

# Coordination Compound

- Transition metals form large number of complex compound (Coordination compd).
- Compd in which metal atoms are bonded to anion/neutral molecule by Coordinate bond is called Coordination Compound.

↓  
Central metal  
atom/ion

↓  
Ligand

- Chlorophyll → Mg
- haemoglobin → Fe
- Vitamin B12 → Co

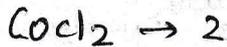
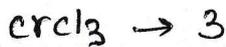
## Werner's Theory

first scientist → to tell abt str of Coordination Compound.

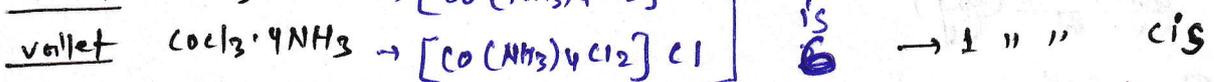
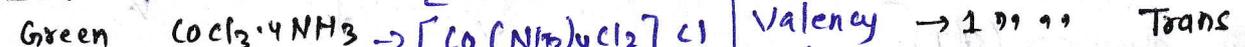
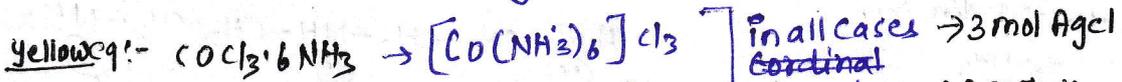
### Postulates of Werner's theory

- Metals shows two types of valance (charge)
  - Primary Valance -
  - Secondary Valance

Primary valency → ~~oxidation~~ oxidation no, ionizable, satisfied by -ve ions, non-directional.



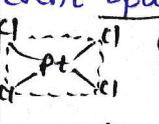
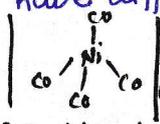
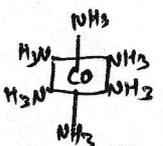
Secondary Valency → Coordination number, non-ionizable, satisfied by neutral, -ve ions, directional, gives definite geometry to compd.



These two have identical formula but diff property → These are cis & trans isomer.

### # ~~Coordination~~ Coordination →

# Coordination polyhedra: The ion/group bonded by secondary linkage with central atom have different spatial arrangements, called coordination polyhedra.

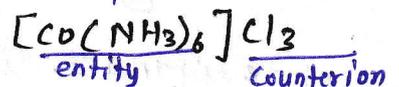


geometry (3d)

most common coordination polyhedra → tetrahedral, sq planar, octahedral.  
 $[Co(NH_3)_6]^{3+}$  → octahedral |  $PtCl_4^{2-}$  → sq planar  
 $[Ni(CO)_4]$  → tetrahedral

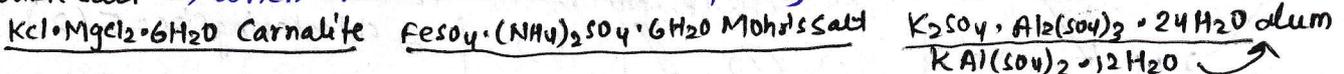
# Coordination entity: Species within square bracket.

Counter ion: species outside the square bracket



### Difference b/w double salt & Complex (Coordination compd)

Double salt → when dissolved in water, it completely breaks into ions.

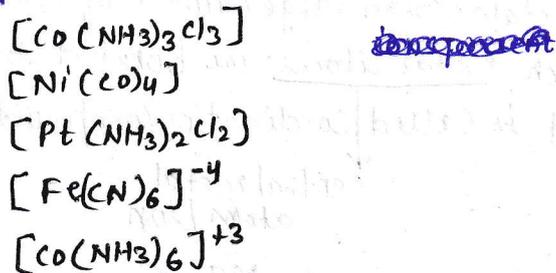


Complex (Coordination compd) → which ~~comple~~ do not dissociate completely ex:  $K_4[Fe(CN)_6]$

# Imp Definition

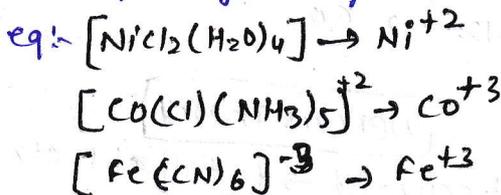
(a) Coordination entity :- Central metal atom/ion bonded to ligands & enclosed in square bracket.

↓  
Species within square brackets



(b) Central atom/ion :- atom/ion to which ligands are bonded by coordinate bond in a definite geometry inside coordination entity.

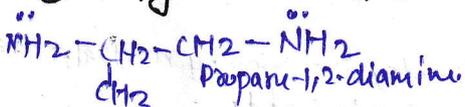
↓  
also a Lewis acid



(c) Ligand → ion/molecule bonded to central atom/ion in coordination entity.

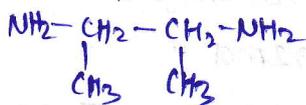
Unidentate → Single donor atom :  $Cl^-$ ,  $H_2O$ ,  $NH_3$ ,  $F^-$ ,  $OH^-$ ,  $O^{2-}$ ,  $O_2^{2-}$ ,  $O_2^-$ ,  $NH_2^-$ ,  $NH^-$ ,  $N^{3-}$   
chloro aqua ammine Hydroxido oxido Peroxo Superoxo Azido Imido Nitrido  
Didentate → two donor atom :  $NH_2CH_2CH_2NH_2$  (en),  $C_2O_4^{2-}$   
ethylenediamine ethane-1,2-diamine oxalate  
Polydentate → Several donor atom

(1) propylene diamine (pn)

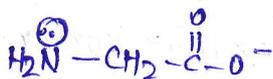


(2) Butylene diamine (bn)

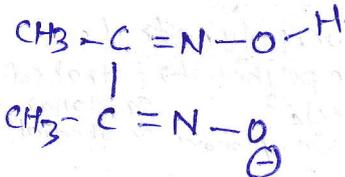
Butane-2,3-diamine



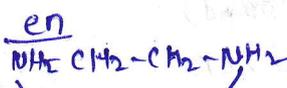
(3) glycinate (gly)



(4) dimethylglyoximate (dmg)



Chelate ligand :- didentate/polydentate forms two or more coordinate bond to give 5 or 6 member ring.

