$\alpha = \frac{4}{3}\delta_0$

Karmanye Vadhikaraste

ma Phaleshu

Kadachanan!

INORG

IOC

cont..

Susnata Chattopadhyay

Name .....

Sub. 208

Std. .....

Roll No. .....

School 208 - CC

COORDINATION COMPOUNDS 3/02/2017

$Salt_1 + Salt_2 \xrightarrow{cryst.}$ Addition compounds / Addn Pdt / Adduct

- $KCl_{(aq)} + MgCl_{2\,(aq)} \xrightarrow{Cryst} KCl.MgCl_2.6H_2O$
- $NH_3 + BF_3 \longrightarrow H_3N: \longrightarrow BF_3$.
- $CuSO_4 + NH_3 \longrightarrow [Cu(NH_3)_4]SO_4$.

When aqueous soln of two or more than two salts is subjected to crystallise new compound is formed which is called addition compound & rxn is called addition rxn.

Types of Addition Compound :-

1) Double Salts — Completely ionise in aq. medium all ions show their presence in aq medium.

2) Complex Salt — Does not ionise completely in aq. medium, Some or all ions loses their presence in aq. medium

Example of double salt.

1) Carnalite — $KCl.MgCl_2.6H_2O$
   Type of ion = 3 (K^+, Mg^{2+}, Cl^-)
   No. of ion = 5

2) Mohr's salt — $FeSO_4.(NH_4)_2SO_4.6H_2O$.
   Type of ion = 3
   No. of ion = 5

3) Alums — $M_2(SO_4)\,M'_2(SO_4)_3.24H_2O$

M = Monovalent $MM'(SO_4)_2.12H_2O$

M' = Trivalent ↳ except Li^+ (small sizes).

Potash Alum →

$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$

No. of ions → 8

Types of ions → 3 K^+ Al^{+3} SO_4^{-}

COMPLEX SALT

$KCN + Fe(CN)_2 \longrightarrow K_4[KCN \cdot Fe(CN)_2]$

$\downarrow H_2O$

Expected — Exp

No. of ion 11 — 5

$2(K^+, Fe^{2+}, (CN^-)_2)$ — $2(Fe^{2+}, (CN^-)_2, K^+)$

$Fe(CN)_2$ also

$Fe^{2+} + CN^- \longrightarrow [Fe(CN)_6]^{-4}$

(+2, −6, −4)

↑ complex ion

CN^-, CN^-, Fe^{2+}, CN^-, CN^-

Ions which do not ionise completely in aq. medium is collectively written in sq. brackets are called complex ion

→ In complex ion atleast, one metal ion is present which is center of complex ion. Act as Lewis Acid surrounded by neutral molecules or ions, is called CENTRAL METAL ION (CMI)

→ CMI is surrounded by neutral molecules/ions which are called Ligands.

Mixed Salts → Salt derived from more than one base or more than one acid → radical.

$NaKCO_3$, $CaOCl_2$.

⇒ Ligands act as Lewis Bases

→ Complex formation is a Lewis Acid base rxn in which coordinate form.

→ Complex salts are also known as COORDINATION COMPOUNDS.

1) Coordination Number.

No. of lone pair (totalized e⁻ pair) accepted by a central metal ion is called its C.N.

ALWAYS

- 3d series → +3 ion = 6
- 3d " → +2 ion → 4/5/6.
- Ni^{+2} with (H_2O, NH_3) → 6; (Cl^-, CN^-) → 4
- Zn^{2+}, Cd^{2+}, Hg^{2+} → 4
- Ag^+, Au^+ → 2
- Pt^{+2}, Pd^{+2}, Ag^{+3}, Au^{+3} → 4
- Pt^{+4}, Pd^{+4} → 6

2) Charge on Complex

Sum of oxidation of CMI & Ligands.

$Ni^{+2} + CN^- \longrightarrow [Ni(CN)_4]^{-2}$

$Pt^{+4} + Cl^- \longrightarrow [PtCl_6]^{2-}$

$Co^{+3} + NH_3 \longrightarrow [Co(NH_3)_6]^{3+}$

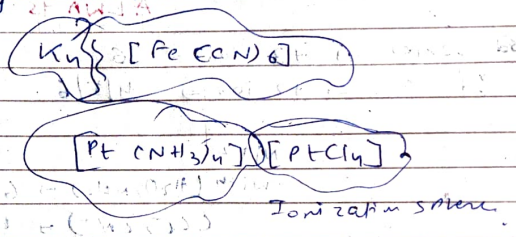
3) Coordination Sphere

Space in 3D where coordinate bond form b/w ligand & CMI is called co-ordination entity.

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

4) Ionization sphere -

Space in 3-D where complex ion form ionic bond with opposite charged ions.



5) Counter - Ion.

Simple ion which neutralise charge of complex ion is called, counter ion.

$[Cu(NH_3)_4]SO_4$ ← counter ion

$K_3[Fe(CN)_6]$

↑ Counter ion.

Species in coordination sphere is non ionizable but species in ionization sphere is ionizable.

Werner's Work

According to Werner Metal ion in complex compound show 2 types of valency

(1) Primary Valency (PV)	(2) secondary Valency (SV)
→ It is OS of CMI.	→ It is CN of CMI
→ satisfy by anions	→ satisfy by ligands
→ Generaly ionizable.	→ Non-Ionizable.
→ Ionic Bond ↳ Non-directional.	→ coordination ↳ Directional.

(i) Counter (anion) ion satisfy only PV

(ii) Neutral ligand satisfy only SV

(iii) Anion ligand satisfy both PV & SV.

Modern Ful.

Eg-	PV	SV	
(1) $Pt.4NH_3.Cl_2$	2	4	$[Pt(NH_3)_4]Cl_2$
(2) $Pt.3NH_3.Cl_2$	2	4	$[Pt(NH_3)_3Cl]Cl$
(3) $Pt.2NH_3.Cl_2$	2	4	$[Pt(NH_3)_2Cl_2]$

Electrolyte

Electrolyte → Cation : Anion ratio

Excess $AgNO_3$

(1)	$2AgCl\downarrow$	(1) 1 : 2
(2)	$1AgCl\downarrow$	(2) 1 : 1
(3)	No ppt.	(3) non-electrolyte

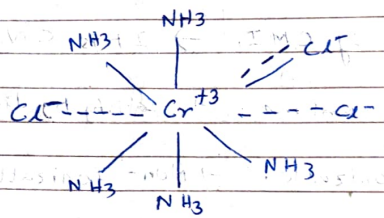
Representation

SV → solid line ——

PV → dotted line - - - -

$Cr^{+3}.5NH_3.Cl_3$.

$[Cr(NH_3)_5Cl]Cl_2$



LIGANDS

- Lewis Base, e⁻ Pair donor,

  LP as well as πe⁻

- Denticity → : No. of lone pair donated (shared) by a ligand to a CMI is called its denticity.

- Classification of Ligands on the basis of "Denticity"

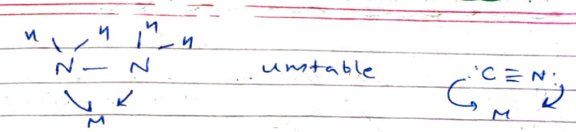
1) Having ONE Donor site.

F^-, Cl^-, Br^-, H^-, I^-, S^{-2}, OH^-, O^{-2}, H_2O, NH_3, NH_2^-, NH^{-2}, PX_3, AsX_3, CH_3^-, $Ph-$

form 1- co-ordinate bond with CMI, acts as Monodentate Ligand

2) Having two Donor site.

(a) form 3-membered Ring with CMI.



So, they act as Monodentate.

eg-

CN^-, SCN^-, NCO^-, N_2H_4, N_3^-, CO, O_2^{2-}, O_2^-, N_2, NO, NO^+.

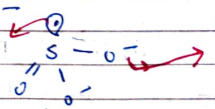
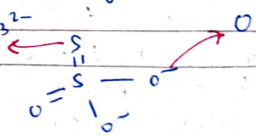
b) Anionic Ligand having two or more different donor site but uses only one type of donor site at a time is called AMBIDENTATE Ligand.

CN^- → CN^- cyanido-C

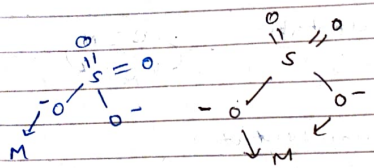
NC^- → NC^- cyanido-N

~~SCN & SNC~~,

In the naming of such ligands First letter of donor site is written is capital letter as suffix.

• thiocyanido	SCN^-	NCS^-
• cyanato	OCN^-	NCO^-
• Nitro	NO_2^-	ONO^- (nitrito)
✱ Thionitro	NOS^- → SNO^-	ONS^-
• Sulphito	SO_3^{2-} 	OSO_2^{2-}
• Thiosulphato	$S_2O_3^{2-}$ 	$OS_2O_2^{2-}$

(6) form 4 membered Ring with CMI.



→ 4 membered.

Now, 4-memb is more stable than 3-mem ring but itself unstable, so generally they act as Monodentate but as per requirement of CN of CMI they can act as bidentate ligands such ligands are called **FLEXIDENTATE LIGAND**.

Ex:- All oxoanion having single C.A

BO_3^{3-}, CO_3^{2-}, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, SiO_4^{4-}, SO_4^{2-}, SO_3^{2-}, ClO_4^-, ClO_3^-, ClO_2^-

(7) form 5/6/7 membered ring.

No-angle strain

Act as bidentate/ didentate.

Note

ONO^- Mono donor O

NO_2^- Mono donor O

O_2N^- Bidentate (O, O')

2 → bi/di

3 → tri

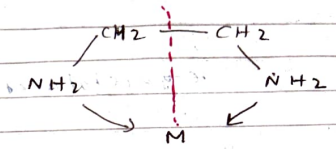
4 → tetra

5 → penta

6 → hexa

} polydentate

1) Ethane - 1,2 diamine (en)

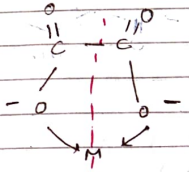


N-N donor

(A,A)

Sym bidentate.

2) Oxalate (ox^{-2})

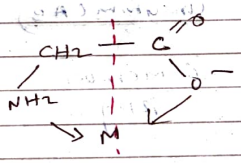


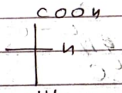
Symm (AA)

5 membe.

3) Glycinato → (Glycine.) (Gly).

(gly^-)



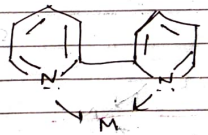


unsymm (AB)

bidentate

5 Membe

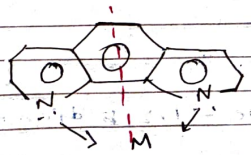
4) Dipyridine. (dipy)



Symm. (AA)

5-Mem. ring.

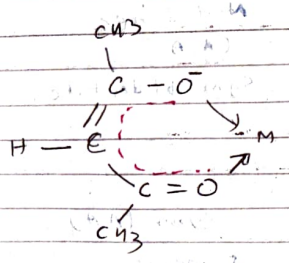
5) Phenanthroliene (phen).



Symm (AA)

5-Memb. ring

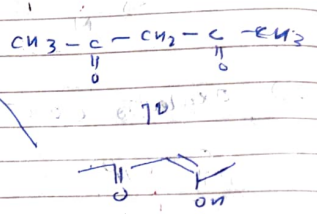
6) Acetyl acetonato. (acac⁻)



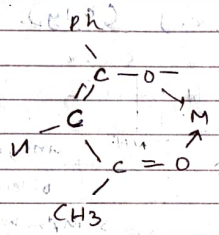
Symm (AA)

6 Mems

eg acetyl acetone



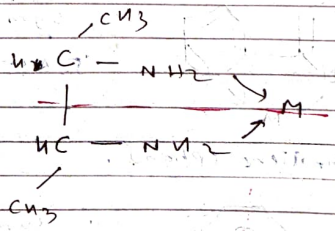
7) Benzyl acetonato (baca⁻)



Unsymm (AB)

6-Member Ring

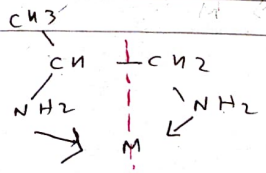
8) bn butane - 2,3, diamine



Symm (AA)

5-membered

9) pn propane - 1,2, diamine.

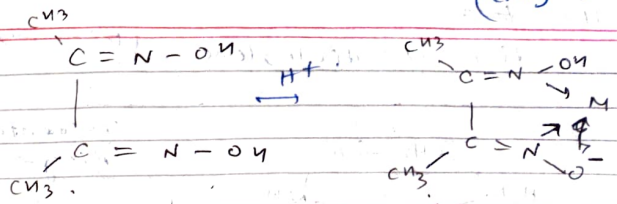


Unsymm (AB)

5-Member.

