

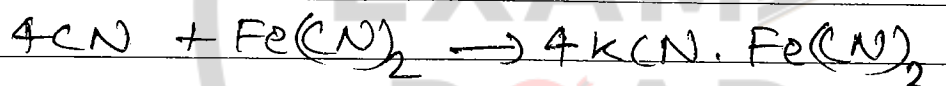
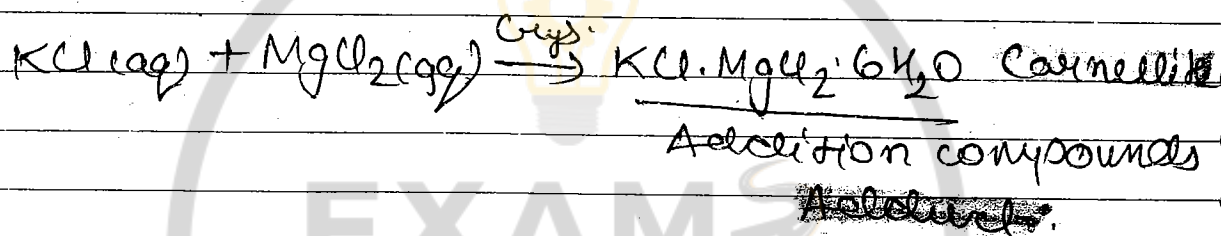
Handwritten Notes on Coordinating Compounds



CO-ORDINATION COMPOUNDS

(Complex Compounds)

When Aq. solⁿ of two or more than salts is subjected to crystallize new compound is formed which contains ions of both salts is called Addition compounds / Adduct. And such reactions are called Addition reaction.

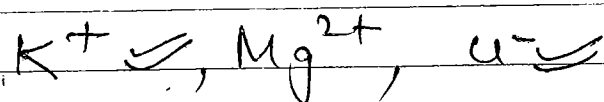
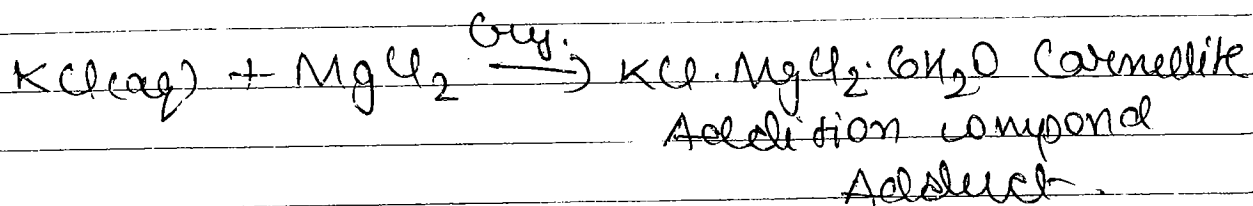


Addition compounds are classified into two categories →

- (1) ~~Double salt~~ → completely ionize in aqueous medium. Exist only in solid state not in aq. medium.

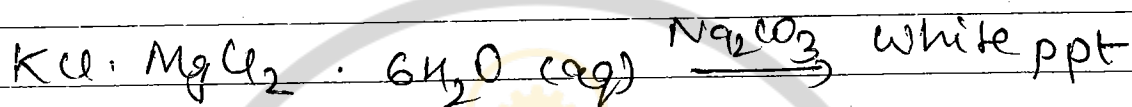
All ions show their presence in aq. medium

All ions gives their ~~test~~

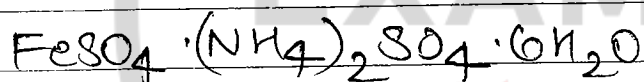


type of ion $\frac{\text{theo}}{3(K^+, 2Mg^{2+})}$ $\frac{\text{Prac}}{3}$
No. of ions. 5 3

flame test ✓



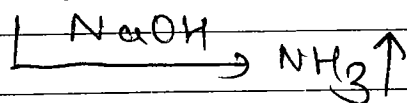
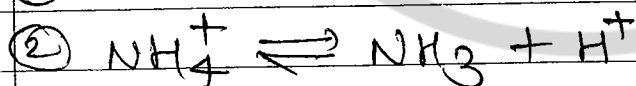
Mohr's Salt



type of ions in aq medium = 3

No. of ions in aq. Medium = 5

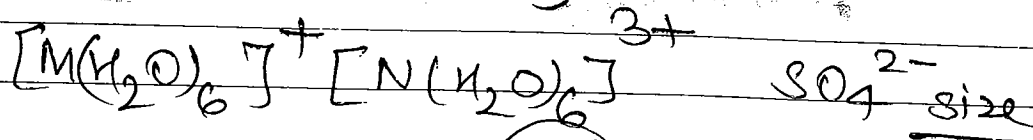
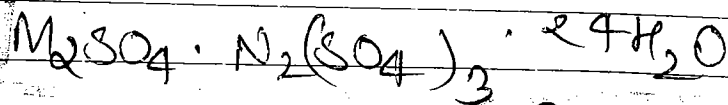
① when react with NaOH gives green ppt of $Fe(OH)_2$



gives basic gas when react with NaOH

③ gives white ppt. when react with
 $BaCl_2 / Pb(NO_3)_2 / SrCl_2$
 $(BaSO_4 / PbSO_4 / SrSO_4)$

Alum



~~M²⁺ monovalent~~ = ~~Li⁺~~, Na⁺, K⁺ \approx NH₄⁺, Cs⁺, Rb⁺
 N³⁺ (trivalent) = due to small size

→ Cr³⁺, Al³⁺, Fe³⁺

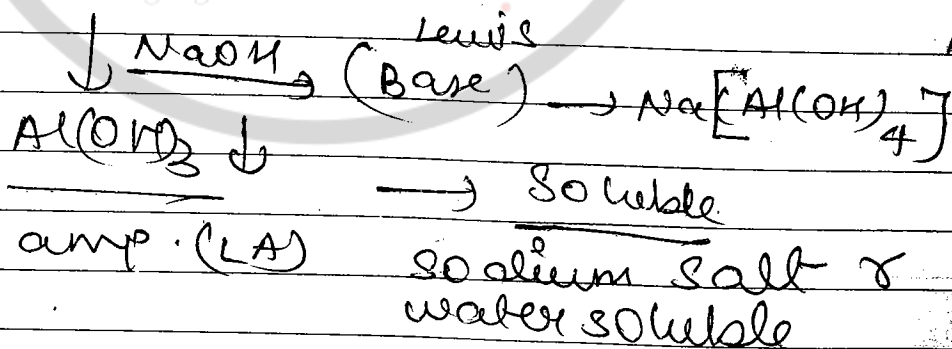
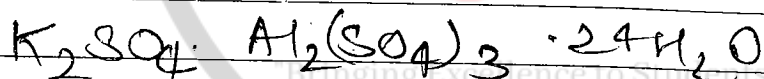
⇒ All alums gives ppt with NaOH

Al³⁺ ions form insoluble hydroxide

⇒ All Alums gives ppt. with BaCl₂
 (white ppt of BaSO₄)

example

Potash alum alum

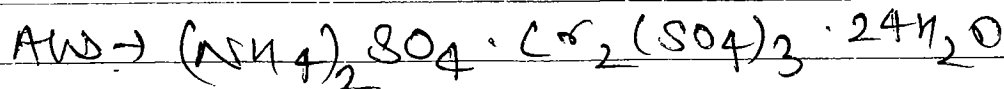


(Q) Find the formula of an alum having following properties →

(1) Gives basic gas when react with NaOH

(2)

⑥ Gives white ppt when React with BaCl_2 .

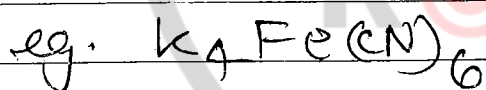


(2) Complex Salts \rightarrow

Does not ionize completely in (aq.) Medium.

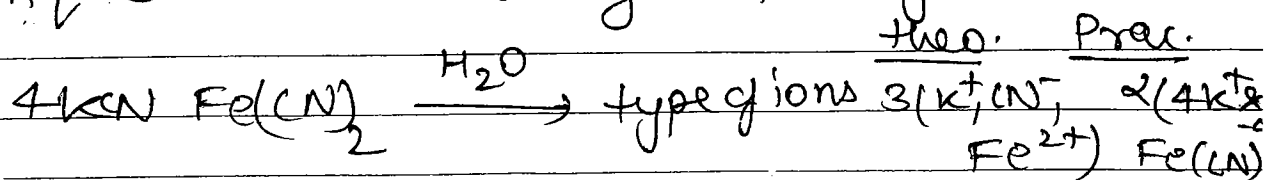
Compound exist in solid state & can exist in (aq.) Medium.

Some of the ions loses their identity in aq. Medium, does not give their true qualitative test, does not show their presence in aq. medium.



KCN & $\text{Fe}(\text{CN})_2$ both are highly poisonous due to presence of $(\text{CN})^-$ ion.

but when they form compound $\text{K}_4\text{Fe}(\text{CN})_6$ its aq. soln is no more poisonous, cyanide ion loses its identity, Aq. soln also not give test of Fe^{+2} .



$\text{K}^+ \checkmark$ $\text{Fe}^{2+} \times$ CN^- No. of ions 11 5

Ions which are not ionized completely in aq. medium loses their identity in aq. medium written in square bracket collectively. Such ions are called complex ions. & ions present in salt which contain such ions are called complex salt.

In Complex ion \rightarrow

At least one metal ion present which is bonded by/surrounded by neutral molecules/ions by coordinate bond. i.e. why complex compounds are also named as Coordination Compounds.

Metal ion which is centre of complex act as Lewis acid is called central Metal ion (CMI).

No. of lone pair accepted by a central Metal ion is called its coordination number.

Properties of CMI \rightarrow

(1) Small Size

(2)



(3) High Z_{eff} .

(4) Presence of vacant orbital of low energy.

General Coordination number \rightarrow

+3 ions of 3d series = 6 always

+2 ions of 3d series = 4/6

$Ni^{2+} \xrightarrow{H_2O/NH_3} 6$

$Cu^+/CN^- \rightarrow 4$

$Pd^{2+}, Pt^{2+}, Au^{3+}, Ag^{3+} (d^8) = 4$ always
 $d^8 sp^2$ sq. planar dia.

$Pd^{4+}, Pt^{4+} = 6$ always
 $d^2 sp^3$ diamag. always

$Au^+, Ag^+ = 2$ always
 Config $\rightarrow d^{10}$ sp hybridization

Neutral Molecules or Ions which act as Lewis base in complex formation are called ligands.

No. of lone pair donated by a ligand is called its denticity.

(Q) Find the denticity of neutral ligand X in given complex.

Ans = 2 $Pt^{4+} \rightarrow CN = 6$

Geometry of complex ion is called coordination polyhedra.

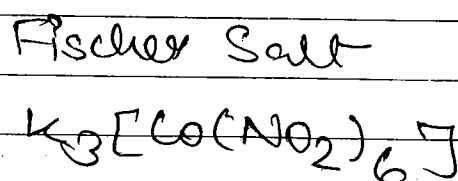
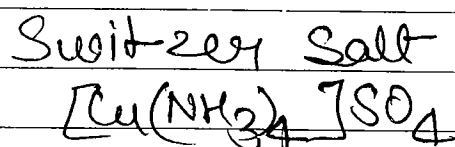
eg → Tetrahedral, square planar

Charge on complex ion is the sum of oxidation state of central metal ion or ligand.

Space in 3d where coordinate bond form b/w central metal ion & ligands is called coordination sphere, Part inside the square bracket represent the coordination sphere.

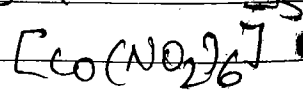
⇒ Species inside a coordination sphere is non-ionizable while species present in ionization sphere is ionizable

Simple ions which form ionic bond with complex ion is called counter ion.

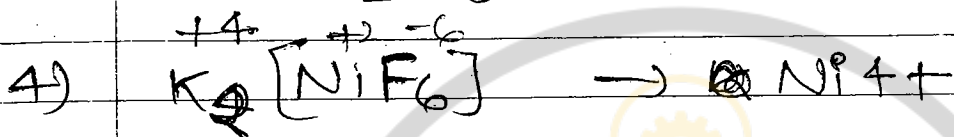
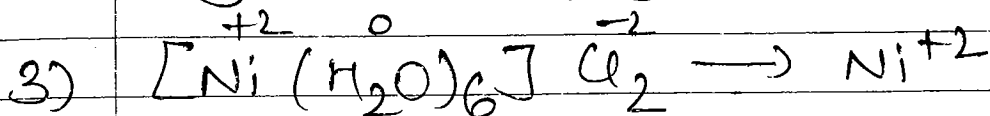
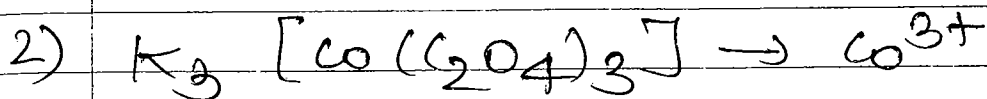
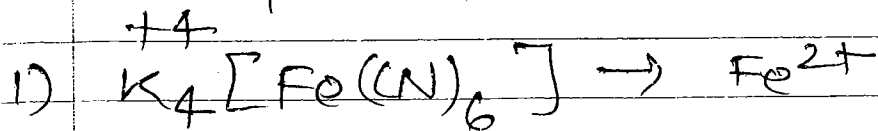


counter ion SO_4^{2-}

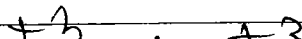
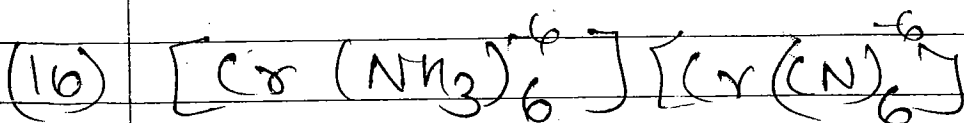
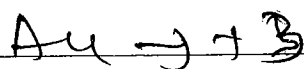
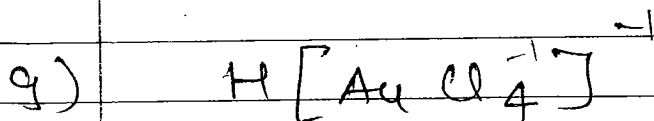
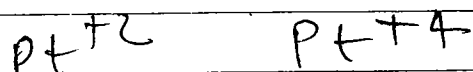
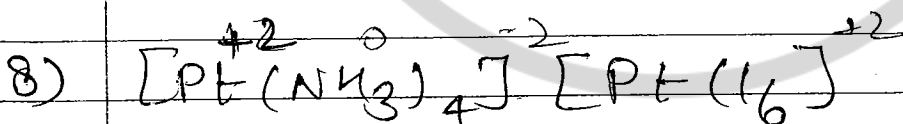
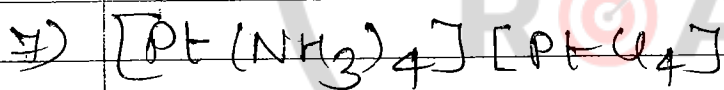
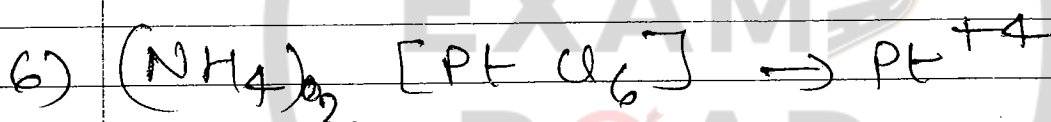
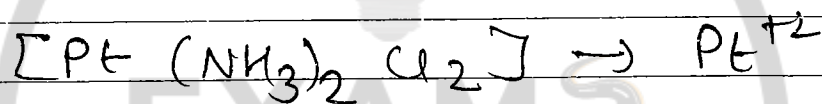
ions in aq. medium $[\text{Cu}(\text{NH}_3)_4]^{2+} \text{SO}_4^{2-} 3\text{K}^+$

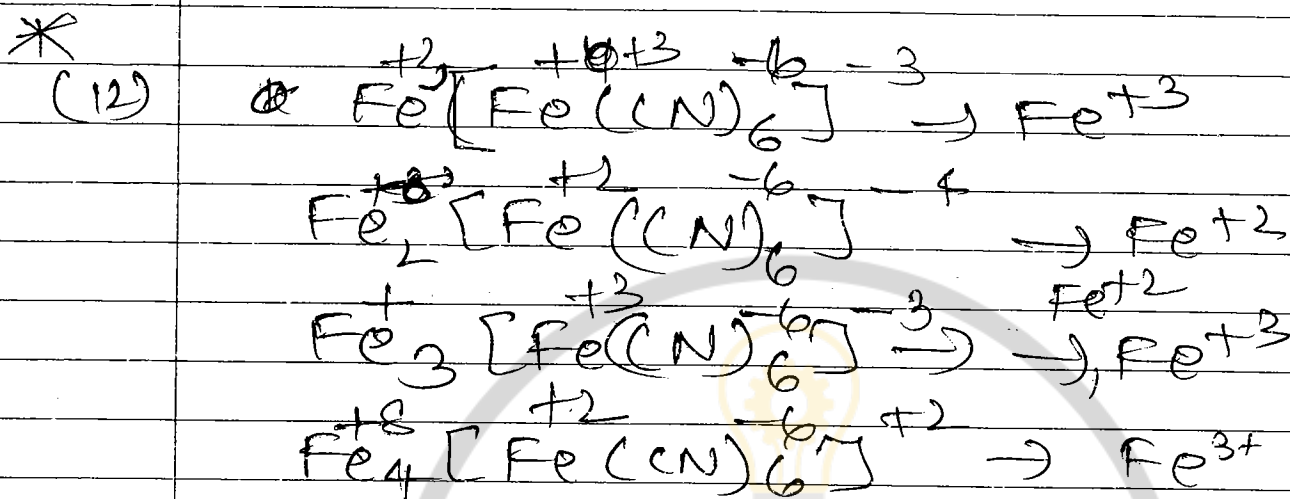
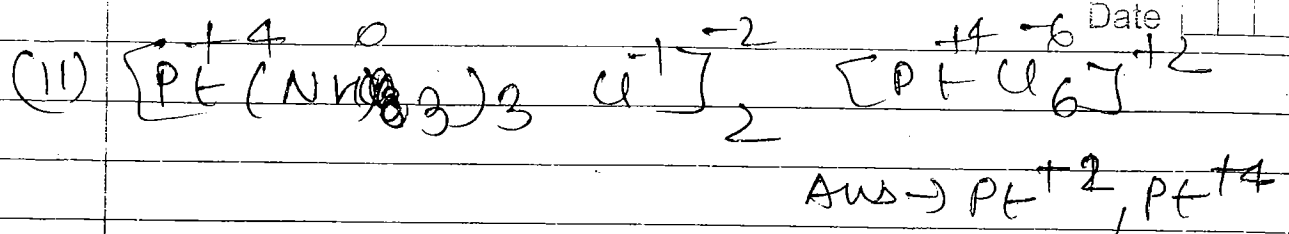


Find Central Metal Ion in given Complexes.



5) Cisplatin (anticancer)





Classification of Complexes \rightarrow

(1) On the basis of charge

Cationic	Anionic	Neutral
$[]^+$	$[]^-$	$[]^0$
So complex compound may be		

① Simple Cation Complex Anion

Fischer's salt $\text{K}_3[\text{Co}(\text{NO}_2)_6]$
Sodium Nitro prusside

$\text{Na}_4[\text{Fe}(\text{CN})_6\text{NO}]$

② Complex Cation Simple Anion

Switzer salt $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$

Brown ring complex $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$

③ Complex Cation Complex Anion

$[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$

④ Neutral complex \rightarrow

Cisplatin (anti cancer)

$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

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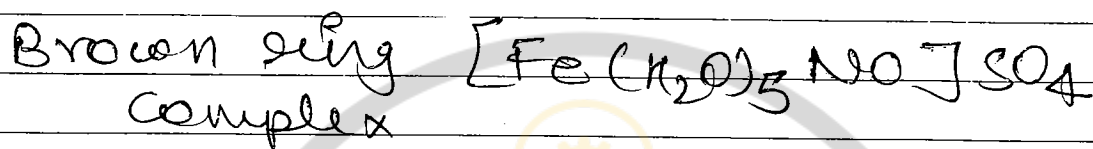
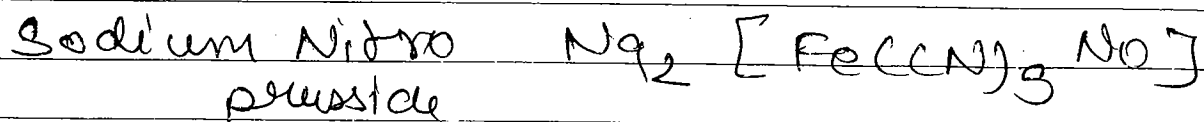
On the basis of type of Ligands \rightarrow

1 Homoleptic \rightarrow Having only one type of ligand in coordination sphere.

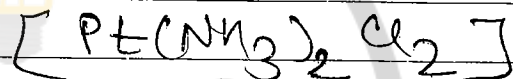
Fischer's salt $\text{K}_3[\text{Co}(\text{NO}_2)_6]$

Switzer salt $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$

2) Heteroleptic \rightarrow More than one type of ligand present in a coordination sphere.



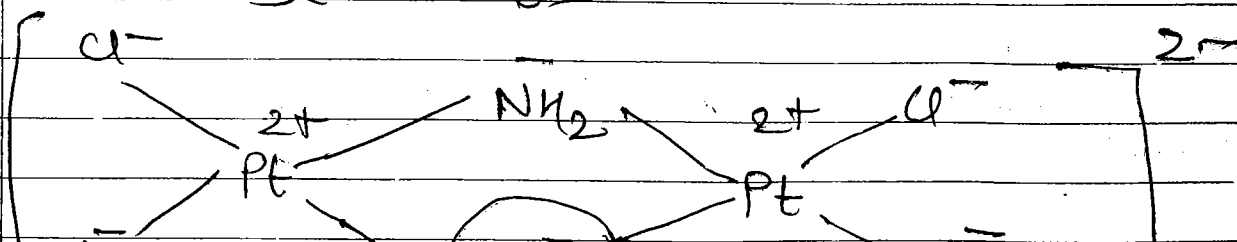
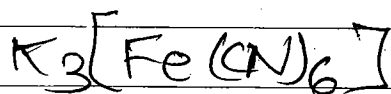
Cisplatin (anticancer).



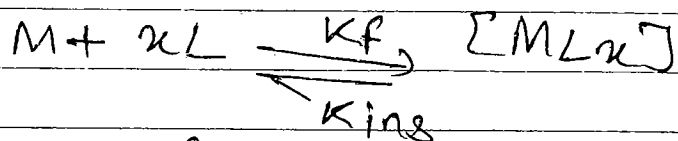
3) On the basis of No. of central Metal ion in a coordination sphere.

(a) Mononuclear complexes \rightarrow Only one central Metal ion present in a coordination sphere.

(b) Poly nuclear complexes \rightarrow More than one ~~to~~ CMT present in a co. sphere.



4) On the basis of Stability \rightarrow



k_f = formation constant

k_{ins} = instability constant

$$K_f = \frac{1}{k_{ins}}$$

$$K_f = \frac{[ML_x]}{[M][L]^x}$$

$$K_f > 1 \quad (K_f \uparrow)$$

$$[ML_x] \gg [M] \& [L]$$

$$K_f < 1 \quad K_f (\downarrow)$$

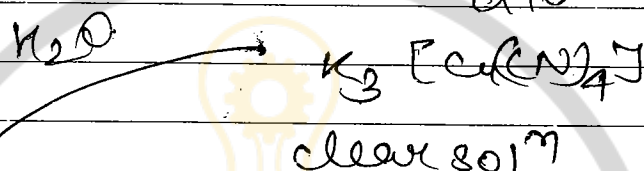
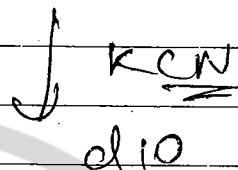
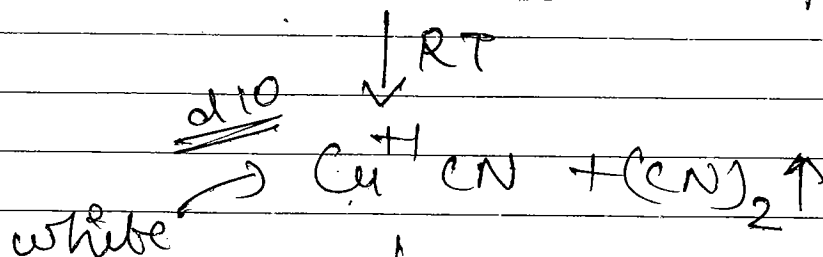
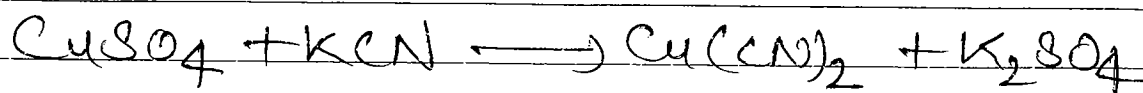
$$[ML_x] \ll [M] \& [L]$$

Perfect Complex \rightarrow

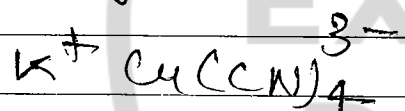
Having high value of formation const.
stable in presence of particular reagent.

Imperfect Complex

Low value of formation const. (K_f)
unstable in presence of particular reagent



type of ions = 2

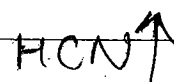


perfect w.r.t H₂O

✗ perfect

w.r.t H₂S

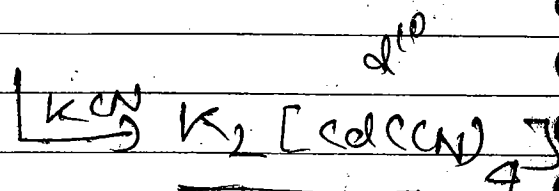
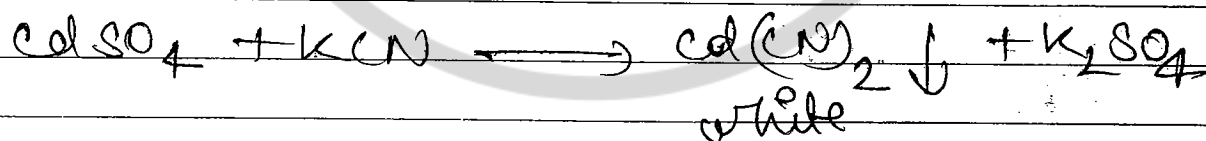
strong acid



imperfect

w.r.t to HCl

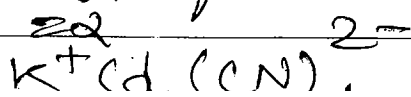
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colourless

H₂O

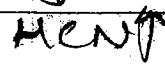
type of ions =



↓ H₂S

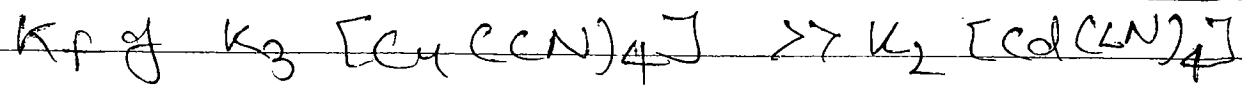
col^d / yellow

↓ HCl



1





All Ammonia and cyano complexes are Imperfect in presence of strong acid.

There is no sharp borderline to distinguish perfect & imperfect complexes.

They are defined in presence of particular reagent.

CLASSIFICATION OF LIGANDS →

On the basis of charge →

(a) Anionic Ligand → In the naming of Anionic ligand suffix 'ide' is replaced 'ido/o'
↓
best

ate → ato
 ide → ite

As a counterion

As a ligand

Cl^-
 SO_4^{2-}
 SO_3^{2-}

chloride
 sulphate
 sulphonate

chlorido
 sulphato
 sulphonato

(b) Neutral Ligands \rightarrow

General name is used in the naming of neutral ligands except

H_2O — aqua

NH_3 — Ammonia

CO — Carbonyl

NO — Nitrosyl

(c) Cationic Ligands \rightarrow

um suffix is used in the naming of cationic ligands

eg $\rightarrow NO^+ \rightarrow$ Nitrosonium/Nitrosylium

$N_2O_5^+ \rightarrow$ Hydrizinium

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On the basis of Denticity \rightarrow

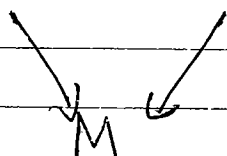
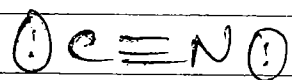
only one donor site = monodentate

because they form only one coordinate bond with a C.M.I.

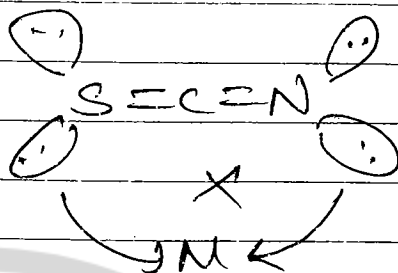
Having two donor site

form three member ring (edge/
corner)

They act as monodentate because their member ring is unstable due to Angle strain



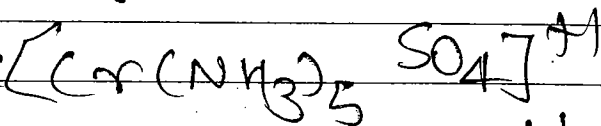
unstable ring



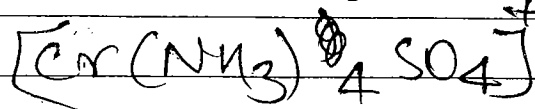
form 4 member ring with CMI

4 member ring is stable than 3 member ring but less stable in comparison S/6/7 member ring due to Angle strain. Such ligands prefer to act as monodentate ligand but as per req. of coordination no. of CMI they can act as bidentate ligand i.e. why such ligands are known as flexidentate ligand. eg. all oxyanions

Mono
dentate

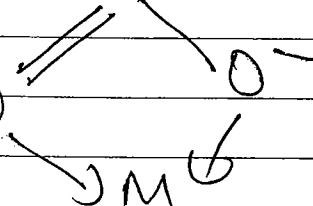


Biden
tate



Cr^{+3} , CN = 6

X (Non metal)



form 3/6/7 member ring \rightarrow act as bidentate, didentate ligand.

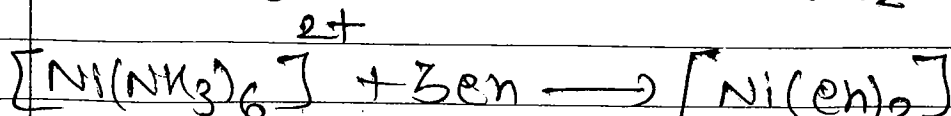
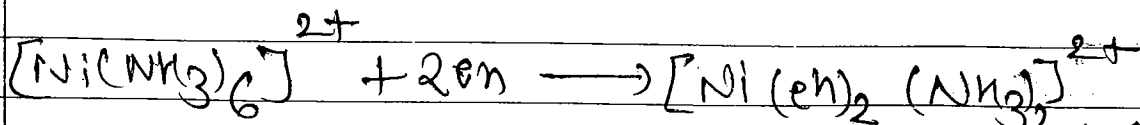
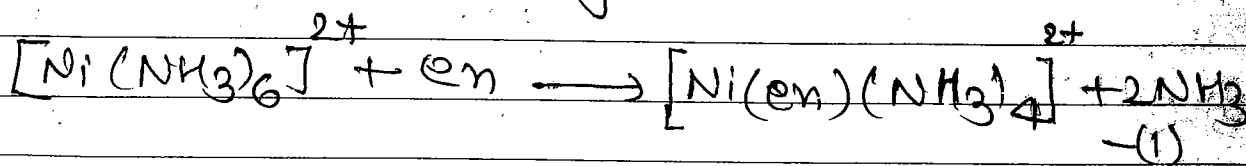
\Rightarrow Ligands Having 3 or more donor site form 3/6/7 member ring act as polydentate.

3 donor \rightarrow tridentate
 4 donor \rightarrow tetradentate
 5 donor \rightarrow pentadentate
 6 donor \rightarrow hexadentate.

CHELLATING LIGAND \rightarrow

When bidentate or polydentate ligand coordinates with a central Metal Ion they form ring like structure. Such rings are called chelate rings and phenomena is called chelation, such ligands are called chelating ligands.

No. of chelate ring formed by a ligand
 $= \text{Denticity} - 1$

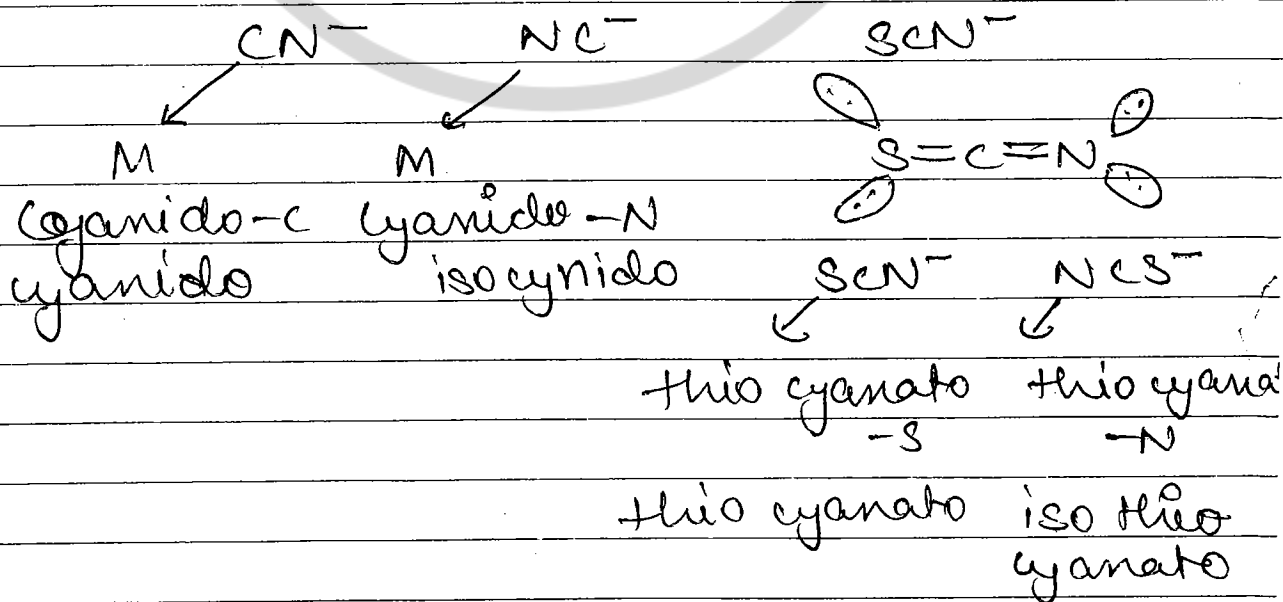


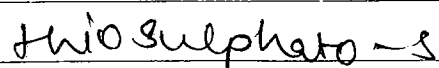
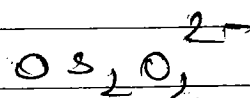
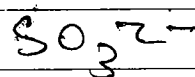
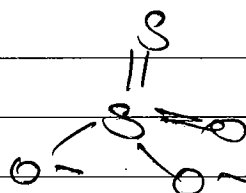
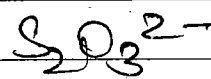
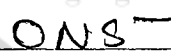
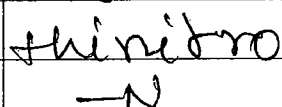
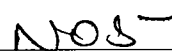
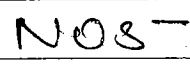
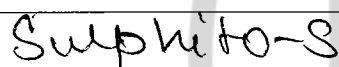
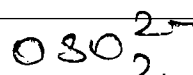
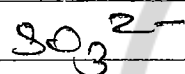
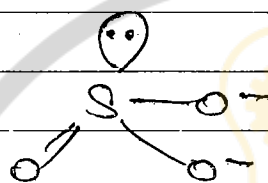
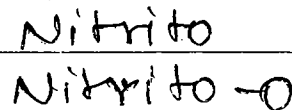
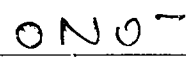
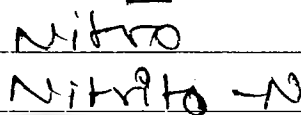
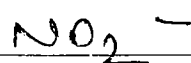
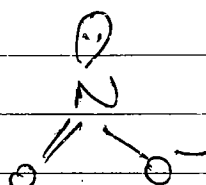
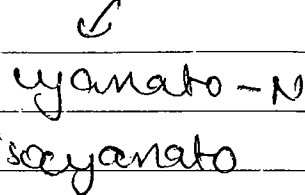
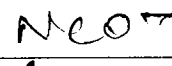
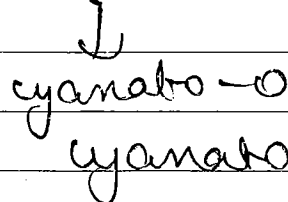
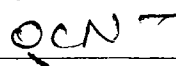
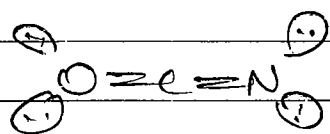
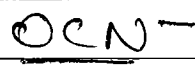
<u>Δn</u>	no. of rings	(i) \rightarrow (ii) \rightarrow (iii)
$(3-2=1)$	1	$\Delta n \uparrow \quad \Delta S \uparrow \quad \begin{matrix} \text{no. of ring} \uparrow \\ \text{chelation} \uparrow \end{matrix}$
$(5-3=2)$	2	$\Delta G \downarrow = \Delta H - T\Delta S \uparrow$
$(7-4=3)$	3	stability \uparrow

stability & chelation
 \propto no. of rings

Ambidentate Ligand \rightarrow

Anionic Ligand having two or more than two diff. donor sites but uses one type of donor site when coordinated with a central metal ion such ligand are called Ambidentate ligands.



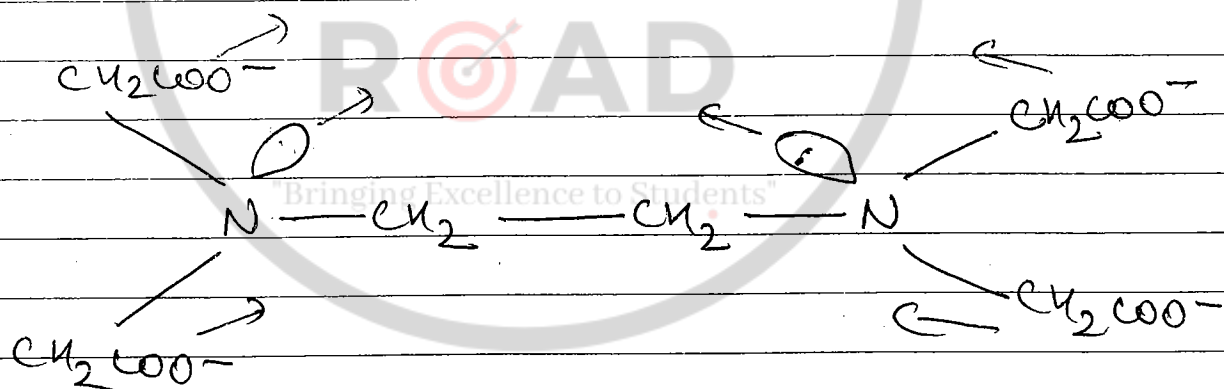
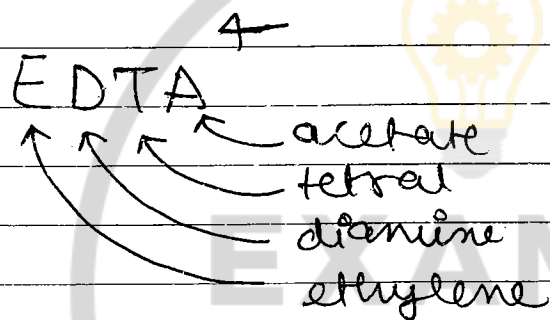


Flexidentate ligands →

Ligands which can show variable denticity.

ex-1) Ligands which form 4 member ring with CMI.

