

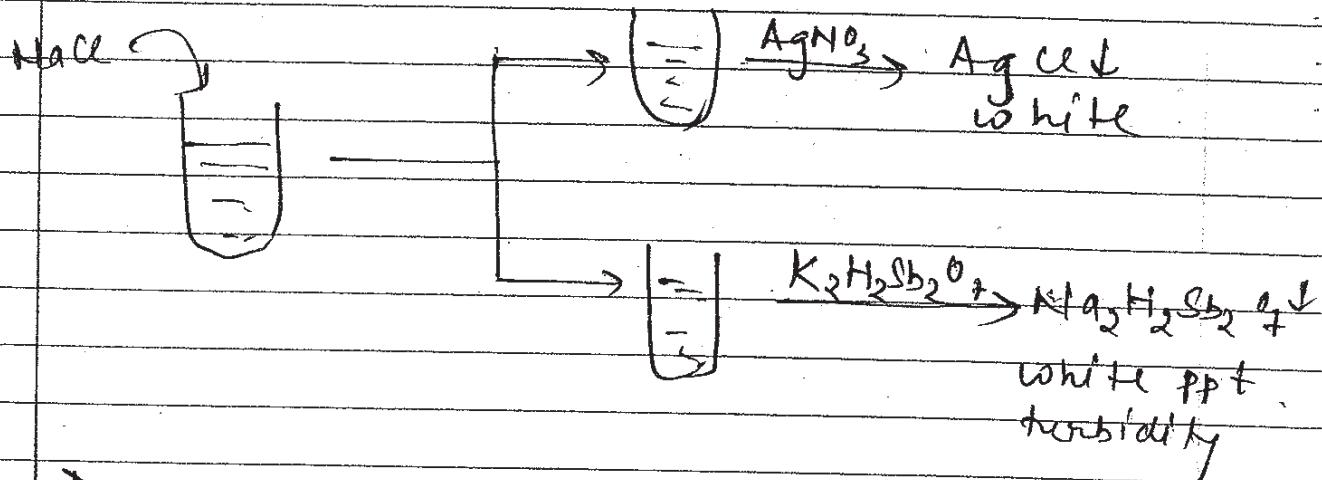
Date

NOTES  
Co-ordination  
Chains

# COORDINATION CHEMISTRY

Date  / 

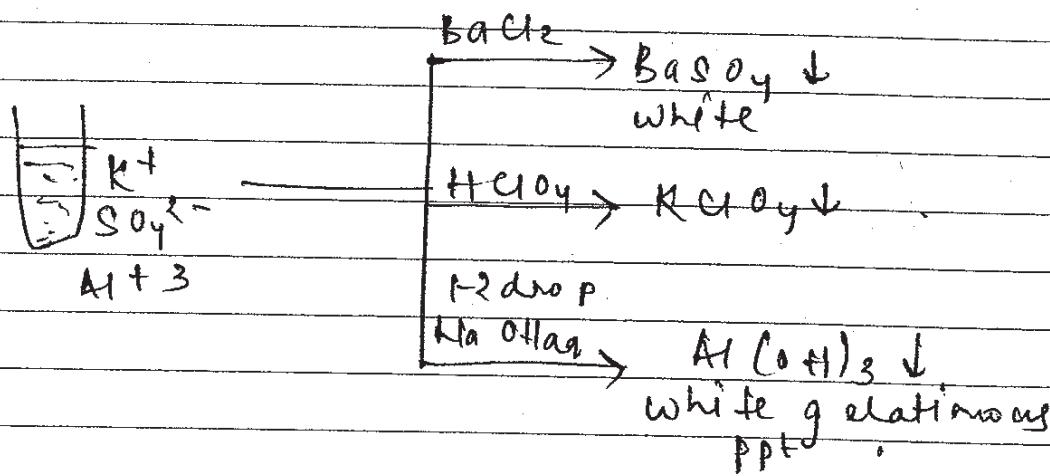
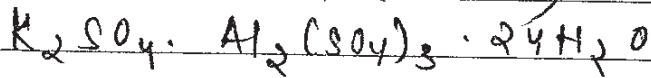
Salt - Substance which are formed by the rxn of acid and base and in aqueous solution all the components of salt give their identification test.



## Double Salt -

Double salt are the addition compound which have their definite identity in solid form but in aqueous soln all the components of double salt give them identification test.

## Potash Alum (white)



(FAS)

Mohr's Salt =  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$   
 (light green)

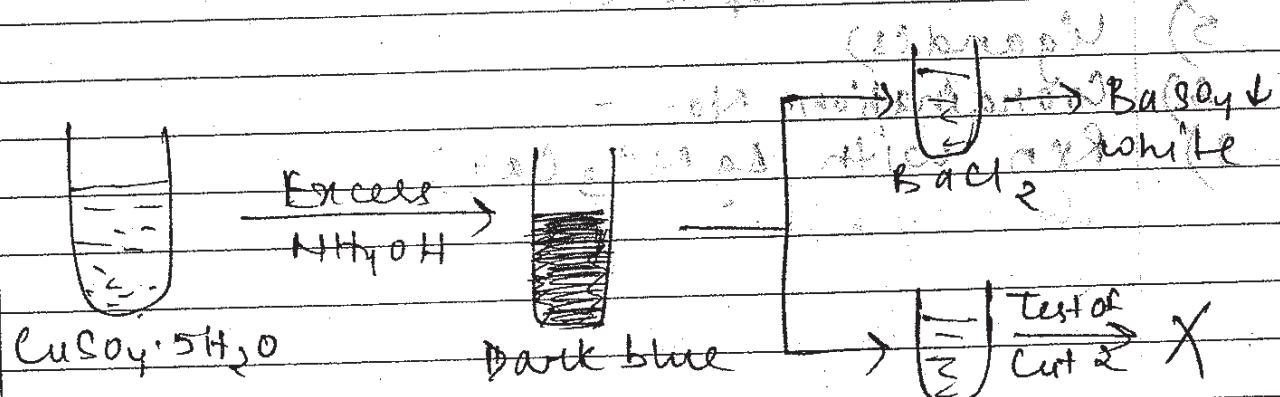
Chrome Alum =  $\text{K}_2\text{SO}_4 \cdot (\text{Mg}(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (violet)

Terrific Alum =  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$   
 (yellow)

Carnallite =  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

Complex Salt

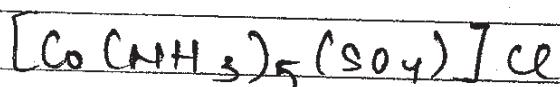
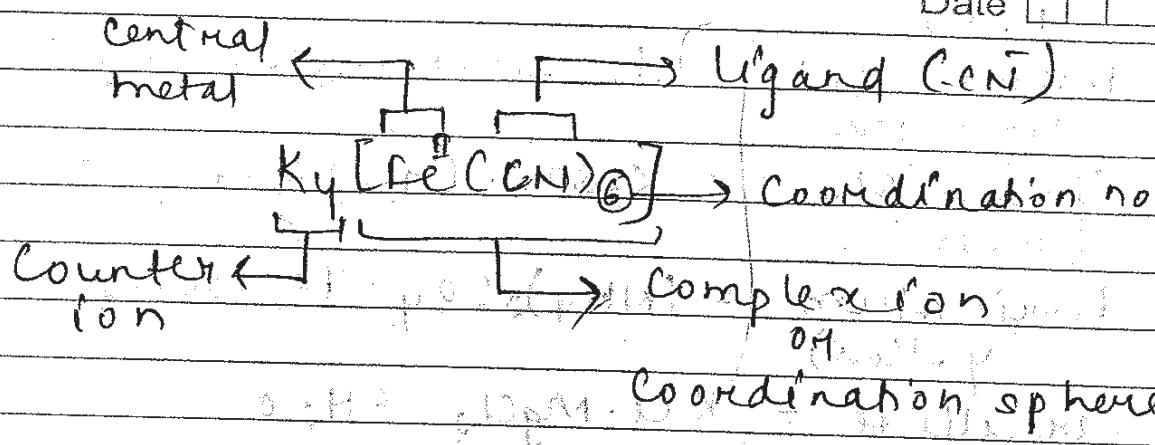
Complex salt are the addition compound formed by two different compound and it has their definite identity in solid state as well as in aqueous solution.



$\text{CuSO}_4 \cdot 4\text{NH}_3$  +  $\text{BaCl}_2 \rightarrow \text{BaSO}_4 \downarrow + [\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot 2\text{H}_2\text{O}$   
 Sustig's salt

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + 6\text{KOH} \rightarrow$  Yellow salt +  $6\text{H}_2\text{O}$   
 +  $[\text{Fe}(\text{CN})_6]^{4-}$  precipitate  
 $\text{K}_3[\text{Fe}(\text{CN})_6]$

Potassium Ferrocyanide



$$n + 0 - 2 = 1/2 \text{ m.e.}$$

$$2 = 3$$

- 1) Counterion :  $\text{Cl}^-$
- 2) Complex ion :  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]^+$
- 3) Central metal ion :  $\text{Co}^{3+}$
- 4) Coordination sphere
- 5) Ligand (3) :  $5\text{NH}_3 \quad \text{SO}_4^{2-}$
- 6) Coordination No. : 6
- 7) Rxn with  $\text{AgNO}_3$  (aq)  
 $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]^{2-} + \text{AgNO}_3 \rightarrow$   
 $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{NO}_3 + \text{AgCl}$

- 8) Rxn with  $\text{BaCl}_2$  (aq) X
- 9) Ag soln shows conductivity - T
- 10) Vant Hoff factors - Q

Q. 0.1M, 1L soln of  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Ba}_2$  when reacts with excess  $\text{AgNO}_3$  produces

- A) 0.2 mole white ppt.
- B) 0.2 mole yellow ppt.
- C) 0.2 mole white + 0.2 mol yellow ppt.
- D) 0.4 mole yellow ppt.

## Central Metal in the salt formation

~~Favourable~~  
WC property is not essential in CM to form complex salt

- A) Small size
- B) High positive charge density
- C) Vacant orbitals of low energy (s)
- D) Variable Oxidation No.



→ Species which accept electron pair from ligand during complex formation is called CM

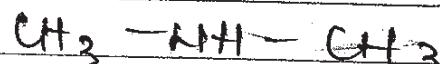
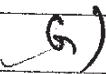
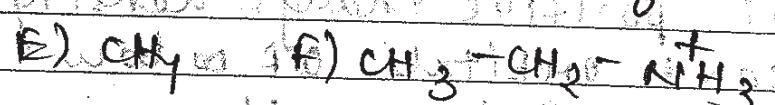
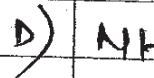
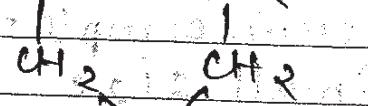
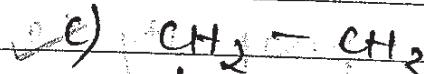
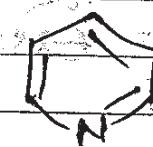
→ CM act as Lewis acid during complex formation

→ Small size, high positive charge density and presence of vacant orbitals of low energy are other favourable conditions for complex formation

→ d-block cations are good complex forming cations because they have all the above specified conditions

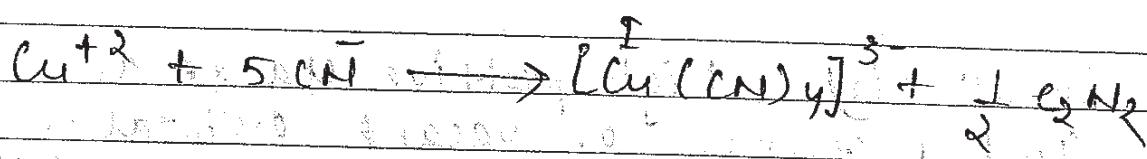
→ s-block cations are not good complex forming cations but  $\text{II(A)}$  ions are better complex forming cations than  $\text{I(A)}$

which is/are can act as ligand.



Ligand - Species which donate  $e^-$  pair to central metal ion during complex formation is called Ligand

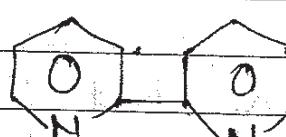
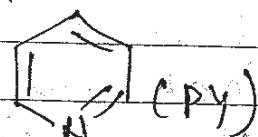
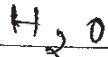
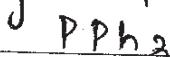
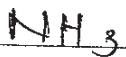
Ligand acts as Lewis Base during complex formation  $\text{M}^{+n} + \text{L} \rightarrow [\text{ML}]^{\pm n}$



### Classification of Ligand

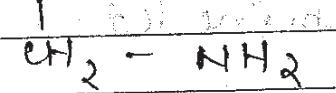
I] On the basis of charge

a) Neutral Ligand



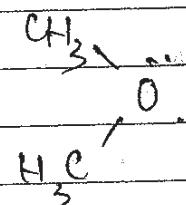
(bipy, dipy)



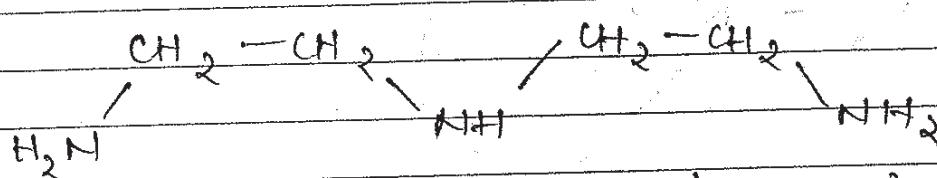


ethylenediamine(en)

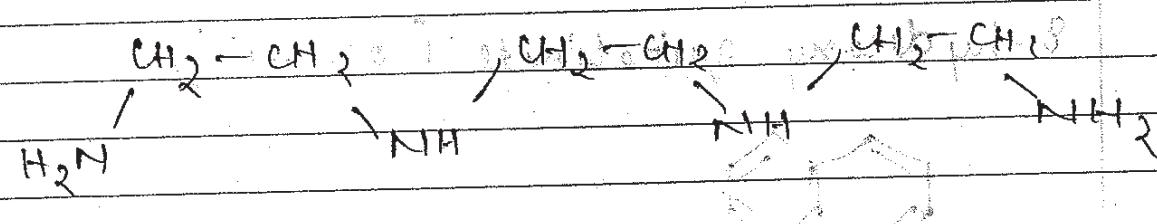
THF



O:



(diethylenetriamine) (di'en)



### (b) Anionic Ligand

$\text{X}^-$  - halide

$\text{NH}_2^-$  - amide

$\text{NH}_2^{2-}$  - imide

$\text{N}^{3-}$  - nitride

$\text{N}_3^-$  - azide

$\text{O}^{2-}$

$\text{O}_2^{2-}$

$\text{O}_3^{2-}$

$\text{CO}_3^{2-}$

Gly

Glycinate

$\text{CH}_2 = \text{C}(\text{O})\text{NH}_2$

$\text{CH}_3\text{COO}^- (\text{OAc})$  a calc

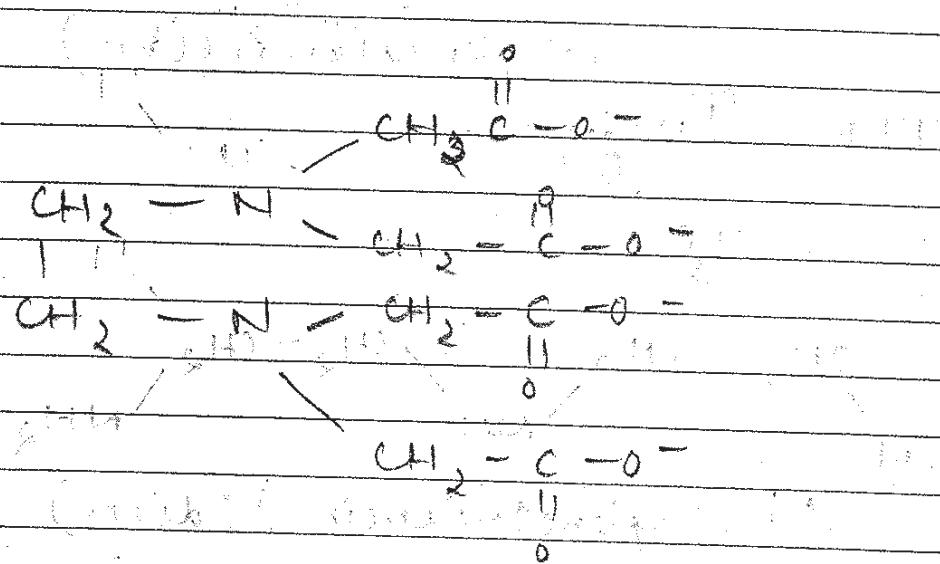
$\text{CH}_3\text{C}(\text{OAc})$  a acetylacetate

Acetyl

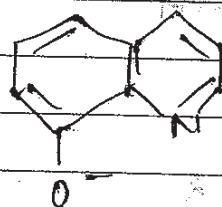
$\text{CH}_3$   $\text{NO}_2^-$

EDTA<sup>4-</sup>

Ethylene diamine tetra acetate.



8-hydroxy quinolinate (oxine-1)



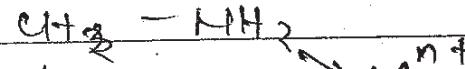
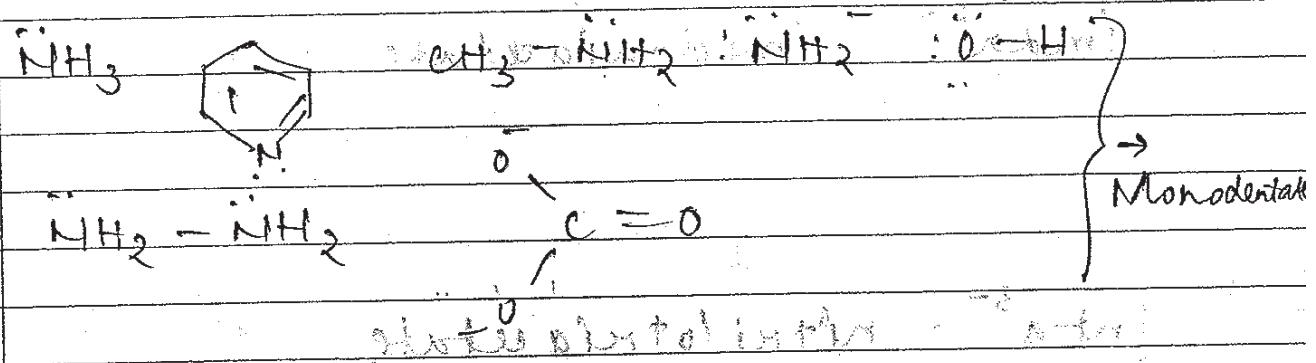
c) Cationic -


 $\text{N}_2\text{H}_5^+ = \text{hydrazinium}$        $\text{N}\equiv\text{O}^+$   
 nitrosonium

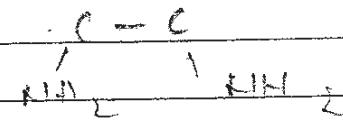
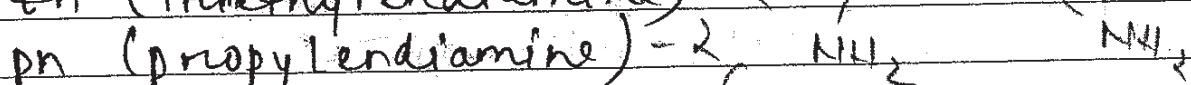
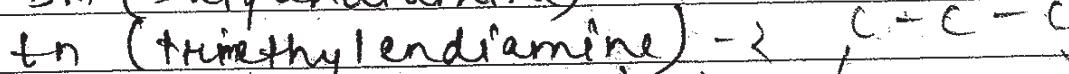
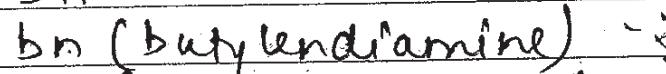
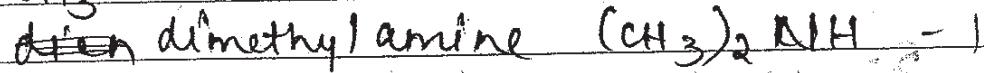
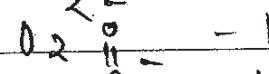
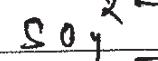
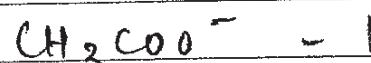
ii] On the basis of denticity.

Denticity  $\rightarrow$  No of  $\sigma$  coordinate bonds formed by a ligand with a central metal. It is defined as denticity of ligand.

No. of donor sites of a ligand bonded with a central metal is defined as denticity of ligand.