10) dimethyl glyoxime (DMG)

→ (dmg⁻¹)



All N-donor are 5 membered.

N-N donor

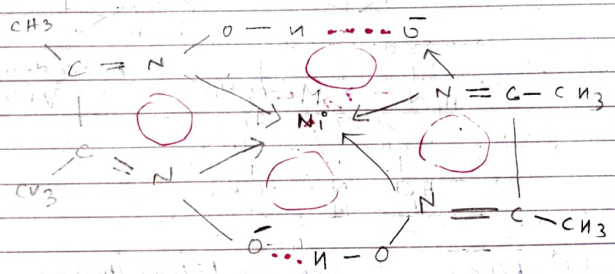
5 member

symm

When

Ni^{+2} + dmg^{1-} → $Ni(dmg)_2 \downarrow$

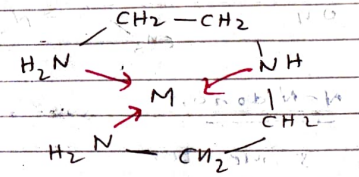
Rosy Red ppt



Note	donor	Membered in Ring
en	N, N	5
dox^{-2}	O, O	5
~~dox~~ gly^-	O, N	5
phen	N, N	5
dipy	N, N	5
acac	O, O	6
bcac	O, O	6
bn	N, N	5
pn	N, N	5
dmg^-	N, N	5

11) ~~dien~~

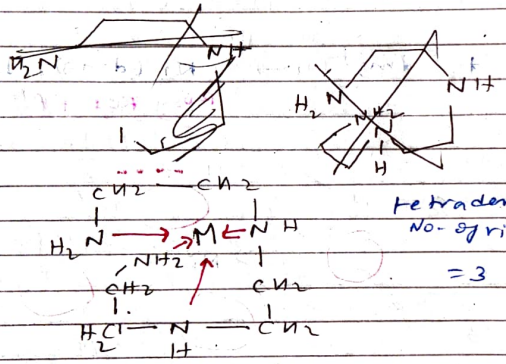
dien → diethylene (triamine)



Tridentate

Ring = 2

12) trien triethylene (tetraamine)

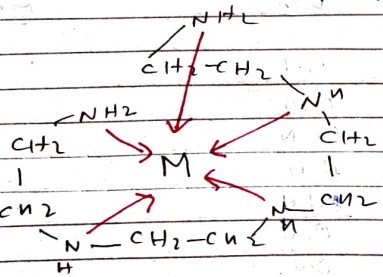


tetradentate

No. of ring

= 3

13) teten ~~tetraethe~~ tetraethylene pentamine.



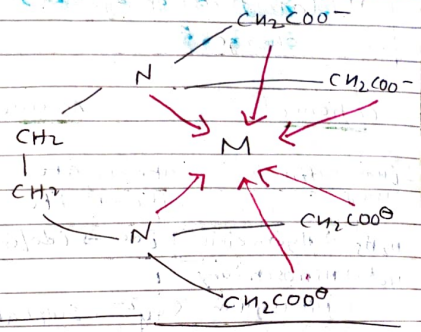
pentadentate

4 ring.

14) $edta^{4-}$ ethylene diamine tetraacetate ion.

Hexadentate

5 ring.



$Edta^{4-}$ is flexidentate & it denticity is ph dependent

Wrong

$edta^{4-} \rightarrow 6$

$Hedta^{3-} \rightarrow 5$

$H_2edta^{2-} \rightarrow 4$

$H_3edta^{-} \rightarrow 3$

$H_4edta \rightarrow 2$

$NH_3 \rightarrow 1$

$NH_4^+ \rightarrow 0$

en → 2

Hen → 1

Ligand is Change ✓ here

Wrong

CHELATING LIGAND. (exception – $Ni(dmg)_2 = 4$)

bi/poly dentate ligand form ring with CM I such ligands are called chelating ligands.

No. of chelate ring form by a ligand = denticity − 1

$[Cr(en)_3]^{3+}$ → 6 − 3 = 3

↳ (3)

" Classification of Ligands on the basis of charge "

Cationic	Anionic	Neutral
-ium suffix is used	ate → ato. ite → ito	except
$N_2H_5^+$ → Hydraziniium	ide → ido/o	CO → carbonyl
NO^+ → Nitrosoniium / Nitrosylium	SO_4^{2-} → Sulphato	NO → Nitrosyl
	SO_3^{2-} → sulphito	H_2O → Aqua
	S^{-2} → sulphido	NH_3 → Ammine
	CH_3^- → Methyl.	General name is used, CH_3NH_2 → Methyl Amine

" Classification of Ligands on the Basis of Bonding Pattern "

CLASSICAL LIGANDS

- lone pair donor.
- σ donor
- only donor.
- M ← L

Eg:- O^{-2}, OH^-, H_2O, F^-, NH_3, NH_2^-, NH^{-2}, CH_3^-, H^-

বিভিন্ন ধরণ, কিন্তু নিচে সবগুলো নাই।

NON-CLASSICAL LIGANDS

- Donor as well as acceptor
- → π-acid ligand (Lewis Acid) ↓ donor
- In π fashion acceptor.
- M ← L give & take. synergic bonding.

Non-Classical Ligands:

σ/Lone Pair Donor

lp donor

σ_{NBMO}

Accept in π*

CO, NO, O_2, NO_2^-, NO^+

B.O in ligand ↓

Accept in e⁻ d-orbital

PPh_3, R_2S, AsR_3

M-L No change in B.O of ligand.

(if π bond is present from before, then can accept in π*)

σ e⁻ donor

σ_{BMO}

H_2 accept e⁻ in σ*

B.O of H_2 < 1

As e⁻ coming is in ABMO.

π e⁻ donor

M ← L

But M-L B.O ↑

Overall stability ↑.

Accept e⁻ in π*

But BO in ligands ↓

π-donor, π-Acceptor.

They are weak donor but they acts as ligand in complex because of synergic bonding.

Metal-ligand, BO > 1 so overall stability ↑, such ligand accept e⁻ in π* so BO in ligand ↓

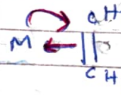
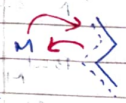
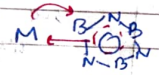
C_6H_6 (Ph) B.O. C-C = 1.5

Cr (Ph) B.O C-C < 1.5

CC - BL, C_6H_6 < Cr(C_6H_6)

Such ligands are written with prefix η^x,

x = hapticity = no of atoms participating in donation.

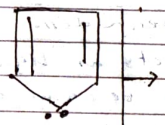
Ligand	Bonding Pattern	e⁻ in donation	Atom in donation	Name
C_2H_4		2	2	η^2 ethylene or π-ethylene
$H_2C=CH-CH=CH_2$		4	4	η^4-butadiene π-butadiene
C_6H_6		6	6	η^6-benzene π-benzene
$B_3N_3H_6$		6	6	η^6-borazine

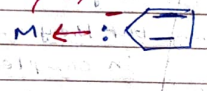
Now

$C_5H_5^-$ # Flexidentate

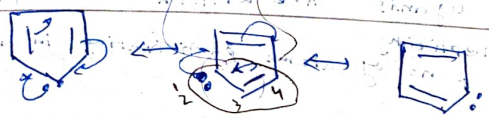
cyclopentadienyl (cp)

N/A e⁻, can't accept

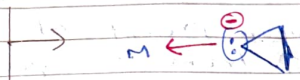




2	1	σ-Cp	η^1-cp
4	3	η^3-cp	
6	5	η^5-cp, π-cp	

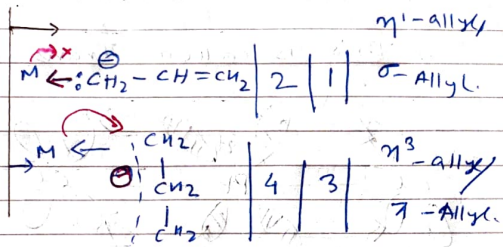


2) $C_3H_5^-$ → cyclopropyl — e^- — atom



2	1	η^1 cyclo propyl

$:\bar{C}H_2-CH=CH_2$ Allyl



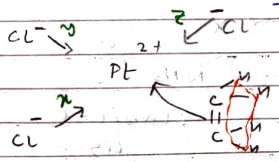
2	1	η^1-allyl, σ-Allyl
4	3	η^3-allyl, π-Allyl

#

Synergic Bonding in Zeise's Salt.

$K[PtCl_3(\eta^2-C_2H_4)]$

Susnata Chattopadhyay

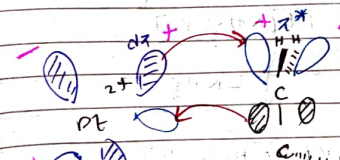


→ $PtCl_3$ plane is $\perp^r$ to C_2H_4 plane.

→ both 'C' atom (σ bond) is also $\perp$ to $PtCl_3$ plane.

→ All 4 H-atoms are present in a plane but not with C–C due to repulsion b/w $d_\pi - \pi^*$ & C–H σ bond.

Here,



Bond length — Bond weak

$x = z < y$ due to TRANS EFFECT.

d_{xy} (metal) → π^*_x (carbonyl)

Q) For complex comp $[Cr(CO)_x(\eta - B_3N_3H_6)_y]$

$x + y = ?$

Cr is in 0 O.S ∴ EAN rule satisfy also

$\therefore 36 = 24 + 2x + 6y \Rightarrow 2x + 6y = 12$

Again as $\eta - B_3N_3H_6$ give 6e⁻ ∴ Denticity $= \frac{6}{2} = 3$

Max m denticity of Cr $= 6$

$\therefore x = 3$ & $y = 1$ ✓ $3 + 1 = 4$.

Q) $[Fe(\eta - C_5H_5)_x(\eta - C_3H_5)_y(CO)_z]$

$x + y + z = ?$ by EAN.

$\eta - C_5H_5$ donate 6e⁻ → D $= \frac{6}{2} = 3$

$\eta - C_3H_5$ → " 4e⁻ → D $= 4/2 = 2$

Max m → $6 = 5 + z$ ∴ $x = 1, y = 1, z = 1$

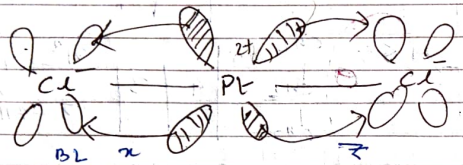
$z = 1$ ∴ (3)

$CN^- > C_6H_5^- > Br^- > NH_3$

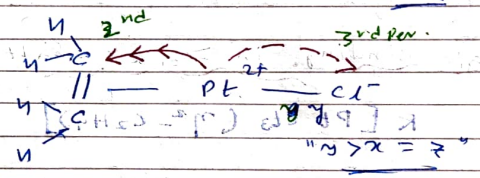
TRANS - EFFECT

In sq. planar / octahedral complexes when good acceptor present at transposition, B.L ↑ from its expected value & when weak acceptor present at trans position, B.L ↓ from its expected value.

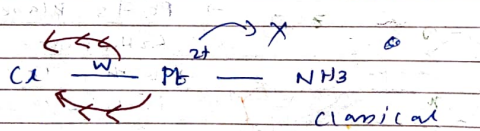
This is called Trans Effect.



(I)

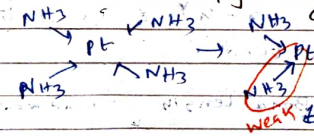


(II)

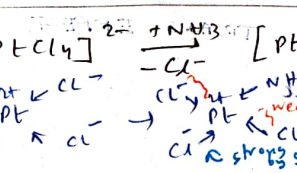


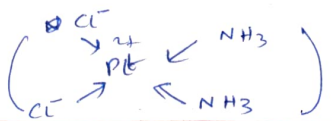
$W < x = z < y$.

Q)) $[Pt(NH_3)_4]^{2+} \xrightarrow{-NH_3} [Pt(NH_3)Cl]^+ \xrightarrow{-NH_3} [Pt(NH_3)_2Cl_2]$



Q) $[PtCl_4]^{2-} \xrightarrow[-Cl^-]{+NH_3} [Pt(NH_3)Cl_3]^- \xrightarrow{+NH_3, Cl^-} [Pt(NH_3)_2Cl_2]$



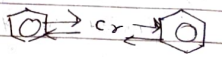


CIS- CIS- platin Anti Cancer.

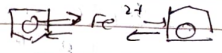
Q) compare BL in (C-C)

1) C_2H_4 < $[PtCl_3(\eta^2-C_2H_4)]^-$

2) C_6H_6 < $Cr(C_6H_6)_2$

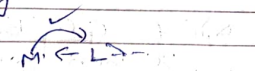


3) $C_5H_5^-$ < $Fe(C_5H_5)_2$ Ferrocene



All synergic bonding.

