

24/10/17

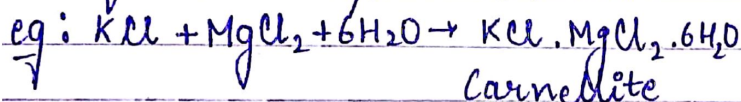
CO-ORDINATION COMPOUNDS

Chlorophyll \rightarrow Mg
Haemoglobin \rightarrow Fe
Vitamin B₁₂ \rightarrow Co

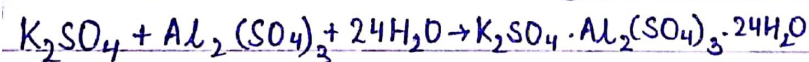
Addition Compounds : When 2 or more salts ^{are} mixed in a fixed proportion and allowed to crystallise then new type of compound formed is known as Addition Compounds.

Double salt

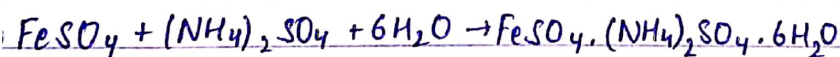
• These addition compds. which are stable in crystalline form and get 100% ionised in aq. medium c/a double salt.



Carnelite



Potash Alum



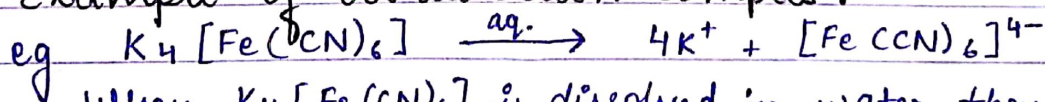
Ferrous ammonium sulphate

Mohr's Salt

Coordination compounds.

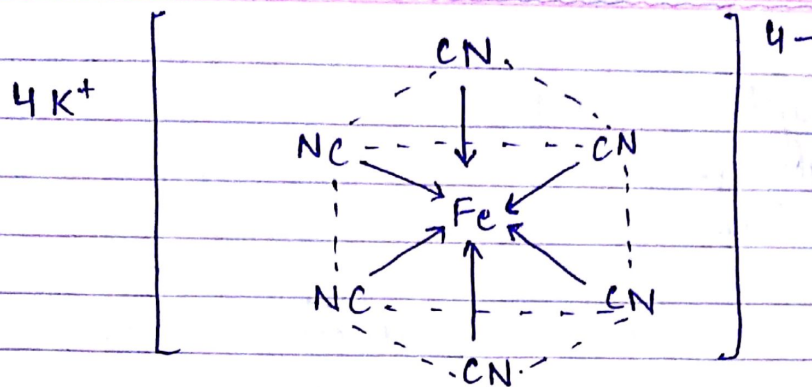
• These addition compds. which are stable in crystalline form as well as in aq. form or medium and do not get 100% ionised is c/a coordination compds.

Example of Coordination Compds :-



When $\text{K}_4[\text{Fe}(\text{CN})_6]$ is dissolved in water then its aq.

solⁿ shows properties of K^+ ions but do not show properties of Fe^{2+} & CN^- ions becoz these are +nt in form of complex ion $[\text{Fe}(\text{CN})_6]^{4-}$



Important terminology related to C.C. :-

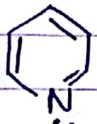
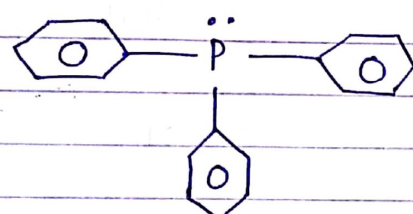
1. Central metal atom and ion :- It is metal atom or ion which have same or nearly same energy vacant orbital to accept lp donated by ligand
* Central metal atom or ion behave as lewis acid.

2. Ligand :- Any atom, molecule or ion which have lp to donate central metal atom or ion.
* Ligand behave as lewis base.

Types of ligand :-

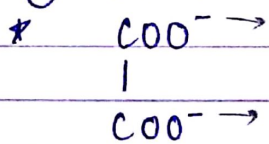
(a) **Monodentate ligand** :- which have one donor atom.

ligand	Name	Charge
1. H_2O	aqua	0
2. NH_3	ammine	0
3. CN^-	cyano	-1
4. X^-	Halido	-1
(F^- , Cl^- , Br^- , I^-)	(Fluorido, Chlorido, Bromido, Iodido)	
5. H^-	Hydrido	-1
6. OH^-	Hydroxo	-1
7. NO_2^-	nitro	-1
8. NO_3^-	nitrate	-1

9. NH_2^-	amido	-1
10. NH^{2-}	imido	-2
11. N^{3-}	nitrido	-3
12. SO_4^{2-}	Sulphato	-2
13. O^{2-}	oxo	-2
14. O_2^{2-}	peroxo	-2
15. S^{2-}	sulphido	-2
16. CH_3COO^-	acetato	-1
17. CO	carbonyl	0
18. NO	nitrosyl	0
19. 	pyridene (py)	0
20. 	triphenyl phosphine	0
21. PH_3	phosphine	0

(b) **Bidentate ligand** : which have 2 donor atom.

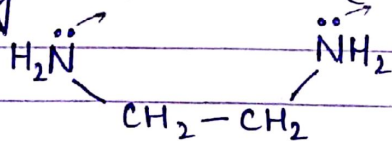
eg: ① oxalato ligand ($\text{C}_2\text{O}_4^{2-}$)



2 donor O-atom

charge = -2

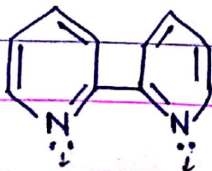
* ② Ethylene diamine (en) or (Ethane-1,2-diamine)



2 donor N-atom

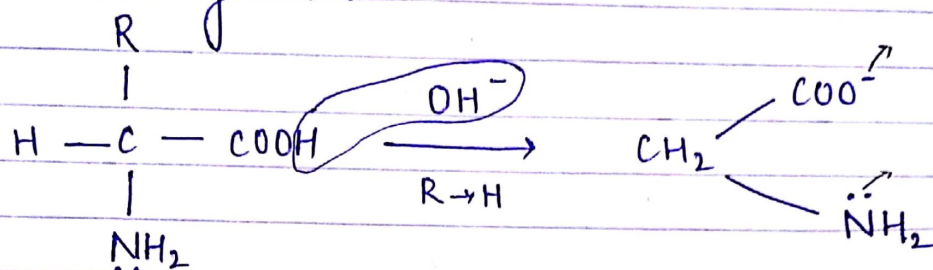
charge = 0

③ 2,2'-bipyridine



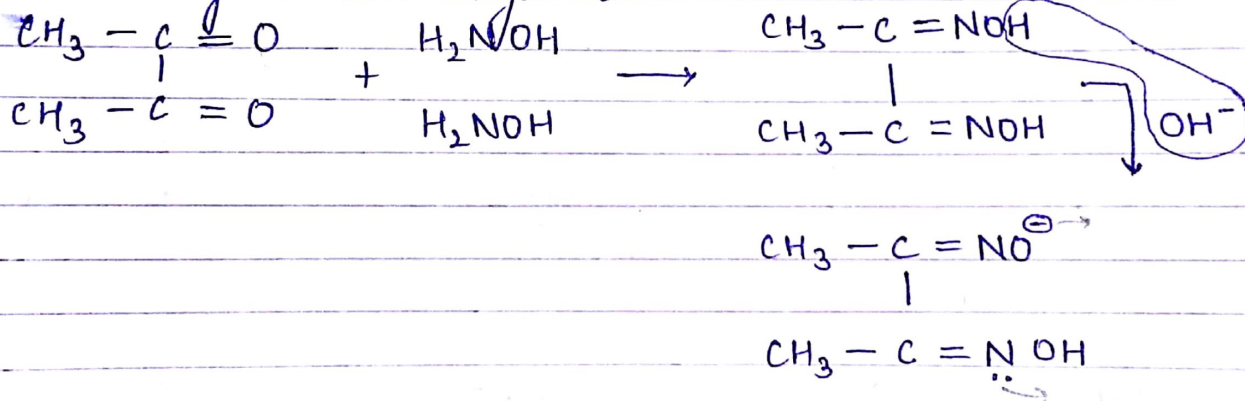
4

4. Glycinato ligand :



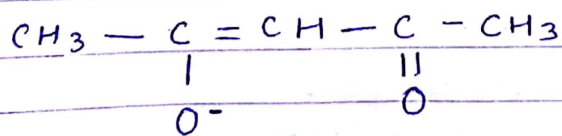
1 donor O-atom & 1 donor N-atom
it is an example of unsymmetrical bidentate ligand.

5. Glyoximate ligand



1 donor O atom & 1 donor N-atom

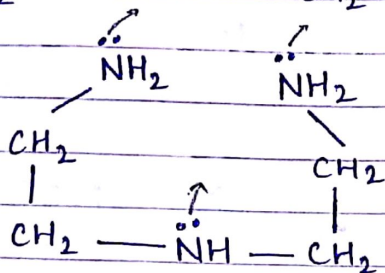
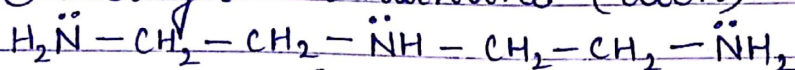
6. Acetyl acetonato (acac)⁻



5

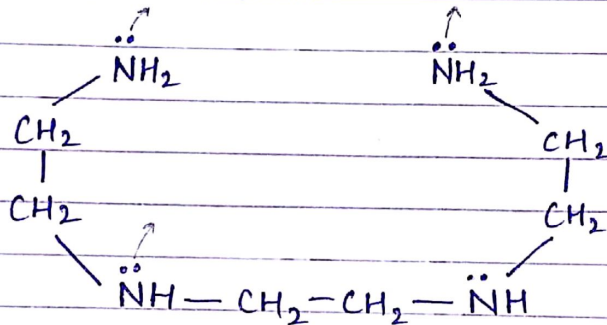
(c) Polydentate ligand : which have more than 2 donor atom

eg : (a) diethylene triamine (dien)



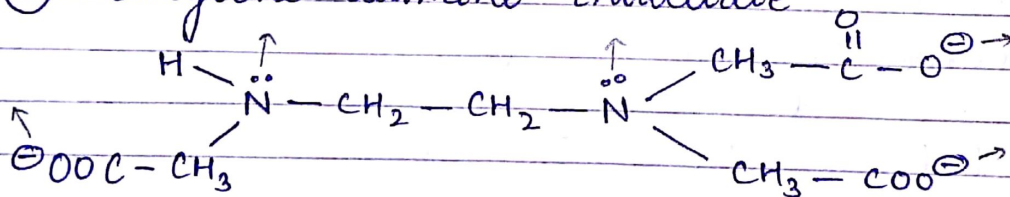
3 donor N-atom
tridentate

(b) triethylene tetramine



4 donor N-atom
tetradentate

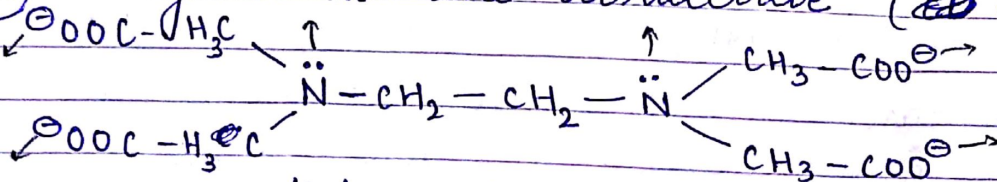
(c) ethylene diamine triacetate



3 donor O-atom & 2 donor N-atom

(Unsymmetrical) Pentadentate

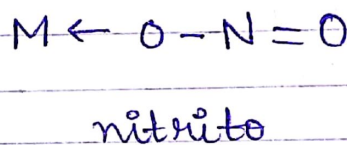
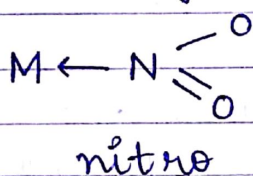
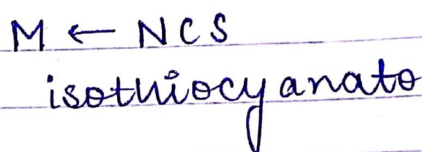
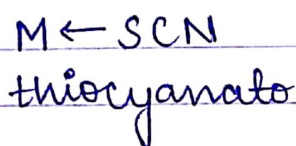
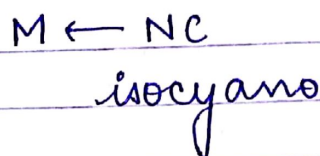
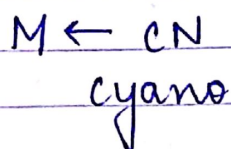
(d) Ethylene diamine tetraacetate (~~ED~~ EDTA)



4 donor O-atom & 2 donor N-atom

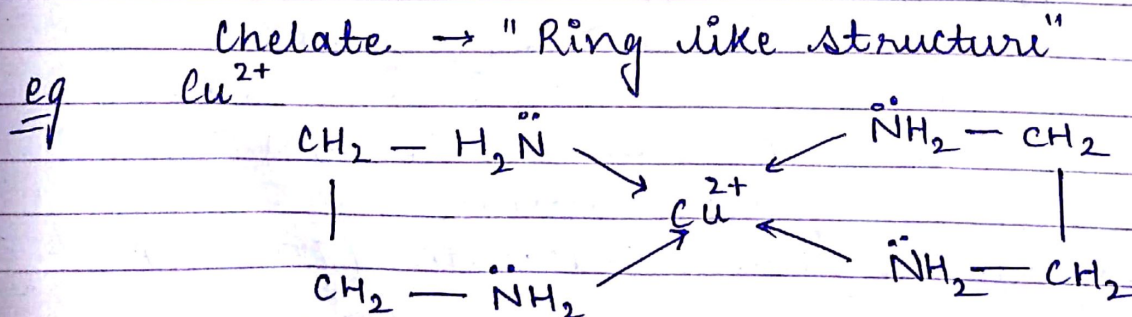
(Unsymmetrical) Hexadentate

(d) **Ambidentate ligand** :- Those ligand which have 2 donor atom^{but} either of them donate one time.



Ambidentate ligands are monodentate ligands.

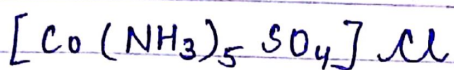
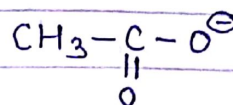
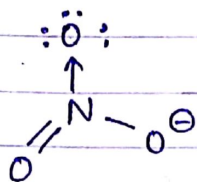
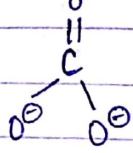
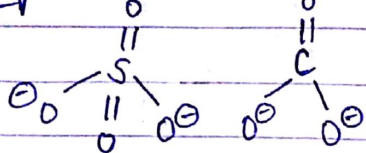
(e) **Chelating Ligand** : When bidentate or polydentate ligand donate simultaneously to central atom. They form ring-like structure c/a chelate ligands.



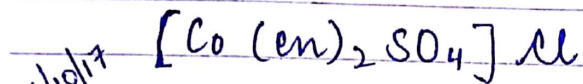
- monodentate can not form ring like structure.
- as no. of donor atoms \uparrow in chelating ligand stability of molecule \uparrow
- EDTA form more stable str. than ethylene diamine.

f) Flexidentate ligand : which can change their denticity.

eg SO_4^{2-} , CO_3^{2-} , NO_3^- , CH_3COO^-



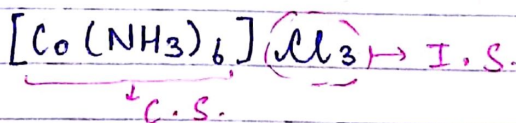
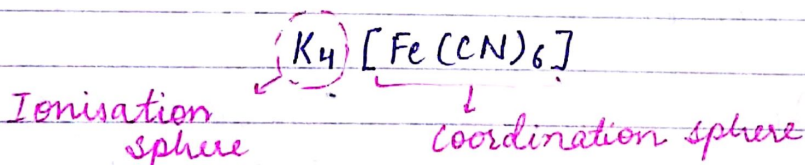
$SO_4^{2-} \rightarrow$ monodentate



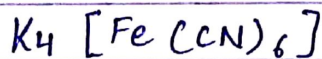
$SO_4^{2-} \rightarrow$ bidentate

3. Ionisation sphere :- species outside coordination sphere form ionisation sphere.

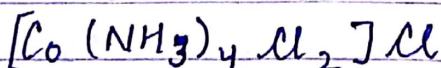
4. Coordination sphere : species +nt in square bracket form coordination sphere.



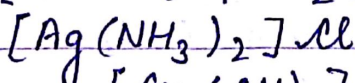
5. Coordination No. :- no. of coordinate covalent bond formed by C.M.A. is c/a c/N.



