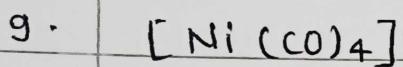
Tris(ethylenediamine)cobalt (III)



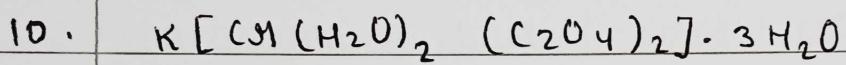
Hexaaquatitanium (III)



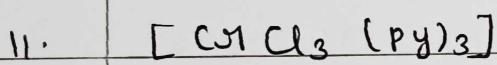
Tetrachloronickelate (II)



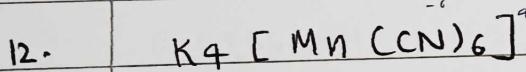
Tetracarbonylnickel (0)



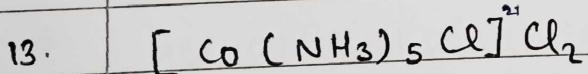
Potassium diaqua dioxalato chromate (III) trihydrate



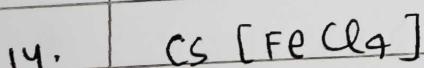
Trichlorido tripyridinechromium (III)



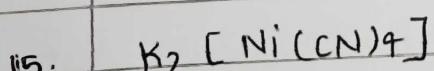
Potassium hexacyanidomanganate (IV)



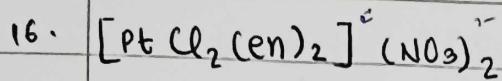
~~Pentaqua~~ Pentaamminechloridocobalt (III) chloride



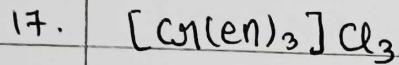
~~Tetraqua~~ Cesium tetrachloroferrate (III)



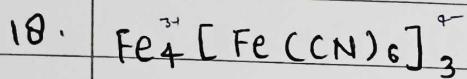
Potassium tetracyanido nickelate (II)



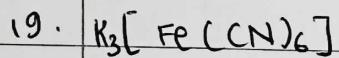
Dichlorido bis(ethylene diamine) platinum(IV) nitrate



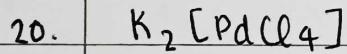
Tris(ethylene diamine)chromium(III) chloride



Iron(II) hexacyanidoferriate(II)



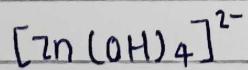
Potassium hexacyanidoferriate(II)



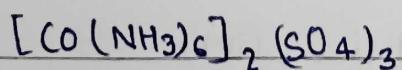
Potassium tetrachlorido palladate(II)

Q. Give formula of following using IUPAC names.

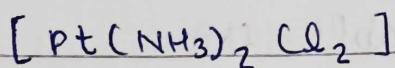
1. Tetrahydroxidozincate(IV)



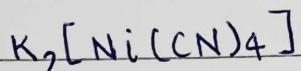
2. Hexaamminecobalt(III) sulphate



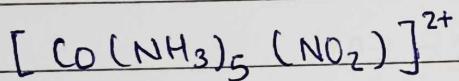
3. Diamminedichloridoplatinum (II)



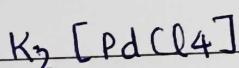
4. potassium tetracyanidonickelate (II)



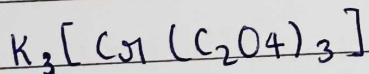
5. pentaamminenitrito-O-cobalt (II)



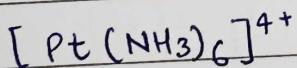
6. potassium tetrachlorido palladate (II)



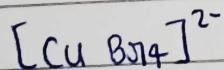
7. potassium trioxalatochromate (III)



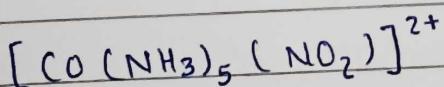
8. hexaammineplatinum (IV)



9. Tetraboronimidocuprate (II)



10. pentaamminenitrito-N-cobalt (III)



## Application of EAN

1. This EAN rule is not applicable for
  - (a) Total odd no. of  $e^-$
  - (b) For  $d^8$  configuration or C.N. = 4  
(For Ni & Pt)
2. To calculate the magnetic moment of the compound.

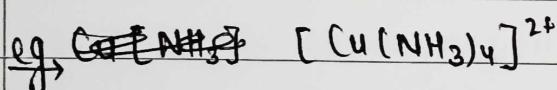
$$\mu = \sqrt{n(n+2)} \text{ BM}$$

where,  $n = (\text{noble gas})_{\text{near}} - \text{EAN}$

$$\text{For } 3d \rightarrow 36$$

$$4d \rightarrow 54$$

$$5d \rightarrow 86$$

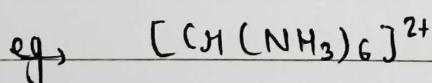


$$\text{EAN} = 29 - 2 + 8$$

$$= 35$$

$$n = 36 - 35 = 1$$

$$\mu = \sqrt{1 \times 3} = \sqrt{3} \text{ BM}$$



$$\text{EAN} = 24 - 2 + 12$$

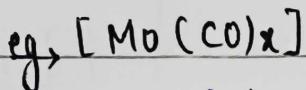
$$= 34$$

$$n = 2$$

$$\mu = \sqrt{8} \text{ BM}$$

3.

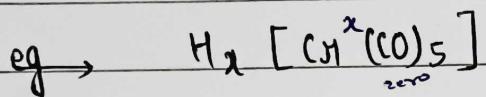
To find the formula of metal carbonyl



$$= 42 + 2x = 54$$

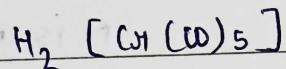
$$2x = 12$$

$$\boxed{x = 6}$$

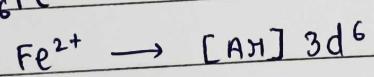
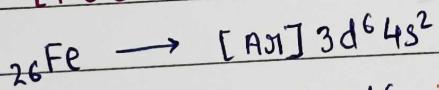
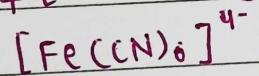
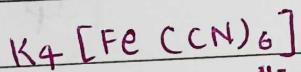


$$24 + x + 10 = 36$$

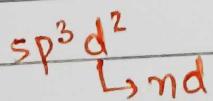
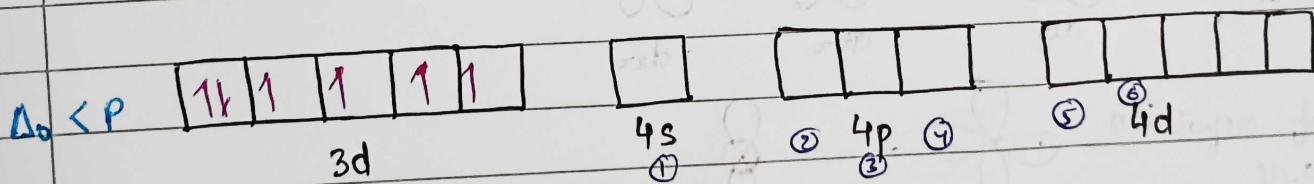
$$\boxed{x = 2}$$



### Valence Bond Theory.



For co-ordinate bond,  
6 vacant orbitals are required



outer orbital complex

$$n = 4e^-$$

$$\mu = \sqrt{24} \text{ B.M.}$$

paramagnetic

$\Delta_o > P$

1s	1s	1s											
3d			4s			4p				4d			

$d^2 sp^3$

↳ Inner d-orbital

(Inner pairing)

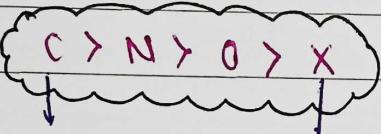
$\mu = 0$

Dimagnetic



### \* Order of ~~steric~~ strength of Ligands :-

C > N > O > X



Carbon  
Containing  
Ligand

Halogen  
Containing  
Ligand.