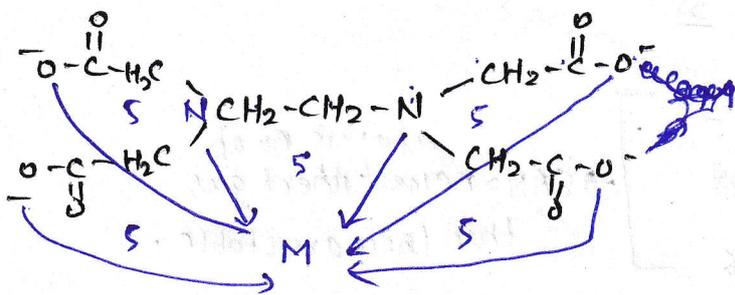


→ M  
Chelate ring size = 5(1)



→ M → chelate ring size = 5(2)

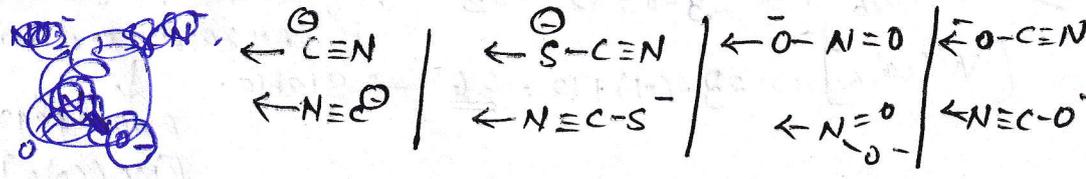
edta



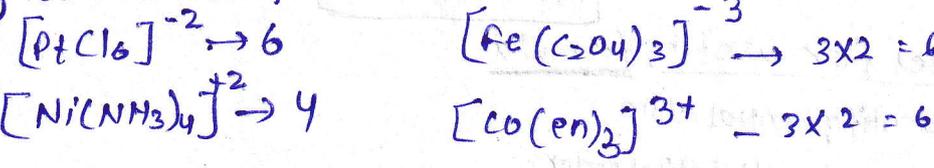
Chelate Ring size = 5 (5)

(2)

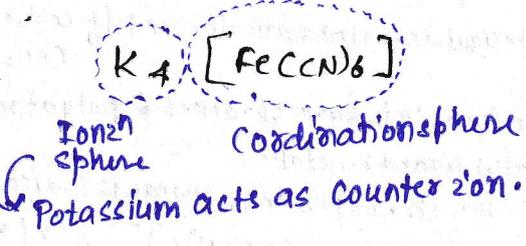
• Ambidentate ligands - a unidentate ligand which can donate through 2 diff atoms.



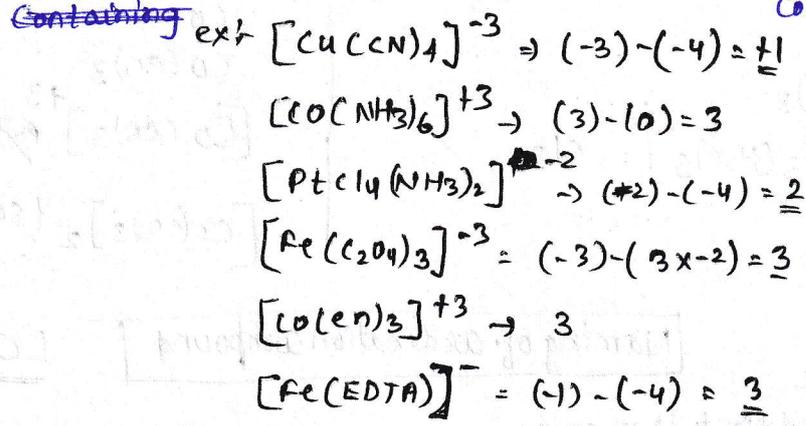
Coordination num:- NO of coordinate bond formed b/w central atom & ligand.



Coordination sphere / coordination sphere & ionization sphere :-



oxidation no :- charge on central atom if all ligands are removed with lone pairs forming coordinate bond.



Homoleptic & Heteroleptic complex :- only one type of ligand  $\rightarrow$  Homo  $\rightarrow [Co(NH_3)_6]^{+3}$   
 more than one type of ligand  $\rightarrow$  Heteroleptic  $[Co(NH_3)_4Cl_2]^+$

EAN  $\rightarrow$  Effective atomic no : no of  $e^-$  of CMA, after forming coordinate bond from ligands.

$EAN = Z - O.S + 2 \cdot CN$

$K_4 [Fe(CN)_6] \rightarrow EAN = 26 - 2 + 2 \times 6 = 36$

$K_3 [Fe(CN)_6] \rightarrow EAN = 26 - 3 + 2 \times 6 = 35$

Sidgwick Theory :- If EAN of metal carbonyl is equal to atomic num of nearest inert gas then that metal carbonyl is stable.