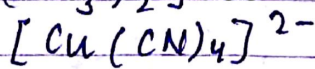
C.N. = 6



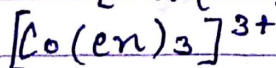
C.N. = 6



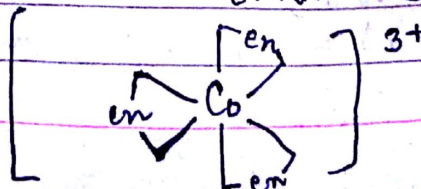
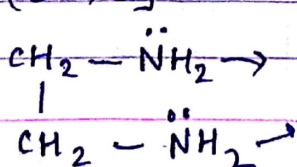
C.N. = 2



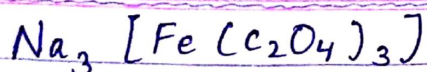
C.N. = 4



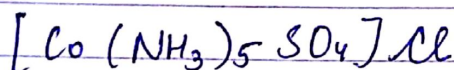
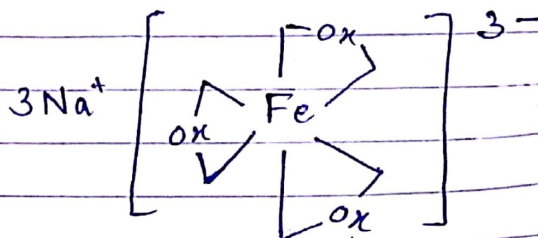
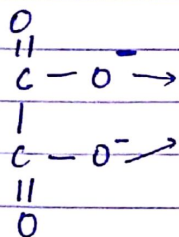
C.N. = $3 \times 2 = 6$



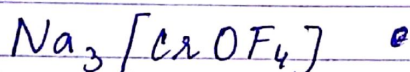
8



$$\text{C.N.} = 3 \times 2 = 6$$



$$\text{C.N.} = 6$$



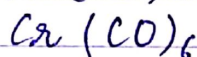
$$\text{C.N.} = 5$$



$$\text{C.N.} = 4$$



$$\text{C.N.} = 5$$

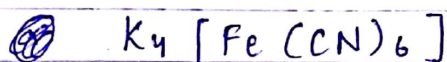


$$\text{C.N.} = 6$$



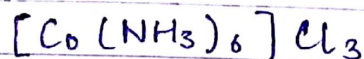
$$\text{C.N.} = 1 \times 6 = 6$$

6. Oxidation Number :-



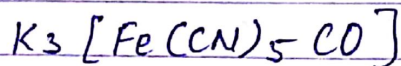
$$x + 6(-1) = -4$$

$$x = -4 + 6 = 2$$



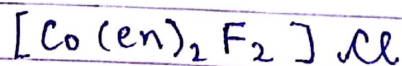
$$x + 0 = +3$$

$$x = 3$$



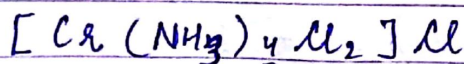
$$x + 5(-1) + 0 = -3$$

$$x = 2$$



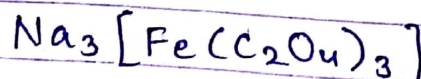
$$x + 2(-1) = +1$$

$$x = 1 + 2 = 3$$



$$x + 4(0) + 2(-1) = +1$$

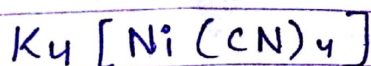
$$x = 3$$



$$x + 3(-2) = -3$$

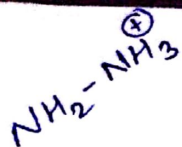
$$x = 3$$

AIEEE

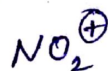
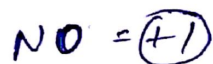


$$x + 4(-1) = -4$$

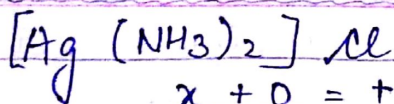
$$x = 0$$



(i)um



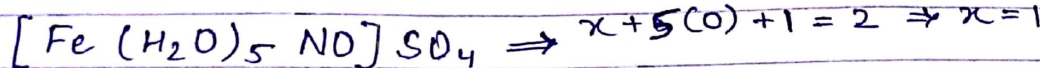
CO = 0 charge



$$x + 0 = +1$$

$$x = 1$$

II

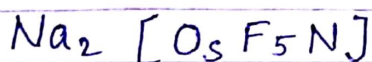


~~$$x + 0 + 1 = +1$$~~

$$x + 5(0) + 1 - 2 = 0$$

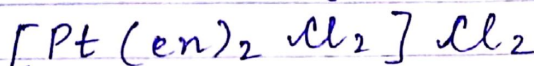
~~$$x = 0$$~~

$$x = +1$$



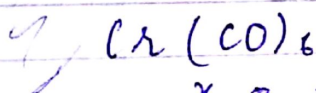
$$x + 5(-1) - 3 = -2$$

$$x = 6$$

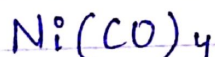


$$x + 0 - 2 = +2$$

$$x = 4$$

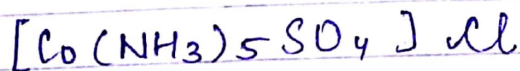


$$x + 0 = 0 \Rightarrow x = 0$$



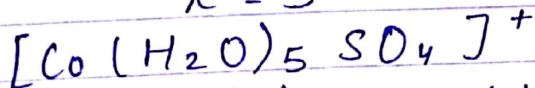
$$x + 0 = 0$$

$$x = 0$$



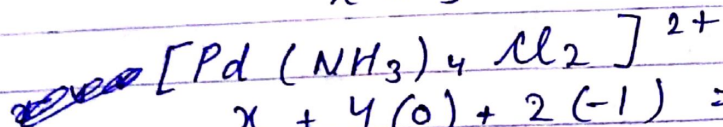
$$x + 0 - 2 = +1$$

$$x = 3$$



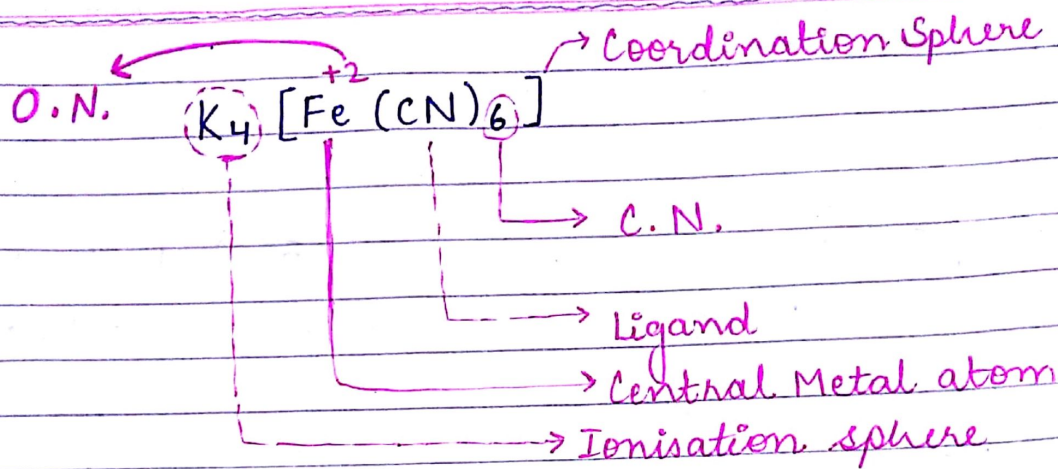
$$x + 5(0) - 2 = +1$$

$$x = 3$$



$$x + 4(0) + 2(-1) = +2$$

$$x = 4$$

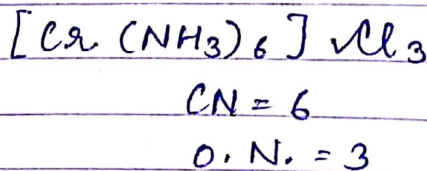
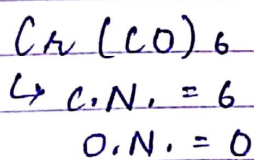


Werner's Theory :-

Every C.M.A. has 2 valency in complex for^m.

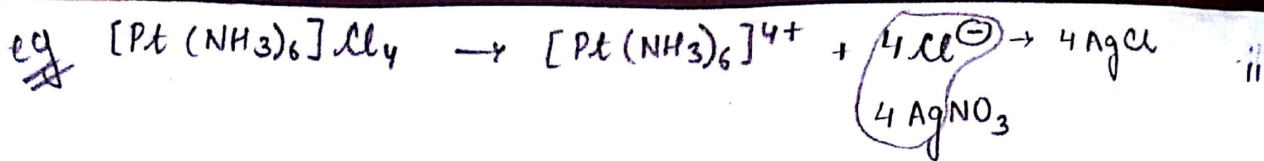
- | | |
|---|---|
| <p>Primary Valency</p> <ul style="list-style-type: none"> • equal to O.N. • due to anions (-ve charge) • ionisable <small>→ means changes its O.N.</small> • non-directional • do not play any role in geometry | <p>Secondary valency</p> <ul style="list-style-type: none"> → equal to C.N. • due to ligand (neutral, -ve, +ve) • non-ionisable <small>→ means not changes its C.N.</small> • directional • decide geometry |
|---|---|

Note :- Every C.M.A. tends to satisfy both valencies.



• Secondary valency i.e. C.N. is fix.

eg Cr^{3+}	6	
Co^{3+}	6	
Pt^{4+}	6	$\text{Pt}^{2+} \rightarrow 4$
Fe^{2+}	6	
Cu^{2+}	4	
Ag^{2+}	2	



Compound	Pri. valency	Sec. valency	No. of Cl^- ions precipitated as $AgCl$ if $AgNO_3$ added	Total no. of ions
1. $[Pt(NH_3)_6]Cl_4$	4	6	4	5 $[Pt(NH_3)_6]^{4+} + 4Cl^-$
2. $[Pt(NH_3)_5Cl]Cl_3$	4	6	3	4 $[Pt(NH_3)_5Cl]^{3+} + 3Cl^-$
3. $[Pt(NH_3)_4Cl_2]Cl_2$	4	6	2	3 $[Pt(NH_3)_4Cl_2]^{2+} + 2Cl^-$
4. $[Pt(NH_3)_3Cl_3]Cl$	4	6	1	2 $[Pt(NH_3)_3Cl_3]^+ + Cl^-$
5. $[Pt(NH_3)_2Cl_4]$	4	6	0	1 $[Pt(NH_3)_2Cl_4]^0$

Question based on table :-

Ques which of the following has max^m conductivity?
conductivity \propto no. of ions.

(1) $[Pt(NH_3)_6]Cl_4$

Ques which of the following will give 3 mol $AgCl$ when mixed with $AgNO_3$.

(2) $[Pt(NH_3)_5Cl]Cl_3$

Ques which of the following is electrically neutral

(5) $[Pt(NH_3)_2Cl_4]$

Ques which of the following do not form white ppt. when mixed with $AgNO_3$.

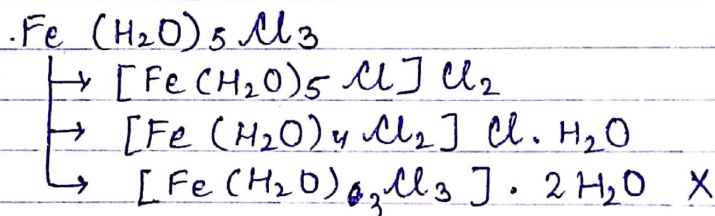
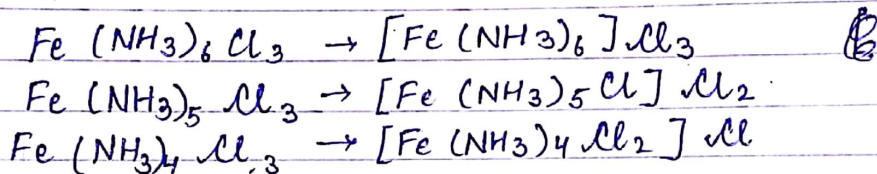
(5) $[Pt(NH_3)_2Cl_4]$

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Ques which of the following will give white ppt. when mixed with $BaCl_2$

- (1) $[Co(NH_3)_4Cl_2]Cl$
 (2) $[Co(NH_3)_5Cl]SO_4$ $[Co(NH_3)_5Cl]^{2+} + SO_4^{2-}$
 (3) $[Pt(en)_2Cl_2]Cl_2$
 (4) $[Pt(NH_3)_5SO_4]Cl_2$
- $BaCl_2$
 \downarrow
 $BaSO_4$

$BaSO_4 \rightarrow$ white ppt.



Effective Atomic Number or Sidgwick Rule :-
 A metal atom or ion continue to accept e^- till no total no. of e^- on metal atom or ion and those accepted from ligand reach to a noble gas configuration.

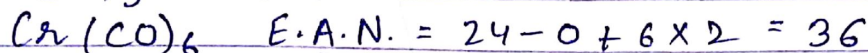
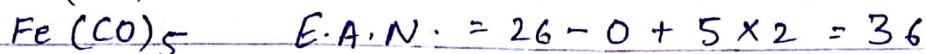
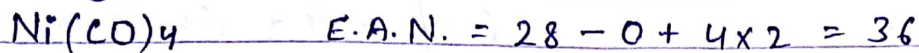
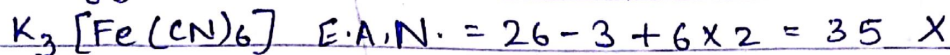
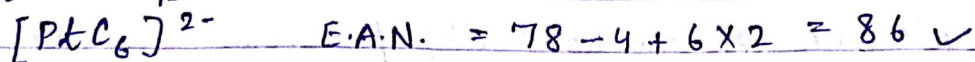
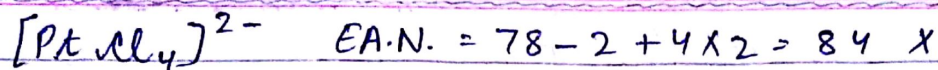
$E.A.N. = \text{Atomic No.} - \text{Ox. No.} + \text{total } e^- \text{ accepted from ligand}$
 or $(2 \times C.N.)$

$[Co(NH_3)_6]Cl_3$ E.A.N. = $27 - 3 + 2 \times 6 = 36$ $\leftarrow Kr$

$K_4[Fe(CN)_6]$ E.A.N. = $26 - 2 + 2 \times 6 = 36$

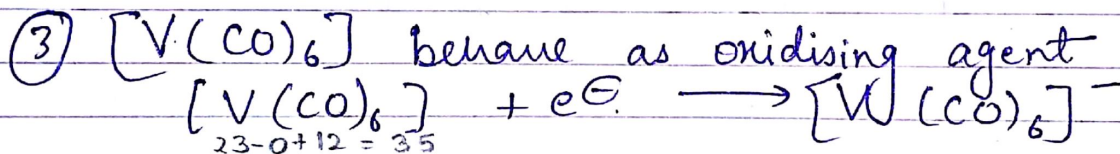
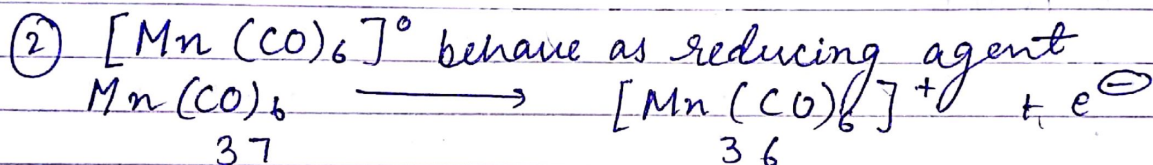
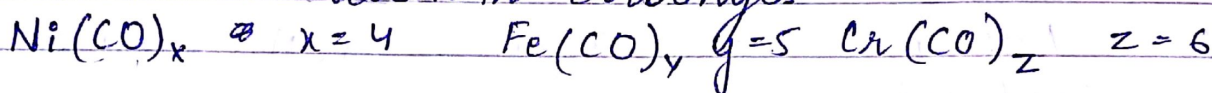
$[Cu(CN)_4]^{3-}$ E.A.N. = $29 - 1 + 2 \times 4 = 36$

$[Pd(NH_3)_4Cl_2]Cl_2$ E.A.N. = $46 - 4 + 2 \times 6 = 54$ Xe



Applications :-

① To calculate no. of π carbon monoxide attached to metal atom in carbonyls.



IUPAC Nomenclature of c.c :-

Rules :-

① If cation is +nt in c.c then it is written is always 1st.

$K_4[Fe(CN)_6]$ Potassium - - -

② Naming of Coordination Sphere :-

First of all name of ligands is written in alphabetical order then name of C.M.A. is written following its O.N. in Roman number.

If multiple ligand are +nt :-

• Then write them in alphabetical order.

• Use di, tri, tetra - - - for monodentate ligands

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If +nt in multiple no.

• For multiple no. of chelate ligand use bis, tris, tetrakis ---

di, tri, tetra are not used in alphabetical order
bis, tris --- ~~is~~ → used ~~is~~ in alphabetical order

Naming of -ve ligand
suffix 'o'

neutral

Cation

$\text{Cl}^- \rightarrow$ Chlorido

$\text{NH}_3 \rightarrow$ amine

NO^+ nitrosonium

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

$\text{H}_2\text{O} \rightarrow$ aqua

NO_2^+ nitronium

$\text{N}^{3-} \rightarrow$ Nitrido

$\text{CO} \rightarrow$ carbonyl

$\text{NH}_2\text{-NH}_3^+$ hydrazinium

$\text{SO}_4^{2-} \rightarrow$ Sulphato

$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ tetra amine dichlorido cobalt (III) ions

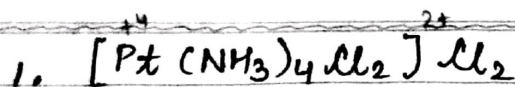
$[\text{Co}(\text{en})_2\text{Cl}_2]^+$ bis (ethane-1,2-diamine) dichloro cobalt (III) ion

③ If coordination sphere is +nt as anionic part then suffix 'ate' is used after name of metal

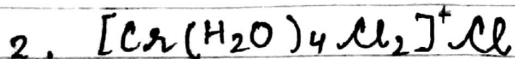
$\text{K}_4[\text{Fe}(\text{CN})_6]^{4-}$ Potassium hexacyano ferrate (II)

④ If anion is +nt outside coordination sphere then name of anion is written at last.