N is containing  
sp

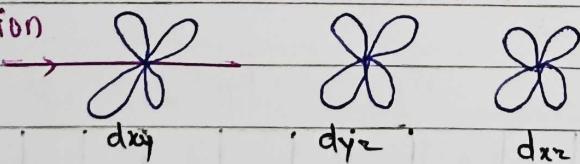
$NO_2^- > ONO^-$

O is containing  
sp



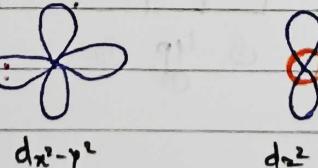
### \* Splitting of d-orbital :-

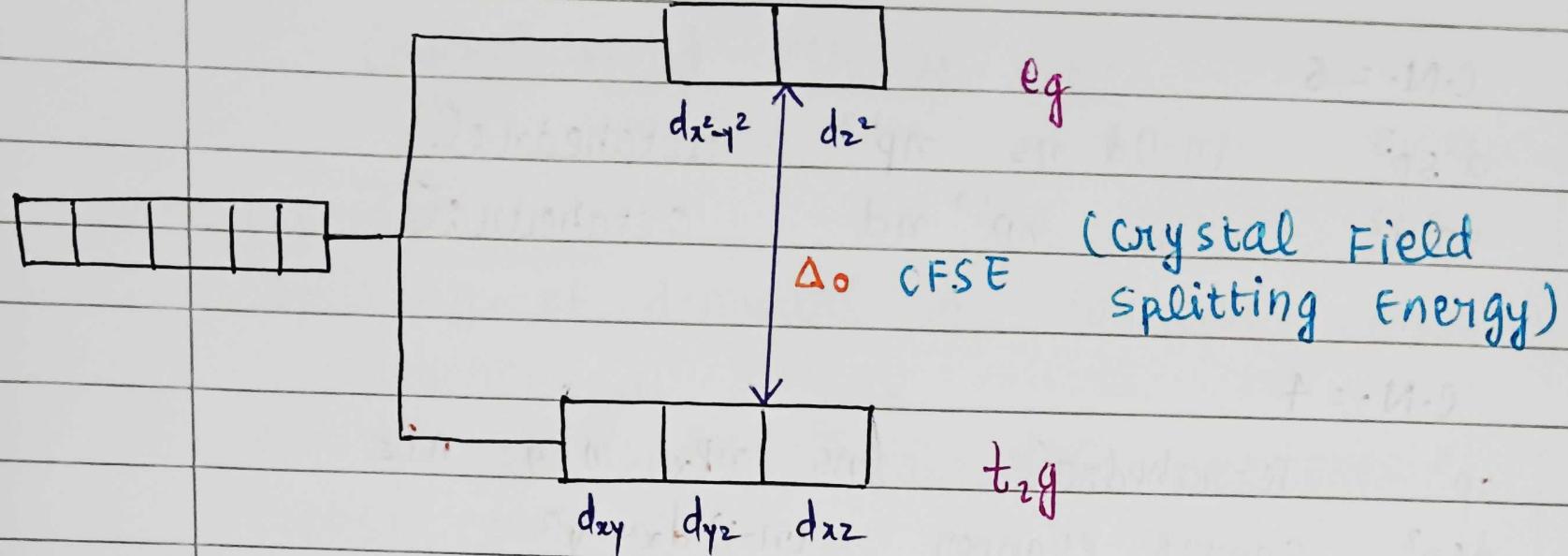
Force of repulsion  
less



Force of repulsion  
more

(Along the axis)





No. of unpaired  $e^-$   
in degenerate  
orbital

No. of unpaired  $e^-$   
in splitted  
orbital

$d^1$

1

1

$d^2$

2

2

$d^3$

3

3

$d^4$

$d^5$

$d^6$

$d^7$

Different unpaired  $e^-$  in both the  
orbitals.

C.N. = 6

$d^2sp^3$

$(n-1)d\ ns\ np^{1-3}$

Octahedral

$sp^3d^2$

$ns\ np^{1-3}\ nd$

Octahedral

C.N. = 4

$sp^3$

Tetrahedral

$ns\ np_x\ np_y\ np_z$

$dsp^2$

Square Planar

$(n-1)d_{x^2-y^2}$

$d^3s$

Tetrahedral

$sp^2d$

Square Planar

# Crystal Field Theory (CFT)

## Introduction

Splitting of d-orbital in octahedral complexes

Spectrochemical series

$e^-$  distribution in octahedral complexes

(CFSE ( $\Delta_o$ ))

Splitting of d-orbitals in tetrahedral complexes

Application of CFT.

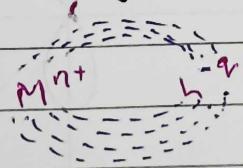
Johann Taylor Distortion (JTD)

## Introduction

H. Breyhey and Van Black had given this CFT. They focused on ionic interaction b/w metal ion ( $M^{n+}$ ) and ligand ( $L^{-q}$ ).

The bond b/w metal ion and ligand is purely ionic, i.e., electrostatic force of attraction (Fe).

negative ligand



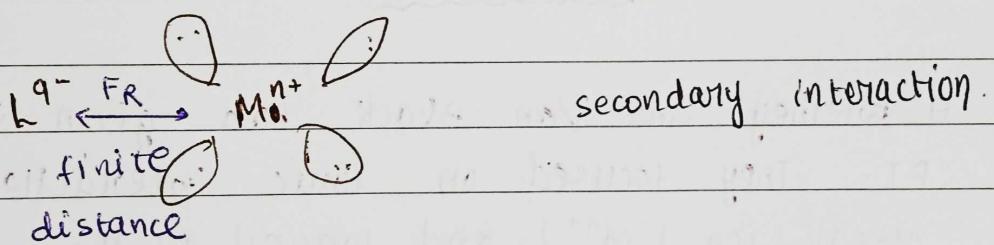
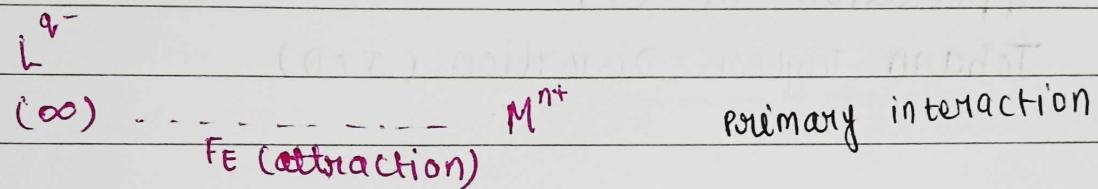
Ion-Ion interaction

Neutral ligand

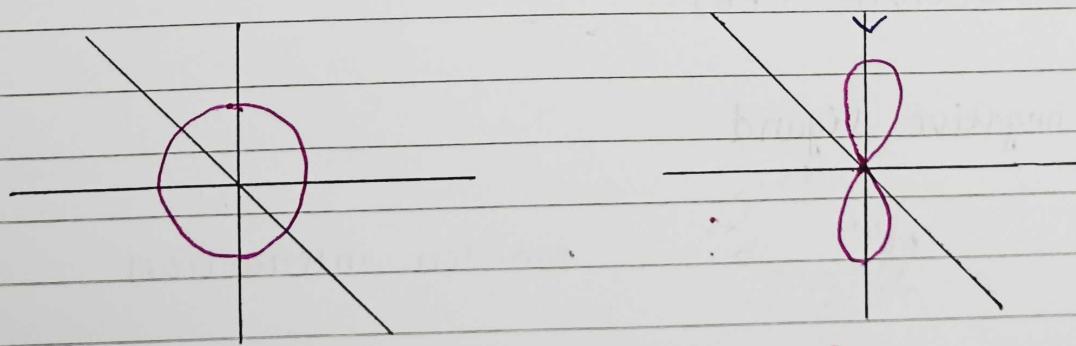


This theory is based on ionic interaction. Hence, no covalent behaviour and overlapping of orbitals.

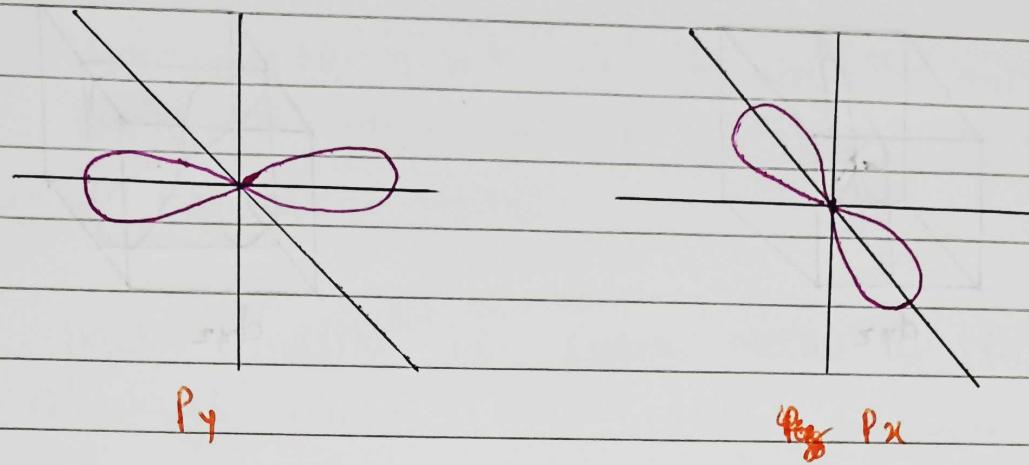
According to CFT, when ligand is at infinity, then it would be primary interaction of attraction but at a certain distance, they start repelling each other.