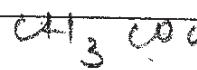
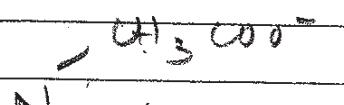
en = Bidentate



$\text{Imda}^{2-}$  - imidodiacetate - 3

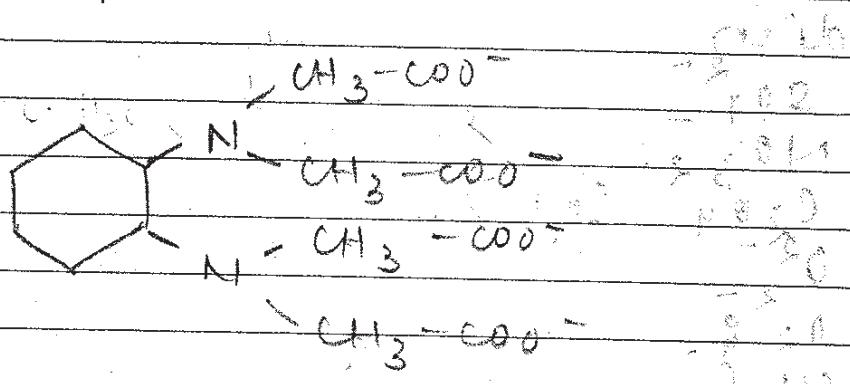


$\text{nta}^{3-}$  - nitrioloacetate - 4

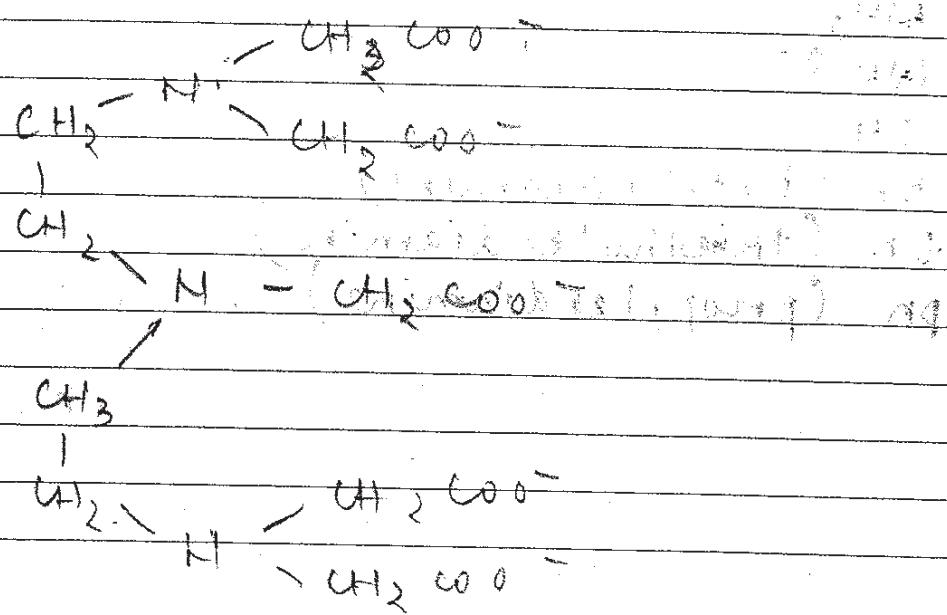


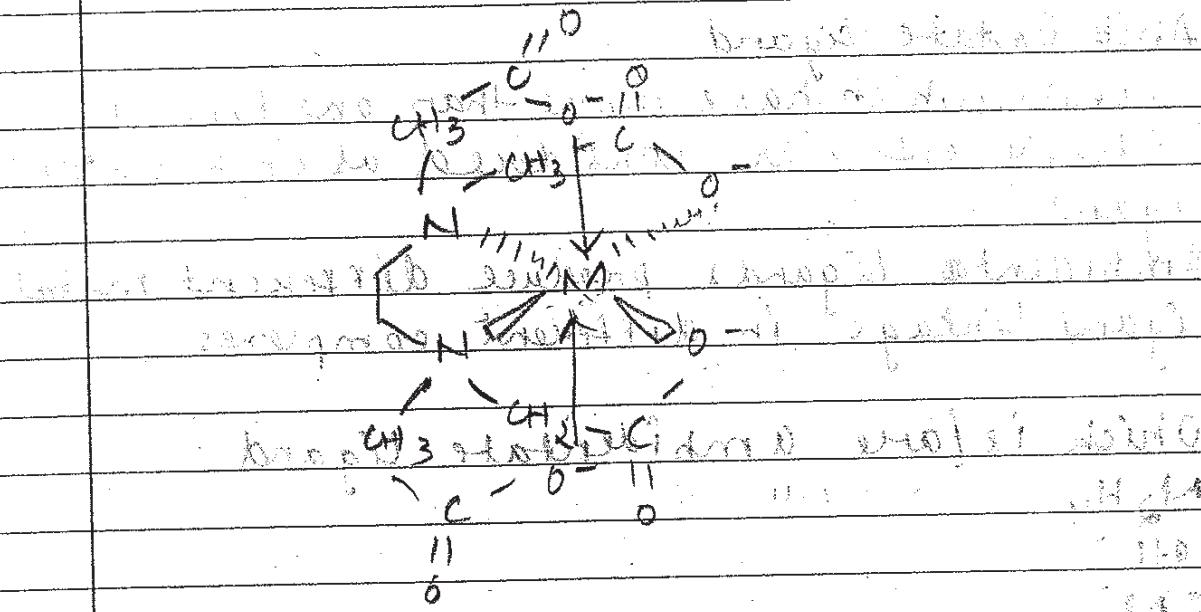
$\text{EDTA}^{4-}$  - 6

$\text{CDTA}^{4-}$  - cyclohexane diamine tetraacetate



$\text{dtpa}^{5-}$  diethylene triamine pentaacetate



PPh<sub>3</sub> - Mono

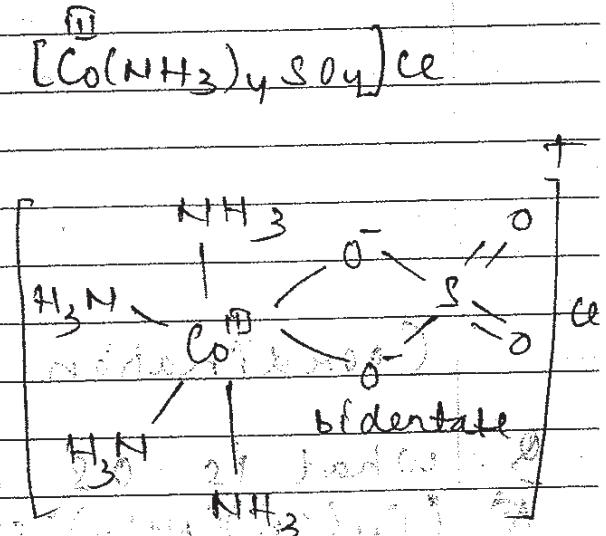
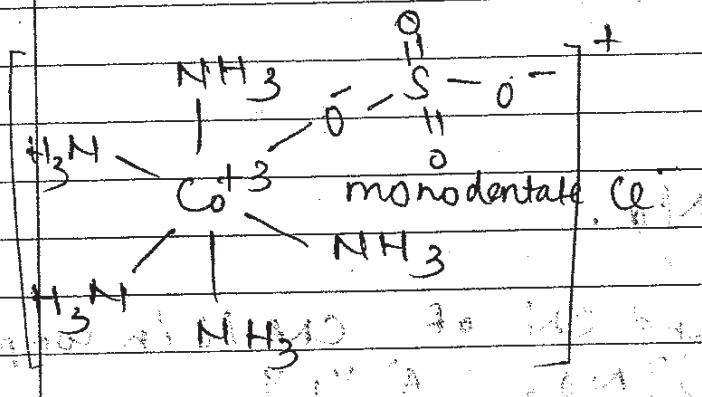
1122 (a)

PMe<sub>3</sub> - Mono

1130 (a)

**flexidentate** - ligands which have 2 or more points of flexible denticity, they are considered as flexidentate ligands.

Eg - SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> are generally monodentate but in some cases they can act as bidentate ligands.

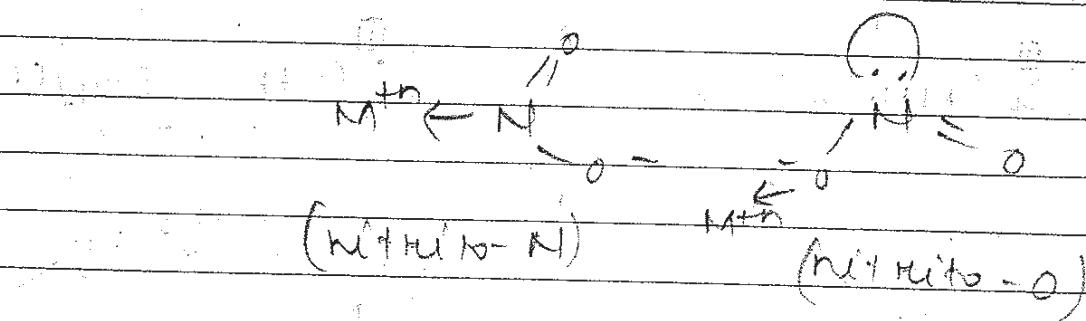


## Ambidentate ligand

- Ligands which have more than one type of donor site, are considered as ambidentate ligand.
- Ambidentate ligands produce different metal ligand linkage in different complexes.

Q. Which is/are ambidentate ligand.

- A)  $\text{N}_2\text{H}_4$        $\text{H}_2\text{N}-\text{NH}_2$   
 B)  $\text{O}^{2-}$   
 C)  $\text{CN}^-$   
 D)  $\text{SCN}^-$        $\text{S-C}\equiv\text{N}$        $\text{M}^{+n} \leftarrow \text{N} = \text{C}=\text{S}$   
 E)  $\text{OCN}^-$       thiocyanato-S      thiocyanato-N  
 F)  $\text{NO}_3^-$        $[\text{M}(\text{SCN})_4]$        $[\text{M}(\text{NCS})_4]$   
 G)  $\text{SO}_4^{2-}$       ditellurite-O       $\text{M}^{+n} \leftarrow \text{O-SO}_4^{2-}$   
 H)  $\text{S}_2\text{O}_3^{2-}$        $\text{M}^{+n} \leftarrow \text{S-SO}_3^{2-}$   
 I)  $\text{C}_2\text{O}_4^{2-}$        $\text{M}^{+n} \leftarrow \text{O-C}_2\text{O}_4^{2-}$   
 J)  $\text{AlO}_2^-$       thiolsulphato-S      thiolsulphato-O

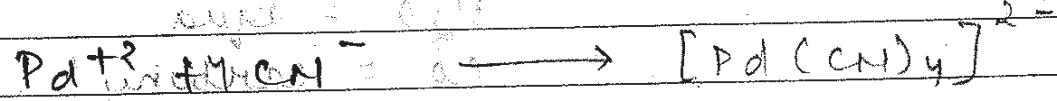
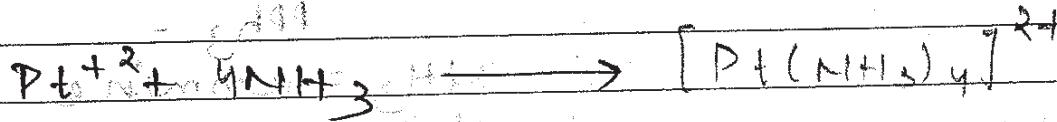
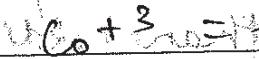
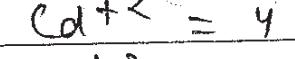
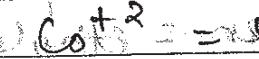
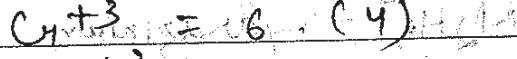
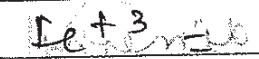
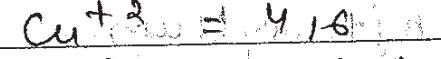
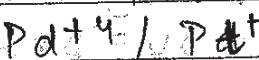
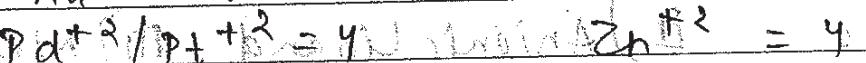
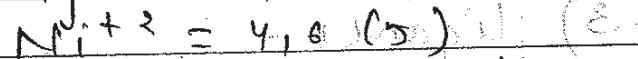
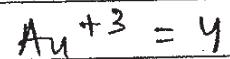
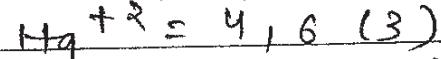
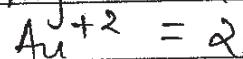
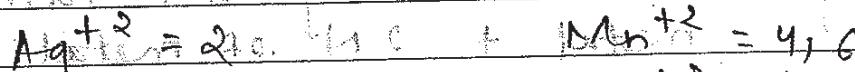


## Coordination No.

- Q. What is OS and CN of  $\text{C}_6\text{H}_5\text{N}_3^-$  in complex
- (Cu(en) $[\text{N}_3\text{Fe}(\text{Cl})_6]$ ) $\text{NO}_3^-$
- n - 1 - 1 = 0      2 + 1 + 1  
 n = 2      : 4
- A) 4, 4  
 B) 4, 2  
 C) 2, 2  
 D) 2, 4

No. of coordinate bonds formed by metal in given complex is called coordination no. of that metal.

Coordination No. is defined for a metal but lenticity is defined for a ligand.



# IUPAC naming of coordination compounds

1] Name of one cation + Name of one anion

2]  $[M(L)_n]^\infty$

No. of ligand + Name of ligand + Name of metal +  $O.N.$  of metal

3)

Ligands - Cationic (I) Anionic Ligand (II) Neutral

$\text{NO}^+$  - nitrosonium

$n$ -nitrolyium

$\text{NH}_2\text{H}_5^+$  - hydrazinium

ide = ido      py = pyridine

ate = ato       $(\text{CH}_3)_2\text{NH} =$

ite = ito      dimethyl amine

en = ethylenediamine  
(ethane-1,2-damine)

$\text{PPh}_3^-$

$\text{NH}_3^-$  = ammonia

$\text{H}_2\text{O}^-$  = aqua

CO = carbonyl

CS = thiocarbonyl

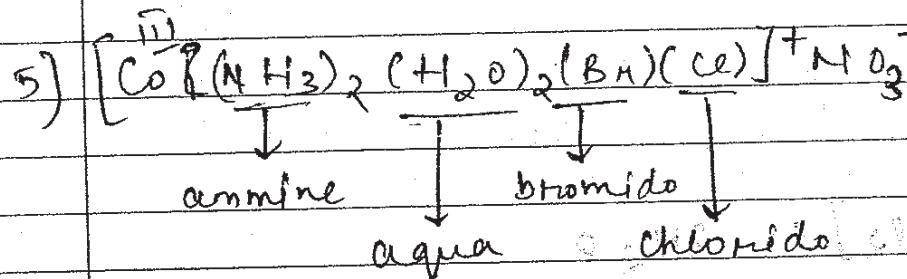
$\text{NO}_2^-$  = nitrosoyl

4)

Ligands which have di, tri, tetra type words in its naming then numerical prefix like, tri-, tetr-, etc are used

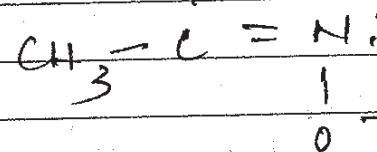
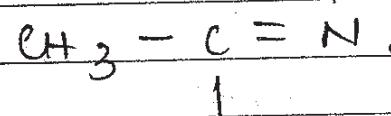
Some ligands are also represented by bis, tris because on using di, tri prefix another compound is formed for eg, pyridine, benzene, etc.

Bis, tris word also used for oxalate and thiosulphate.



diamminedi aquabromochloridocobalt(II) nitrate

DMG<sup>-1</sup> - dimethyl glyoximate



6) If complex is anionic  $[\text{M}(\text{OR})_n]^-$   
 Fe = ferrocate.

Co → Cobaltate

Cu → Cuprate

Mn → Manganate

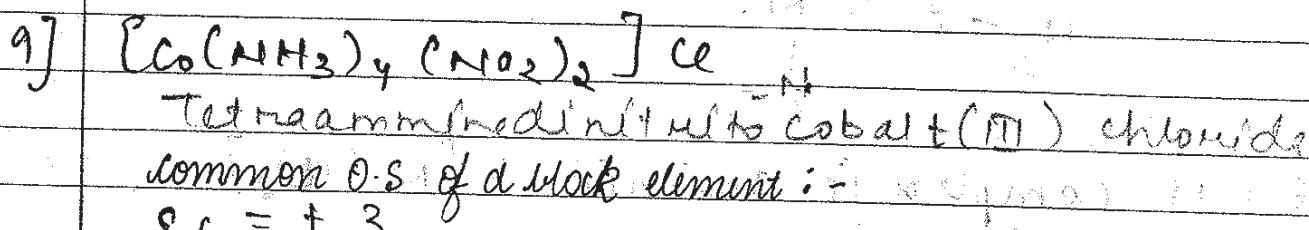
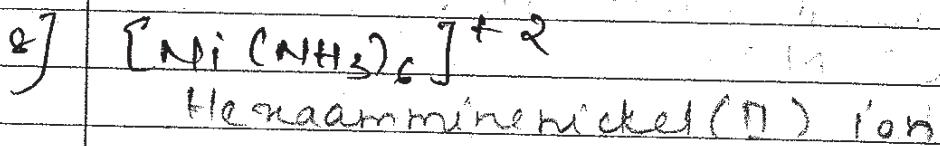
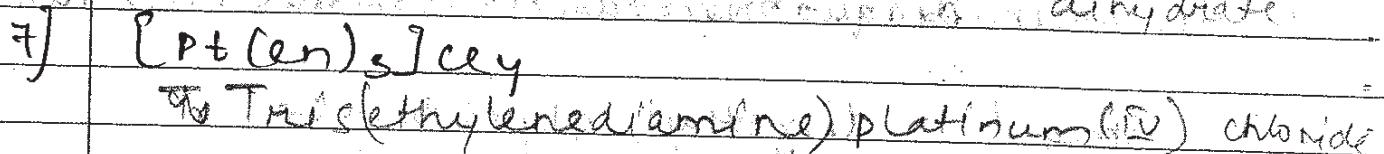
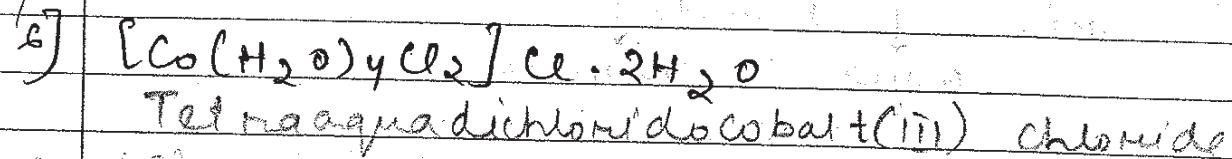
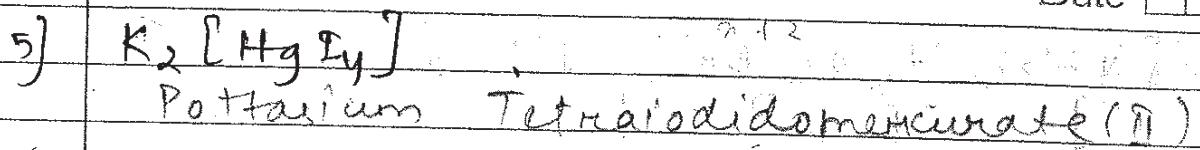
Mg → Magnate

1) Switzer salt -  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$   
 Tetraamminecopper(II) sulphate

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

3)  $\text{Na}_2[\text{Zn}(\text{OH})_4]$  - Sodium tetrahydroxozincate(II)  
 n + 3 - c

4)  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$  - Fischel's Salt.  
 Potassium hexanitro cobaltate(II)



$$Sc = +3$$

$$Ti = +2, +3, +4$$

$$V = +2 \cancel{, +3}, +3$$

$$Cr = +3 \cancel{, +6}$$

$$Mn = +2, +4, +7$$

$$Fe = +2, +3$$

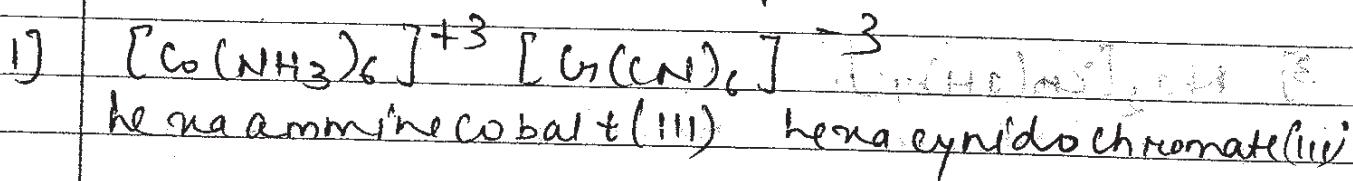
$$Co = +2, +3$$

$$Ni = +2, +3$$

$$Cu = +1, +2$$

$$Zn = +2$$

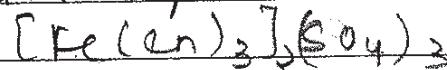
$$Pd, Pt = +2, +4$$



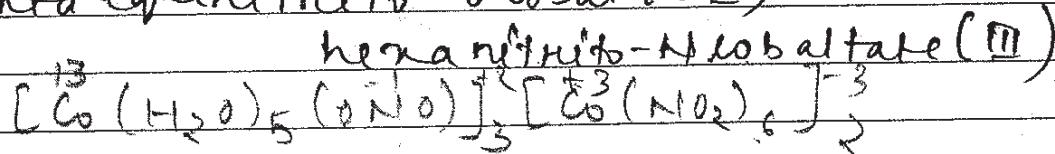
- 2)  $\left[ \overset{+2}{\text{Pt}}(\text{NH}_3)_4 \right]^2 \left[ \overset{+2}{\text{Pt}}\text{Cl}_4 \right]^{-2}$   
 Tetraammineplatinum(II) Tetrachloroplatinate(II)
- 3)  $\left[ \overset{+3}{\text{Fe}}(\text{NH}_3)_5 \text{SCN} \right]^{\frac{1}{2}} \left[ \overset{+3}{\text{Co}}(\text{NH}_3)(\text{NCS})_5 \right]^{-\frac{5}{2}}$   
 Pentaamminemethiocyanato cobalt(III)  
 Bis(ethylenediamine)Amminepentaaquothiocyanato cobaltate(II)
- 4)  $\left[ \overset{+3}{\text{Fe}}(\text{en})_3 \right]^{\frac{1}{2}} \left[ \overset{+3}{\text{Co}}(\text{C}_2\text{O}_4)_3 \right]^{-\frac{3}{2}}$   
 Tris(ethylenediamine)iron(II) Tris(oxalato)cobaltate(II)

Write formula of following compds.