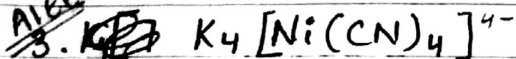
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ hexaammine Cobalt (III) Chloride



tetra ammine dichlorido Platinum (IV) Chloride



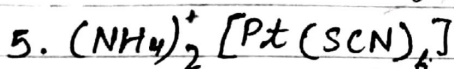
Tetra aqua dichlorido chromium (III) Chloride



Potassium tetracyano nickelate (0)



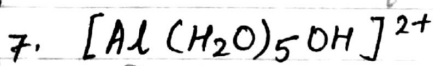
Potassium carbonyl pentacyano Ferrate (II)



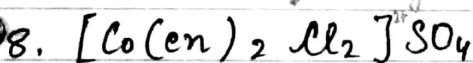
hexathiocyanato Platinate (IV)



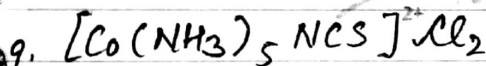
Sodium tetrafluorido oxo chromate (IV)



Penta aqua hydroxo aluminium (III)



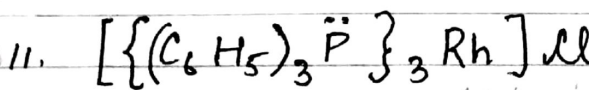
dichlorido di (ethane 1,2-diamine) cobalt (IV) Sulphate



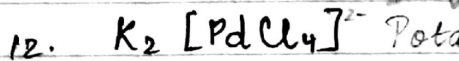
Penta ammine iso thiocyanato cobalt (III) Chloride



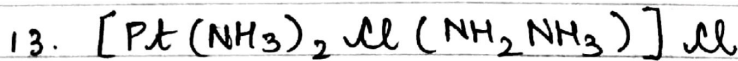
Lithium tetra hydrido aluminate (III)



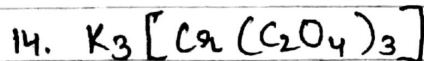
tris (tri phenyl phosphine) Rhodium Chloride



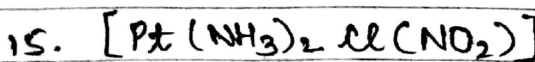
Potassium tetra chlorido pallidumate (II)



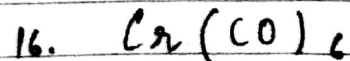
Diamine chlorido hydrazinium Platinum (I) Chloride



Potassium tris-oxalato Chromate (III)

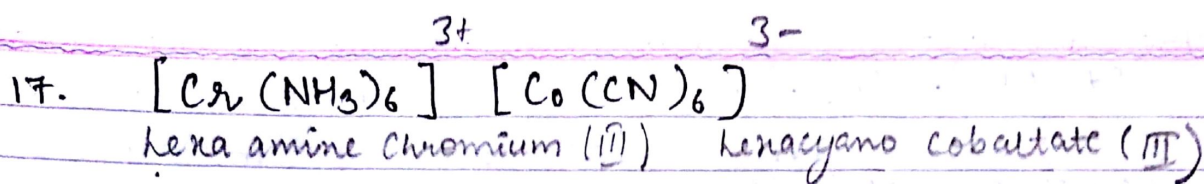


diamine chlorido nitronium Platinum
 $x + (-1) + (+1) = 0$
 $x = 0$



hexa carbonyl chromium

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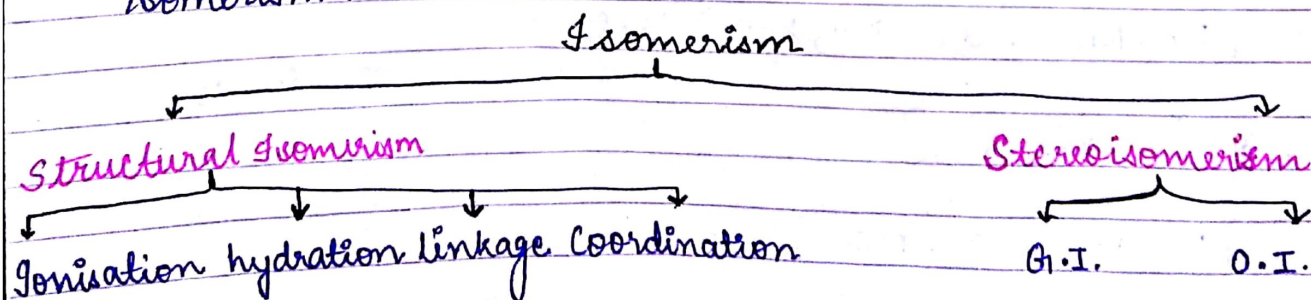


Ques: Write formula of following :-

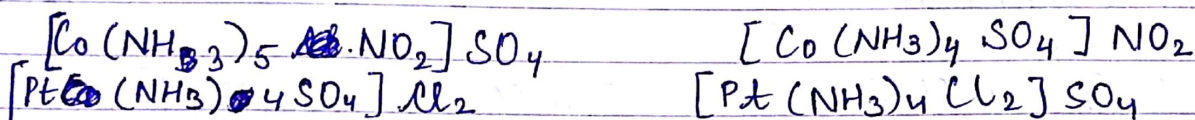
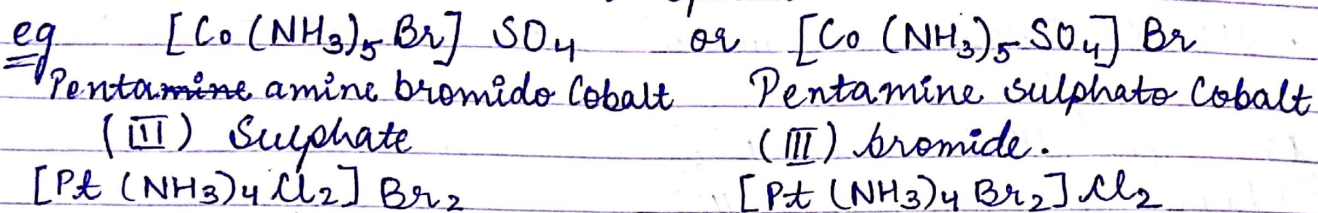
- tetra carbonyl Nickel (0)
 $Ni(CO)_4$
- tetra amine aqua chlorido cobalt (III) Chloride
 $[Co(NH_3)_4(H_2O)Cl]Cl_2$
- bis (ethane -1,2-diamine) dibromido Chromium (II)
 $[Cr(en)_2Br_2]$
- Ammine bromido chlorido nitro - N-Platinate (II)
 Pt
- Iron (III) hexacyano ferrate (II) Fe^{3+} $[Fe(CN)_6]^{4-}$ $Fe_4[Fe(CN)_6]_3$
- Potassium tetracyano nickelate (II)
 $K_2[Ni(CN)_4]$
- Potassium tris oxalato aluminate (III)
 $K_3[Al(C_2O_4)_3]$

1 Q. NEET/AIIMS

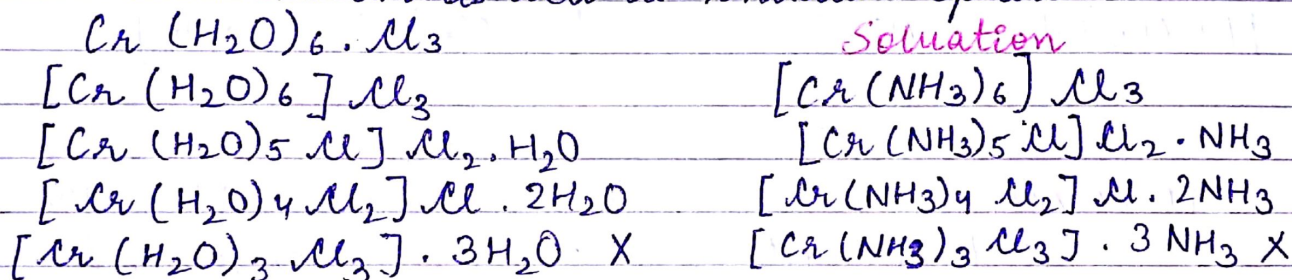
Isomerism :- Compds which have same molecular formula but different structural formula are k/n as isomers & phenomena is k/n as isomerism.



1. **Ionisation isomerism** : In these type of isomerism, interchange of ligands takes place b/w coordination & ionisation sphere



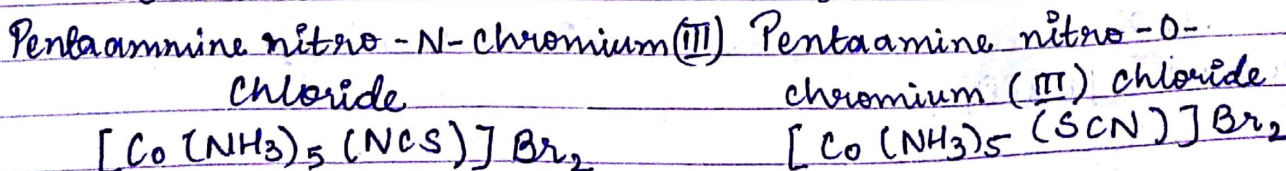
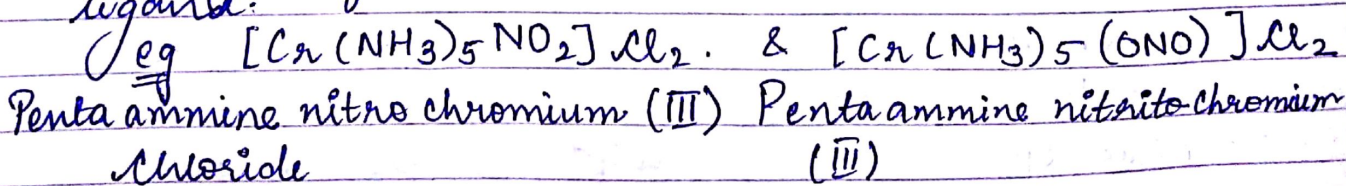
Hydration isomerism : water molecule are +nt in coordination as well as ionisation sphere



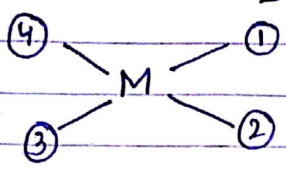
Hydration isomerism is a special case of ionisation isomerism

Linkage Isomerism :- shown by those coordination compd which have ambidentate ligand.

• This type of isomerism takes place due to change of donor atom due to ambidentate ligand.



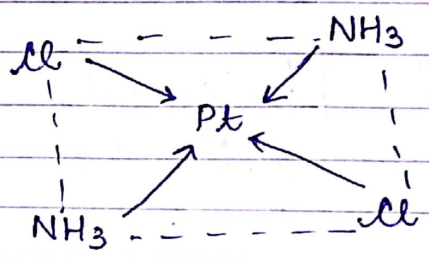
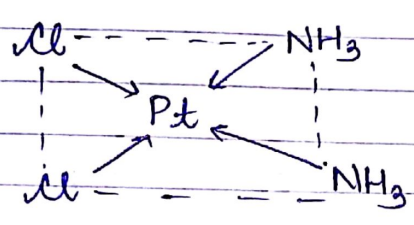
Type-I Ma_2b_2



$M \rightarrow C.M.A.$
a \rightarrow Monodentate
b \rightarrow Monodentate

cis 1-2, 2-3, 3-4, 4-1
trans 1-3, 2-4

$[Pt(NH_3)_2Cl_2]$

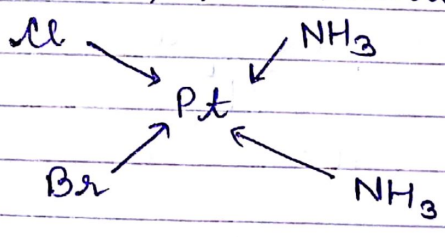
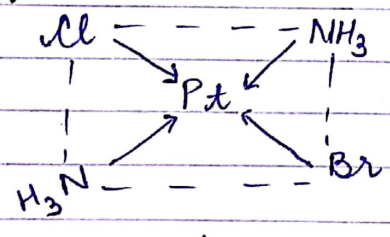


cis platin
anti cancerous used
in chemotherapy

trans-platin

Type-II Ma_2bc

$M \rightarrow CMA$
a, b, c \rightarrow monodentate ligand

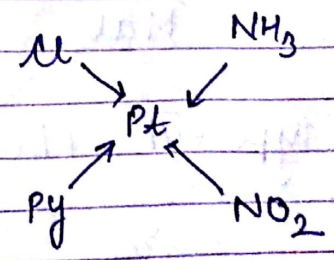
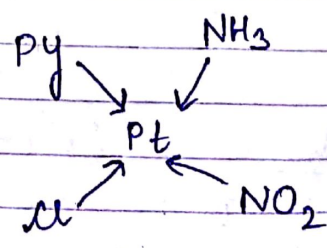
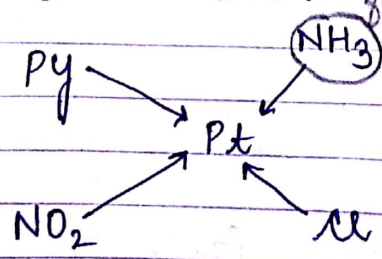


trans

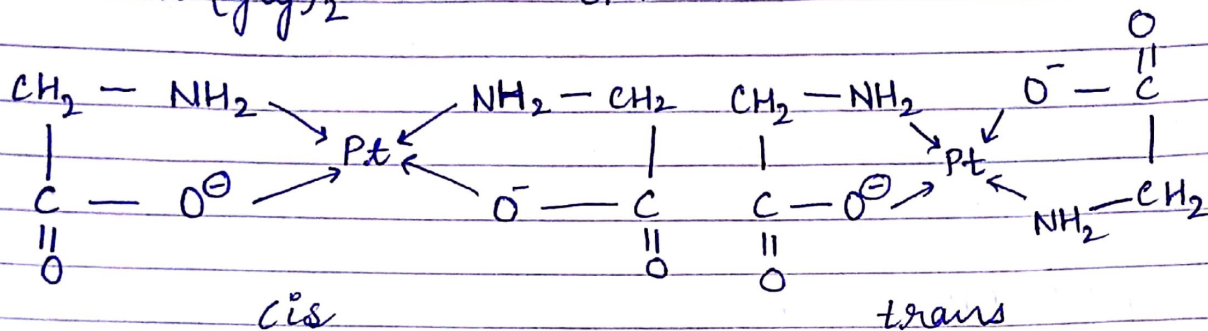
cis

Type-III $Maabcd$

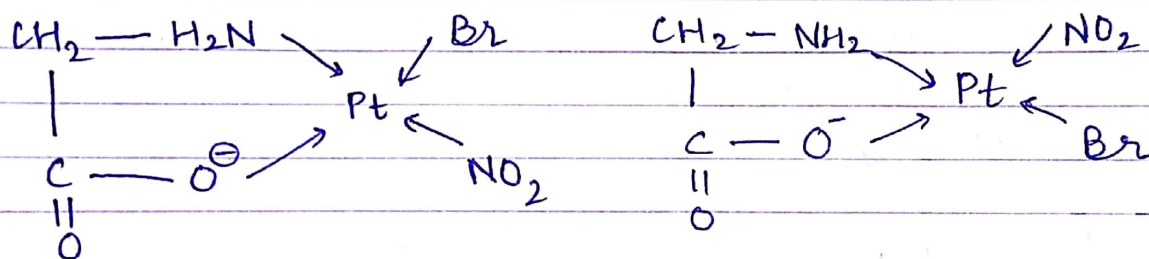
G.I. = 3



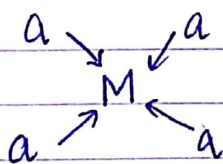
2/11/17
Type-IV $[M(ab)_2]$
unsymm. bidentate
Pt (gly)₂ G.I. = 2



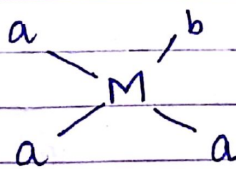
Type V $[M(ab)cd]$
unsy. bi mono
G.I. = 2



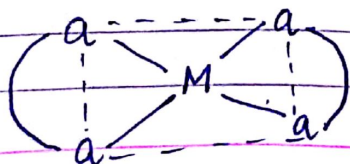
Type VI Ma_4
G.I. = 0



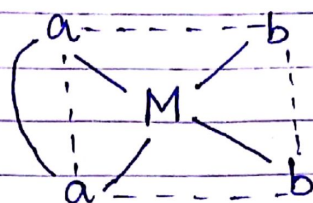
Type VII Ma_3b or Mab_3
G.I. = 0



Type VIII $M(aa)_2$ Pt (en)₂
G.I. = 0



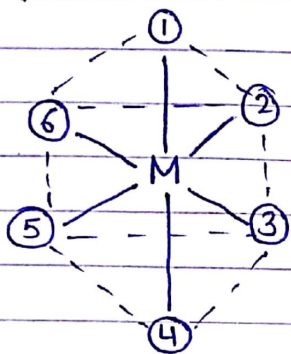
Type $M(aa)b_2$



G.I. = 0

C.N. = 6

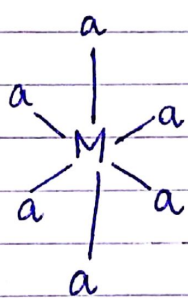
d^2sp^3 / sp^3d^2 Octahedral



cis $\rightarrow (1,2) (1,3) (1,5) (1,6) (4,3)$
 $(4,2) (4,6) (4,5)$
 $(2,6) (2,3)$
 $(5,6) (5,3)$