Ques  $[Mn(CO)_5] = 25 - 0 + 2 \times 5 = \underline{35}$

$[Mn(CO)_5]^- = 25 - (-1) + 2 \times 5 = \underline{36}$

$[Mn(CO)_6] = 25 - 0 + 3 \times 6 = \underline{37}$

$[Mn(CO)_6]^+ = 25 - 1 + 12 = \underline{36}$

atomic no of inert gas  $\rightarrow$  EAN = nearest inert gas then these are stable.

Ques  $V(CO)_6 \rightarrow 23 - 0 + 12 = \underline{35}$

$[V(CO)_6]^- \rightarrow 23 - (-1) + 12 = \underline{36}$

atomic no of inert gas  $\rightarrow$  if EAN < inert gas  $\rightarrow$  Reducing agent  
if EAN > atomic no of inert gas  $\rightarrow$  Stable.

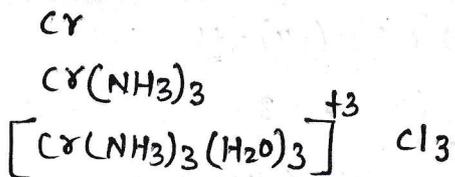
oxidizing agent  $\rightarrow$  bcoz gains one  $e^-$   
 $\downarrow$   
Reducing agent  $\rightarrow$  bcoz loses one  $e^-$   
 $\downarrow$   
oxidizing agent

### Nomenclature

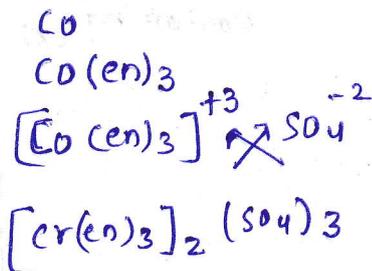
#### Rules for writing formula

- Identify central atom
- write ligands in alphabetical order
- polydentate ligands  $\rightarrow$  alphabetical order; if abbreviated ligand comes, consider first letter for alphabetical order. (en, pn, bn)
- write the formula in square bracket; polyatomic ligand abbreviation  $\rightarrow$  parenthesis.
- no space b/w ligand & metal.
- if counter ion is not present, charge is indicated on square bracket.

Trigonal bipyramidal aquachromium(III) chloride



tris(ethane-1,2-diamine)cobalt(III) sulphate



### Naming of coordination compound

#### LCOR Rule.

#### $\rightarrow$ naming of coord comp

- Cation is named first then anion
- Ligands are named first (alphabetical order) then central atom is named then oxidation state is written in Roman.

#### $\rightarrow$ naming of ligand

- anionic ligand - name - ends in o (Cl<sup>-</sup>)  $\rightarrow$  chlorido  
C<sub>2</sub>O<sub>4</sub><sup>-2</sup>  $\rightarrow$  oxalato  
O<sup>-2</sup>  $\rightarrow$  oxido  
OH<sup>-</sup>  $\rightarrow$  Hydroxido.

- neutral ligand  $\rightarrow$  same name  $\rightarrow$  NH<sub>3</sub> - ammine  
H<sub>2</sub>O  $\rightarrow$  aqua  
CO  $\rightarrow$  Carbonyl  
NO  $\rightarrow$  nitrosyl.

- cationic ligand  $\rightarrow$  ends in ium NO<sup>+</sup>  $\rightarrow$  nitrosylium NO<sub>2</sub><sup>+</sup>  $\rightarrow$  nitronium,

Prefix mono, di, tri, tetra are used to denote no. of ligands.

If name of ligands already have (di, tri, tetra) then use b/s - 2

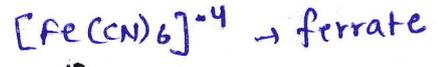
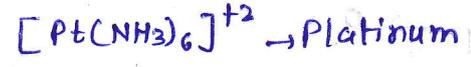
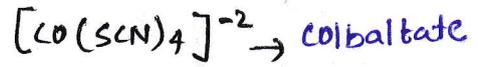


dichlorobis(triphenylphosphine)nickel(II)

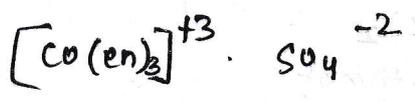
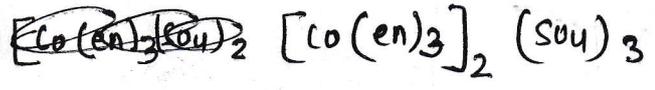
tris - 3  
tetraakis - 4

if complex is cation → central atom has same nomenclature.

if complex is anion → central atom naming ends with ate.

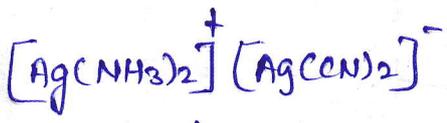


LCO

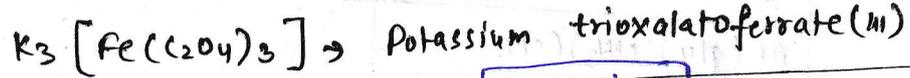
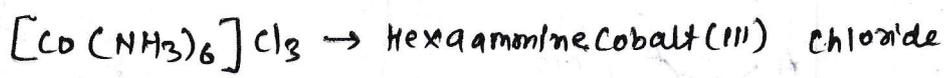


~~triethylened~~ tris(ethylenediammine) cobalt(III) Sulphate.

tris(ethane-1,2-diammine) cobalt(III) Sulphate.



diamminesilver(I) dicyanoargentate(I)



Isomerism

def:- same chemical formula but different ~~chem~~ physical/chemical property.

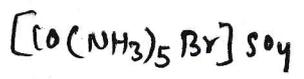
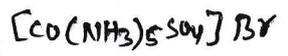
↳ <sup>bcuz of</sup> different arrangement of atoms.