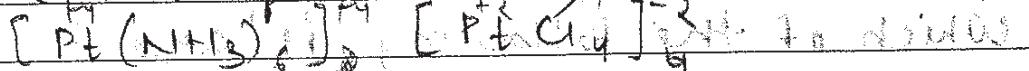
1) tris(ethylenediamine)iron(II) sulphate.



2) penta aquanitrito-o cobalt(II)



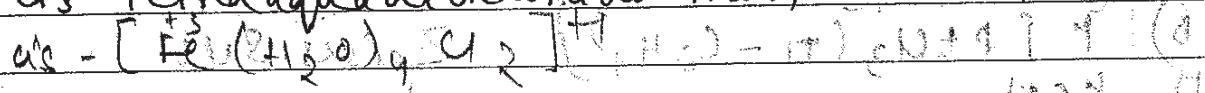
3) hexaammineplatinum(0) tetrachloroplatinate(II)

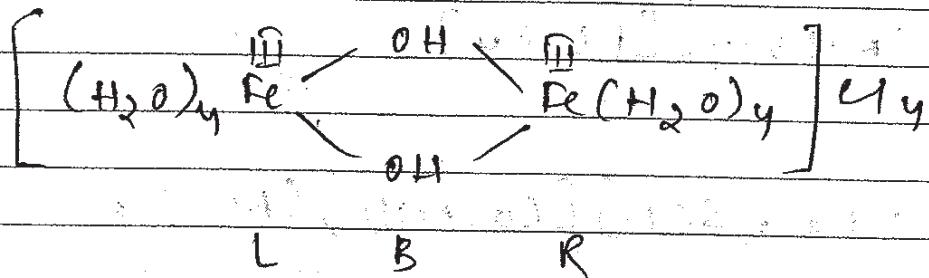


4) iron(II) hexacyanido ferrate(II)



5) C<sub>2</sub>-tetra aquadichlorido Iron(II) (cyan)<sup>+</sup>



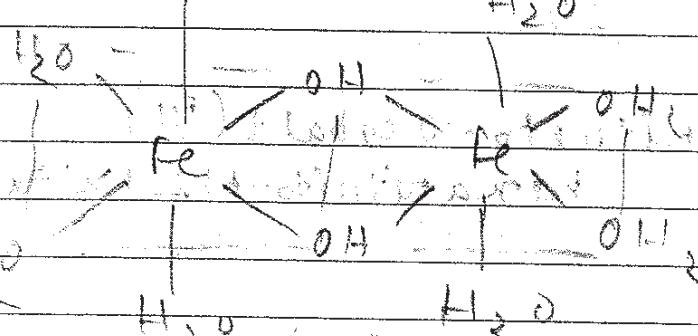


1) tetraaquairon(III) di-H-hydroxidotetraqua iron(III) chloride

2) di-H-hydroxidobis(tetraaquairon(III)) chloride

3) di-H-hydroxido octaaquadiiron(II) chloride

4) bis{H-hydroxidotetraaquairon(II)} chloride



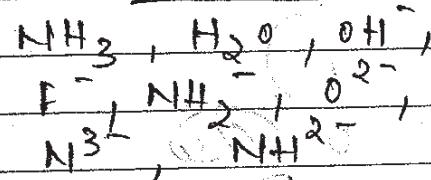
Q. Which of the following is/are organometallic compound.

- A)  $\text{H}_3\text{C}\text{MgBH}_4$
- B)  $\text{K}_3[\text{Al}(\text{CH}_3\text{O})_6]$
- C)  $[\text{Ni}(\text{CO})_4]$
- D)  $\text{P}[\text{PtCl}_3(\text{H}-\text{C}_2\text{H}_4)]$  Zeiss's Salt
- E)  $\text{KCN}$

Compounds which have metal-C linkage are called organometallic compounds  
Ionic carbide and ionic cyanide - not organometallic.

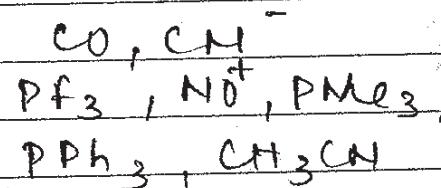
# Classification of Ligands on the basis of bonding.

## Classical ligand

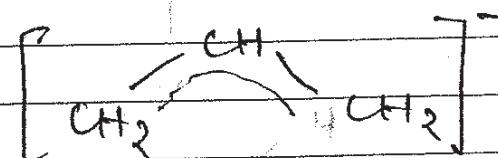


## Non classical (π-acid (acceptor))

(σ-donor)  
(π-acceptor)



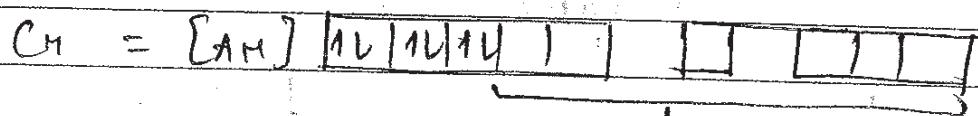
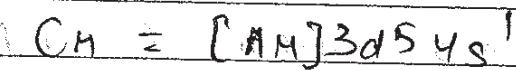
cyclopentadienyl



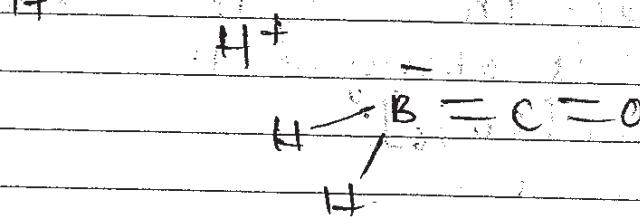
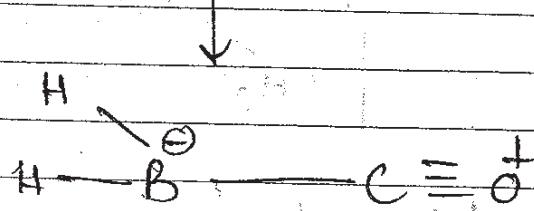
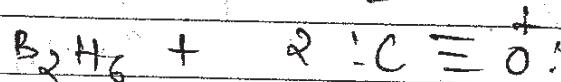
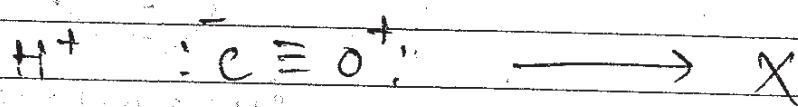
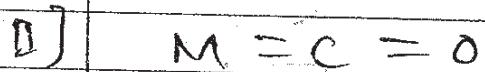
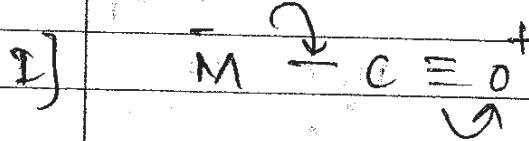
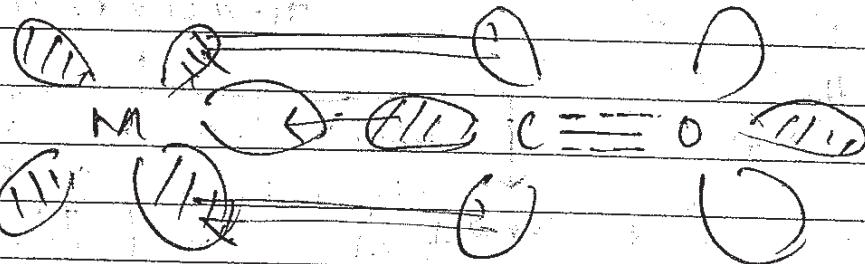
### I] σ-donor π-acceptor ligand

Q1. C-O bond length in CO is  $1.128 \text{ \AA}$ . What C-O length is observed in  $[\text{Cr}(\text{CO})_6]^0$ .

- A)  $1.128 \text{ \AA}$
- B)  $1.118 \text{ \AA}$
- C)  $1.158 \text{ \AA}$
- D)  $1.78 \text{ \AA}$

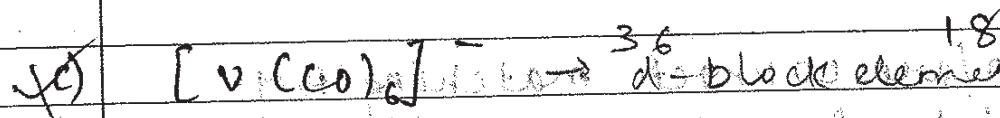


$d^2sp^3$



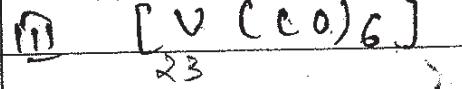
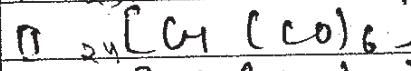
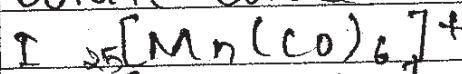
JEE 2007

which have minimum C-O bond order.

EAN      Valence e<sup>-</sup>

positive hexa carbyl stage 3R-V + on group 16S only when there M<sub>3</sub> C<sub>6</sub> - acceptor ligand

Q1. Write correct order for



i) CO bond length.

ii) CO : BE.

iii) No. of e<sup>-</sup>.

iv) π-character in M-C bond.

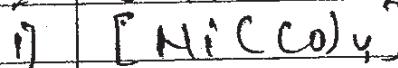
v) IR F. required to stretch C-C bond.

vi) IR ν

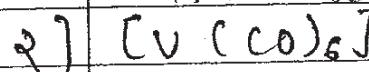
vii) IR δ

viii) Total valence e<sup>-</sup> = I + II + III

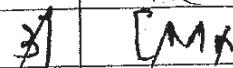
Q. Write IUPAC naming



Tetracarbonylnickel(0)

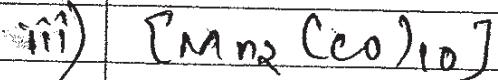


Hexacarbonylvanadate (-I) ion

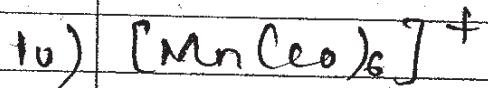


All  $Hg^{2+}$  compds are diamagnetic  
because it is isoelectronic to  $Hg^{2+}$

Date: [ ]



Decacarbonyldimanganese(0)



Hexa carbonylmanganese(I) ion (Co) and (Mn)

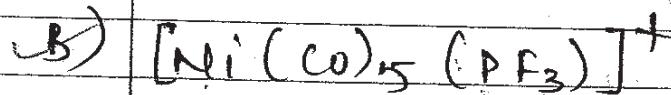
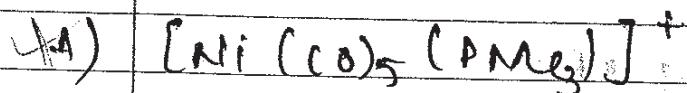
Q. Which of the following correctly matches the  $\pi$ -orbital of  $\pi$ -acceptor ligand which overlap with metal.

- A)  $NO_2$  ( $\pi^*$ )
- B)  $CN^-$  ( $\pi^*$ )
- C)  $PF_3$  ( $\pi_d$ )
- D)  $PH_3$  ( $\pi^*$ )
- E)  $R-C\equiv N$  ( $\pi^*$ )
- F)  $H_2C=CH_2$  ( $\pi^*$ )

Q. Which of the following has highest  $\pi$ -acceptor ability?

- A)  $PCl_3$
- B)  $PI_3$
- C)  $PMe_3$
- D)  $NNAr_3$

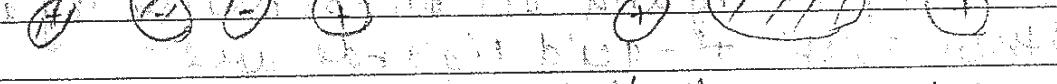
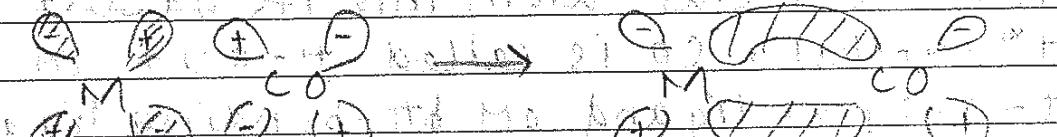
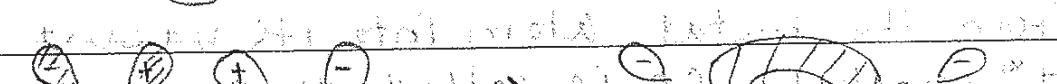
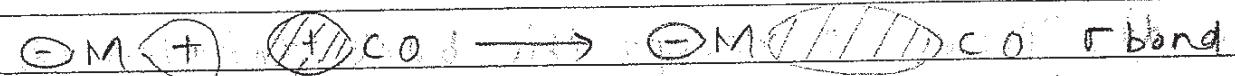
Q. Which complex requires highest energy to stretching of C=O bond?



tot

## Bonding in Metal Carbonyl

Ex:  $[\text{Fe}(\text{CO})_5]$ ;  $[\text{Ni}(\text{CO})_4]$ ;  $[\text{Cr}(\text{CO})_6]$



dative  $\pi$ -bond is formed by fully filled  $\sigma$  orbital

on M to empty antibonding molecular orbital on CO

a) The metal - carbon bond can in metal carbonyls may be represented as the donation of an electron pair from carbon to vacant orbital of metal and form  $\sigma$ -bond ( $\text{M} \leftarrow \text{CO}$ ) .

b) A second bond is formed by back bonding sometimes called dative  $\pi$ -bonding . This arises from side ways overlap of a full orbital on the metal with the empty antibonding  $\pi^*_{\text{p}_y}$  /  $\pi^*_{\text{p}_z}$  (if  $n$ -axis is molecular axis) molecular orbital of the carbon monoxide , thus forming a  $\pi \text{M} \rightleftharpoons \text{CO}$  bond ( $\sigma\text{-M-CO}$  + back bond)

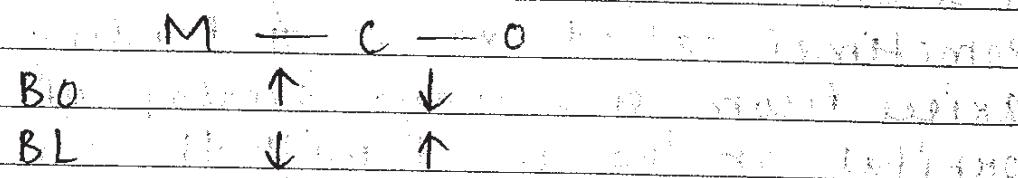
c) The filling or partial filling of the antibonding orbital on CO reduces the bond order of C-O bond from the triple bond in CO towards a double bond . This is shown by the increase in C-O bond length

from  $1.128\text{ \AA}$  to  $\text{In-CO}$  to about  $1.15\text{ \AA}$  in many carbonyls.

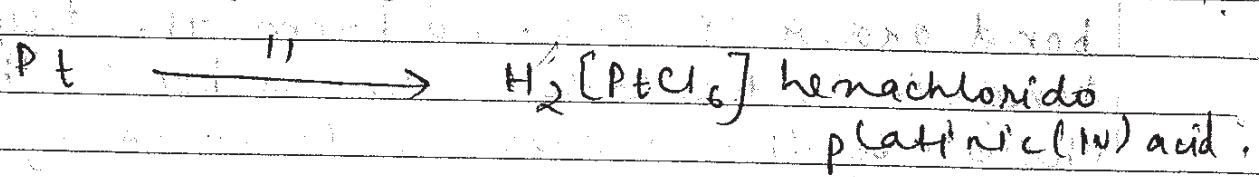
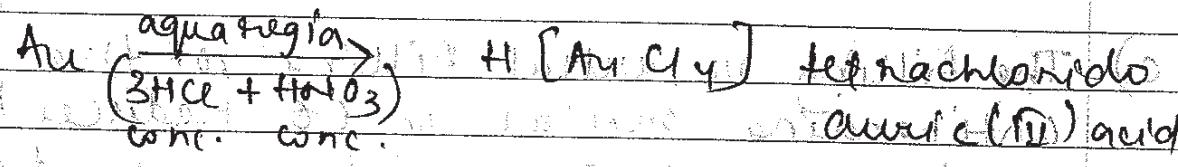
- d) Since CO accept the back donated electrons from the metal atom into its vacant  $\pi^*$  orbital, CO is called  $\pi$ -acid or  $\pi$ -acceptor ligand or  $\pi$ -bonding ligand. Other such  $\pi$ -acid ligands are  $\text{CN}^-$ ,  $\text{RCN}$ ,  $\text{NO}^+$ .

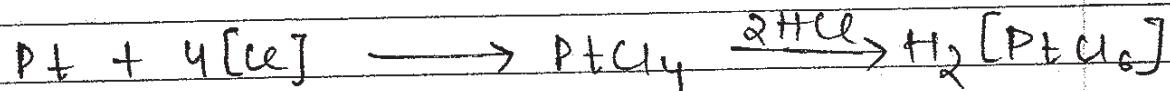
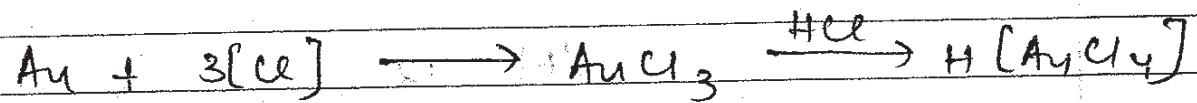
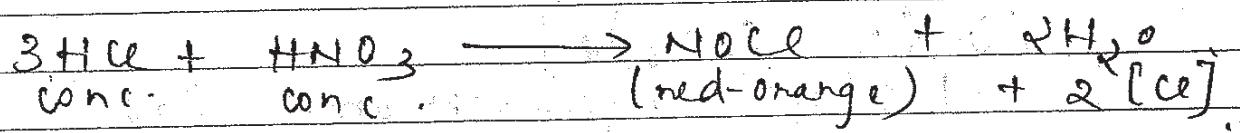
NOTE :  $\pi$ -acid ligands like  $\text{PF}_3$ ,  $\text{PPh}_3$ ,  $\text{AsCl}_3$ , etc accept the back donated electrons from the metal atom into its vacant d-orbital of central atom.

- e) As bond order increases, bond length decreases; bond energy increases & stretching / vibrational frequency increases.

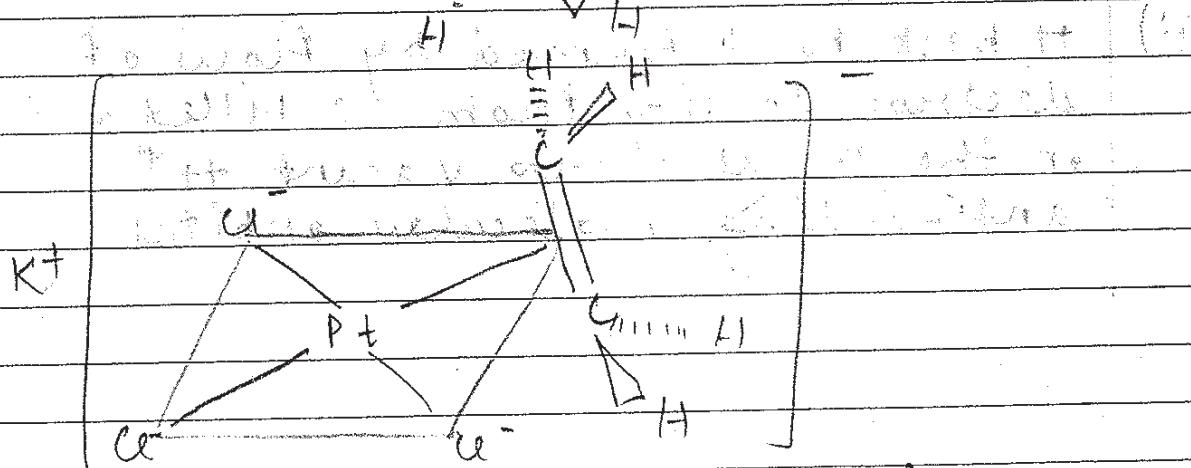
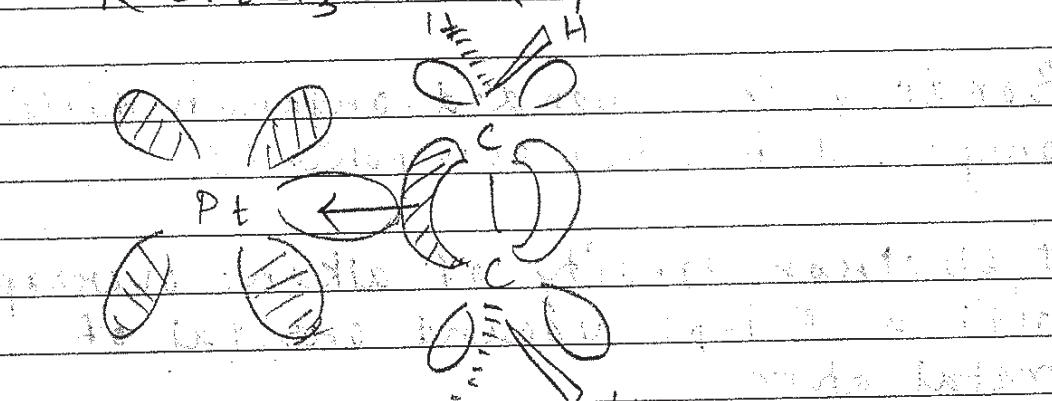
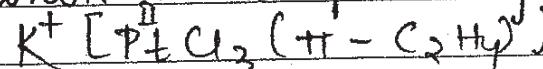


Complex in which  $\text{H}^+$  ion is counterion, that type of compounds are considered as complex acids.