2) EDTA⁴⁻ has pH dependent denticity



Denticity = 6

Denticity

pH ↓	EDTA ⁴⁻	6
	HEDTA ³⁻	5
Denticity ↓	H ₂ EDTA ²⁻	4
	H ₃ EDTA ⁻	3

Ligands Formula Name Identity Comments

1) H^-

Hydrido

1

2) F^-

Fluorido

1

3) Cl^-

chlorido

1

4) Br^-

Bromido

1

5) I^-

Iodido

1

6) O^{2-}

Oxido

1

7) N^{3-}

Nitrido

1

8) O_2^{2-}

Peroxido

1

9) O_2^{2-}

Superoxide

1

10) OH^-

Hydroxido

1

3 member ring

paramagnetic

Date



EXAMSROADOFFICIAL



EXAMSROAD



EXAMSROAD



EXAMSROAD

1. ligands formula

- 1) CN_3^-
- 2) OCN^-
- 3) SCN^-
- 4) SO_4^{2-}
- 5) SO_3^{2-}
- 6) SO_3^{2-}
- 7) N_3^-
- 8) NH_2^-
- 9) NH_2^{2-}
- 10) NO_2^-
- 11) ND_3^-
- 12) CN^-
- 13) Acetato $C_2H_3O_2^-$
- 14) CO_3^{2-}
- 15) CH_3^-
- 16) $CH_3CH_2^-$

Methoxide
Cyanato
Thiocyanato
Sulphato
Sulphito
Thiosulphato
Azido
Amido
Imido
Nitrido-N
Nitrate
Cynido
Acetato
Carbonato
Methyl
Ethyl

1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1
1

Ambidentate

— " — ligand

Flexidentate (4 members ring)
Ambi as well as flexi

Ambi. and flexi

Ambi and flexi

flexi

Ambi

flexi

flexi

Organic ligand

— " —

— " —

Ligand Formula

$6H_5^-$
 NC_3^-
 NH_3^-
 $2O$
 $2O$
 $2O$
 2
 2
 H_3
 Me_3
 PH_3
 $2H_4$
 $2NH_2$
 $2O$
 $2O$

Phenyl
 Trichloro
 stannite
 Amm
 Aqua
 Carbonyl
 Nitrosyl
 dioxygen
 diNitrogen
 phosphane
 Trimethyl phosphene
 Triphenyl phosphene
 Hydrocarone
 Methyl Amine
 Dimethyl ether
 Dimethyl phos ether

organic ligand

monodentate

Paramagnetic ($3e^-$ donors)

Date

1 1 1 1 1 1 1 1 1 1 1 1 1 1 1



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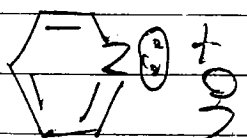
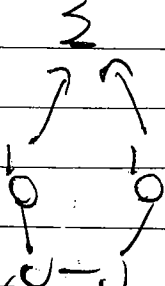
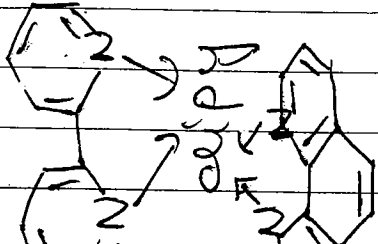
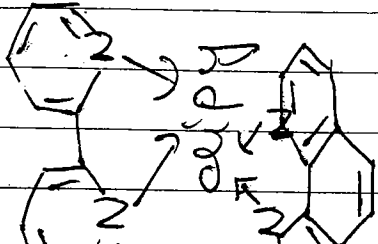
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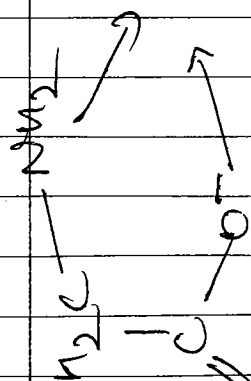


EXAMSROAD



EXAMSROAD

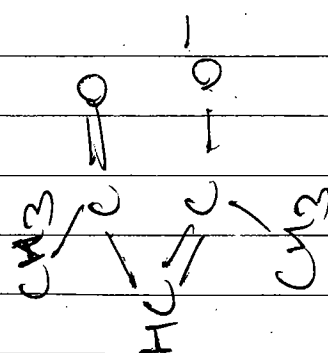
	pyridine	1	
$2H_5^+$	Nitrosonium/ Nitrosylum	1	
$2-NH_2^+$	Hydrazinium	1	$CH_2-NH_2 \rightarrow M$
$2-NH_2$	Ethylene diamine (en)	2	CH_2-NH_2 Symmetrical bidentate no. of ring 1
$2-O^-$	Oxalato	2	Symmetrical bidentate 3 member ring
	ethylenediamine	2	Sym. bidentate
	diphenyl ether	2	"
	biphenyl	2	"



Glycinate

2

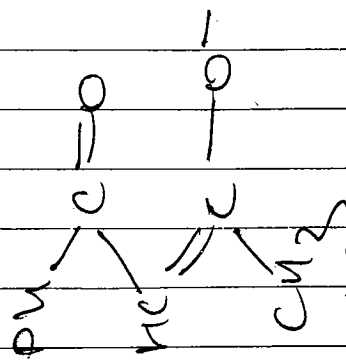
unsymmetrical
bidentate



Acetylacetonato
acac⁻

2

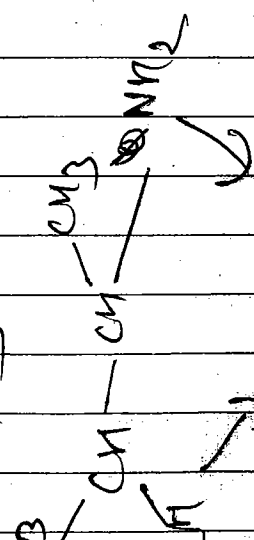
symm.
bidentate



Benzoyl acetonato
bcac⁻

2

unsymm.
bidentate



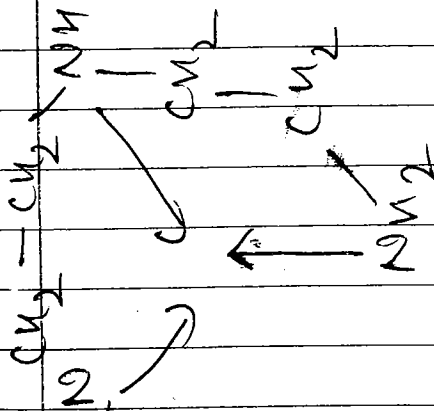
butylene diamine
bn

2

Symm.
bidentate
optically
active

Date

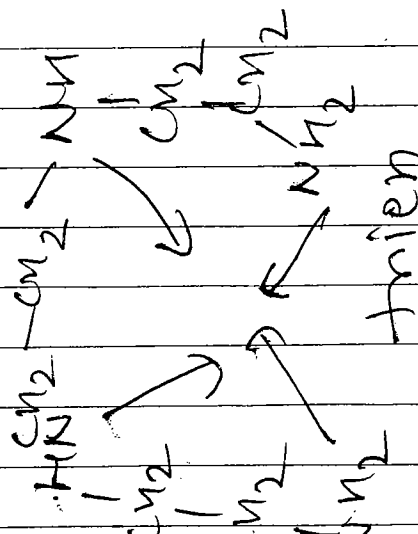




diethylene triamine

olien

3



trien

+ diethylene
tetraamine

4

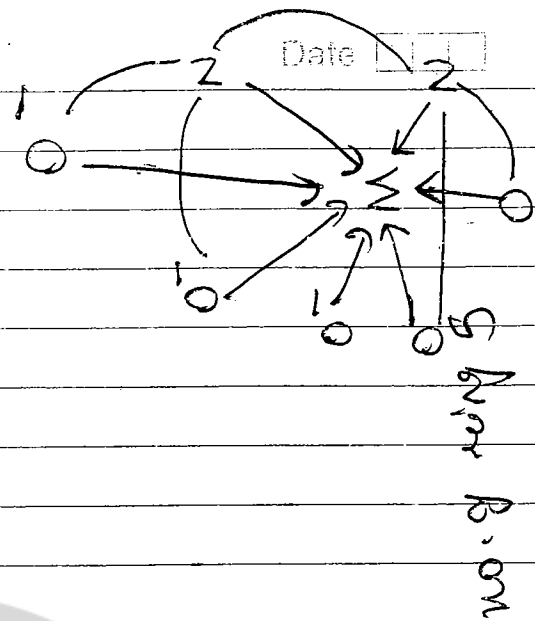
+ eten

tetraethylene
pentaamine teten

5

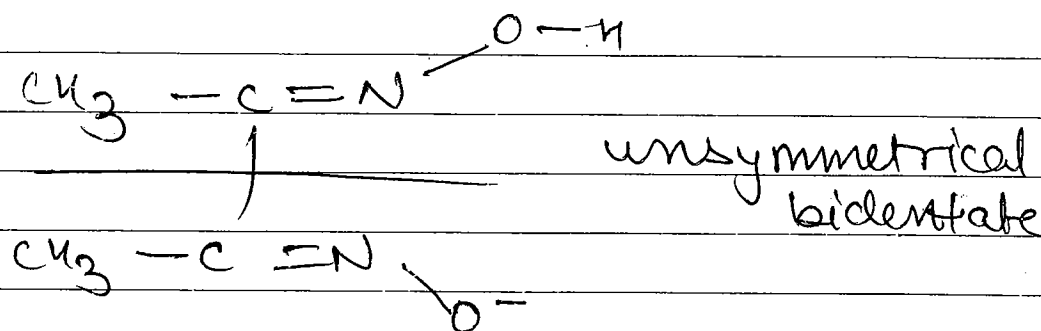
EDTA⁴⁻

6



Date

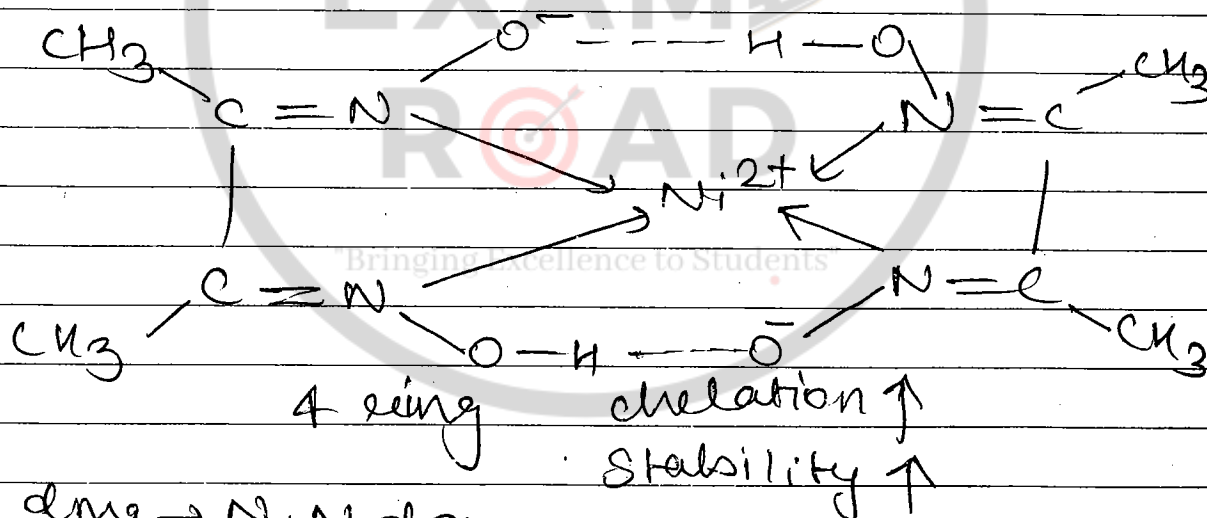
dmg⁻ - dimethyl glyoximate



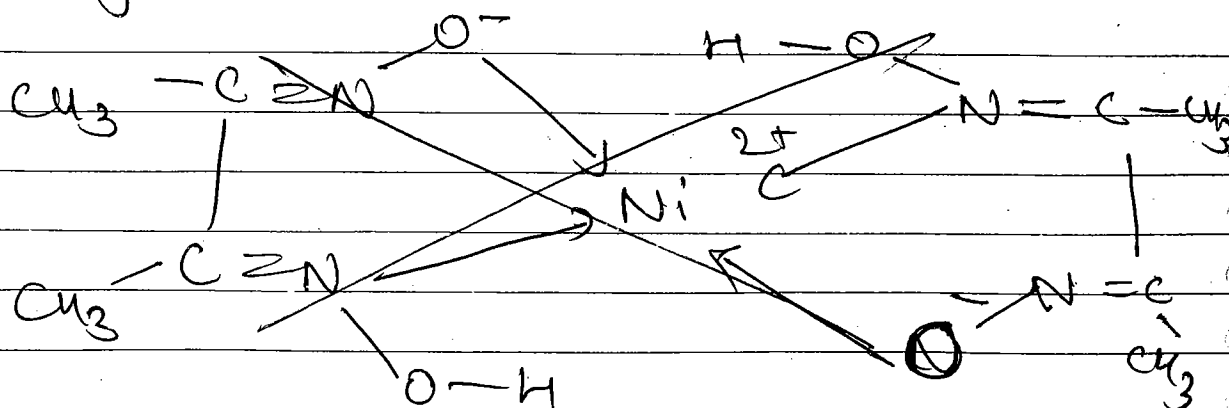
dmg⁻ is used to detect Ni^{2+}



rosy red ppt



dmg⁻ → N, N donor



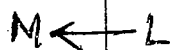
Classification of ligands on the Basis of Bonding Pattern

Classical

Non-Classical

(σ donor)
(only donor)

(donor as well as acceptor)



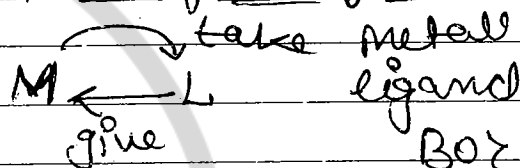
BO = 1

absence of vacant orbital

(2nd & 1st period donor, absence of π -bond)

$NH_3, H_2O, OH^-, F^-, en, dien, trien, N_3^-, H^-, NH_2^-, NH_3^+, O^{2-}$

π -acid ligand
accept in form of π



BO > 1

give + take = synergic bond

Non-classical ligands

σ -donor - π acceptor
donates lp. accept in form of π

π donor π acceptor
donate πe^- / accept in form of π

lone pair donor
accept e^- in π^*

example $\rightarrow 15/14/16e^-$
diatomic species

CO, NO, NO^+, CN^-, N_2

lone pair donor
accept πe^- in d-orbital

example \rightarrow

PMe_3, PH_3, PF_3
 PPh_3, R_3S, R_2AS

always accept e^- from CMI in π^* orbital

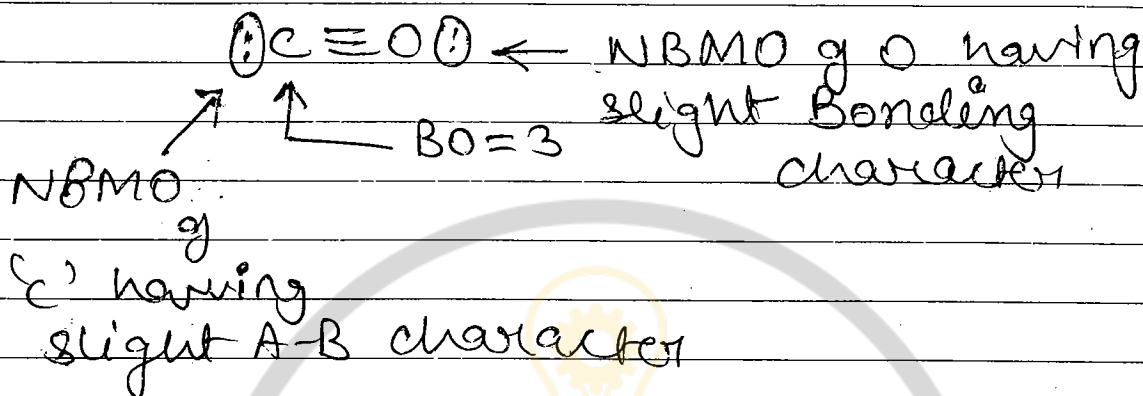
due to synergy
ML BO > 1

so they can act as ligand in complex form



Synergic Bond in Metal carbonyl

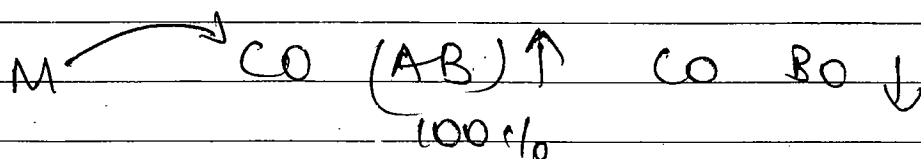
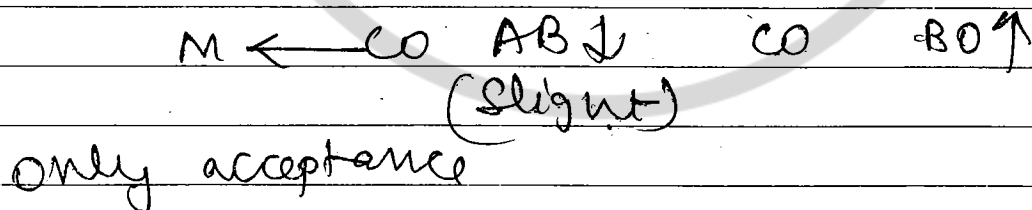
Acc. to MOT $CO \Rightarrow 14e^-$



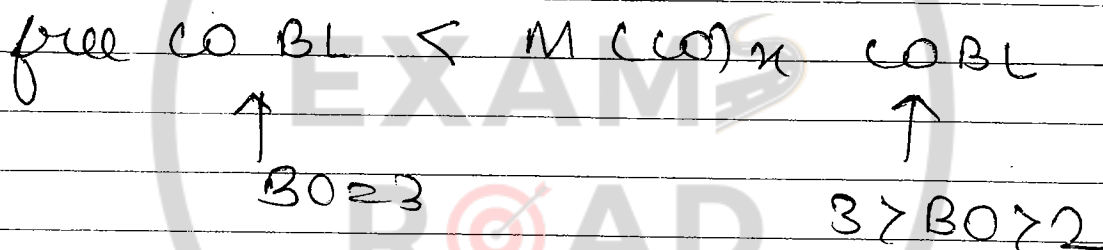
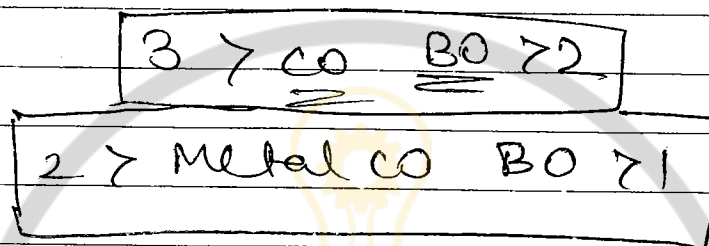
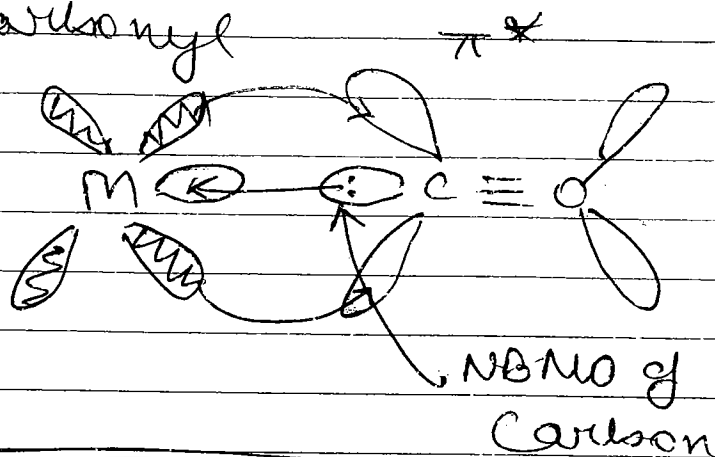
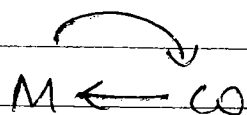
In 'C' atom is donor -

$\text{C} \equiv \text{O}$
 Reason 1) EN of C < O
 2) Energy of NBMO(C) > NBMO(O)

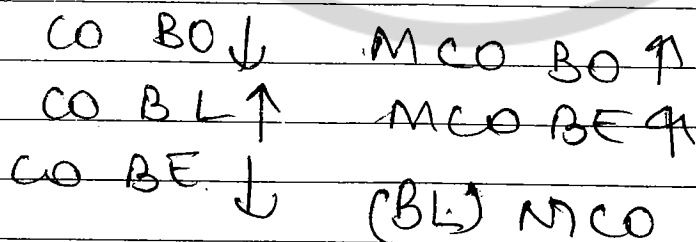
CO is $14e^-$ system so it accept new e^- in π^* (100% AB character)
 Only donation



So in metal carbonyl

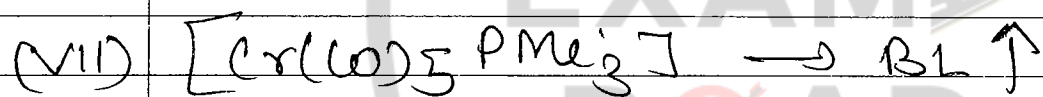
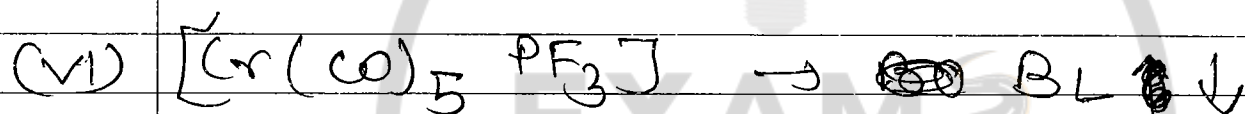
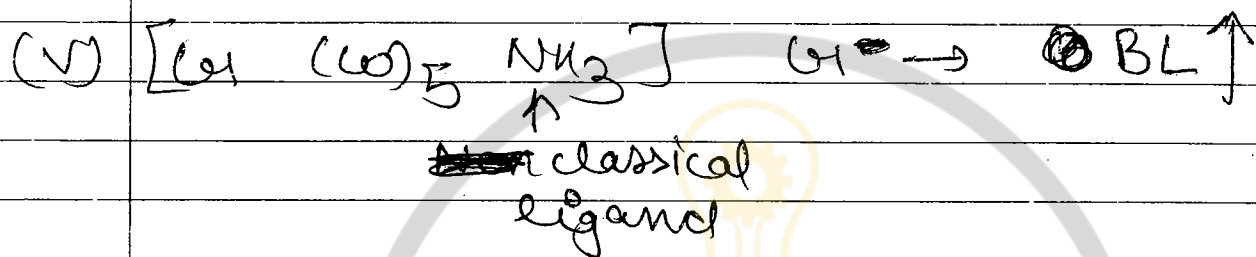
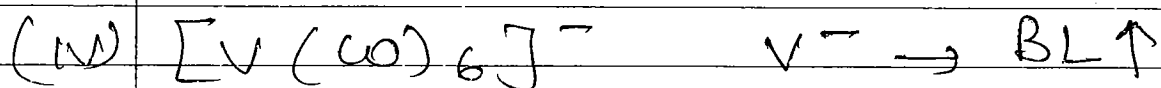
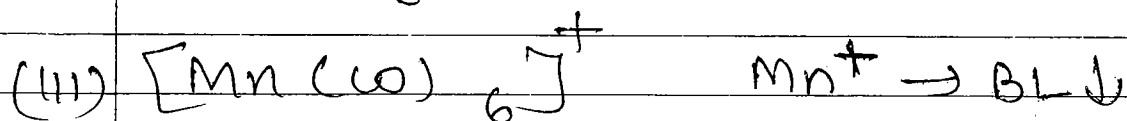
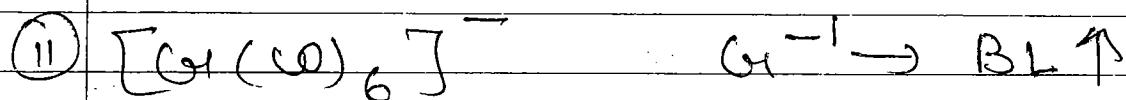
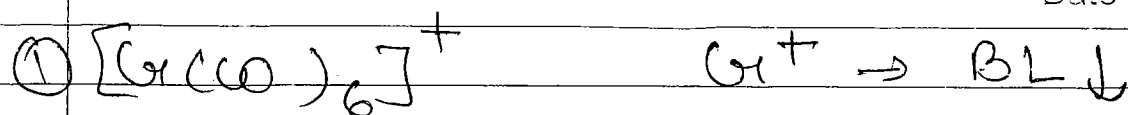


As donation of metal \uparrow
 e^- in ABMO of CO \uparrow



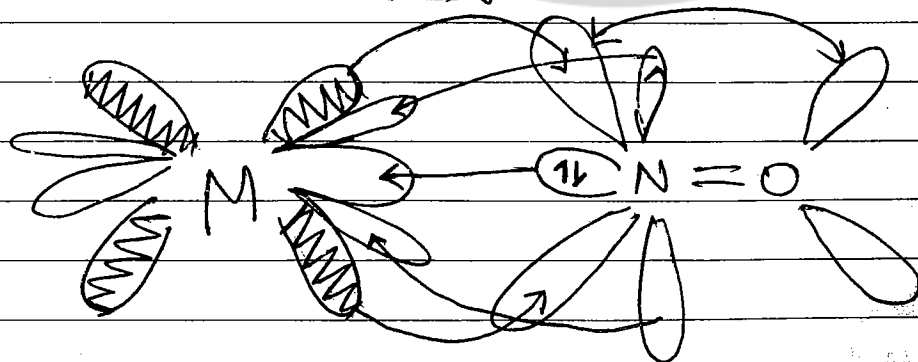
NO comments.

(Q) Comment on CO BL in given complexes
 with respect to π where π is
 CO BL in $[Cr(CO)_6]$



acceptance tendency of
 $\text{PF}_3 > \text{CO} > \text{PMe}_3$

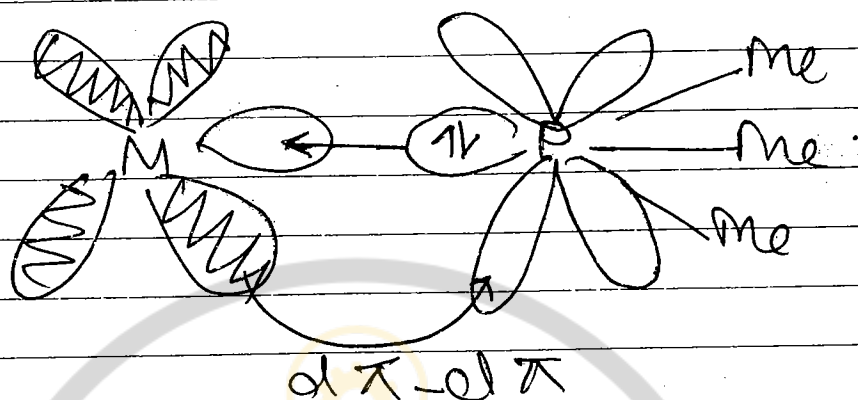
NO as a ligand π^*



NO is a three e^- donor ligand
 σ donor, π donor,
 π acceptor

$\text{PF}_3 / \text{PMe}_3 / \text{PPh}_3 / \text{PH}_3 / \text{R}_2\text{S} / \text{R}_3\text{As}$

As a ligand



No effect on P-Me bond order
because 'P' accept e^- in $\sigma^* \pi^*$ orbital

Practical evidence of CO BL

Stretching frequency method

CO	BL	↑	↓
CO	BO		
CO	BE	↑	

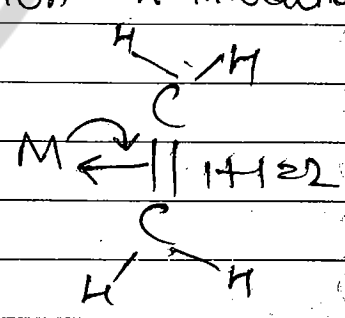
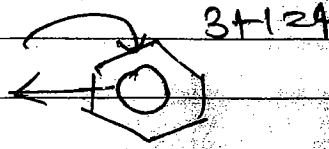
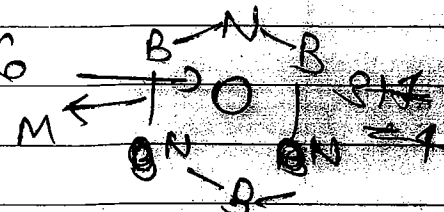
to stretch CO BO Ad req. energy ↑
frequency related to energy ↑

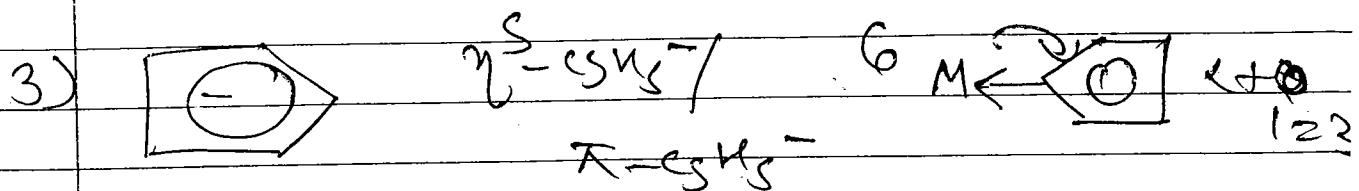
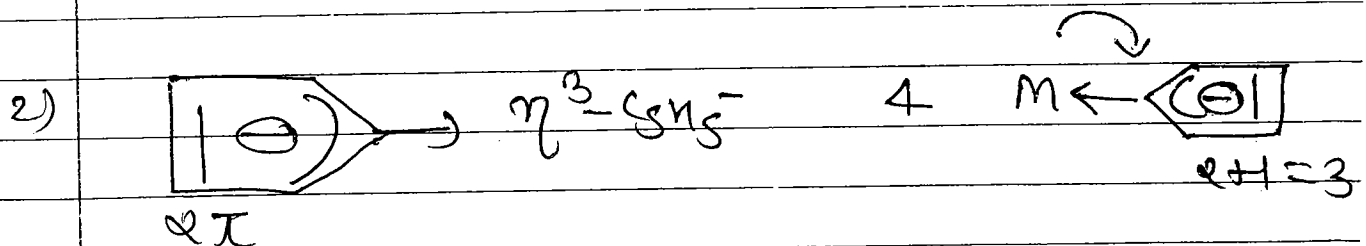
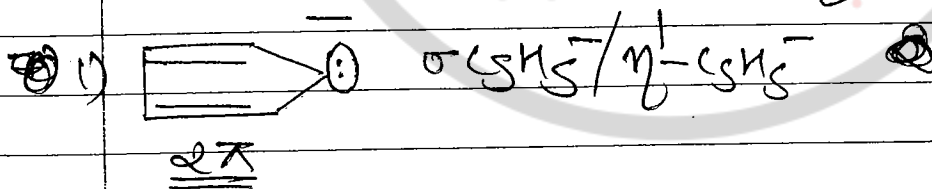
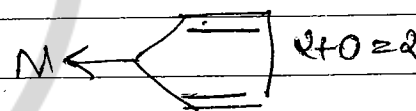
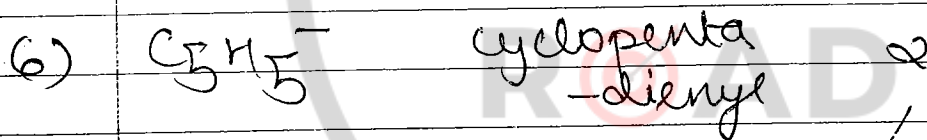
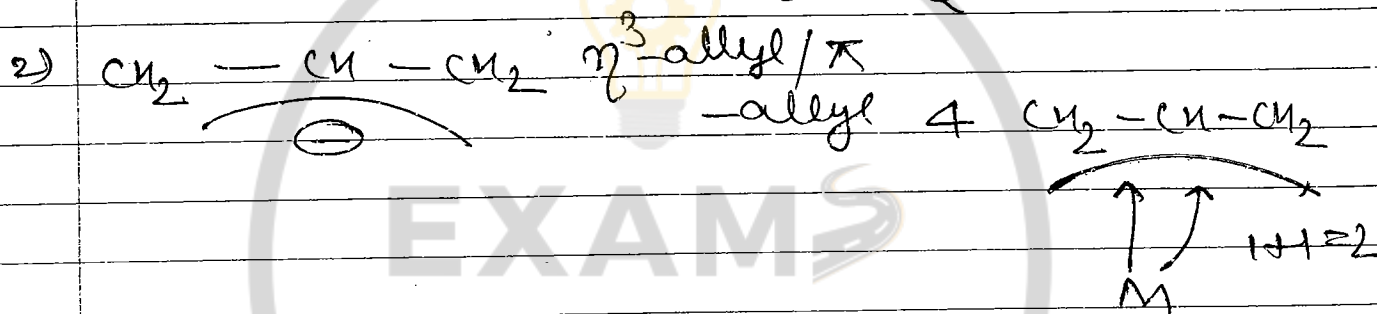
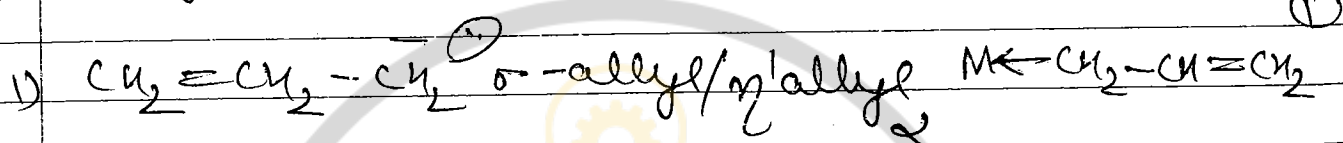
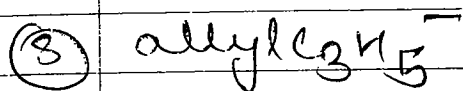
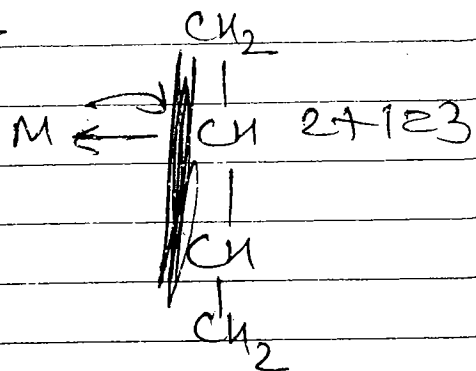
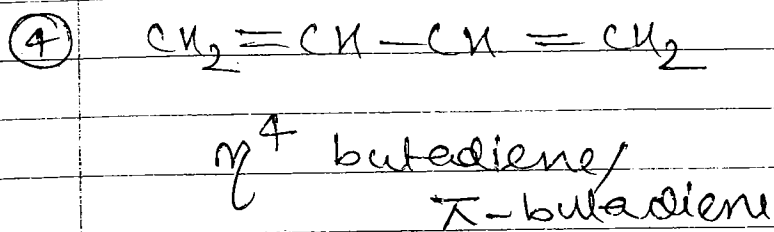
so stretching frequency of CO

← $\frac{1}{\text{synergic Bond}}$

π donor - π acceptor \rightarrow

- 1) They are not Lewis base.
- 2) They can act as ligand in complex formation due to synergic bonding.
- 3) They accept e^- pair from filled d -orbital of central metal ion in their π^* orbital.
- 4) Due to synergic metal ligand B.O. increases stability of complex \uparrow but ligand B.O. \downarrow .
- 5) Such ligands are written with prefix η^x where x is hapticity of ligands or no. of atoms participate in donation.

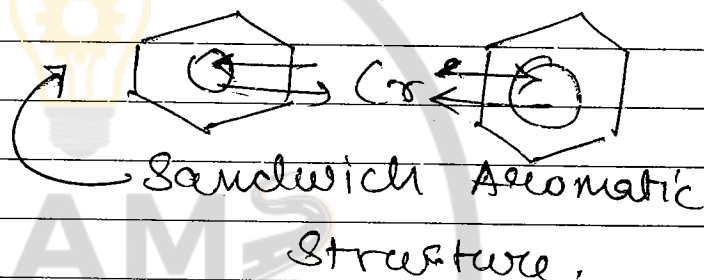
Ligand	Name	e^- donation	π -interaction
1) C_2H_4	η^2 -ethylene/ ethylene	2	
2) C_6H_6	η^6 -benzene/ π -benzene	6	
3) $B_3N_3H_6$	η^6 -borazine/ π -borazine	6	



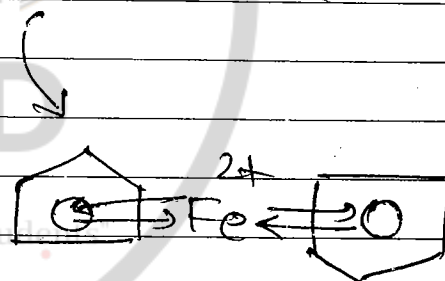
Note: Denticity is not defined for π -donor & π -acceptor ligand when delocalize π e⁻s participate in donation.

(Q) Compare C-C BL in

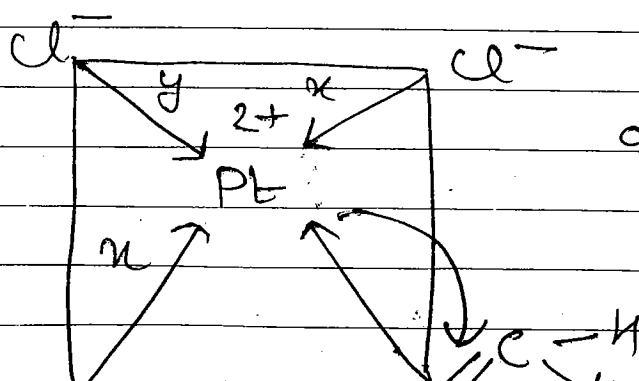
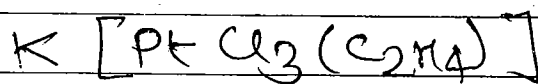
- 1) C_2H_4 & Zeise's salt ($K[PtCl_3(C_2H_4)]$)
- 2) C_6H_6 & $Cr(C_6H_6)_2$



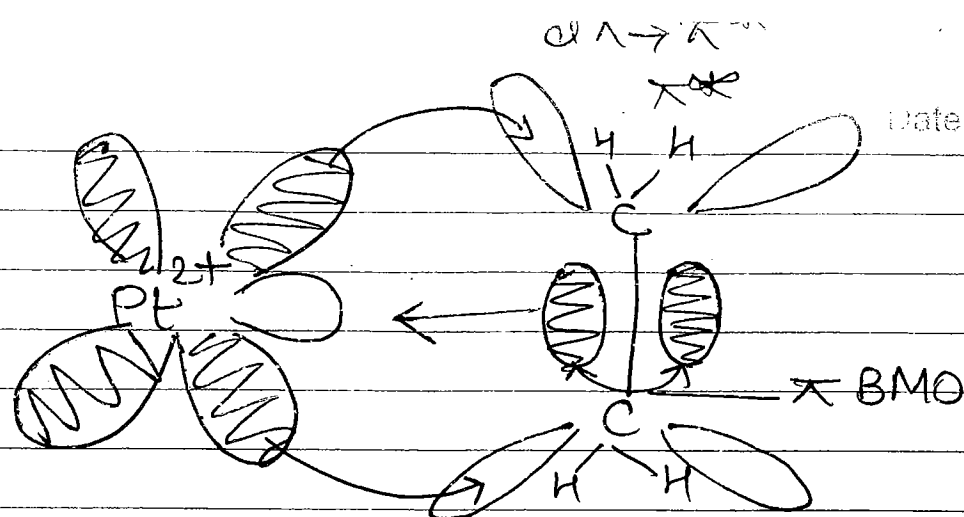
- 3) C_5H_5 & Ferrocene $[Fe(C_5H_5)_2]$



Synergic bonding in Zeise's salt



due to trans effect



⇒ PtCl_2 plane is \perp due to C_2H_4 Plane

⇒ In free C_2H_4 all atoms are present in a plane but in PtCl_2 salt due to π b/w $\text{Pt}-\text{C}_2\text{H}_4$ back bond & $\text{C}-\text{H}$ bond all H atoms are present out of the plane.

⇒ trans effect \rightarrow when strong acceptor present at transposition bond length is larger than from its normal value.

"Bringing Excellence to Students"

WERNER'S THEORY \rightarrow

According to Werner in complex formation CMI show two types of valencies

Primary Valency

Secondary valency

1) O.S of central metal ion. Coord. Number of CMI.

2) Satisfy by anions. Satisfy by ligands.