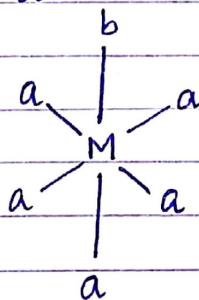
trans $\rightarrow (1,4) (2,5) (3,6)$

① Ma_6



G.I. = 0

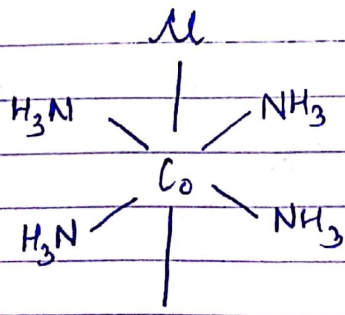
② Ma_5b



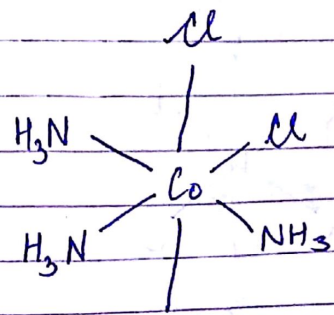
G.I. = 0

③ Ma_4b_2

G.I. = 2

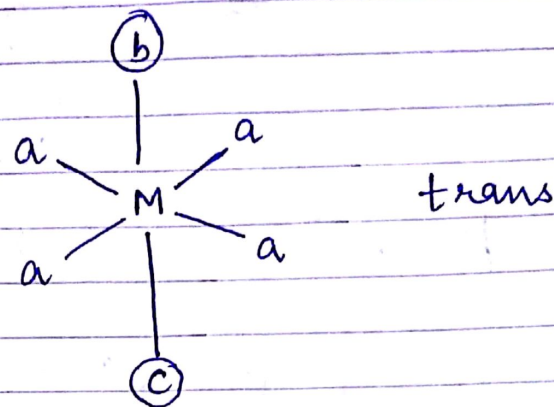
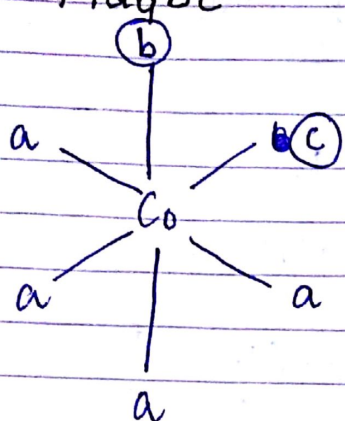


trans



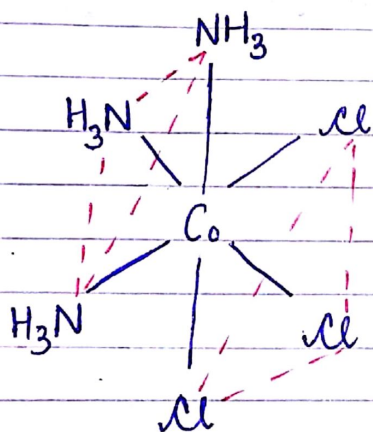
cis

(4) Ma_4bc $G.I. = 2$

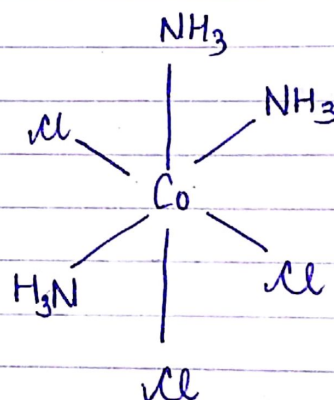


trans

(5) Ma_3b_3 $G.I. = 2$

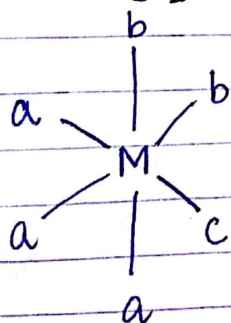


Facial or
fac isomer

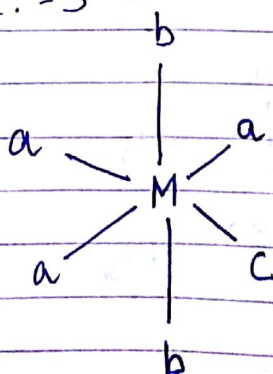


Meridional
or mer isomer

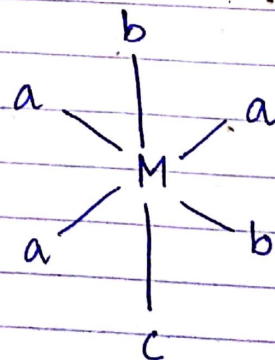
(6) Ma_3b_2c $G.I. = 3$



$a-b$
 $a-c$ } trans
 $b-b$
 $a-b$
 $a-c$ } cis



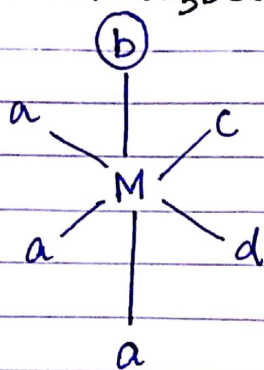
$a-a$
 $a-c$
 $b-b$ } trans
 $a-a, ac, bc, ab$ } cis



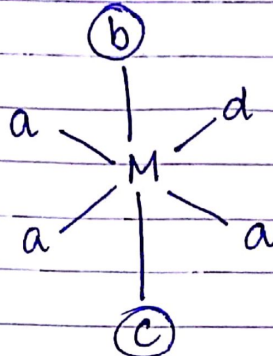
ab, aa, bc } trans
 aa, ab, ca, cb, ba
 $, bb$ } cis

(7) Ma_3bcd

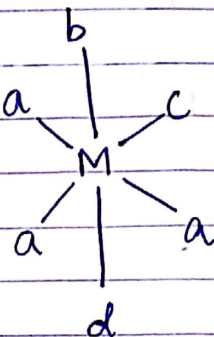
G.I. = 4



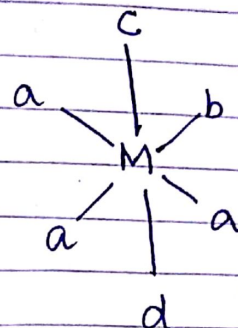
a & b trans



b & c trans



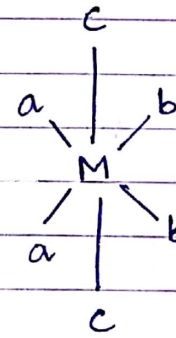
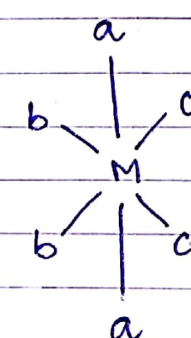
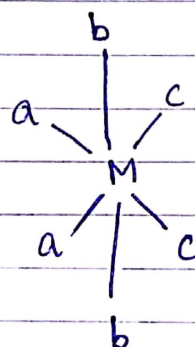
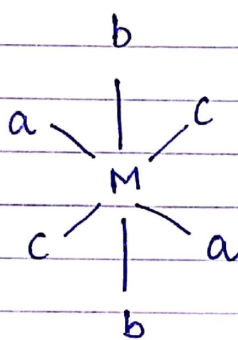
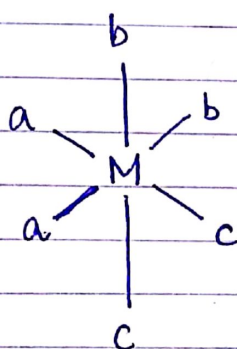
b & d trans



c & d trans

(8) $Ma_2b_2c_2$

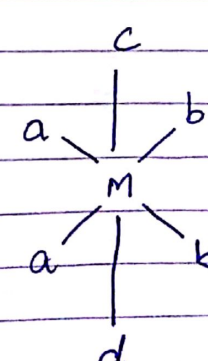
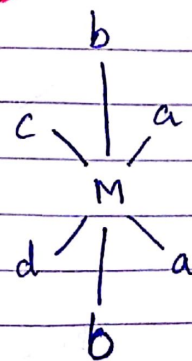
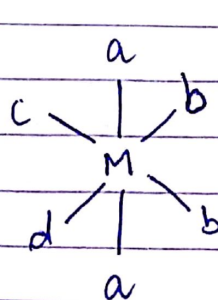
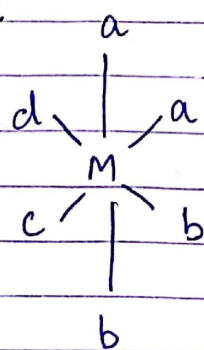
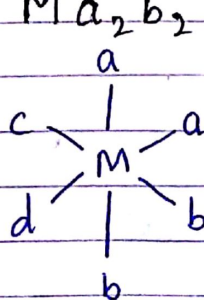
G.I. = 5



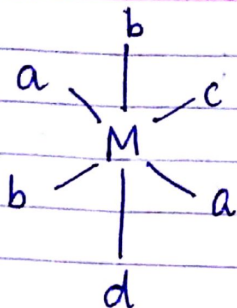
$a \rightarrow b/c/d \rightarrow 3$
 $a, b \rightarrow c, d \rightarrow 2$
 $a, b, c \rightarrow d \rightarrow 1$

 6

(9) Ma_2b_2cd

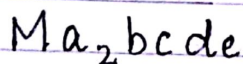


24

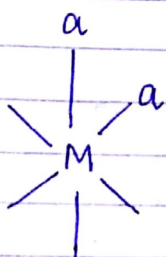


4/11/17

(10)



a-a cis



fix

(b) - c, d, e → 3

(b, c) - d, e → 2

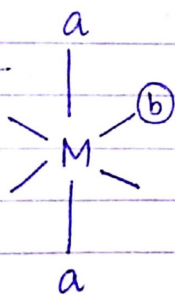
(b, c, d) → e → 1

(6)

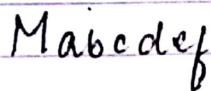
(b) → c, d, e → 3

total = 6 + 3 = 9

a-a trans



(11)



(a) → bcdef → 5

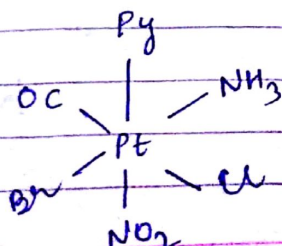
a, b → cdef → 4

a, b, c → d, e, f → 3

a, b, c, d → e, f → 2

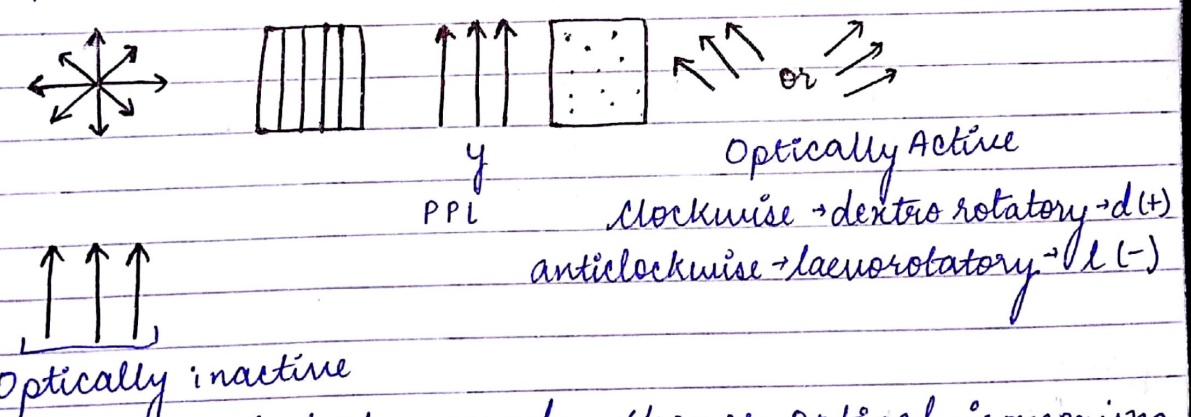
abcde → f → 1

15



	G.I.	O.I.
M_{abcdef}	15	<u>30</u>
M_{a_2bcde}	9	12
$M_{a_2b_2cd}$	6	
$M_{a_2b_2c_2}$	5	
M_{a_3bcd}	4	
$M_{a_3b_2c}$	3	
$M_{a_3b_3}$	2	
M_{a_4bc}	2	
<u>30</u> $M_{a_4b_2}$	2	
M_{a_5b}	0	
M_{a_6}	0	

Optical Isomerism :- which form \neq non-super imposable mirror images of each other c/a optical isomers and phenomena c/a optical isomerism



Note : Unsymmetrical compds shows optical isomerism i.e. posⁿ, centre and axis of symmetry is absent in optically Active compds.

Note : cis give O. Active

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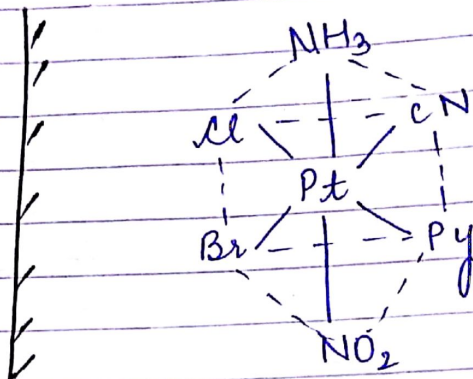
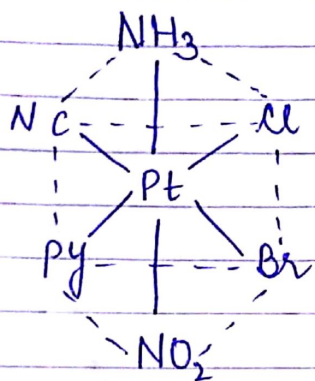
43,44 Gyanodaya Tower, Kota
9416566619, 7340250100

Be Wise Classes

learn here, lead everywhere

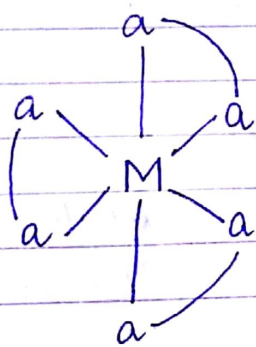
26

Mabcdef

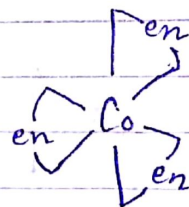
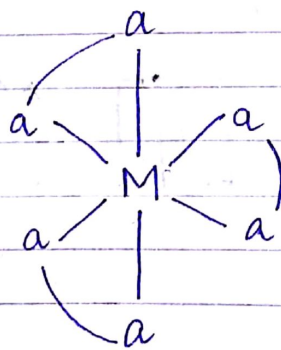


G.I. = 15
O.I. = 30

$M(aa)_3$



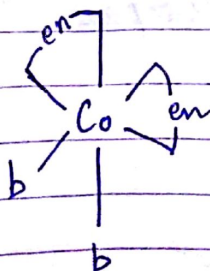
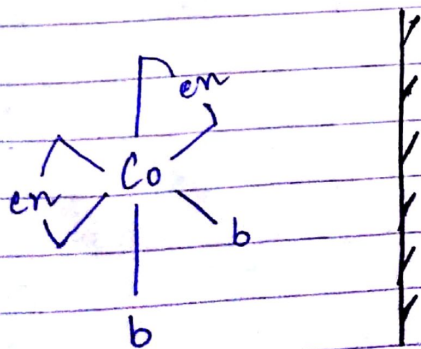
eg $[Co(en)_3]^{3+}$



O.A.

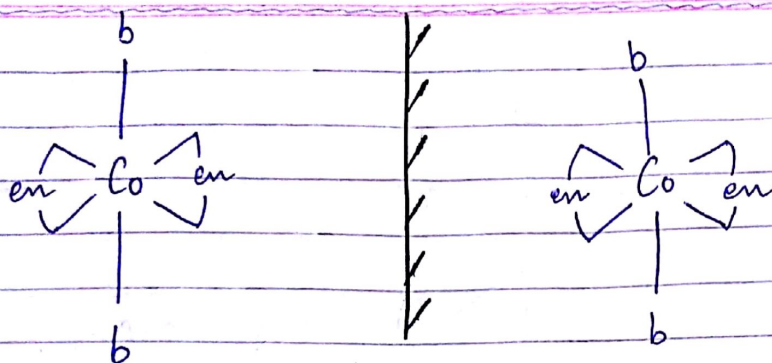
v. imp

$M(aa)_2b_2$

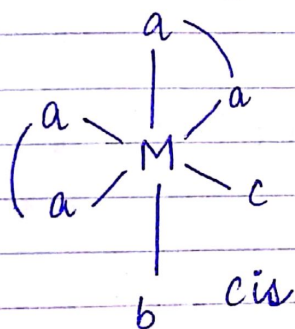
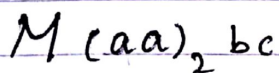


cis

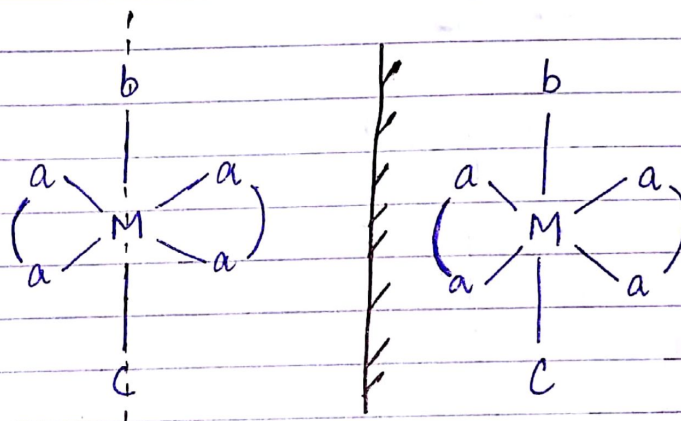
O.A.