2)  $\pi$ -donor II-acceptor ligand

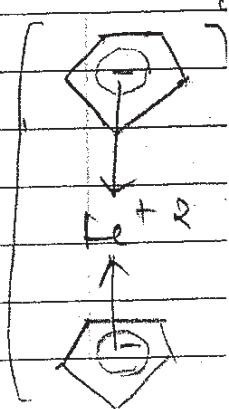


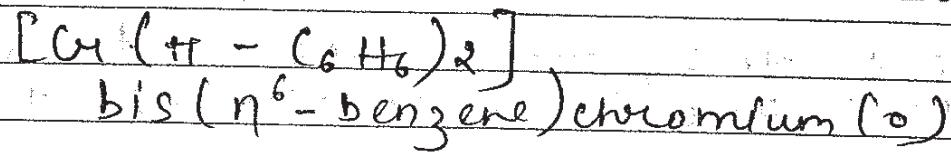
Potassium trichlorido( $\eta^2$ -ethene)platinate(II)

$[\text{Fe}(\pi-\text{C}_5\text{H}_5)_2]$  - Ferrocene

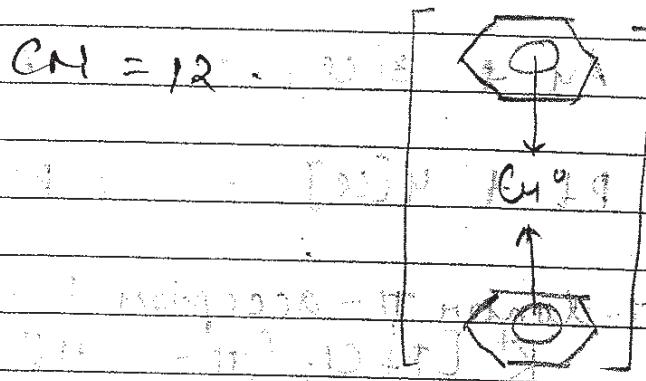
bis( $\eta^5$ -cyclopentadienyl)iron(II)

CN = 10





$$\text{CN} = 12$$



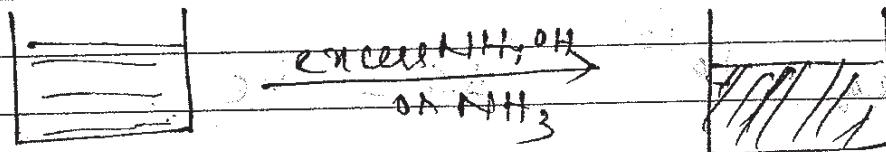
Bonding in  $\pi$  bonded organometallic compound has two components:

- i)  $\pi$  electron density of alkene overlaps with a  $\sigma$  type vacant orbital of metal atom.
- ii)  $\pi$  back bond formed by flow of electron density from a filled d-orbital on the metal into vacant  $\pi^*$  antibonding molecular orbital

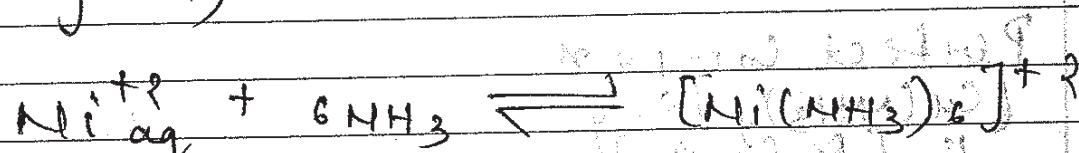
Q. Which is most stable complex.

- A)  $[\text{Ni}(\text{NH}_3)_6]^{+2}$
- B)  $[\text{Ni}(\text{en})_3]^{+2}$
- C)  $[\text{Ni}(\text{CH}_3\text{NH}_2)_6]^{+2}$
- D)  $[\text{Ni}(\text{en})(\text{NH}_3)_4]^{+2}$

Exp-1

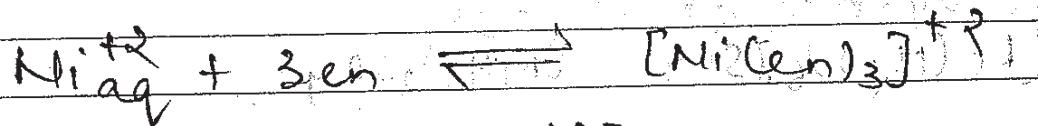
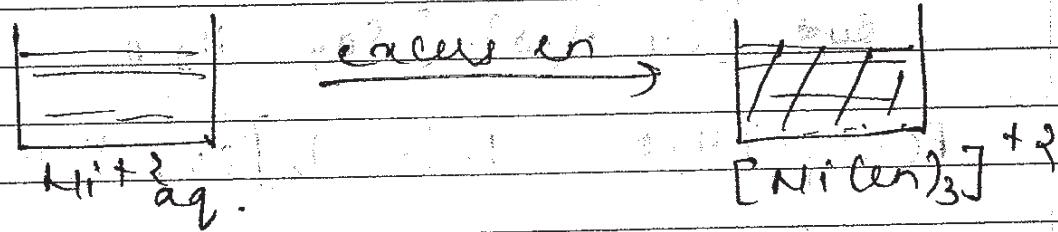


$\text{Ni}^{+2}\text{aq}$ .  
(green)

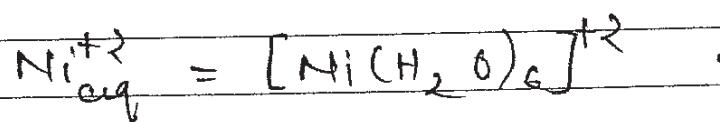


$$K_f = \frac{[\text{Ni}(\text{NH}_3)_6]^{+2}}{[\text{Ni}^{+2}][\text{NH}_3]^6} = 10^8$$

Exp-2

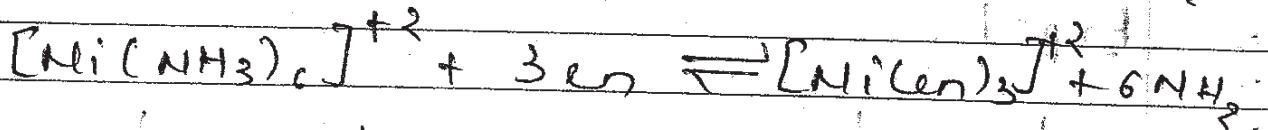
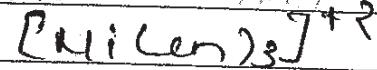
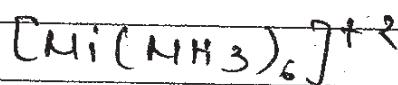
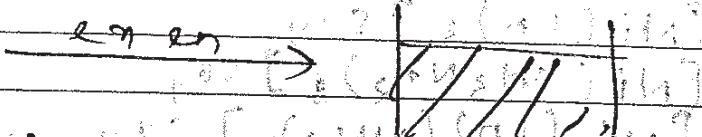


$$K_f = \frac{[\text{Ni}(\text{en})_3]^{+2}}{[\text{Ni}^{+2}][\text{en}]^3} = 10^{18}$$



Expt - 3

even even

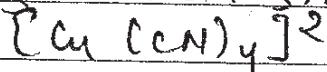
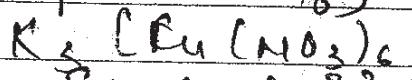
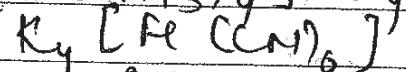
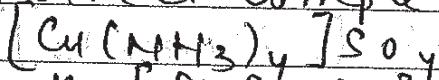


$K_{\text{eq}} = 10^{10}$

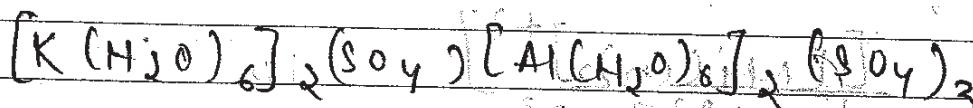
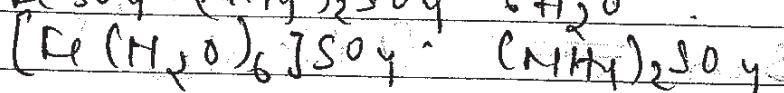
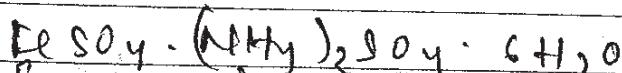
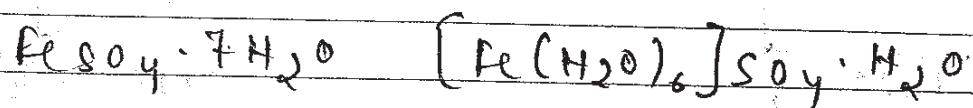
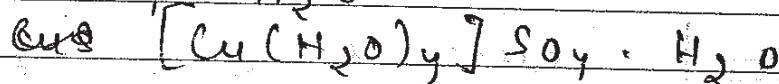
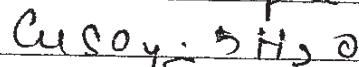
$\Delta G^\circ = -nFE$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

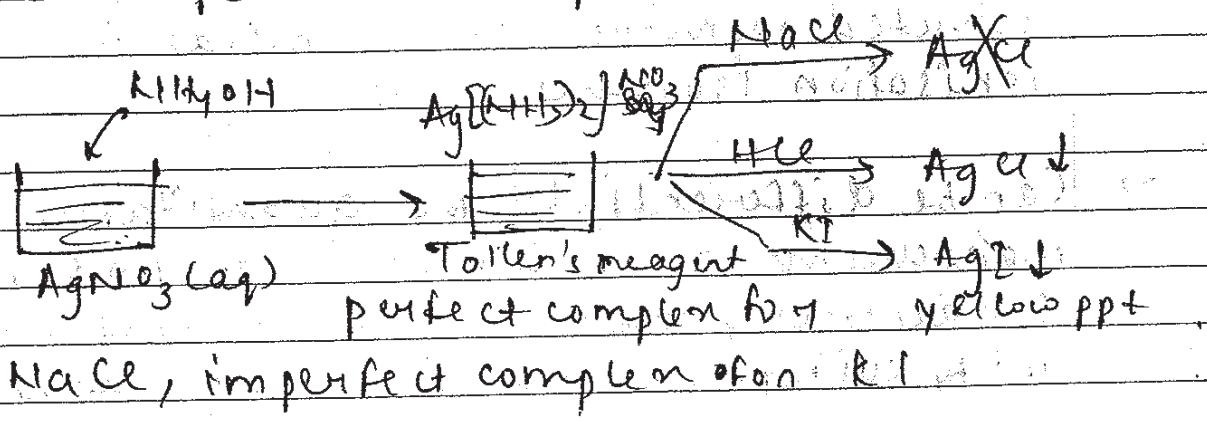
Perfect Complex



Imperfect Complex



- Stability of complex salt depends on their formation constant. Higher the  $K_f$  greater will be the stability of coordination compound.
- It is observed that chelate complexes have relatively higher  $K_f$  so that they are more stable. It is called chelation effect.
- Extra stability of chelating complexes is explained by thermodynamic factors entropy.
- In general, complex salts which have higher formation constant are relatively more stable and considered as perfect complex.
- Some other complex which have relatively low  $K_f$  and give identification test of their components are called imperfect complex.
- Most of the aqua complex of 3d-series are imperfect complex.



# Isomers



## Structural Isomerism

- 1) Ionization
- 2) Hydrated
- 3) Linkage
- 4) Coordination
- 5) Ligand
- 6) Coordination Positions

## Stereo Isomerism

- 1) Geometrical

- 2) Optical

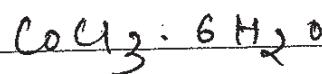
### Ionization Isomerism

- Two complex which have same MF but produce different types of ions in aqueous soln are called ionisation iso.
- This type of isomers can be differentiated by precipitation method or conductivity measurement (e.g.  $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{say } [\text{Pt}(\text{NH}_3)_4\text{Cl}_2\text{Br}_2$ ,  $[\text{Co}(\text{NH}_3)_5\text{SO}_4] \text{ i.e. } [\text{Pt}(\text{NH}_3)_4\text{Br}_2\text{Cl}_2$ )

### Hydrated Isomers

(Solvated)

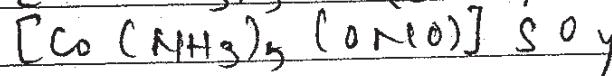
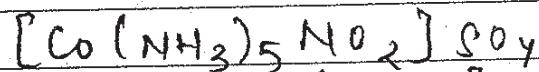
- Complex salts which have same NAE but have different water of crystallization are called hydrated isomers or solvated isomers. It is similar to ionisation isomers.
- Can be differentiated by quantitative measurement estimation of ppt, conductivity measurement, colligative properties and by using suitable dehydrating agent.



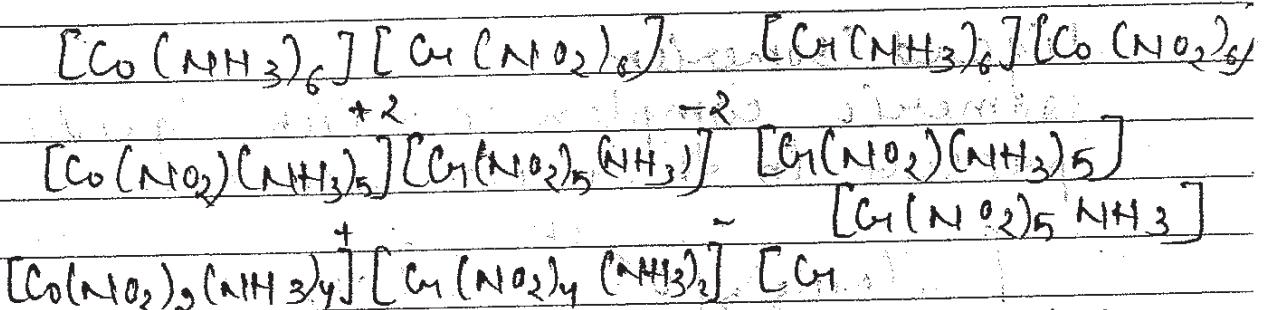
- 1)  $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$
- 2)  $[\text{Co}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
- 3)  $[\text{Co}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot [2\text{H}_2\text{O}] \quad [\text{Co}(\text{H}_2\text{O})_3]$
- 4)  $[\text{Co}(\text{H}_2\text{O})_3\text{Cl}_3] \cdot 3\text{H}_2\text{O}$

Linkage Isomerism.

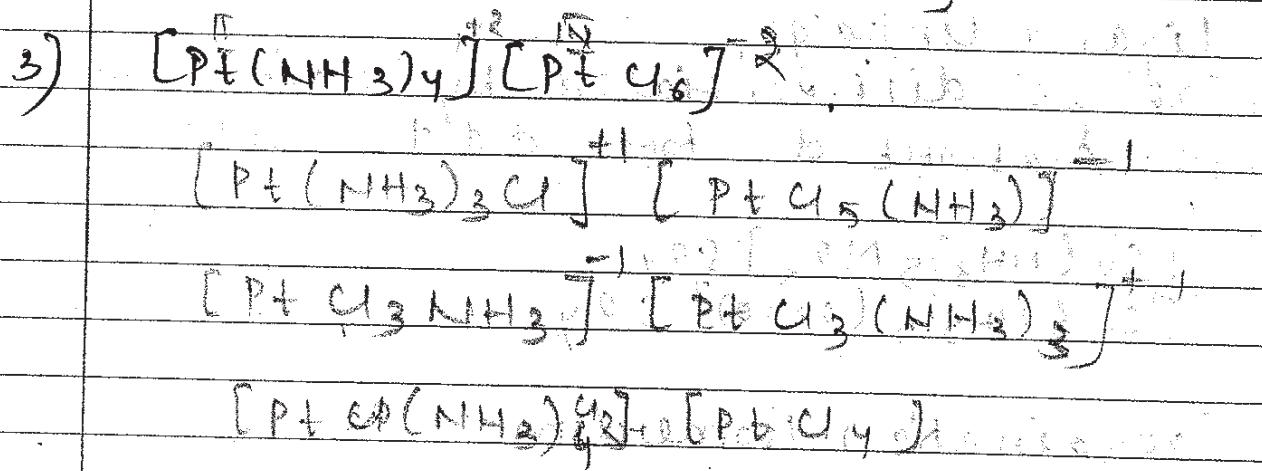
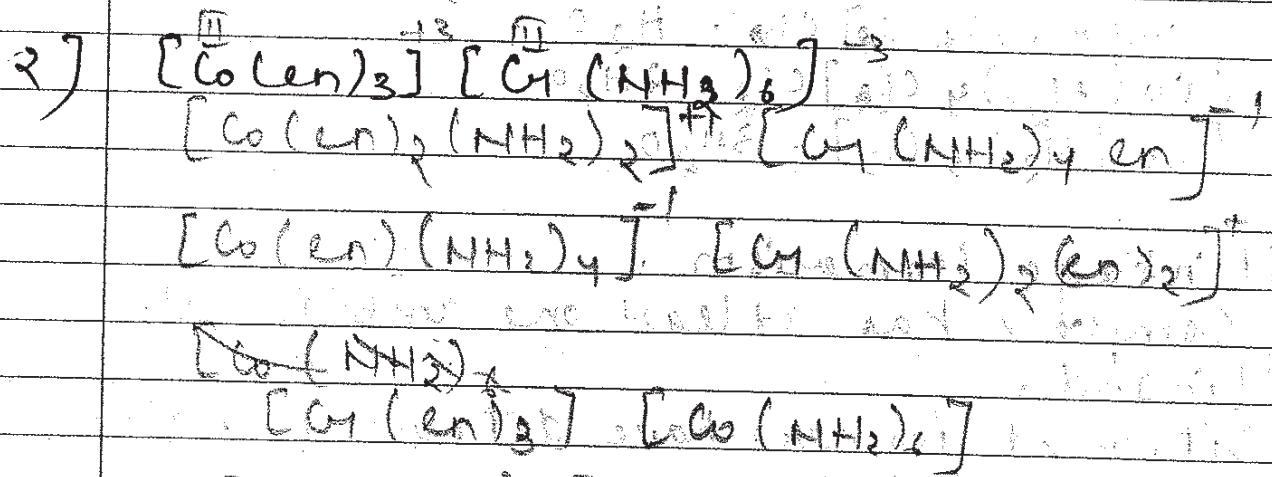
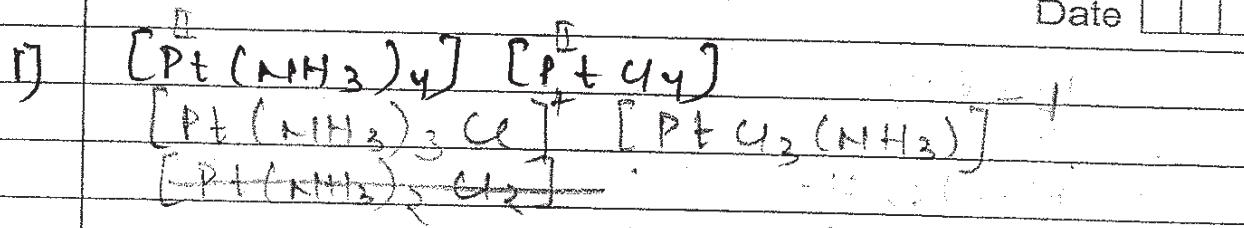
- Complex  $\alpha$  has at least one ambidentate ligand.
- Different isomers have different metal ligand linkage.
- Can be differentiated by their colours or absorbed by d-d transition.