Structural Isomerism

having different ligand in coordination sphere.

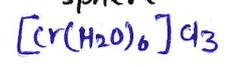
Ionization

compounds which give different ions in solution.



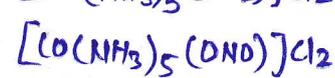
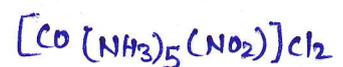
Solvate/hydrate.

no of water molecules is different inside & outside coordination sphere.



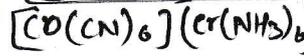
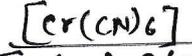
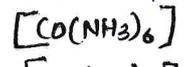
Linkage

ambidentate ligand's present.



Coordination

Both the ~~part~~ and negative ions are complex.



# Stereoisomerism

Same chemical formula, same chemical bond, diff arrangement in 3D space.

## Geometrical

- Tetrahedral → X
- Sq. planar ✓
- Octahedral ✓

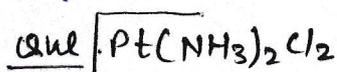
$Ma_4 \rightarrow 0$

$Ma_3b \rightarrow 0$

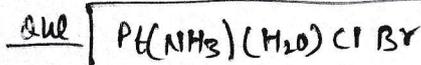
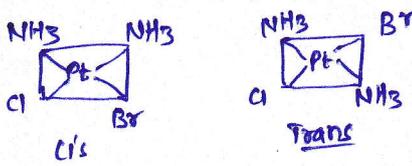
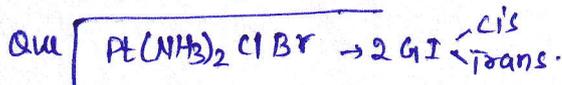
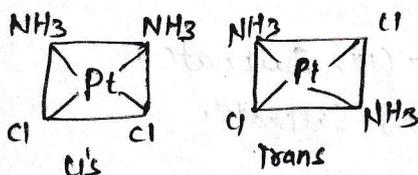
$Ma_2b_2 \rightarrow 2$  (1 cis + 1 trans)

$Ma_2bc \rightarrow 2$  ( " )

$Maabcd \rightarrow 3$  (2 cis + 1 trans)

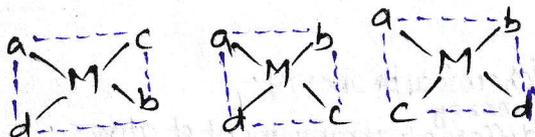


2 GI  $\begin{cases} \text{cis} \\ \text{trans} \end{cases}$



$Maabcd$

(ab cd) (ac bd) (ad bc)



ab → standard

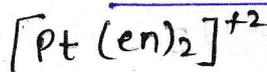
str 2 & str 3 → ab at 90° → cis

str 1 → trans.

## Geometrical

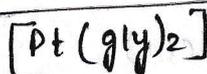
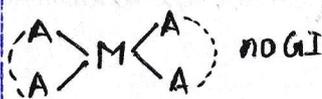
## optical

### Bidentate

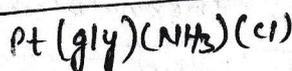


$M(AA)_2$

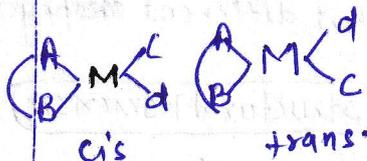
2 donor atoms of bidentate ligand never lies at 180°.



$M(AB)_2$



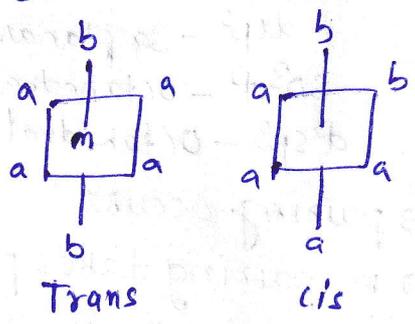
$M(AB)cd$



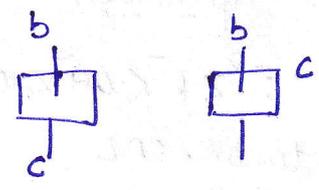
GI & OI in octahedral

	GI	Pair of enantiomer	no of stereoisomer (OI + OI)
$MA_6$	0	0	0
$MA_5b$	0	0	0
$MA_4b_2$	2	0	2
$MA_4bc$	2	0	2
$MA_3b_3$	2	0	2
$MA_3b_2c$	3	0	3
$MA_3bcd$	4	1	5
$MA_2b_2c_2$	5	1	6
$MA_2b_2cd$	6	2	8
$MA_2bcde$	9	6	15
$Mabcdef$	15	15	30

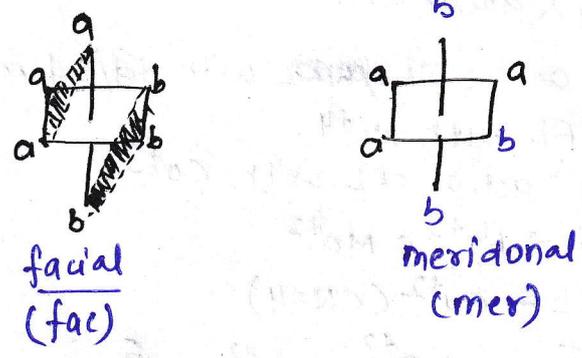
Qw  $[Pt(NH_3)_4Cl_2]Cl_2$   
 or  $[Co(NH_3)_4Cl_2]^+$   
 $\rightarrow MA_4b_2 \rightarrow 2GI$