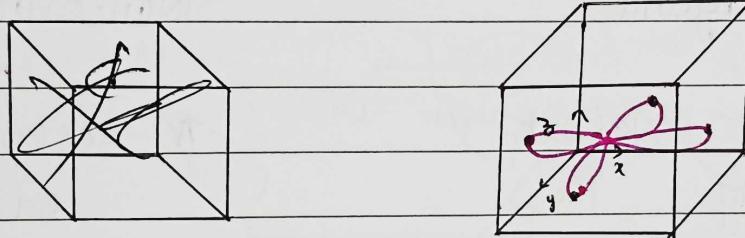
- \* When ligand reaches at finite distance, secondary interaction:-



FA is same along  
x, y & z axis

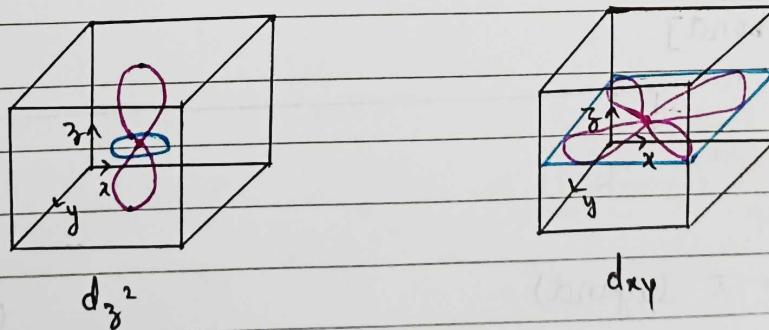


(axial bond)  $p_x, p_y, p_z$  angle for axial bonding  
 $F_n$  remain same  
 (axial bonding)

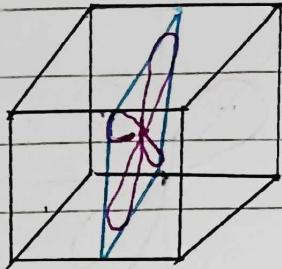


$d_{x^2-y^2}$

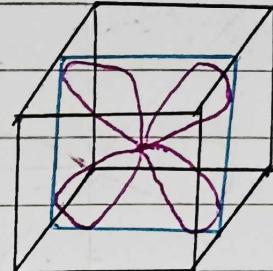
All four lobes of  $d_{x^2-y^2}$   
 are touching face centre



Both the lobes  
 are touching  
 face centre.



$d_{yz}$



$d_{xz}$

## Classification of ligand based on chemical Bonding

↓  
classical ligand

or  
Co-ordinate covalent bonding

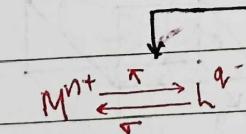
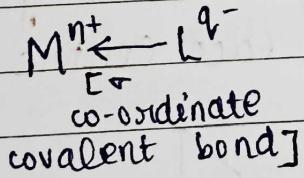
or  
 $\pi$ -ligand

↓  
Non-classical ligand

or  
 $\pi$ -acceptor ligand

or

synergic ligand.

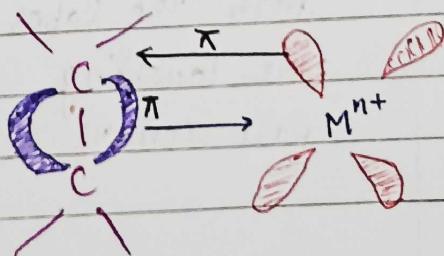


( $\sigma, \pi$  ligand)

- CO
- $P(Ph_3)_3$
- $NO^+$



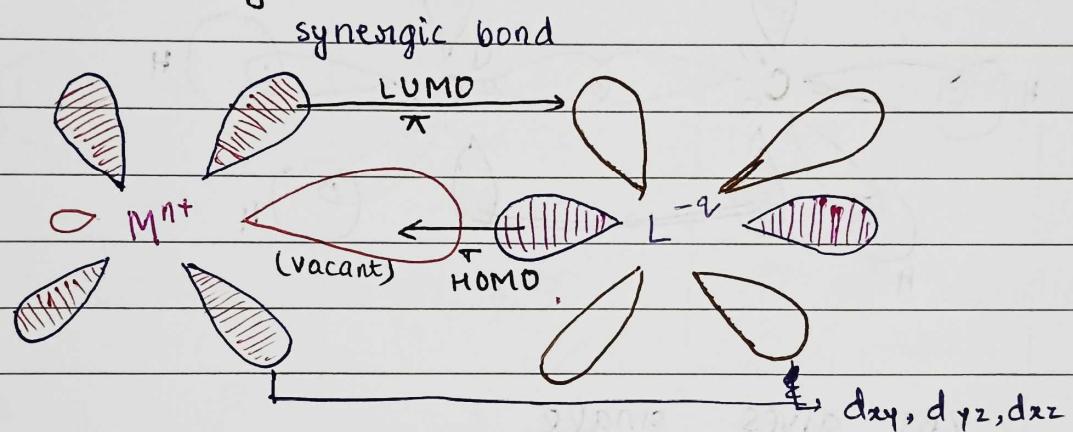
( $\pi, \pi$  ligand)



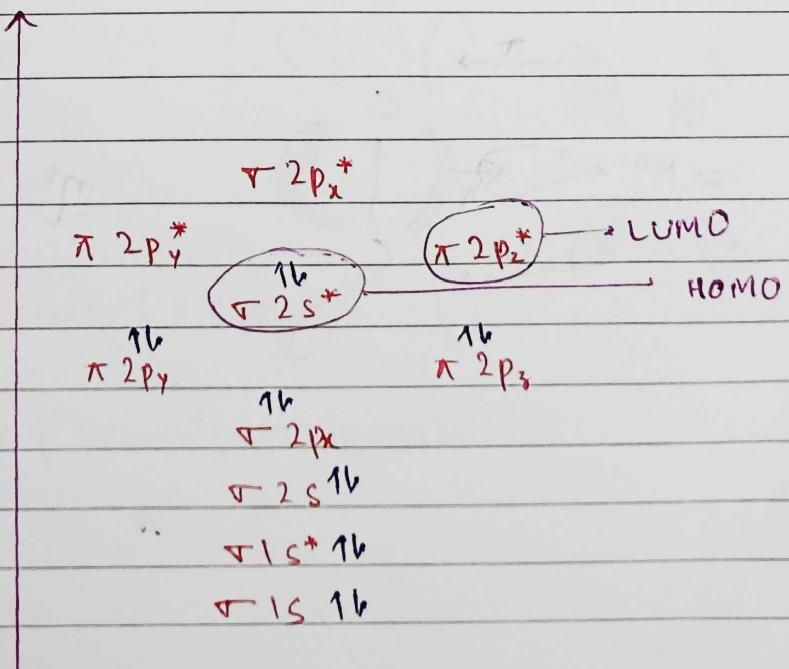
Ligand to metal bond is always from BMO which is also called as HOMO (Highest Occupied Molecular Orbital).

For back bonding i.e. from metal to ligand, bond is always from LUMO (Lowest Unoccupied Molecular orbital)

\*  $\pi, \pi^*$  bonding.

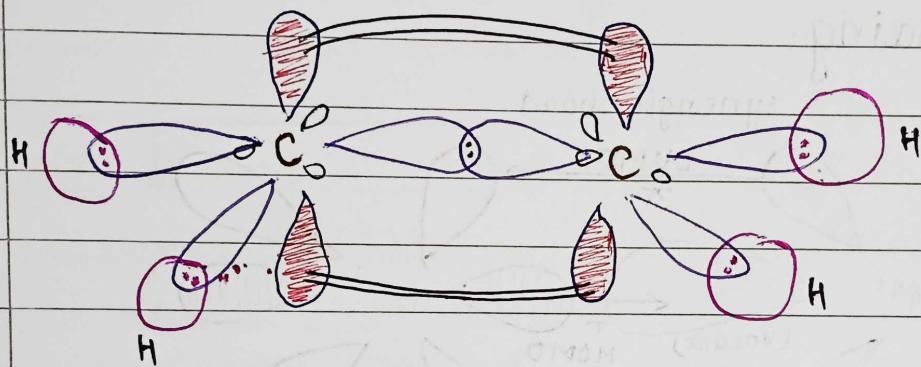
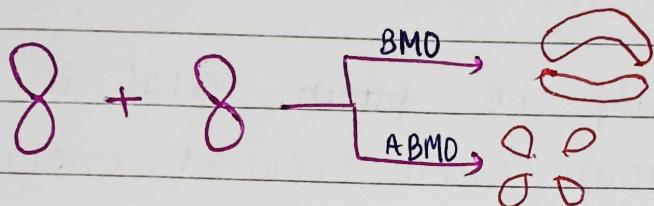