Satisfy

in Werner representation

Date

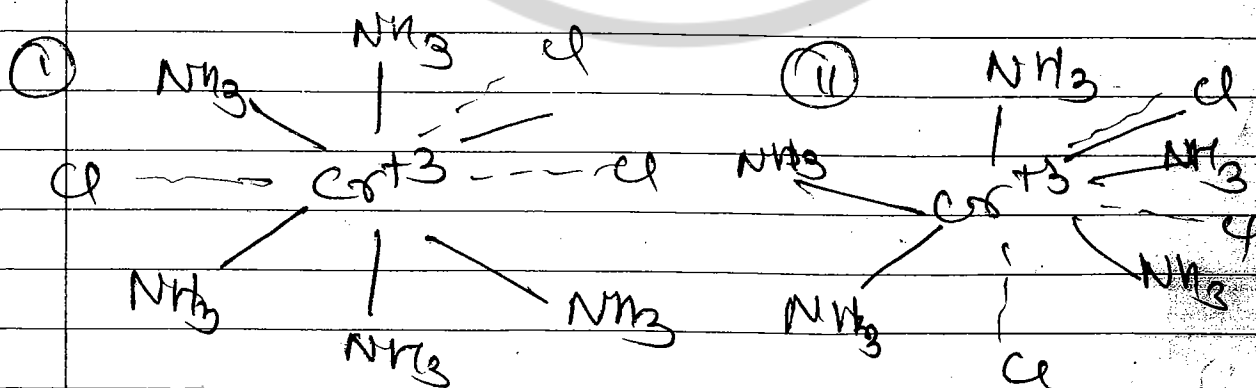
Counter ion	only PV	(----) dotted line
Neutral ligand	only SV	(—) solid line
Anionic ligand	PV & SV	(=) solid with dotted line

		(Cation: electrolyte)	PV	SV
1) Cr. 6 NH ₃ Cl ₃	[Cr(NH ₃) ₆]Cl ₃	1:3	3	6
2) Cr. 5 NH ₃ Cl ₃	[Cr(NH ₃) ₅]Cl ₃	1:2	3	6
3) Cr. 4 NH ₃ Cl ₃	[Cr(NH ₃) ₄]Cl ₃	1:1	3	6
4) Cr. 3 NH ₃ Cl ₃	[Cr(NH ₃) ₃]Cl ₃	Nonelectrolyte	3	6

ppt of AgCl formed when react with excess AgNO₃

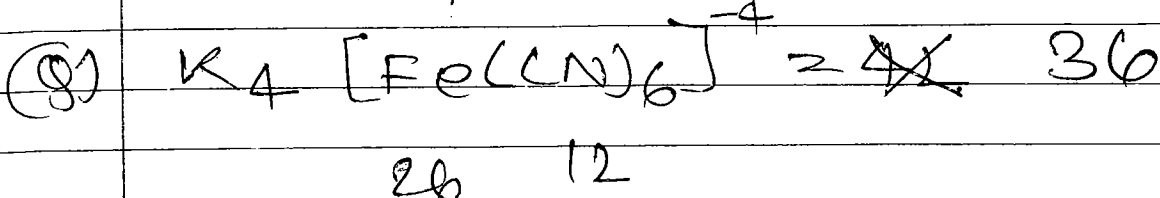
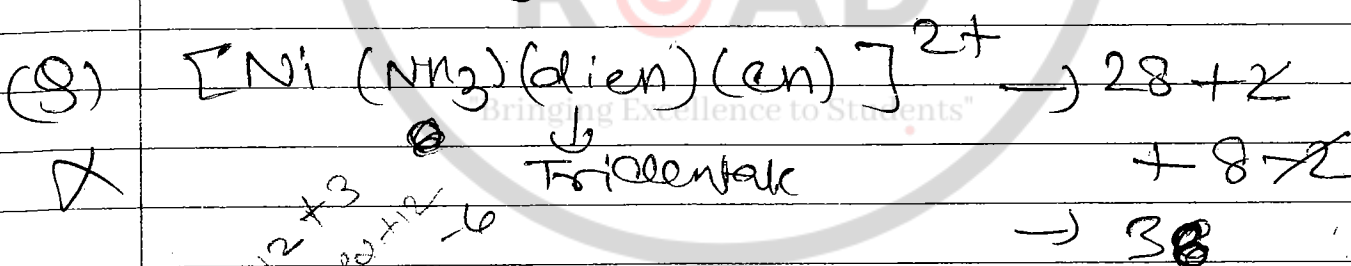
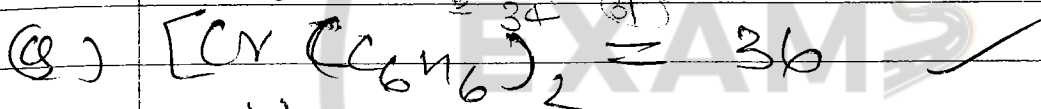
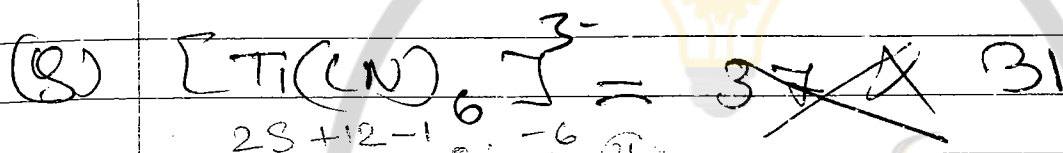
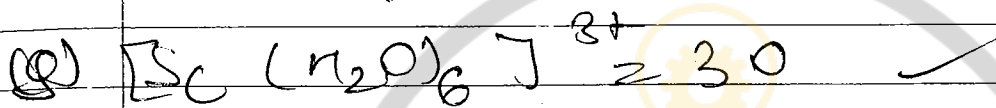
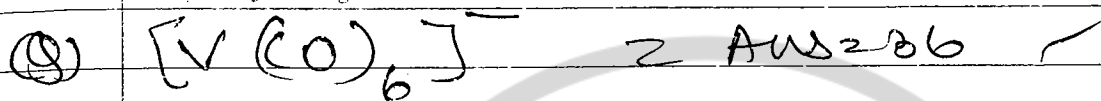
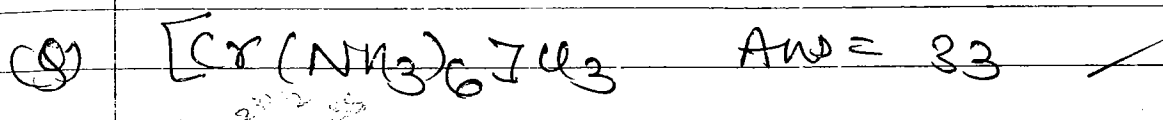
3
2
1
zero

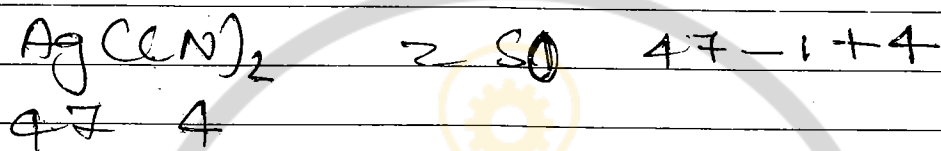
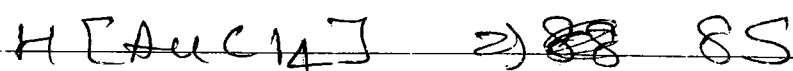
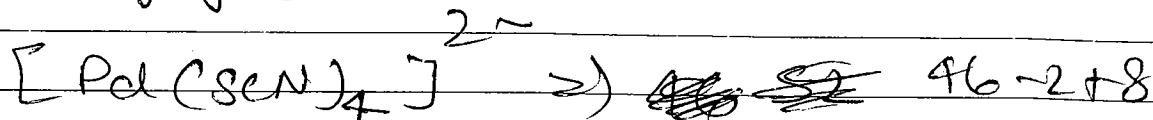
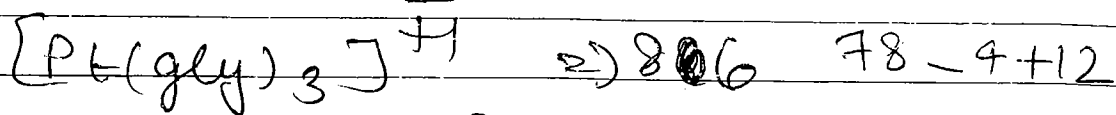
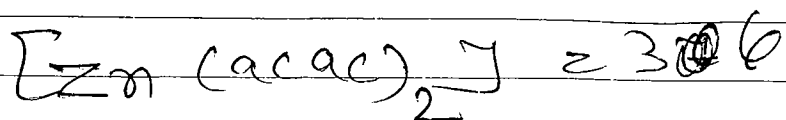
conductivity I > II > III > IV



Effective Atomic Number \rightarrow (EAN)

Total no. of e^- s in CMI after complex formation is called (EAN) of CMI in that complex.





SIDWICK (EAN) RULE \rightarrow (18e Rule)

According to Sidwick to gain stability CMI in complex want to achieve EAN = next inert gas at no.

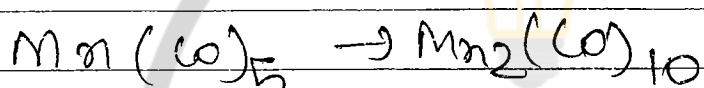
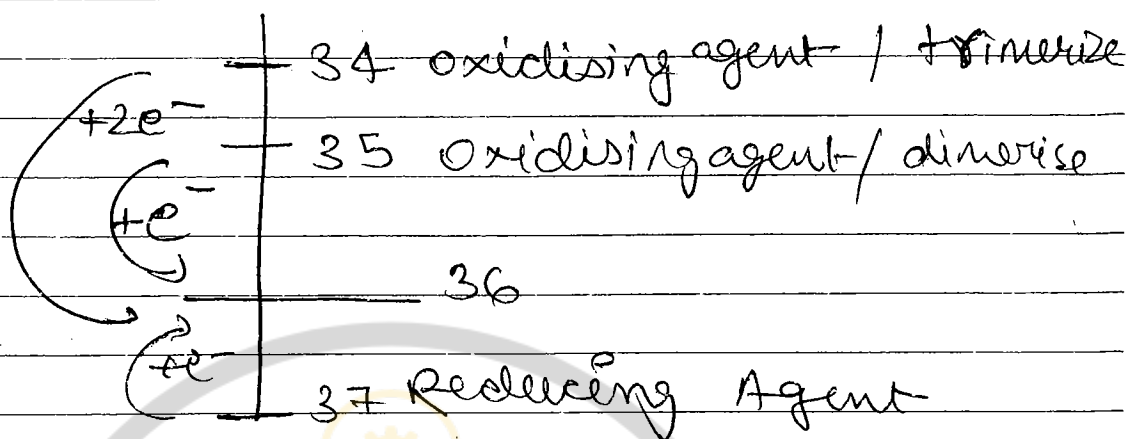
Complex follow EAN rule means EAN of CMI for 3d series 36, 4d series 54, 5d series 86

APPLICATION OF EAN RULE

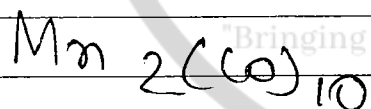
Metal Carbonyls follow EAN rule

(Q) Find the value of x, y, z in given complexes

Oxidising/Reducing Nature & Dimerisation tendency of Metal carbonyls

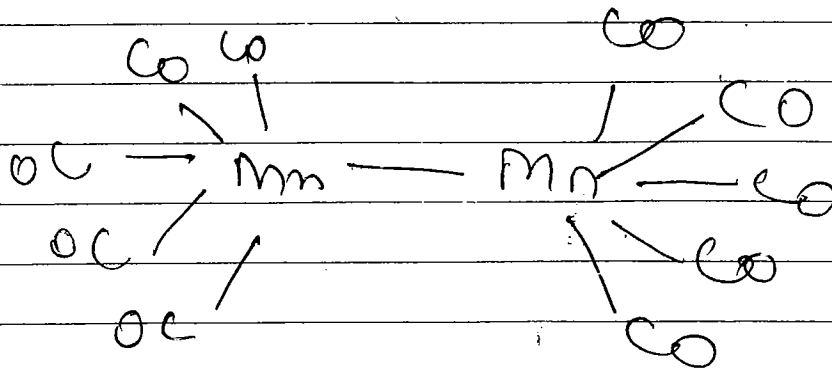


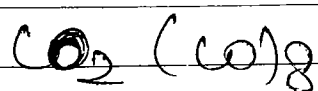
To find Metal - Metal Bonds in poly nuclear carbonyls.



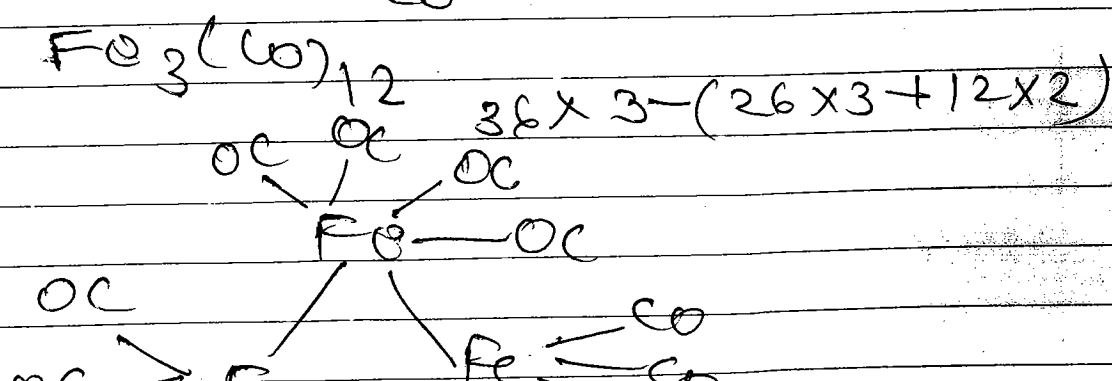
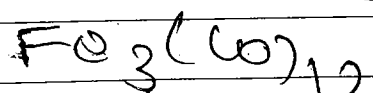
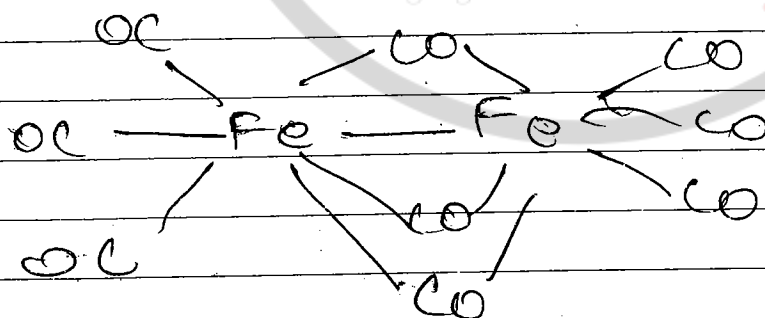
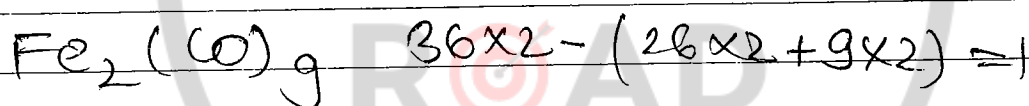
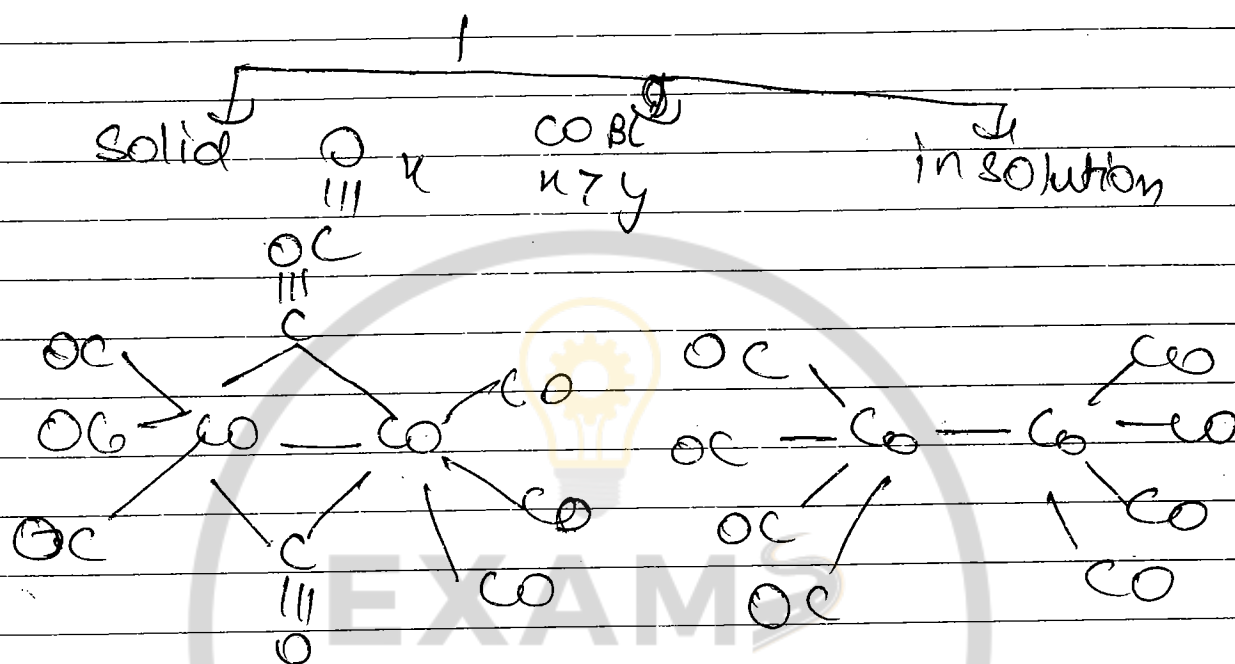
$$\text{No. of } e^- \text{ in sharing} = 36 \times 2 - (28 \times 2 + 2 \times 10) = 2$$

$$\text{No. of Bonds} = \frac{2}{2} = 1$$





$$\frac{36 \times 2 - (27 \times 2 + 8 \times 2)}{2} = 1$$



VALENCE BOND THEORY & COORDINATION COMPOUNDS →

According to VBT. Central Metal Ion provides vacant orbital equal to its coordination no. These vacant orbitals undergoes hyb. and form equal energy hybrid orbitals and these hybrid orbitals are configured at 3D in Min. repulsion which defines geometry around C.M.I.

CN	Hyb	geo
2	sp	linear
3	sp ²	triagonal planar
4	sp ³ d ³ s (dxy dx ² -y ² dy ²) } Tetrahedral dsp ² (dx ² -y ²) } - real sq. planar	
5	dsp ³ /sp ³ d T.B.P dsp ³ /sp ³ d square pyramidal	
6	d ² sp ³ /sp ³ d ² Sq. bipyramidal, octa	

Orbital

Inner orbital complex \rightarrow when $n-1$ d orbital participate in hys.

Outer \rightarrow n \rightarrow when n d orbital participate in hys.

Classification of Ligands on the basis of Bond strength \rightarrow

- ① SFL (strong field ligand)
 \rightarrow form strong bond with CMT
- ② WFL \rightarrow (weak \rightarrow) form weak \rightarrow

Properties of SFL

- 1) good donor Lewis base
size \downarrow
-ve charge \uparrow
EN \downarrow

- 2) good acceptor

SFL \rightarrow $C > P > N$

WFL \rightarrow O, halogen
General strength of ligand

$C > N > O > F$
Ce.

SPECTROCHEMICAL SERIES →

It is a relative strength of ligand in terms of Thermodynamics (ΔH) w.r.t a particular CMI

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < NO_3^- < F^- < OH^-$
 Itra Bura Iha @kale Shamu Nai Fulle Hath

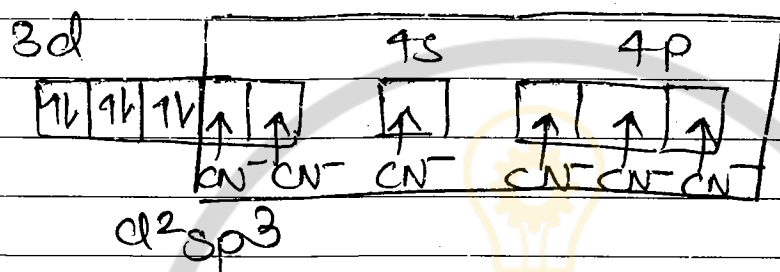
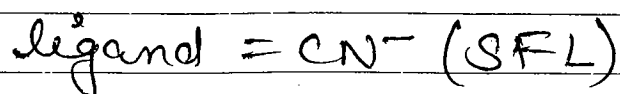
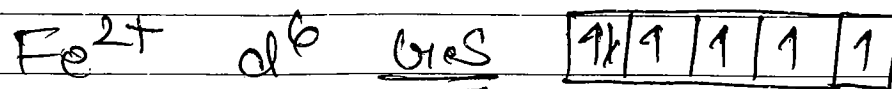
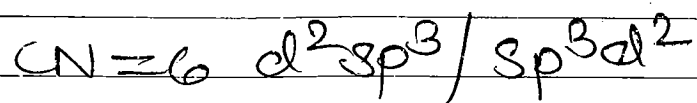
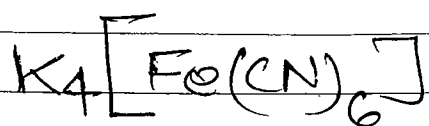
$< CH_3COO^- < C_2O_4^{2-} < H_2O$
 aise uske pani
 bhara

$< NES^- < EDTA^{4-} < NH_3 \approx Py < en \approx dipy$
 Navinchandra In di no Amman dimer
 Saxena Paame

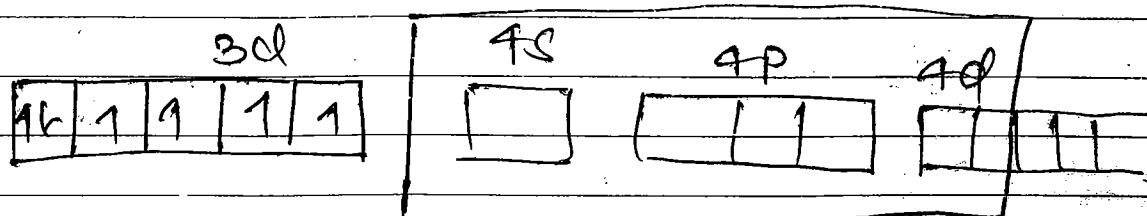
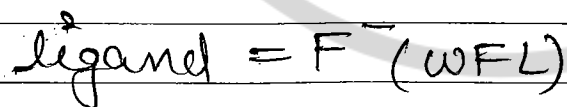
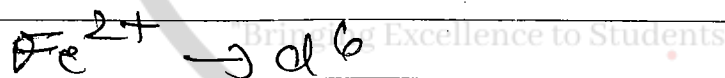
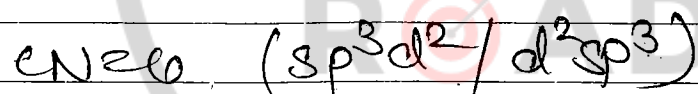
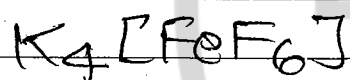
$< NO_2^- < CN^- < CO$
 Naan Sena Cowe
 Gkhum rakh the

In presence of strong field ligand e^- s are forced to pair so that no. of unpaired e^- s
 ↓ value of spin only magnetic moment
 ↓ such complexes are called low spin complex. In presence of WFL there is no effect on no. of unpaired e^- s value of spin only magnetic moment is high in comparison of low spin complexes such complexes are called high spin complexes.

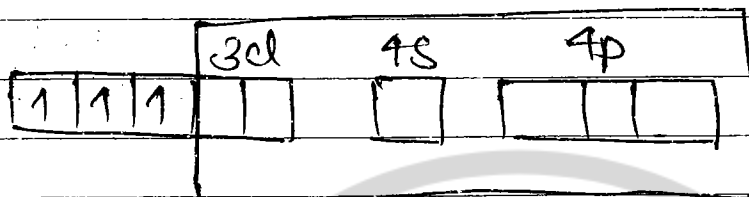
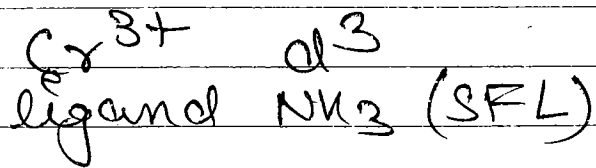
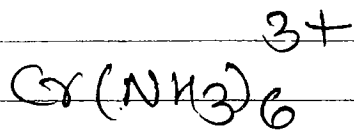




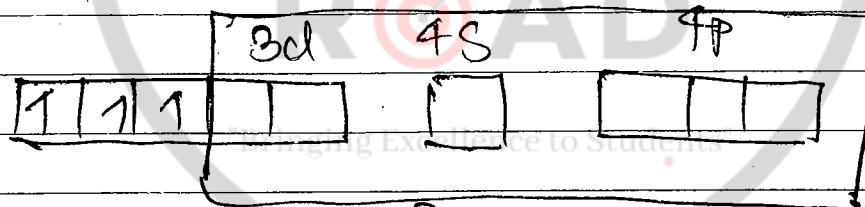
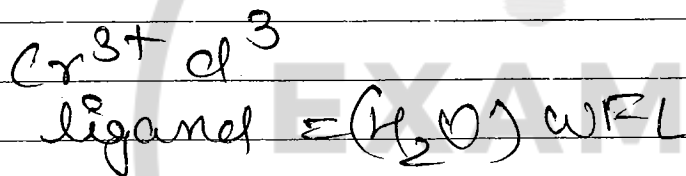
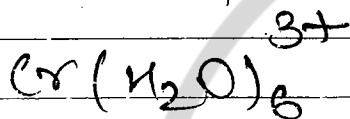
low spin complex, inner orbital, Dia



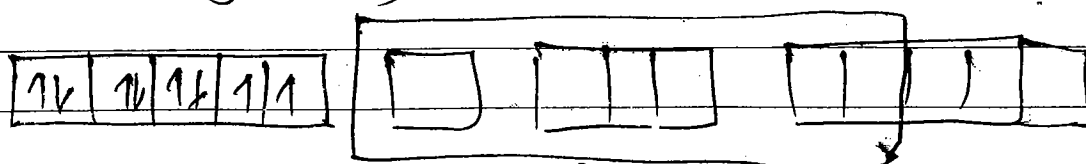
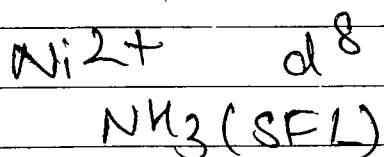
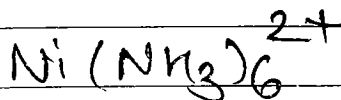
High spin, para
 sp^3d^2 , outer orbital



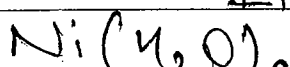
d^2sp^3 , inner, para

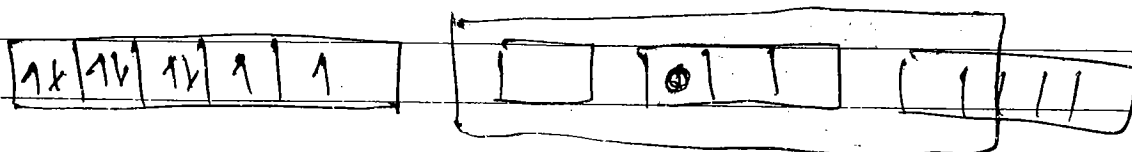


d^2sp^3 , inner



$2+ \quad sp^3d^2$



 sp^3d^2

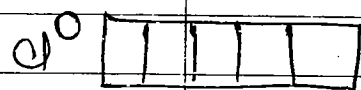
In CN = 6

WFL

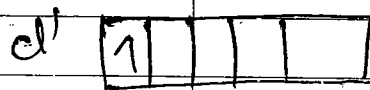
Config

Hyb

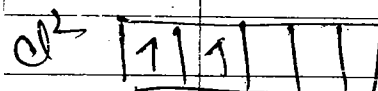
Para/Dia

 d^2sp^3

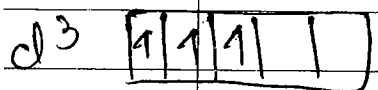
Dia

 d^2sp^3

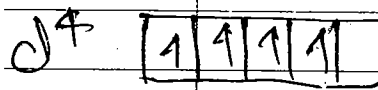
para

 d^2sp^3

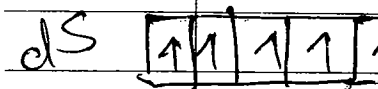
para

 d^2sp^3

para

 sp^3d^2

para

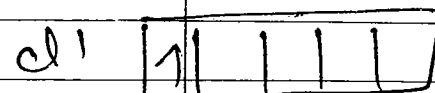
 sp^3d^2

para

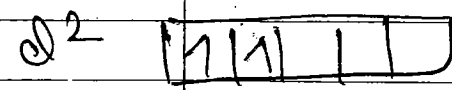
SFL

 d^2sp^3

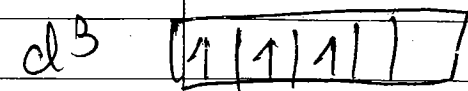
Dia

 d^2sp^3

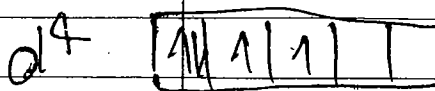
para

 d^2sp^3

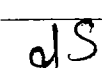
para

 d^2sp^3

para

 d^2sp^3

para



WFL

SFL

Date

d6
d7
d8
d9
d10

1	1	1	1	1
1	1	1	1	1
1	1	1	1	1
1	1	1	1	1
1	1	1	1	1

$sp^3 d^2$ p
 $sp^3 d^2$ p
—
—
 $sp^3 d^2$ D

1	1	1		
1	1	1	1	
1	1	1	1	1
1	1	1	1	1
1	1	1	1	1

$d^2 sp^3$ R
excited to 4p
 $sp^3 d^2$ p
 $sp^3 d^2$ D
 $sp^3 d^2$ D

Ex 1

Q. A central metal ion form inner orbital complex in presence of SFL while in presence of WFL it form para. complex. Metal ion can be in CN 6.

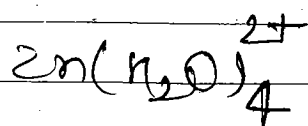
Mn^{2+} Fe^{2+} Co^{3+} Pt^{4+}
d6

(Q) Find total no. of CMI which can form diamagnetic complex in CN=6
 Sc^{3+} , Ti^{4+} , V^{5+} , Cr^{0} , Mn^{3+} , Fe^{3+} , Co^{3+} , Zn^{2+} , Cd^{2+} , Ni^{4+} , Pd^{4+} , Cu^{2+}

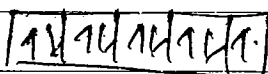
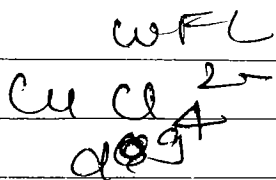
CN=4 (sp^3 / dsp^2)

$Ni(CO)_4$ $NiCl_4^{2-}$ $Ni(CN)_4^{2-}$ $Zn(NH_3)_4^{2+}$
CN=4

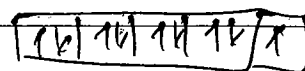
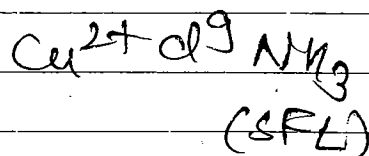
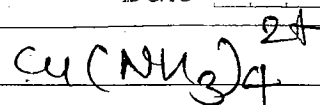
sp^3	sp^3	dsp^2	dsp^2
D	P	d	sp^3



sp^3



sp^3



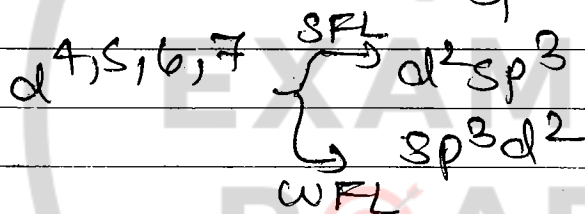
$d\text{sp}^2$
para

#IMPORTANT POINTS →

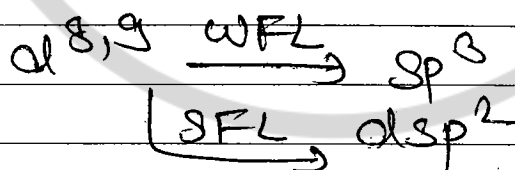
(1) In coordination no. 6

$d^0, 1, 2, 3 \rightarrow d^2\text{sp}^3$ always

$d^8, 9, 10 \rightarrow \text{sp}^3d^2$ always



(2) In coordination no. 4



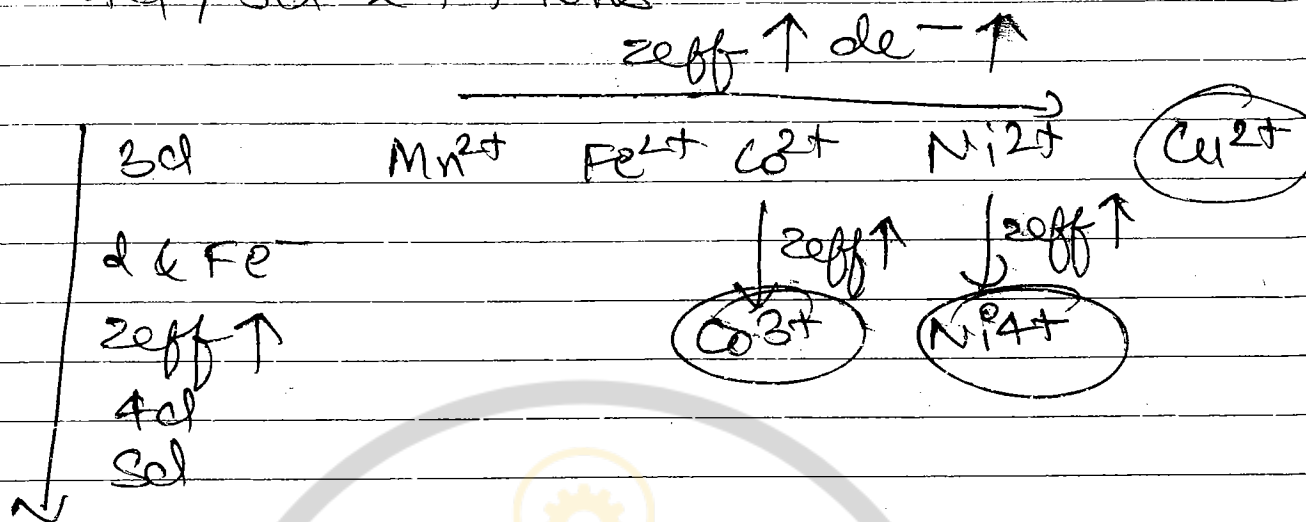
$d^{10} \rightarrow \text{sp}^3$

1) In general NH_3 is SFL but in case of $\text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}$ it acts as WFL

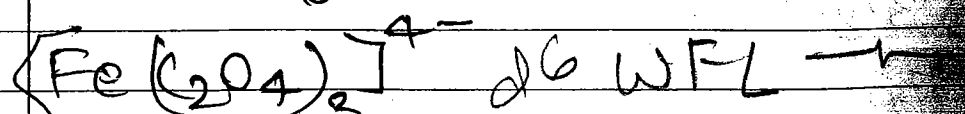
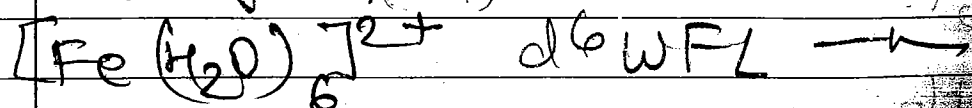
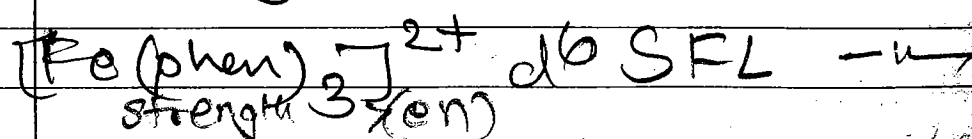
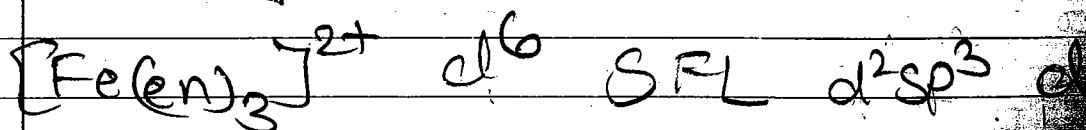
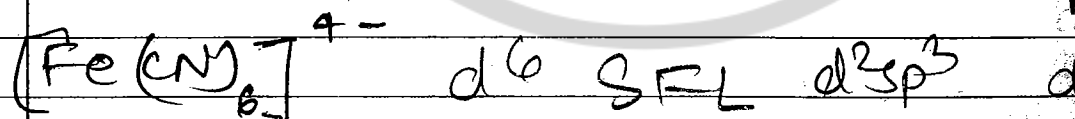
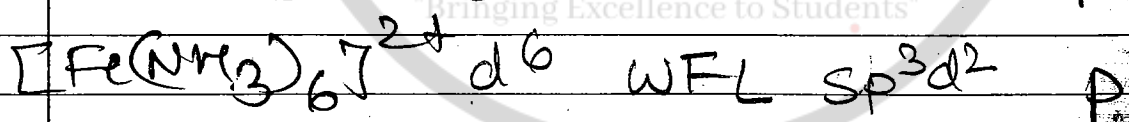
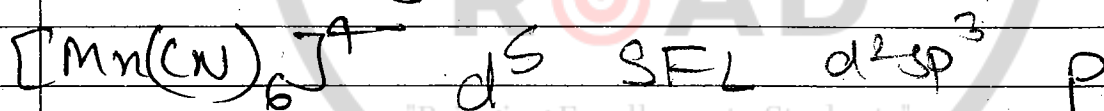
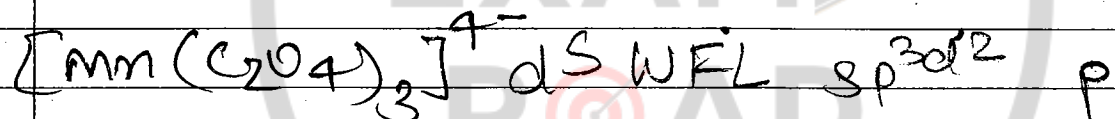
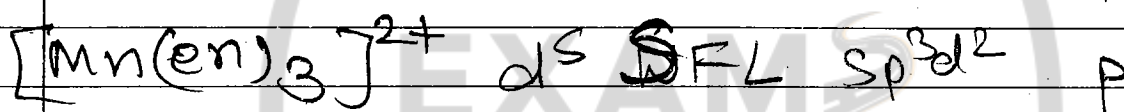
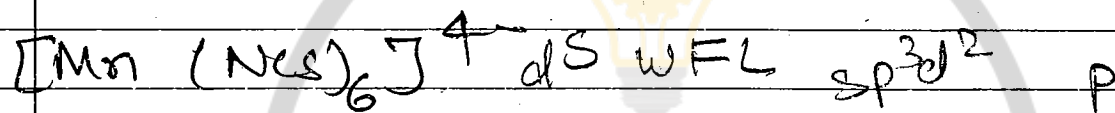
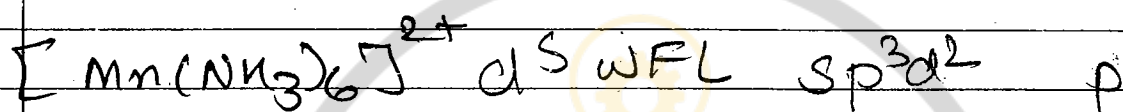
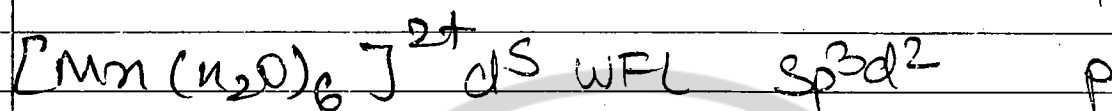
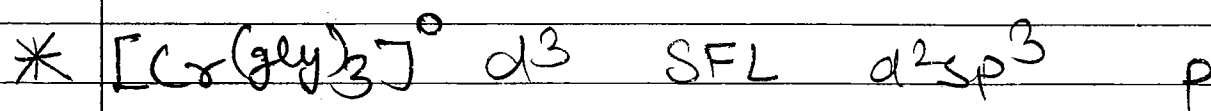
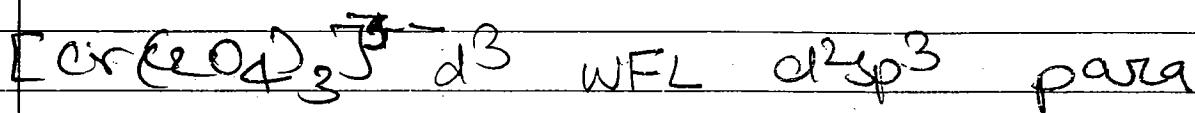
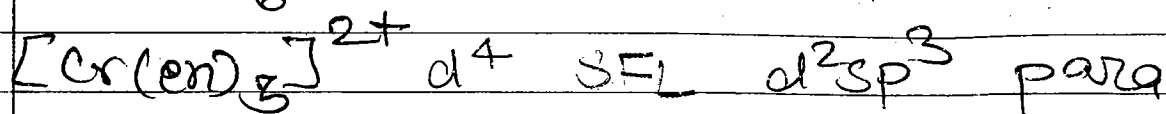
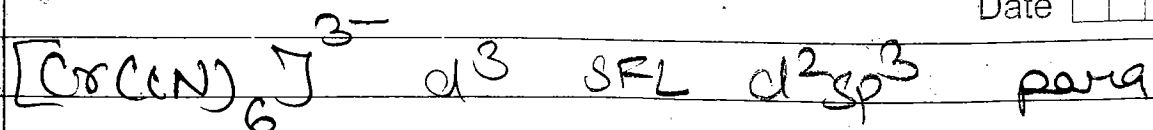
2) In general, O donor Metals are Ligands are WFL but in case of Co^{3+} & Cu^{2+} they act as SFL (except NO_2^- , it

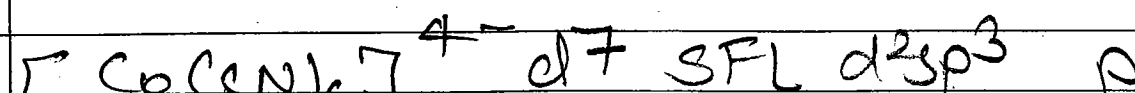
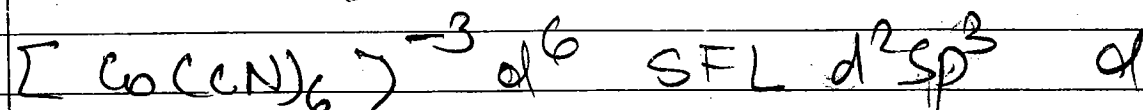
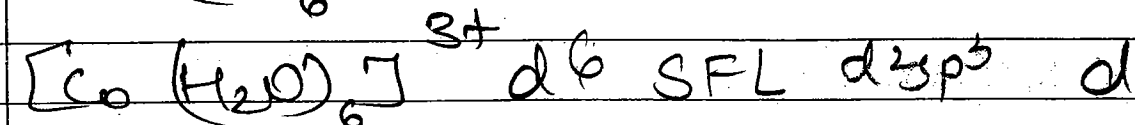
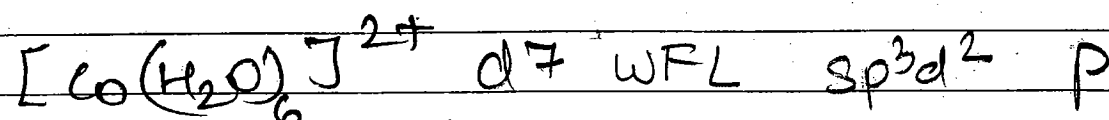
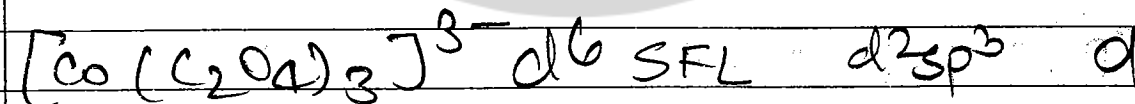
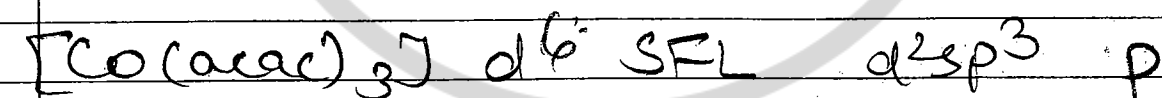
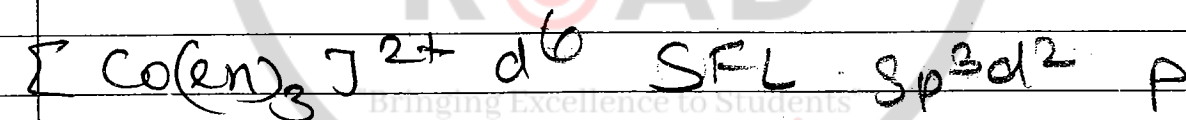
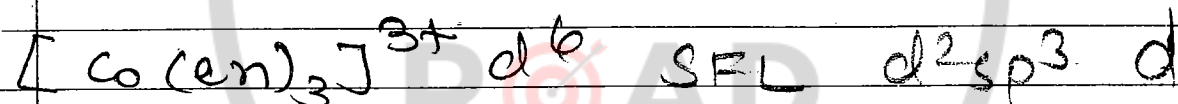
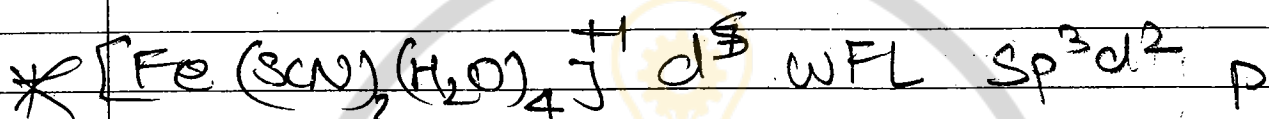
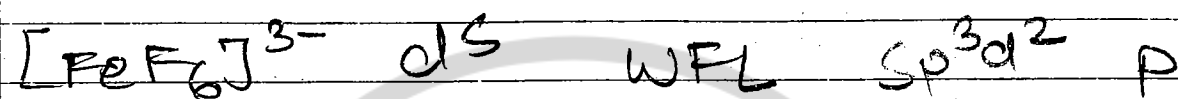
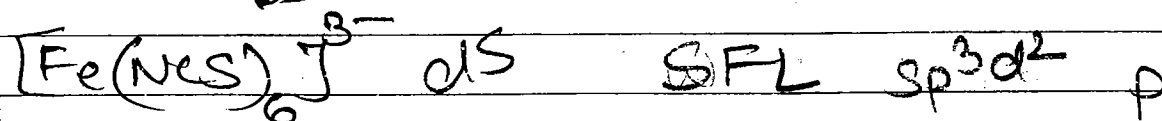
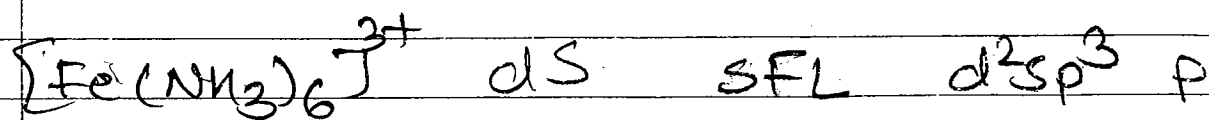
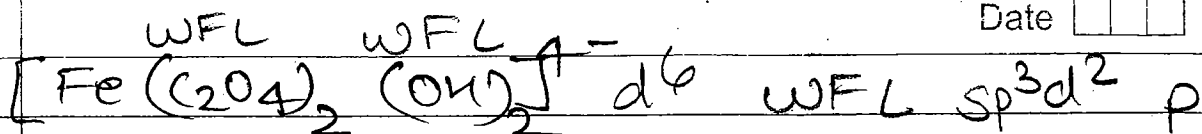