Qw  $[Pt(NH_3)_4ClBr]$   $MA_4bc \rightarrow 2GI$

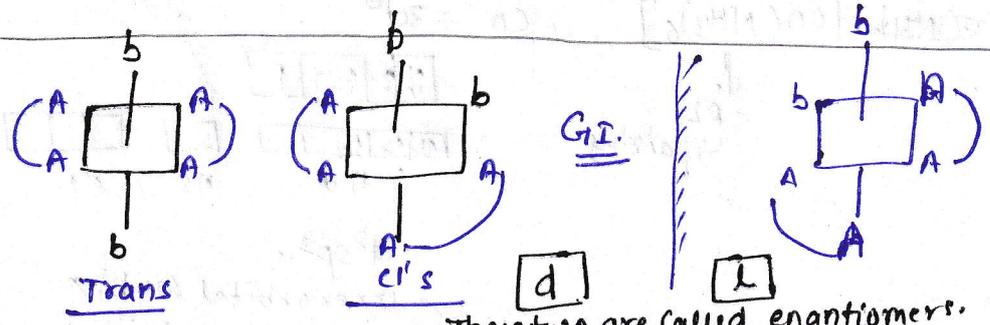


Qw  $[Co(NH_3)_3Cl_3]$   $MA_3b_3$   
 or  $[Co(NH_3)_3(NO_2)_3]$

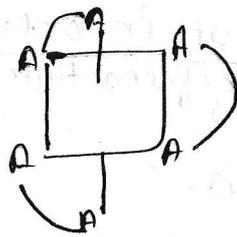
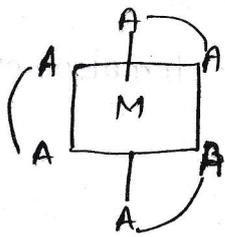
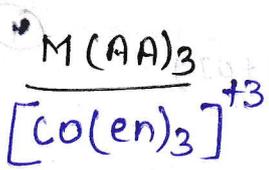


Bidentate

$(Co(Cl_2)(en)_2)$   
 $[M(AA)_2b_2]$



These two are called enantiomers.  
 'cis' shows optical isomerism because it has non superimposable mirror image. (also, it is chiral)  
 but don't have pos/cis



non superimposable mirror image

(d)

(l)

Valence Bond Theory

Under influence of ligand central metal uses two types of orbital for ~~complexing~~ hybridization

1) inner orbital  $\rightarrow (n-1)d, ns, np$

2) outer orbital  $\rightarrow ns, np, nd$

• Vacant orbitals undergo hybridization & gives octahedral, tetrahedral, square planar geometry

$sp^3$  - Tetrahedral

$dsp^2$  - Sq planar

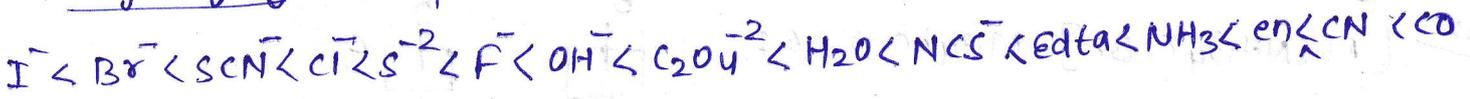
$sp^3d^2$  - octahedral

$d^2sp^3$  - Octahedral

• In SFL  $\rightarrow$  pairing occurs.

• In WFL  $\rightarrow$  no pairing takes place.

Strength of ligand - Spectrochemical series



C/N donor - SFL

O/X donor - WFL

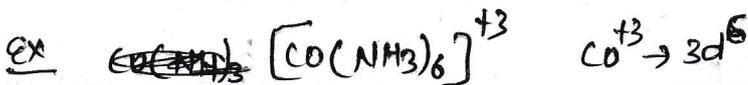
• All ligands act as SFL with  $4d/5d$  metal ions.

•  $F^-$  acts as SFL with  $Ni^{+4}$ .

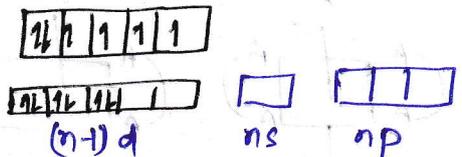
•  $H_2O$  &  $C_2O_4^{2-}$  act as SFL with  $Co^{+3}$ .

•  $NH_3 \rightarrow$  WFL  $\rightarrow Fe^{+2}$  &  $Mn^{+2}$

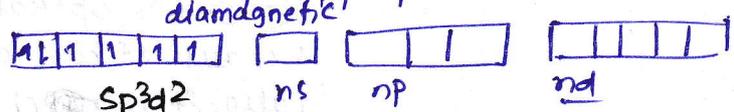
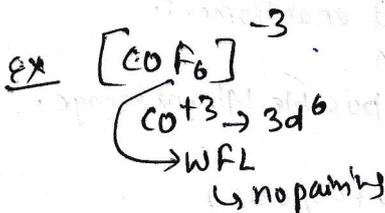
•  $H_2O \rightarrow$  SFL  $\rightarrow Cu^{+2}$  (CN=4)



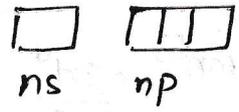
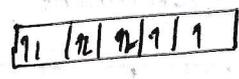
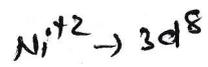
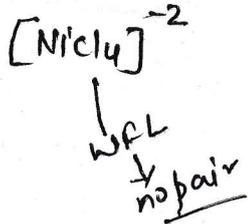
$\downarrow$   
SFL  
pairing