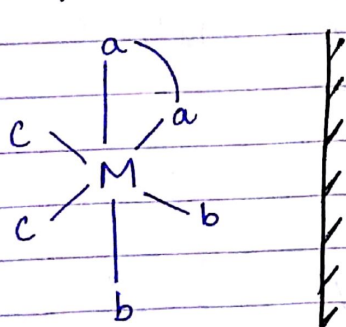
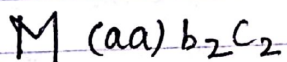
trans O.A. X



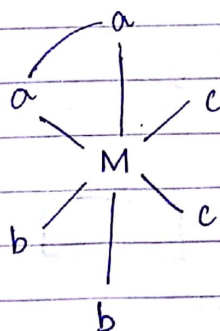
O.A.



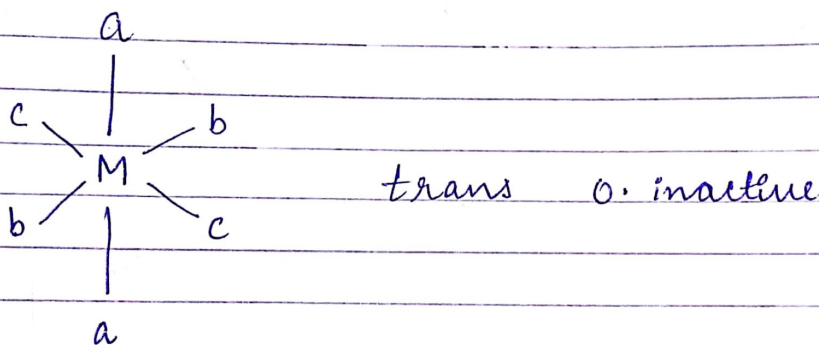
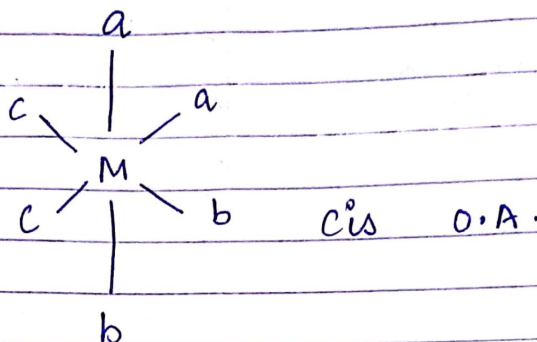
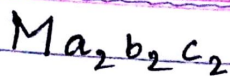
Optically Inactive



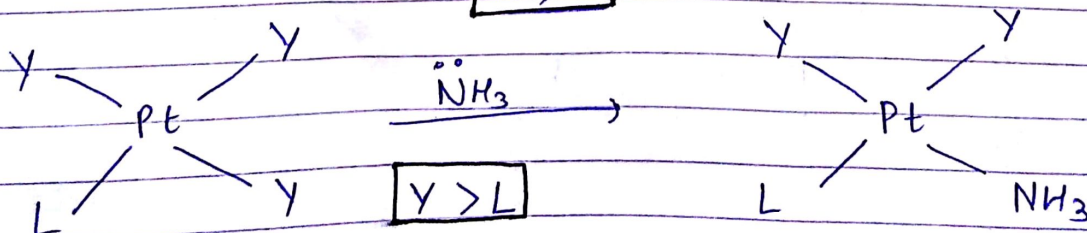
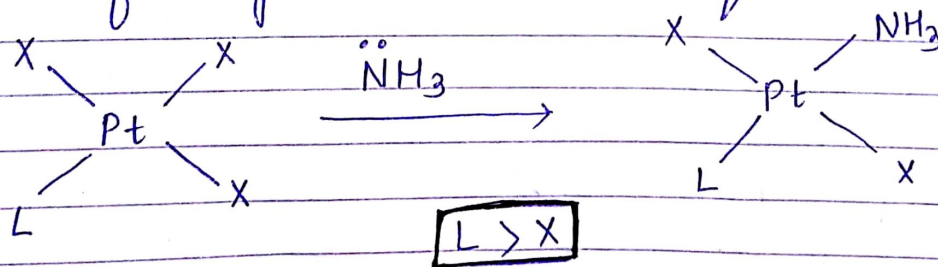
O.A.



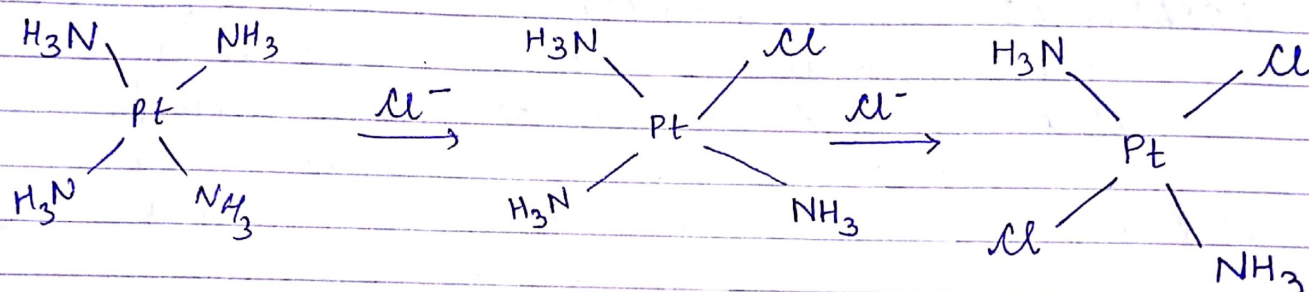
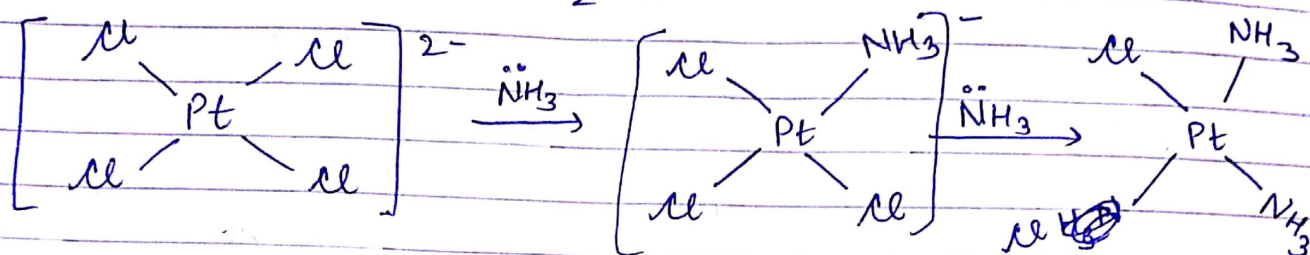
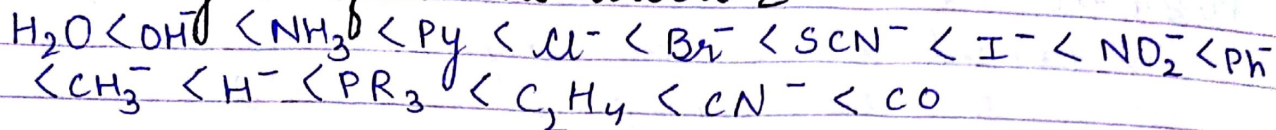
28



Trans-Effect : It is kinetic phenomena which means that it promotes faster substitution rate for ligands trans to itself than cis to itself.



Strength of trans director

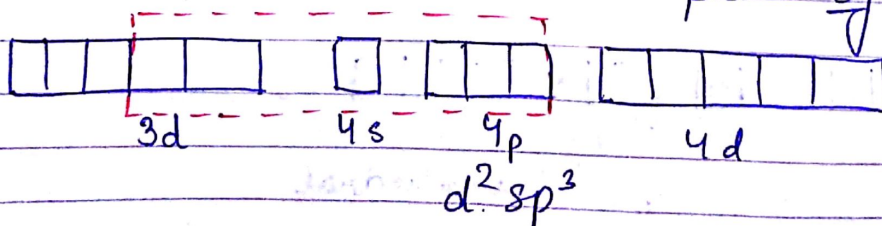


Valence Bond THEORY :- given by Pauling.

Postulate 1 : C.M.A or ion must have vacant orbitals to accept sp donated by ligands.

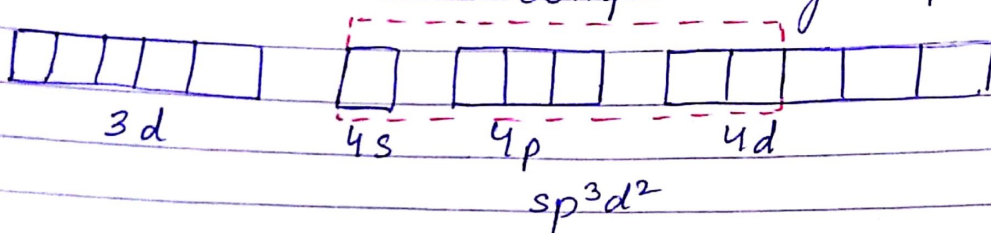
Postulate 2 : Vacant orbitals of same or nearly same energy undergoes hybridisation & forms new set of —

Postulate 3 : If inner $(n-1)d$ take part in hybridisation complex formed is k/n as.
Inner orbital complex eg d^2sp^3

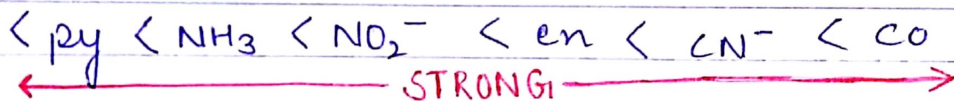
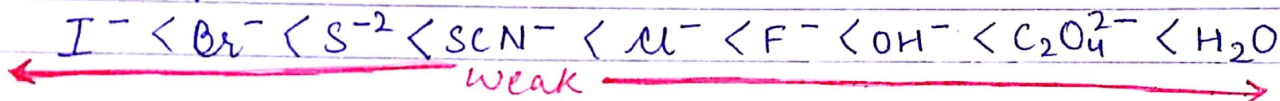


30

Postulate - 4 : If outer 'n.d' orbitals take part in hybridisation then complex formed is K/n as outer orbital complex eg: sp^3d^2



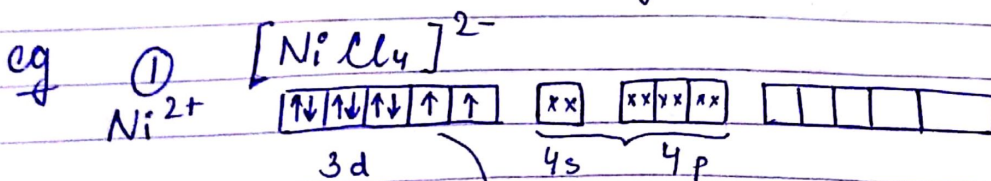
Postulate 5 :- Outer low orbital complex is formed in +ve of weak ligand while inner orbitals complex is formed in +ve of strong ligand. Ligands are arranged in a series accⁿ to their strength known as spectrochemical series



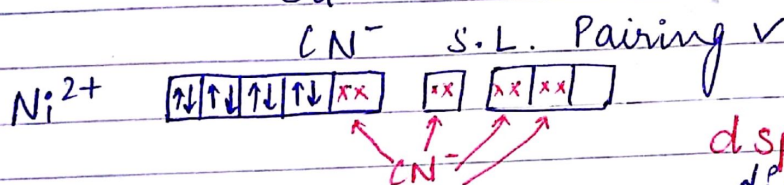
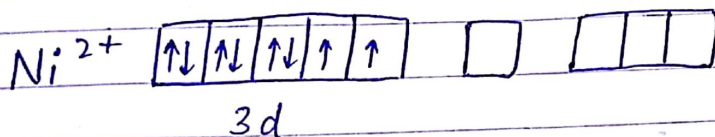
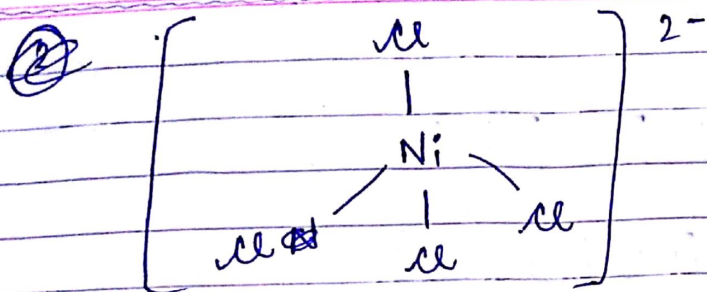
Halogen atom < O-donor < N-donor < C-donor

Postulate - 6

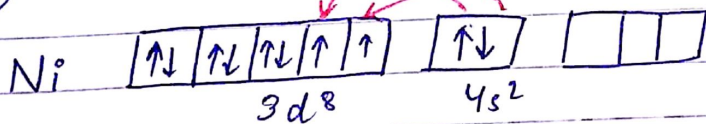
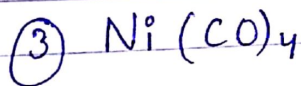
Generally complex are diamagnetic in +ve of strong ligand \therefore SL cause pairing e^- .
 + Inner orbital complex / low spin complex
and in +ve of weak ligand complex are paramagnetic \therefore WL do not cause pairing of e^- .
 \rightarrow Outer orbital complex / high spin complex.



$Cl^- \rightarrow$ W.L pairing X \rightarrow sp^3 tetrahedral
 2 unpaired, Paramagnetic



*dsp², Square Planar
diamagnetic*

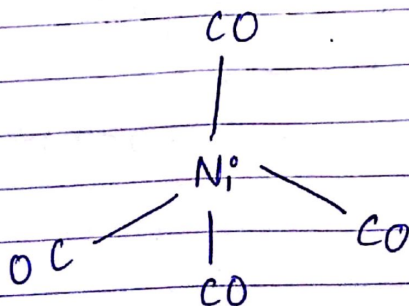


CO → s.l., pairing ✓

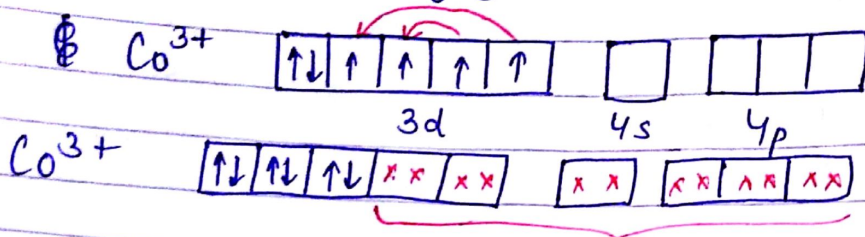
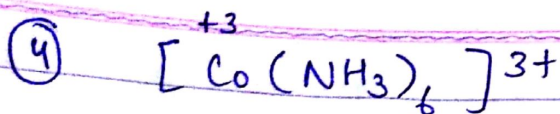


sp³, tetrahedral

dia



32

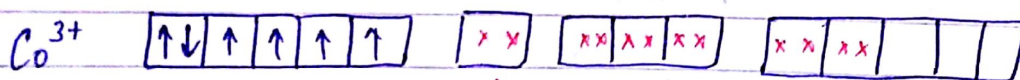
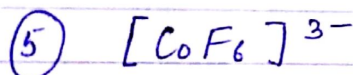
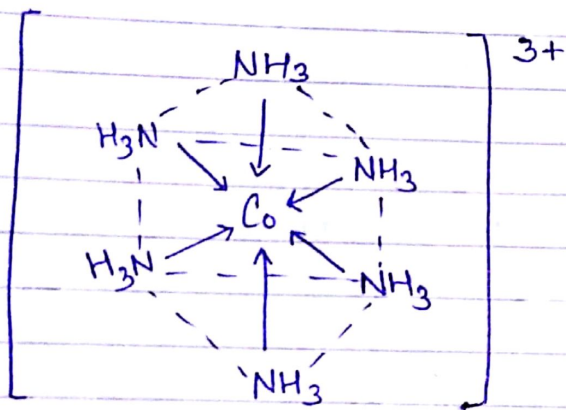


$NH_3 \rightarrow S.L.$
Pairing

d^2sp^3 , Octahedral
dia. IOC / LSC

Inner orbital complex

low spin complex



$F^- \rightarrow W.L.$
pairing x

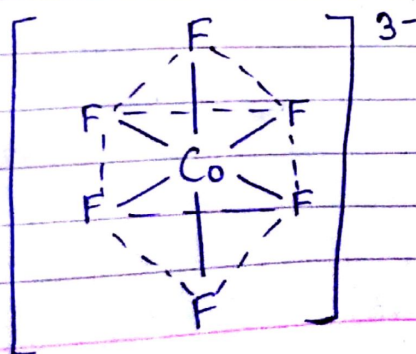
sp^3d^2 , Octahedral

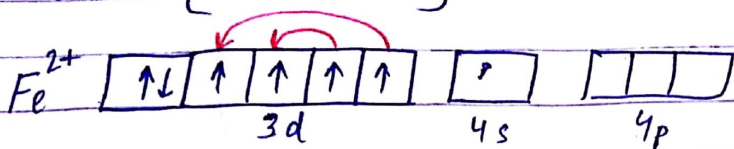
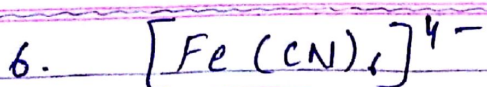
$n=4$, Paramagnetic

Outer orbital complex

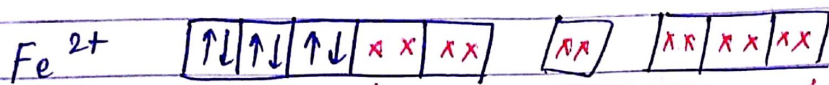
IOC / HSC

High spin complex





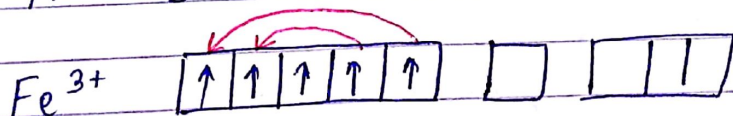
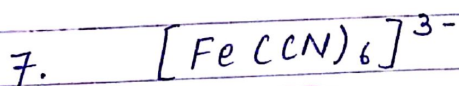
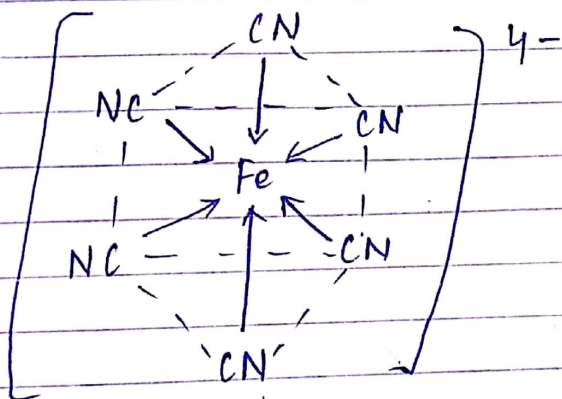
CN⁻ → S.L.