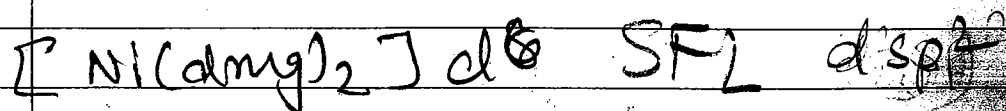
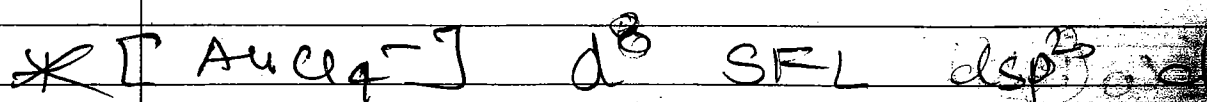
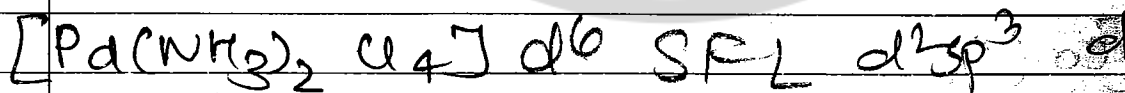
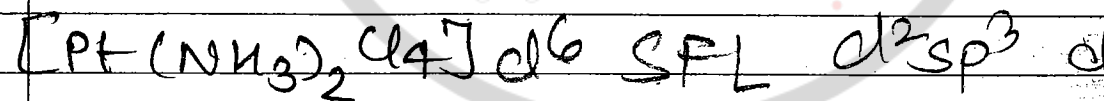
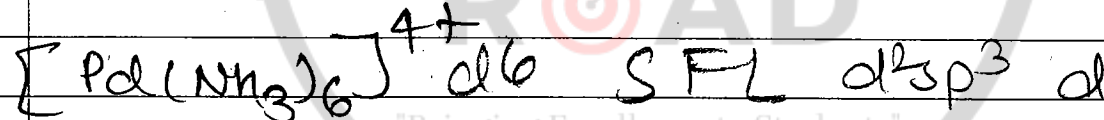
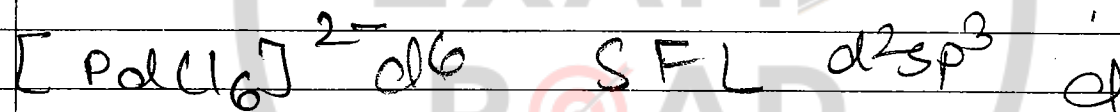
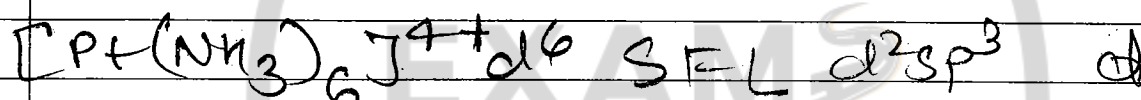
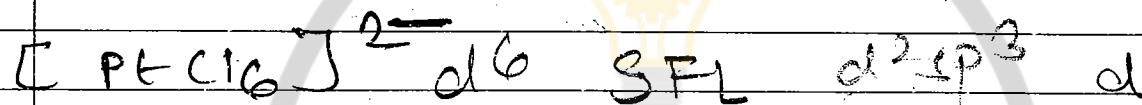
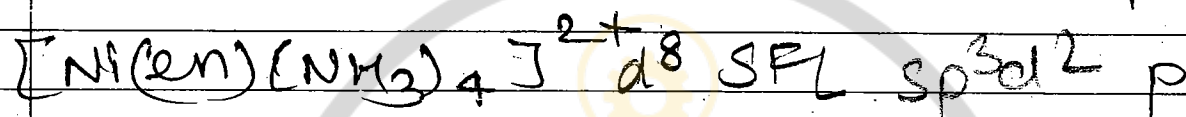
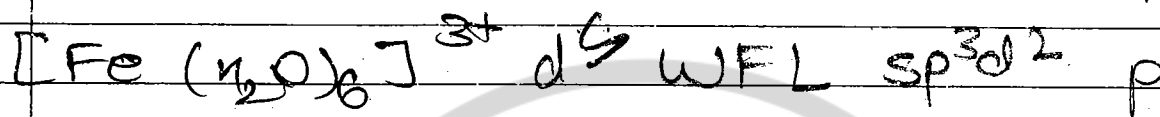
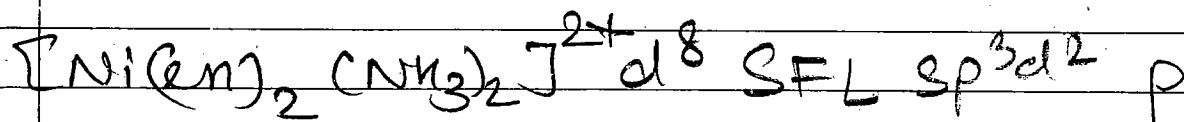
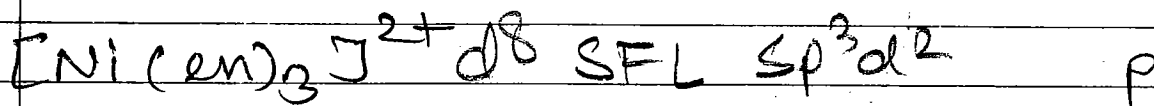
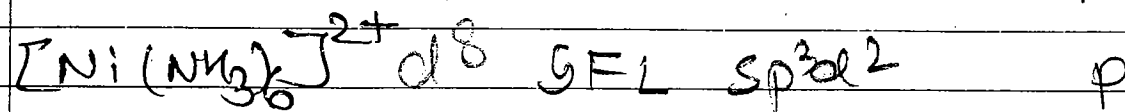
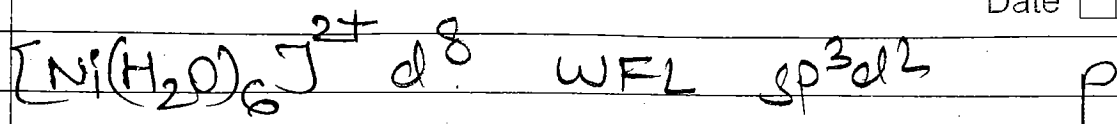
3) In general all ligands are SFL for 4d, 5d & +4 ions.



	Config	Ligand	Hyb.	para dia
$[Sc(H_2O)_6]^{3+}$	d^0	—	d^2sp^3	dia
$[Fe(NCS)_6]^{4-}$	d^6	WFL	sp^3d^2	para
$[Ti(H_2O)_6]^{3+}$	d^1	WFL	d^2sp^3	para
$[V(CO)_6]^-$	d^6	SFL	d^2sp^3	dia
$[Cr(CO)_6]$	d^6	SFL	d^2sp^3	dia
$[Cr(NH_3)_6]^{3+}$	d^3	SFL	d^2sp^3	para
$[CrF_6]^{3-}$	d^3	WFL	d^2sp^3	para
$[Cr(H_2O)_6]^{3+}$	d^3	WFL	d^2sp^3	para
$[Cr(NH_3)_3(H_2O)_3]^{3+}$	d^3		d^2sp^3	para
	SFL	WFL		

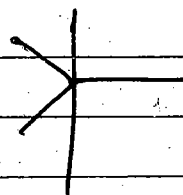
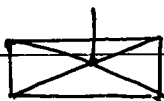
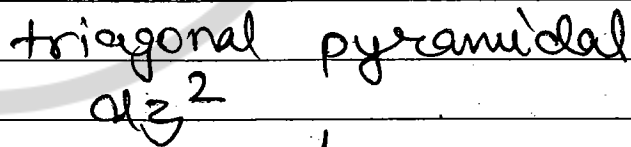
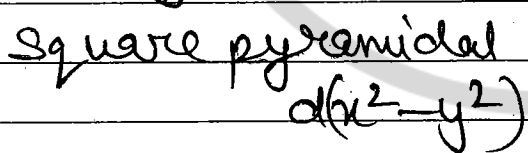
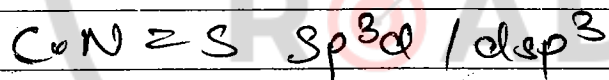
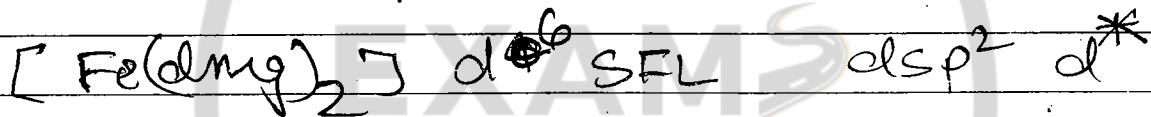
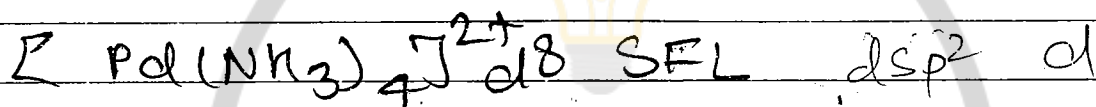
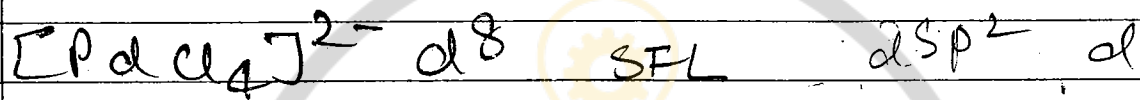
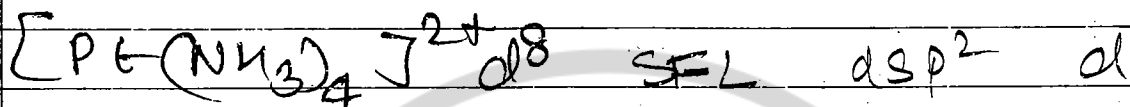
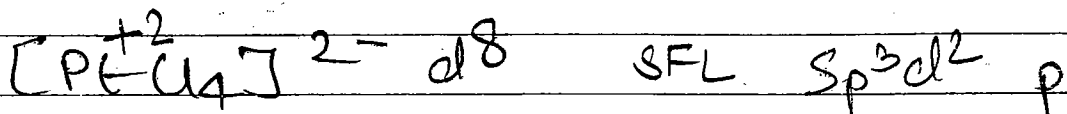
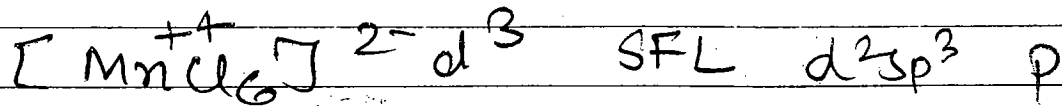
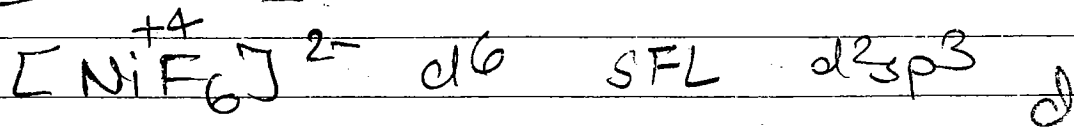
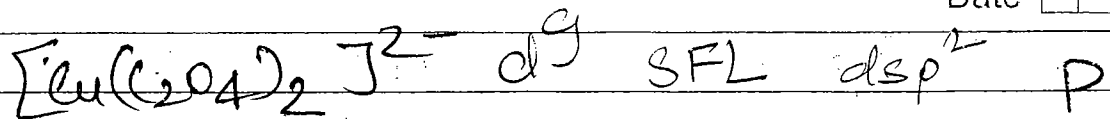






Date

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ligand: - SPL except 'Co'

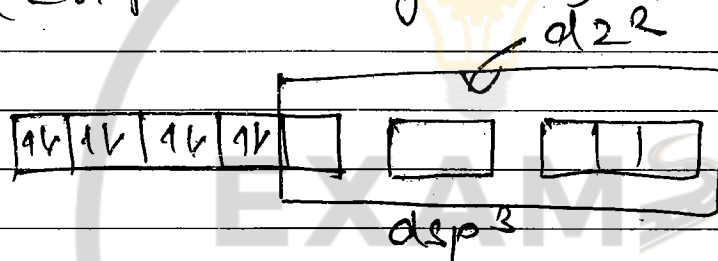
ligand :- WFL
& CO
geometry

example $\text{Fe}(\text{CO})_5$ TBP
 $\text{Mn}(\text{CO})_5$ TBP
 $\text{Co}(\text{CO})_4^+$ YBP
 $\text{Cu}(\text{CO})_3^+$ TBP
 $\text{Ni}(\text{CN})_5^{3-}$ SP

$\Rightarrow \text{Fe}(\text{CO})_5$

$\text{Fe}(\text{at. s}) 3d^6 4s^2$

$\text{Fe}(\text{In presence of SFL}) 3d^8$



Limitations of VBT \rightarrow

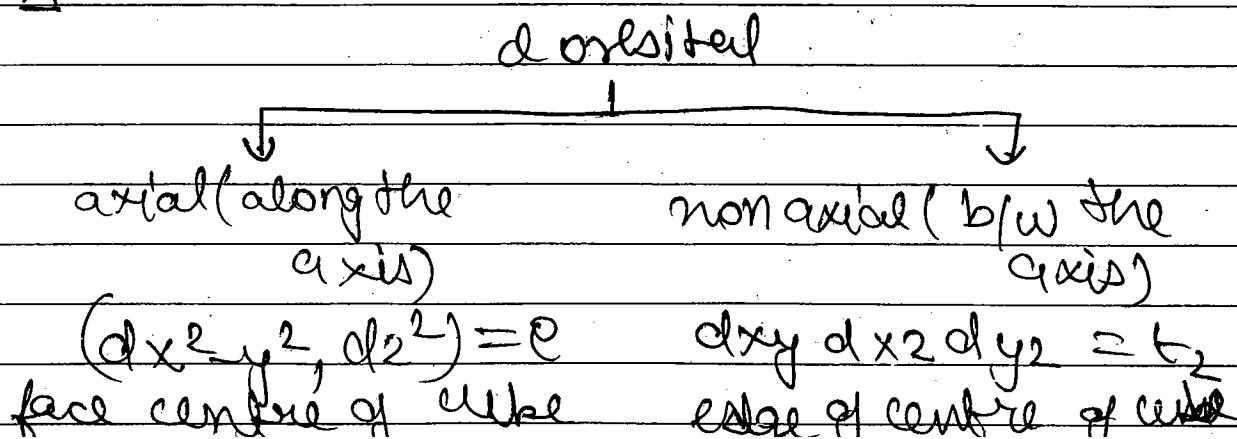
- 1) There are so many Assumptions
- 2) It does not explain \rightarrow
 - a) colour of complexes
 - b) stability of complexes
 - c) SFL & WFL

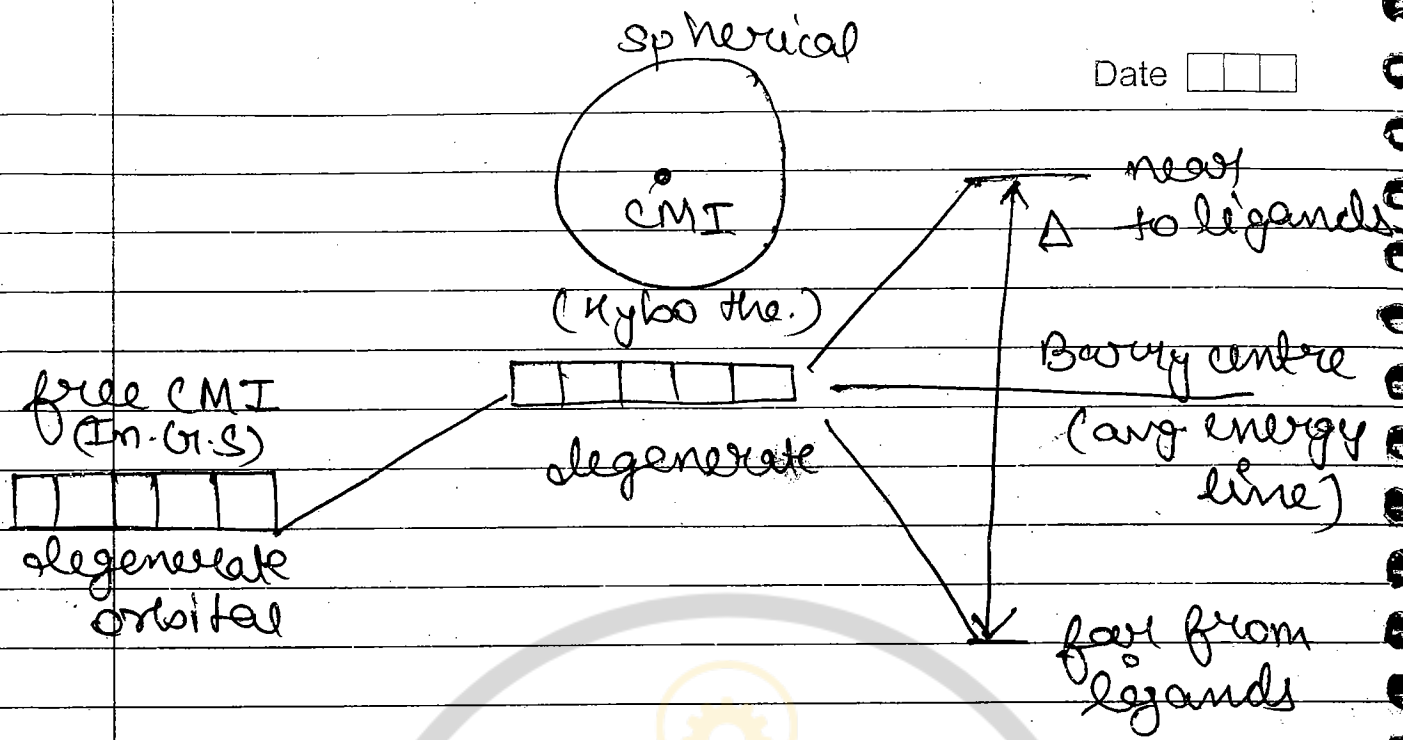
CRYSTAL FIELD THEORY

According to CFT central metal ion equal to (+ve) point charge. Anionic ligand = negative point charge. Neutral ligand equal to Dipole, So interaction b/w ligand & CMI is Electrostatic.

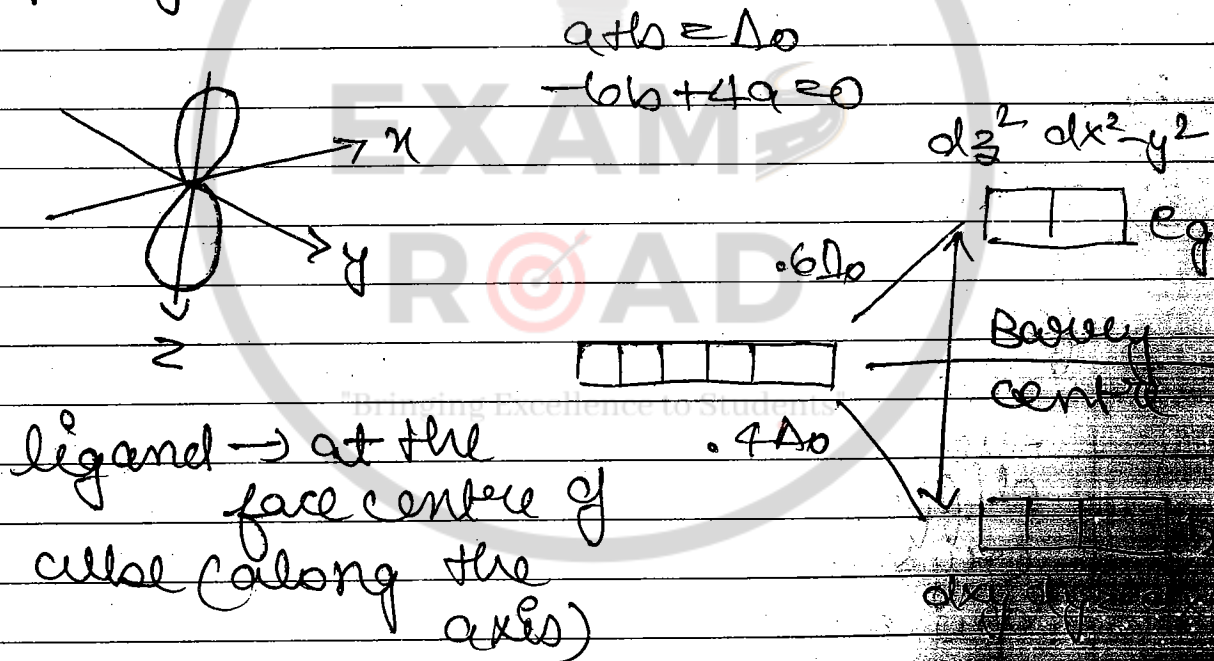
When ligand approaches CMI it experiences two types of forces →

- 1) Force of Attraction due to nucleus of CMI.
- 2) Force of Repulsion due to d-orbital e⁻s of CMI.
- 3) In particular geometry d-orbital ligands are near to some of the d-orbitals and far from other d-orbitals, so d-orbitals experience different-different repulsive forces so d-orbital split into different energy set which is called crystal field splitting. Energy difference b/w orbitals is called splitting energy Δ

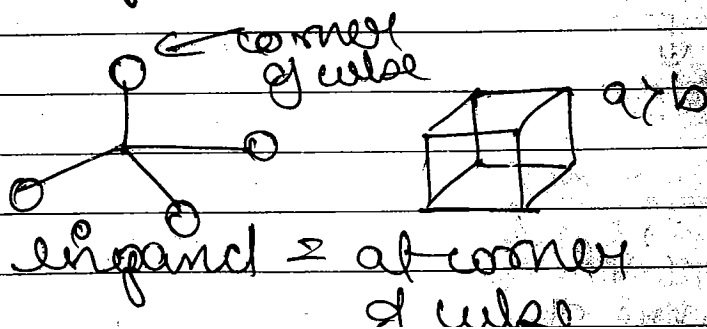


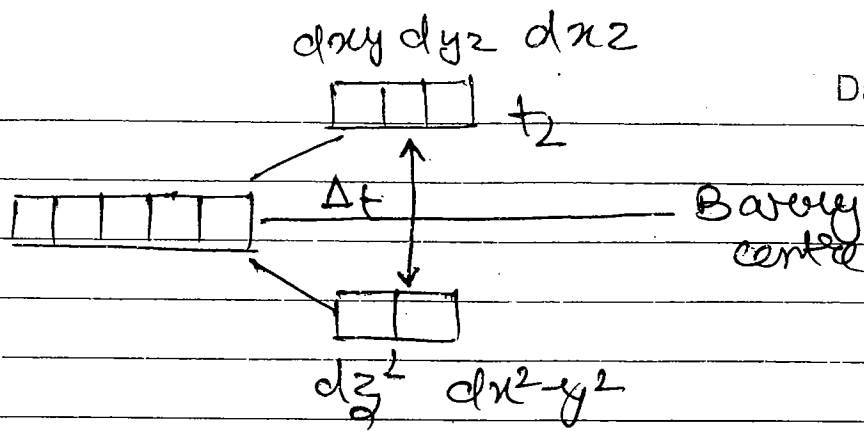


Splitting in octahedral \rightarrow

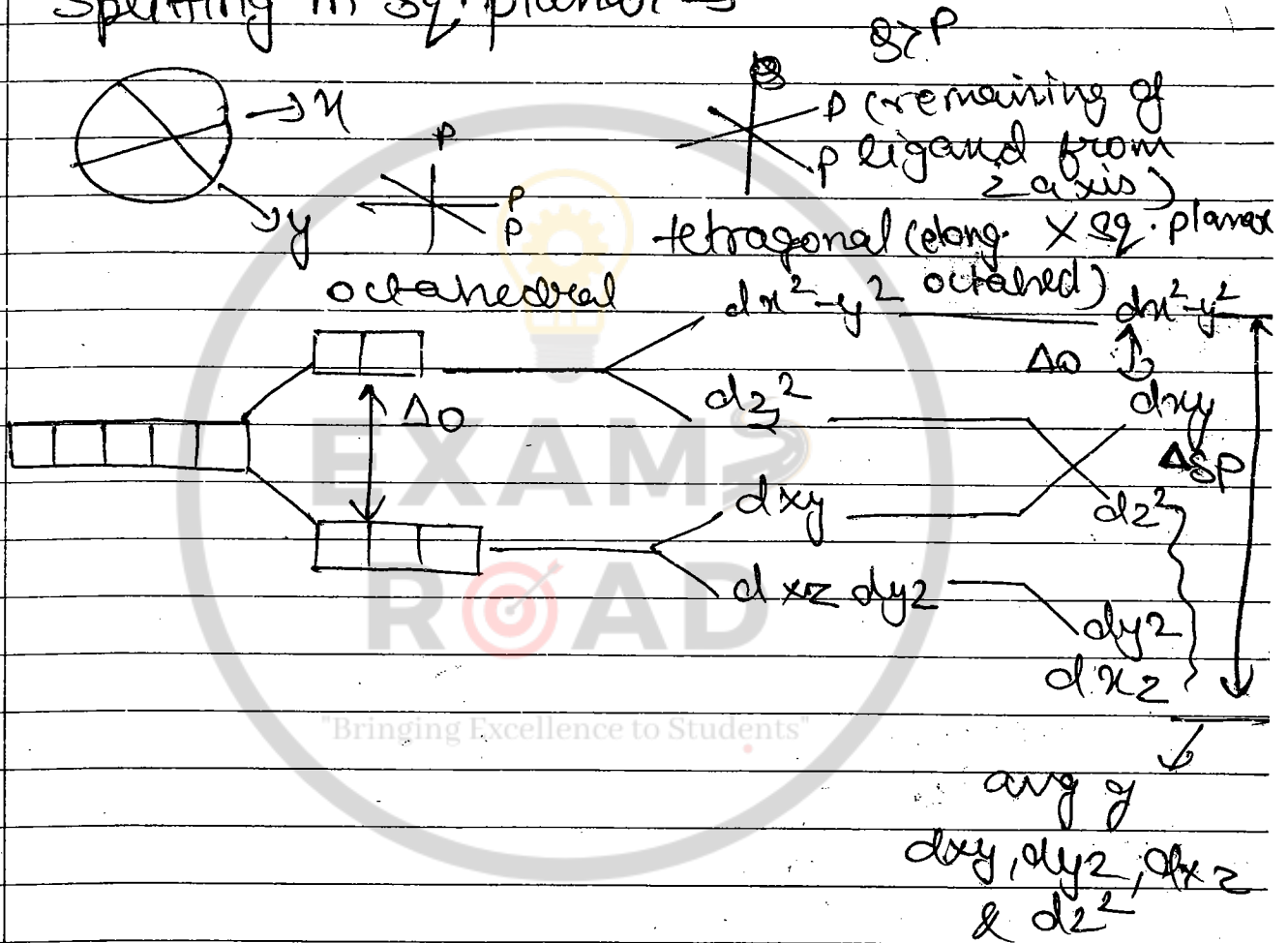


Splitting in tetrahedral \rightarrow





Splitting in sq. planar \rightarrow



Relation b/w Δ_o , Δ_t , Δ_{sp}

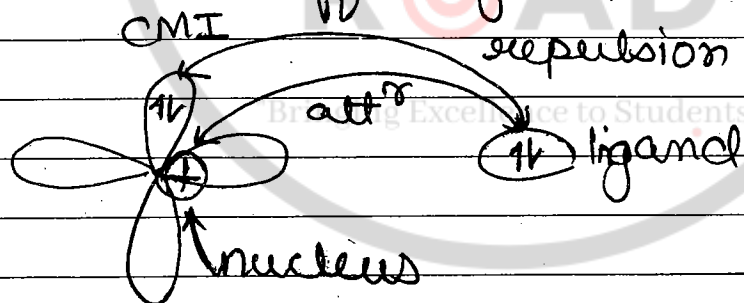
	$\Delta_{sp} > \Delta_o > \Delta_t$		
orbital	1	2	3
ligand	4	6	4

$$\frac{4}{6} \Delta_o = \frac{3}{4} \Delta_t$$

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

$$\frac{1}{4} \Delta_{sp} = \frac{2}{6} \Delta_o$$

$$\boxed{\frac{3}{4} \Delta_{sp} = \Delta_o}$$

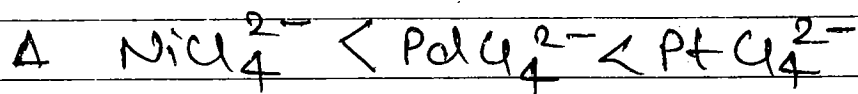
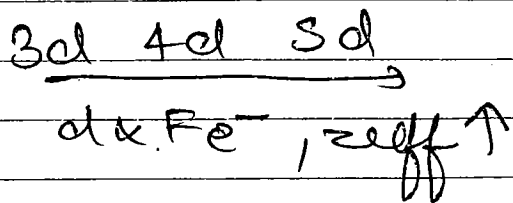
Factors affecting splitting energy \rightarrow 

As attrⁿ b/w CMI and ligand \uparrow
 distance \downarrow repⁿ b/w d⁻ & Ligand \uparrow
 splitting \uparrow

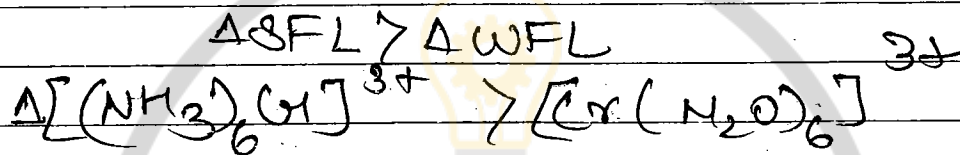
1) $\Delta \propto (+ve)$ the charge on CMI.



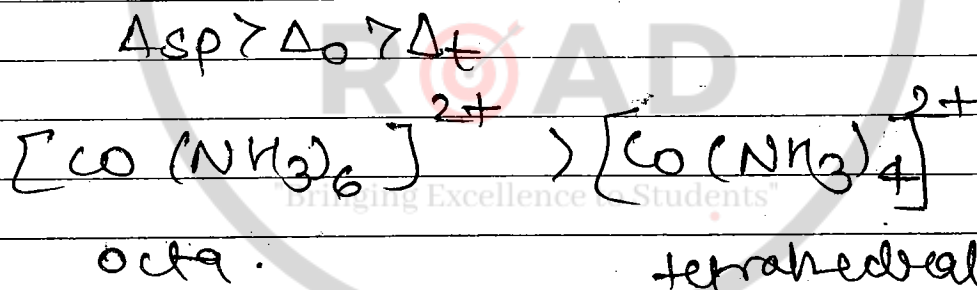
(2) $\Delta \propto Z_{eff}$ of CMI

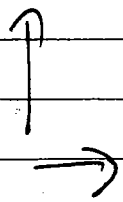


(3) $\Delta \propto$ strength of ligand



(4) geometry \rightarrow





TRICKS

Zinda

SC
Science
Scooter

Ti
Teacher
Ti

Cr
Teacher
Woh

Fe
fe
Feros

Co
core
Coker

Ni
ni
Ni

Cu
Cu
Cu

Zn
Zn
Zn

4

yaari
yanaha
Zara

Zr
Zara
Zara

Nb
Naha
Naha

Mo
Maut
Mol

Ru
Rukmal
Ruh

Pd
Padi
Padage

Ag
Age
Ag

Co
Cage
Cage

La

La
La

Hg

Hogi
Hog

Hf

Hafte
Haaf

Ta

Tha

W

Werna
Wala

Re

Re
Re

Ds

Osang
Si

Ir

Osang
Ikhari

Pt

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Date



EXAMSROADOFFICIAL



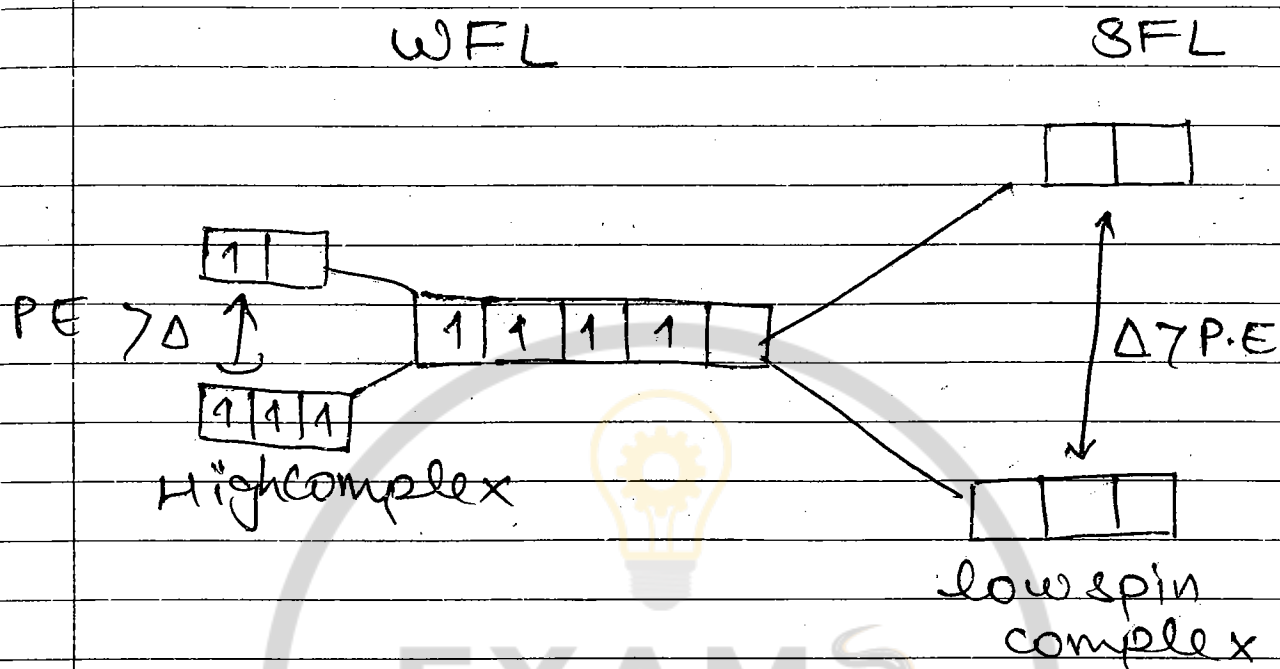
EXAMSROAD



EXAMSROAD

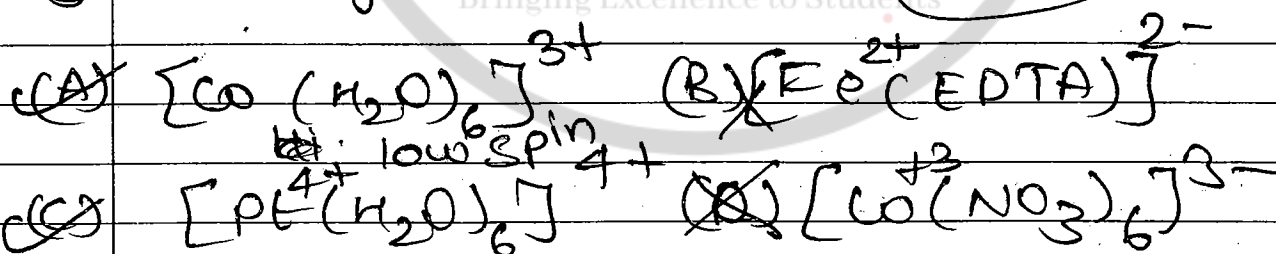


EXAMSROAD

low spin & High spin Complex \rightarrow 

Pairing energy :- energy req to pair e^- in an orbital

(Q) Which of them is/ have $\Delta_o > P.E$ SFL



Co^{3+}

Crystal Field Stabilization energy (CFSE)

Decrement in energy due to crystal field splitting

$$CFSE_{(0)} \rightarrow 0.4 \Delta_0 \times n_1 - \Delta_0 \times 0.6 n_2 - \lambda \times P.E$$

$\lambda \Rightarrow$ no. of extra pair

$n_2 \Rightarrow$ no. of e^- in eg set

$n_1 \Rightarrow$ no. of e^- in t_{2g} set

	WFL	SFL
	Config, CFSE	Config, CFSE
d ⁰	t _{2g} ⁰ e _g ⁰ 0	t _{2g} ⁰ e _g ⁰ 0
d ¹	t _{2g} ¹ e _g ⁰ 0.4 Δ ₀	t _{2g} ¹ e _g ⁰ 0.4 Δ ₀
d ²	t _{2g} ² e _g ⁰ 0.8 Δ ₀	t _{2g} ² e _g ⁰ 0.8 Δ ₀
d ³	t _{2g} ³ e _g ⁰ 1.2 Δ ₀	t _{2g} ³ e _g ⁰ 1.2 Δ ₀
d ⁴	t _{2g} ³ e _g ¹ (0.4 - 0.6) Δ ₀	t _{2g} ⁴ e _g ⁰ 1.6 Δ ₀
d ⁵	t _{2g} ³ e _g ² 0 Δ ₀	t _{2g} ³ e _g ² 2.0 Δ ₀
d ⁶	t _{2g} ⁴ e _g ² 0.4 Δ ₀	t _{2g} ⁶ e _g ⁰ 2.4 Δ ₀
d ⁷	t _{2g} ⁵ e _g ² 0.8 Δ ₀	t _{2g} ⁶ e _g ¹ 1.8 Δ ₀
d ⁸	t _{2g} ⁶ e _g ² 1.2 Δ ₀	t _{2g} ⁶ e _g ² 1.2 Δ ₀
d ⁹	t _{2g} ⁶ e _g ³ 0.6 Δ ₀	t _{2g} ⁶ e _g ³ 0.6 Δ ₀

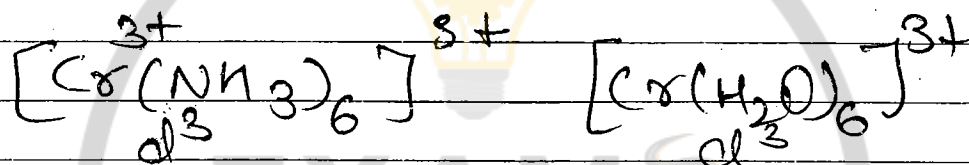
$$CFSE_{\text{(Tetrahedral)}} = -0.4\Delta_t \times n_1 + 0.6\Delta_t \times n_2 - x \times p \times e$$

n_2 = no. of extra pair

n_2 = no. of e^- pair set

n_1 = no. of e^- in t_2 set

(Q) which of the properties are similar in



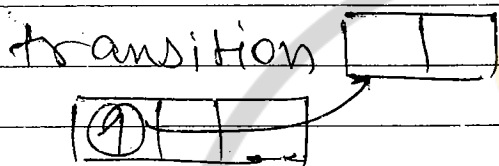
- ① no. of $d e^-$ ✓
- ② Hyb. of CML ✓ d^2sp^3
- ③ geometry ✓ octa
- ④ Magnetic moment ✓ no. of unpaired
- ⑤ Magnetic nature ✓ Same
- ⑥ G.F.S.E ✗ as expression same but value is not same as Δ differs.