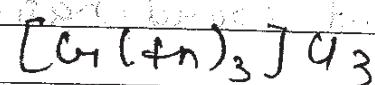
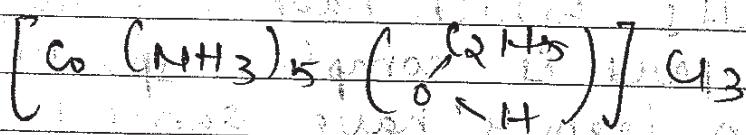
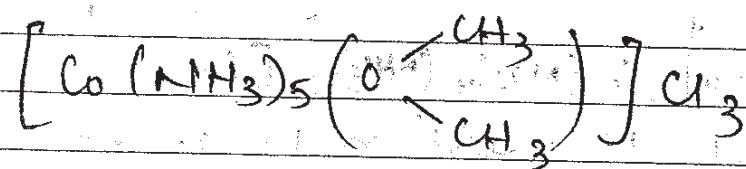
Coordination Isomerism

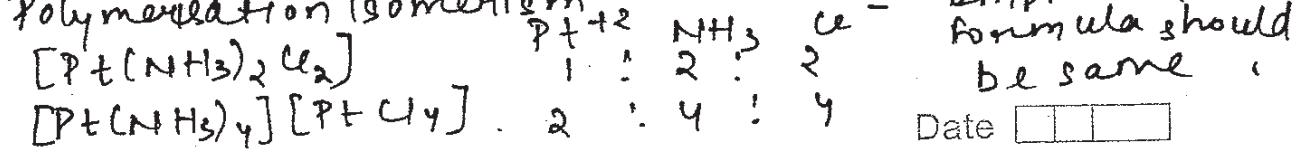


This type of isomerism is observed in complex salts which have cationic as well as anionic part of complex sphere. Coordination isomers have same N.F. but different coordination sphere.

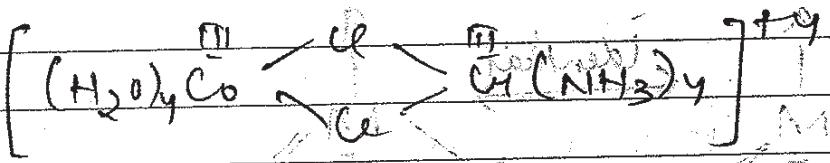
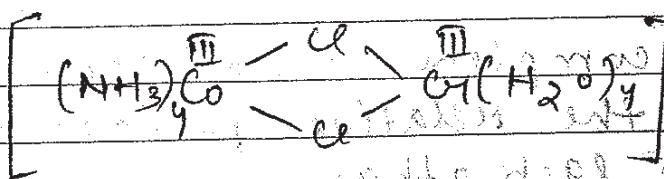


Ligand Isomerism  
 Isomeric complex in which ligands are present in their isomeric form



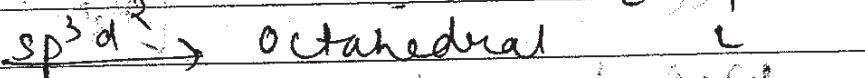
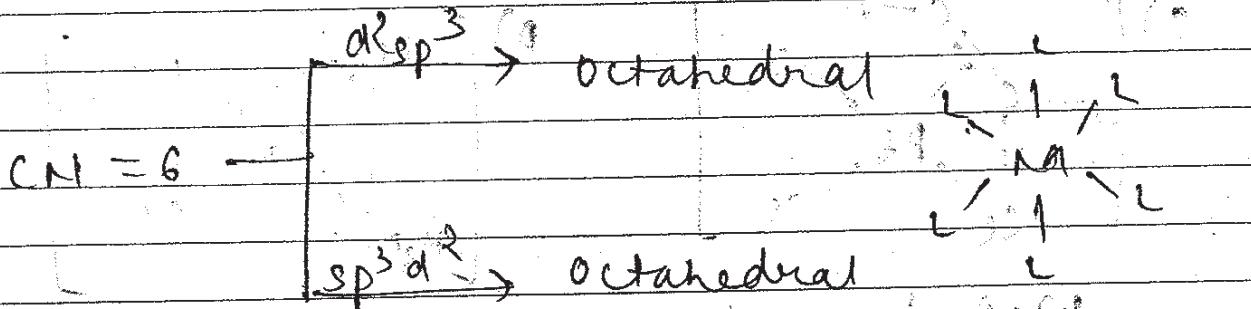
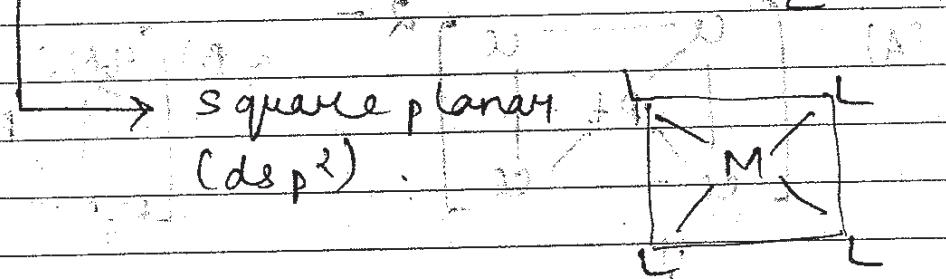
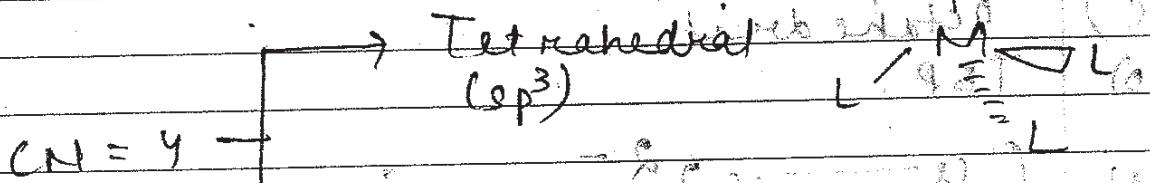


### 6) Coordination Position Isomerism



### Stereo Isomerism

Complex which have same Mf, same structural formula but different space orientation of ligands are called stereoisomers of each other.

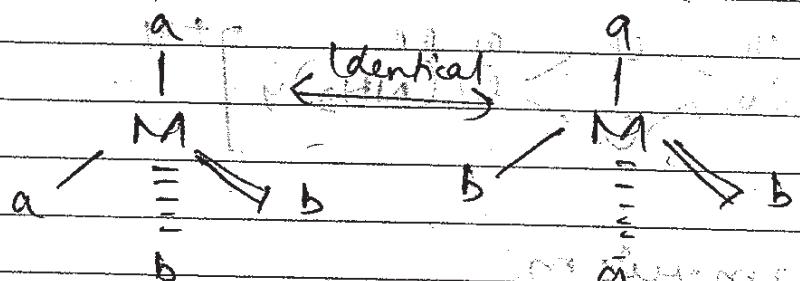


Complex which have same molecular formula, same structural formula but different relative position of ligands (axial distance) are called geometrical isomers

$$CN = 4$$

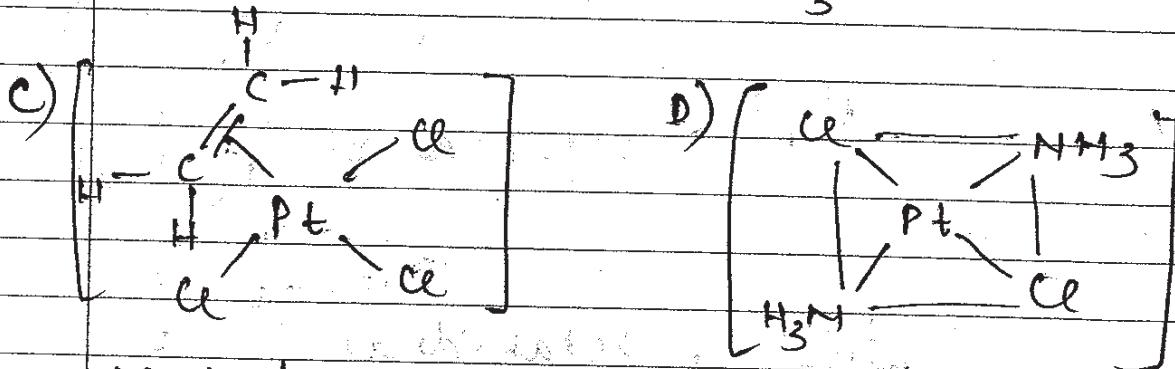
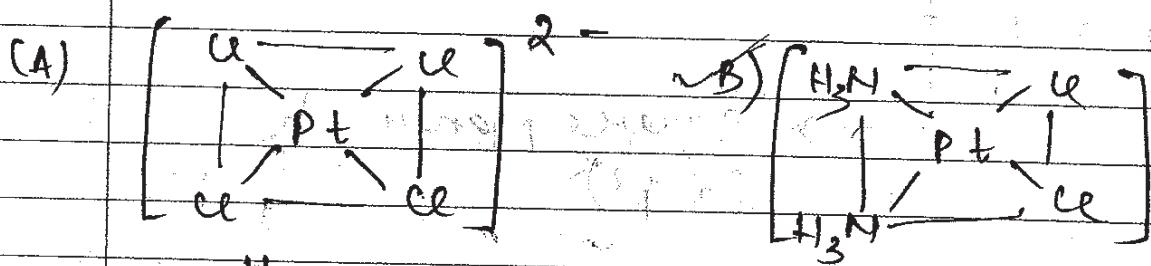
i) Tetrahedral

Tetrahedral complex do not show  $G_I$  because all the relative positions are identical to each other.



$[M(a_3 b)]$  does not show  $G_I$ . What is shape?

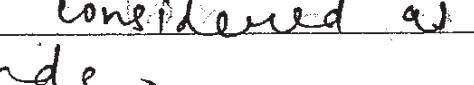
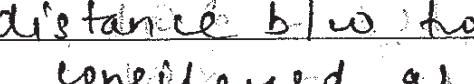
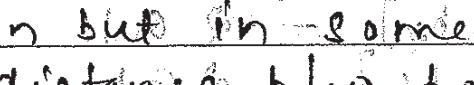
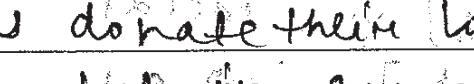
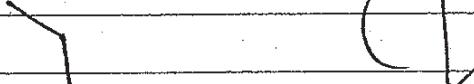
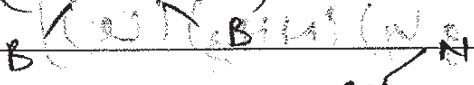
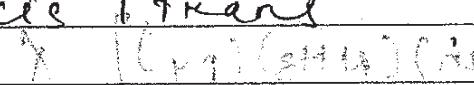
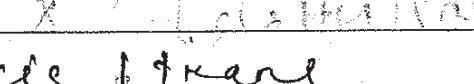
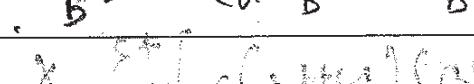
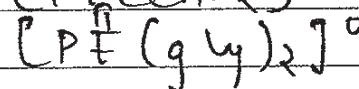
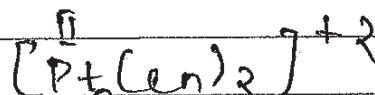
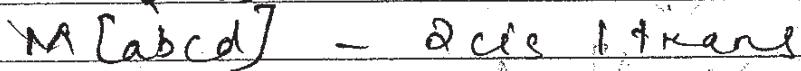
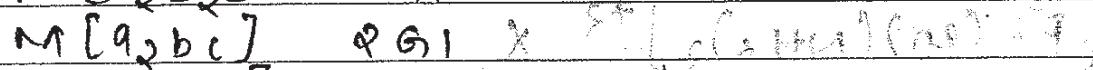
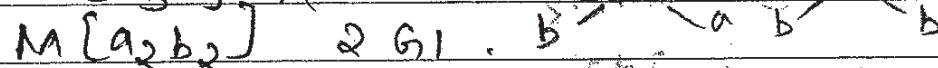
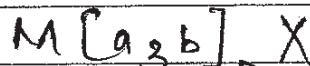
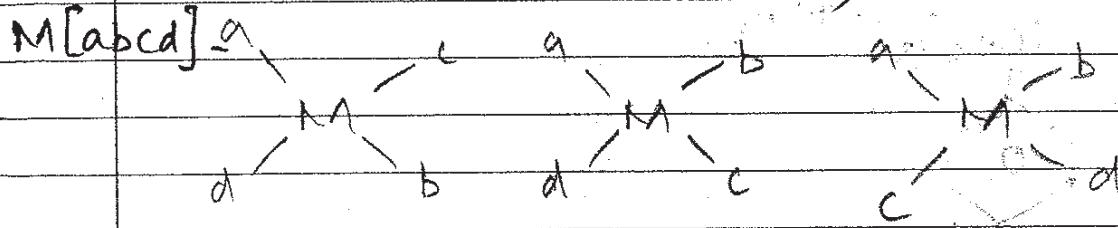
- (A) tetrahedral
- (B) sq. planar
- (C) octahedral
- (D) TBP



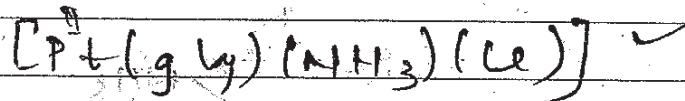
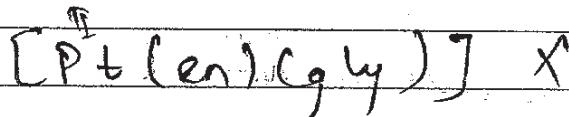
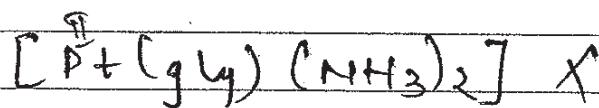
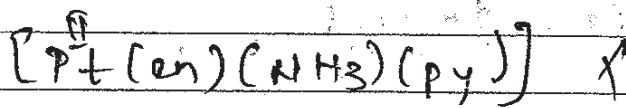
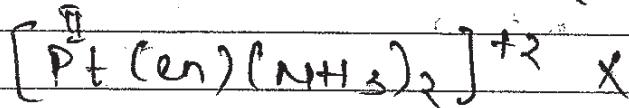
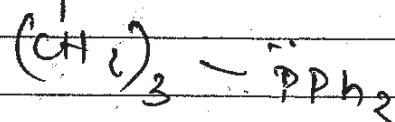
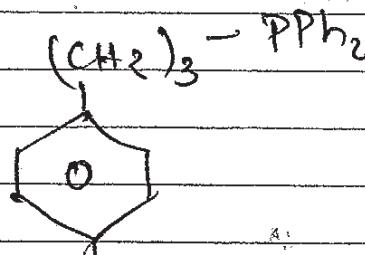
Wof is used as a antitumor agent!

$Pt^{+2}$ ,  $Pd^{+2}$ ,  $CN = 4$ , always produce square planar complex

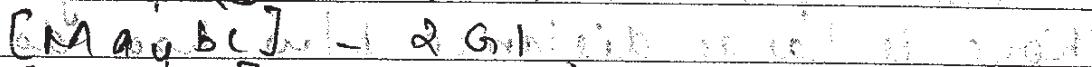
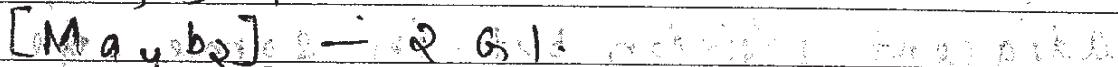
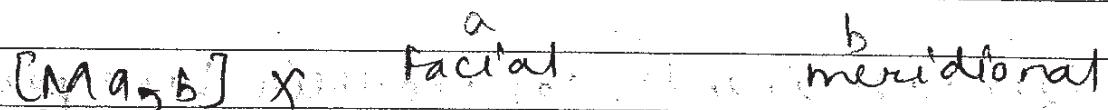
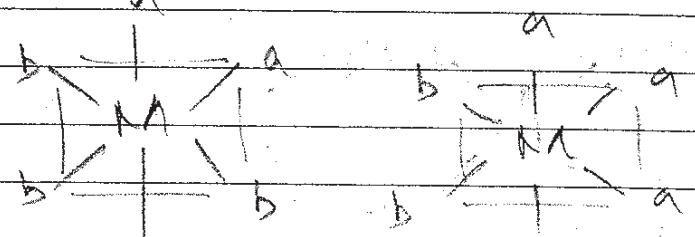
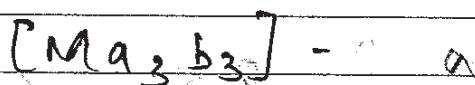
Stereoisomerism (Sq. Planar) (G1) Date [ ]

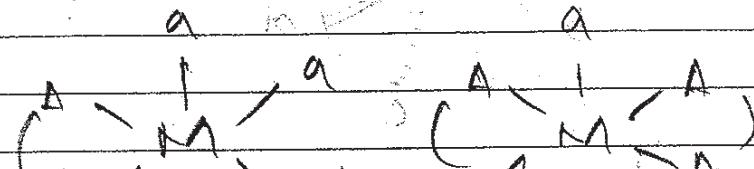
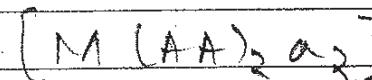
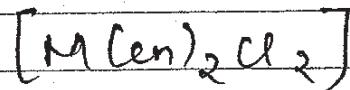


→ Bidentate ligands donate their lone pair on adjacent position but in some, e.g., there is large distance b/w donor sites. They are considered as trans-chelating ligands.

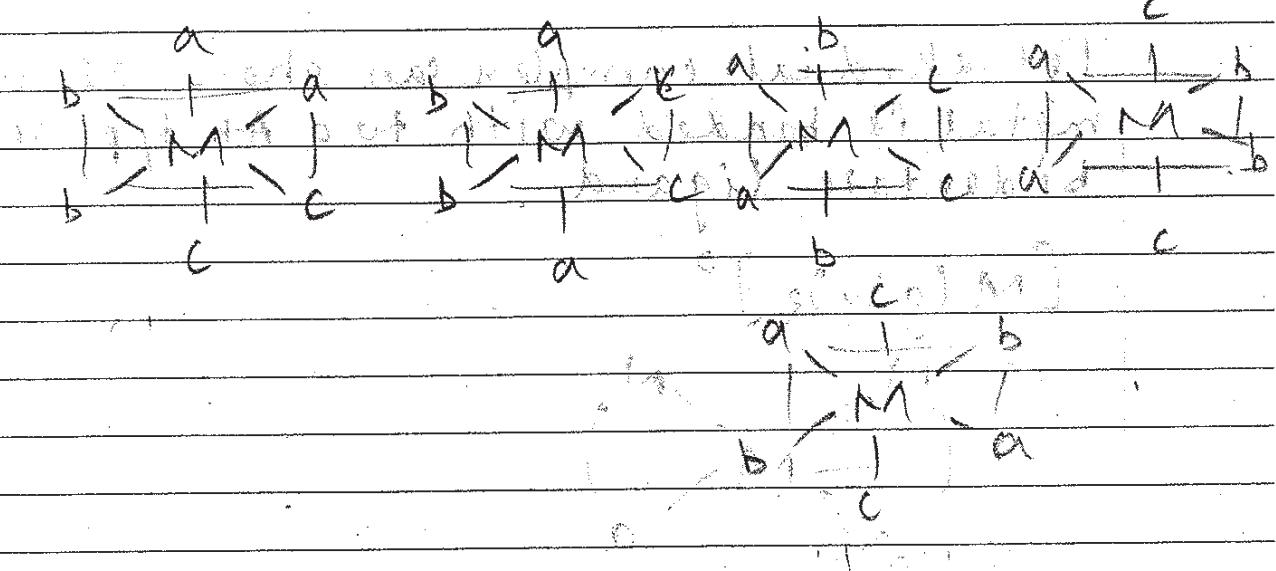
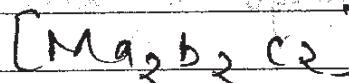


$\text{CM} = 8$   
(Octahedral)





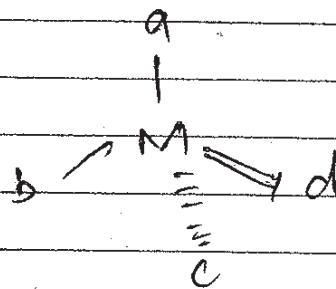
~~in 10 f. Water & Ethanol at 0° C  
possible with Thioacetone & a with the ligand  
extremely strong & no such effect due  
to C's with the same ligand  
but in acidic condition general effect is seen~~



Optical Isomerism: ~~is a phenomenon in which~~  
 Complex which have same molecular formula,  
 same structural formula and same  
 relative position but different behaviours  
 towards PPL, are called optical isomers  
 of each other.

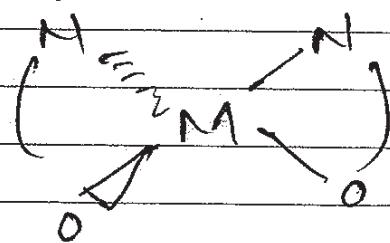
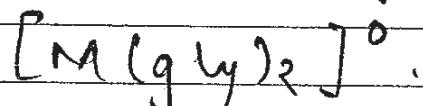
CN = 4

Tetrahedral -

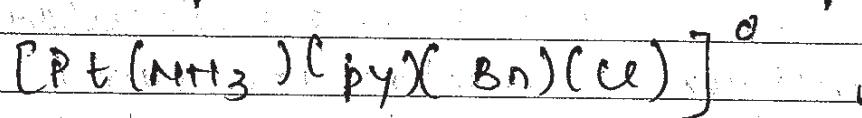


In tetrahedral complex, OI is possible when all the 4 ligands are different but this type of tetrahedral complexes are not stable because of their labile nature (undergo ligand exchange rxn)

Tetrahedral complex can show OI when metal is bonded with two AB type of bidentate ligand.