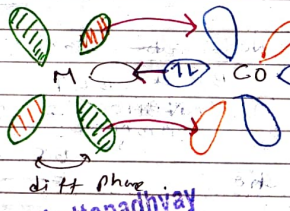
(↑) e⁻ in



Synergic Bonding in Metal Carbonyl.

"M ← CO"

$d\pi \rightarrow \pi^*$



from MOT

C.O → 14e⁻

BO = 3

HOMO = σ NBMO of C

LUMO = π^* 2p orbital

having slight AB char

M-C BO ↑

M-C BE ↑

M-C BL ↓

Sushata Chattopadhyay

if M ← CO

then AB e⁻ of CO ↓

∴ BO ↑ slight

$BO = \frac{1}{2}(N_b - N_{ab})$

N_{ab} ↑

BO ↓

Now M ← CO in 100% ABMO

BO ↓ Rapidly

So, in M - CO, decreasing effect more

2 < C-O > B.O is < 3

Thus d- block elements also show -ve / low O.S due to stability of -ve charge by synergic bonding.

So,

→ CO B.L in Metal carbonyl is greater than CO B.L in free 'CO'.

→ As negative charge on Metal ↑, So donation tendency of Metal ↑.

So, e^- in ABMO of CO ↑ ∴ $BO = \frac{1}{2}(N_a - N_b)$

CO B.O ↓

B.L ↑

Q) If C.O Bond length in $Cr(CO)_6$ is x then comment in CO bond length in

(i) free CO < x

Cr → C ≡ O

BO ↓ BL ↑

(ii) BH_3CO

No donation sharing

BL < x.

BO ↓ BL ↑

$BH_3 \leftarrow CO$ ABMO — give

So, BO > 3

only donation.

(iii) $Cr(CO)_6^+$

(I) Less e^- give by M

$Cr(CO)_6$ (II)

Donation tendency ↓ 0

+1 More

So, e^- in ABMO of CO More

I < II

∴ CO Bond order (I) ↑ More

CO B.L, I < x.

(iv) $Cr(CO)_6^-$ $Cr(CO)_6$

(I) ↓ (II) ↓

(1) Donation tendency of e^- ↓ 0

More ←

(2) So, neg e^- in ABMO of CO ↓ (II)

More ←

(3) BO of CO in (I) < (II)

(4) BL in CO (I) > x.

Follow the 4 steps Always, to solve every question.

(v) $V(CO)_6^-$ > x.

(1) donation tendency V^- > Cr

(2) ∴ e^- in ABMO of CO $V(CO)_6^-$ > $Cr(CO)_6$

(3) ∴ CO BO <

(4) CO BL > x.

(vi) $Mn(CO)_6^+$

(1) donation tendency Mn^+ < Cr

(2) No. of e^- ABMO of CO < $Cr(CO)_6$.

(3) CO BO >

(4) BL < x

(vii) $[Cr(CO)_5NH_3]$ | $Cr(CO)_6$, LP in 6.

↑ classical ligand.

(1) Here 1 LP is divided in 5 CO.

∴ e^- in ABMO of CO >

∴ Co BO ↓ Len

CO BL More, > x

(viii) $[Cr(CO)_5PF_3]$

Acceptance tendency

$PF_3 > CO > PCl_3$

PF_3 take maximum e⁻

So,

e⁻ in ABMO of CO ⊕ then -

BO ↓ More in

BL ↓ $< x$

(ix) $[Cr(CO)_5PCl_3]$.

Now, More

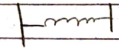
e⁻ in ABMO in CO

∴ More

CO BO ↓

BL ↑ $> x$

COMPARISON of CO BL with stretching frequency Method.



As like spring

As strength of spring ↑

to stretch spring required energy ↑

$E = h\nu$

↑ frequency

So, related frequency also ↑

This frequency is called stretching frequency.

As, CO BO ↑, CO BE ↑,

stretching frequency of CO ↑.

a) compare ν_{CO} (Stretching frequency)

(1) (a) $[Cr(CO)_5NH_3]$ (a)

(b) $[Cr(CO)_4(en)]$ (b)

(c) $[Cr(CO)_3(dien)]$ (c)

NH₃, (en), dien are ~~not~~ classical

1 Lp → 5 CO So, Not accept

Only donation, No. of ABMO e⁻ in CO

(a) < (b) < (c)

∴ BO (a) > (b) > (c) & BE

$\nu_a > \nu_b > \nu_c$

(2) $[Cr(CO)_5PF_3]$ $[Cr(CO)_5PCl_3]$ $[Cr(CO)_5PMe_3]$

(a) (b) (c)

These are non classical

Good Accept

(a) More e⁻ take by PF_3

So, No. of ABMO e⁻ in CO ↓

BO ↑

BL ↓

(c) PMe_3 More en take

∴ BL c > b > a

BE b < a

ν_a

BO a > b > c

BE > >

∴ $\nu_a > \nu_b > \nu_c$ ν_{CO}

(3) $Ni(CO)_4$ $Co(CO)_4^-$ $Fe(CO)_4^{2-}$

Donation tendency.

Now $Fe^{2-} > Co^- > Ni$

∴ ABMO e⁻ in CO ↑

> >

BO < <

BE < <

∴ ν α < < <

Here

$Ni(CN)_4^{2-} \rightarrow Ni^{+2}$ $3d^8$

28, → 2+8 = 10
−2
8

similarly

$Fe(CO)_4 \rightarrow Fe^{-2}$

2+6 = 8 $3d^{10}$
+2
10

$Na_2[Fe(CN)_5 NO]$ (d⁵, d¹)

sodium Nitro prusside.

$[Fe(CN)_5 NO]^{-2}$ (Fe: +2)

Fe = 26

$\therefore Fe^{+2}$, 2+6−2 = 6

→ $3d^6$

TRICKSHOT

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
At no	21	22	23	24	25	26	27	28	29	30 → $3d^{10}4s^2$
distrib	3 4 5	6	7	8	5	10	11			

Eg:- (n−1)d + ns

∴ For Co^{+2} → $x+7-x = 7$

∴ $3d^7$

Ni^{+4} → 10−4 = 6 → $3d^6$

∴ For Pd^{+2} → $x+8-x = 3d^8$

(Same for, Ni)

Note

INNOCENT LIGAND	NON-INNOCENT LIGAND
In which charge on ligand is predictable.	Charge on ligand is not predictable.
Cl^-, $(H_2O)^0$, $(NH_3)^0$, ...	$O_2 \rightarrow O_2^-$; O_2, O_2^{-2}
Ox^{-2} → $(O)^{-2}$	$NO \rightarrow NO^+$, NO.

In Non-innocent ligand any hint is given to predict charge.

i) conf of CMI, O.S of CMI, Unpaired e⁻ on CMI

2) BL of of ligand, BO, geometry, (-2)

Q) $Zn(O_2)_2(CN)_2$ (+2, 0, −2) + liq NH_3 → $K_2[Zn(O_2)_2(CN)_2]$ (+2, −2)

O_2^0

(-2) → $(O_2)_2$

∴ −1 → $O_2^{(-)}$

(a) ~~$K_3[Cr(NH_3)(O)(O_2)(CN)]$~~

$K_3[Cr(C_2O_4)(O_2)(CN)_5] \rightarrow -3$

x −2 y −1×5

x + y − 2 − 5 = −3

x + y − 7 = −3

x + y = 4

Cr → +6 (x)

O → y → −2

Cr → +5

O → y → −1

Cr → +4

O → 0

Familiar

Ans

How to Find charge on NO in complexes.

Q1) $Na_2[Fe(CN)_5NO]$ → NO → Fe^{+3} / → NO^+ → Fe^{+2}

Clearly, ~~Fe^{+3} ~~ NOm

∴ less diff. charge.

More stable. ✓

∴ Fe^{+2}, NO^+.

Q2) $[Fe(CH_2O)_5NO]SO_4$.

x y

$x + y = +2$ | But NO^+ Fe^+

$y \neq 0$ | more stable

$x = +2$ ~~✓~~ | OV

X

Q) $Fe(NO)_4$

Fe → 0 | NO^+

NO → 0 | Fe^{-4}

Effective Atomic Number (EAN)

Total no. of e^- in CMI after complex formation is called it's EAN.

$K_4[Fe(CN)_6]$ → Fe^{2+}

↓ 26 e^- ∴ 0 ↓ 26−2

CN ligand → 2 6 − 2 + 2 × 6

= 36 Total e^-.

$EAN = Z - (O.S) + 2 \times CN$

IUPAC Naming.

1) Cations are written before anions. $MgCl_2$

2) Never consider no. of ions.

$FeCl_2$ Iron(II) chloride

$FeCl_3$ Iron(III) chloride.

3) In the naming of complex,

(a) Ligand are written before CMI.

(b) To represent no. of ligands prefix

2 – di

3 – tri

4 – tetra

5 – penta

6 – hexa

Eg. $(Py)_2$ → dipyridine but ↓ (dipy)

(c) When prefixes (di, tri, tetra) already present in the name of ligand, for organic ligand oxo anion prefixes.

2 → bis

3 → tris

4 → tetrakis

5 → pentakis.

4) When more than one type of ligand present in complex then alphabetic priority is used.

Eg. $[Pt(NH_3)_3 \cdot H_2O]^{2+}$.

triammine aqua

But for (dipy) we consider ∵ ligand name.

5) Never consider prefixes when they are not part of name of ligand in priority order.

primary SAQ II

(6) Naming of central Metal Ion.

Fe^{+2} Iron(II) — Ferrate (II).
Cd^{+2} Cadium(II) — Cadmate (II).

CMI = [ ]$^{+/0}$ CMI = [ ]$^{-}$

Use General Name (OS) : Latin name + ate
roman No. OS

(7) Name to formula.

[CMI L_1 L_2 L_3]
Alphabetic priority

1) potassium hexa nitroferrate(II) (Nitro-N)

$K_4[Fe(NO_2)_6]$

NO_2^-

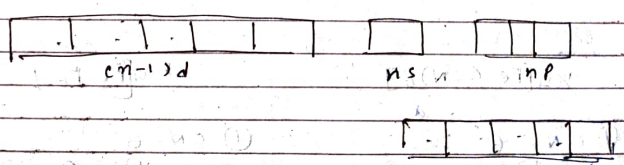
$2+ -6 = -4$

(8) Poly nuclear Complex → Not in syllabus
(Last) JEE Main/Adv.

VALENCE BOND THEORY (VBT)

- CMI → provide vacant orbital
- Ligand → lp.
- Coordinate bond = σ bond + ~~π~~.
- ∴ No. of hybrid orbital = CN of CMI (σ bond).

CN	Hyb.	Geometry
2	sp	Linear
3	sp^2	Trigonal planar
4	sp^3, dsp^2 →	
5	dsp^3, d^2sp^3	tbp,
6	d^2sp^3, sp^3d^2	oct.



- if (n-1)d orbital used in Hyb →
  - inner orbital complex
  - Low Spin.

d^2sp^3, dsp^2, dsp^3

- If nd orbital used in Hyb
  - → outer orbital complex
  - → High spin

sp^3d, sp^3d^2, sp^3d^3

→ sp^3d, dsp^3d^2, sp^3d^3

inner e⁻, are closer to nucleus → stereochemically inactive.

LIGAND

1) SFL (strong Field Ligand)

→ CN^-, CO, en, NO_2^-, NH_3

CH_3 ~ C, N donor.

2) Weak Field Ligand (WFL)

→ O, halogen, S donor.

Note

- in presence of SFL e^- are ~~forced~~ forced to pair, as per requirement of d-orbitals in Hybridisation

- In WFL, no pairing, Normal config is used (no force).

Eg

$K_4[Fe(CN)_6]$

① $CN = 6$ → 2d

② Fe^{+2} ∴ conf $26-6-2$ → d^6

③ CN^- = SFL

free CMI 3d6

Now, in presence of SFL

inner orbital d^2sp^3

$n = 0$ $M = 0$ Low spin

$K_4[Fe F_6]$

① $CN = 6$

② Fe^{+2} d^6

③ WFL = F^-

free CMI, 3d6

In presence of WFL

same

$n = 4$

$M = \sqrt{n(n+2)}$ sp^3d^2

$= 4.$

$M \neq 6$

High Spin

As per req. keep 2 d-orbitals for SFL.