Application of CFT →

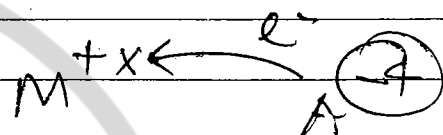
- 1) Colour of complex
- 2) Stability of complex

Colour of complexes

d-d transition



Charge transfer



⇒ b/w two atom

⇒ In an atom (CMT) ⇒ potential difference

⇒ Self excitation

⇒ external force x ⇒ external force v

⇒ No. of transition ↓ ⇒ No. of transition ↑

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⇒ Intensity ↓ ⇒ Intensity ↑

d-d Transition

⇒ $\Delta_{sp} > \Delta_o > \Delta_t$

gap b/w d orbitals in sq. planar > octa
 > Tetra

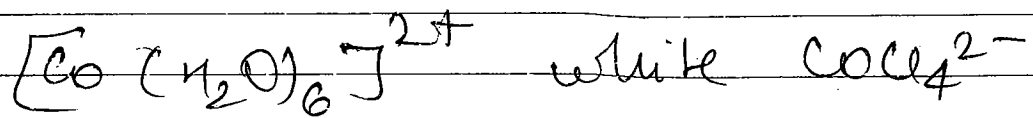
transition of e^- <

Intensity <

<

<

Sq. planar complexes are colourless generally



light pink

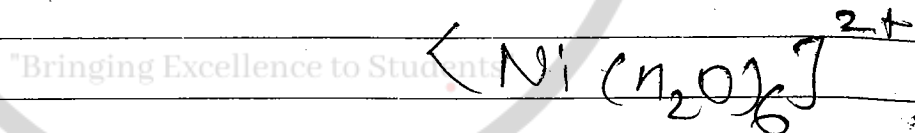
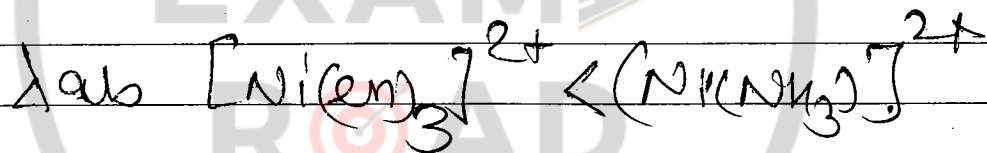
intense blue

d orbital

due to splitting
 \downarrow
 d orbitals

$$\text{gap} = \Delta(\epsilon) = h\nu = \frac{hc}{\lambda_{\text{abs}}}$$

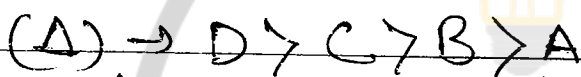
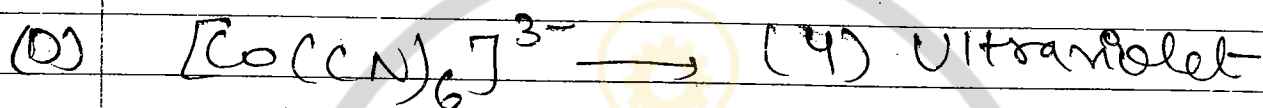
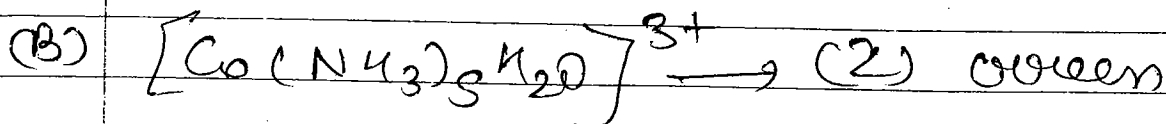
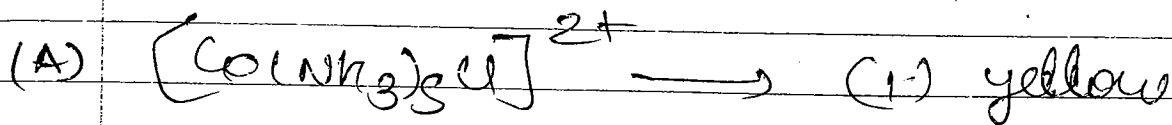
$\Delta \uparrow \Rightarrow \lambda_{\text{abs}} \downarrow$





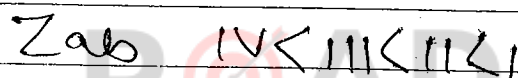
Date

(Q) Match them correctly absorbed wave length

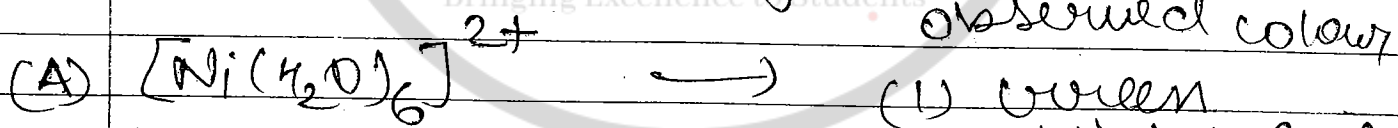


$\Delta \uparrow$ then λ absorbs \downarrow

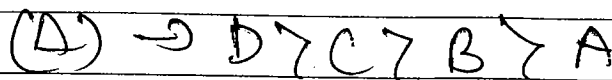
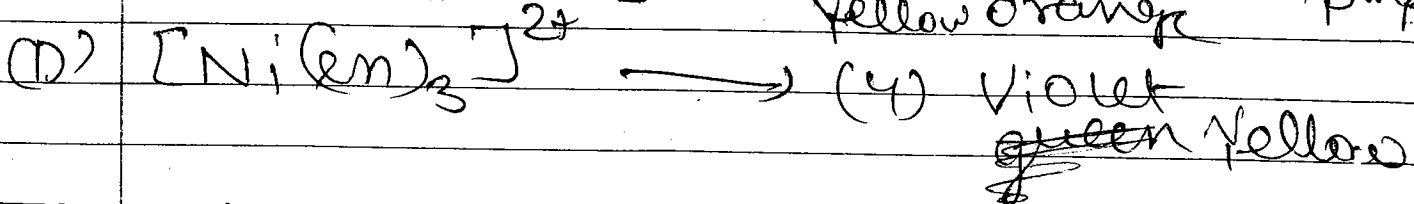
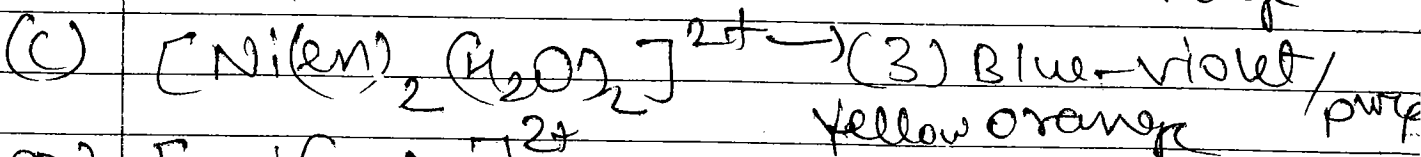
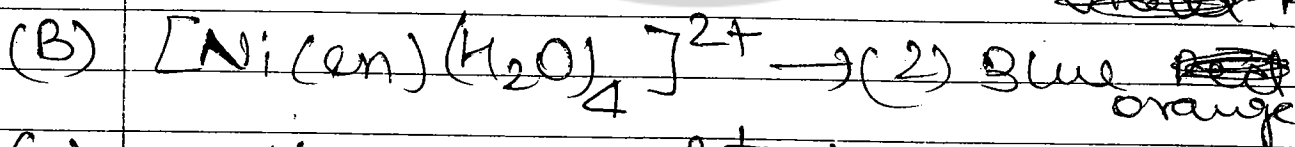
λ abs $\rightarrow D < C < B < A$



Match them correctly \rightarrow



~~Violet~~ Red



$\lambda_{\text{abs}} \rightarrow D < C < B < A$



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→ Anhydrous CuSO_4 is white in color while hydrated CuSO_4 is blue colour compound because in hydrated form H_2O act as ligand d -orbitals are splitted and $d-d$ transition possible while in absence of ligand all d orbitals are degenerated so $d-d$ transition not occurs.

→ Emerald (green) is a mineral beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) it is coloured bcz some of Cr^{3+} are present in place of Al^{3+} at octahedral sites

→ Ruby (Red) is an impure Al_2O_3 it contains impurity of Cr^{3+} which is reason of color.

→ $d-d$ transition is not possible in

(1) d^0 due to absence of e^- s

(2) d^{10} ~~for~~ absence of vacancy

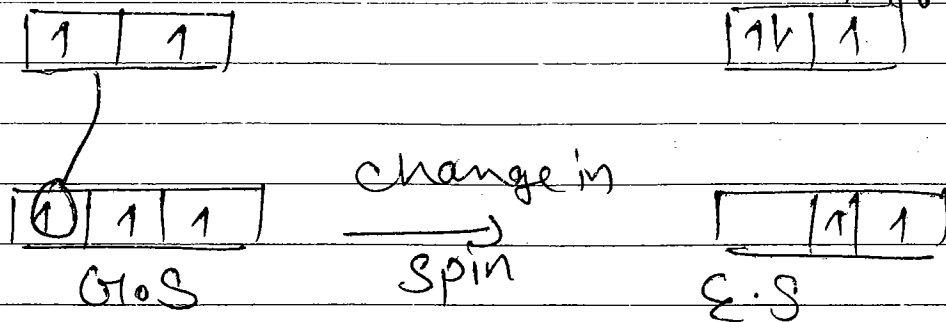
(3) d^5 WFL Symmetrical distributed

④



d⁵ WFL

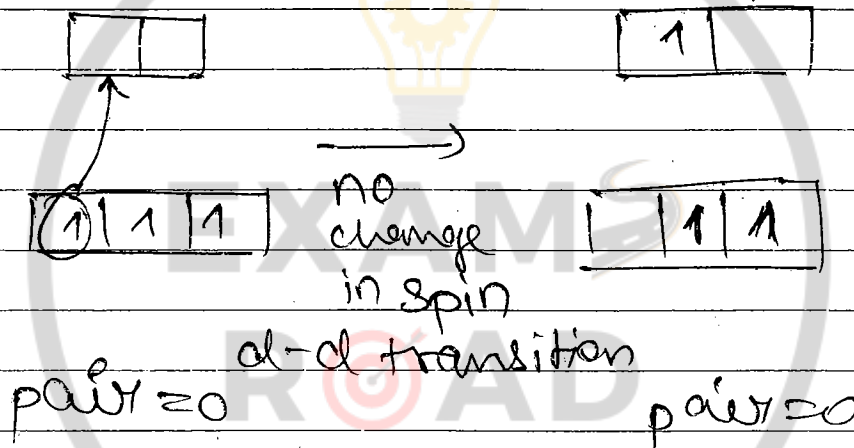
Spin not allowed
spin forbidden



pair = 0 d-d transition pair = 1

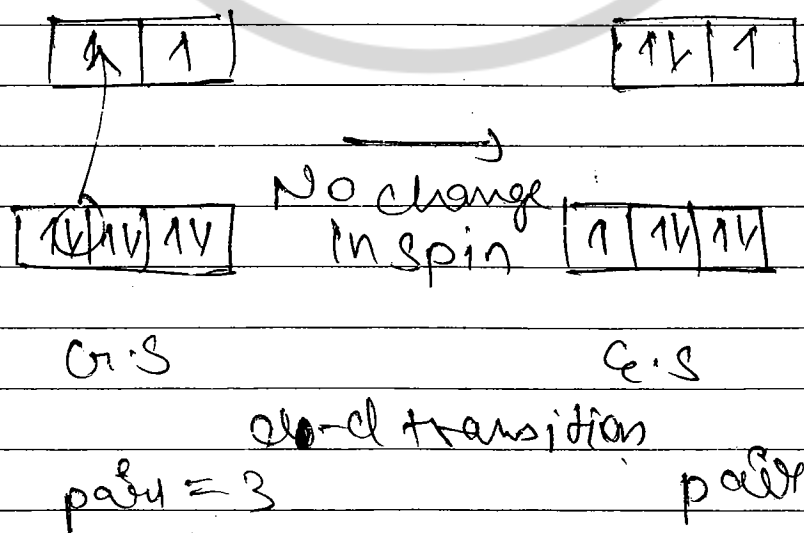
d³

spin allowed



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d⁸



$[\text{Mn}(\text{H}_2\text{O})_6]^{2+} \rightarrow \text{light pink / colourless}$

$[\text{FeF}_6]^{3-} \rightarrow \text{colourless}$

$[\text{Fe}(\text{H}_2\text{O})_6]^{3+} \rightarrow \text{light yellow}$

$[\text{Co}(\text{H}_2\text{O})_6]^{3+} \rightarrow \text{violet}$

$[\text{Cr}(\text{H}_2\text{O})_3 \text{X}]^4 \rightarrow \text{Green}$

$\text{X} = \text{SO}_4^{2-} / \text{Cl}^- / \text{NO}_3^-$

$[\text{Ni}(\text{H}_2\text{O})_6]^{2+} \rightarrow \text{green}$

Colour of Hydrate ion \rightarrow

Same no. d^0 & $d^{10} \rightarrow \text{colourless}$

of unpaired d^1 & $d^9 \rightarrow \text{Blue (except Ti}^{3+} \text{ purple)}$

d^2 & $d^8 \rightarrow \text{Green}$

(ye koi concept nahi hai
ye observed hai)

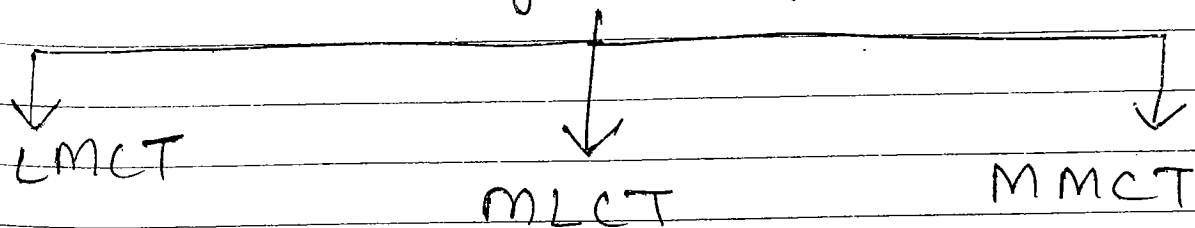
$\text{Fe}^{2+}, \text{Ni}^{2+} \rightarrow \text{Green}$

$\text{Cu}^{2+}, \text{Cr}^{2+} \rightarrow \text{Blue}$

$\text{Mn}^{2+}, \text{Co}^{2+} \rightarrow \text{Light pink / colourless}$

$\text{Fe}^{3+} \rightarrow \text{light yellow}$
 $\text{Cr}^{3+} \rightarrow \text{violet}$

Charge Transfer



1) LMCT (Ligand to metal charge transfer)

Example

- 1) ionic compounds
- 2) d-block oxyanions
 $(\text{MnO}_4^-, \text{CrO}_4^{2-}, \text{Cr}_2\text{O}_7^{2-}, \text{MnO}_4^{2-})$

• Oxyanions are formed by acidic oxide & d block metal form acidic oxide in +5, +6, +7 OS (High O.S)

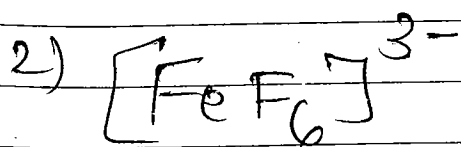
(3) d^0, d^{10}, d^s WFL (If they are coloured)

explain

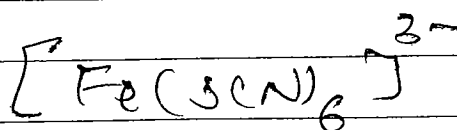
	+5	+6	+7
	VO_4^{3-}	CrO_4^{2-}	MnO_4^-
	colourless	yellow	purple

$\xrightarrow{\text{+ve charge} \uparrow \text{ transition} \uparrow \text{ Intensity}}$

d^s WFL

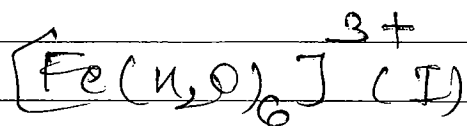


colourless

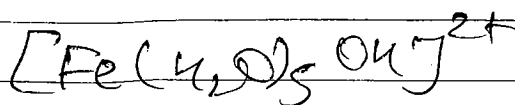


Blood red colour

②



light yellow

 $\text{Fe}^{3+} d^5$ WFL

yellow brown

d-d transition

CT ✓

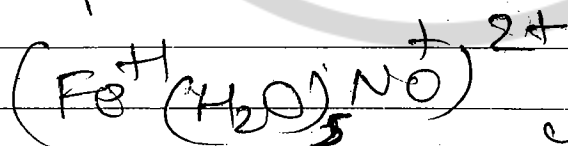
polarizability
Intensity $\text{H}_2\text{O} < \text{OH}^-$
 $\text{I} < \text{II}$ MLCT \rightarrow (Metal Ligand to charge Transfer)

Metal is in low

O.S. (-1, -2, 0, +1)

 \Rightarrow ligand good acceptor (π^*) $\text{C}_6\text{H}_6, \text{C}_5\text{H}_5^-, \text{C}_3\text{H}_5^-, \text{NO}, \text{NO}^+, \text{CO}$

example

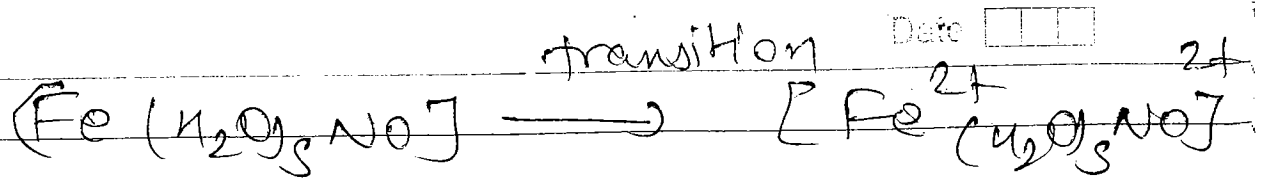
 Fe^{+1} NO^{+1} unpaired e⁻ practically ✓

3

 Fe^{2+} NO^0

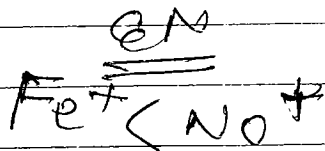
4

x

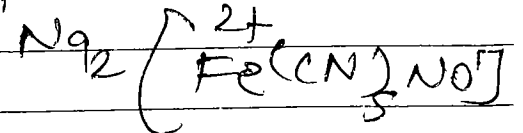


G.S

E.S



Sodium Nitro prusside



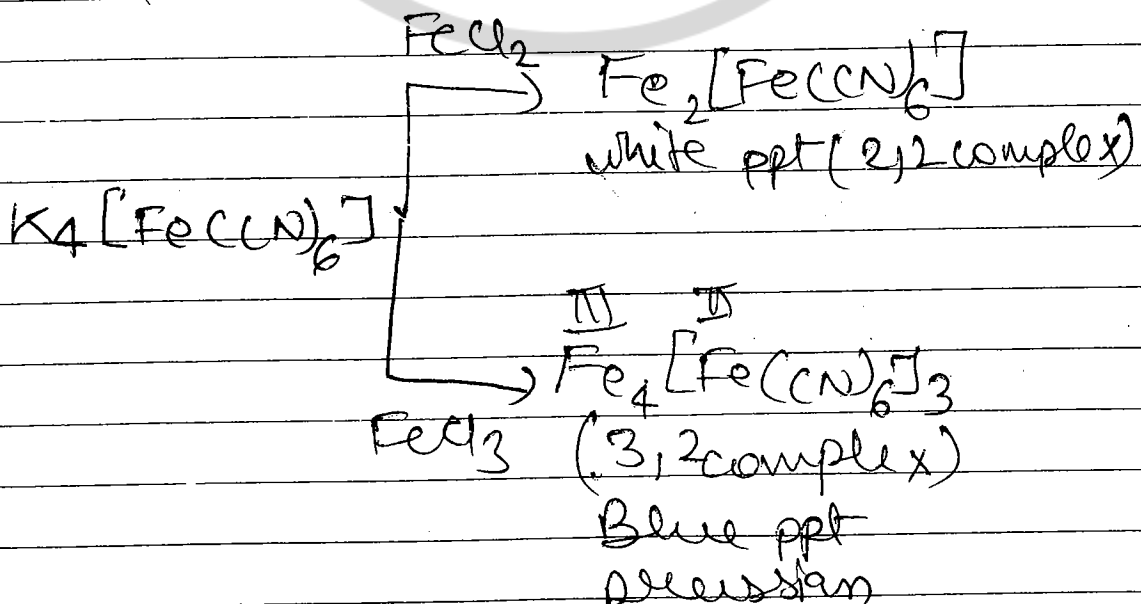
diamagnetic

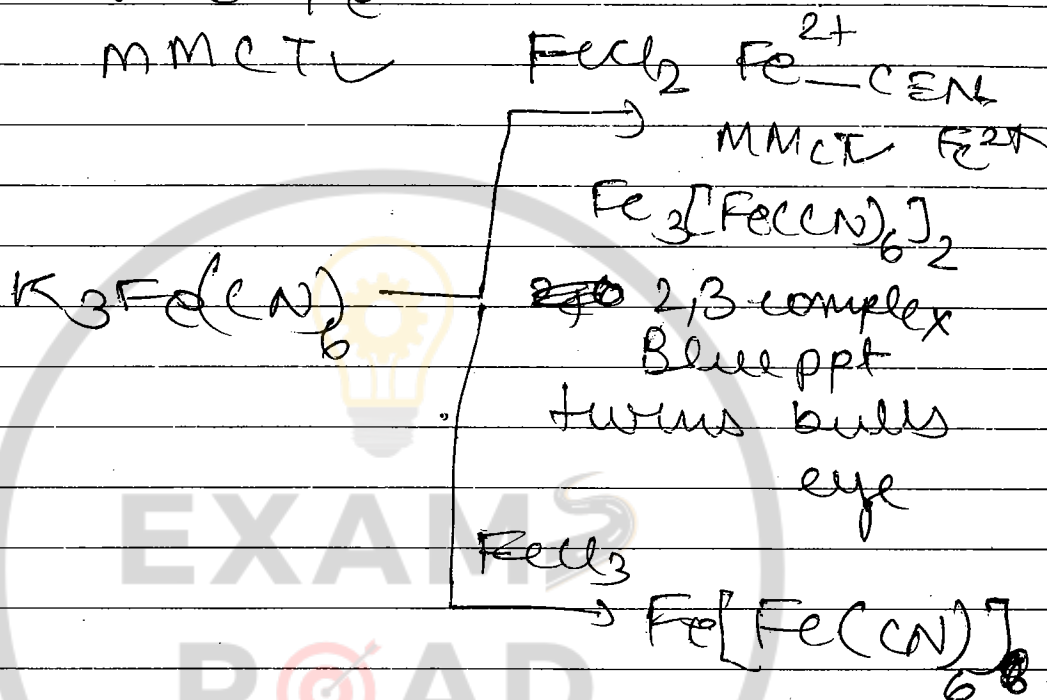
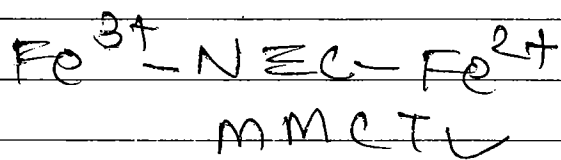
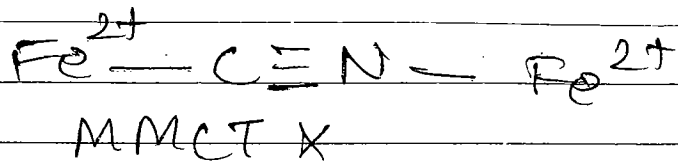
CTx $\text{Fe}^{+2} \text{NO}^+$ colourless
d-d transition x ligand CN^-

splitting ↑

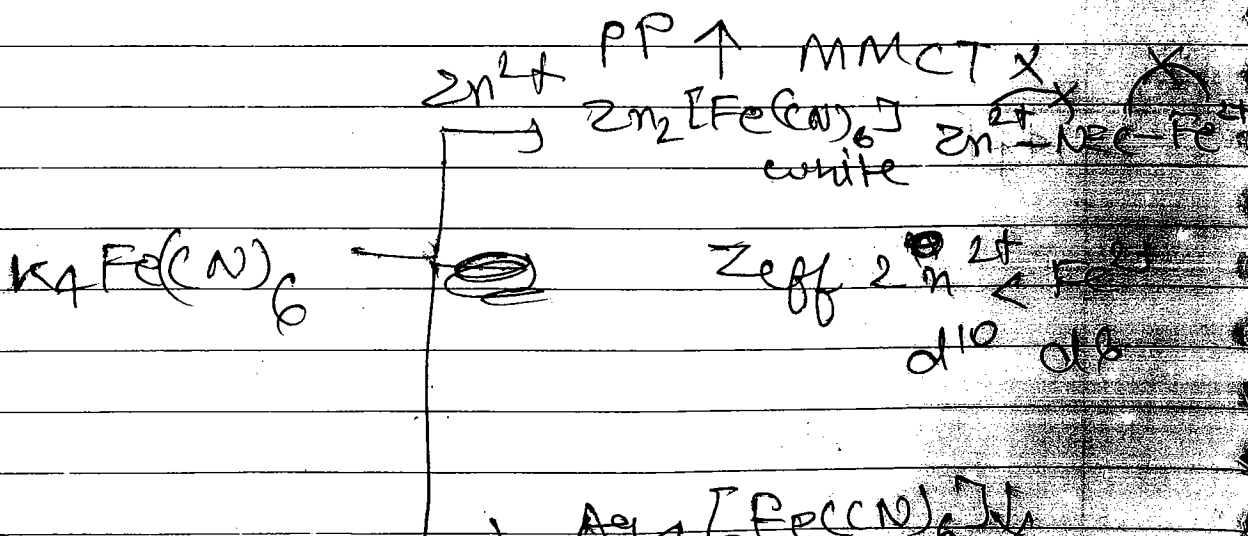
• Metal to Metal Charge transfer (MMCT)

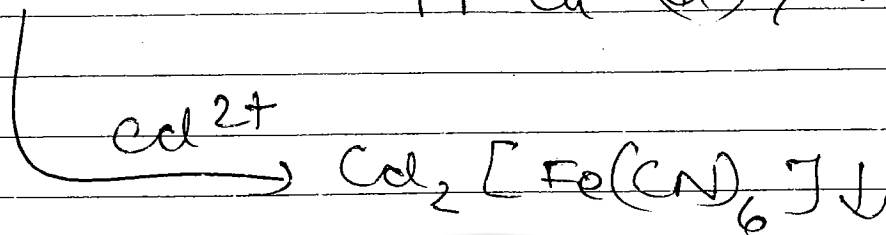
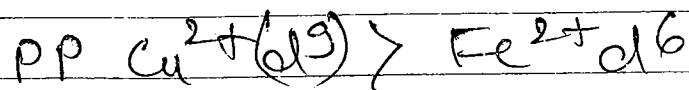
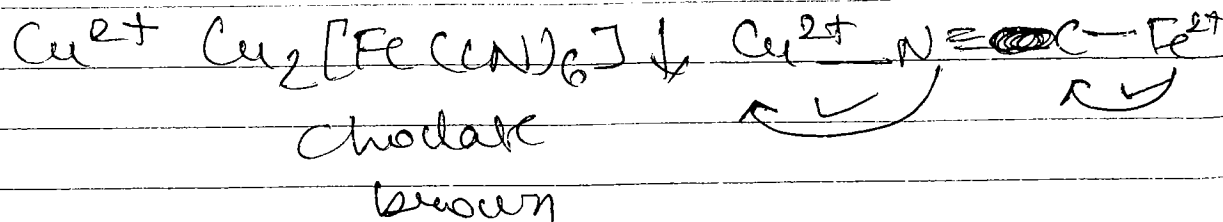
when two d-block metals present
in complex $[\text{AMLx}]$ at different potential



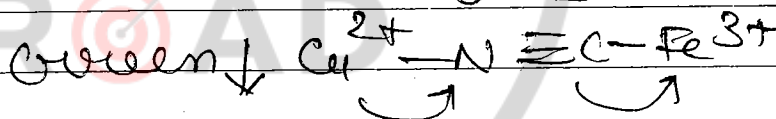
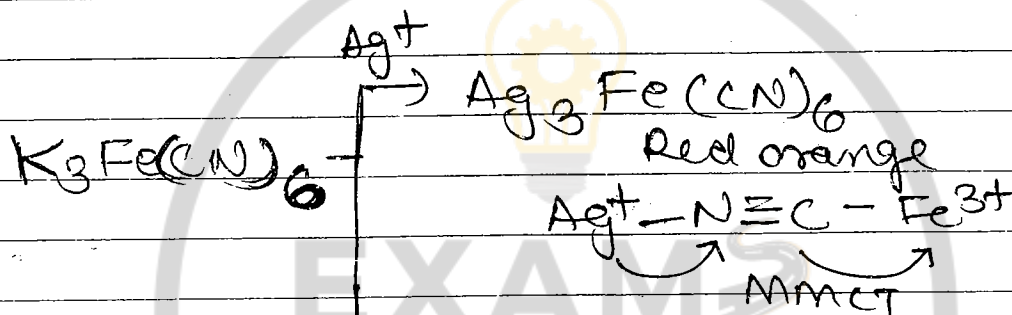


Red colouration
 (3,3 complex) (polarization)



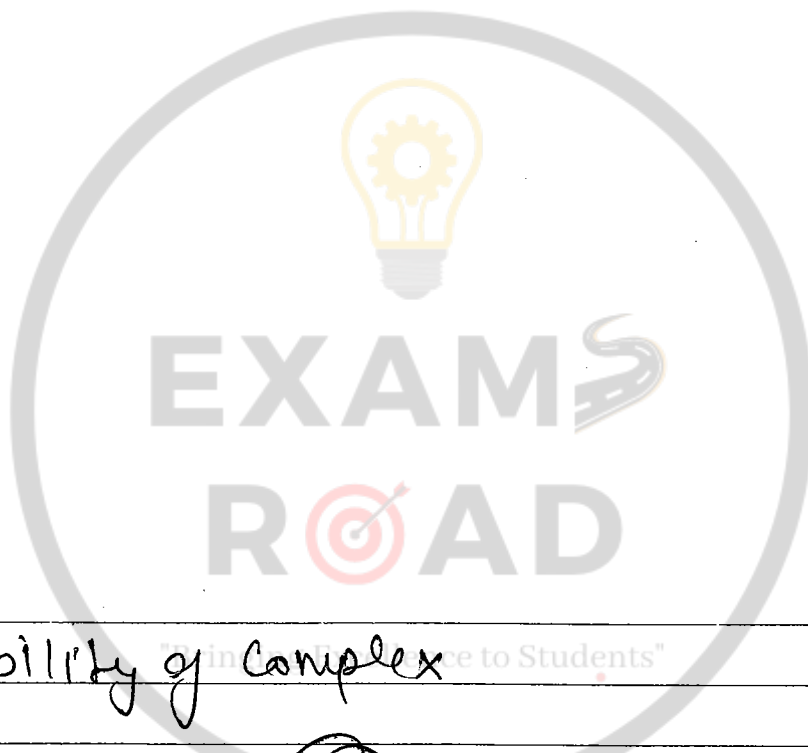


Bluish white ppt



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MMCT



Stability of Complex

$$\Delta G = \Delta H - T(\Delta S) \rightarrow \text{chelation (ring formation)}$$

↑
Bond formation
CFSE

As chelation ↑
Stability ↑

CFSE $\propto \Delta$

Δ & +ve charge on
CMI

chelation & no. of
rings
for same no. of
rings

$\propto Z_{eff} (3d < 4d < 5d)$

\propto Strength of ligand

$\Delta_{sp} > \Delta_o > \Delta_t$



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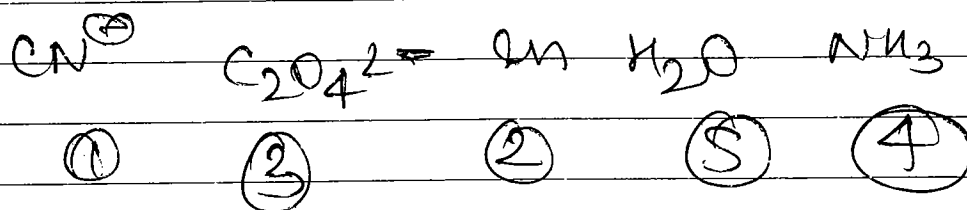
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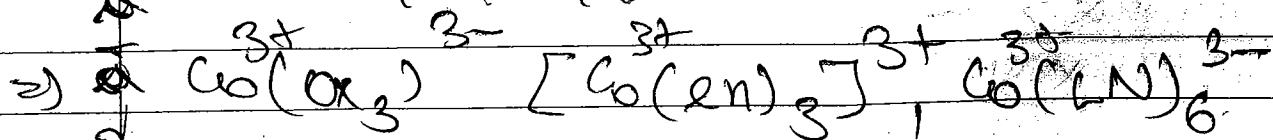
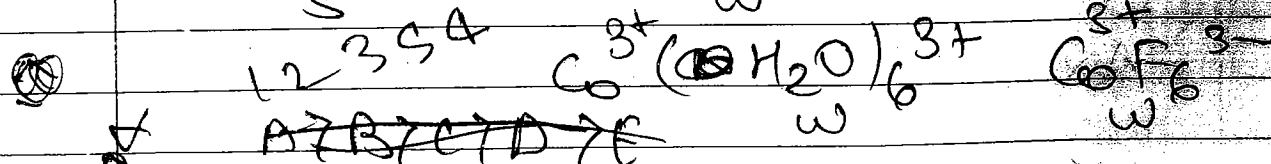
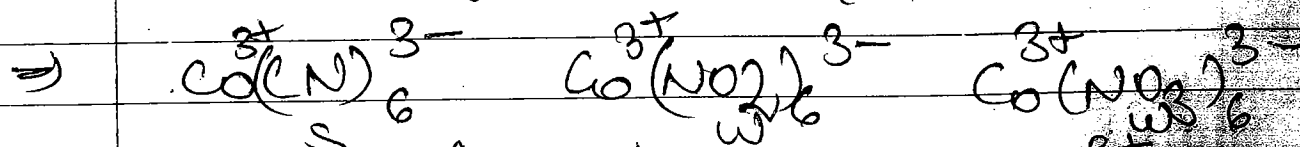
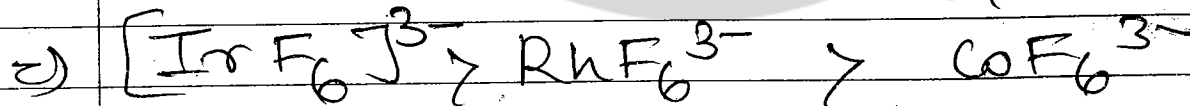
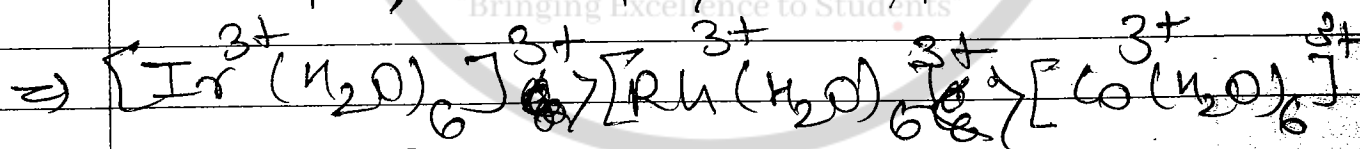
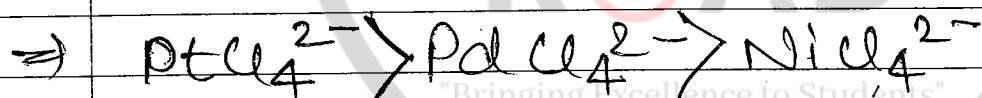
Priority order of same CMI

Strength \equiv chelation > strength of ligand

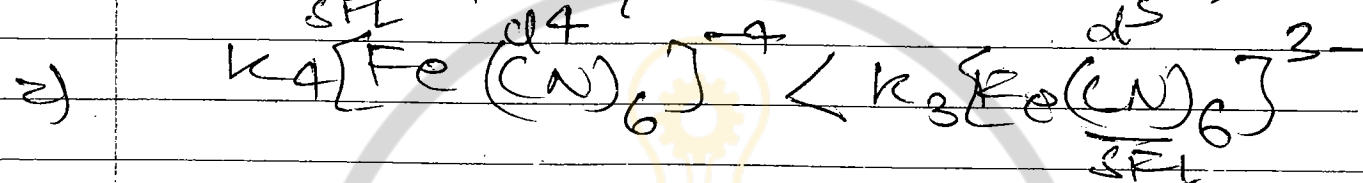
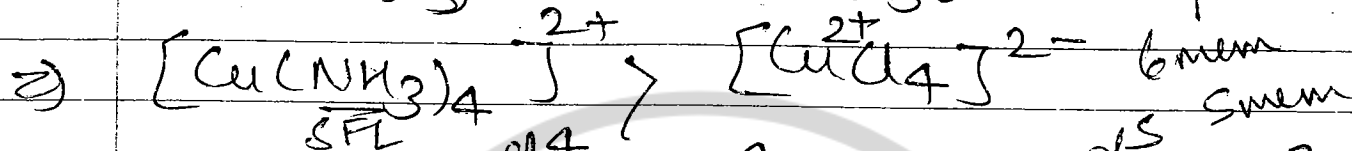
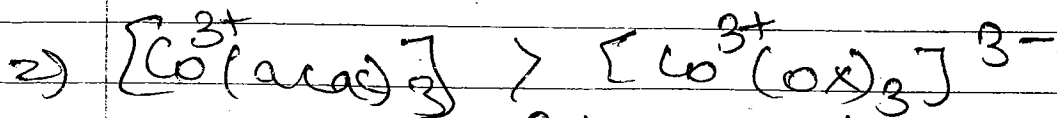
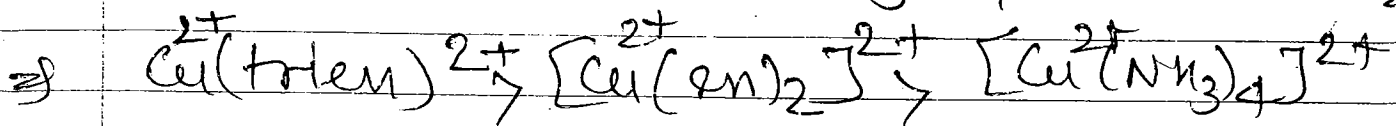
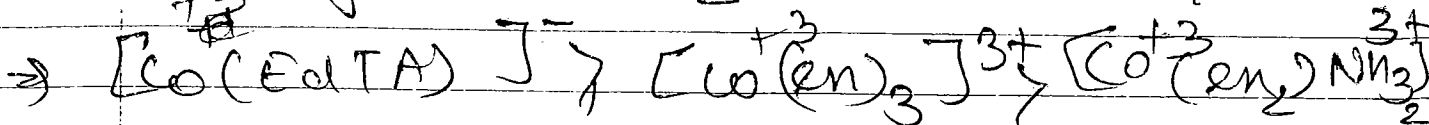
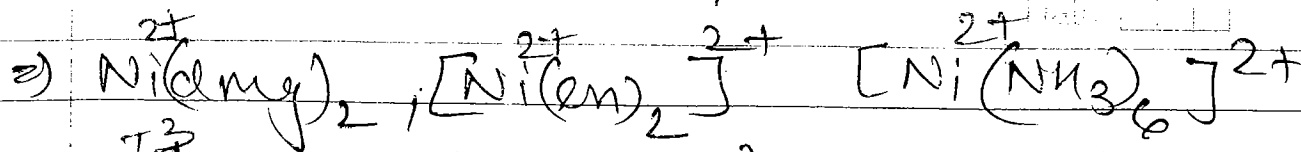


Bidentate ligands always present at cis as at trans Angle strain more.

Q Arrange following in correct order of stability \rightarrow



A > B > C



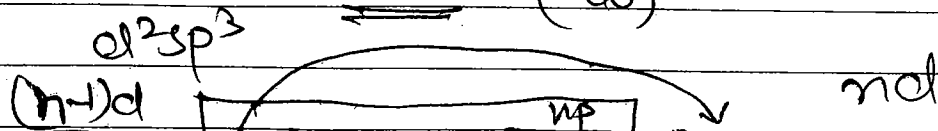
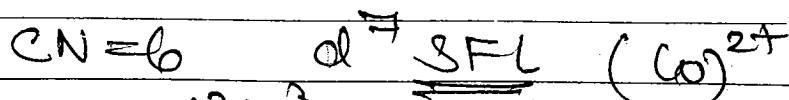
IMPORTANT POINTS

1) $Pt^{2+}, Pd^{2+}, Au^{3+}, Ag^{3+} \rightarrow$ always $d^8 sp^2$ diamagnetic

2) $Pt^{4+}, Pd^{2+} d^2 sp^3$ diamag. always.