Molecular Orbital Diagram for CO

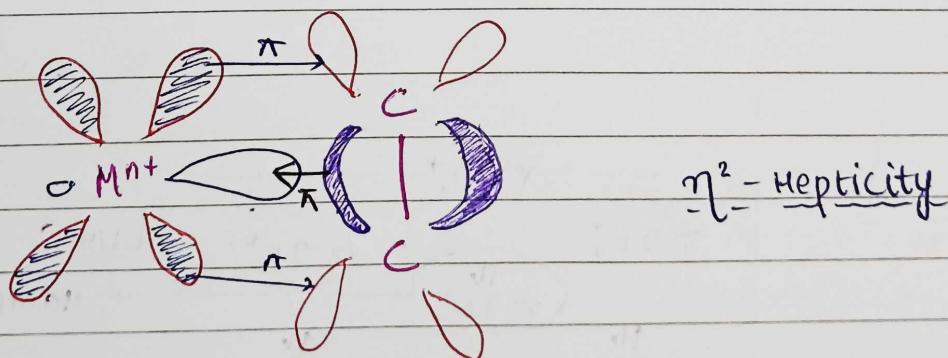


\*  $\pi, \pi$  ligand

Only formed by alkene derivative

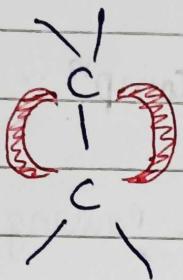


VBT gives single  
MOT gives double



## Hepticity - Fastening number

$C_2H_4$



Senticity

1

Heptacity

$\eta^2$ -ethylene

$C_4H_4$

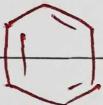


2

cyclo

$\eta^4$ -butadiene

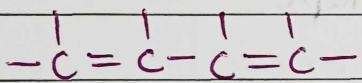
$C_6H_6$



3

$\eta^6$ -Benzene

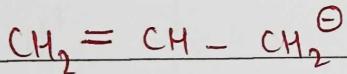
$C_4H_6$



2

$\eta^4$ -butadiene

$C_3H_5^{\ominus}$



1  
2

$\eta^3$ -allyl

$C_5H_5^{\Theta}$



1  
3

$\eta^5$ -cyclopenta dienyl ion

Q.  $[Mn(\sigma C_3H_5)_2(\pi C_3H_5)_3]^{3-}$

Bisallyl- $\eta^3$ trisallylmanganate (II)

## Bonding in Co-ordination Compounds

- Theories to explain co-ordination compn:-

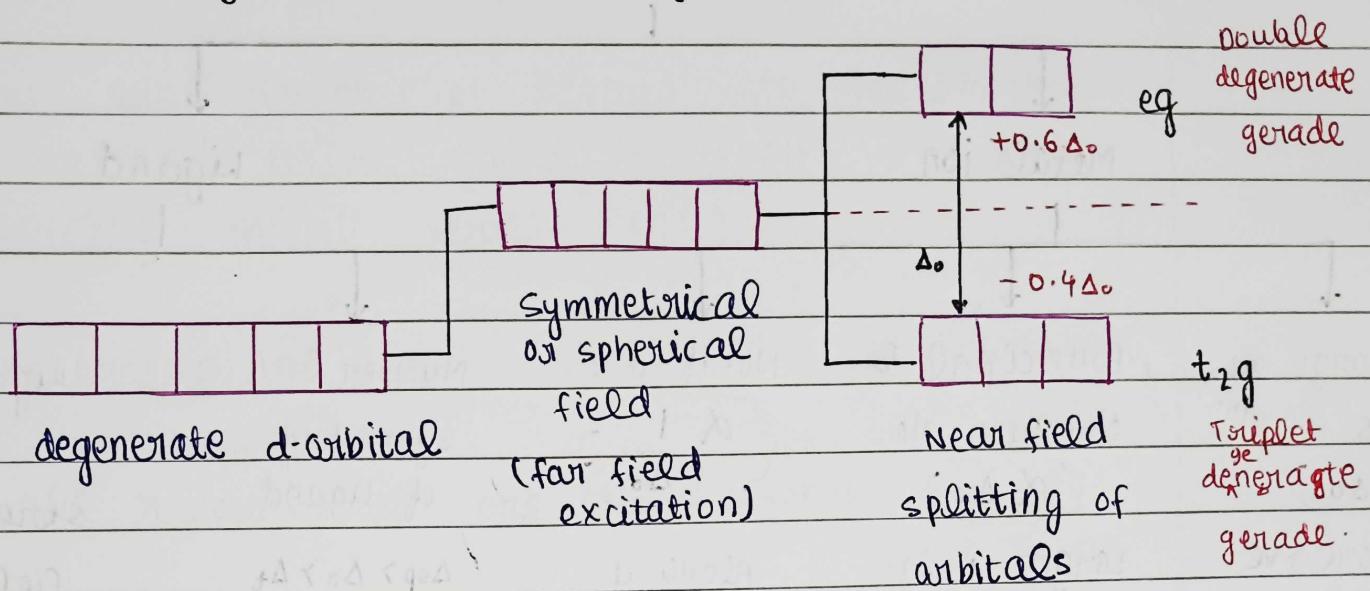
1. VBT (Valence Bond Theory) → L. Pauling
2. CFT (Crystal Field Theory) → Brønsted & van Vleck
3. LFT (Ligand Field Theory)
4. MOT (Molecular Orbital Theory)

} Beyond syllabus

CN	Hybridisation	Shape
2	sp	Linear
3	sp <sup>2</sup>	Triangular Planar
4.	sp <sup>3</sup> dsp <sup>2</sup> d <sup>3</sup> s sp <sup>2</sup> d	Tetrahedral square Planar Tetrahedral square Planar
5	sp <sup>3</sup> d	TBP
6.	sp <sup>3</sup> d <sup>2</sup>	Octahedral

In syllabus

## Crystal Field Theory:-



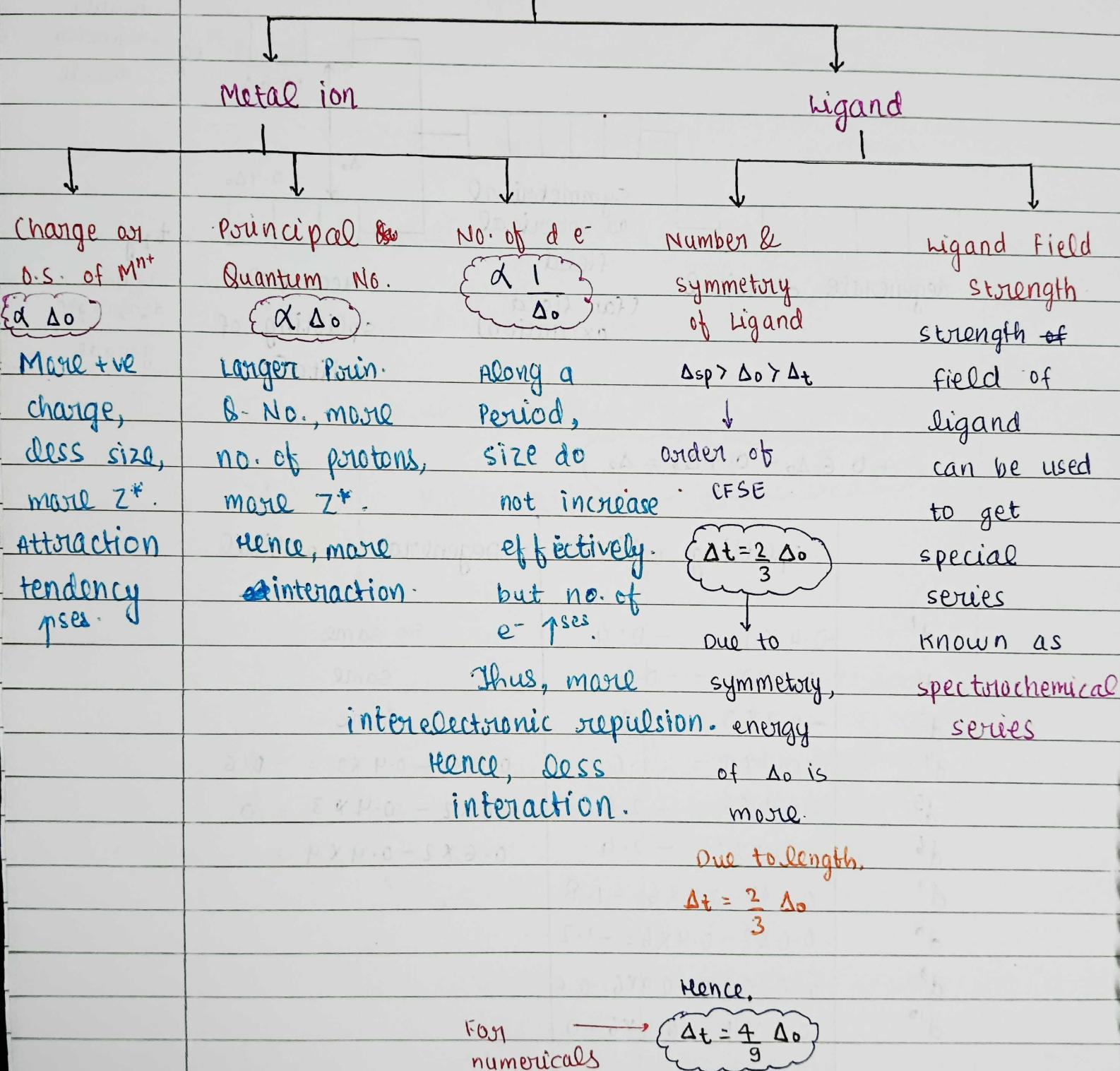
$$+ 0.6 \Delta_0 - 0.4 \Delta_0 = \Delta_0$$

	splitting orbital	Degenerate orbital
$d^1$	$-0.4 \times 1 = -0.4$	same
$d^2$	$-0.4 \times 2 = -0.8$	same
$d^3$	$-0.4 \times 3 = -1.2$	same
$d^4$	$-0.4 \times 4 = -1.6$	$0.6 \times 1 - 0.4 \times 3 = -0.6$
$d^5$	$-0.4 \times 5 = -2.0$	$0.6 \times 2 - 0.4 \times 3 = 0$
$d^6$	$-0.4 \times 6 = -2.4$	$0.6 \times 2 - 0.4 \times 4 =$
$d^7$	$0.6 \times 1 - 0.4 \times 6 = -1.8$	
$d^8$	$0.6 \times 2 - 0.4 \times 6 = -1.2$	
$d^9$	$0.6 \times 3 - 0.4 \times 6 = -0.6$	
$d^{10}$	$0.6 \times 4 - 0.4 \times 6 = 0$	

More negative  $\Delta_0$ , more is release of energy and more is the stability.  
-  $\Delta_0 \propto$  stability.