Q. Total possible GI & OI n-eep form



- Ans: 021 101 4  
 A) 1021 4  
 B) 012  
 C) 316  
 D) 310

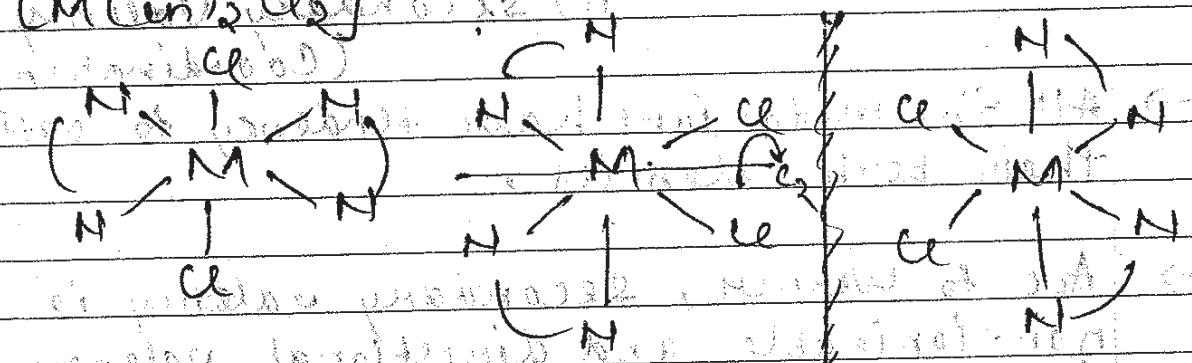
$\text{CN} = 4$  : Square Planar

Q1 is not possible for square planar complex because they have D<sub>2</sub>S but if ligand has chiral centre, then Q1 is possible  
 Ans -  $[PtCl_2(pn)]^0$

$CN = 6$  all Octahedral (six nearest) To right

(All photos)

$\text{CM}(\text{Cent}_2 \text{Cl}_2)$



69 =

ED =

$$S_{100} = 3.2 \text{ cm}^{-2} \text{ sr}^{-1} \text{ Hz}^{-1} \text{ mJy} [M_{95\%}]^{0.8} x$$

$$0 \text{ Active} = 9$$

0 Inactive =

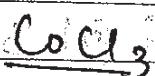
[May b<sub>2</sub>]. 2 Gt but

(or not)

# Theories of the formation of coordination compound.

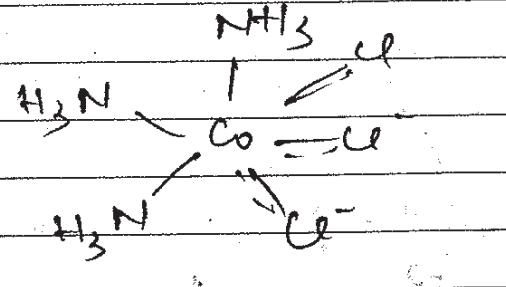
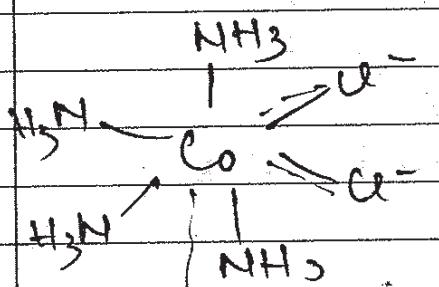
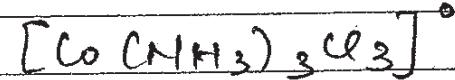
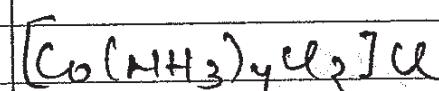
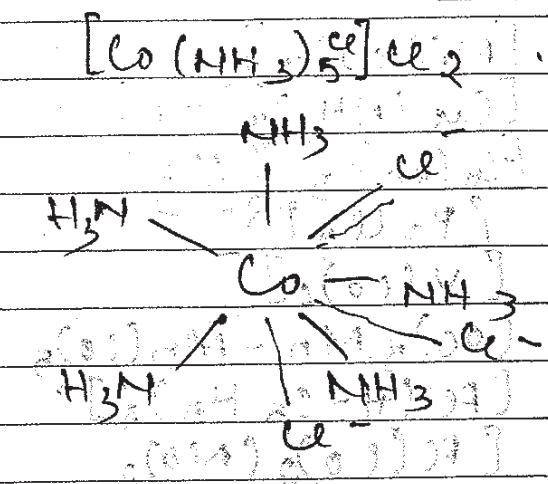
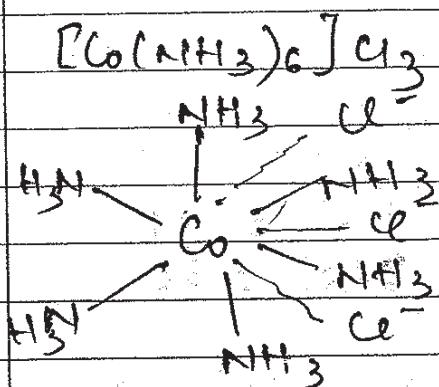
## i) Werner Theory.

- According to Werner, metal ions have 2 type of valencies i) Primary Valency (Co<sup>n</sup> No.)
- ii) Secondary Valency (Coordination No.)
- All the metal ions have tendency to satisfy their both valencies.
- Acc. to Werner, secondary valency is non-ionisable and directional valency (because he observed stereo isomerism in some coordination compounds).
- Primary valency is the ionisable valency.



100% in BP

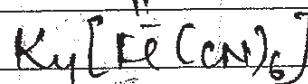
|    | $\text{CoCl}_3 \cdot 6\text{NH}_3$ | $\text{Rxn with AgNO}_3$ | Conductivity | Elevation              |
|----|------------------------------------|--------------------------|--------------|------------------------|
| 1) | $\text{CoCl}_3 \cdot 6\text{NH}_3$ | 3 mole AgCl.             | Excellent    | $\uparrow i = 4$       |
| 2) | $\text{CoCl}_3 \cdot 5\text{NH}_3$ | 2 mole AgCl              | Moderate     | $\uparrow i = 3$       |
| 3) | $\text{CoCl}_3 \cdot 4\text{NH}_3$ | 1 u                      | "            | poor. $\uparrow i = 2$ |
| 4) | $\text{CoCl}_3 \cdot 3\text{NH}_3$ | x                        | x            | $\uparrow i = 1$       |



Limitations  $\Rightarrow$

$\rightarrow$  Werner's theory does not explain colouration, magnetic nature, shape and relative stability of complex salts.

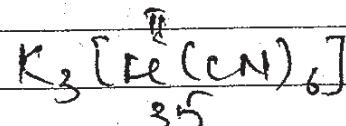
## 2) EAN ( Sidgewick Effective Atomic Number Theory )



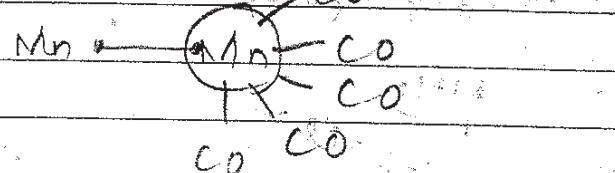
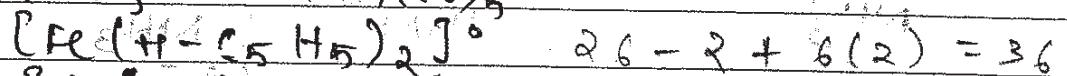
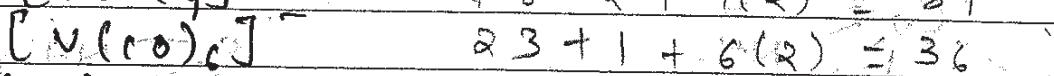
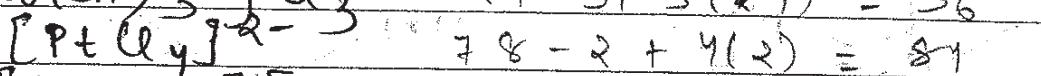
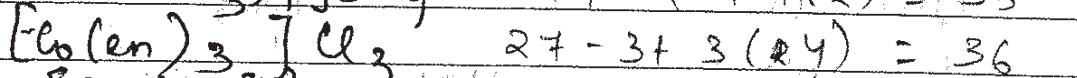
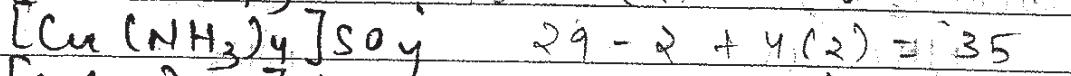
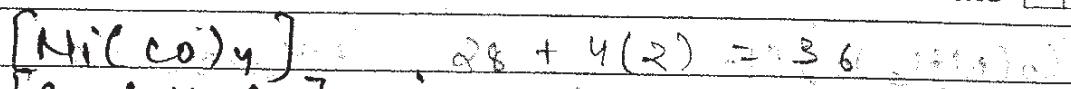
26  
- 2

24  
12

$$\text{EAN} = 36 \text{ (K1)}$$



35

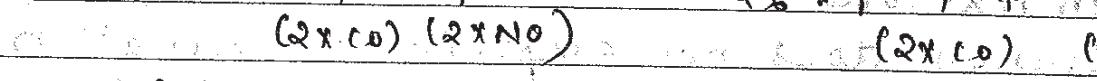


$$25 + 10 + 1 = 36$$

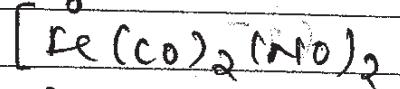
$$9 + 2 = 11 \quad 9 + 8 = 17$$



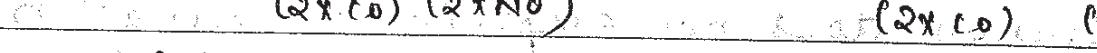
$$26 + 2 + 4 + 4$$



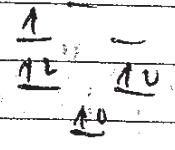
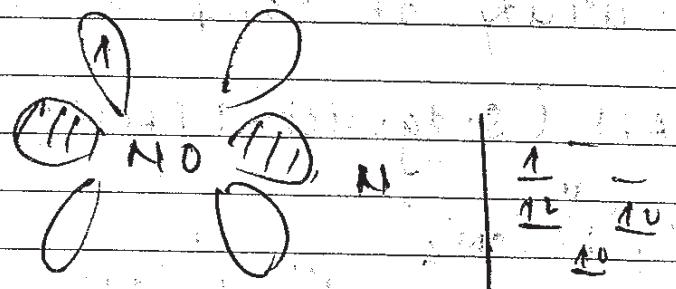
$$= 36$$



$$26 + 4 + 4 + 6$$



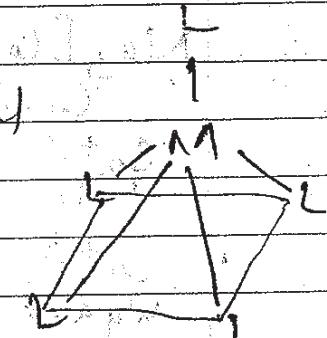
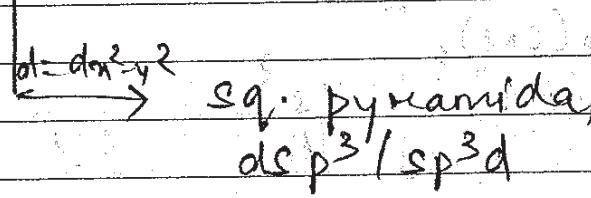
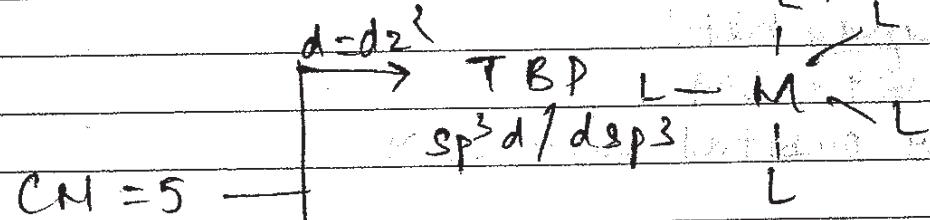
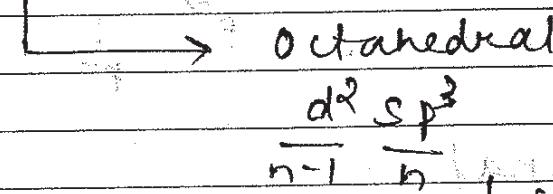
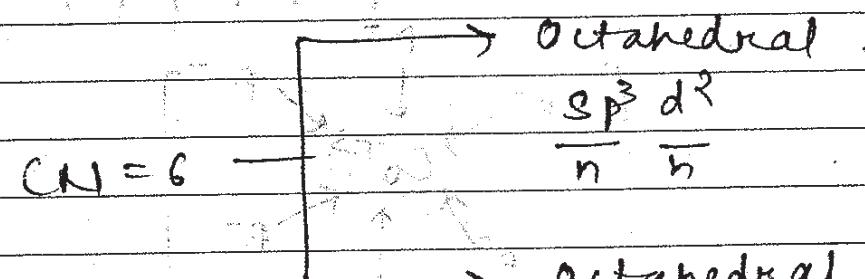
$$= 36$$

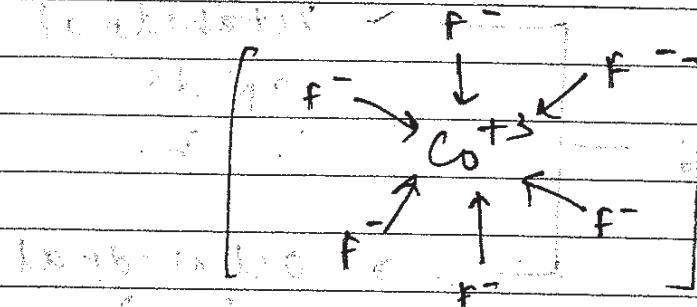
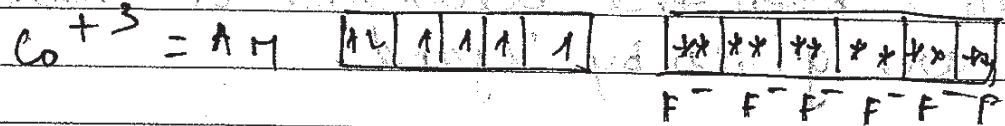
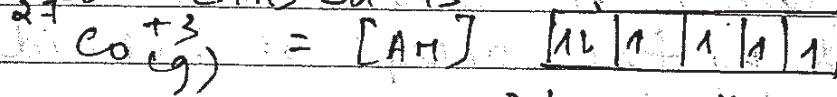
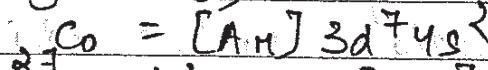


VBT (Valence Bond Theory)

→ VBT explained formation of coordination compound by the concept of hybridisation and overlapping.

→ In complex formation, central metal use its vacant orbitals for hybridisation because both the electrons of shared pair are given by ligand.



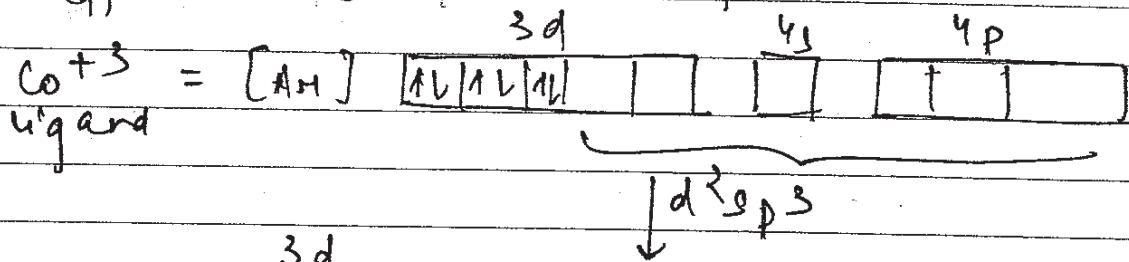
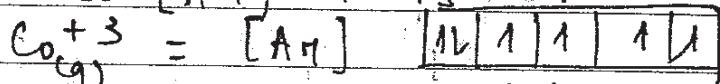
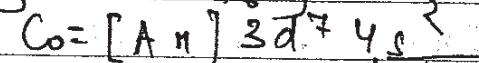
1)  $\text{Na}_3[\text{CoF}_6]$  $\Rightarrow \text{sp}^3 \text{d}^2$ 

→ Octahedral

→ Paramagnetic

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

→ Outer orbital complex

2)  $\text{Na}_3[\text{Co}(\text{CN})_6]$ 

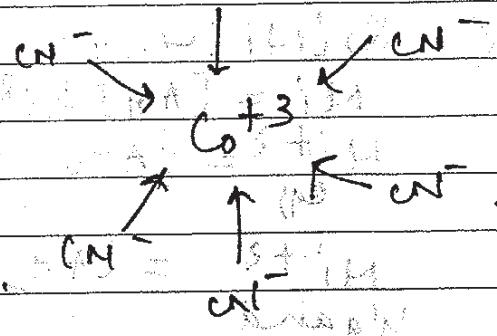
3d



Grate

- d<sup>3</sup>sp<sup>3</sup>
- Octahedral
- D<sub>4h</sub>
- H<sub>2</sub>O

→ Inner Orbital Complex.



Strong FL - CN<sup>-</sup>, CH<sub>3</sub><sup>-</sup>, CO, NO<sub>2</sub><sup>-</sup> etc

Weak FL - F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, H<sub>2</sub>O<sup>0</sup>, OH<sup>-</sup>, SCN<sup>-</sup>, ONO<sup>-</sup>.

Ni<sup>2+</sup> → +2 (weak)

Ni<sup>3+</sup> → +3 (strong)

3) K<sub>2</sub>[NiCl<sub>6</sub>]

Ni = [Ar] 3d<sup>8</sup> 4s<sup>2</sup> 3d<sup>8</sup>

Ni<sup>+2</sup> = [Ar] 1L 1L 1L 1 1  
(g)

Ni<sup>+3</sup> = [Ar] 1L 1L 1L 1 1

Ligand

Ni<sup>+3</sup> = [Ar] 1L 1L 1L 1 1 | 4x sp<sup>3</sup> sp<sup>3</sup> sp<sup>3</sup> sp<sup>3</sup> sp<sup>3</sup>

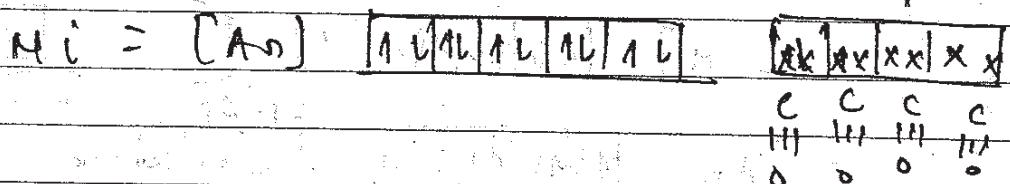
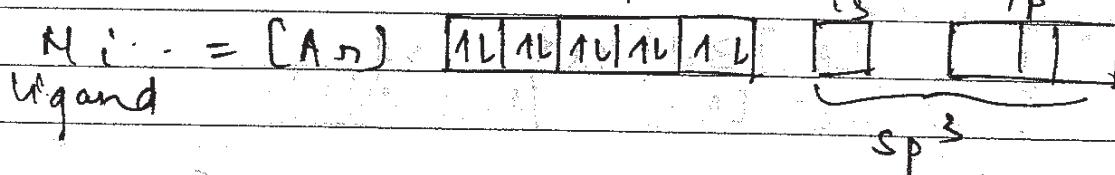
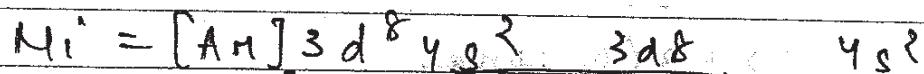
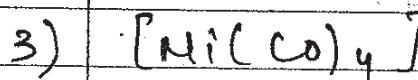
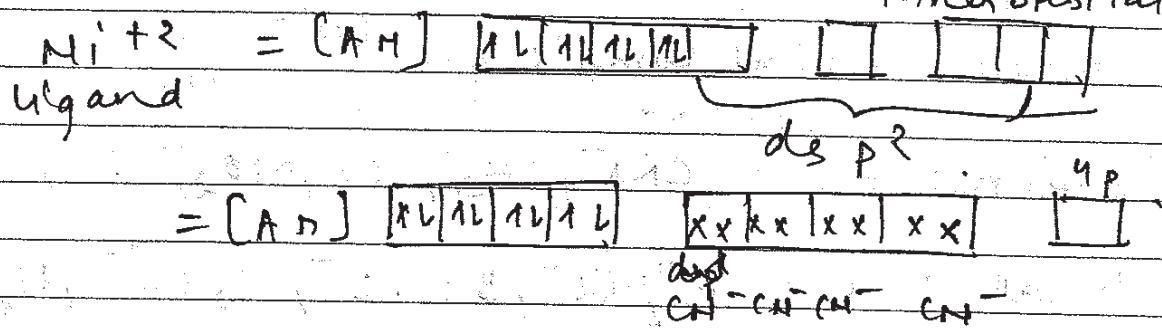
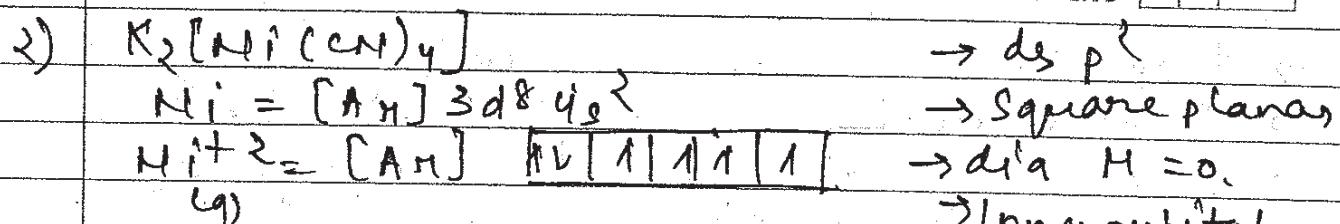
→ sp<sup>3</sup>

2) Tetrahedral

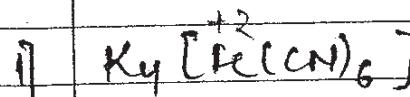
para

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

Date



- $sp^3$
- tetrahedral
- $d^0$
- $\mu = 0$



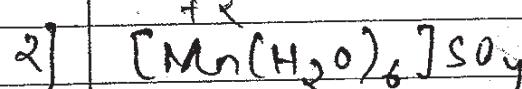
Fe:  $3d^6 4s^2$ ,  $[1\bar{1}\bar{1}1\bar{1}1\bar{1}]$

$\text{Fe}^{+2} = [1\bar{1}\bar{1}1\bar{1}1]$

$\text{Hyb} = d^2 s p^3$ .