③ Interference of e^-

when highest energy d orbital contain single e^- in presence of SFL



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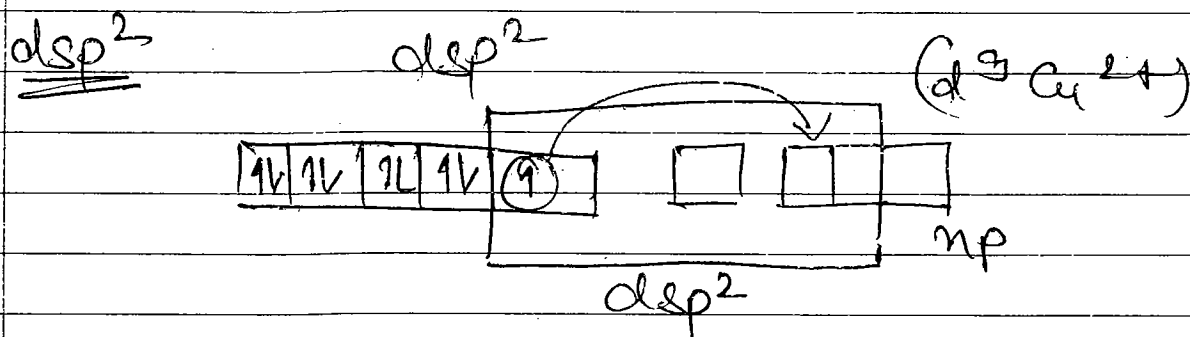


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CN=4 dsp^2 (d^9, Cu^{2+})



CN=5 dsp^3 (d^9, Cu^{2+})



$Co(II) \xrightarrow[CN=6]{SPL} Co(III) - (a) \text{ removal of } e^- \text{ from } e$

$Cu(II) \xrightarrow[CN=4]{SPL} Cu(III) - (b) \text{ removal of } e^- \text{ from } 4p$

also $IE / Z_{eff} (Cu^{2+} > Co^{2+})$

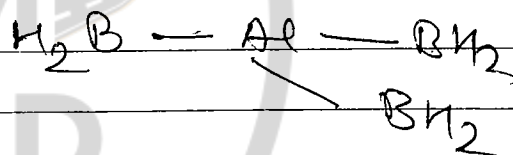
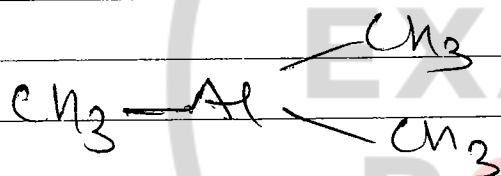
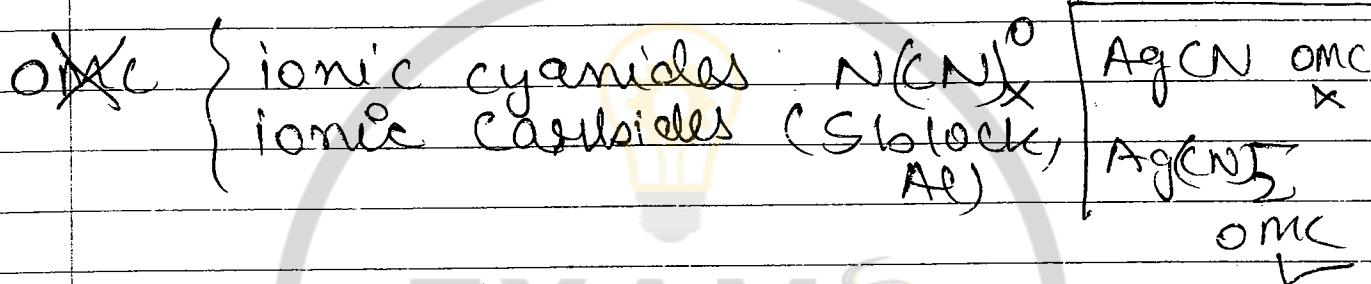
Q. A is ~~more~~ spontaneous in comparison to B as B is non spont. bcoz removal of e^- is easy from d orbital in comparison of $4p$ orbital.

OMC organo metallic compounds

Metal + C/B/Si
Covalent / coordinate

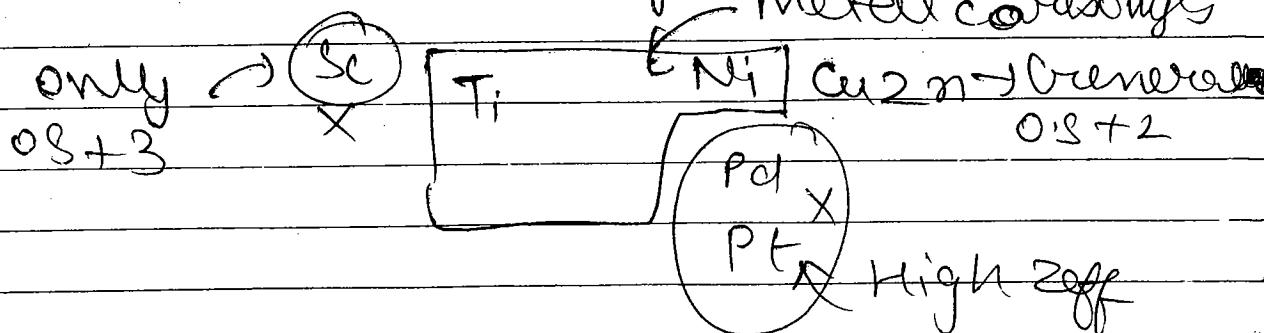
σ donor

π donor



\Rightarrow CO is not a good donor but it is a good acceptor so it form complex with metals having low OS. (-2, -1, 0, +1)

generally all d-block metals form metal carbonyls

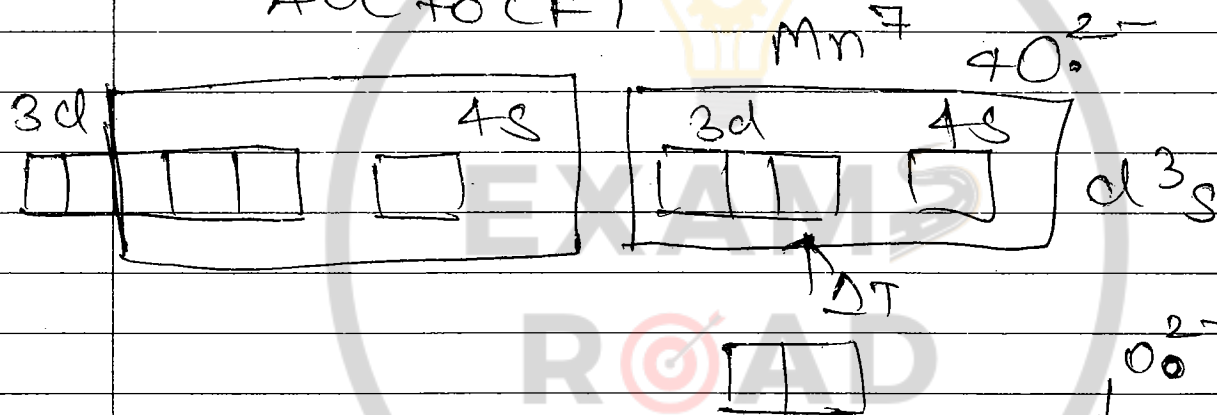


⇒ In CN = 4 d^0, d^1, d^2

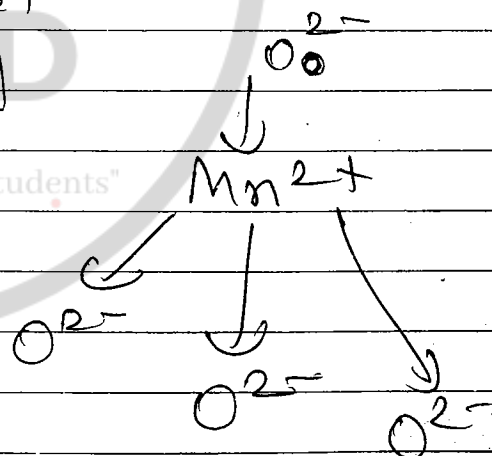
Acc to CFT → d^3s
 practically → d^3s as well as sp^3

example :- MnO_4^- , ~~MnO_4^{2-}~~ , CrO_4^{2-} ,
 $Cr_2O_7^{2-}$, VO_4^{3-} , MnO_4^-

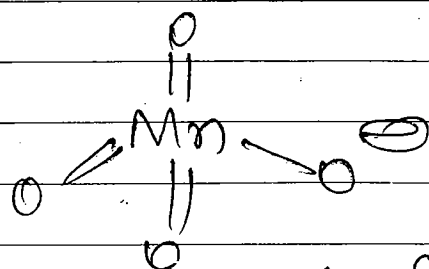
Acc to CFT



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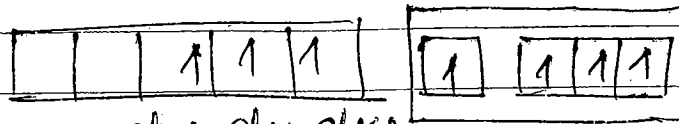


Practically →



4 bonds

Cr's ↑↑↑↑↑



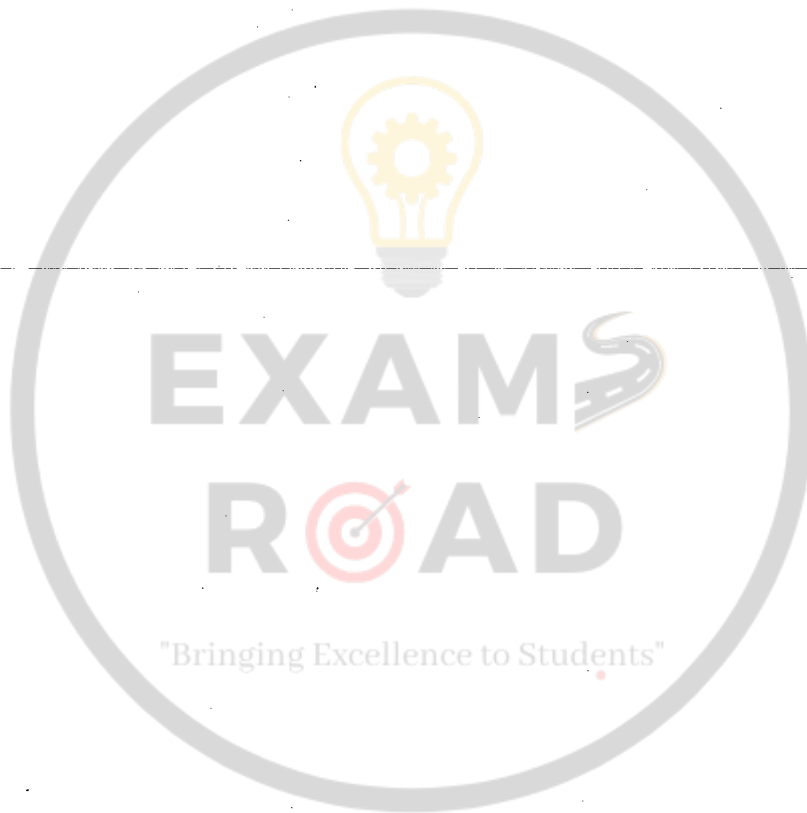
dx_y dx_z dx₂
form π bond

sp^3

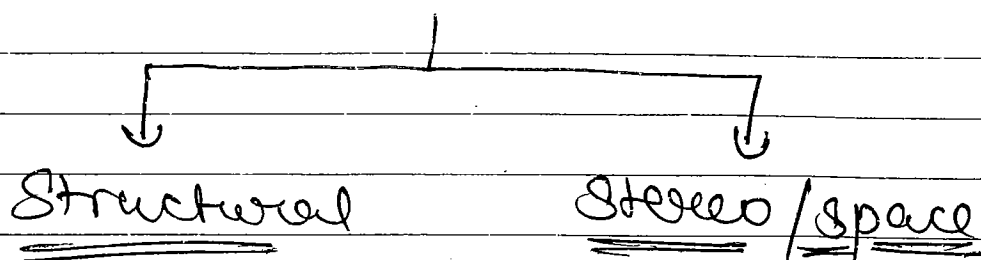
can't distinguish

can't distinguish

Colour of complexes



ISOMERISM

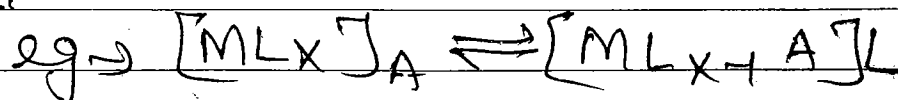


- 1) Ionization
- 2) Hydrate/solvate
- 3) linkage
- 4) co-ordination
- 5) coordination position
- 6) ligand isomerism
- 7) polymerisation

- 1) Geometrical
- 2) optical

IONIZATION ISOMERISM →

Complexes having same molecular formula but furnishes different type of ions in aq. medium. In such complexes counter ion can act as ligand and ligand act as C.E.T.



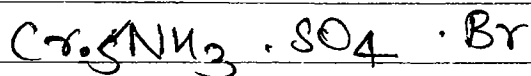
Ionisation isomers can be distinguished by

- 1) Qualitative Analysis (Precipitation)

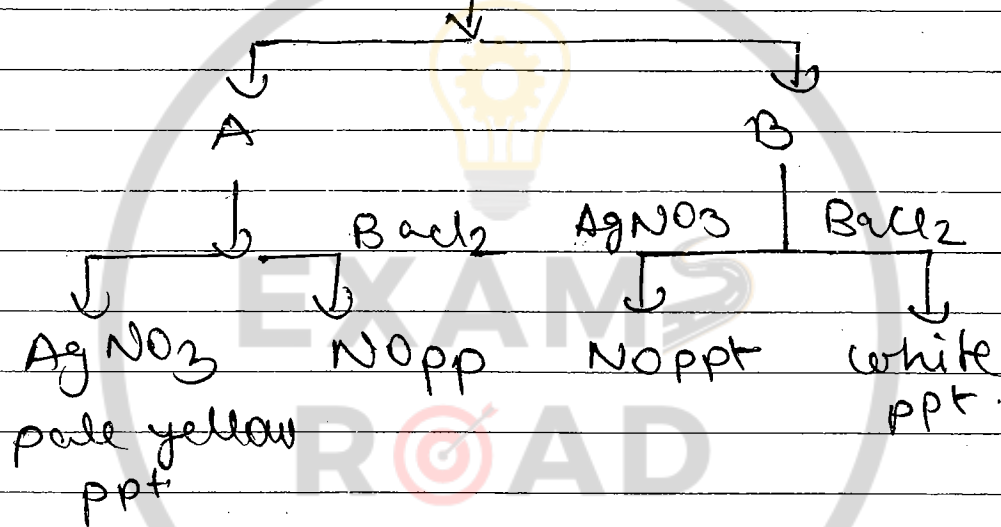


2) Conductivity Measurement (conductivity & charge $\propto \frac{1}{\text{Hydrated size}}$)
 & charge dominates over size.

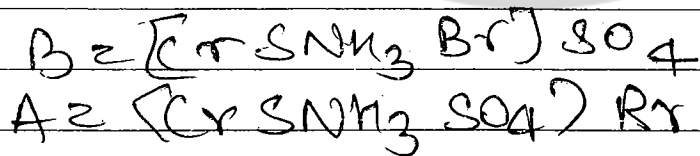
(Q)



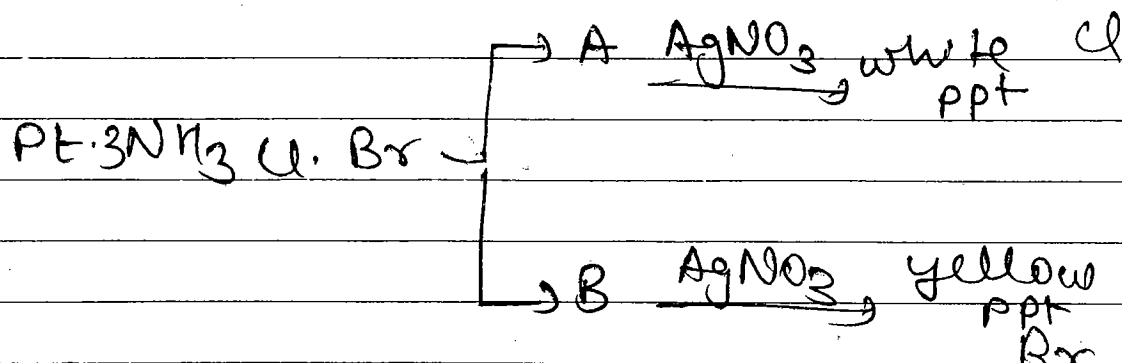
Ionisation Isomer



Identify complexes A & B.



(Q)



Hydrate/Solvate Isomerism \rightarrow

In complex compound H_2O molecule act as ligand inside the coordination sphere and act as crystalline water outside the coordination sphere in Ionic Lattice

Complexes having same molecular formula but diff. no. of water molecules inside or outside coordination sphere are hydrate isomers of each other.

Hydrate isomers, $[M(H_2O)_6]Br_2$

$[M(H_2O)_5Br]^+ Br^- \cdot \text{crystalline } H_2O \text{ water}$

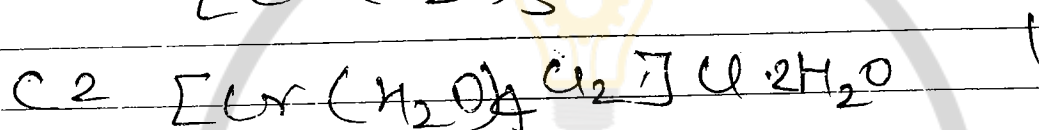
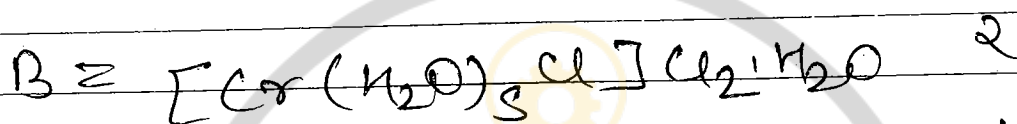
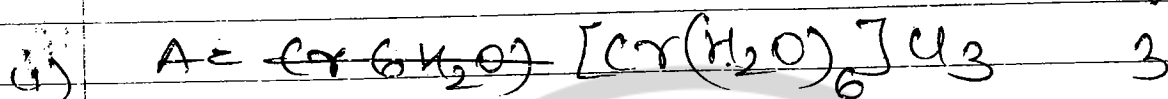
~~$[M(H_2O)_4Br_2] \cdot 2H_2O$~~

Hydrate isomers can be distinguished by

- 1) Quantitative Analysis (Difference in no. of moles of ppt)
- 2) Conductivity Measurement
- 3) By weight loss measurement or

(Q) $\text{Cr} \cdot 6\text{H}_2\text{O} \cdot \text{Cl}_3$ exist in 3 isomeric form A, B, C. (i) find conductivity of A, B, C. (ii) find order of weight loss of A, B, C or \rightarrow with conc. H_2SO_4 (iii) find moles of AgCl precipitated when each mole of A, B, C separately reacts with excess of AgNO_3 .

AgCl



(ii) ~~A, B, C~~ conc. H_2SO_4

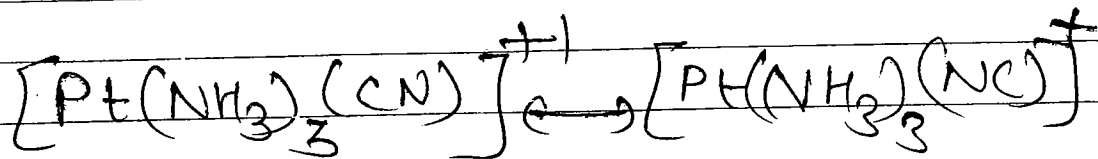
No wt. loss

$\left. \begin{array}{l} 1\text{H}_2\text{O} \\ 2\text{H}_2\text{O} \end{array} \right\} \text{loss}$

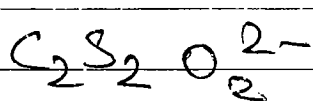
"Bringing Excellent Students"

LINKAGE ISOMERISM \rightarrow

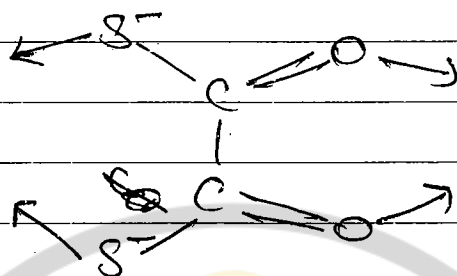
This type of isomerism arises when complex contain ambidentate ligand because Ambidentate ligand can be coordinated with different-different donor sites with CN^-



donor site	CN ⁻	NCO ⁻	SCN ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₃ ²⁻	S ₂ O ₃ ²⁻
	2	2	2	2	3	2	2



identifiable
& ambident



(8) Which of them can show linkage isomerism

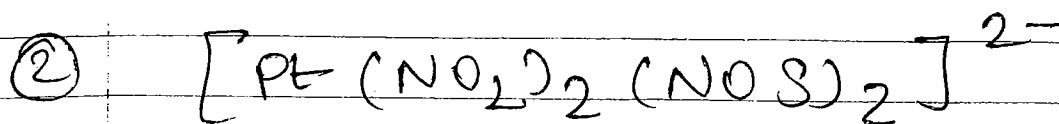
- ① $[\text{Fe}(\text{SCN})_6]^{3-}$
- ② $[\text{Pt}(\text{CN})_4]^{2-}$
- ③ $[\text{Cr}(\text{NH}_3)_4\text{SO}_3]^{+}$
- ④ $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$
-

(9) Find possible linkage isomers of

1) $\text{Pt}(\text{CN})_4^{2-}$	C	N
	4	0
	3	1
	2	2
	1	3

Ans = 3

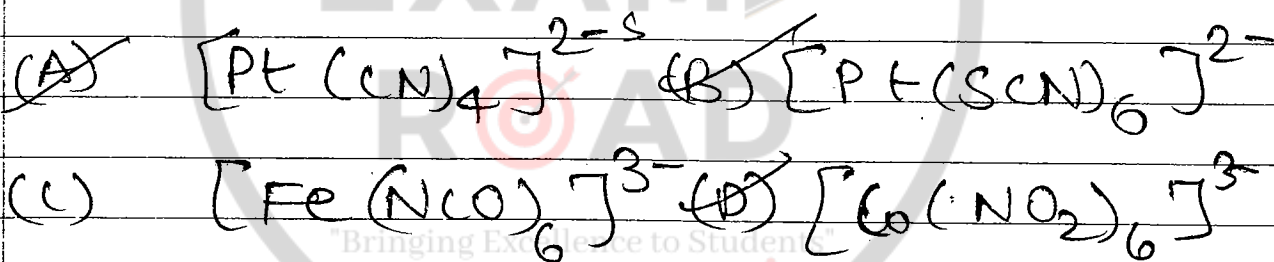




	NO₂	NO₃	N	O	S
NO ₂	2	0	1	0	0
2 O			1	1	0
1 1			0	1	1
0 2			2	0	0
			0	0	2
			0	2	0

⇒

Hybridization of which complex & its homoleptic linkage isomer is same.

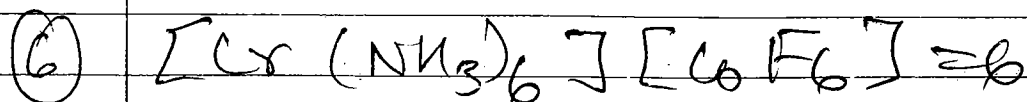
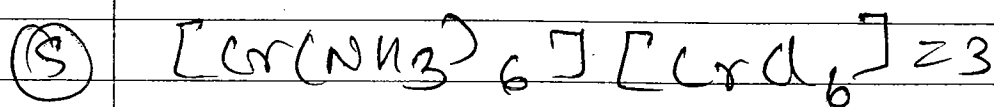
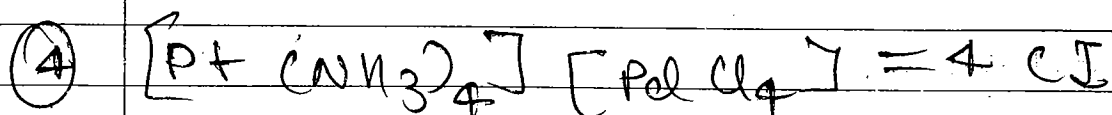
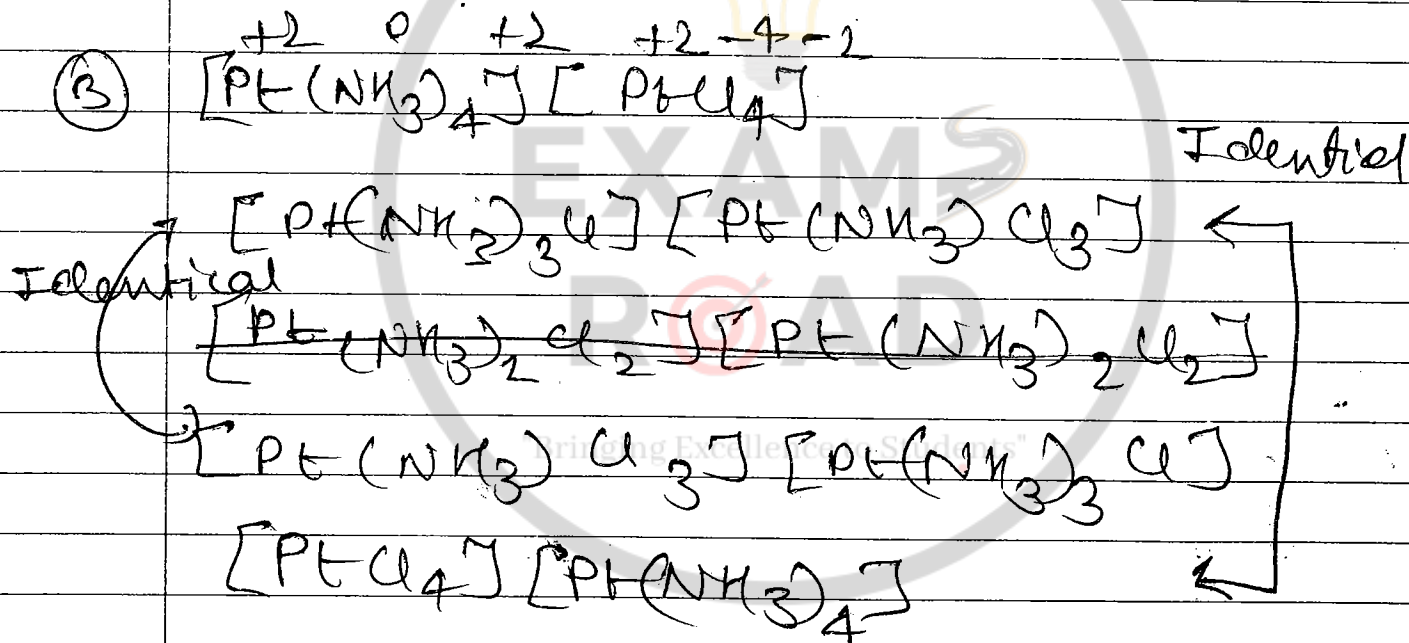
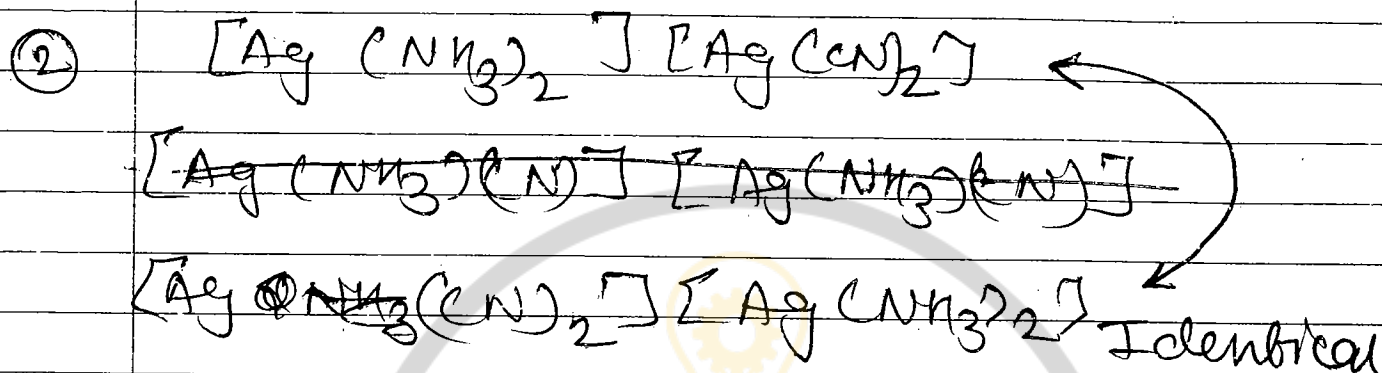
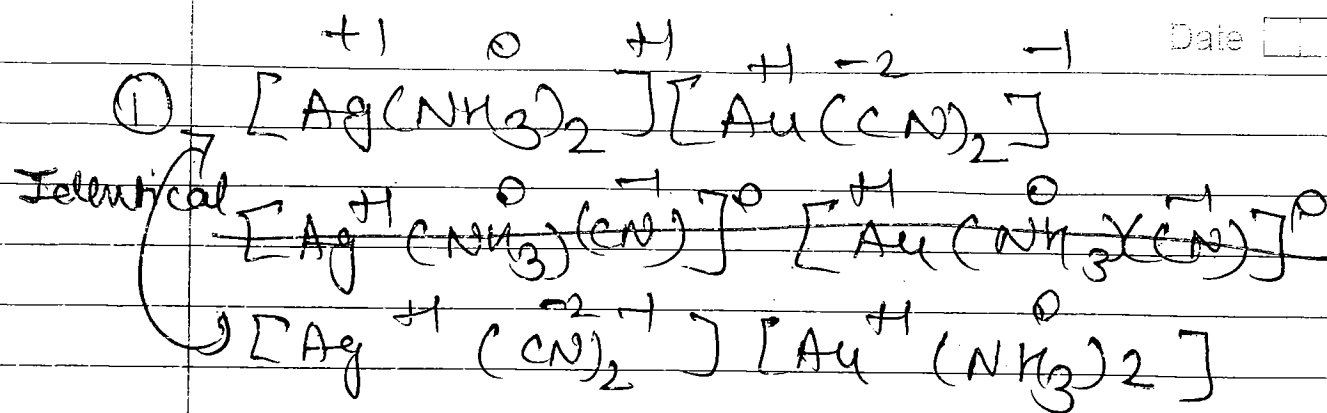


COORDINATION ISOMERISM →

This type of isomerism arises in compound having complex cation as well as complex anion.

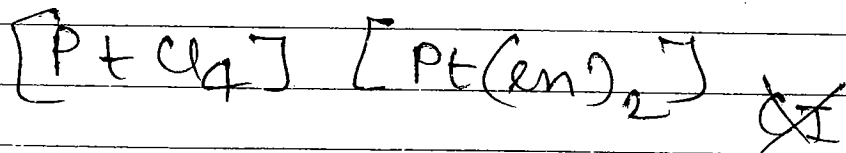
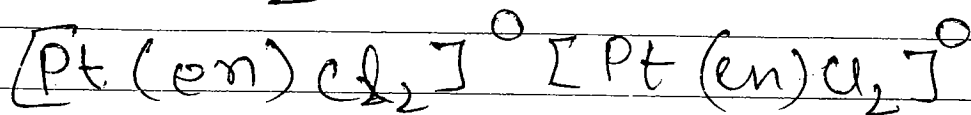
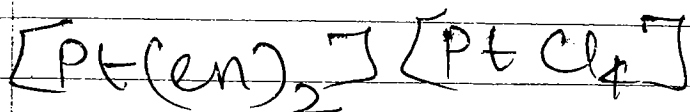
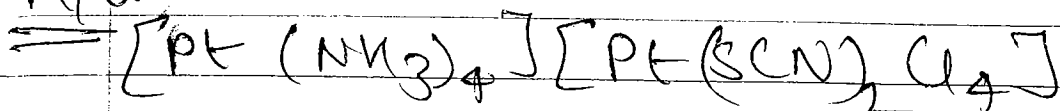
Complexes having same molecular formula but ligands or CMI present in diff-diff coordination sphere.



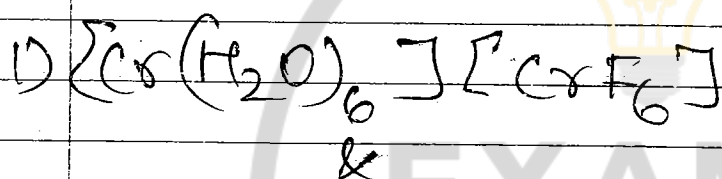


H/W

Date

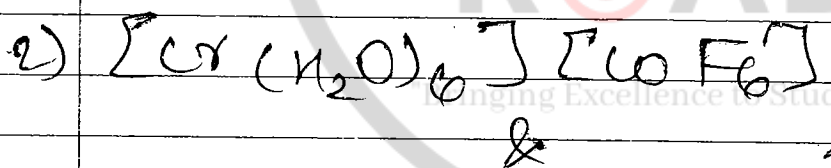
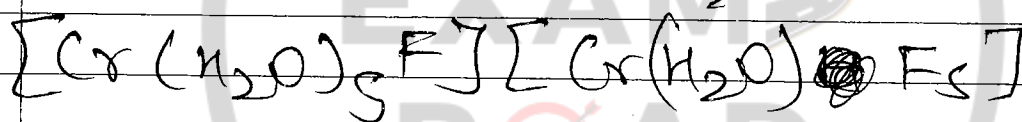


match them can distinguish by

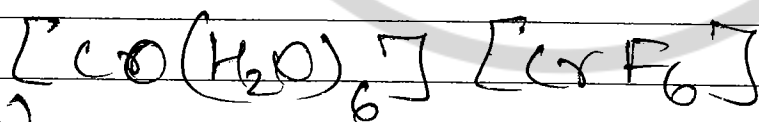


(A) molar

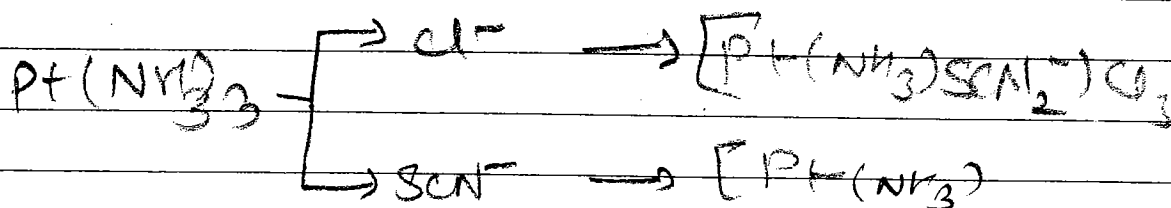
conductivity



(B) Electrolysis



H/W



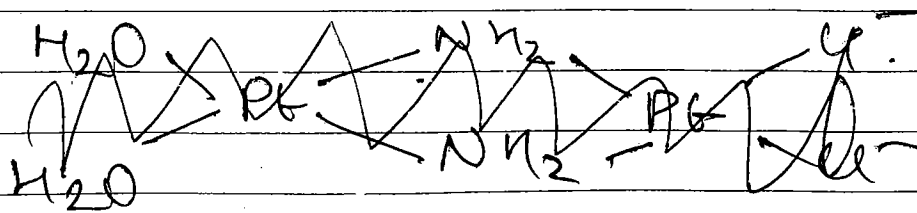
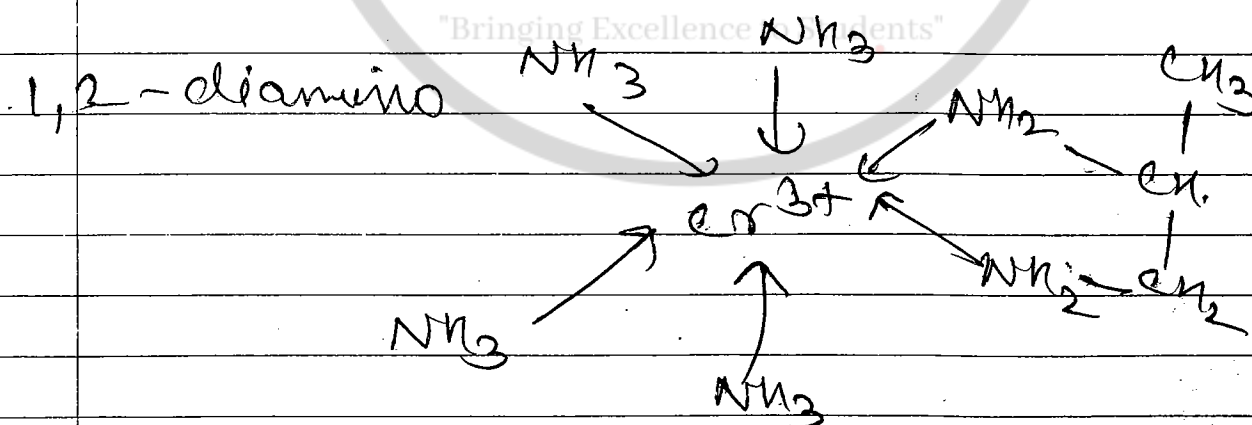
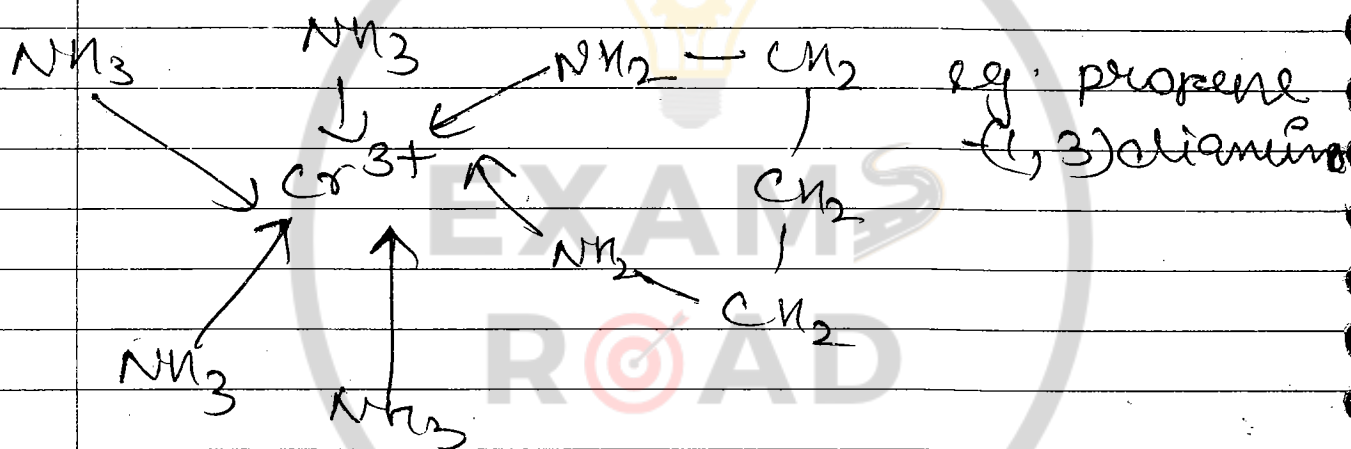
Next two pages



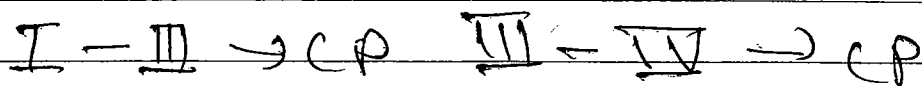
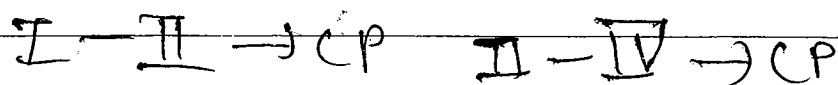
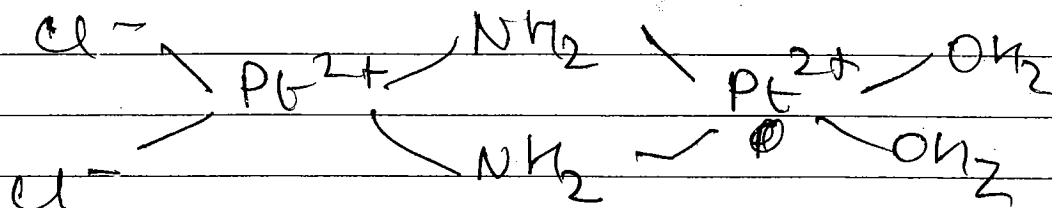
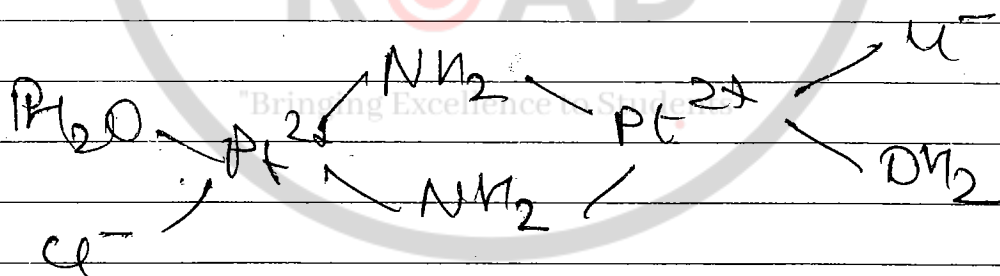
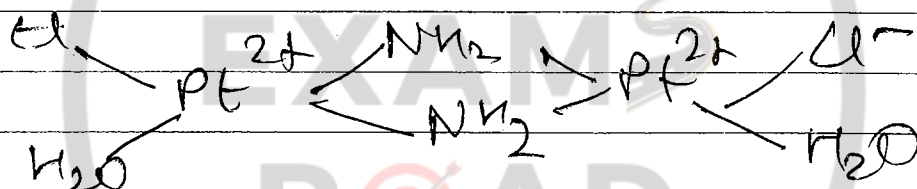
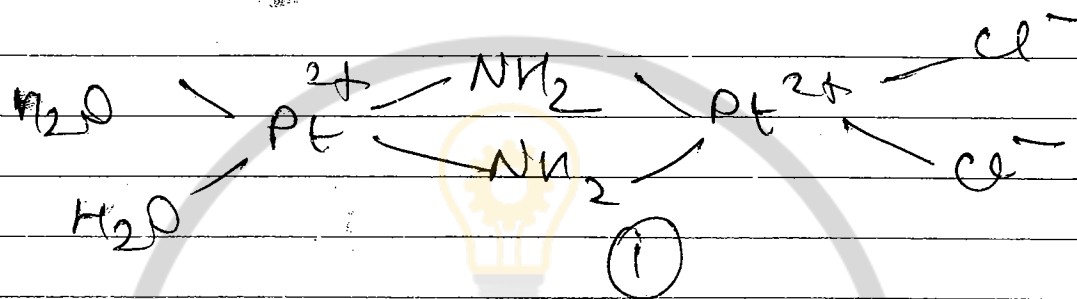
LIGAND ISOMERISM →

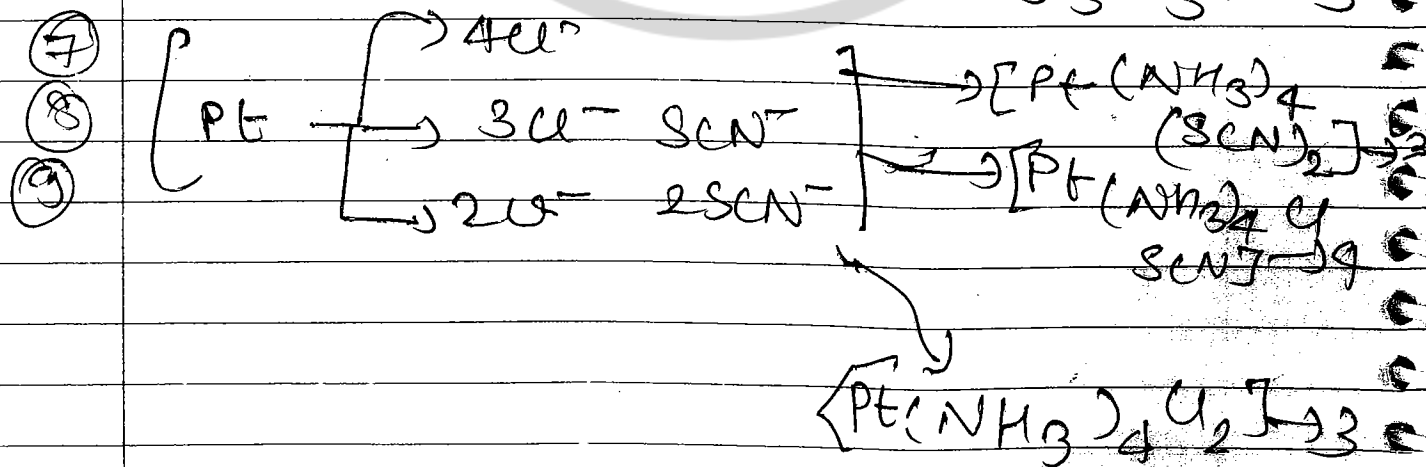
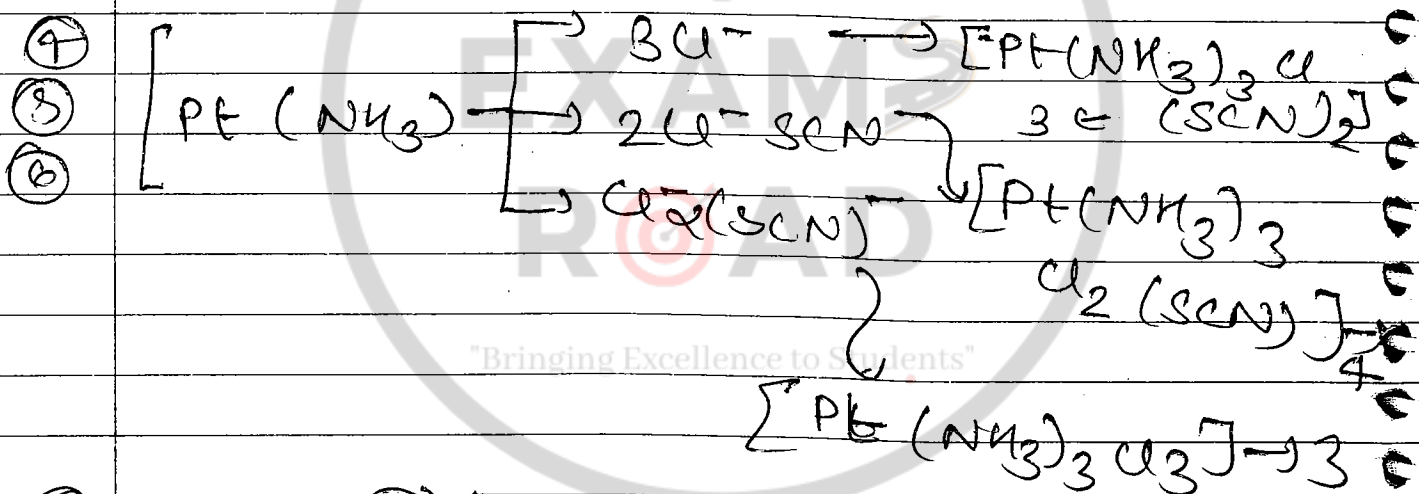
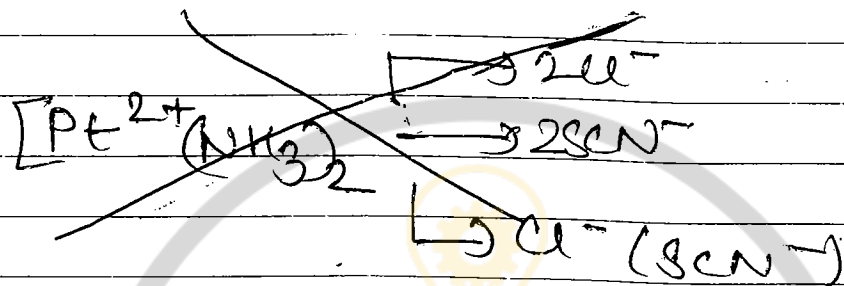
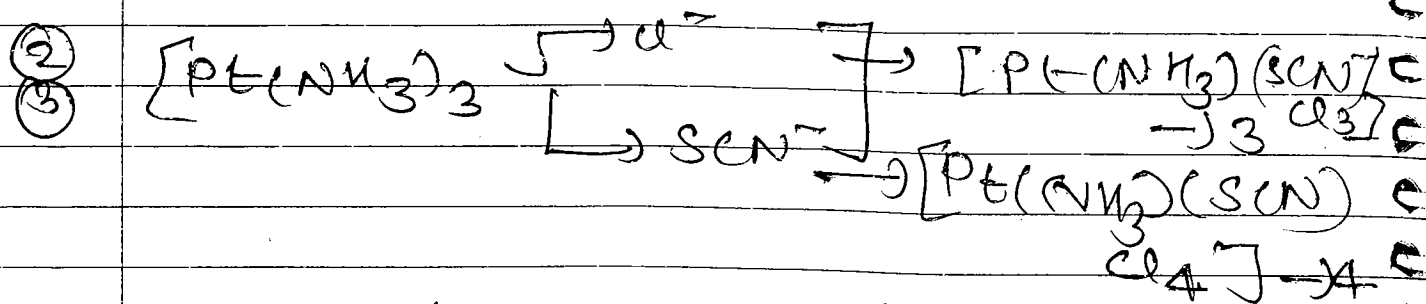
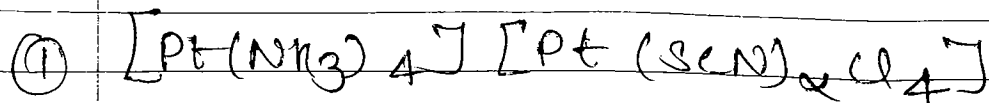
This type of isomerism when ligands can show position isomerism.