$d^5$  &  $d^{10}$  always form low spin complex

## Factors affecting $\Delta_o$ (applicable to $\Delta_t$ ):-



Outer orbital  $\rightarrow$  High spin  $\rightarrow$  No. of unpaired  $e^- \uparrow$ ,  $\Delta_o < P$   
 Pairing do not occur  $\hookleftarrow$

Inner orbital  $\rightarrow$  Low spin  $\rightarrow$  No. of unpaired  $e^- \downarrow$ ,  $\Delta_o > P$   
 Pairing occurs

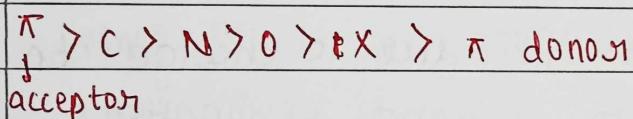
## Spectrochemical series

The arrangement of ligand into increasing order of their field strength is called spectrochemical series (SCS).

According to this,

All  $\pi$  acceptors are <sup>strong</sup>~~weak~~ field ligand.

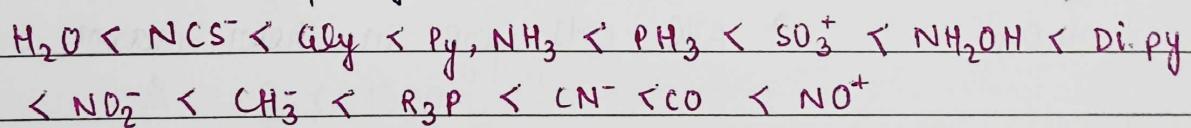
All  $\pi$  donors are weak field ligands.  
(Alkene derivative)



In SCS, water is taken as reference ligand.

weak ligand  $\leftarrow \text{H}_2\text{O} \rightarrow$  strong ligand

$\rightarrow$  Glycinate



↓

have tendency for inner orbital complex

VBT

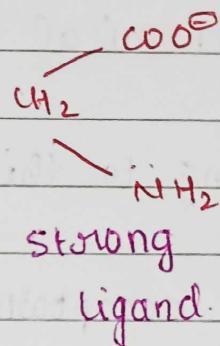
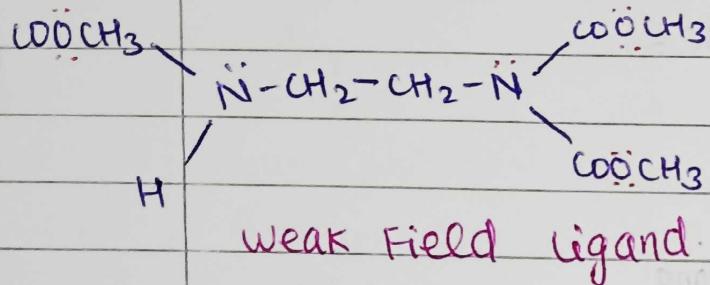
weak field ligand - X<sup>0</sup>, O

strong Field Ligand - N, C

## Salts of Complex Ion



glycinate

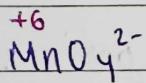
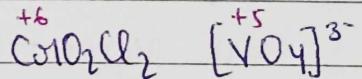
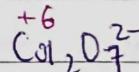
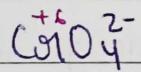
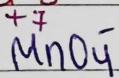
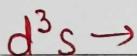


$\text{sp}^3\text{d}^2 / \text{sp}^3 \rightarrow$  weak field ligand

$\text{d}^2\text{sp}^3 / \text{dsp}^2 / \text{d}^3\text{s} \rightarrow$  strong field ligand



This hybridisation is due to charge on CMI not due to ligand strength.



→ All CMI are in their maxm. o.s.

\*

[symmetry.  $\propto \Delta_0$ ]

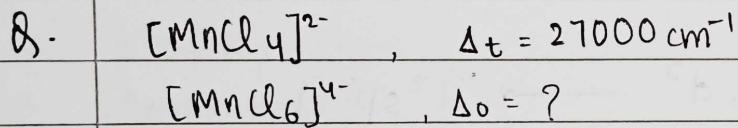
{  $\Delta_{\text{sq. planar}} > \Delta_{\text{octahedral}} > \Delta_{\text{Tetrahedral}}$  }

sq

$\Delta$   $\propto$  C, N > X, O  $\propto \Delta$   
 $\Delta$   $\propto$  charge on c.m.f (Z\*)  $\propto \Delta$   
 $\Delta$   $\propto$  Symmetrical arrangement of ligand  $\propto \Delta$   
 $\Delta$   $\propto$  d - e<sup>-</sup> in c.m.f  $\propto \frac{1}{\Delta}$

This all is applicable for 3d p only.  
 For 4d & 5d, all are strong field ligand.

$$\Delta_t = \frac{4}{9} \Delta_0$$



Soln:-  $\Delta_t = \frac{4}{9} \Delta_0$

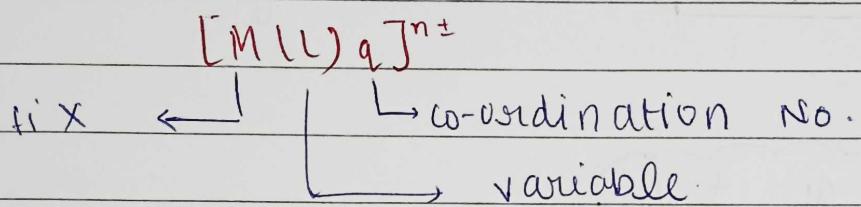
$$\Delta_0 = \frac{9}{4} \Delta_t$$

$$\Delta_0 = \frac{9}{4} \times 27000^{6750}$$

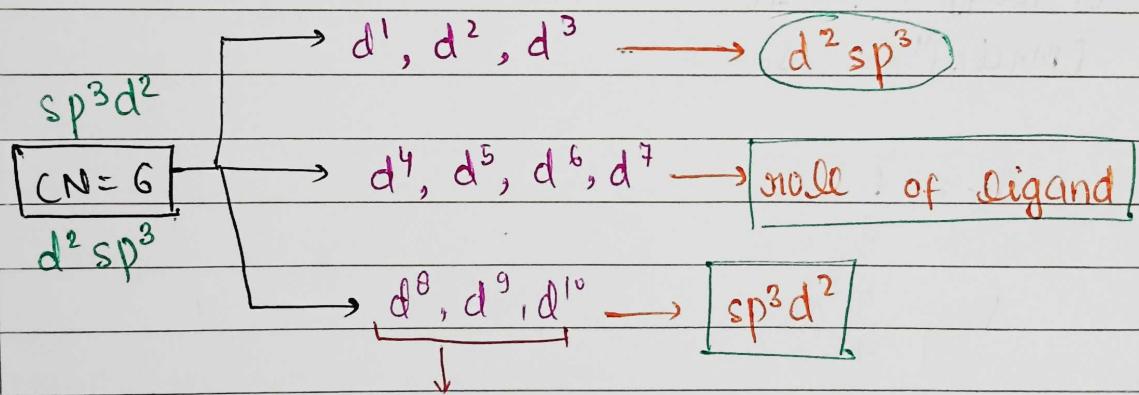
$$\Delta_0 = 60750 \text{ cm}^{-1}$$

$$(\Delta \propto \bar{v} \propto 1)$$

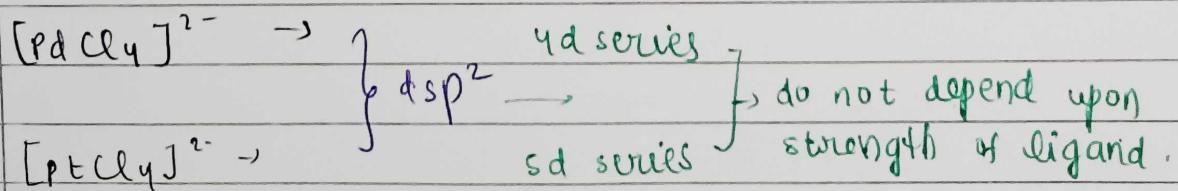
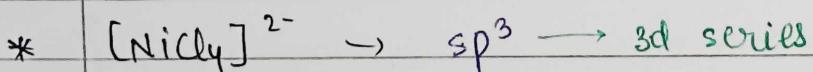
\* Concept of weak field and strong field ligand is applicable upto 3d series only. For 4d & 5d all are strong field ligand. because in 4d and 5d, screening effect decreases and  $Z^*$  increases. Thus, attraction tendency increases of CMF making the ligand strong ligand.