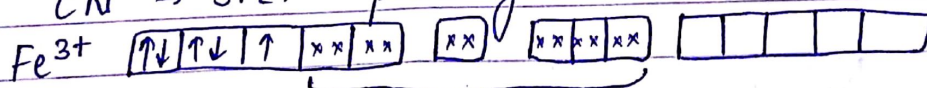
CN⁻
 $d^2 sp^3$, Octahedral

n = 0 dia

IOC / L.S.C.



CN⁻ → S.L. → pairing ✓



$d^2 sp^3$, Octahedral

n = 1 Paramagnetic

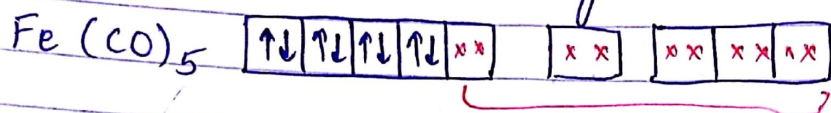
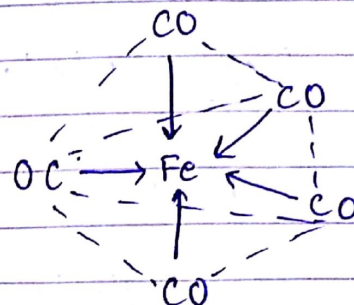
IOC / L.S.C.

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8. $Fe(CO)_5$

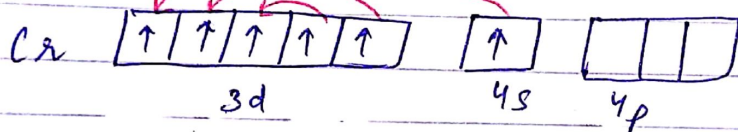


$CO \rightarrow s.l. \rightarrow$ Pairing

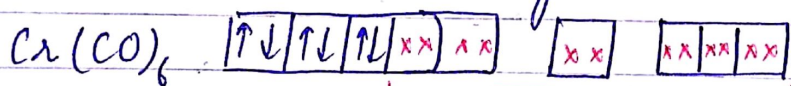


dsp^3 , Trigonal Bipyramidal
 $n=0$ dia
IOC / LSC

9. $Cr(CO)_6$



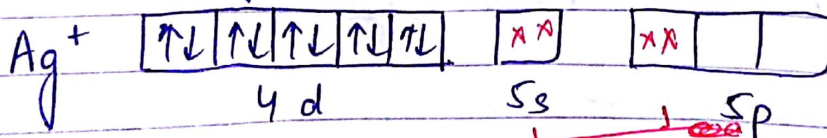
$CO \rightarrow s.l. \rightarrow$ pairing



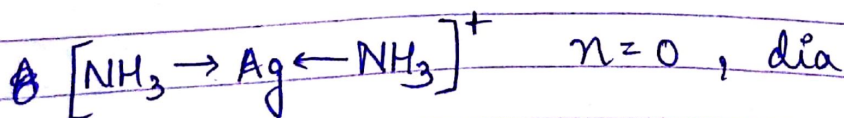
d^2sp^3 , Octahedral

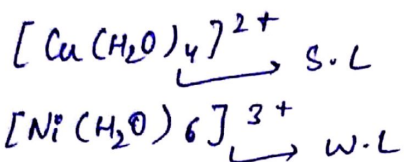
$n=0$, dia
IOC / L.S.C.

10. $[Ag(NH_3)_2]^+$



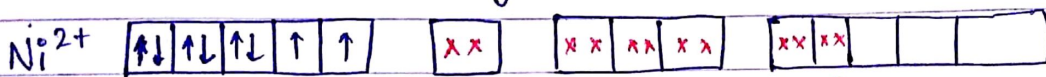
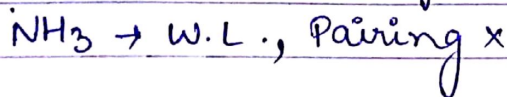
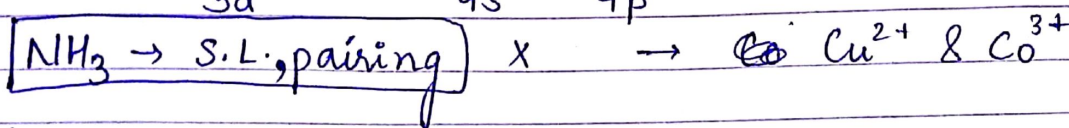
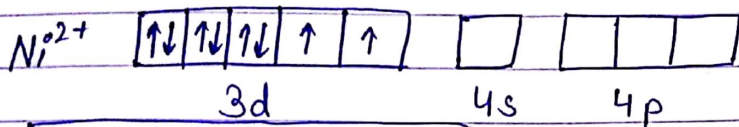
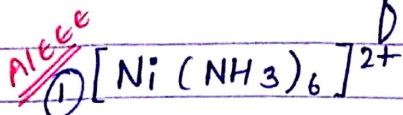
sp , linear



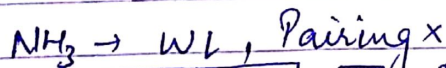
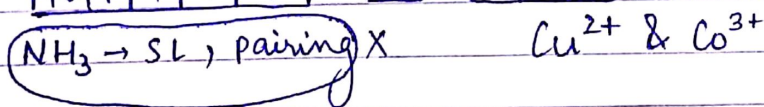
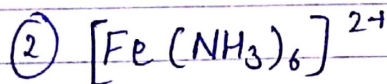


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Note :- 1. NH_3 & H_2O works as strong ligand in case of Cu^{2+} & Co^{3+} .



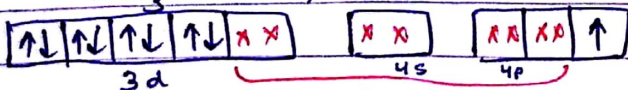
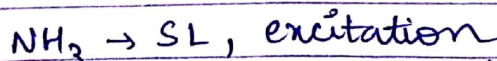
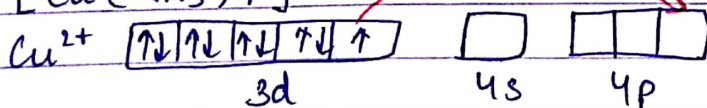
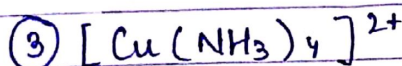
sp^3d^2 , Octahedral
 $n=2$, Paramagnetic
OOC / HSC



sp^3d^2 , Octahedral

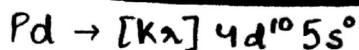
OOC / HSC

$n=4$, Para



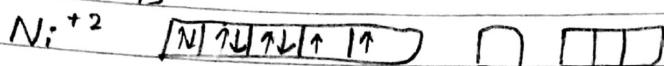
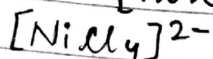
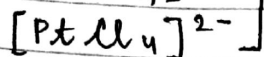
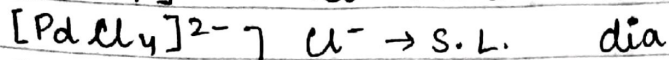
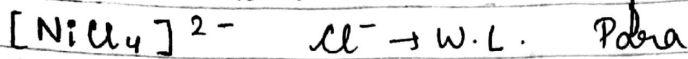
OOC / HSC

dsp^2 , square Planar
 $n=1$ Paramagnetic

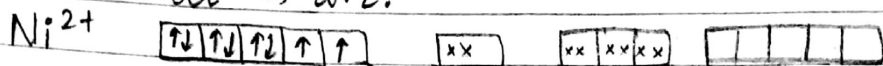


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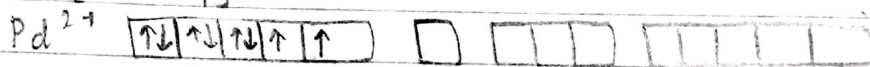
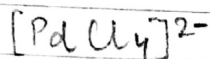
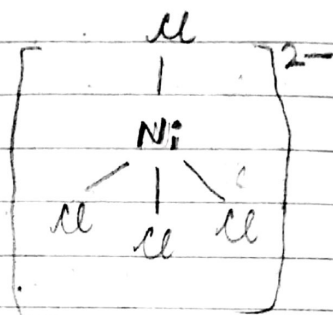
Note : W.L. works as S.L. in +ve of 4d & 5d metals



$Cl^- \rightarrow$ W.L.

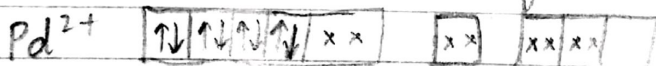


sp^3 tetrahedral
 $n = 2$ Para.



$Cl^- \rightarrow$ W.L. Pairing \times \times

$Cl^- \rightarrow$ S.L. Pairing \checkmark



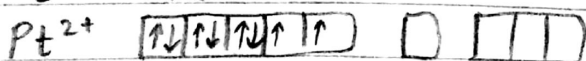
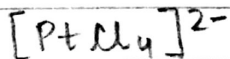
4d

$5s^2$
 dsp^2

5p

Square Planar

diamagnetic



$Cl^- \rightarrow$ W.L. Pairing \times \times

$Cl^- \rightarrow$ S.L. Pairing \checkmark



5d

6s

6p

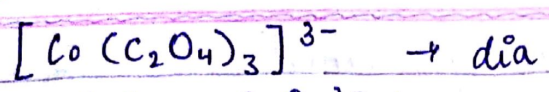
dsp^2

Square Planar

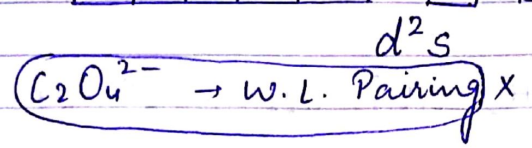
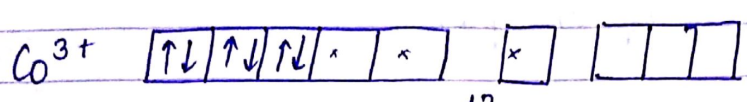
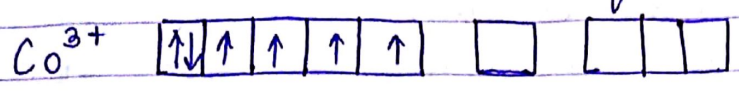
$n = 0$

diamagnetic

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oxalato $\rightarrow C_2O_4^{2-}$ in +ve of Co^{3+} works as S.L.

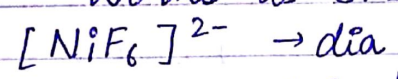


$C_2O_4^{2-} \rightarrow$ Pairing, S.L.

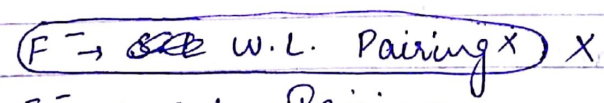
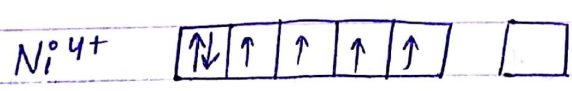
diamagnetic

AIIMS

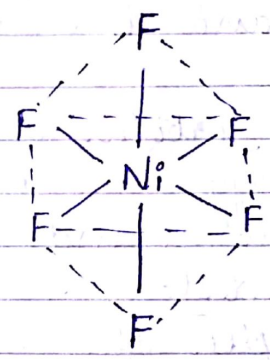
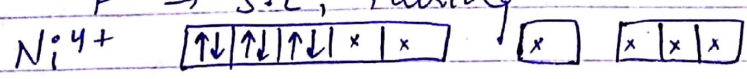
F^- works as S.L. in +ve Ni^{4+}



$\rightarrow d^2sp^3$



$F^- \rightarrow$ S.L., Pairing



d^2sp^3 , Octahedral
diamagnetic.

LIMITATIONS OF V.B.T. :-

1. It ~~could not~~ involves a no. of assumptions.
2. It does not give quantitative-titathue interpretation of magnetic data.
3. It does not explain color exhibit by V.B.T. compd.

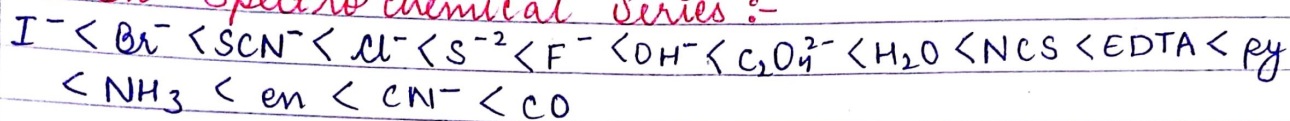
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4. It does not explain stability of Δ coordination compd.

5. It ~~do~~ could not distinguish w.l. and s.l.

6. It could not explain tetrahedral and square planar structures of compd.

Sto Spectrochemical Series :-



C.F.T. :-

1. Ligands are considered as point charges². There is only electrostatic force of attraction b/w metal orbital & ligand orbital i.e. bond b/w metal & ligand is purely ionic.

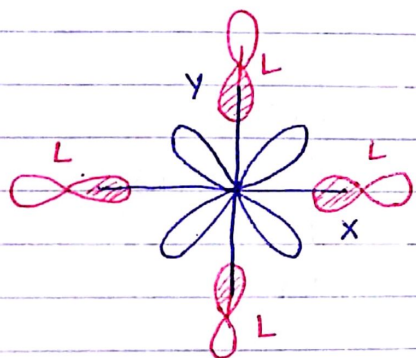
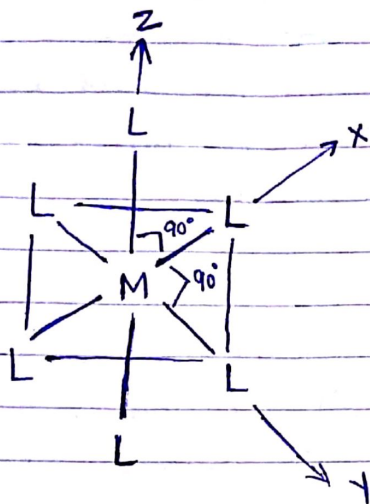
3. 5 d orbitals are degenerate orbitals i.e. have same energy.

When ligands approach these degenerate orbitals they destroy degeneracy of these 5 d orbitals and split them into 2 new sets of orbitals i.e. t_{2g} orbitals & e_g orbitals.

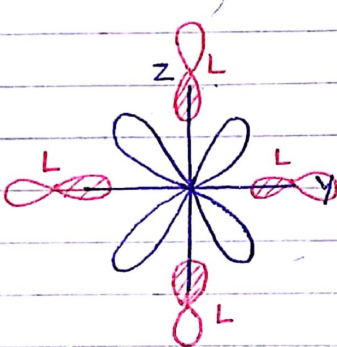
This splitting of orbitals into is c/a Crystal Field Splitting and amt. of energy released is c/a Crystal Field Stabilisation Energy (CFSE)

The amt. of energy released in +ve of strong ligand is more than the amt. of energy released in +ve of weak ligand. So strong field ligand form more stable complex than weak field ligand.