Complexes having same molecular formula containing ligands which are position isomers of each other are ligand isomers of each other.



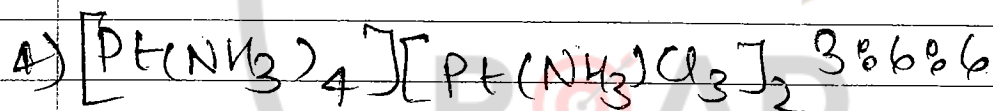
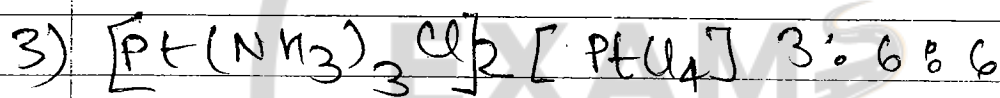
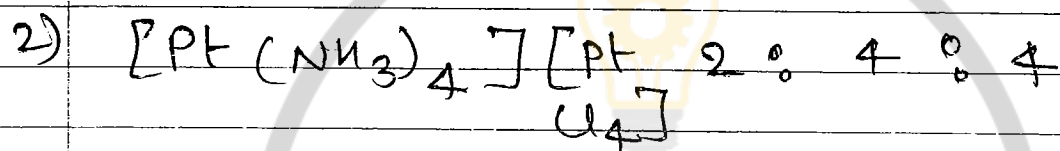
This type of isomerism arises in polynuclear complexes. Polynuclear complexes having same molecular formula but metal ion is coordinated diff-diff ligands are coordination position isomers of each other.





Polymerization Isomerism

Complexes having different Molecular formula but same empirical formula are polymers isomers of each other
It is not a true isomerism



~~1:2, 1:3, 1:4, 2:4~~

1-2, 2-3, 1-3, 1-4, 2-4 polymer isomer

3-4 coordination isomer

Stereo/space Isomerism \rightarrow

geometrical \rightarrow Diff distance, diff type
of bond angle

Optical \rightarrow ~~POS~~

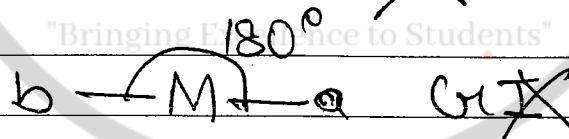
let \rightarrow

$$CMI = M$$

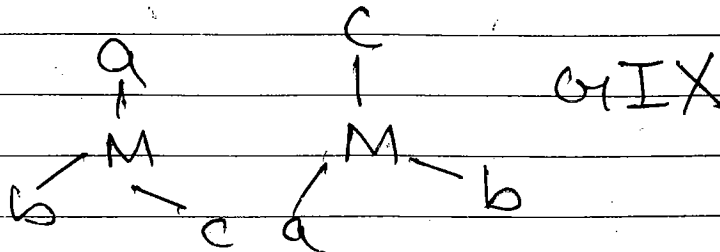
a, b, c, d, e, f, ... = Monodentate ligand
AA, BB, CC = bidentate (symmetrical)
(en, alpy, ox, phen, acac)
AB, AC, BC = bidentate (unsymmetrical)
(gly, bcar, dmg)

CN=2 linear (planar)

POS \checkmark OI ~~X~~



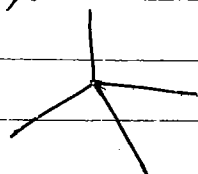
CN=3 linear POS \checkmark OI X
 ↑
 triangular



CN=4

Tetrahedral

OI X

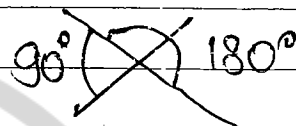


can show OI

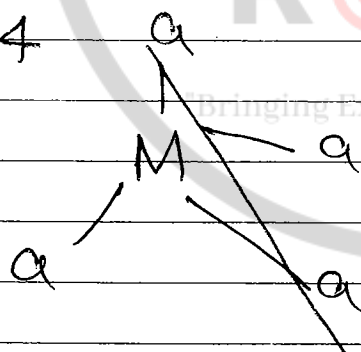
→ only type of BA

Square Planar

POS ✓ OI

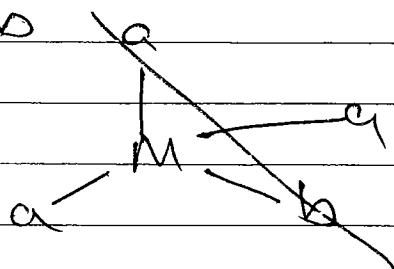


can show bti

OI in tetrahedral →① Ma_4 

POS ✓

OI X

② Ma_3b 

POS ✓

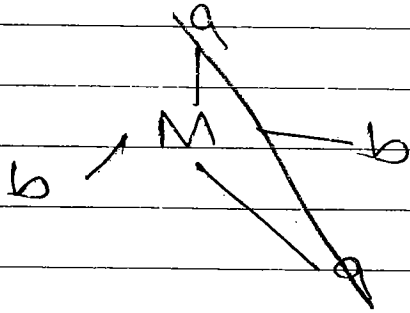
OI X



③

$M a_2 b_2$

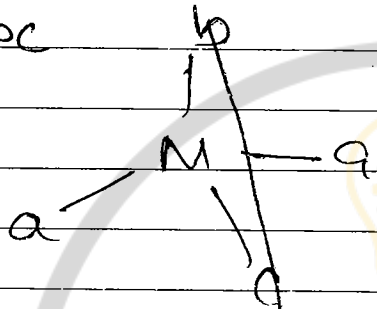
POS ✓
OIX



④

$M a_2 b c$

POS ✓ OIX

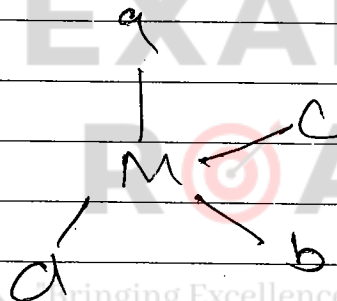


⑤

$M a b c d$

POS X

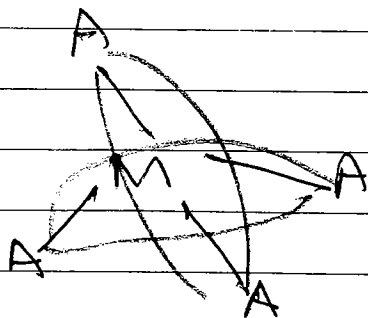
OIX ②



⑥

$M(AA)_2$

POS ✓ OIX



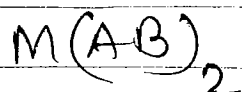
⑦

$M(AA)(BC)$

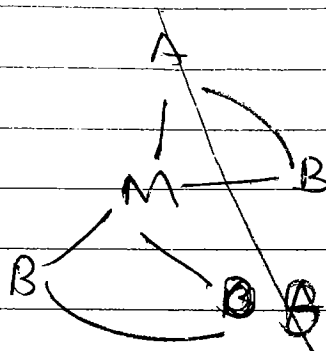
B
|

POS ✓
OIX

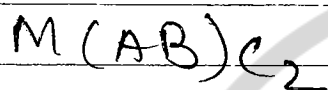
(8)



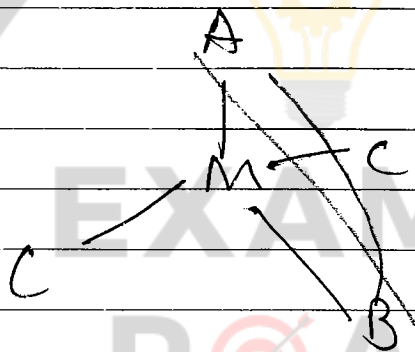
POS X OI ✓

Symmetry wrt
donor atomsbut unsymmetrical due to atoms of
ligand.

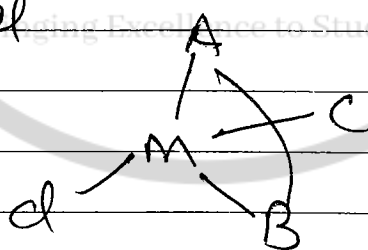
(9)



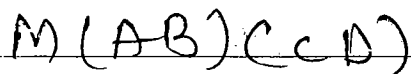
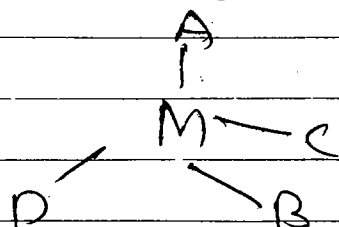
POS ✓ OI X

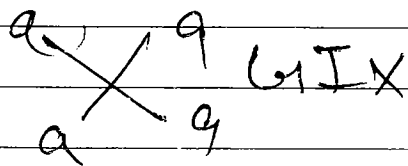
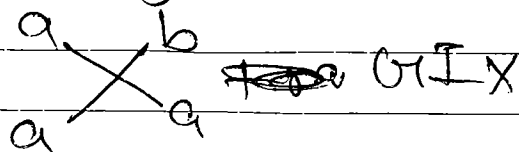
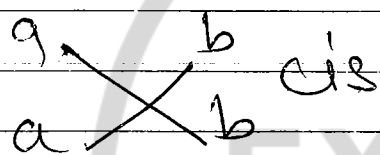
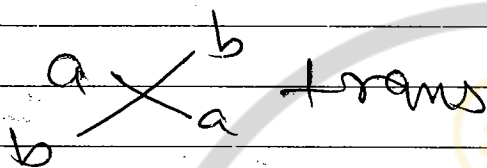
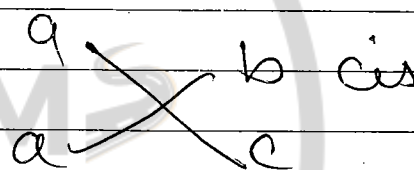
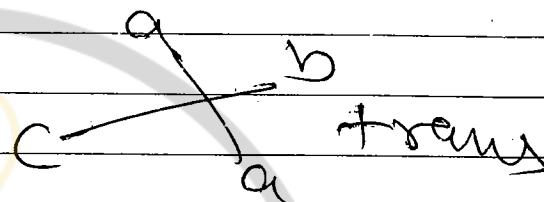
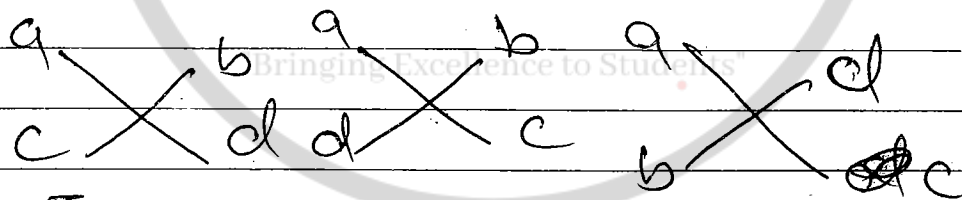


(10)

POS X
OI ✓
(2)

(11)

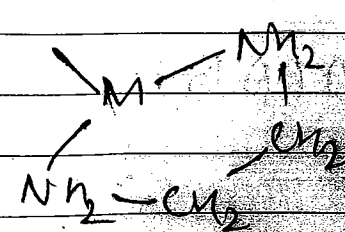
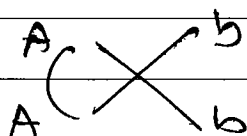
POS X
OI ✓
(2)

GI in square planar \rightarrow ① Ma_4 ② Ma_3b ③ Ma_2b_2
(aa, ba, bb)④ Ma_2bc ⑤ $Maabcd$ 

GI = 3

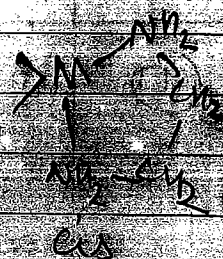
2 cis + 1 trans.

⑥

 $M(AA)b_2$ 

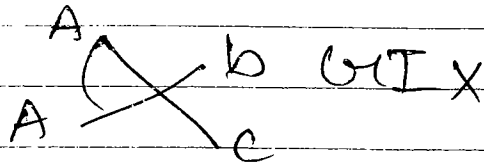
(trans)

unstable

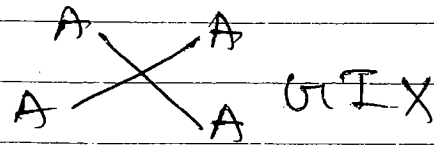


stable

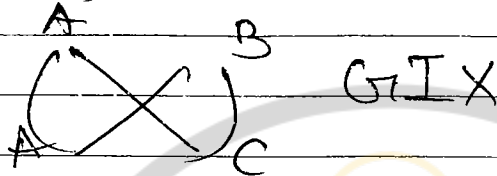
⑦ $M(AA)bc$



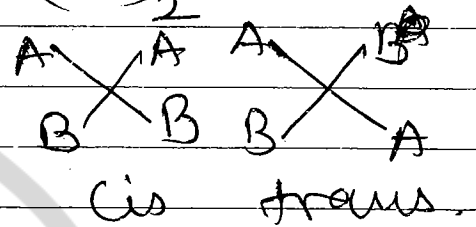
⑧ $M(AA)^2$



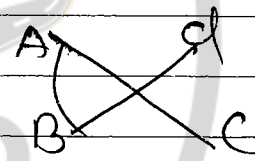
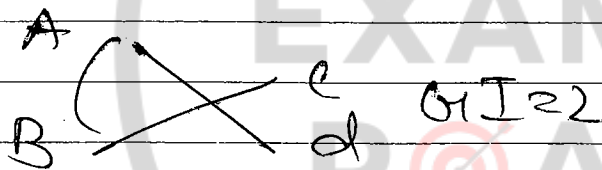
⑨ $M(AA)BC$

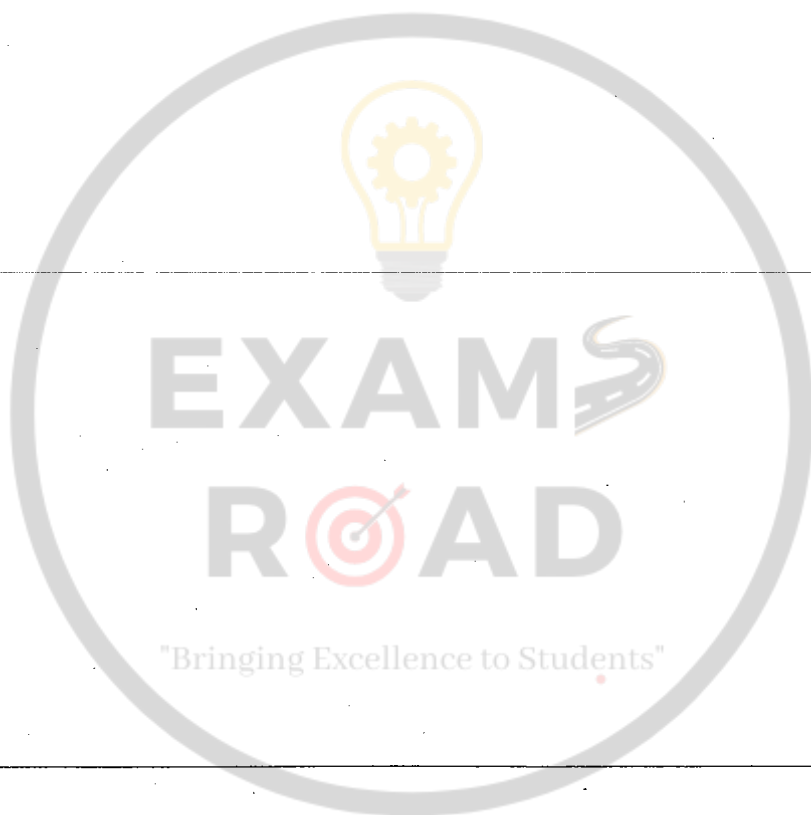


⑩ $M(AB)^2$



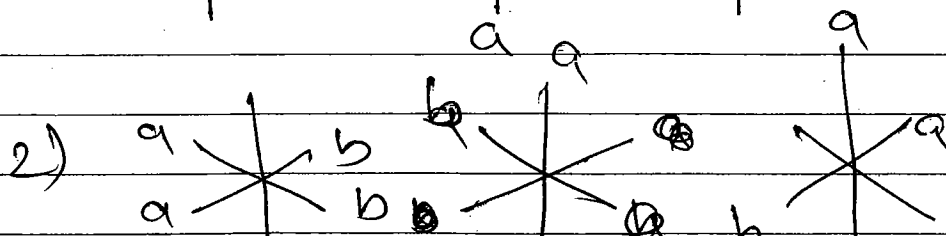
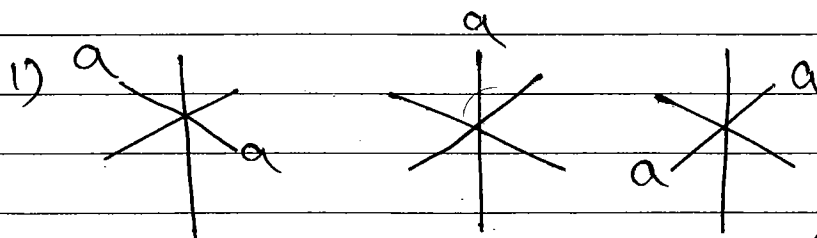
⑪ $M(AB)cd$





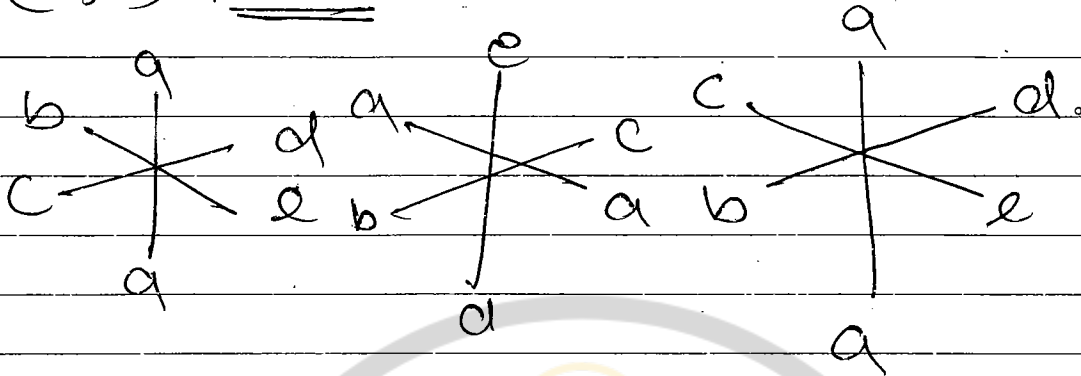
STEREO ISOMERISM in $CN=6$

POS

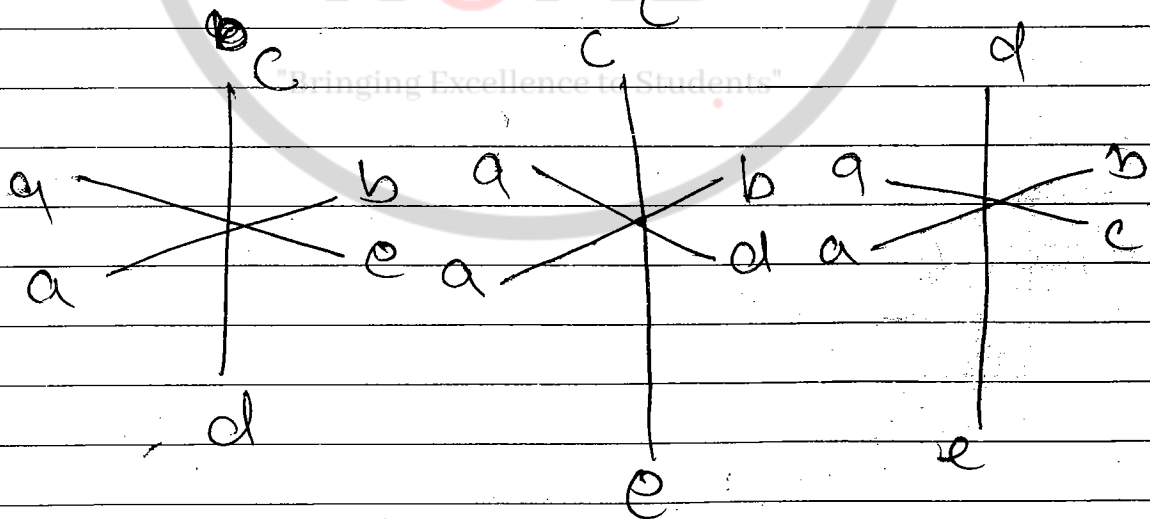
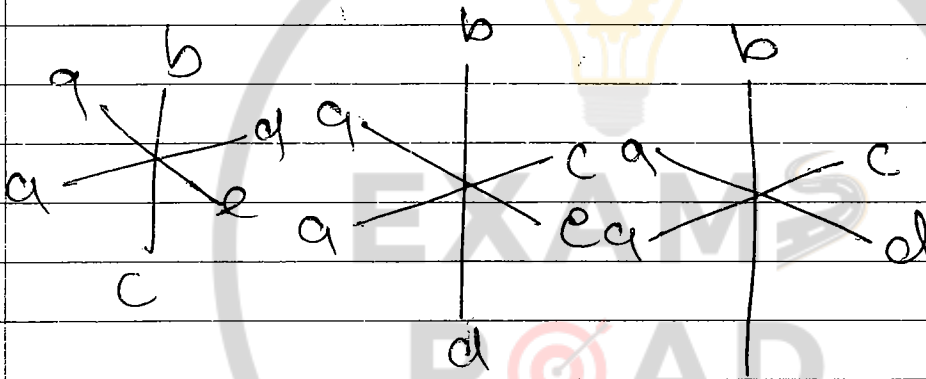


Ma₂ bcde

(a, a) trans



$GI = 3 \quad OI$

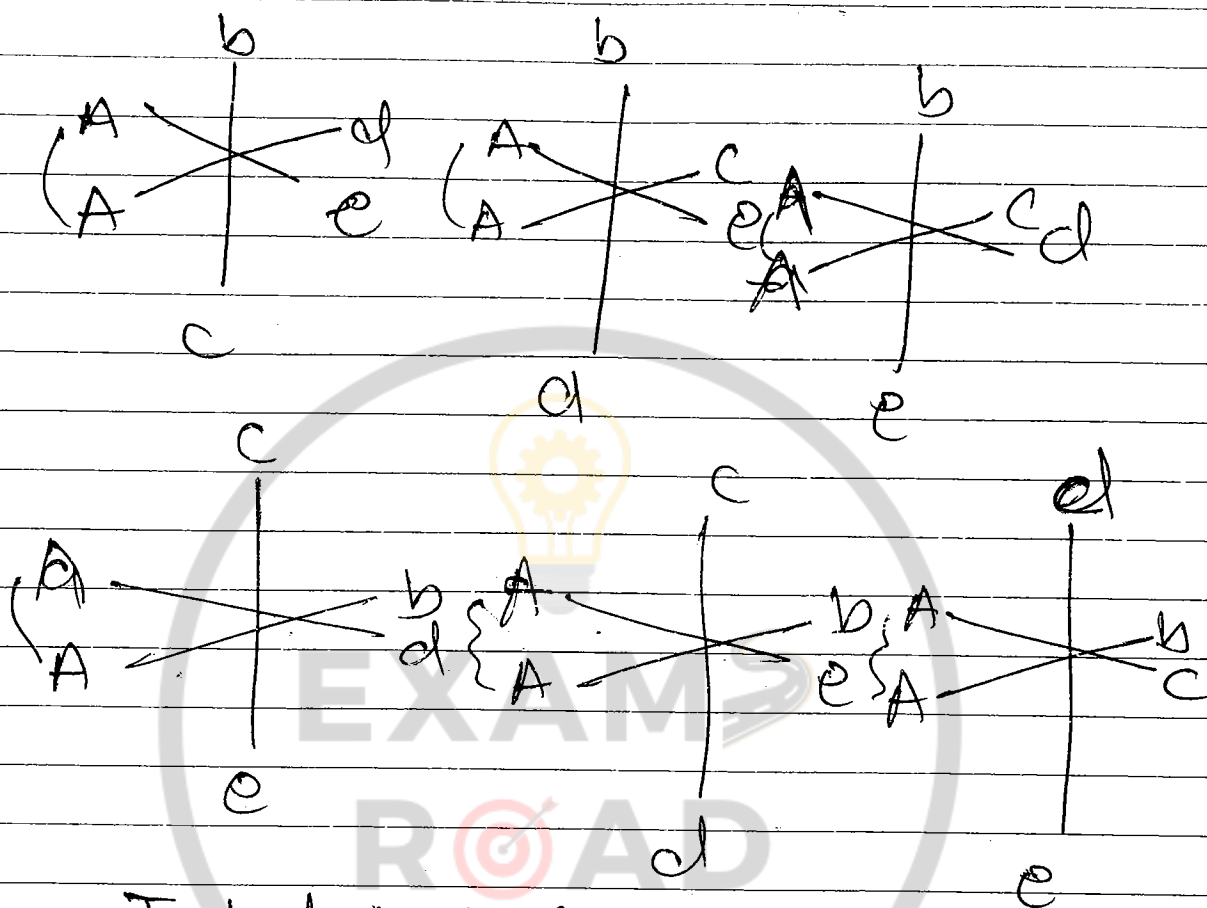


$GI = 6 \quad OI = 6$

Total $GI = 9$

$OI = 3$

$M(AA)bcde$



Total $GI = 6$

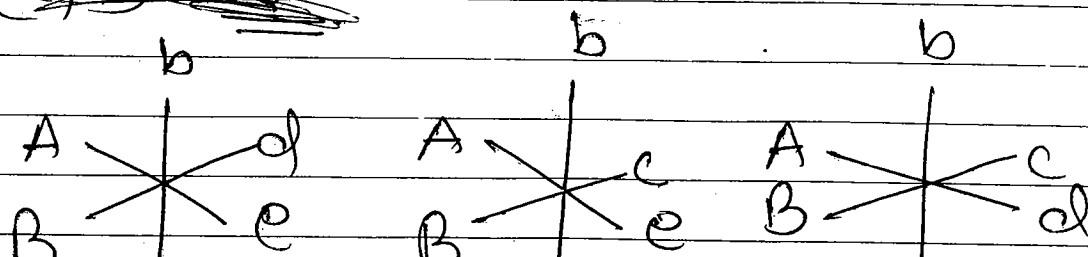
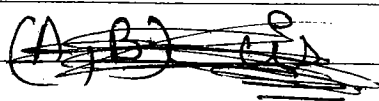
$OI = 20$

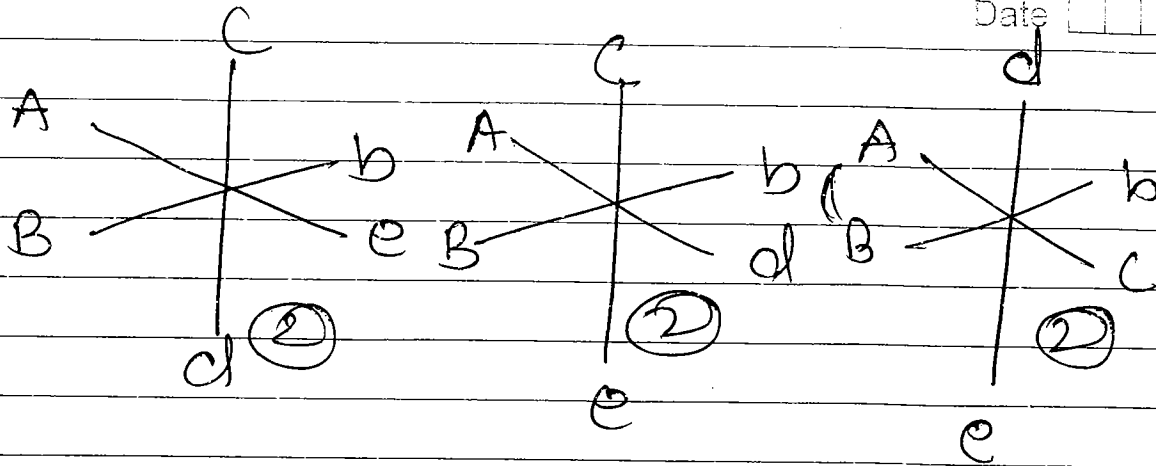
$OA = 12$

$O \text{ isomer} = 12$

Stereo isomer = 12

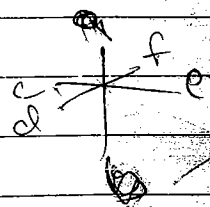
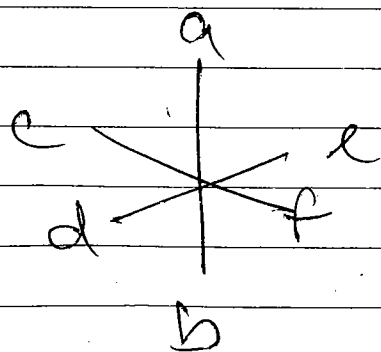
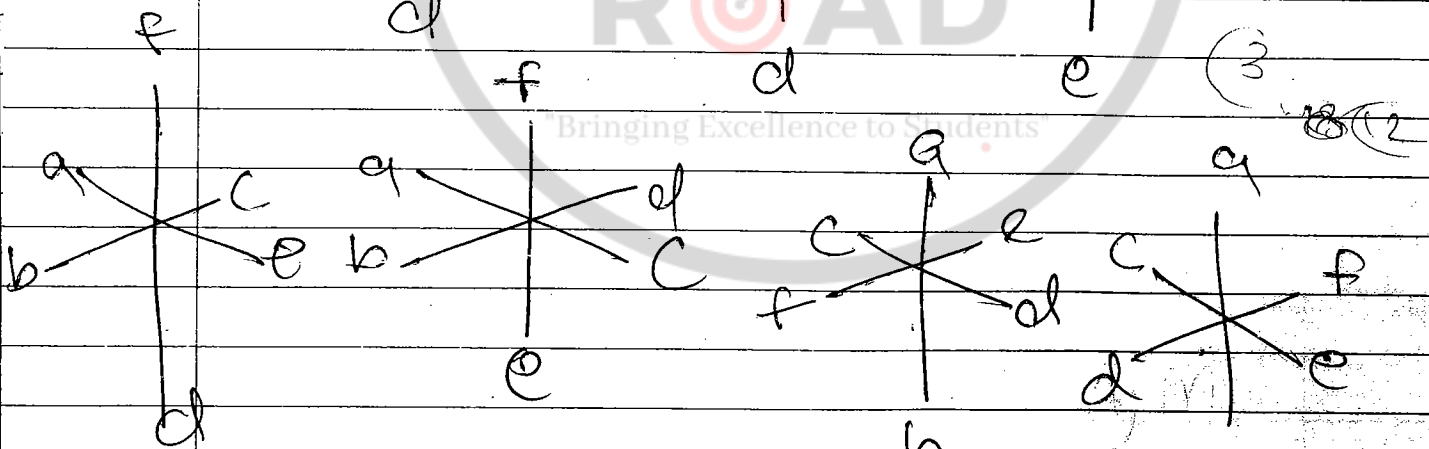
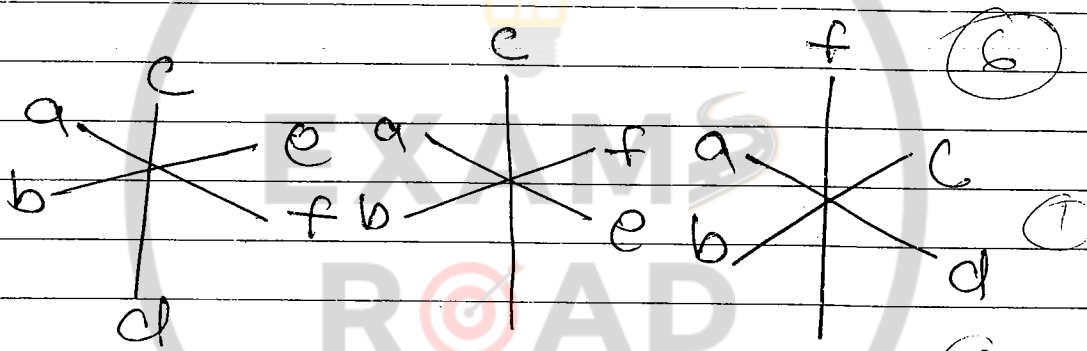
$M(AB)bcde$



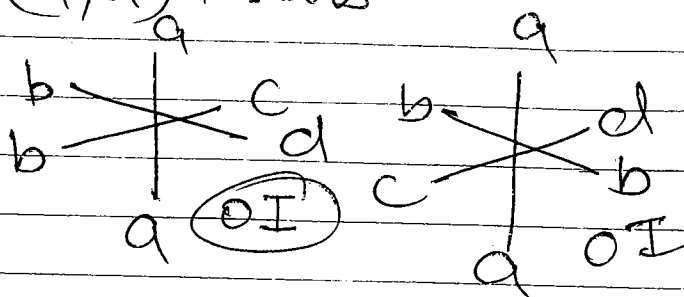


Total GI = 12
OA = 24

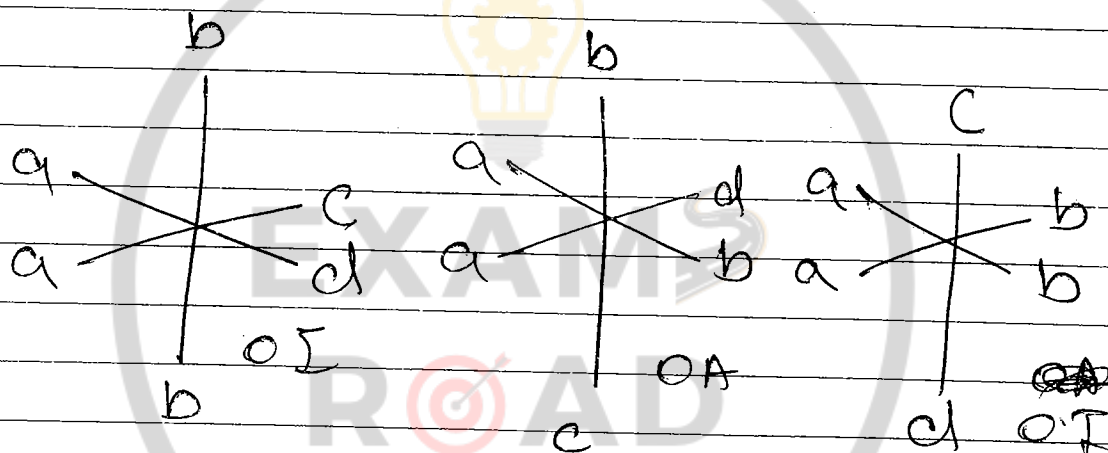
Also def



$M a_2 b_2 c d$
 $(a, a) + trans$



$(a, a) cis$



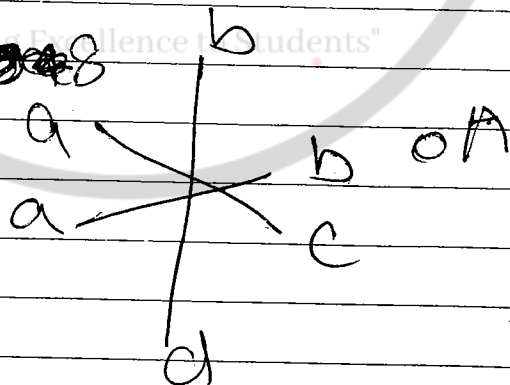
$G.I. = 6$

$O.I. = 8$

$O.A. = 2$

$O.I. = 4$

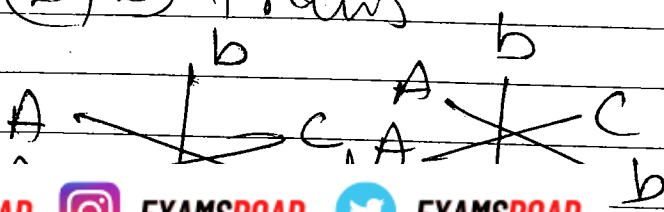
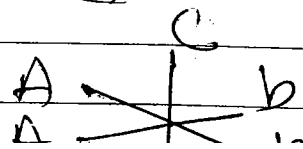
$S.I. = 8$