DIA

Octahedral      Inner orbital     $M = 0$



Mn:  $3d^5 4s^2$

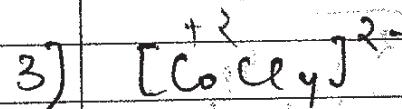
$\text{Mn}^{+2} = [\bar{1}\bar{1}\bar{1}1\bar{1}1]$

$\text{Hyb} = s p^3 d^2$ .

Para

Outer orbital

$$M = \sqrt{5 \times 7} = \sqrt{35}$$



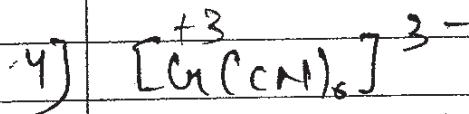
Co:  $3d^7 4s^2$

$\text{Co}^{+2} = [1\bar{1}\bar{1}1\bar{1}1]$

$\text{Hyb} = s p^3$

Tetrahedral

$$\text{Para} \quad M = \sqrt{3 \times 5} = \sqrt{15}$$



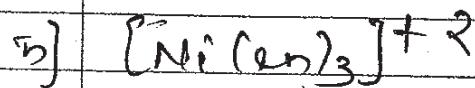
Cr:  $3d^5 4s^1$

$\text{Cr}^{+3} = [1\bar{1}\bar{1}1\bar{1}]$

$\text{Hyb} = d^2 s p^3$

Octahedral

$$\text{Para} \quad M = \sqrt{3 \times 5} = \sqrt{15}$$

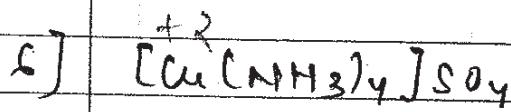


$\text{Ni} : 3d^8 4s^2$

$\text{Ni}^{+2} : \boxed{1L|1U|1L|1|1} \quad \boxed{\phantom{0}} \quad \boxed{\phantom{0}}$

$sp^3 d^2$

Outer  $M = \sqrt{8}$



$\text{Cu} : 3d^{10} 4s^1$

$\text{Cu}^{+2} : \boxed{1L|1U|1L|1L} \quad \cancel{\boxed{\phantom{0}}} \quad \cancel{\boxed{\phantom{0}}} \quad \cancel{\boxed{\phantom{0}}} \quad \cancel{\boxed{\phantom{0}}}$

$sp^3 \quad M = \sqrt{3} \quad \text{Para}$

$\text{Cu}^{+2}_{eq} = [\text{AM}] \quad \boxed{1L|1L|1L|1L|1}$

$\text{Cu}^{+2} = [\text{AM}] \quad \boxed{1L|1L|1L|1L} \quad \underbrace{\boxed{\phantom{0}} \quad \boxed{\phantom{0}} \quad \boxed{\phantom{0}}}_{\text{d}sp^2} \quad \boxed{11}$

$\text{Cu}^{+2} = [\text{AM}] \quad \boxed{1L|1L|1L|1L} \quad \boxed{xx|xx|xx|x} \quad \boxed{1}$

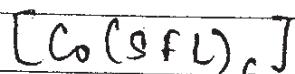
$dsp^2$

Sq. Planar

Para

$$M = \sqrt{3} BM$$

Inner Orbital



$$M = \sqrt{3} BM$$

$\text{Co}^{+2} = [\text{AM}] \quad \boxed{1L|1U|1L|1|1}$

$\text{Co}^{+2} = [\text{AM}] \quad \boxed{1L|1L|1L|1} \quad \underbrace{\boxed{\phantom{0}} \quad \boxed{\phantom{0}} \quad \boxed{\phantom{0}}}_{\downarrow d^2 sp^3} \quad \boxed{1111}$

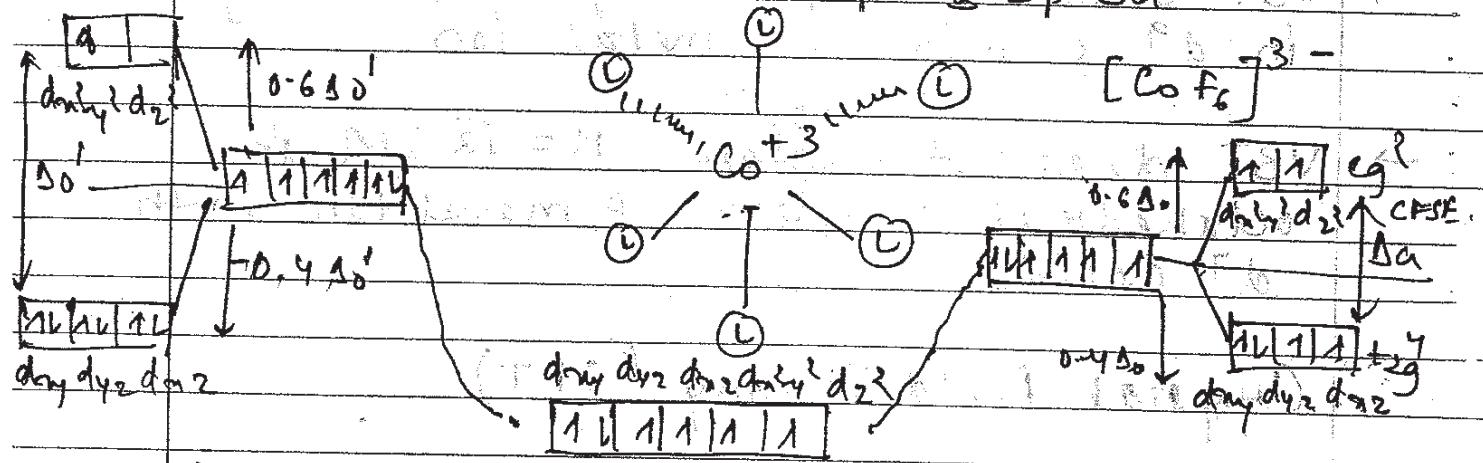
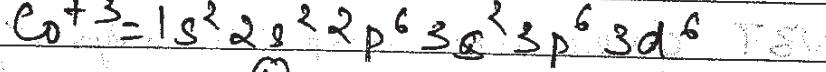
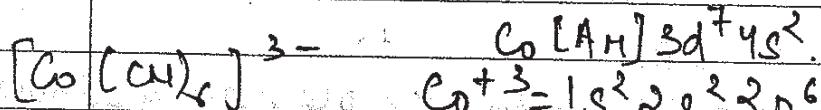
### Limitations of VBT:

- VBT does not explain back pairing, colouration, relative strength of ligand and stability of coordination compounds.
- VBT does not <sup>justify</sup> explain square planar geometry in  $d^9$  config. of metal ion.
- VBT does not <sup>justify</sup> explain  $M = \sqrt{3} BM$  in octahedral complex of metal ion with  $d^7$  config.

### Crystal Field Theory (CFT)

- CFT consider pure coulombic force b/w metal and ligand.
- Acc. to CFT, metal ion is point positive charge, anionic ligands are point negative charge and neutral ligands are considered as point dipoles.
- Acc. to CFT, when suitable no. of ligands approach towards central atom ion, valence shell d orbitals of metal ion lose their degeneracy and splitted to subenergy levels. For eg.  $t_{2g}$  and  $e_g$  in octahedral.
- RF Energy difference b/w splitted orbitals is called Crystal Field Splitting Energy (CFSE).
- CFT explain back pairing in coordination compound by considering CFSE and PE.

Date: \_\_\_\_\_



Octahedral

$$D_{\text{fa}}, M=0$$

low spin

$$t_{2g}^3 e_g^0 \\ (\Delta_g' > \Delta_{\text{PE}})$$

Octahedral

$$\text{Para } M = \sqrt{2}/4 \text{ BM}$$

high spin

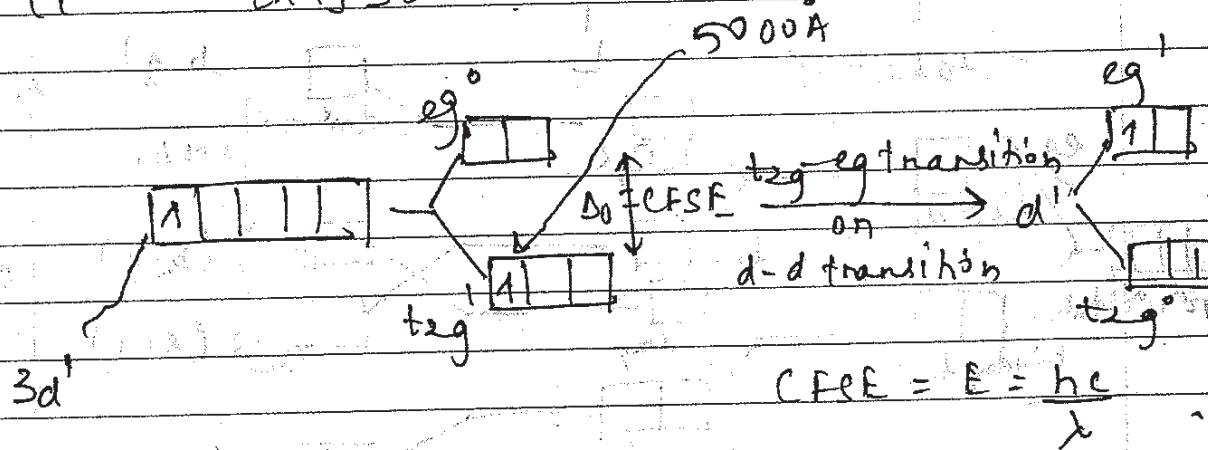
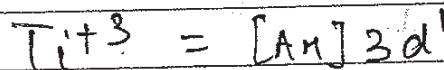
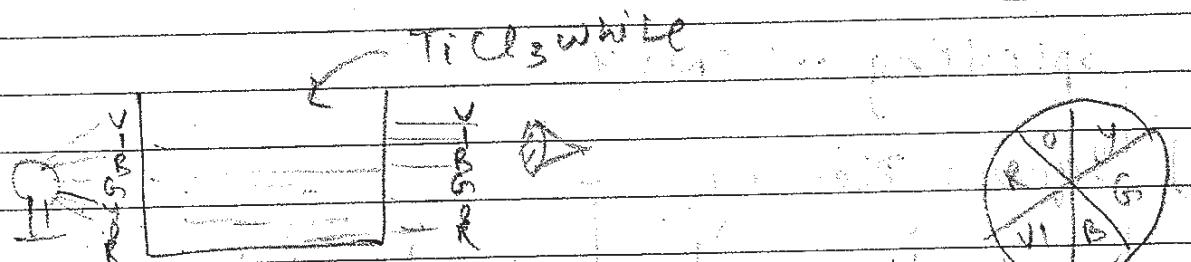
$$t_{2g}^4 e_g^2 (\Delta_g < \text{PE})$$

low spin

$$\begin{array}{ll} t_{2g}^3 e_g^0 & d^4 \\ t_{2g}^5 e_g^0 & d^5 \\ t_{2g}^6 e_g^0 & d^6 \\ t_{2g}^8 e_g^1 & d^7 \end{array}$$

high spin

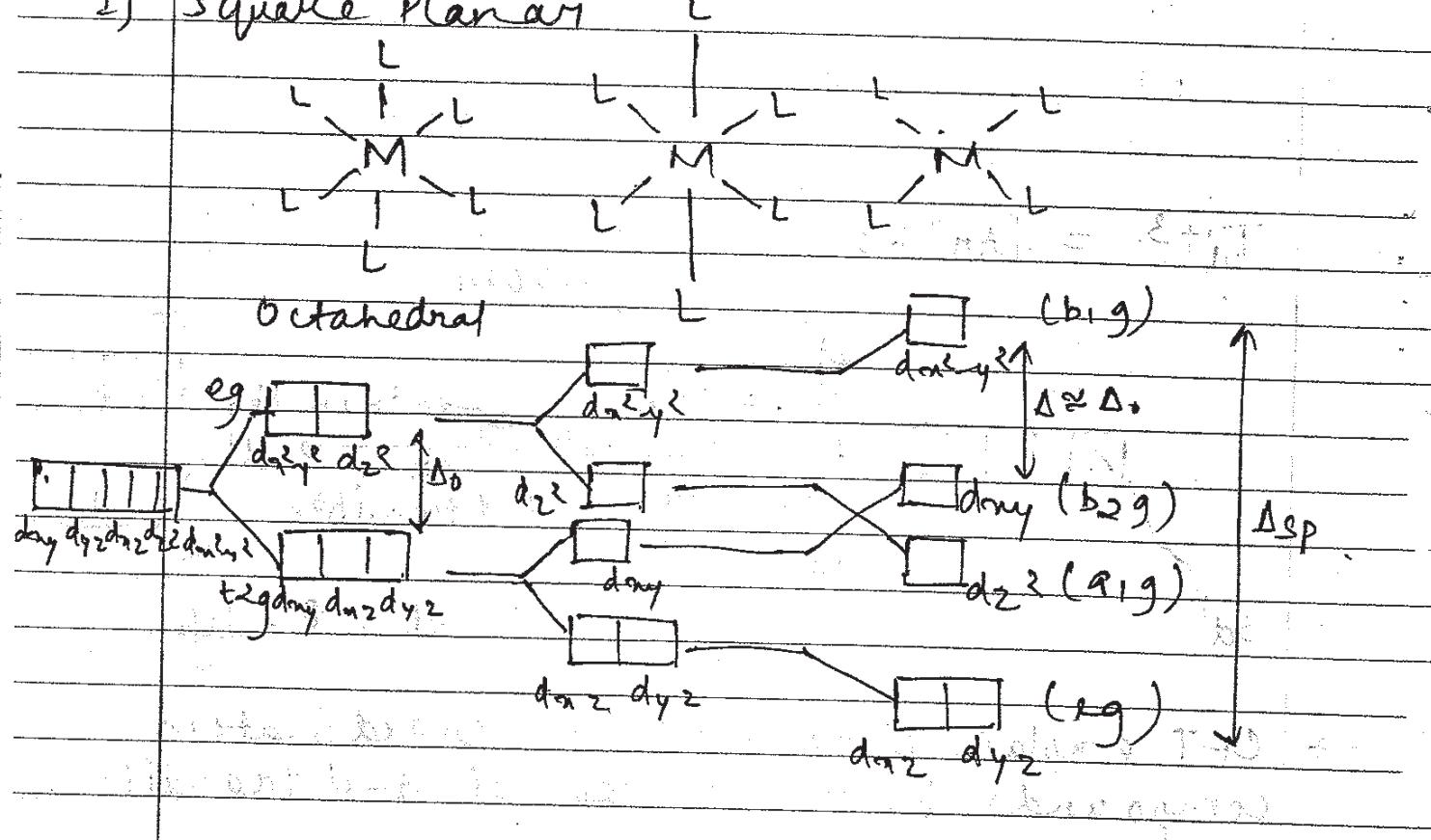
$$\begin{array}{ll} t_{2g}^3 e_g^1 & \\ t_{2g}^3 e_g^2 & \\ t_{2g}^4 e_g^2 & \\ t_{2g}^5 e_g^2 & \end{array}$$



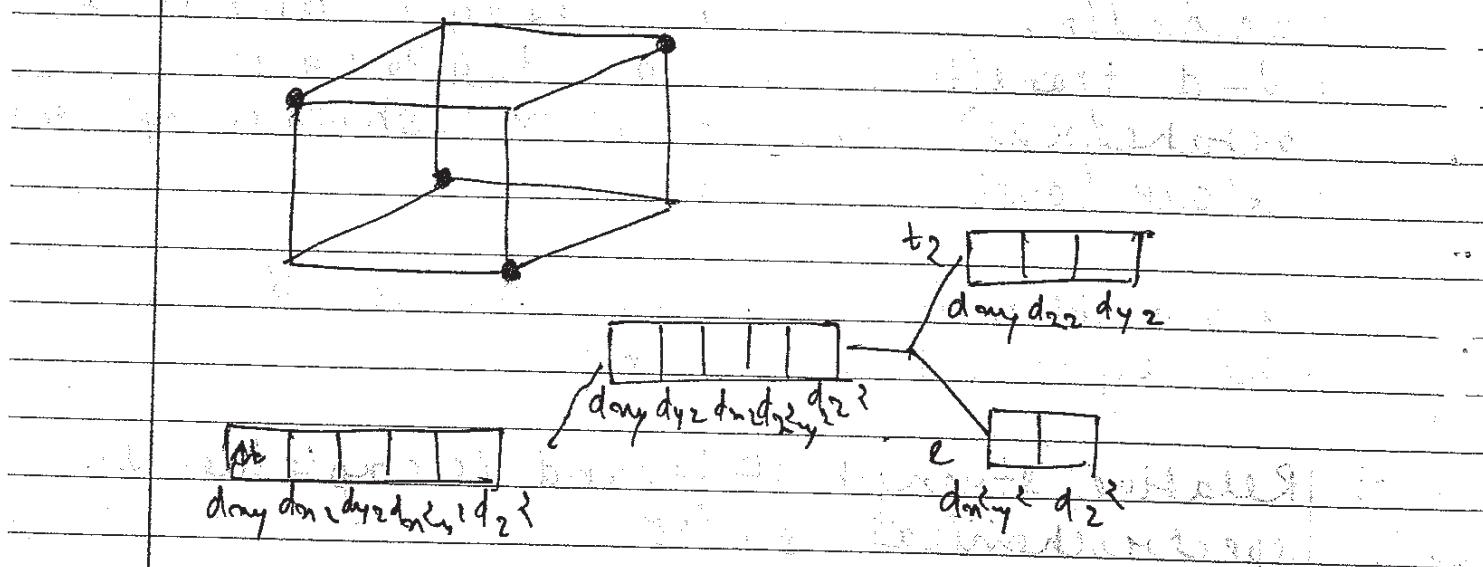
- CFT explain colouration in coordination compounds by the concept of d-d transition.
- Complex absorb suitable visible light according to splitting energy and show d-d transition (for eg - t<sub>2g</sub> to eg in octahedral) and complex show complementary colour (observed colour).
- Colouration in coordination compounds is the eg of absorption spectra.
- Relative strength of ligand is explained by spectrochemical series.
- Ligands which cause large value of  $\Delta_o$  are considered as strong field ligand.