CN = 6 } d^2sp^3 / sp^3d^2

Config.	WFL	SFL
d^0	(n-1)d, d^2sp^3	(n-1)d, d^2sp^3
d^1	1, d^2sp^3	1, d^2sp^3
d^2	1 1, d^2sp^3	1 1, d^2sp^3
d^3	1 1 1, d^2sp^3	1 1 1, d^2sp^3
d^4	1 1 1 1, sp^3d^2	1 1 1, d^2sp^3
d^5	1 1 1 1 1, sp^3d^2	1 1 1, d^2sp^3
d^6	1 1 1 1 1 1, sp^3d^2	1 1 1, d^2sp^3
d^7	1 1 1 1 1 1 1, sp^3d^2	1 1 1 1, 4d excite (maximum), d^2sp^3
d^8	1 1 1 1 1 1 1 1, sp^3d^2	1 1 1 1 1, no more, sp^3d^2
d^9	1 1 1 1 1 1 1 1 1, sp^3d^2	1 1 1 1 1, sp^3d^2
d^{10}	1 1 1 1 1, $n = 0$	1 1 1 1 1, $n = 0$

Transference

V. Important

We learnt:

CN=6

- $d^{0,1,2,3}$ Always d^2sp^3 inner orbital
- $d^{4,5,6,7}$ SFL d^2sp^3 inner, low spin.
  WFL sp^3d^2 Outer, high spin.
- $d^{8,9,10}$ sp^3d^2 Always.

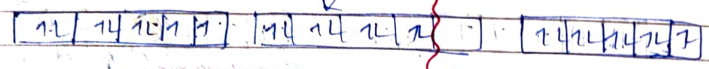
Diamagnetic
d^0, d^{10}, d^6 – SFL.

CN=4 → sp^3 / dsp^2

$Ni(Cl_4)^{2-}$ | $Ni(CN)_4^{2-}$ | $Ni(CO)_4$ (SFL)

Ni^{2+} d^8 | Ni^{2+} d^8 | Ni^0 d^{10}

WFL | SFL | SFL



sp^3 | dsp^2 (1d requirement) | sp^3

para | dia | dia

High spin | low spin | low spin

(Sq. planar)

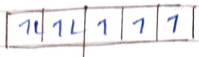
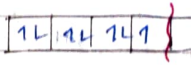
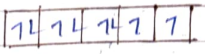
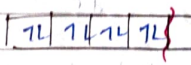
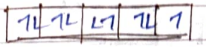
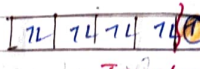
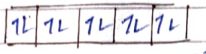
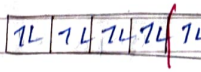
Now

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Noble EAN
										36

d^6 CN = 6 (generally)

$d^{7,8,9,10}$ CN=4

sp^3/dsp^2

	WFL	SFL
d^7	 sp^3	 dsp^2
d^8	 sp^3	 dsp^2
d^9	 sp^3	 dsp^2 (4P, Transference)
d^{10}	 sp^3	 sp^3

$d^{7,8,9}$ SFL → dsp^2; WFL → sp^3

Dia: d^0, d^{10}, d^8 – SFL

d^{10} → sp^3

CN=5

→ dsp^3 or sp^3d

Dia → same as before
d^0, d^{10}, d^8 – SFL,

So, by observation

CN=5 → WFL, CO

CN=5 → SFL, except CO

Geometry



(d_{z^2})

trigonal bipyramidal



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

square pyramidal

Q) Find Hybl Geometry, unpaired e^- in $Fe(CO)_5$ also comment on Fe–C B.L.

At No. = 26

= 8

Fe → $3d^8$

CN = 5 → dsp^3 / sp^3d Hybd

Geometry is

Unpaired $e^- = 0$.

Now B.L

pd (n-1)d

sp^2 ? (ns, np)

Axial Fe–C bond < Equatorial Fe–C.

Exception of VBT :-

1) Generally 'O' donor are WFL but act as SFL for Co^{3+} & Cu^{2+} in 3d series.

2) NH_3 is SFL but acts as WFL for Co^{2+}, Fe^{2+}, Mn^{2+} (also NCS⁻, edta⁴⁻)

3) All ligands are SFL for 4d, 5d series & M(+4) ions

$\therefore$ C > N > O (SFL) > F > Cl > Br > I (WFL)

Explanation of Exception.

1) SFL is SFL ?

- Because good donation.

3d series. Mn^{2+} Fe^{2+} Co^{2+} Ni^{2+} Cu^{2+}

Z_{eff} ↑ ; Z_{eff} ↑ . (Nuclear ↑)

Co^{3+}

4d & 5d

Z_{eff} ⇑ (poor shield).

$\therefore$ SFL ligand form strong bond with CMI.

As Z_{eff} of CMI ↑ WFL ligand can act as SFL.

for 4d, 5d series, Good pair easily,

So, O donor are WFL but act as SFL for Co^{3+} & Cu^{2+} in 3d series.

MATRIX

21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn

always inner orbital

complex → d^3 → Properties

(A) $M(CN)_6^{-2}$

(B) $M(en)_3^{x+}$

(C) $M(NH_3)_6^{x+}$

(D) $M(H_2O)_6^{x+}$

(E) $M(C_2O_4)_3^{x-}$

(F) MF_6^{x-}

(G) MCl_6^{x-}

(H) $M(NCS)_6^{-x}$

(P) M = Cr^{+3} inner orbital complex

(Q) M = Mn^{2+} outer orbital

d^6 (R) M = Pt^{+4} diamagnetic

d^5 (S) M = Fe^{3+} paramagnetic

d^4 (T) M = Fe^{2+} High spin(C)

d^6 (U) M = Co^{3+} Low spin.

(A) (A) SFL

A ①

(P) – A B C D E F G H ✓ ✓

(Q) – D, E, F, G, C, H

(R) – A, B, C, D, E, F, G, H

(S) – A B C D E F, H always paran addo

(T) – C, D, E, F, G, L, H

(U) – A, B, C D E, H

Fe^{26} → d^5 / d^6

$8-3$, $8-2$

Matrix Match:

① CN=4

(A) $M(CN)_4^{2-}$ (P) M = Zn^{2+} diamagnetic
(B) $M(en)_2^{2+}$ (Q) M = Cu^{2+} paramagnetic
(C) $M(C_2O_4)_2^{2-}$ (R) M = Pt^{2+} sq. planar dsp^2
(D) MCl_4^{2-} (S) CN = 4

② d^9

WFL

M = M^{2+} d^8 tetrahedral sp^3

A →	R	Q	P	
B →	R	Q	P	
C →	R	Q	P	S
D →	R	Q	P	S

dsp^2

d^9, CN = 4 → SFL WFL

↓ Diamag. Para

Pt^{2+} → All SFL

Zn^{2+}

$3d^{10}4s^2$

Zn^{2+} $3d^{10}$ Always

Ni^{2+} → CN, d^8

∴ d^8 → SFL → dia.

Spectrochemical Series (Relative strength of ligand).

- $I^- < Br^- < SCN^- < Cl^- < S^{-2} < NO_3^-/N_3^- < F^- < OH^- < CH_3COO^- < C_2O_4^{2-} < H_2O <$

Itna Bura Jha Kalu Shyamu Nayi, Aule hath ese, wske pani bhara ho jaisi

- $NCS^- < EDTA^{4-} < NH_3 < Py < en < dipy < NO_2^- < CN^- <$ (Gly-1, dmg-1) No.

Naveen Chandra Saxena — Enn dino — Amman Pune — ke bolke double-2 — Nosena court — ke chakkar lage rahe thai

'p' donor - gen. SFL.

Mixed Field Ligand

When

- SFL > WFL : Effective SFL
- SFL < WFL : Effective WFL
- SFL = WFL : Generally SFL except

$[Co(H_2O)_3F_3]$
$[Ni(PPh_3)_2Cl_2]$
$[Ni(NH_3)_2Cl_2]$.

CRYSTAL FIELD THEORY.

Drawbacks of VBT:-

(i) It involves a no. of assumption.
(ii) It does not explain —
(ii) Quantitative interpretation of Magnetic data.
(iii) Colour Property.
(iv) Stability of complex.
(v) CN=4 exact prediction of tetra & sq. planar.
(vi) diff b/w SFL & WFL.

Acc to CFT,

interaction b/w ligand and central metal ion is ionic

CMI

Ligand → +ve point charge

Ligand → Anionic Ligand → -ve point charge
→ Neutral ligand → Dipole.

When ligand approaches CMI to form complex type of forces is present

(i) attr b/w lp of ligand & Nucleus of CMI.

(ii) repn b/w lp of ligands & d-orbital of CMI.

So, in

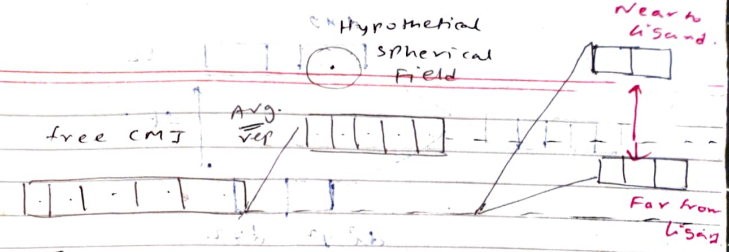
- free CMI all d-orbitals are degenerate.
- If ligand approaches CMI in a spherical field, repulsion on d-orbitals is equally applicable.
- So, energy of d-orbitals equally increases, degeneracy of d-orbitals is maintained.

Now,

Practically ligand approaches CMI in a particular geometry. So acc to geo geomery, some d-orbital near to ligands experienced more repulsion in comparison of other d-orbitals which are far from ligands.

So, d-orbitals are splitted into different energy set, loss of degeneracy is called CRYSTAL-FIELD SPLITTING.

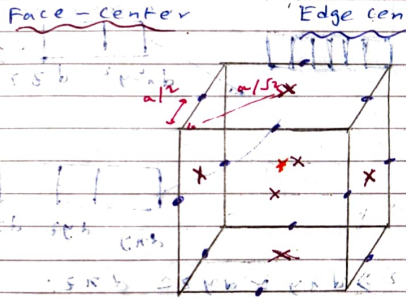
Energy diff b/w d-orbitals is called splitting energy (Δ).



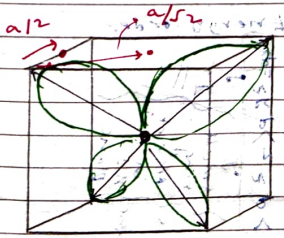
Dr orbital

Axial, dz^2, dx^2-y^2

Non Axial dxy, dyz, dxz



★ Splitting in Tetrahedral.



∴ Ligand → Near to Non Axial d-orbital.

So, corner of ligand near edge center.

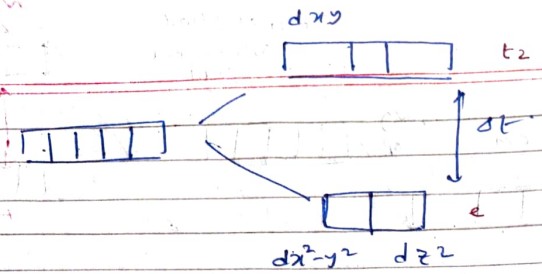
∴ Each point (corner) cover 3 edge center.

4 point → 12 edge

So, Energy order.

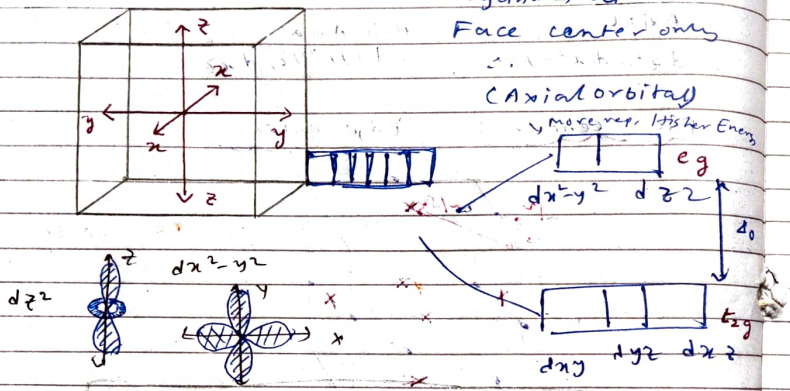
$$dxy = dyz = dxz > dz^2 = dx^2-y^2$$

t2 e



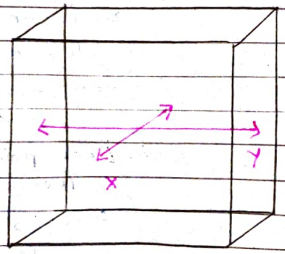
* Splitting in Octahedral.

Ligand → at Face center only
∴ (Axial orbital)



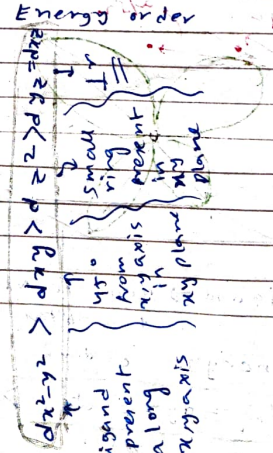
∴ $d_{x^2-y^2} = d_{z^2} > d_{xy} \approx d_{yz} \approx d_{xz}$.

* Splitting in Square planar.