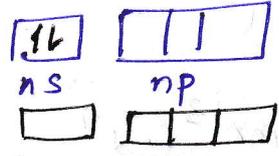
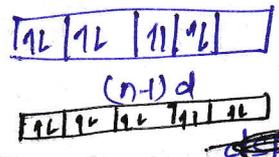
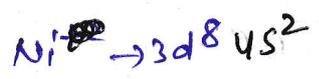
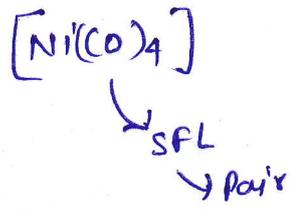
$d^2sp^3$ ,  
inner orbital complex  
low spin / spin paired.  
diamagnetic



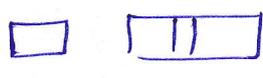
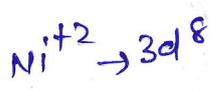
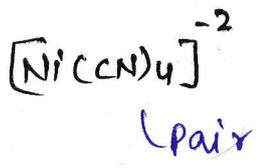
$sp^3d^2$  outer orbital complex  
Paramagnetic High spin / spin free complex



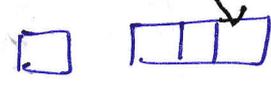
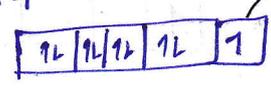
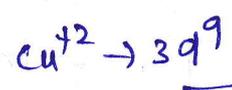
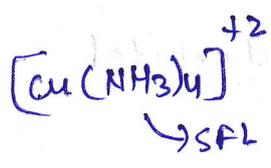
$sp^3$   
Tetrahedral  
paramagnetic



~~$sp^3$~~   
~~planar~~  
 $sp^3$   
Tetrahedral  
diamagnetic



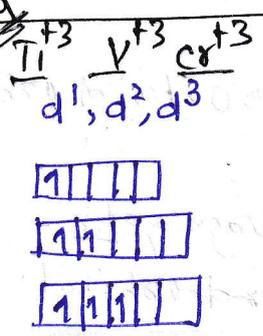
$dsp^2$   
Sq. planar  
diamagnetic



excite in presence of SFL.

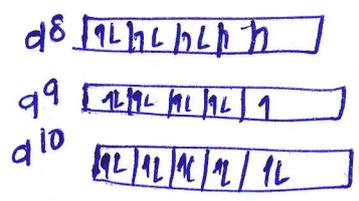
$dsp^2$   
Sq planar  
Paramagnetic

only octahedral



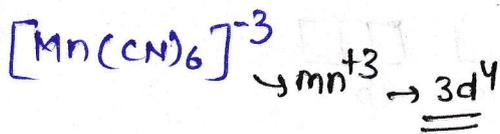
magnetic property of c.c

always 2 d orbital available,  
 $\downarrow$   
 $dsp^3$   
Octahedral  
 SFL / WFL  $\rightarrow$  no pairing occurs

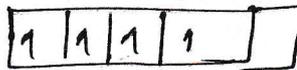


2 inner d orbital  
 can't be available,  
 $sp^3d^2$  always  
 SFL / WFL  $\rightarrow$  no pairing occurs.

$d^4 \quad d^5 \quad d^6 \quad d^7$  }  $\rightarrow$  check  $\rightarrow$  SFL  $\rightarrow$  pairing  
 $\rightarrow$  WFL  $\rightarrow$  pairing X



magnetic moment



only one pairing req  $\rightarrow$  for 2 d orbital

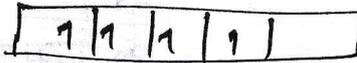
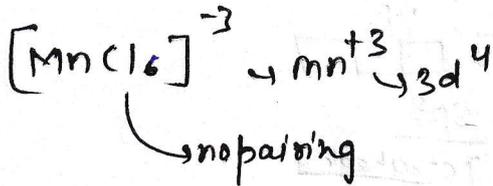


$\rightarrow$  inner d orbital

$n=2$  paramagnetic

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

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

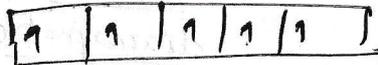
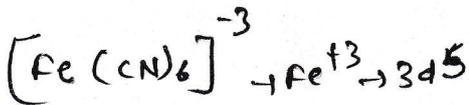


$\rightarrow$  outer d orbital

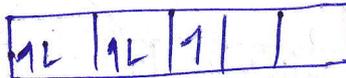
$n=4$  paramagnetic

$\text{MM} = \sqrt{4(4+2)} \text{ BM}$

$= \sqrt{24} \text{ BM}$

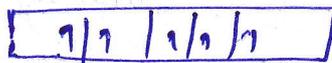
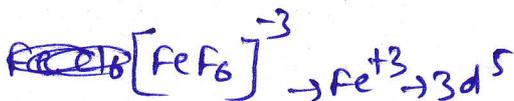


for two 2 d orbital  $\rightarrow$  2 pairing req.

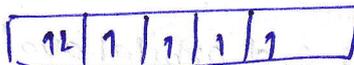
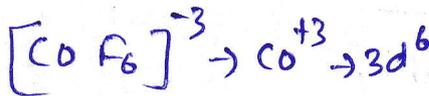


$\rightarrow$  inner d orbital

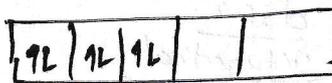
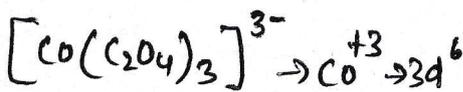
$n=1$   
paramagnetic