Thus, strength of ligand can be known.



4d and 5d series will give this.



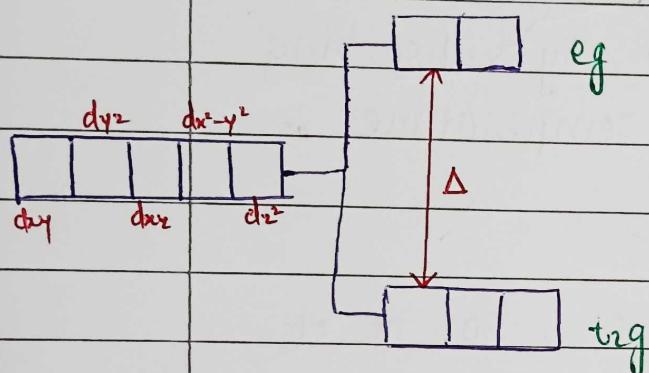
## Colour of Complex Ions:

d-d transition

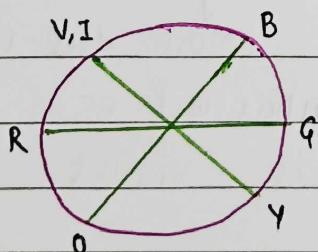
Principal Quantum

No. do not change.

charge transfer



$e^-$  jump from  
lower energy level  
to higher energy  
level and emits  
radiation.



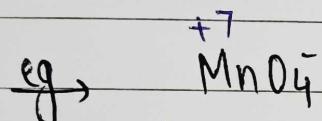
$$\Delta\lambda = \frac{hc}{\lambda} \text{ violet}$$

This wheel tells  
about colour &  
anti-colour.

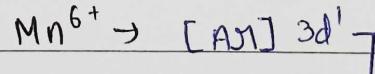
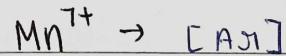
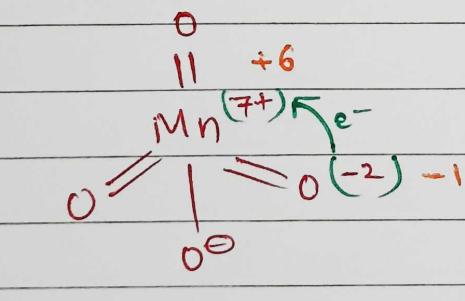
## Colour due to Charge Transfer

We know that many of the complex compounds except  $d^0$  and  $d^{10}$  are coloured due to  $d-d$  transition.

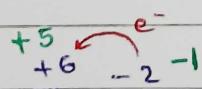
But in some of the comp<sup>n</sup>, colour is due to transfer of charge ( $e^-$ ) by absorbing available energy at Room Temperature.



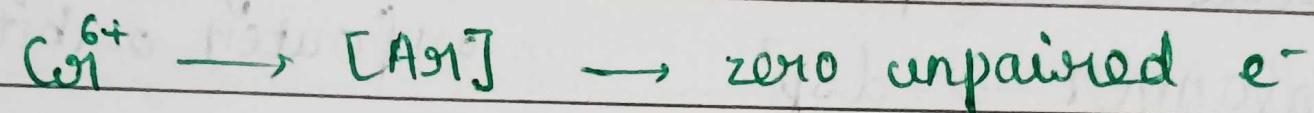
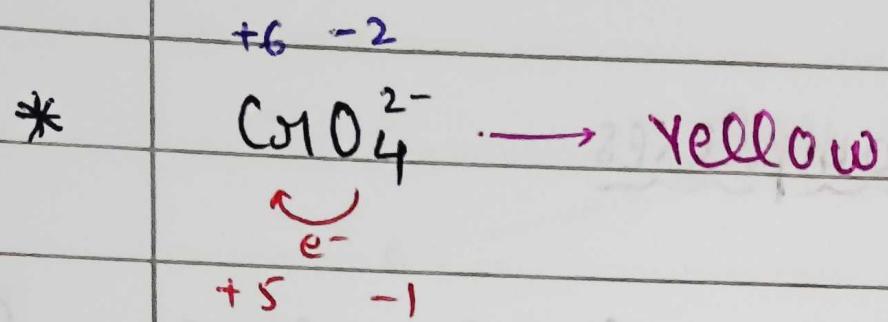
Here, Mn is in +7 O.S. So, no. of unpaired  $e^- = 0$ . So, it must be colourless. But actually, it is **deep violet** due to transfer of charge from O to Mn at Room Temperature.



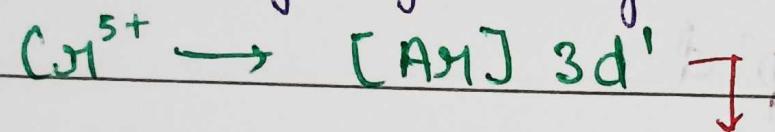
Now, due to one unpaired  $e^-$ , colour is violet.



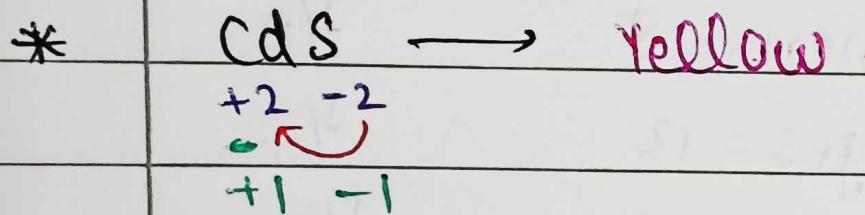
orange colour



Now, by gaining 1  $e^-$  from Oxygen.



Now, due to 1 unpaired  $e^-$ ,  
it gives yellow colour.

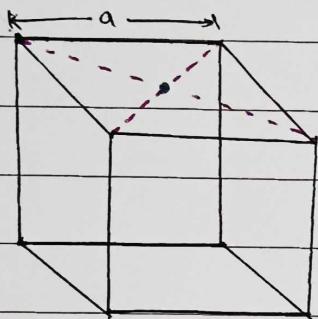


## CFT for tetrahedral complexes

tetrahedral  $\rightarrow$   $sp^3 \rightarrow \Delta t \rightarrow$  (High spin complex)  
 square planar  $\rightarrow$   $dsp^2$  or {outer orbital complex}

tetrahedral  $\rightarrow d^3 s$   
 square planar  $\rightarrow sp^2 d$

### Cubical structure :-



	Contribution
Corneris = 8	$\frac{1}{8}$
Edges = 12	$\frac{1}{4}$
Face = 6	$\frac{1}{2}$
Body diagonals = 12	
Face diagonal = $6 \times 2 = 12$	

Body diagonal :-

$$\sqrt{3}a$$

Face diagonal :-

$$\sqrt{2}a$$

\* Distance of :

$$\text{corner-edge centre} : - a/2 = 0.5a$$

$$\text{corner-face centre} : - \sqrt{2}a/2 = a/\sqrt{2} = 0.7a$$

$$\text{corner-body centre} : - \sqrt{3}a/2 = 0.85a$$

\* In a cubical structure

$$\text{Tetrahedral voids} = 8$$

$$\text{Octahedral voids} = 4$$

## Voids in cubical

planar voids

Triangular planar

Square planar

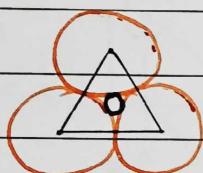
Non-planar voids

Tetrahedral

Octahedral

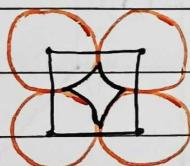
### \* Planar voids

#### 1. Triangular planar void.



~~Tetra~~

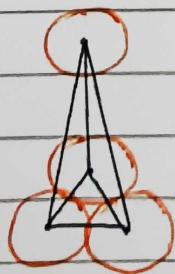
#### 2. square planar void.