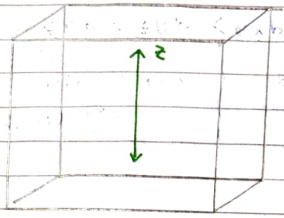


Ligand at face center of 4 sides, ∴ More rep, More Energy

Energy order



* Splitting in Linear Geometry.



∘ Ligand ● on z axis,

$d_{z^2} > d_{yz} = d_{xz} > d_{x^2-y^2} = d_{xy}$

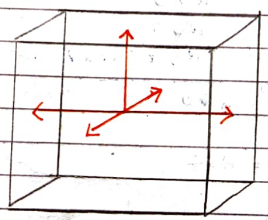
↓ along z axis — 45° to z Axis — ⊥r to z axis,

Energy order.

Ligand on X-Axis.

$d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{yz} = d_{xz}$.

* Splitting in Square Pyramidal.

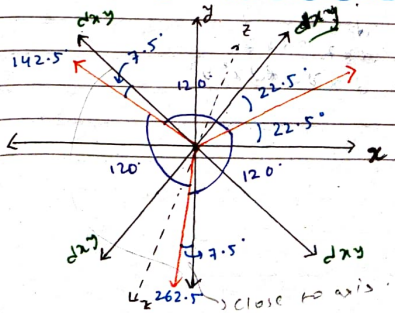


Now,
Energy order.

$d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{yz} = d_{xz}$.

2 Ligands in each xy axis — Ligands in z axis — 4 Ligand near to dxy at 45° — Ligand near at 45°,

* Splitting in Trigonal Planar.

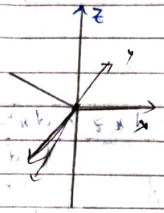


So, Same dist

$d_{x^2-y^2} = d_{xy} > d_{z^2} > d_{xz} = d_{yz}$

dxy → b/w two axis.

* Splitting in trigonal bipyramidal.

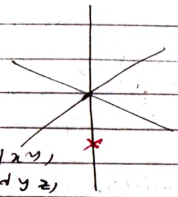


$d_{z^2} > d_{x^2-y^2} = d_{xy} > d_{yz} = d_{xz}$

two ligand on z lobe | 3 ligand & lobes | Not in direction of ligands

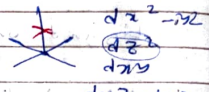
Analysis

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

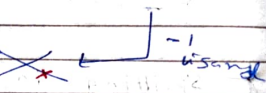


d_{xy}, d_{yz}, d_{xz}.

- 1 ligand → from z axis.



- 2 ligand → z Axis.

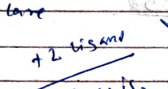


- 1 ligand xy plane

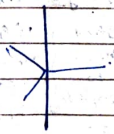
$d_{x^2-y^2}$
d_{xy}
d_{z^2}
$d_{yz} = d_{xz}$

- 1 ligand xy plane

+ 2 ligand z axis.

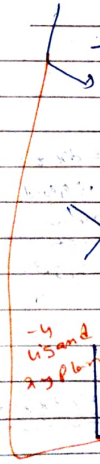


$d_{x^2-y^2} = d_{xy}$
d_{z^2}
$d_{yz} = d_{xz}$



d_{z^2}
$d_{x^2-y^2} = d_{xy}$
$d_{yz} = d_{xz}$

- 3 ligand xy plane





d_{z^2}
$d_{yz} = d_{xz}$
$d_{xy} = d_{x^2-y^2}$

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

Relation b/w Δ_o, Δ_t, Δ_{sp}.

	Δ_o	Δ_t	Δ_{sp}
No. of ligand.	6	4	4
Orbitals in direction of ligands.	2	3	1

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

Avg.

$\frac{1}{4}\Delta_{sp} = \frac{2}{6}\Delta_o$ ⟹ $\Delta_{sp} = \frac{4}{3}\Delta_o$

$\frac{2}{6}\Delta_o = \frac{3}{4}\Delta_t$ ⟹ $\Delta_t = \frac{4}{9}\Delta_o$

Factor Affecting Splitting Energy.

As aHr b/w ligand & Nucleus of CMI ↑ dist. b/w ligands ⊖ & ⊕ of CMI ↓
dist. b/w ligand & d-orbitals ↑
repulsion ↑ Δ ↑

But Δ ∝ strength of bond.

1). +ve Charge on CMI.

WFL SFL

$[Co(H_2O)_6]^{2+}$ < $[Co(H_2O)_6]^{3+}$

$[Fe(NH_3)_6]^{2+}$ < $[Fe(NH_3)_6]^{3+}$

Δ ∝ +ve charge.

2) Z_{eff}

$\Delta \propto Z_{eff}$.

$NH_3 \rightarrow$ WFL ; NH_3 - SFL.

Mn^{2+} Fe^{2+} Co^{2+} Ni^{2+} Cu^{2+}

$Z_{eff} \uparrow$ $\Delta \uparrow$

SFL

$NiCl_4^{2-}$ $PdCl_4^{2-}$ $PtCl_4^{2-}$

$\Delta \uparrow$

3d → 4d → 5d

$Z_{eff} \uparrow$

3) ~~Streagth~~ Strength of ligand.

SFL > WFL

Properties of SFL → Good donor (L Base)
Good Acceptor.

Strength

$C > N > O > F > Cl > Br > I$.

Always SFL.

Why Low spin & high spin complexes are formed?

$\Delta < PE$

WFL

Δ less

SFL

$\Delta > PE$

Δ more.

To pair here, P energy require.

Free CMI

because in d^5 ↑ ↑ ↑ ↑ ↑ their 2 pair-d extr

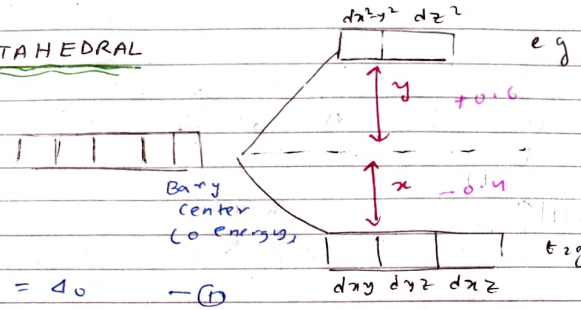
but in d^6 ↑↓ ↑ ↑ ↑ ↑

but in exam, if given 3PE (✓) already one pair so, extra pair occur 3-1 = 2P

CFSE: Crystal Field Stabilization Energy

" Decreament in energy due to crystal field Splitting."

In OCTAHEDRAL



$x + y = \Delta_o$ — (I)

And if fully filled

$-6x + 4y = 0$ — (II)

g → gerade

Solving we get, $x = 0.4\Delta_o$

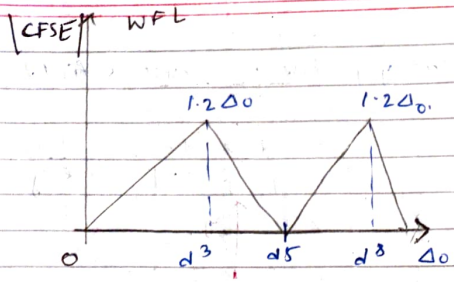
$y = 0.6\Delta_o$

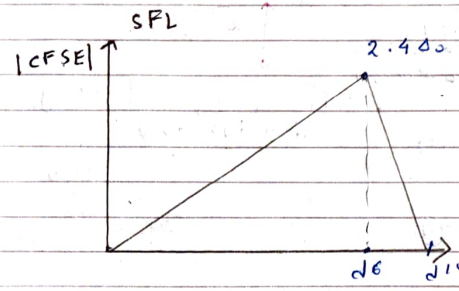
In Oct, system is stabilised by $0.4\Delta_o$/e⁻ and destabilised by $0.6\Delta_o$/e⁻

Note

Δ_o ← depends on Ligands. Energy ↓ Stabilisation ↑

WFL		Conf	CFSE	SFL		Conf	CFSE
		$t_{2g}^0 e_g^0$	0			$t_{2g}^0 e_g^0$	0
d^1	↑	$t_{2g}^1 e_g^0$	$-0.4\Delta_o$	↑	d^1	$t_{2g}^1 e_g^0$	$-0.4\Delta_o$
d^2	↑ ↑	$t_{2g}^2 e_g^0$	$-0.8\Delta_o$	↑↑	d^2	$t_{2g}^2 e_g^0$	$-0.8\Delta_o$
d^3	↑ ↑ ↑	$t_{2g}^3 e_g^0$	$-1.2\Delta_o$	↑↑↑	d^3	$t_{2g}^3 e_g^0$	$-1.2\Delta_o$
d^4	↑↓ ↑ ↑	$t_{2g}^4 e_g^0$	$-0.6\Delta_o$	↑↓ ↑↑	d^4	$t_{2g}^4 e_g^0$	$-1.6\Delta_o + P$
d^5	↑↓ ↑↓ ↑	$t_{2g}^5 e_g^0$	0	↑↓ ↑↓	d^5	$t_{2g}^5 e_g^0$	$-2.0\Delta_o + 2P$
d^6	↑↓ ↑↓ ↑↓	$t_{2g}^6 e_g^0$	$-0.4\Delta_o$	↑↓ ↑↓ ↑↓	d^6	$t_{2g}^6 e_g^0$	$-2.4\Delta_o + 3P$ *
d^7	↑↓ ↑↓ ↑ ↑	$t_{2g}^5 e_g^2$	$-0.8\Delta_o$	↑↓ ↑↓ ↑	d^7	$t_{2g}^6 e_g^1$	$-1.8\Delta_o + 1P$ *
d^8	↑↓ ↑↓ ↑↓ ↑ ↑	$t_{2g}^6 e_g^2$	$-1.2\Delta_o$	↑↓ ↑↓ ↑↓ ↑ ↑	d^8	$t_{2g}^6 e_g^2$	$-1.2\Delta_o + 0P$
d^9	↑↓ ↑↓ ↑↓ ↑↓ ↑	$t_{2g}^6 e_g^3$	$-0.6\Delta_o$	↑↓ ↑↓ ↑↓ ↑↓ ↑	d^9	$t_{2g}^6 e_g^3$	$-0.6\Delta_o$
d^{10}	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	$t_{2g}^6 e_g^4$	0	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	d^{10}	$t_{2g}^6 e_g^4$	0
				No pairing occur.			





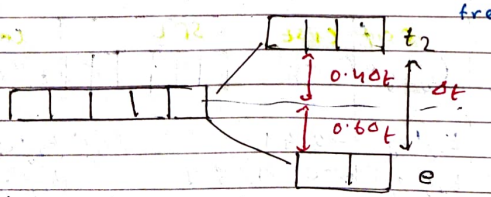
$(CFSE)_o = -0.4\Delta_o \times \eta_{t_{2g}} + 0.6\Delta_o \times \eta_{eg}$

($\eta_{t_{2g}}$: e⁻ in t_{2g}; η_{eg}: e⁻ in e_g)

$+ x \cdot PE$

↑ no. of extra pair wrt free CMI

CFSE in tetrahedral



$(CFSE)_t = -0.6\Delta_t \eta_{e^-} + 0.4\Delta_t \eta_{t_2} + x \cdot PE$

As WFL, so, tetrahedral only form.

Note → Splitting Energy

Q) If CFSE for Oct. as 18,000, than CFSE for tetra? Splitting Energy?

i.e,

$\Delta_t = \frac{4}{9}\Delta_o = \frac{4}{9} \times 18,000$

$= 8000$

Eg-

$[M^{+x}(NH_3)_6]$

$de^- \rightarrow (CFSE)_{\Delta_o}$

Let d^6,

$(CFSE)_o = 0.4\Delta_o$

Given $0.4\Delta_o = 18,000$

Now, $(CFSE)_t$ for d^6 WFL

$0.6\Delta_t = ?$

} then correct

Q) Find numbe for $Co(dmg)_2$ →

- No. of e⁻ in non axial orbital
- no. of e⁻ in axial orbital → dxy.
- Find name of orbital which contain unpaired e⁻.

dxz dyz dz² dxy dx²-y²

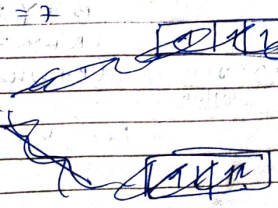
Square Planar

A CN = 4, ∴ ~~Tetrahedral~~

SFL Co+2 ~~d9~~

CN=4 → 27, → 9-2 = 7

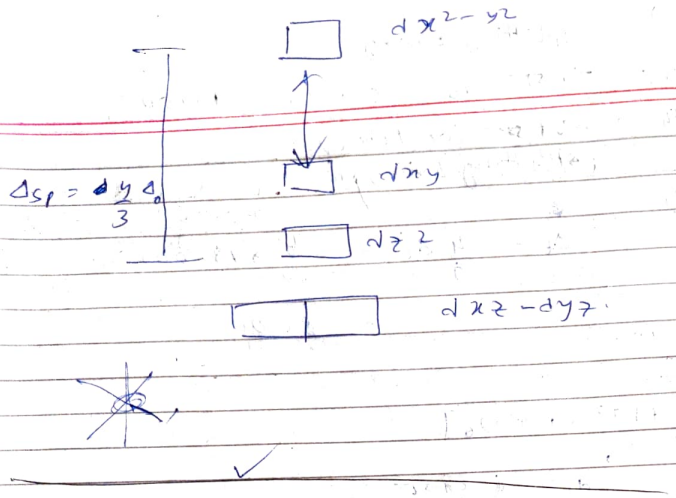
d7



SFL

Non axial orbital = 5

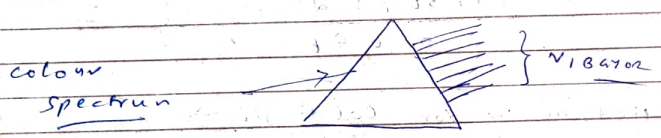
e⁻ in axial orbital = 2.