$n=5 \rightarrow$  outer d orbital



$n=4 \rightarrow$  outer d orbital

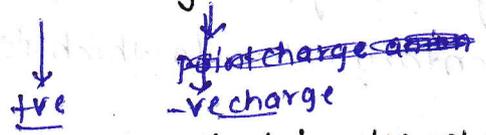


$n=0$  diamagnetic  
 $\rightarrow$  inner d orbital

Limitation of VBT

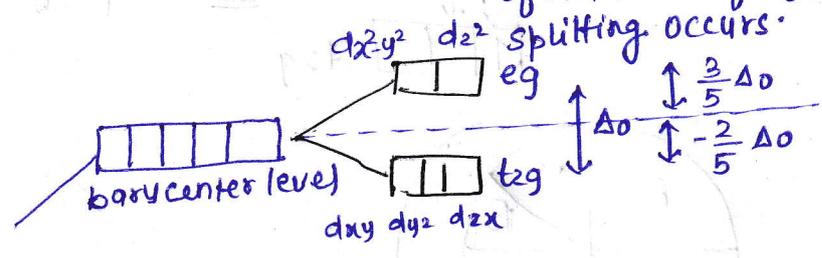
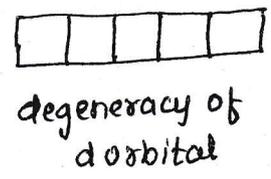
- based on number of assumption.
- does not distinguish b/w SFL & WFL
- does not explain color of c.c.
- failed to predict tetrahedral, square planar complex.
- can't explain kinetic, thermodynamic stability of c.c.
- can't explain magnetic properties.

- electrostatic model.
- Considers metal-ligand bond to be ionic.

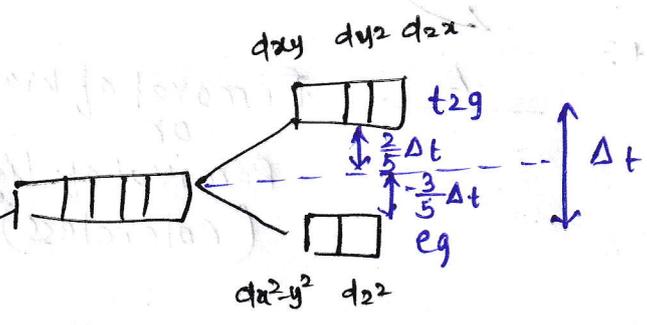
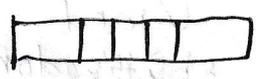


- Degeneracy of d orbitals breaks when ligand approaches central atom.
- repulsion between electron of d orbital of metal & e<sup>-</sup> of ligand. So, d orbital

Octahedral



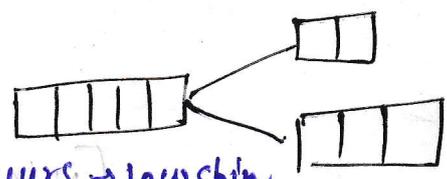
tetrahedral



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

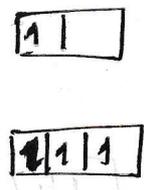
if  $\Delta_o < P \rightarrow$  WFL  $\rightarrow$  no pairing occurs  $\rightarrow$  high spin

Splitting energy  $\downarrow$   
Pairing energy  $\downarrow$

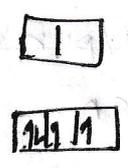


if  $\Delta_o > P \rightarrow$  SFL  $\rightarrow$  pairing occurs  $\rightarrow$  low spin

$d^4$  in case of WFL  
 $t_{2g}^3 e_g^1$



$d^4 \rightarrow$  SFL  
 $t_{2g}^4 e_g^0$



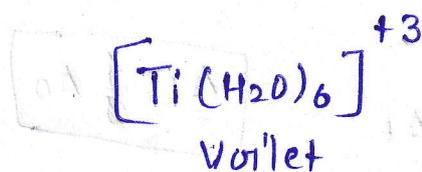
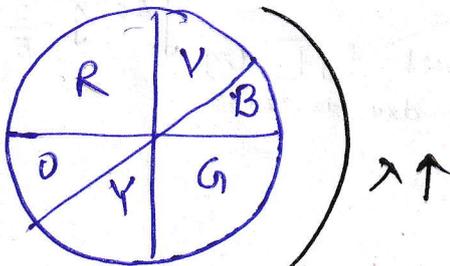
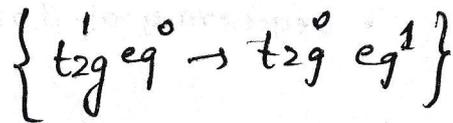
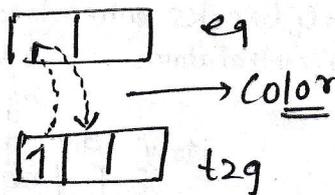
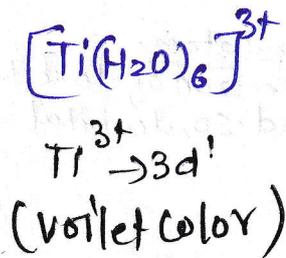
Factors affecting crystal field splitting energy

- $\Delta_o \propto$  charge of CMA
- $\Delta_o \propto$  Zeff of CMA
- 3d < 4d < 5d (CFSE  $\uparrow$ )
- $\Delta_o \propto$  strength of ligand
- octahedral > tetrahedral

color → d-d transition

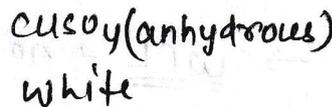
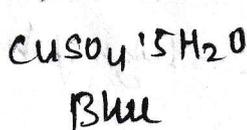
$e^-$  jump from  $t_{2g} \rightarrow e_g$ .

• gt shows complementary color to which it's absorbed.