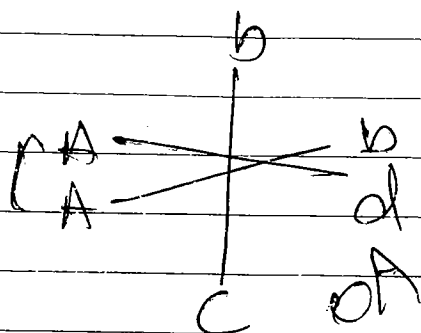


$M (AA) b_2 c d$

$(b, b) cis$

$(b, b) trans$



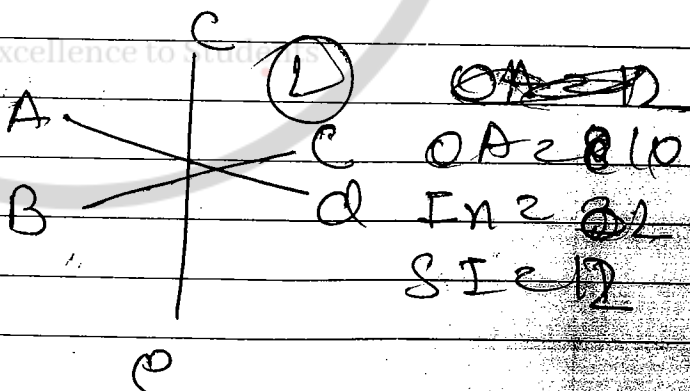
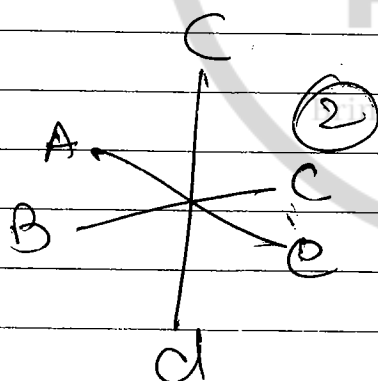
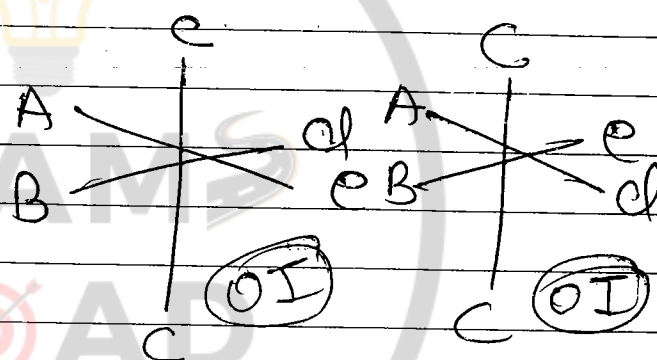
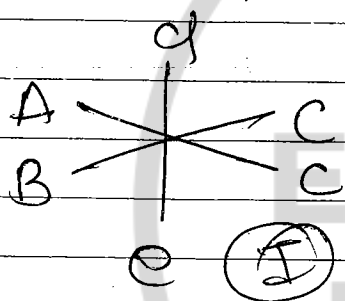


GI = 4
 OA = 4
 OI = 0m = 6
 SI = 6
 OI = 2 = 2

M(AB)C₂de

(C-C) cis

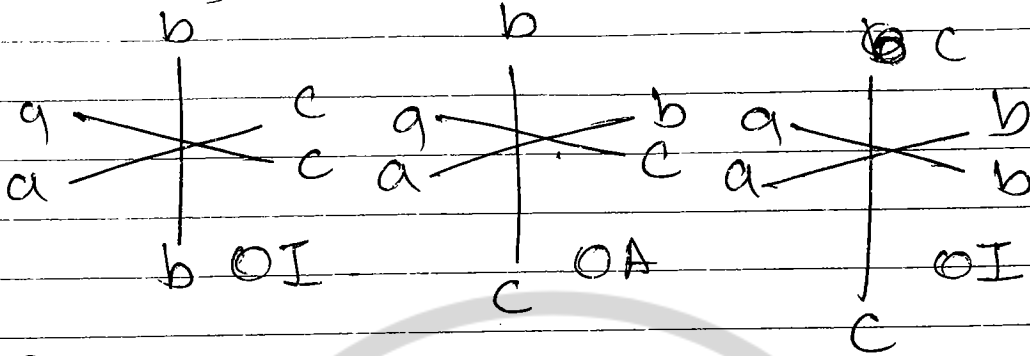
(C,C) trans



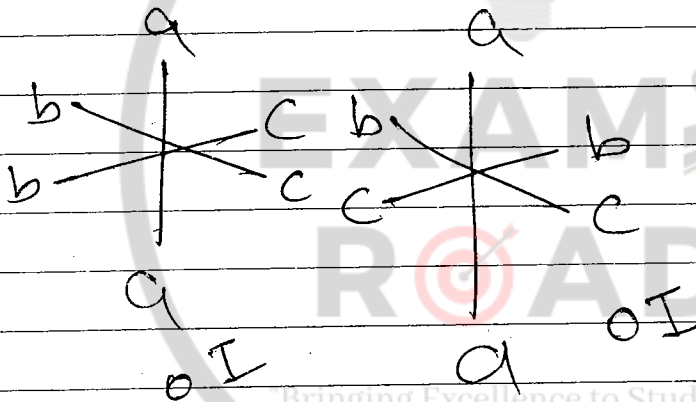
~~OA = 10~~
 OA = 10
 In = 2 = 2
 SI = 12

$M_{a_2 b_2 c_2}$

$(a-a)_{is}$



$(a-a)_{trans}$

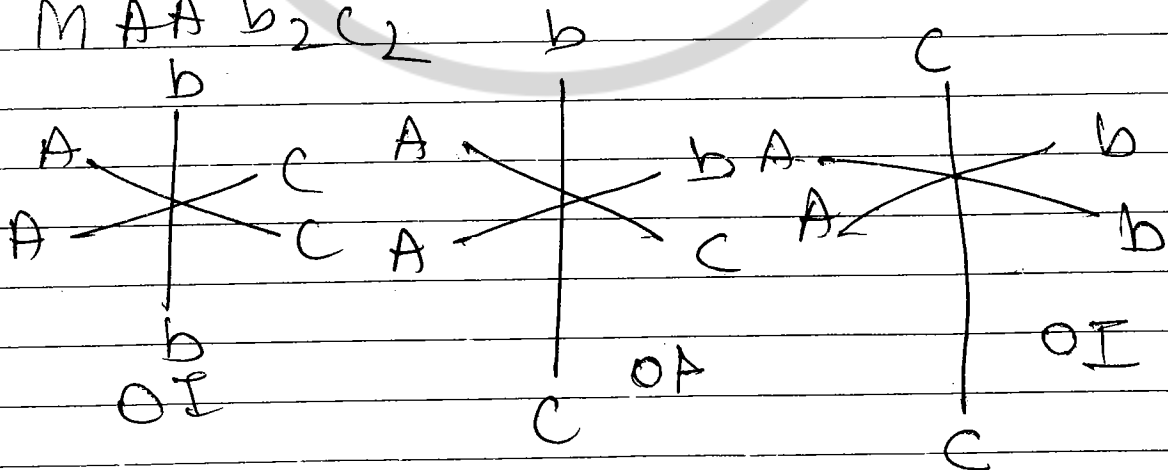


$OA = 1 \times 2$

$OI = 4$

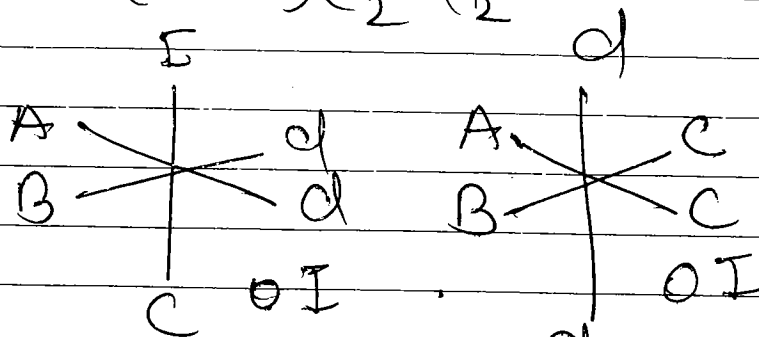
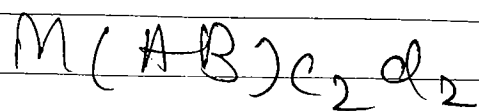
$SI = 6$

$M_{AA b_2 c_2}$



$G_I = 3$

$OI = 2$

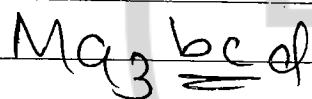
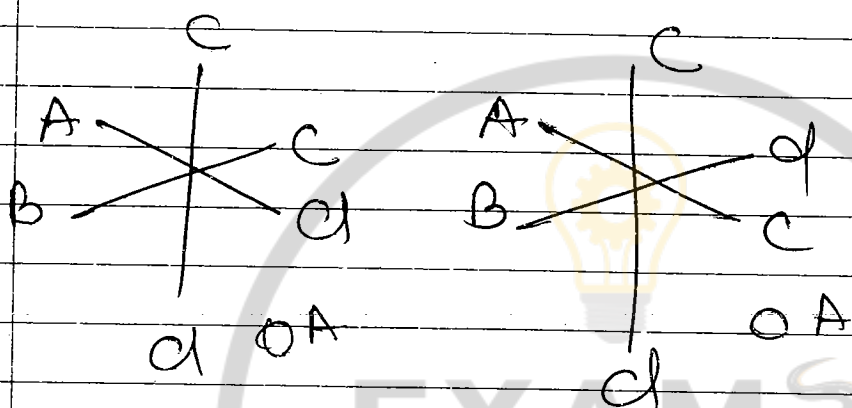


$GI = 4$

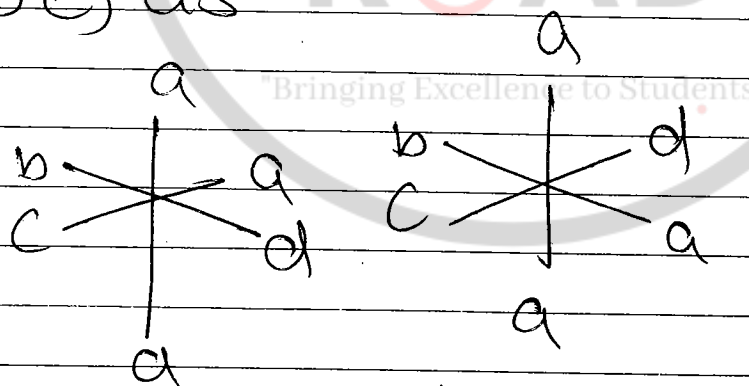
$A = 4$

$I = 2$

$\theta = 120^\circ$



(bc) cis



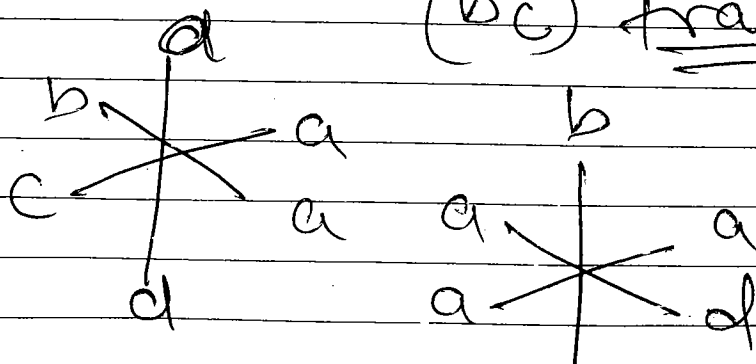
$GI = 4$

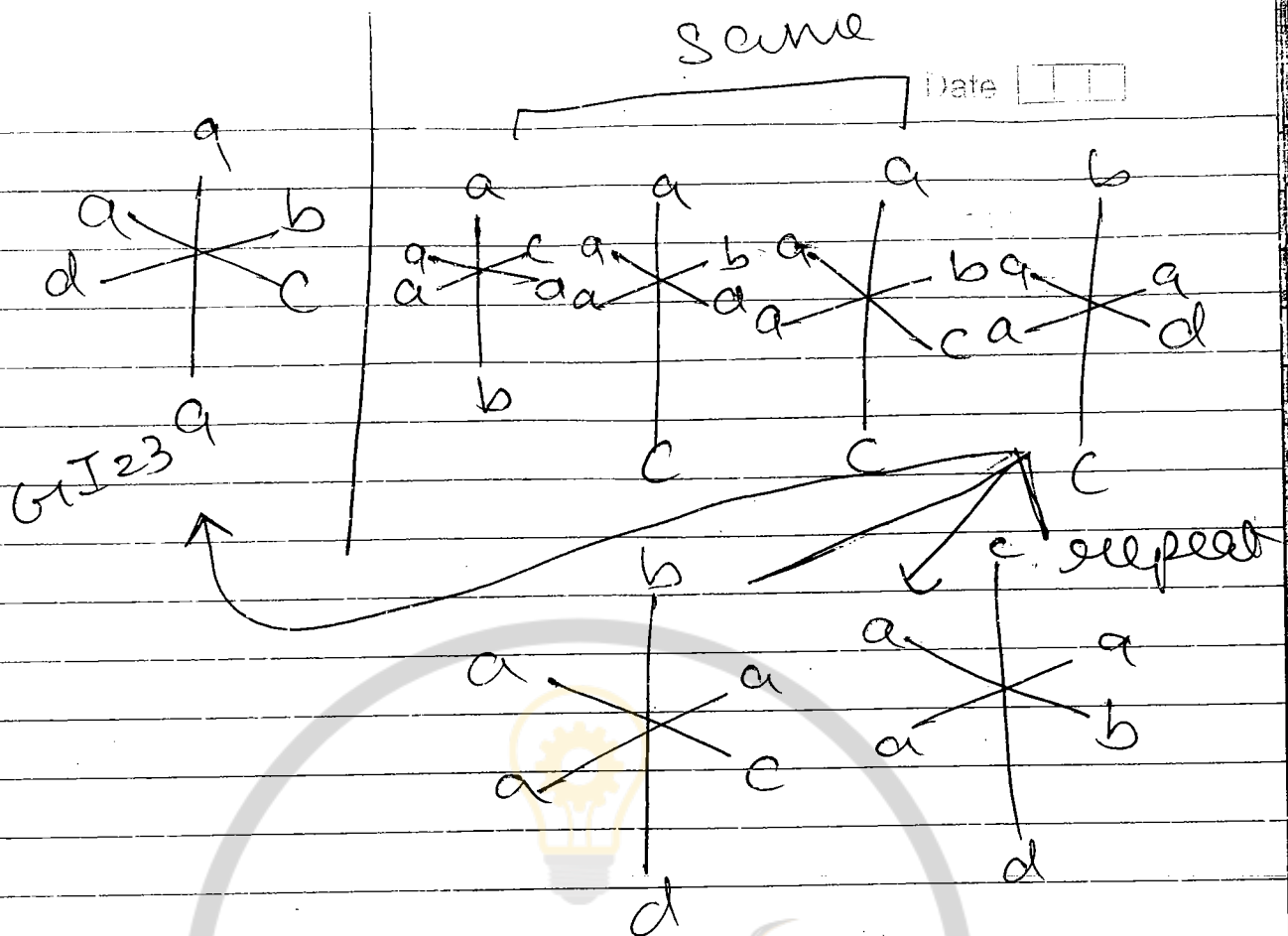
$OA = 2$

$I = 3$

$SI = 2$

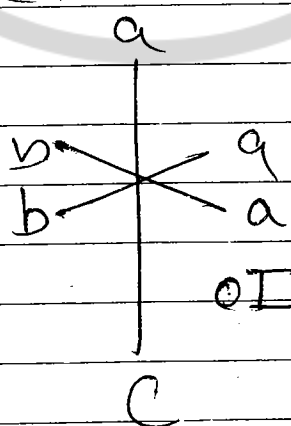
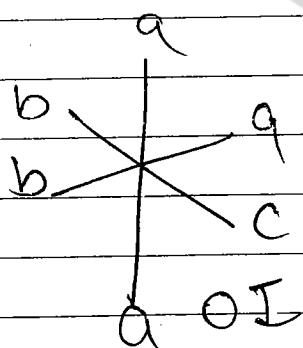
(bc) trans





When 3 same type of monodentate present in $CN=6$ only one isomer possible

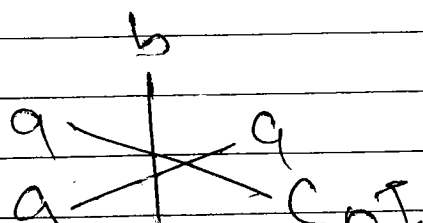
Ma_3b_2c (b, b) is



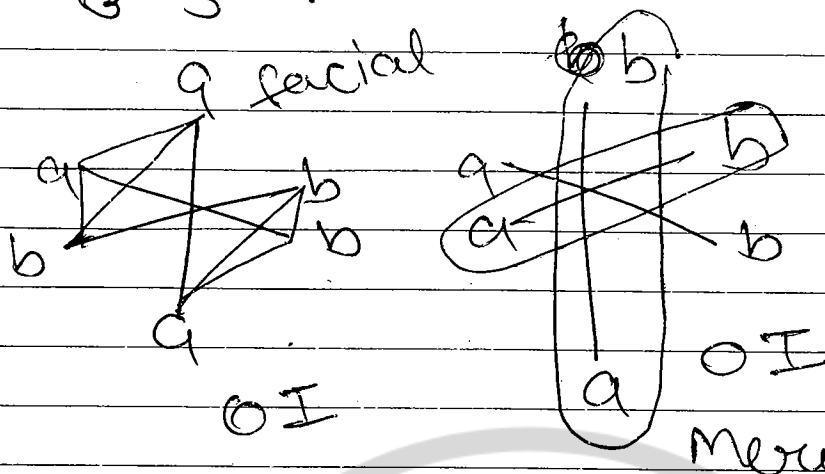
GI 23

OI 23

SI 23

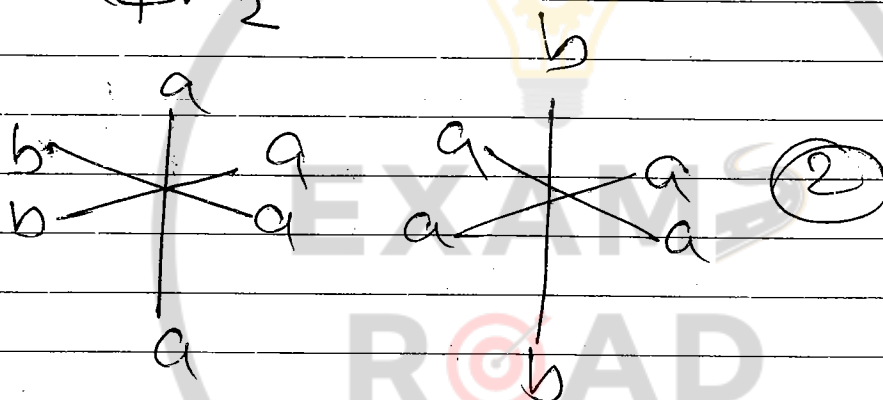


Ma_3b_3 face-mer

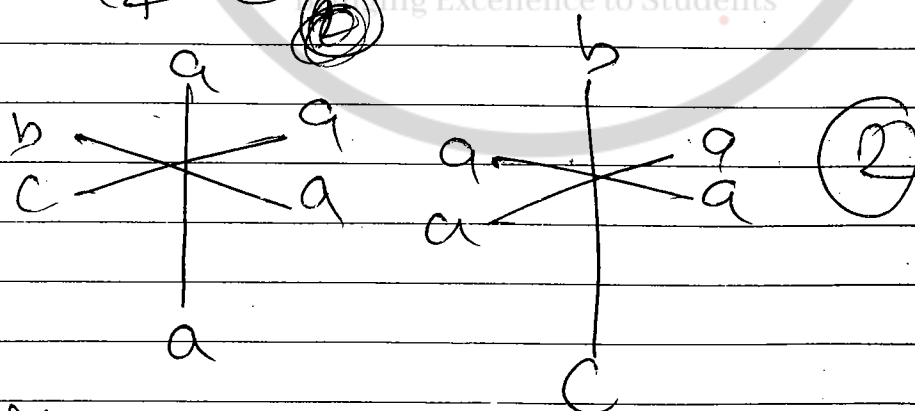


GI 22
OI 22
SI 22

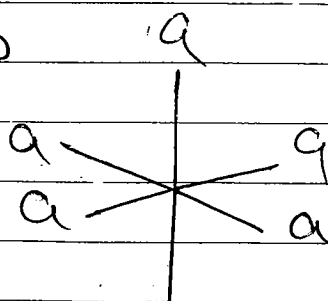
Ma_4b_2



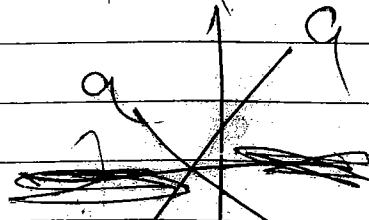
Ma_4bc



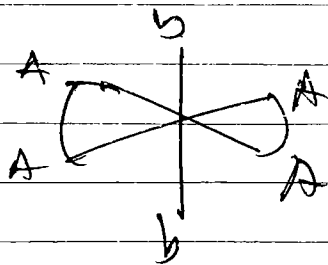
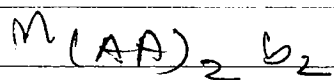
Ma_5b



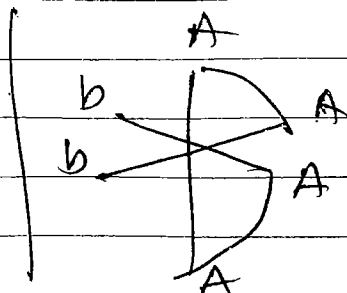
Ma_6a



No CIL



OIA



OA

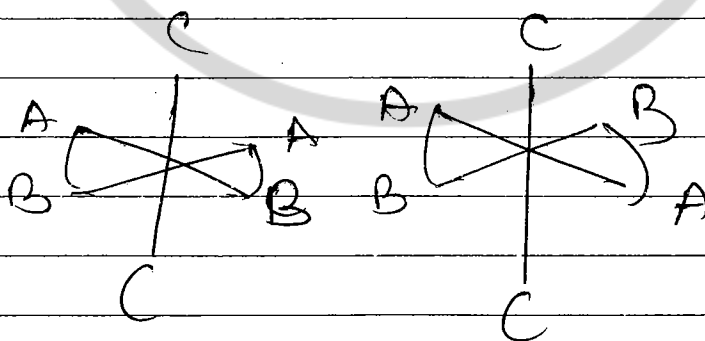
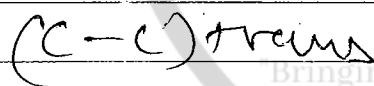
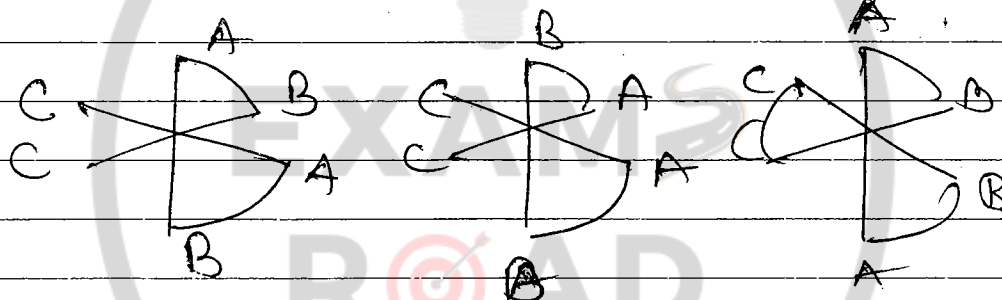
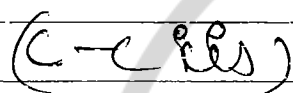
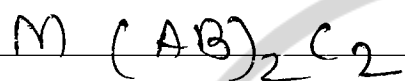
$GI = 2$

$OIA = 1$

$OA = 2$

$OI = 3$

$SI = 3$



$GI = 5$

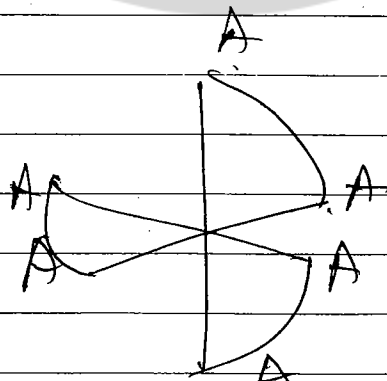
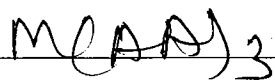
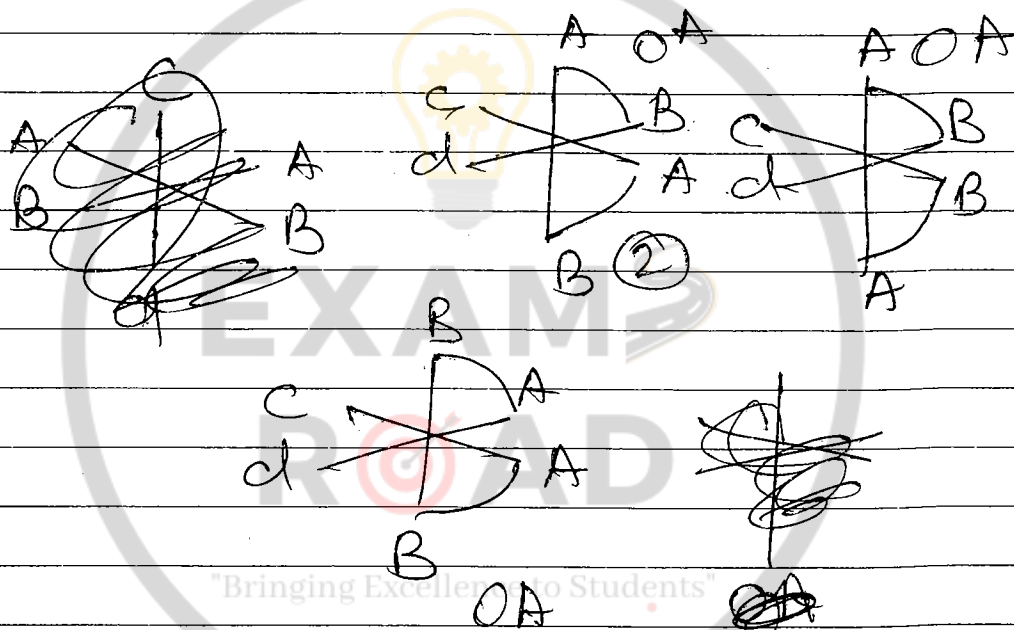
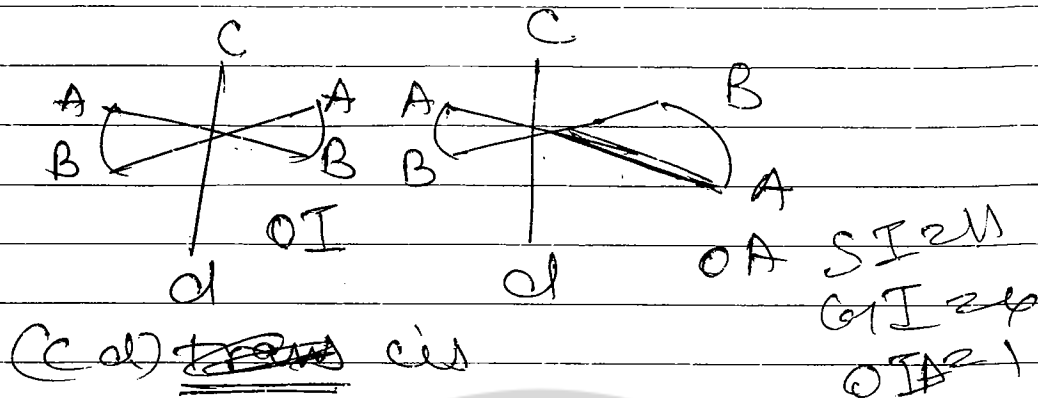
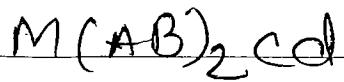
$OA = 3 \times 2 = 6$

$OI = 2$

$OI = 8$

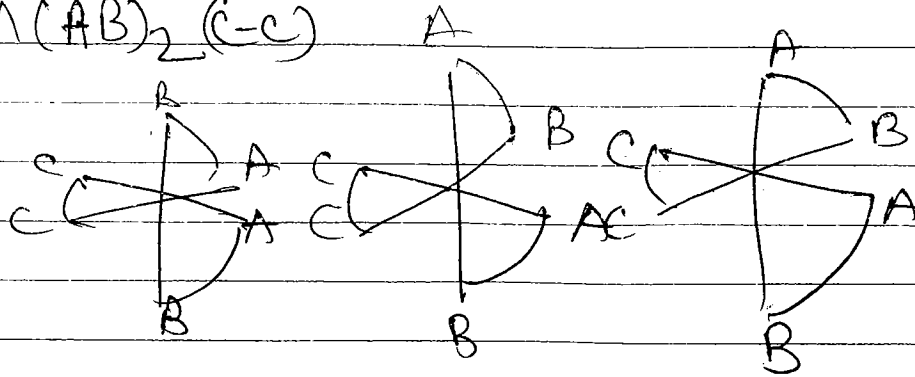
$SI = 8$

When two bidentated ligand present in coordination no. of cis isomer is always odd no. of trans isomer is always even no.



when 2 well bidentate ligand
present in coordination
no. 6 complex is always 2

$M(AB)_2(C-C)$



$GI = 3$

$OA = 6$

$OI = 6$

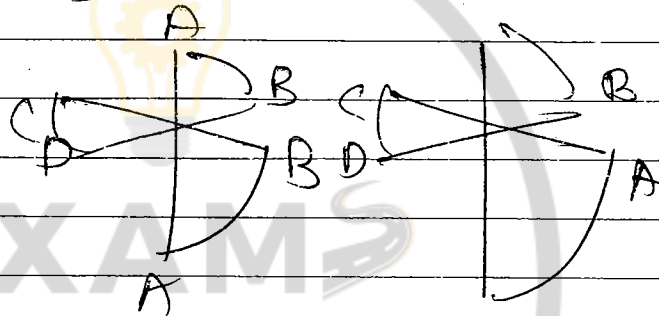
$SI = 8$

$M(AB)_2(C-D)$

$GI = 4$

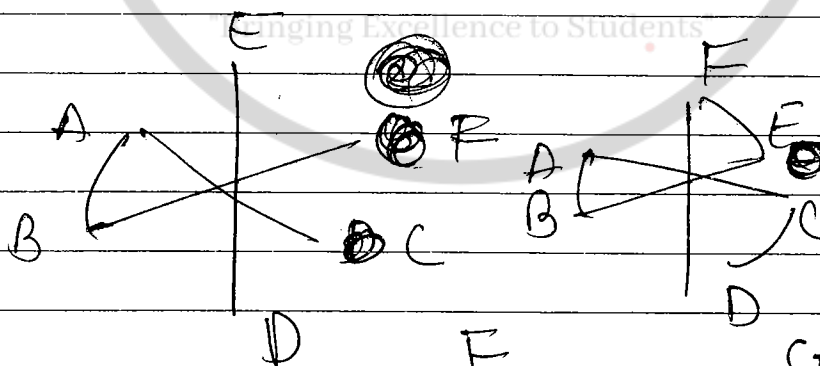
$OA = 8$

$SI = 8$

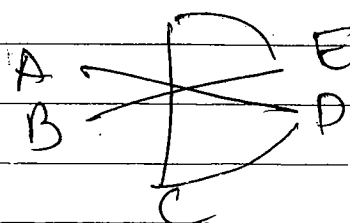


$M(AB)(C-D)(E-F)$

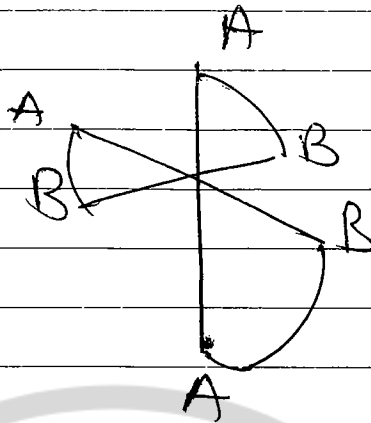
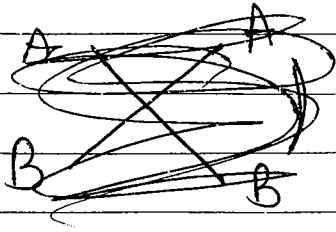
$GI = 8$



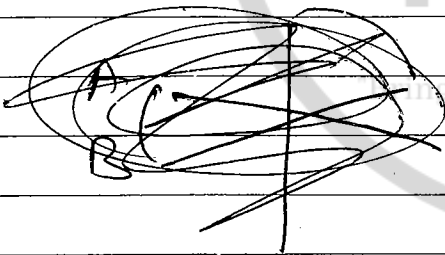
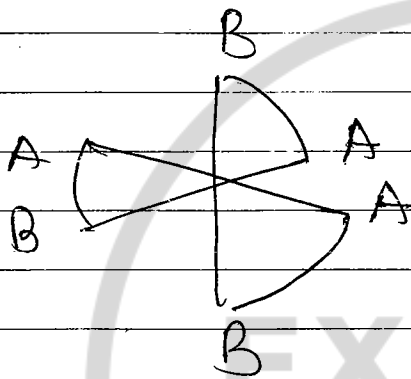
$GI = 8$

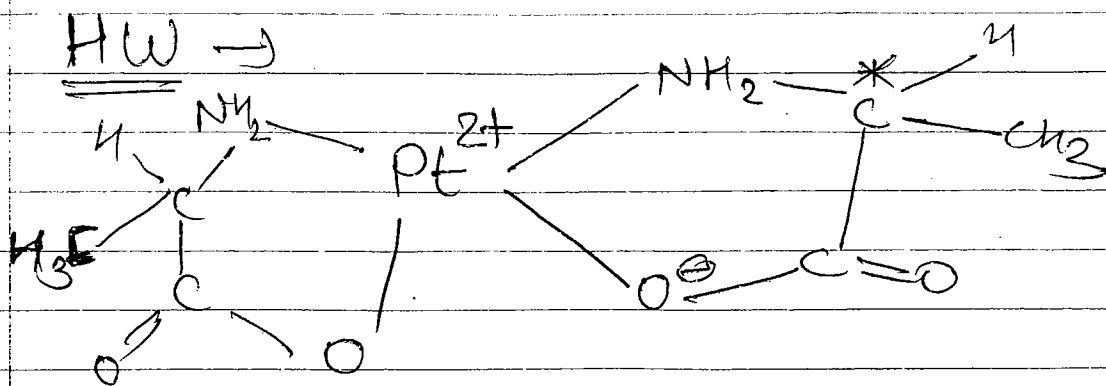


$M(AB)_2$



3 trans



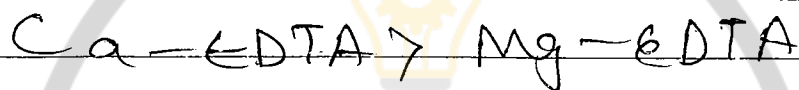


Application of Coordination Compounds

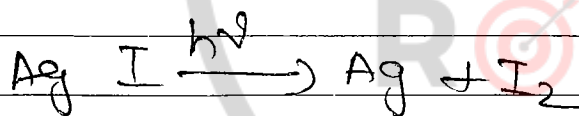
- (1) Haemoglobin \rightarrow hae means iron & globin \rightarrow protein. It is complex of iron.
- (2) Vitamin B₁₂ is complex of cobalt.
- (3) Chlorophyll is complex of Magnesium.
- (4) In treatment of lead poisoning EDTA⁴⁻ is used. EDTA is hexadentate ligand which forms stable complex with Pb²⁺. So, identity of Pb²⁺ loses its. Calcium EDTA is used instead of Sodium EDTA bcoz increment in sodium conc. in body adversely affects cell membranes.
- (5) Cisplatin $\text{cis}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is used to control growth of tumour cells.

(6) Wilkinson catalyst $[Rh(PPh_3)_3Cl]$ is used in hydrogenation of Alkenes

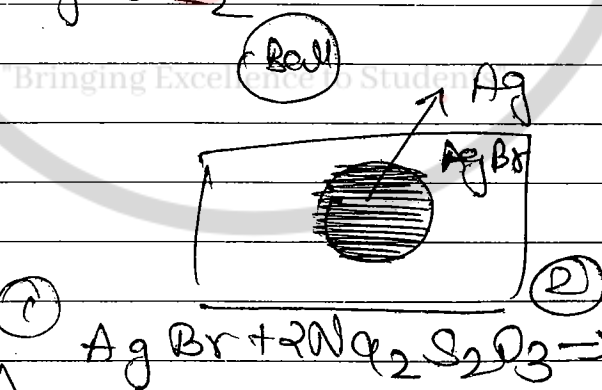
(7) $EDTA^{4-}$ is used to estimate water hardness, hardness of water produced due to presence of calcium & magnesium. $EDTA^{4-}$ is also used in selective estimation of Ca^{2+} because KF of



(8) In Black & white photograph to dissolve undecomposed $AgBr$ Hypo solⁿ is used




photographic plate
photo sensitive
($AgI/AgCl/AgBr$)

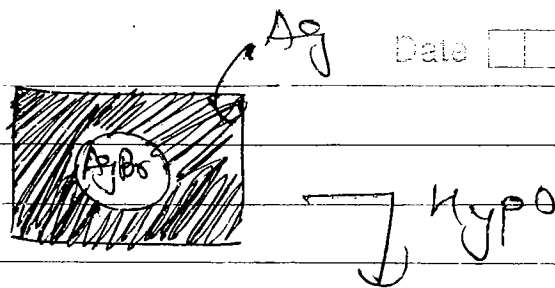


positive
Hypo solⁿ
 $Na_2S_2O_3$

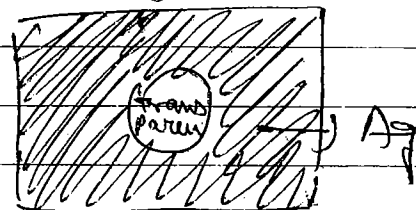
transparent
 Ag



photographic
plate
repetition of
(1, 2, 3)

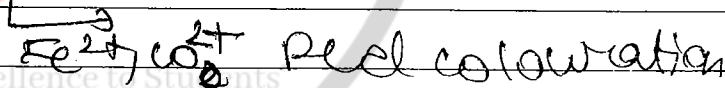
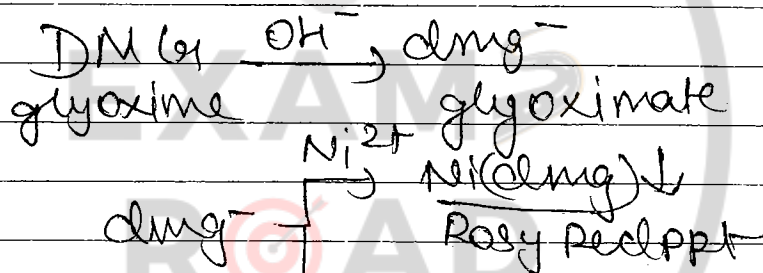


Negative



(9) In qualitative analysis

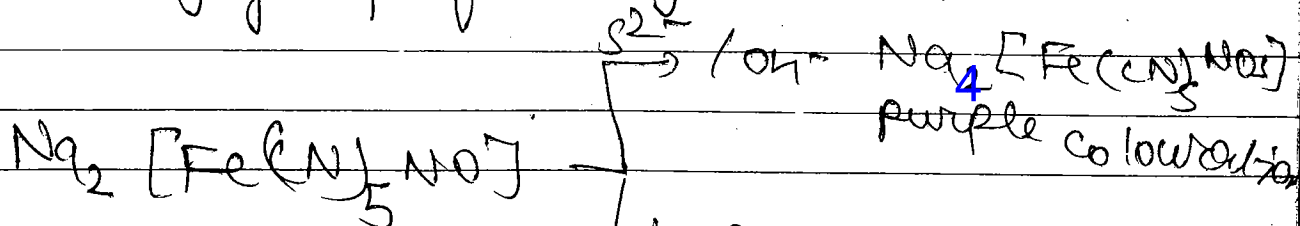
A



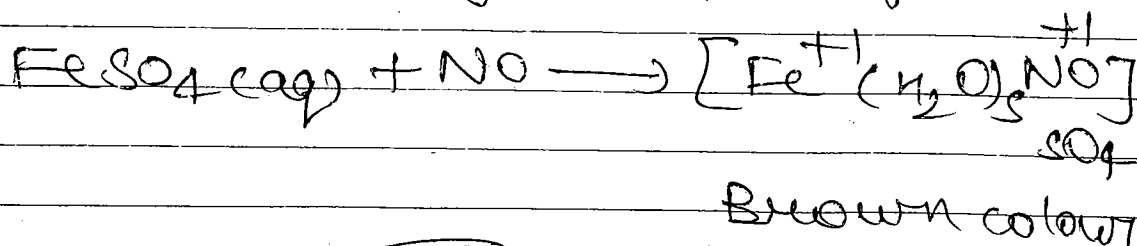
(10) Sodium nitroprusside is used in detection of S²⁻ ion in Basic medium

prusside

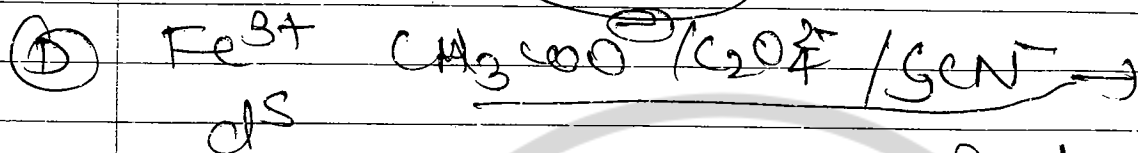
when one CN⁻ is replaced by any
any group from cyano complex



(C) Brown ring complex formation



WFL



Red colouration
Colour due to
CT

(E) Strong Lewis base form complex with strong Lewis acid weak Lewis base form complex with weak Lewis acid

complex formation tendency

d block > p block
except

Hg

size \uparrow d10

e.g mixture of d block & p block cations

KCN

Complex formation
by d block
cations

p block & Hg don't

WFI
excess KI

Complex formation by

p block & Hg not by
d block

excess
 $\text{NH}_3/\text{NH}_4\text{OH}$

Complex formation by

d block except Mn, Fe

, Hg not by p block

★ Fe^{3+} complexes are more stable
with O donor in comparison of N
donor (exception in stability order)

(10) In Metallurgy

① Mac Arthur forest cyanide
process (for Ag & Au)

② Mond's process (in purification of
Ni)



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