COLOUR OF COMPLEXES

1) Colour of compounds.

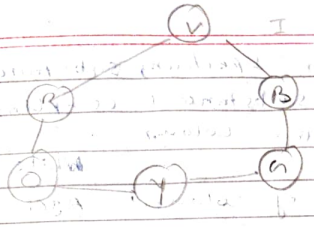
White Light.



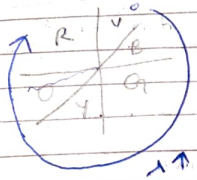
UV, VBGYOR, IR

- Primary colour = R, B, Y
(P)
- Secondary colour = R+B = V
(S) B+Y = G.
R+Y = O
- Tertiary colour = (P+S)C

ie, V + B = I
↑
Indigo



Color Wheel



- Range of Red is largest

NEUTRAL COLOUR

White → All colour are present
Black → All colour are absorbed
Grey → combination of two colour.

Complementary colour Relationship

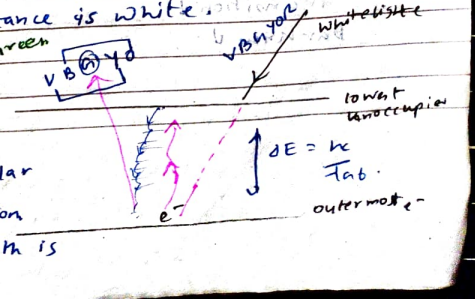
R + G
B + O
V + Y
→ Grey

- Pair of colour which neutralise each other

White ↔ Black
Red ↔ Green
Blue B ↔ Orange
V → Yellow
Violet

COLOUR THEORY.

- When all colours are absorbed, no colour present on surface of substance, substance become black
- When all colour are reflected, no colour is absorbed substance is white.



⇒ When white light ~~applied~~ applied on a substance
it's ~~loosely~~ ~~or absorbed~~ outermost e⁻ particular absorb wavelength for excitation
If absorb wavelength is

related to colour spectrum substance is coloured and colour of substance is complimentary colour of absorbed colour

1) comparison of colour.: AgCl (white) AgBr (Pale Yellow) AgI (Yellow) → darkness ↑

Gap ↑ White (∵ N⊗ abs)

2) Match the colour:

4 compound ⟷ 4 colour

Sunata Chattopadhyay

3) Learn colour of particular compounds.

4) Reason of Colour

5) Can't Predict

Reason of Colour (Type of Transition)

Intra-atomic	Intramolecular	Interatomic
Complexes	For Halogens (HOMO-LUMO transition).	Charge transfer
d-d transition		Momentary redox
Self excitation		1) LMCT: Ligand to Metal, $A \xrightarrow{-y} M^{+x}$
Transition ↓		2) MLCT: Metal to Ligand, $M \rightarrow L$
Darkness ↓		3) MMCT: $M' \leftrightarrow M$
		transition ↑
		Darkness ↑

1) d-d - transition:

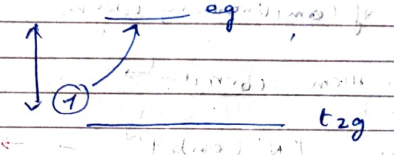
→ due to splitting of d-orbitals.

- $CuSO_4$ Anhydrous is white, while hydrated $CuSO_4 \cdot 5H_2O$ is blue.
- In presence of H_2O splitting of d-orbitals take place,

→ $FeSO_4 \cdot 7H_2O \xrightarrow{\Delta} FeSO_4$

Green → White.

→ For octahedral



∴ Absorbed colour (λ) $\propto$ $\frac{1}{\text{Splitting Energy}}$

→ λab of $[Ni(NH_3)_6]^{2+}$ < $[Ni(H_2O)_6]^{2+}$

Ammonia Complex → both Ni^{2+}, Cu^{2+} Blue.

Δ_0 | $NH_3 > H_2O$

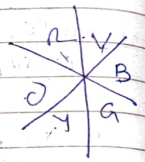
colour → Blue, Green

compliment → Orange, Red

(λab) ↓ ↑

Q) Match Correctly.

A) $[Co(CN)_6]^{3-}$	→	(i) Violet
B) $[Co(en)_3]^{3+}$	→	(ii) Green
C) $[Co(NH_3)_6]^{3+}$	→	(iii) Blue
D) $[Co(H_2O)_6]^{3+}$	→	(iv) Yellow



Δ_o of

$CN > en > NH_3 > H_2O$

$\therefore$ λ_{ab} : $CN^- < en < NH_3 < H_2O$

of complimentary colour.

Match them correctly → Colour of Complexes

(A)	$[Ni(en)_3]^{2+}$ →	(P) Violet
(B)	$[Ni(en)_2(H_2O)_2]^{2+}$ →	(Q) Violet–Blue
(C)	$[Ni(en)(H_2O)_4]^{2+}$ →	(R) Blue
(D)	$[Ni(H_2O)_6]^{2+}$ →	(S) Green

Now

Δ : A > B > C > D

λ_{ab} : A < B < C < D

↓	↓	↓	↓	
Y	O–Y	O	R	

Try. V V–B B, G.

Note: Color matching question always λ_{ab} & – कितना relate करता है।

Now

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

So, darkness / No. of transitions

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

① ⇒ When square planar complexes are colourless / Pale Yellow.

$\Delta \uparrow$ $\lambda_{ab} \downarrow$ (gem-violet/UV)

λ_{abs} in ↓

And colour = Yellow.

② ⇒ $CoCl_4^{2-}$ is intense blue, while $[Co(H_2O)_6]^{2+}$ is light pink

③ ⇒ octahedral cyano complexes are Pale Yellow generally

$K_4Fe(CN)_6$ / $K_3Fe(CN)_6$ → Pale Yellow.

CN^- is strongest ligand

Δ_{max} ↑ → λ_{ab} min (complementary)

i.e., UV/Violet

④ d^0, d^{10}, (d^5 – WFL) (d–d transition is not possible.)

d^5 → Symmetrically filled

d^{10} → Fully filled, No space

No e^-

LMCT & MLCT, written (part) under Ionic Compounds.

Color of ions in aq. Medium

1) S/p block cation →

has inert gas config.

No splitting ✗

∴ Colourless

2) d-Block →

Except → d^0, d^{10} | coloured

d^1 – d^9

d–d transition → except d^5-WFL, LMCT,

3) f-block cation.

except f^0, f^{14} | → All coloured

↓

f–f transition

d^0, d^{10} → colourless.

Fe^{3+} (aq) → pale yellow.	Fe^{2+}, Ni^{2+} → Green	d^1 & d^9 → Blue
	Cu^{2+}, Cr^{2+} → Blue.	(Ti^{+3} → Violet)
	Mn^{2+}, Co^{2+} → Pink light	d^2 & d^8 → Green.

But, Cr^{3+} (aq) in chemical rxn → Green

coz, $[Cr(H_2O)_5SO_4]^+$

Cr^{3+} (aq) in pure → VIOLET $[Cr(H_2O)_6]^{3+}$

Aq. medium only H_2O is ligand,

d^5-WFL → given colour due to LMCT

Ligand to Metal Charge Transfer (Polarization)

(1) d^1–WFL

F^- H_2O OH^- CH_3COO^- SCN^- transition ↑

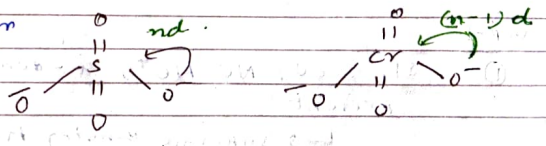
polarizability ↑ darkness ↑

FeF_6^{3-} colourless | $Fe(H_2O)_6^{3+}$ Pale-Yellow | $[Fe(OH)(H_2O)_5]^{2+}$ Yellow Brown

$Fe(CH_3COO)_6^{3-}$ Red | $Fe(SCN)_6^{3-}$ Blood Red.

(2) d-block oxoanions are coloured while p-block oxoanions are colourless

Eg SO_4^{2-} colourless | CrO_4^{2-} coloured.



More ΔHrn

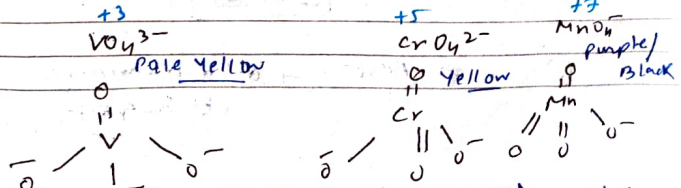
ΔHrn on e⁻ of O⁻ ↑

Polarization ↑

Intensity ↑ Darkness ↑

- H_2SO_4 (aq) soln is colourless
- H_2CrO_4 (aq) " " pale-Yellow

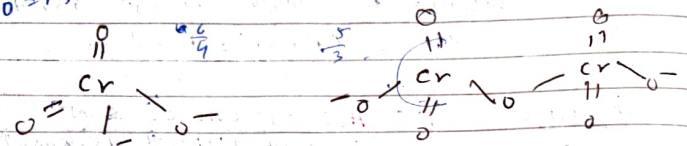
Eg



+ve charge on CAT ↑, polarization ↑

Intensity ↑ Darkness ↑

Q1 CrO_4^{2-} (+6) $\quad Cr_2O_7^{2-}$ (+6)



Yellow $\quad$ orange

Bond order ↑

Dist. b/w Cr–O ↓.

Transition ↑ Darkness ↑.

Summary How to identify which type.

Given :– [< formula + Ligand >].

Step-1

① If, CO, NO, NO^+, π-donor ligand present

↳ synergic Bonding take place

↓ [MLCT]

② If Not, Check d orbital config.

d^0, d^{10}, d^5 – WFL

↳ [LMCT]

③ Rest → d–d transition.

~~Charge Transf~~

Metal – Metal Charge Transfer.

MMCT

$K_4[Fe(CN)_6]$ (2+)

Fe^{+2} → $Fe_2[Fe(CN)_6]\downarrow$ White.

Fe^{3+} → $Fe_4[Fe(CN)_6]_3\downarrow$ Prussian Blue.

Zn^{2+} → $Zn_2[Fe(CN)_6]\downarrow$ White.

Cu^{2+} → $Cu_2[Fe(CN)_6]\downarrow$ Chocolate Brown.

Ag^+ → White ppt. ↓

$K_3[Fe(CN)_6]$ (+3)

Fe^{+2} → $Fe_3[Fe(CN)_6]_2\downarrow$ Turnbull's Blue.

Fe^{3+} → $Fe[Fe(CN)_6]$ Red colouration.

Ag^+ → Coloured ppt

Cu^{2+} → coloured ppt

$Fe^{2+} \leftarrow C\equiv\overset{\ominus}{N}: \rightarrow M^{+x}$

Fe^{2+} | White | MMCT ✗

P.P $Fe^{2+} > Zn^{2+}$ | Zn^{2+} | White | MMCT ✗

Fe^{3+} | Blue | MMCT ✓

$Fe^{2+} < Cu^{2+}$ | Cu^{2+} | choc. Brown | MMCT ✓

Ag^+ | White | MMCT ✗

2 for Prn Prussian Blue.

$Fe^{2+} \leftarrow C\equiv N \rightarrow Fe^{3+}$

Both are same after formation.

$Fe^{+3} \leftarrow :C\equiv N: \rightarrow M^{+x}$

↑ very high PD, itself take. Coloured Always.

Fe^{3+} | Fe^{3+} MMCT ✗ | ✓ LMCT

Fe^{2+} MMCT ✓

Cu^{2+} MMCT ✓

3 for Prn Ag^+ MMCT ✓ Turnbull's Blue

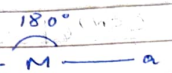
$Fe^{3+} \leftarrow C\equiv N \rightarrow Fe^{2+}$

PTO after 2 page

CN = 2

1) Linear.