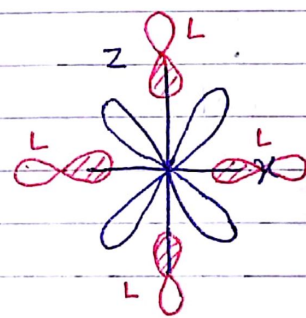
CFS in Octahedral Complex :-



d_{xy}

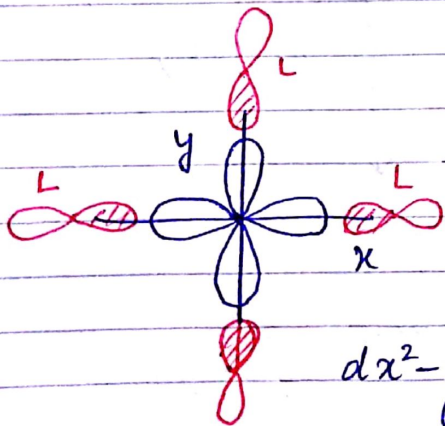


d_{yz}

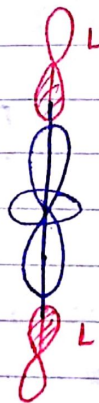


d_{zx}

t_{2g} orbitals



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



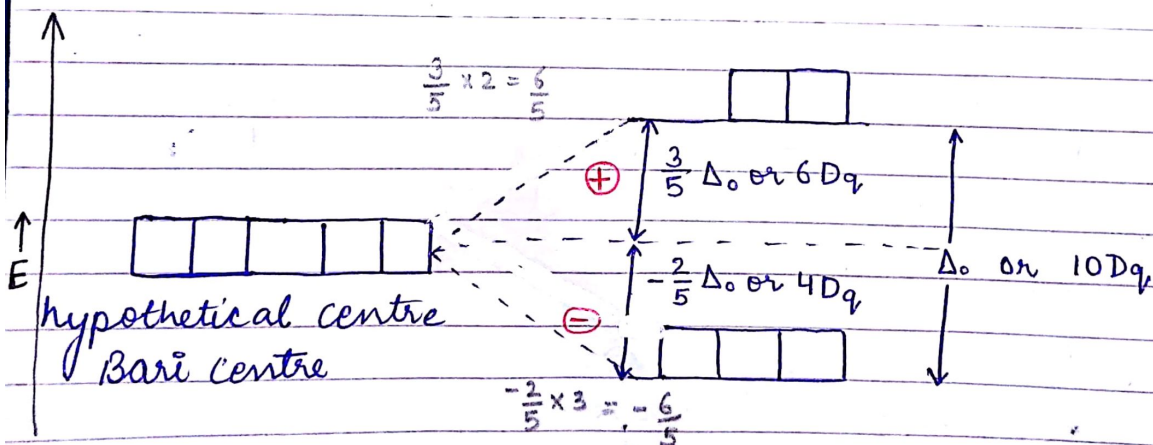
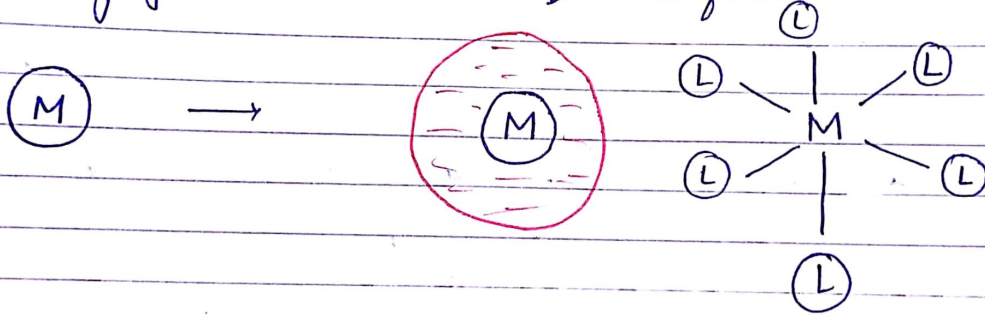
d_{z^2}

e_g orbitals

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→ Accⁿ to CFT, ligands always approach along the axes.
d_{xy} , d_{yz} & d_{xz} orbitals does not come directly in path of approaching ligand so that there is less repulsion b/w metal orbital & ligand orbital hence lower energy t_{2g} orbital (tripally generate orbitals) are formed.

$d_{x^2-y^2}$ & d_{z^2} orbitals comes direct in path of approaching ligands so there is more to repulsion b/w metal orbital & ligand orbital hence higher energy e_g orbitals (doubly generate orbitals) are formed.



Δ_0 → CFSE for Octahedral complex

e^\ominus are filled accⁿ to Hund's Rule

(e^- are filled in t_{2g} / lower energy orbitals accⁿ to Hund's Rule)

Conf.	weak ligand $\Delta_0 < P$			strong ligand $\Delta_0 > P$		
	n	μ		n	μ	
d^1	1	1.73	$t_{2g}^1 e_g^0$	1	1.73	$t_{2g}^1 e_g^0$
d^2	2	2.84	$t_{2g}^2 e_g^0$	2	2.84	$t_{2g}^2 e_g^0$
d^3	3	3.90	$t_{2g}^3 e_g^0$	3	3.90	$t_{2g}^3 e_g^0$
d^4	4	4.92	$t_{2g}^3 e_g^1$	2	2.84	$t_{2g}^4 e_g^0$
d^5	5	5.	$t_{2g}^3 e_g^2$	1	1.73	$t_{2g}^5 e_g^0$
d^6	4	4.	$t_{2g}^4 e_g^2$	0	0	$t_{2g}^6 e_g^0$
d^7	3	3.90	$t_{2g}^5 e_g^2$	1	1.73	$t_{2g}^6 e_g^1$
d^8	2	2.84	$t_{2g}^6 e_g^2$	2	2.84	$t_{2g}^6 e_g^2$
d^9	1	1.73	$t_{2g}^6 e_g^3$	1	1.73	$t_{2g}^6 e_g^3$
d^{10}	0	0	$t_{2g}^6 e_g^4$	0	0.	$t_{2g}^6 e_g^4$

P → Pairing energy required for pairing of e^- in an orbital.

in case of $d^1, d^2, d^3, d^8, d^9, d^{10}$ conf. does not depend upon strength of ligand.
but in case of d^4, d^5, d^6, d^7 conf. depend upon strength of ligand.

Ques Which of the following configuration will show magnetic moment equal to 2.84 BM?

- ① d^3
- ② d^5 (in case of weak ligand)
- ③ d^7 (in case of strong ligand)
- ④ d^4 (in case of weak ligand)

Ans

Ques Which of the following have least value of magnetic moment?

- ① $[Fe(CN)_6]^{3-}$ $3d^5, n=1$
- ② $[Co(CN)_6]^{3-}$ $3d^6, n=0$
- ③ $[Cr(CN)_6]^{3-}$
- ④ $[Mn(CN)_6]^{3-}$

$CN^- \rightarrow S.L.$

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CFSE for Octahedral complex = $[-0.4 \times n_{t_{2g}} + 0.6 n_{e_g}] \Delta_o + P$

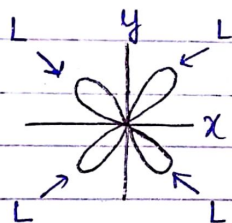
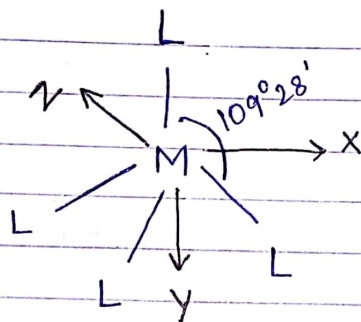
P → Pairing energy

Δ_o → CFSE for Octahedral complex

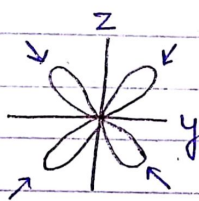
$n_{t_{2g}}$ → no. of e^- in t_{2g} orbitals

n_{e_g} → no. of e^- in e_g orbitals.

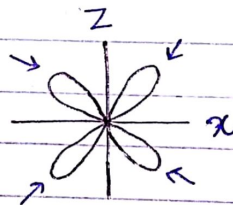
CFSE in Tetrahedral complex :-



d_{xy}



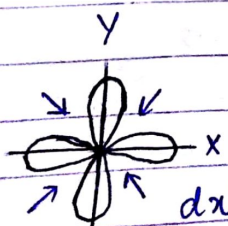
d_{yz}



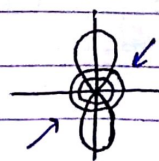
d_{zx}

t_{2g}

t_{2g} orbitals point directly to ligand
repulsion ↑
energy ↑



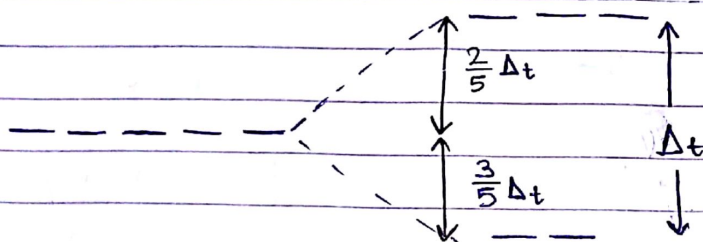
$d_{x^2-y^2}$



d_{z^2}

e_g

eg orbitals does not point directly to ligand
repulsion ↓
energy ↓



$\Delta_t \rightarrow$ CFSE for Tetrahedral complex

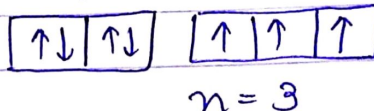
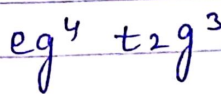
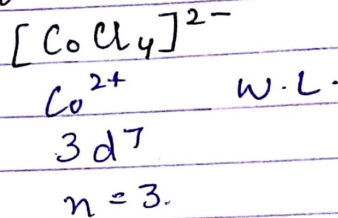
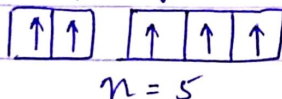
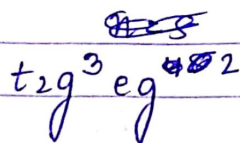
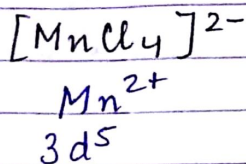
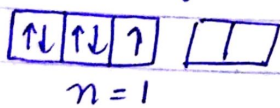
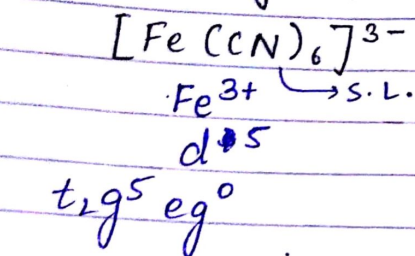
$$CFSE = (+0.4 \Delta_t) n_{t2g} + (-0.6 \Delta_t) n_{eg} + P$$

Note : Tetrahedral Complex are formed in +ve of W.L. Conf.

Conf.	Weak ligand $\Delta_t < P$	n	μ
d^1	$t_{2g}^0 e_g^1$	1	1.73
d^2	$t_{2g}^0 e_g^2$	2	2.84
d^3	$t_{2g}^1 e_g^2$	3	3.87
d^4	$t_{2g}^2 e_g^2$	4	4.90
d^5	$t_{2g}^3 e_g^2$	5	5.92
d^6	$t_{2g}^3 e_g^3$	4	4.90
d^7	$t_{2g}^3 e_g^4$	3	3.87
d^8	$t_{2g}^4 e_g^4$	2	2.84
d^9	$t_{2g}^5 e_g^4$	1	1.73
d^{10}	$t_{2g}^6 e_g^4$	0	0

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Que Arrange following in \uparrow order of magnetic moment



Factor affecting CFSE :-

1. Nature of metal
 Energy $3d < 4d < 5d$

2. O.S. on C.M.A. $CFSE \propto$ O.S. of C.M.A.
 $[Fe(CN)_6]^{3-} > [Fe(CN)_6]^{4-}$
 $+3 \quad +2$

3. Nature of ligand : S.L. > W.L.
 $Fe(CO)_5 > [Fe(CN)_6]^{3-} > [Fe(CN)_6]^{4-}$
 $CO > CN^- \quad O.S.$

4. Nature of complex Octahedral > tetrahedral

$$\Delta_t = \frac{4}{9} \Delta_o = 0.45 \Delta_o = 45\% \Delta_o$$

JOHN TELLER EFFECT :-

Accⁿ to John Teller effect, distortion in ^{regular} octahedral geometry occurs when unsymmetric configuration in of easy orbitals of C.M.A.

In ~~of~~ Octahedral field if all d e⁻ are symm. arranged then they will repel six lang ligands equally. Thus the structure will be a complete regular octahedral.

	t _{2g}	e _g	
d ⁰	$\square \square \square$	$\square \square$	[Cr(CN) ₆] ³⁻ [Cr(NH ₃) ₆] ³⁺
d ³	$\uparrow \uparrow \uparrow$	$\square \square$	S.L. or W.L. [TiCl ₆] ²⁻
d ⁵	$\uparrow \uparrow \uparrow$	$\uparrow \uparrow$	S.L. or W.L. [Cr(CN) ₆] ³⁻
d ⁶	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\square \square$	W.L. [Fe(H ₂ O) ₆] ³⁺
d ⁸	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \uparrow$	S.L. [Fe(CN) ₆] ⁴⁻
d ¹⁰	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow \downarrow$	S.L. or W.L. [Ni(NH ₃) ₆] ²⁺ [Ni(CN) ₆] ⁴⁻
			S.L. or W.L. [Zn(NH ₃) ₆] ²⁺ , [Zn(H ₂ O) ₆] ²⁺

In Octahedral field if d e⁻ are unsymm. arranged then some of ligands will repel more than other hence geometry will be distorted octahedral

	t _{2g}	e _g	
d ⁴	$\uparrow \uparrow \uparrow$	$\uparrow \square$	WL ^{HSC} Cr(II)
d ⁷	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \square$	SL Co(II) Ni ⁰ (III)
d ⁹	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow$	S.L. or WL Cu(II)

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Ques Which does not undergo John Teller distortion?
 (1) d⁴ (2) d⁷ (3) d⁸ (4) d⁹

If e_g orbitals point directly at ligands so unsymm. filling of e⁻ in e_g orbitals cause distortion in Octahedral geometry.

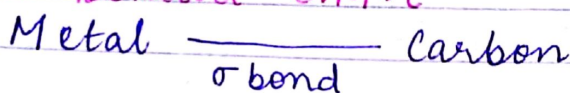
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t_{2g} orbitals lies b/w ligand approaching dirⁿ so in unsymm. filling of e^- in t_{2g} orbital cause less distortion which is negligible.

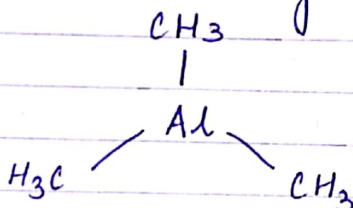
Organo Metallic Compound :-

Those compd in which metal atom is attached to carbon atom of some organic group are c/a O.M.C.

1. Sigma bonded O.M.C



eg : $Al(CH_3)_3 \rightarrow$ Trimethyl aluminium



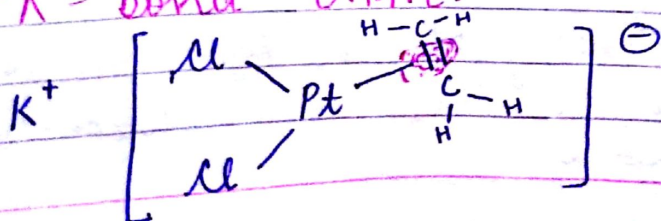
$R-Mg-X$ Grignard Reagent
 $(CH_3)_2Zn$ Frankland Reagent
 $(C_2H_5)_4Pb \rightarrow$ tetraethyl lead
TEL \rightarrow used as antiknocking agent in petrol.

$(C_2H_5)_2Zn$ Frankland Reagent

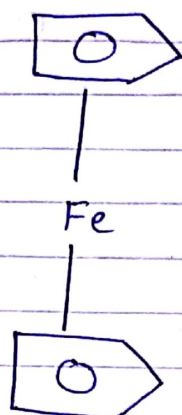


phenyl lithium

2. π -bond O.M.C.