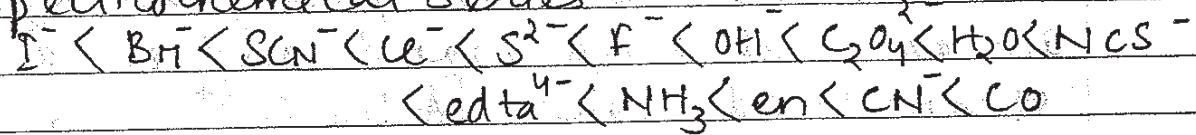
Splitting in CN = 4

I) Square Planar

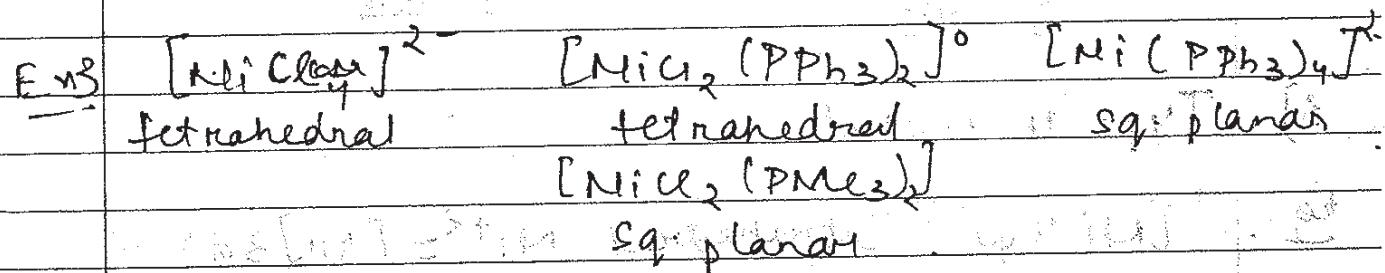
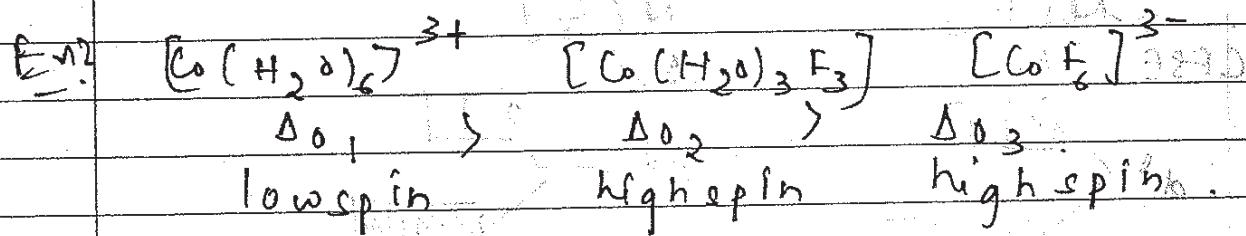
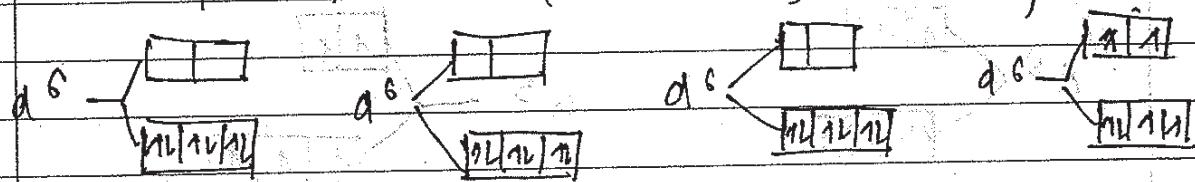
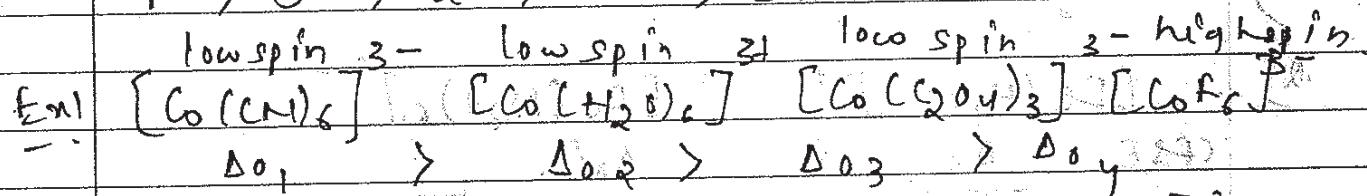
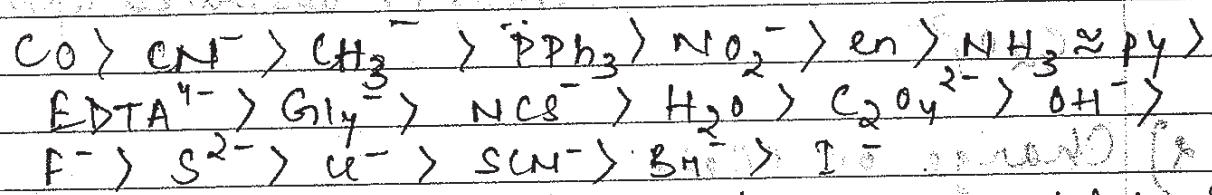


II) Tetrahedral



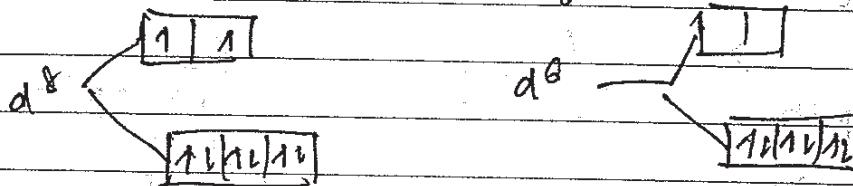
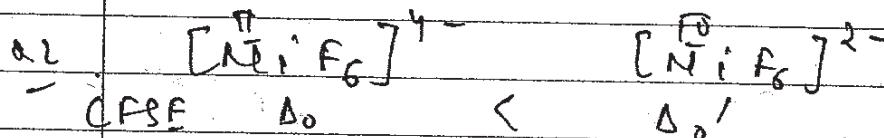
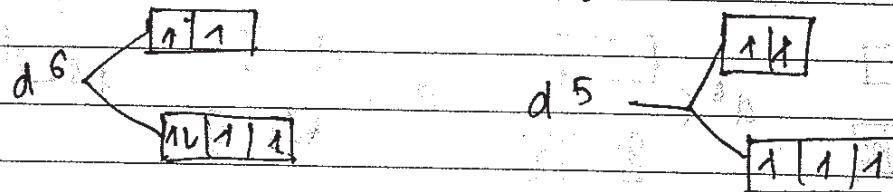
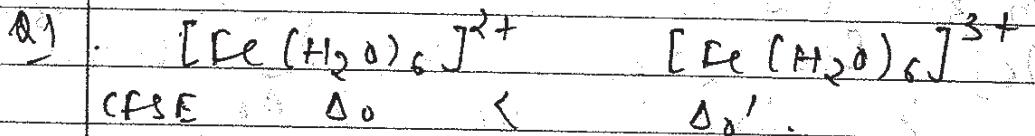
Spectrochemical Series -Factors affecting CFSE -

## 1) Type of Ligand



- Form +2 ions of 3d series,  $\text{NH}_3$  and  $\text{H}_2\text{O}$   
 Act as weak field ligand and can act as strong field ligand. [After  $\text{Co}^{2+}$ ,  $\text{NH}_3$  becomes strong ligand]
- Form +3 ions of 3d series  $\text{NH}_3$  act as SFL but  $\text{H}_2\text{O}$  act as WFL but in case of  $\text{Co}^{3+}$ , back pairing is observed upto  $\text{C}_2\text{O}_4^{2-}$ .

### 2) Charge on Metal

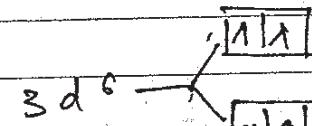
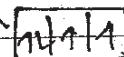
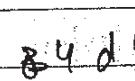
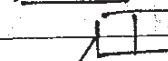
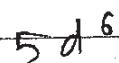
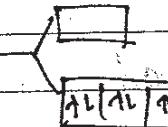


### 3) Type of Metal

Eg:  $[\text{Ni}(\text{Cl}_4)]^{2-}$  Tetrahedral  $\text{Ni}^{+2} = [\text{Ar}] 3d^8$ .

$[\text{Pd}(\text{Cl}_4)]^{2-}$  Sq. Planar  $\text{Pd}^{+2} = [\text{Kr}] 4d^8$

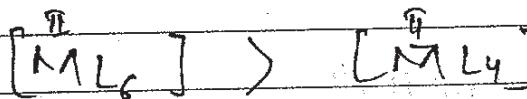
$[\text{Pt}(\text{Cl}_4)]^{2-}$  Sq. Planar  $\text{Pt}^{+2} = [\text{Xe}] 4f^{19} 5d^8$

$\text{Eg}^2$ High spin  $[\text{CoF}_6]^{3-}$  $\Delta_{\text{o}}^1$ Low spin  $[\text{CrF}_6]^{3-}$  $\Delta_{\text{o}}^2$ Low spin  $[\text{InF}_6]^{3-}$  $\Delta_{\text{o}}^3$ 

## 4) Type of geometry



$$( \Delta_{\text{sp}} = 1.33 \Delta_{\text{o}} )$$

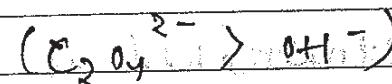


Octahedral

Tetrahedral

$$\Delta_t = \frac{4}{9} \Delta_{\text{o}}$$

## 5) Chelation

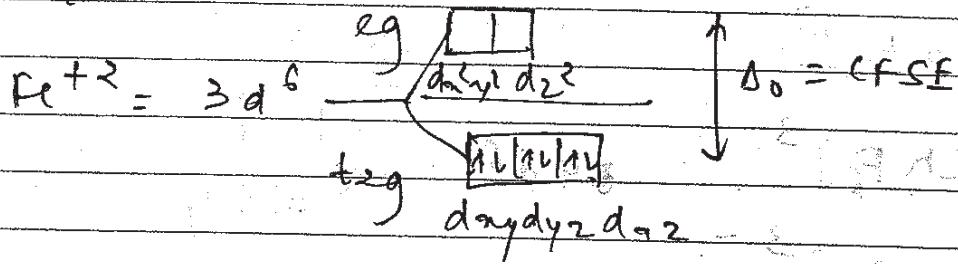


★

## 6) Synergic Bonding

Ligand which show synergic bonding behave as SFL because they approach more close towards  $\text{CM}^+$  and it is explained by MOT.

1)  $K_3[Fe(CN)_6]$   
yellow



Octahedral

D<sub>1</sub>a $M = 0$ 

(CFSE) PE

 $t_{2g}^6 eg^0$ 

low spin

coloured

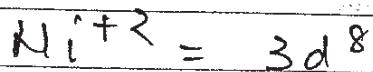
d<sub>2g</sub>p<sub>3</sub>

inner orbital octa complex

$$CFStabilization = (-0.4\Delta_o \times 6) + 2PE$$

$$= -2.4\Delta_o + 2PE$$

2)

 $[NiCl_4]^{2-}$ 

tetrahedral

para

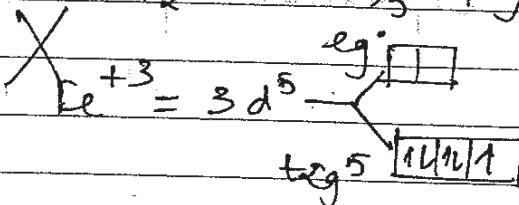
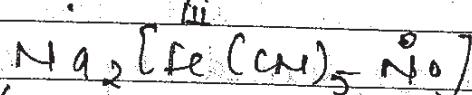
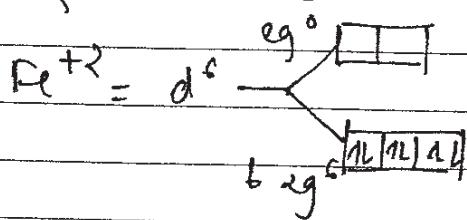
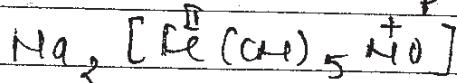
 $M = t_8 BM$ 

CFSE &lt; PE

 $e^4 t_2^1$  sp<sup>3</sup>

Coloured

Sodium Nitrocyanide

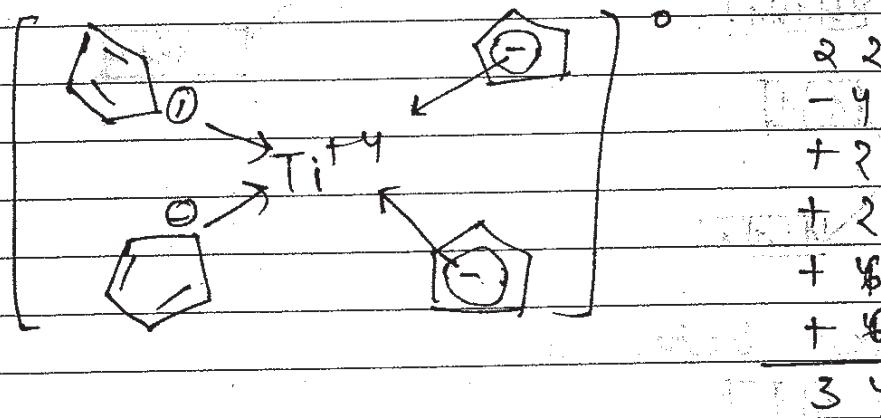
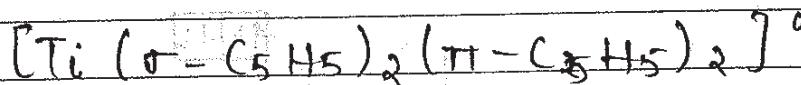
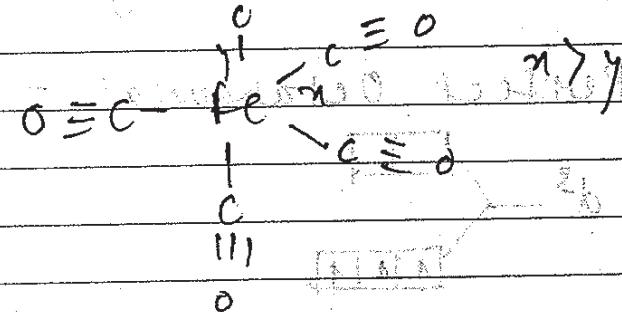


$\text{Fe} = [\text{Ar}] 3d^6 4s^2$

$\text{Fe} = [\text{Ar}] \quad 1\ 1\ 1\ 1\ 1\ 1\ 1$

$d_{sp^3}$  hybridization

$xx \quad xx \quad xx \quad | \quad xx \quad xx$  next

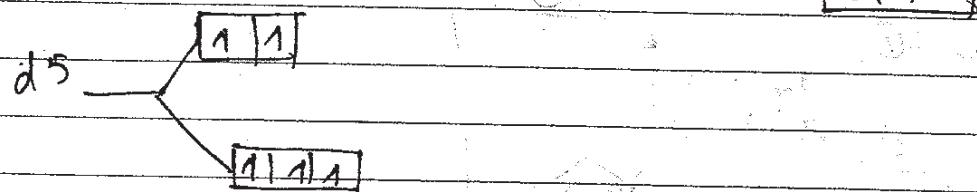
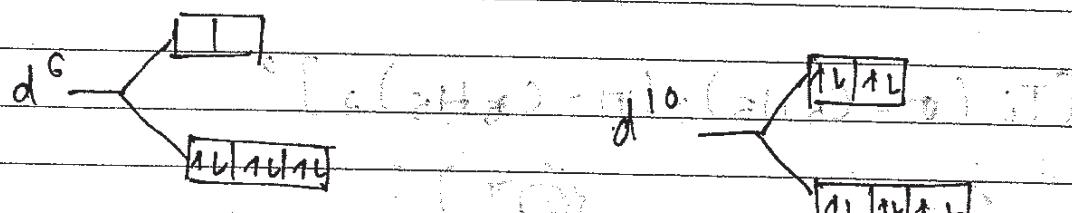
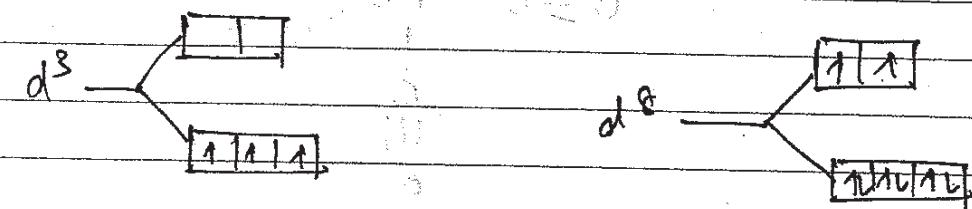


bis( $\eta^5$ -cyclopentadienyl)bis( $\eta^5$ -cyclopentadienyl)  
titanium(IV)

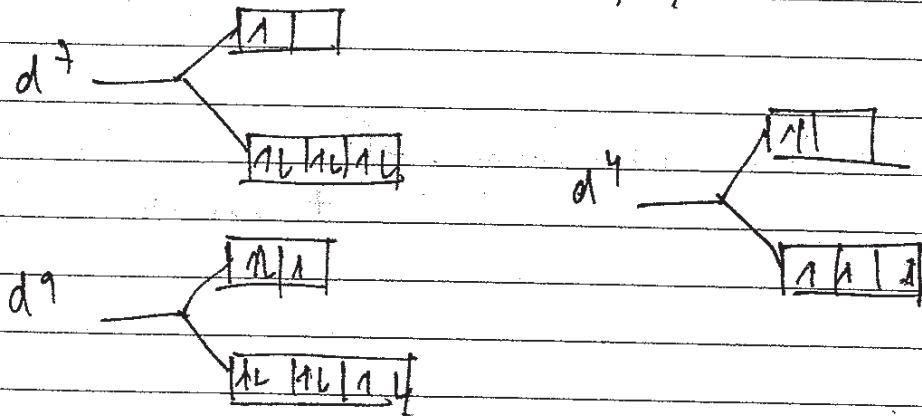
According to Jahn-Teller distortion if electronic distribution is unsymmetric in eg orbitals (Octahedral complex) then significant distortion is observed in geometry.

Slightly distorted octahedron is formed when electronic distribution is not symmetric in t<sub>2g</sub> orbitals.

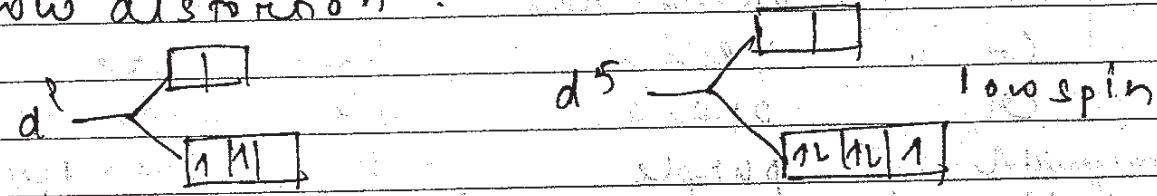
Perfect Octahedral -



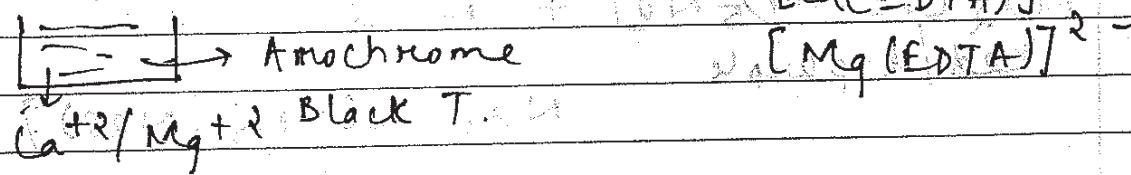
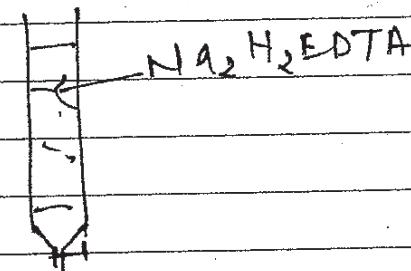
Distorted Octahedron



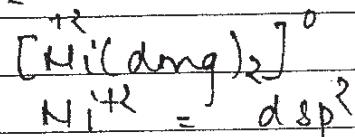
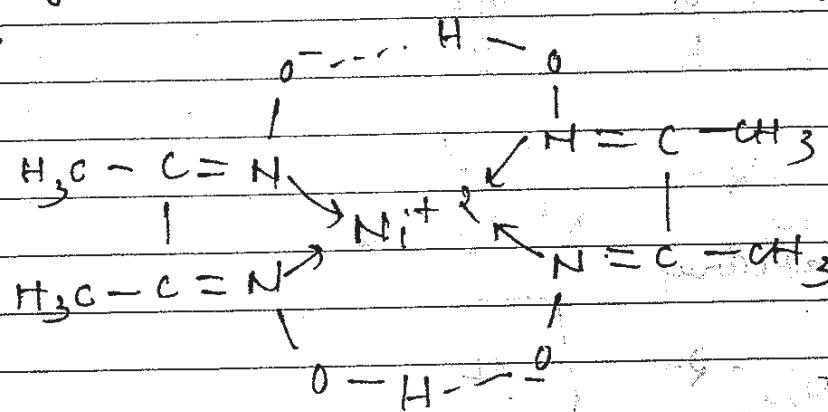
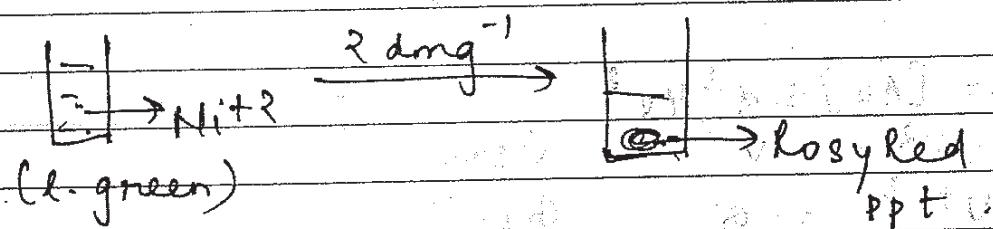
low distortion



Hardness of water is estimated by complexometric titration using  $\text{EDTA}^{4-}$

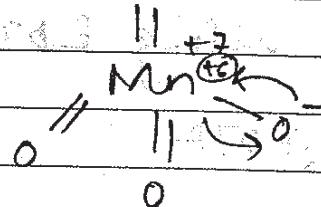


Wilkinson catalyst -  $[\text{RhCl}(\text{PPh}_3)_3]$



Square Planar

|   |            |   |
|---|------------|---|
| $\text{CrO}_2\text{Cl}_2$               | Orange red | they all are<br>coloured due to<br>charge transfer<br>(L $\rightarrow$ M) |
| chromate $\text{CrO}_4^{2-}$            | yellow     |   |
| dichromate $\text{Cr}_2\text{O}_7^{2-}$ | orange     |   |
| permanganate $\text{MnO}_4^-$           | purple     |   |



$\text{L} \rightarrow \text{MCT}$