Mab

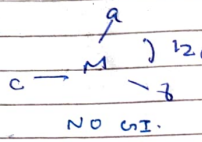


No GI.

CN = 3

Trigonal Planar

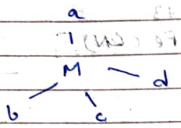
Same type band angle only.



NO GI.

CN = 4 Tetrahedral:

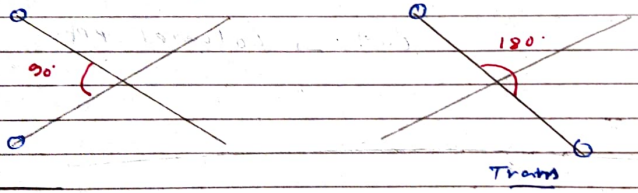
Mabcd



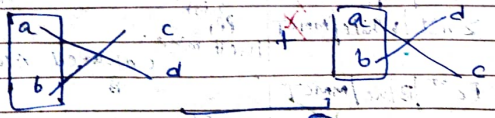
NO GI.

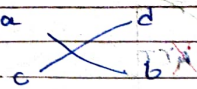
GI X

CN = 4 Square Planar.



(A) Mabcd



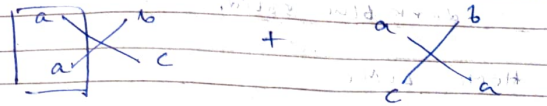


Trans = 1

Total = 3

Take 2 at a time.

(B) Ma2bc

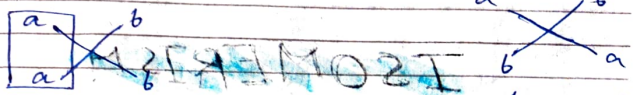


cis = 1

Trans = 1

Total = 2.

(C) Ma2b2

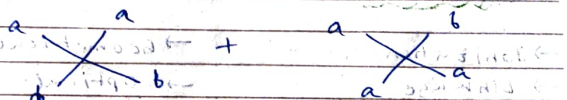


cis = 1

Total = 2

trans = 1

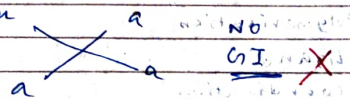
(D) Ma3b.



Both same.

Compound = 1, NO GI.

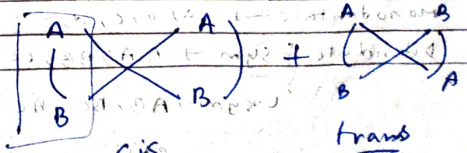
(E) Ma4.



NO GI

• Bidentate - ligand is always present in cis position.

(F) M(AB)2



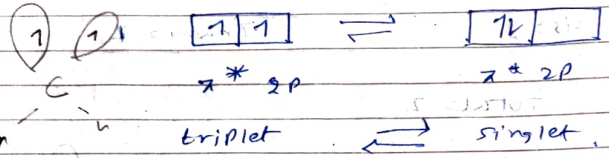
GI = 2

cis

trans

O_2 ≈ – Colourless gas, pale-blue liquid, dark blue solid.

HOMO = LUMO



ISOMERISM

Structural

→ Ionization
→ Linkage
→ Hydrated
→ Co-ordination

Extra
→ Polymerisation
→ Ligand
→ Coordination posi.

Stereo

→ Geometrical.
→ Optical.
↳ (Adv X)

GEOMETRICAL ISOMERISM

CN = 4 & 6

CMI = M

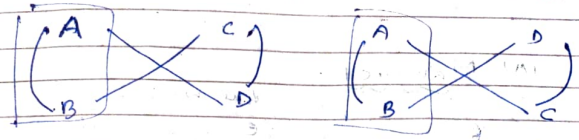
Monodentate → (a), b, c, d, - - -

Didentate { sym → AA, BB, CC (en, ox, dipy, phen, acac)
unsym → AB, BC, AC (gly, bcac).

Contd
Future.

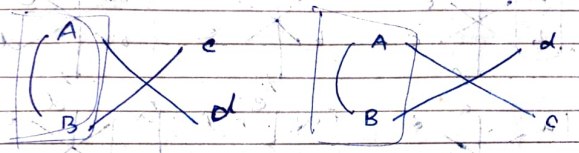
take one fix.

(G) M(AB)(CD).



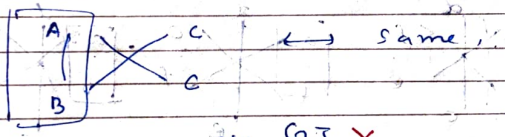
GI = 2

(H) M(AB)cd.



GI = 2

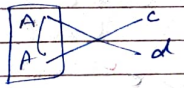
(I) M(AB)c_2



No GI ✗

(J) M(AA)cd
M(AA)(CD)
M(AA)c_2
M(AA)(BB)

both same in cis, trans

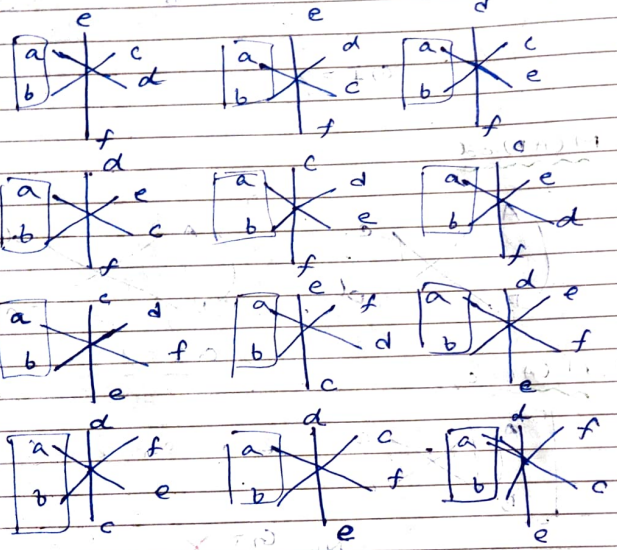


When sym. bidentate present in CN = 4, it will not show GI.

CN = 6 Octahedral.

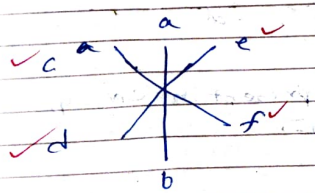
(A) M_{abcdef}.

line wise.



∴ 12 cis (a, b).

Now, (a, b) trans.



sq. planar type

↳ +3 GI

Trans

OA = 15 × 2 = 30

OIA = 0

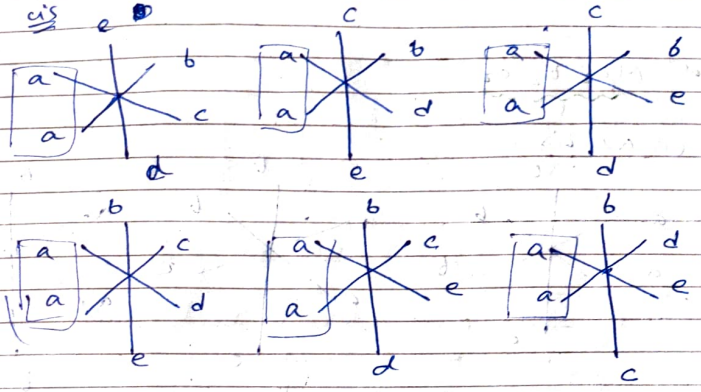
OI = 30

SI = 30

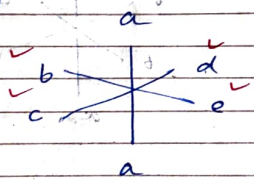
Total = 15

(b) M_{a_2bcde}

cis



Ans. trans

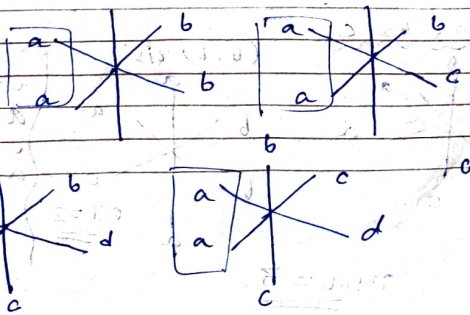


GI = 3

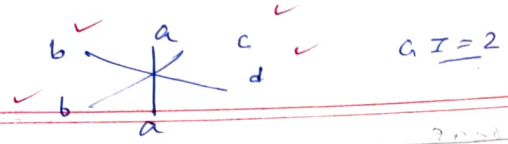
Total = 9

(c) $M_{a_2b_2cd}$

cis (a, a)



GI = 4

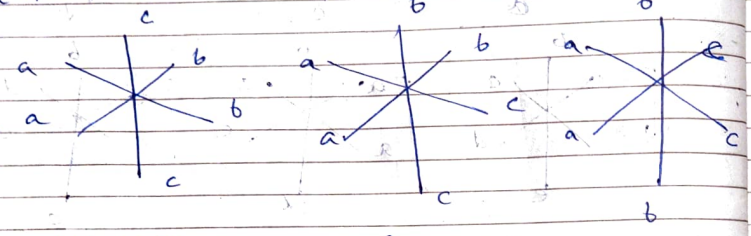


GI = 2

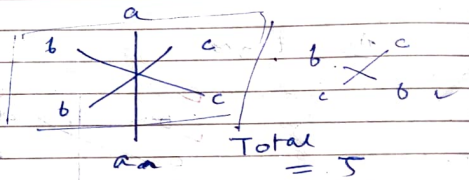
Total = 6

d) $Ma_2b_2c_2$

(a,a) cis.



(a,a) trans



GI = 2

Total = 5

GI = 5

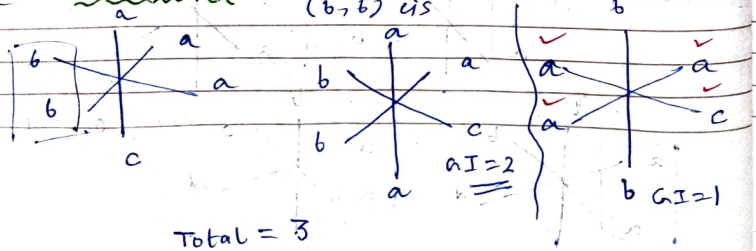
OIA = 4

OA = 2×2 = 2

OI = 6

SI = 6

(e) Ma_3b_2c



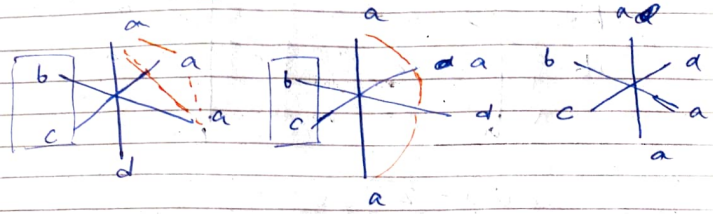
Total = 3

(f) Ma_3b

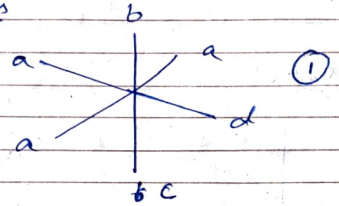
M(a3) xyz

cis isomer only 1.

cis



bc trans

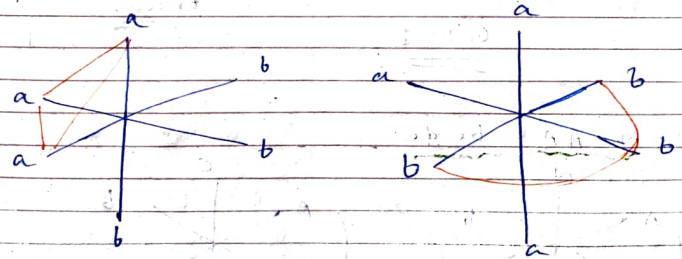


(1)

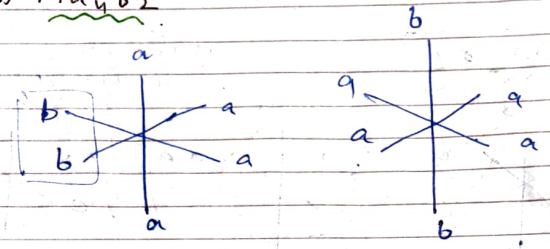
Total = 4

(g) Ma_3b_3

fac-Mer isomerism.

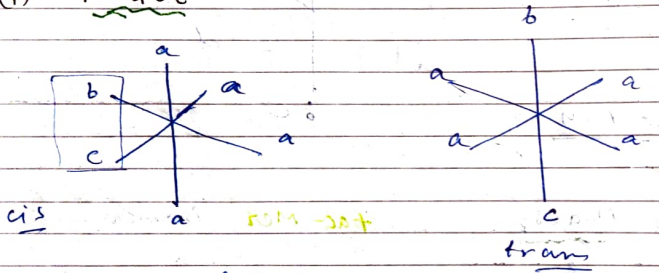


(h) Ma_4b_2.