Zeise's salt $K^+ PtCl_3 \eta^2 (C_2H_4)]^- \cdot x H_2O$

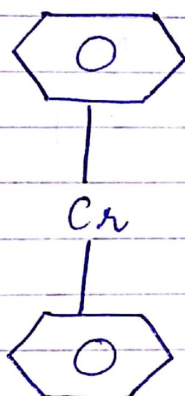


$\eta^5 (C_6H_5)_2 Fe (II)$

Ferrocene

bicyclo Pentadienyl Iron (II)

~~di~~ dibenzene Chromium (0)



$\eta^6 (C_6H_6)_2 Cr (0)$

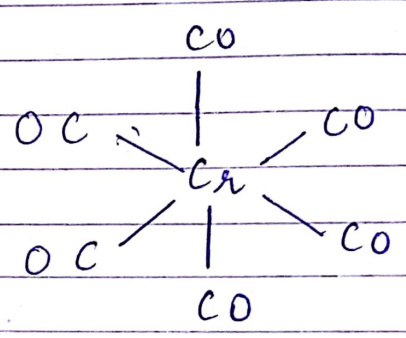
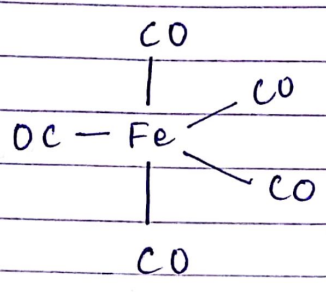
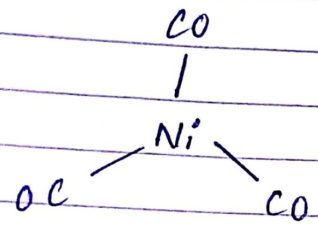
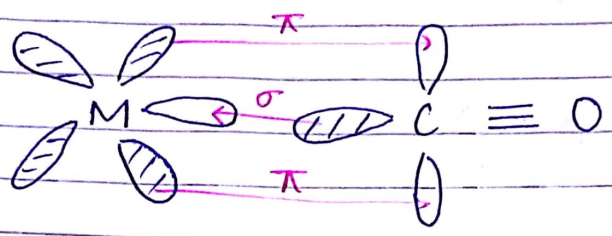
σ and π bond

→ include metal carbonyls like $Ni(CO)_4$, $Fe(CO)_5$

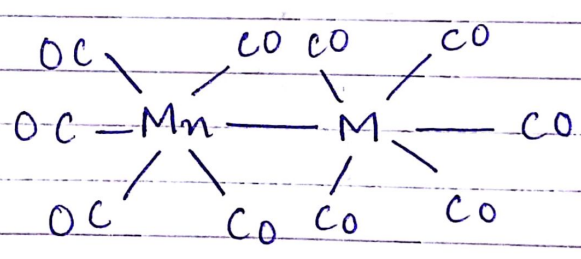
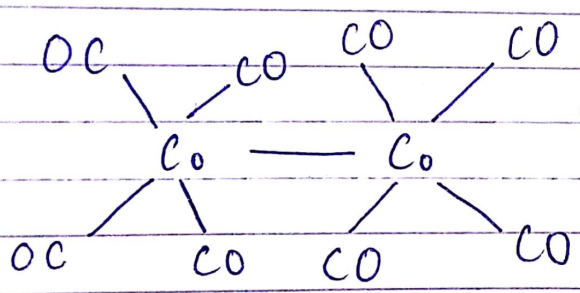
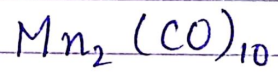
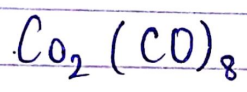
→ In this compd, σ bond formed b/w vacant hybrid orbital of metal & lp of carbon atom in CO.

→ While a π bond is formed b/w antibonding orbital (π^*) of CO & filled orbital of Metal atom. This bonding is also k/n as synergic bonding.

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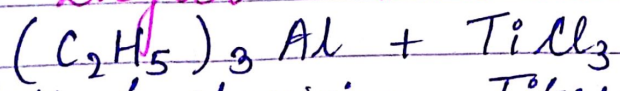


C-O B.L. order $[\text{Fe}(\text{CO})_5]^- > [\text{Cr}(\text{CO})_6]^0 > [\text{V}(\text{CO})_6]^+$



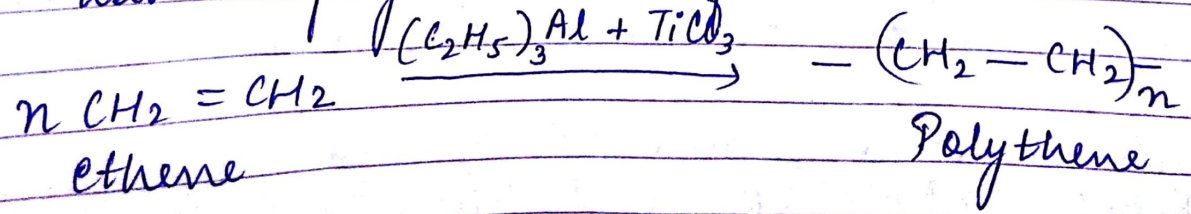
Appⁿ of O.M.C.

1. Ziegler Natta Catalyst :-

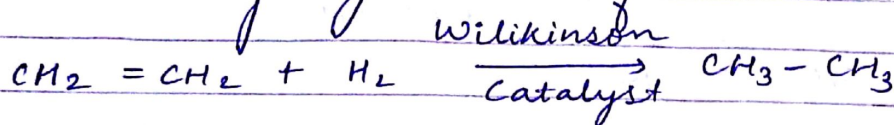


Triethyl aluminium Titanium chloride

→ used in polymerisation of alkene



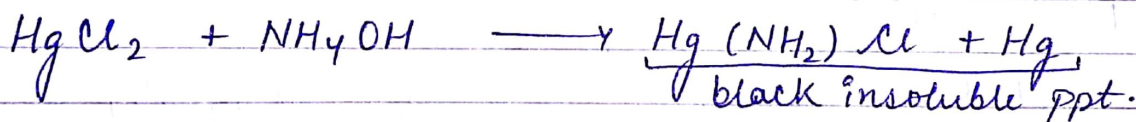
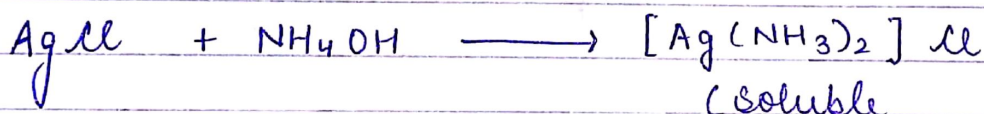
2. Wilkinson's catalyst $[\{(\text{C}_6\text{H}_5)_3\text{P}\}_3\text{Rh}] \text{Cl}$
used in hydrogenation of alkene



3. $\text{C}_2\text{H}_5\text{HgCl}$ (ethyl Mercury Chloride)
used as fungicide in agriculture (Toxic)

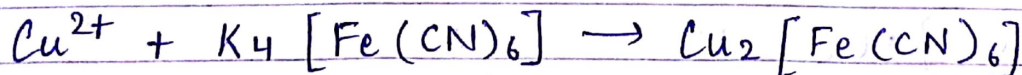
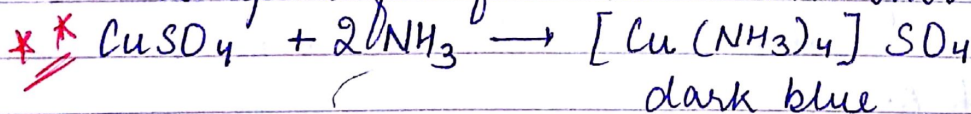
Application of Coordination Compd :- In Qualitative Analysis

1. To separate group I radical like Ag^+ & Hg^{2+}
complexation formation with NH_4OH is done



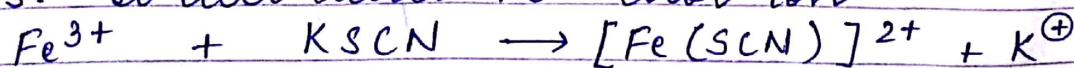
2. To detect Cu^{2+} ion

Complex for Cu^{2+} with ammonia is done



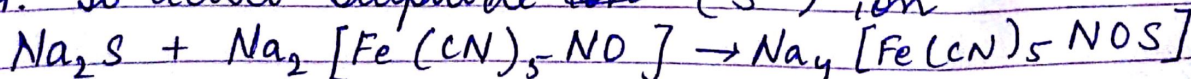
Chocolate brown

3. To detect Fe^{3+} color ion



blood red color

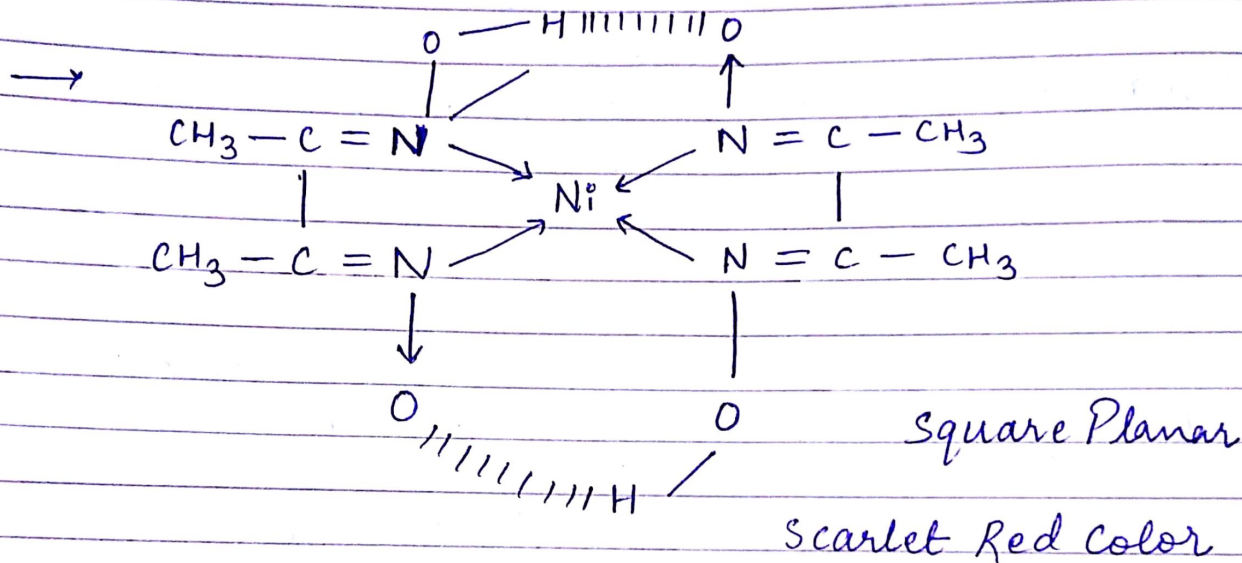
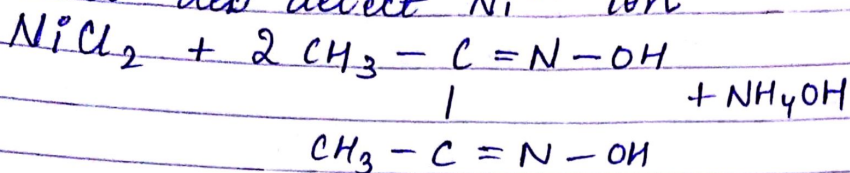
4. To detect sulphide ion (S^{2-}) ion



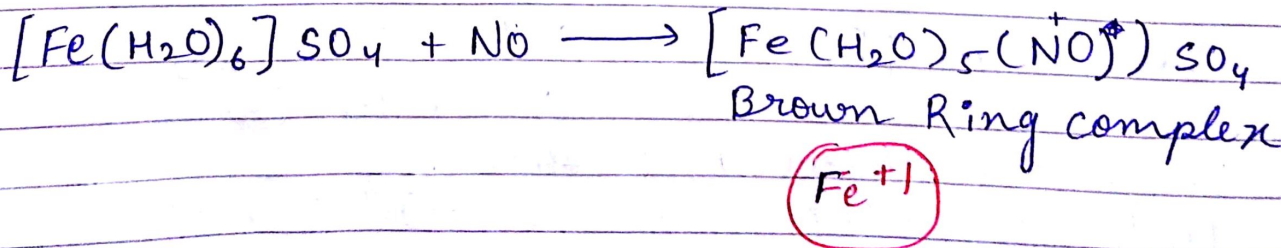
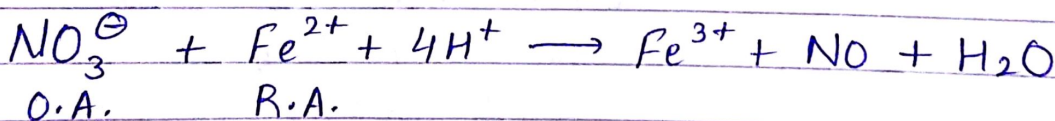
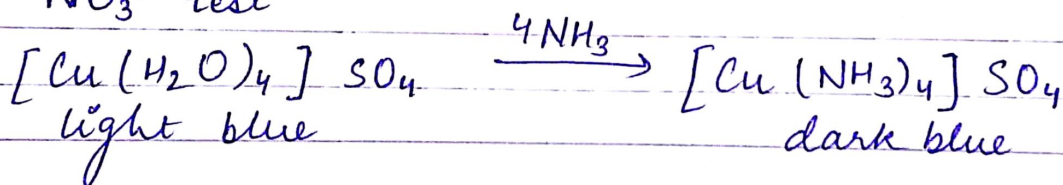
Sodium Nitro
Prusside

Violet color

5. To detect Ni^{2+} ion



NO_3^- test



In Medical field :-

① cis-platin is used in anti-cancer drug.

② Ca-EDTA is used for treatment of patients suffering from lead poisoning.

Ca-EDTA dissociates lead into inside the body & more stable Pb-EDTA complex is formed which is excreted through urine by body. while harmless Ca^{2+} ions remains inside the body.

Vitamin B12 : cyanocobalamin is a cobalt vitamin in which Co^{2+} is central metal ion. It is anti-pernicious anemia factor.

Chlorophyll (Mg^{2+})

AIIMS-13

Haemoglobin (Fe^{2+})

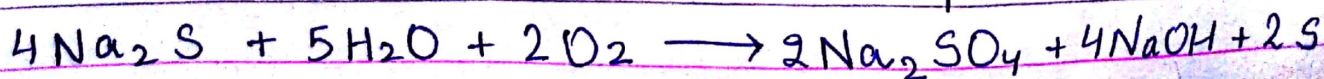
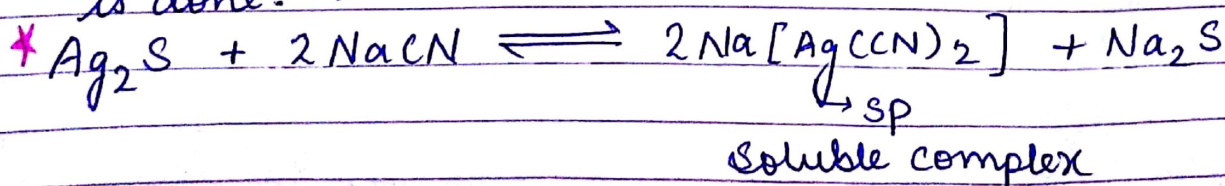
Myoglobin (Fe^{3+})

Insulin (Zn)

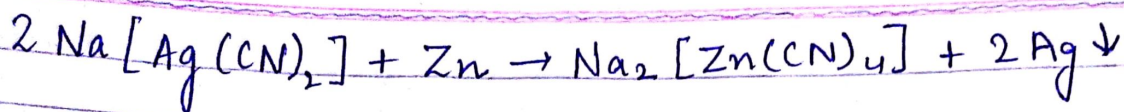
Carboxypeptide (Zn)

In Metallurgy :-

In extraction of metals like silver & gold, complex form with sodium cyanide ($NaCN$) solⁿ is done.



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In Electroplating :-

In electroplating of noble metals like silver & gold, their complex forming tendency is used.

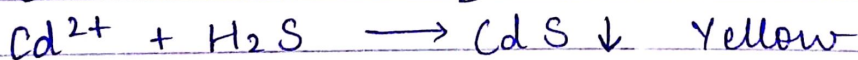
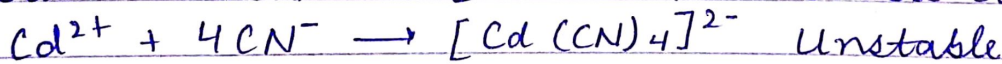
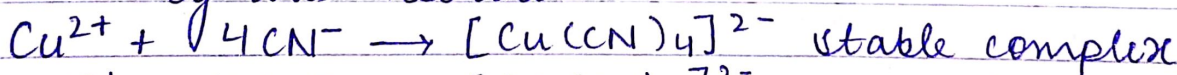
For eg :-

In electroplating of silver complex potassium dicyano argento (I) - $\text{K}[\text{Ag}(\text{CN})_2]$ is formed due to which Ag^+ ions are not available for displacement & layer over silver remain stable for a longer time.

In a masking agent :-

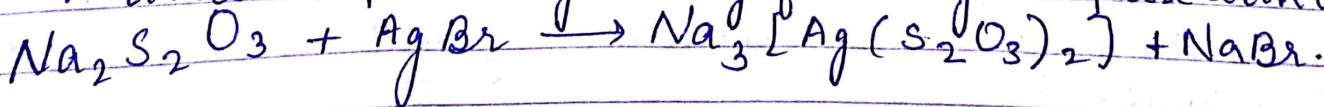
To detect a particular ion in +ve of other ions. A specific ligand is added which form stable complex with all the other ions. Except the ion to be detected, this is k/n as masking Method.

For eg : Cd^{2+} ions are detected in +ve of the Cu^{2+} ions by this method.



In photography :-

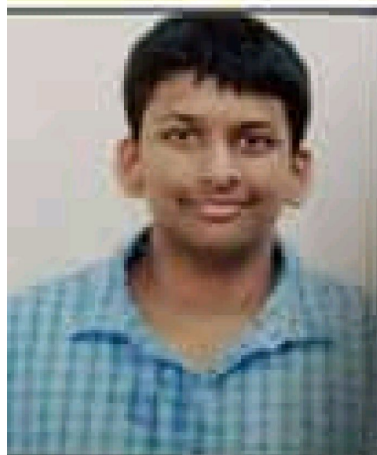
Sodium Thiosulphate is used in photography becoz of its complex forming tendency as it removes undecomposed AgBr by forming complex with it.



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