### \* Non-planar voids

#### 1. Tetrahedral void.

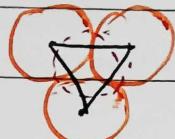
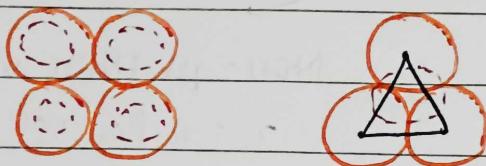
For our convenience, it is made like :



actual

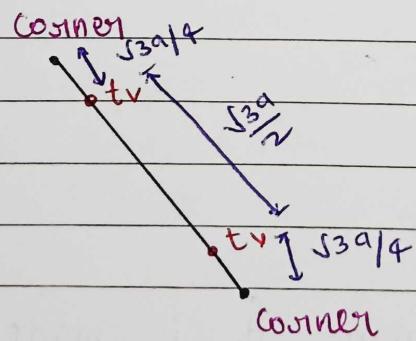
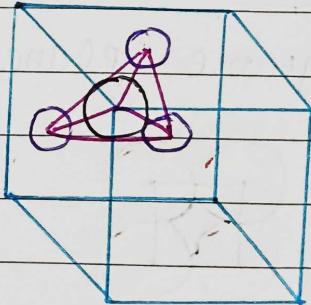
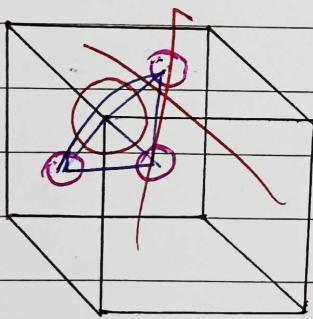
$$r_t = 0.225 R$$

2. Octahedral Void :-

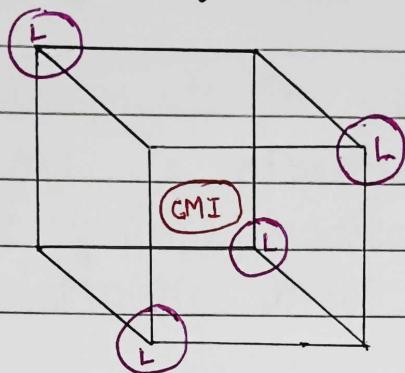


$$r_o = 0.414 R$$

\* Tetrahedral Void :-



## Arrangement of comp<sup>n</sup> in Tetrahedral Geometry:-

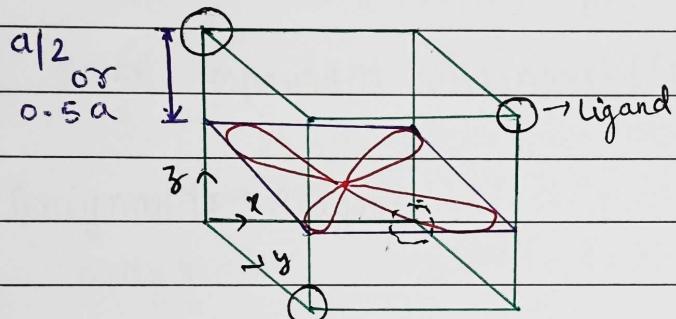


CMI = Central Metal

Ion

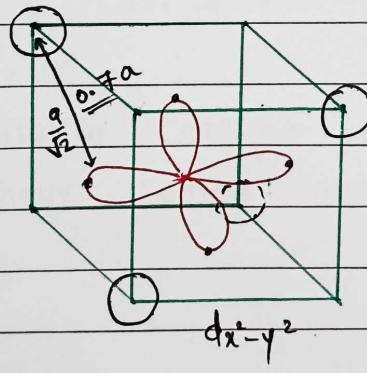
l = ligand.

### \* Arrangement for $d_{xy}$ , $d_{yz}$ , $d_{xz}$

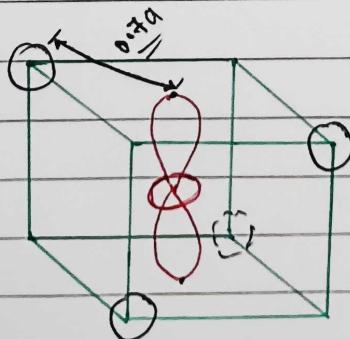


Distance b/w  
ligand & lobe  
i.e.,  $0.5a$  is  
same for  $d_{xy}$ ,  
 $d_{yz}$  and  $d_{xz}$ .

### \* Arrangement for $d_{x^2-y^2}$ , $d_{z^2}$



Distance b/w  
ligand & lobe  
i.e.,  $0.7a$  is  
same for  
 $d_{x^2-y^2}$  and  $d_{z^2}$



## Organometallic Compounds

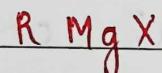
Those compounds in which transition metal or CM's is directly connected to organic groups / radical / ions are called organometallic comp<sup>n</sup>.



metal carbon bond

Some important organometallic comp<sup>n</sup> :-

1. Grignard's Reagent



2. Gilmann's Reagent



3. Wilkinson's catalyst :  $[Rh(PPh_3)_3Cl]$

4. TEL (Tetraethyl lead)  $(C_2H_5)_4Pb$

Anti-knocking comp.

\* Lead makes poisonous comp so it should be removed by adding ethylene bromide which on reacting forms  $PbBr_2$ .

\* Classification of Organometallic Comp:-

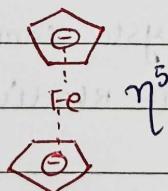
Main group element OMC

Transition metal OMC

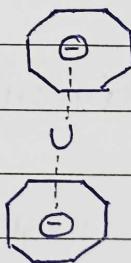
Inner-transition metal OMC

- $R-MgX$
- $R-Li$
- $(C_2H_5)_3Al$
- $EtNa$

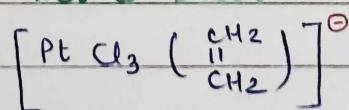
- $R_2CuLi$
- $[Rh(PPh_3)_3]Cl$
- Ferrocene



• Uranocen



• Zeise's salt



•  $Fe(CO)_4$

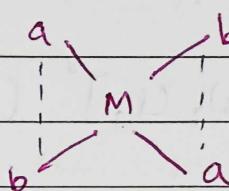
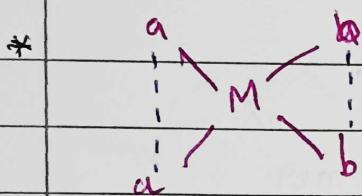
Colmann's Reagent

## Geometrical Isomerism:-

$Ma_2b_2 \rightarrow a \Rightarrow \text{monodentate}$

$b \Rightarrow \text{monodentate}$

$M(AA)BB \rightarrow A \Rightarrow \text{Bidentate}$



[Square  
planar]

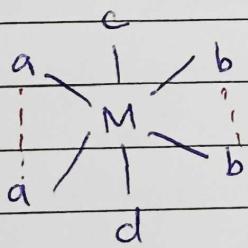
cis w.r.t. a

cis w.r.t. b

trans w.r.t. ba

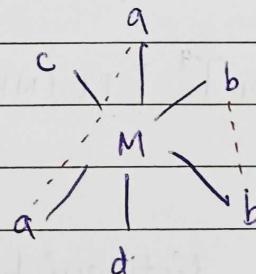
w.r.t. b

A complex comp<sup>n</sup> can be both cis and trans.



cis w.r.t. a

cis w.r.t. b



~~cis~~ w.r.t. a

cis w.r.t. b

[Octahedral  
shape]

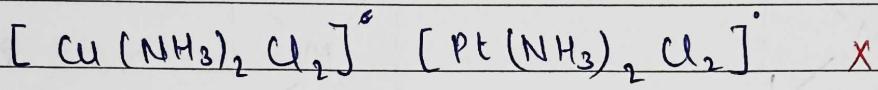
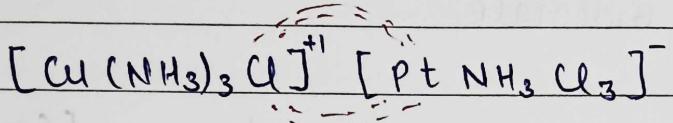
If to trace path b/w two ligands,  
we have of cross central metal,  
then trans.

If we can directly trace, then cis.

\* For tridentate, chelation occurs and cyclic ring is formed.

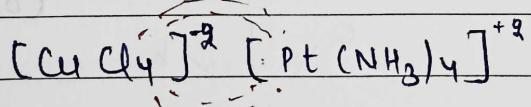
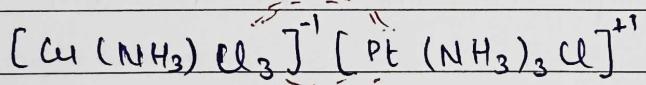
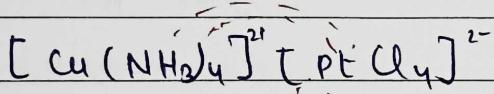
Q. The total number of possible structural isomers for the complex comp<sup>n</sup>  $[\text{Cu}(\text{NH}_3)_4][\text{PtCl}_4]$  are.

Sol<sup>n</sup>:-



They are not structural isomers  
because net charge is zero.

so, no interaction b/w them.

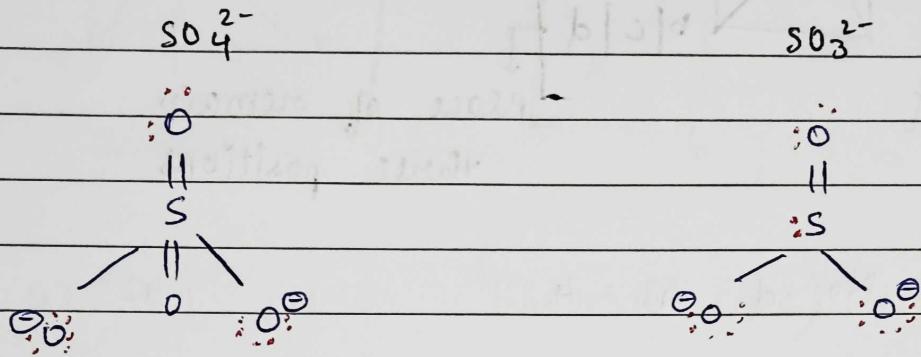


\* Test to distinguish -

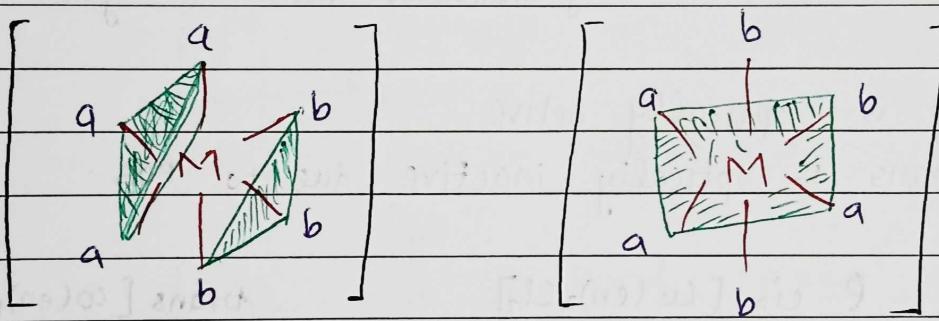
Partial co-ordination Isomerism - Measurement of molar conductance.