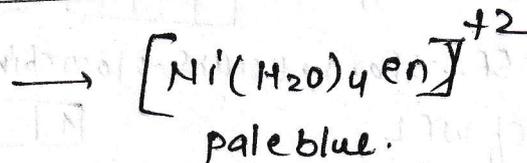
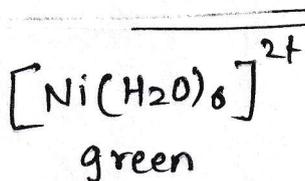


Removal of water  
 or  
 Removal of ligand  
 (colorless)

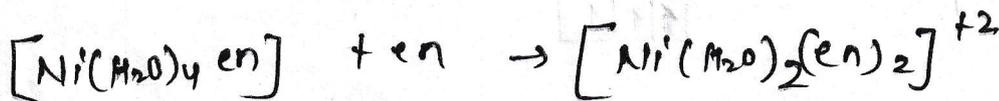
$\left\{ \begin{array}{l} \text{bcO}_2 \\ \text{without} \\ \text{ligand} \\ \text{splitting does not} \\ \text{occur} \end{array} \right\}$



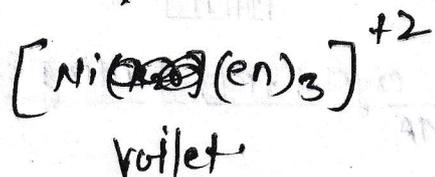
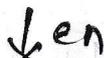
$\left\{ \begin{array}{l} \text{ligand is removed,} \\ \text{splitting does not} \\ \text{occur} \end{array} \right\}$



$\left\{ \begin{array}{l} \text{CFSE added} \\ \downarrow \\ \text{CFSE} \uparrow \\ \downarrow \\ \text{color change} \end{array} \right\}$



blue/purple



CFSE  $\uparrow$  en  $\uparrow$   $\therefore$   $\uparrow \downarrow$ .

Blue  $\rightarrow$  purple  $\rightarrow$  violet

Limitation to CFT

• do not consider  $\pi$  bonding in complex.

Bonding in metal Carbonyl

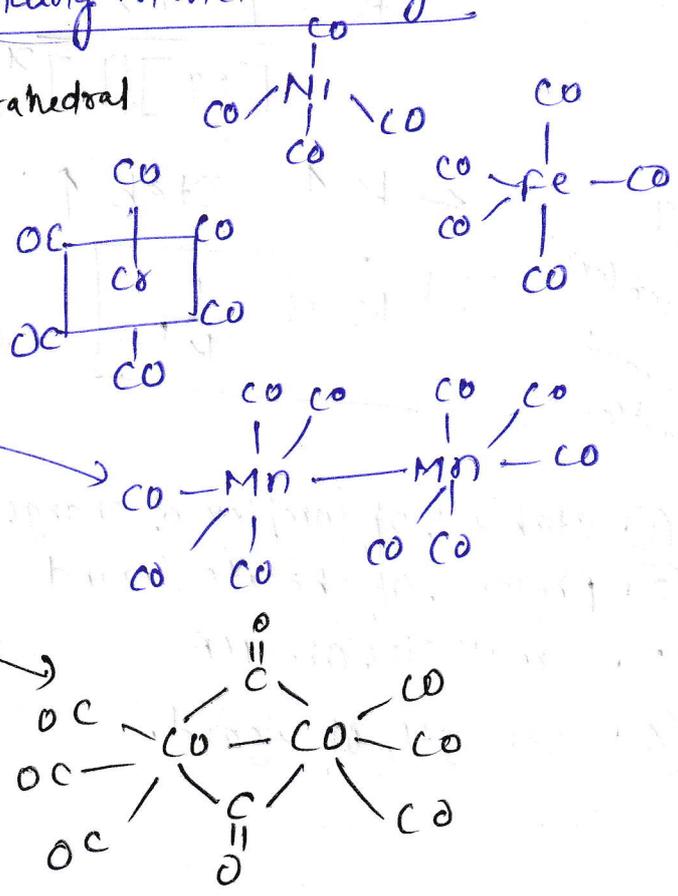
$Ni(CO)_4 \rightarrow sp^3 \rightarrow$  Tetrahedral

$Fe(CO)_5 \rightarrow sp^3d \rightarrow$  TBP

$Cr(CO)_6 \rightarrow sp^3d^2 \rightarrow$  octahedral

$Mn_2(CO)_{10} \rightarrow$

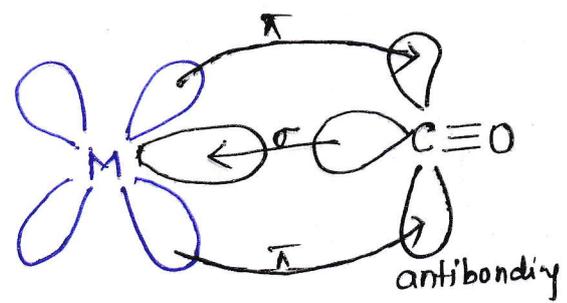
$Co_2(CO)_8 \rightarrow$



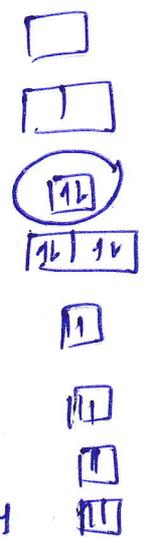
metal-carbon bond in metal carbonyl has both  $\sigma$  and  $\pi$  bond.

$\sigma$  bond b/w M-C :  $\pi$  2p orbital of CO  $\xrightarrow{\text{donates}}$  empty metal orbital

$\pi$  bond b/w M-C : Filled d orbital of M  $\xrightarrow{\text{donates}}$  antibonding ( $\pi^*$ ) molecular orbital of CO



This is synergic bond



CO  $\rightarrow$  14