Complete co-ordination Isomerism - Electrolysis of aqueous solution.

\*  $\text{SO}_4^{2-}$  can't show linkage isomerism because there is no d.p. on sulphur in this compn.  
Only O can donate d.p.



GI for  $\text{CN}=6$   $[\text{Ma}_3\text{b}_3]$  Type



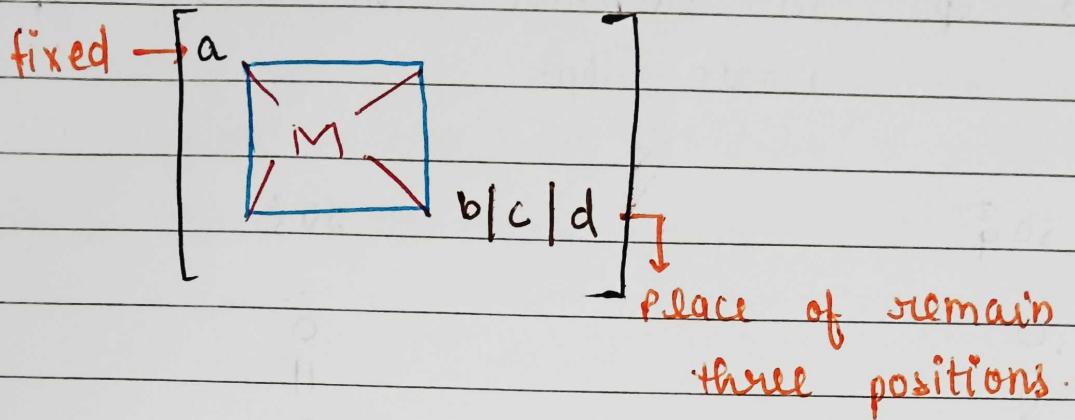
All same  $\sigma$  ligands  
can't be joined  
without crossing  
CMI.

facial isomer  
(fac)

while joining  
all ligands of  
same type, we  
have to cross  
CMI.

Meridian Isomer  
(mer)

GI for CN = 4 [Mabcd] Type:-



No. of GI = 4

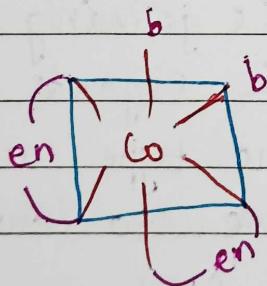
GI for  $[M(AA)_2b_2]$  (CN=6)

↳ symmetrical bidentate ligand.

cis is optically active.

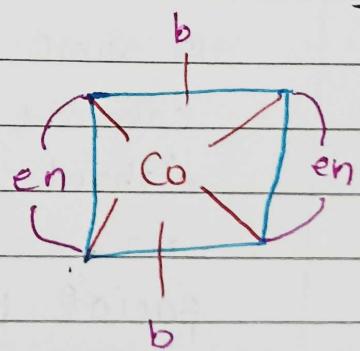
trans is optically inactive due to pos.

e.g., P cis  $[Co(en)_2Cl_2]$



O I ✓

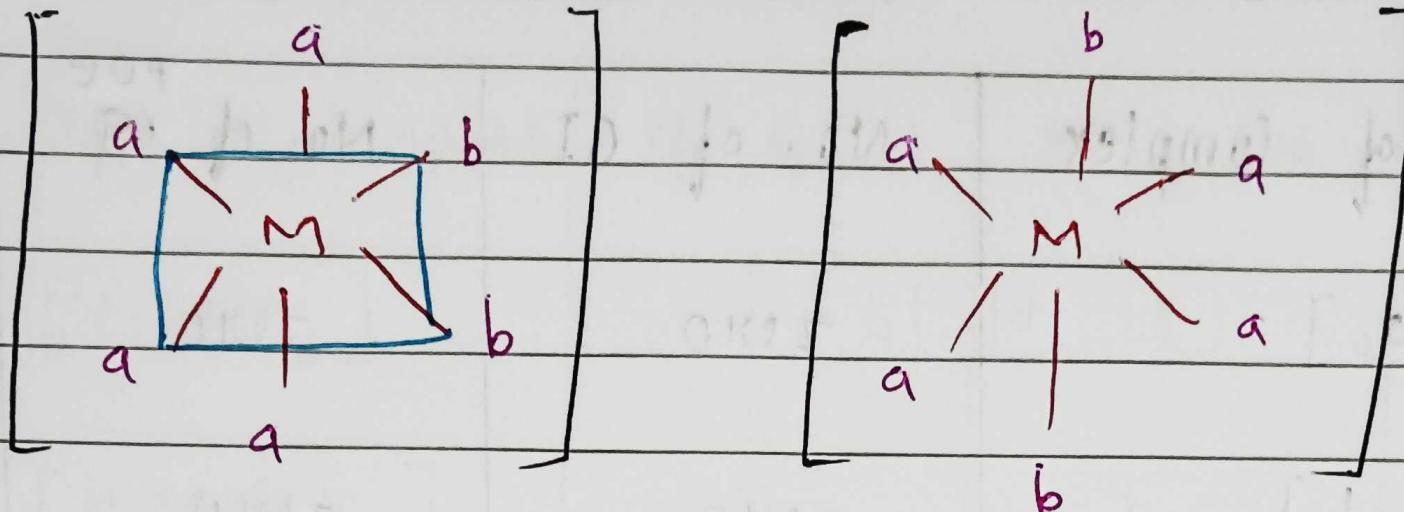
- trans  $[Co(en)_2Cl_2]$



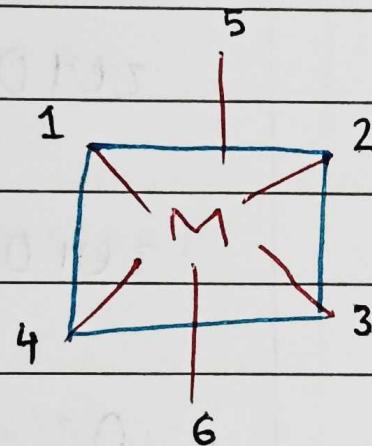
contain plane  
of symmetry.

O I ✗

GI for  $[M a_4 b_2]$   $CN = 6$ .



\* GI for  $CN = 6$  (General case)



GI for CN = 6

Type of Complex	No. of GI	No. of POE	No. of SI
[Ma <sub>6</sub> ]	zero	zero	1
[Ma <sub>5</sub> b]	zero	zero	1
[Ma <sub>4</sub> b <sub>2</sub> ]	2	zero	2
[Ma <sub>4</sub> b <sub>2</sub> c]	2	zero	2
[Ma <sub>3</sub> b <sub>3</sub> ]	2	zero	2
[Ma <sub>3</sub> b <sub>2</sub> c]	3	0	3
* [Ma <sub>3</sub> bcd]	4	1	5
[Ma <sub>2</sub> b <sub>2</sub> c <sub>2</sub> ]	5	1	6
[Ma <sub>2</sub> b <sub>2</sub> cd]	6	2	8
[Ma <sub>2</sub> bcde]	9	6	15
[Mabcdef]	15	15	30

$\text{AA} \rightarrow$  symmetrical Bidentate  
 $\text{AB} \rightarrow$  unsymmetrical Bidentate

GI form CN=6 (Bidentate ligand)

Type of complex	No. of GI	No. of POE	Total no. of SI
$[\text{M(AA)}_3]$	1	1	2
$[\text{M(AA)}_2 \text{b}_2]$	2	1	3
$[\text{M(AA)}_2 \text{bc}]$	2	1	3
$[\text{M(AA)} \text{b}_4]$	1	0	1
$[\text{M(AA)} \text{abcd}]$	6	6	12
$[\text{MM(AA)} \text{a}_2 \text{bc}]$	4	2	6

GI form CN=6 (Bidentate Unsymmetrical ligand)

Type of Complex	No. of GI	No. of POE	Total no. of SI
$[\text{M(AB)}_3]$	2	2	4
$[\text{M(AB)}_2 \text{a}_2]$	5	3	8
$[\text{M(AB)}_2 \text{ab}]$	6	5	11