GI = 2

(i) Ma_4bc

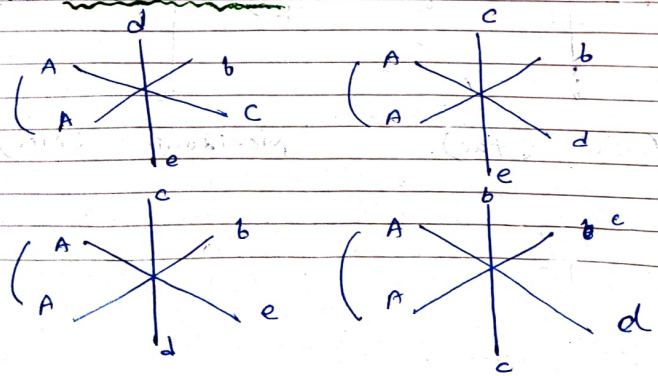


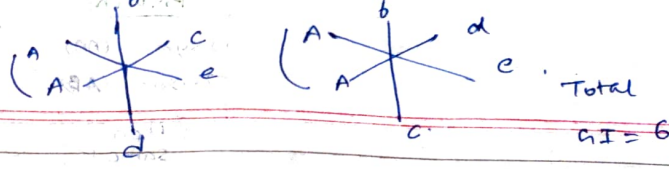
cis

trans

GI = 2

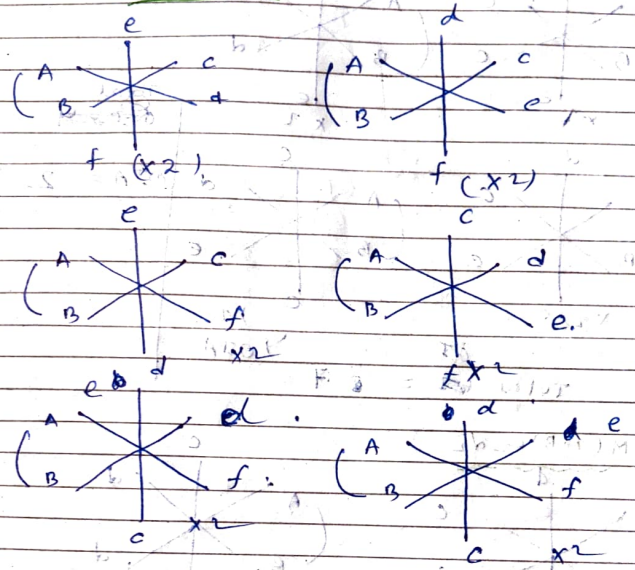
(j) M(AA) bcde





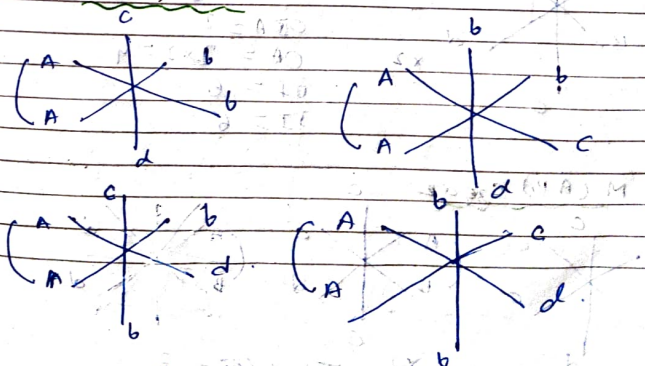
Total GI = 6

(k) M(AB) cdef.



Total GI = 12.

(l) $M_{(AA)}b_2cd$

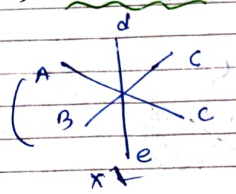


GI = 4

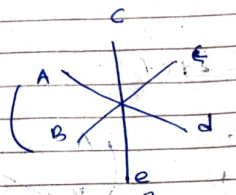
Priority

1) Sym (AA)
2) Unsym (AB)
3) 2 Mono same

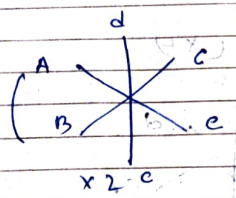
(m) M(AB)C_2de



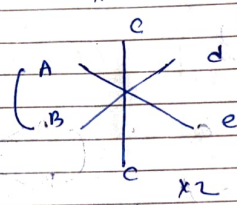
x1



x2



x2



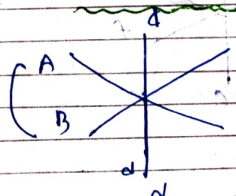
x2

Total
OIA = 2

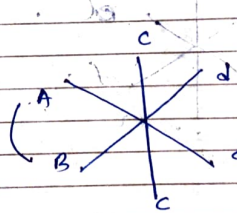
GI

Total = 7

(n) M(AB)C_2d_2



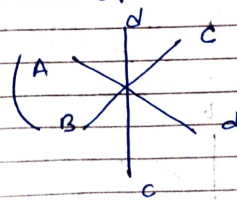
x1



x1

OIA

OIA



x2

GI

Total = 4

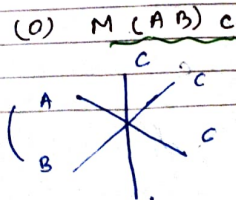
OIA = 2

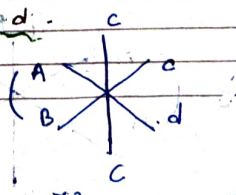
OA = 2×2 = 4

OI = 6

SI = 6

(o) M(AB)C_3d.



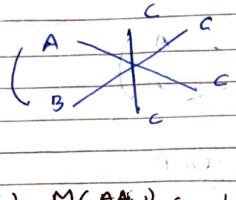


x2

Total = 3

GI

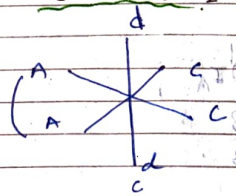
(p) M(AB)C_4.

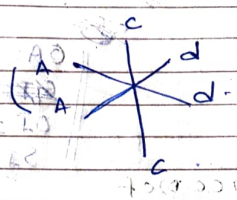


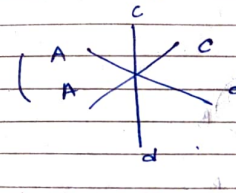
GI ✗

(1)

(q) M(AA)C_2d_2

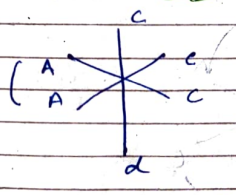


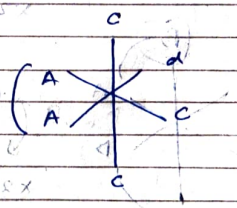




GI = 3

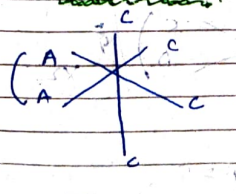
(r) M(AA)C_3d.





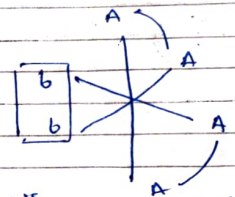
Total GI = 2.

(s) M(AA)C_4.

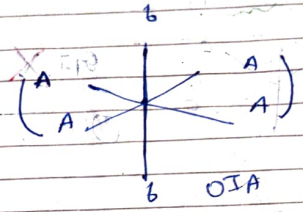


No GI. ✗

(t) $M_{(AA)_2 b_2}$



cis



OIA

$C_nI = 2$

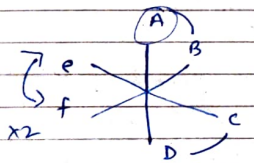
OA $= 2 \times 1 = 2$

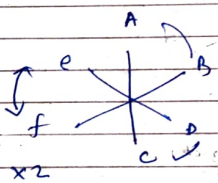
$OI_A = 1$

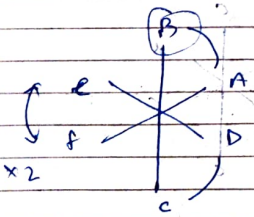
$OI = 3$

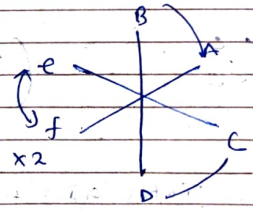
$SI = 3$.

(u) $M_{(AB)(CD)ef}$

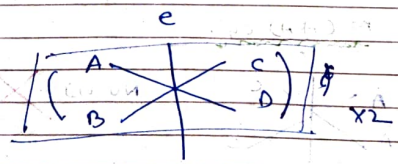








cis = 8



trans = 2

$\therefore$ Total $C_nI = 10$

OIA = 0

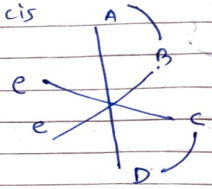
OA $= 10 \times 2 = 20$

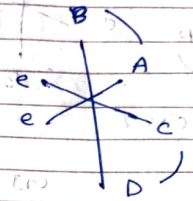
OI = 20

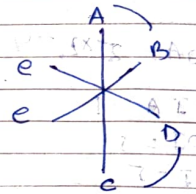
SI = 20.

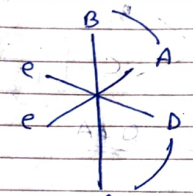
(v) $M_{(AB)(CD)e_3}$

cis





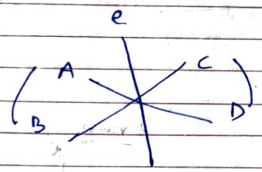


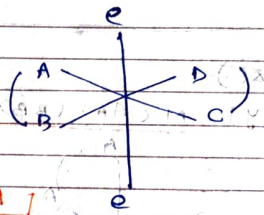


cis = 4

OA

Trans





Total $C_nI = 6$

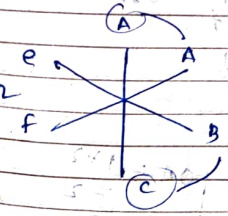
OIA = 2

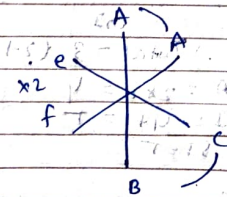
OA $= 4 \times 2 = 8$

OIA

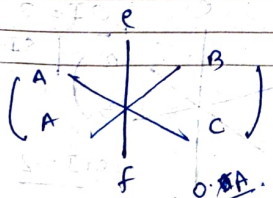
SI = 10, OI = 10.

(w) $M_{(AA)(BC)ef}$.





cis = 4



Trans = 1

Total = 5

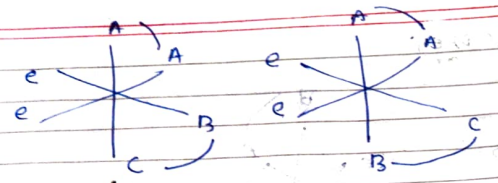
OIA = 0

OA $= 5 \times 2 = 10$

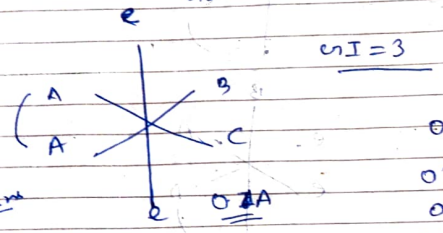
OI = 10

SI = 10

(x) M(AA)(BC) e_2



cis = 2



trans

OIA

mI = 3

OA = $2^{1} \times 2 = 4$

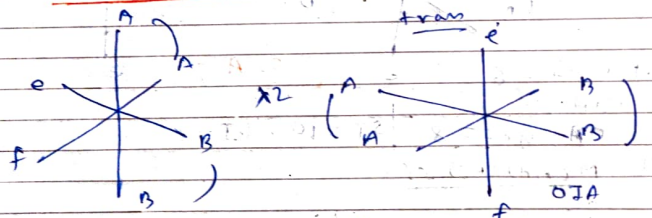
OIA = 1

OI = 5

SI = 5

~~(x)~~

(y) M(AA)(BB) ef.



cis = 2

OI

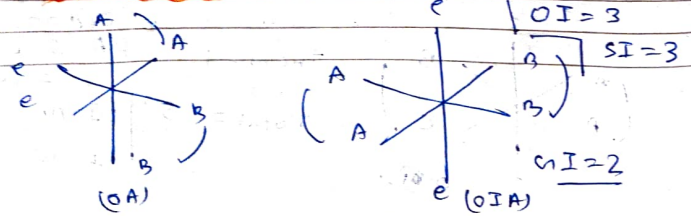
Total = 3 (2+1)

OA = 2×2 = 4

OI = 4+1 = 5

SI = 5

(z) M(AA)(BB)e_2



OA = 1×2 = 2

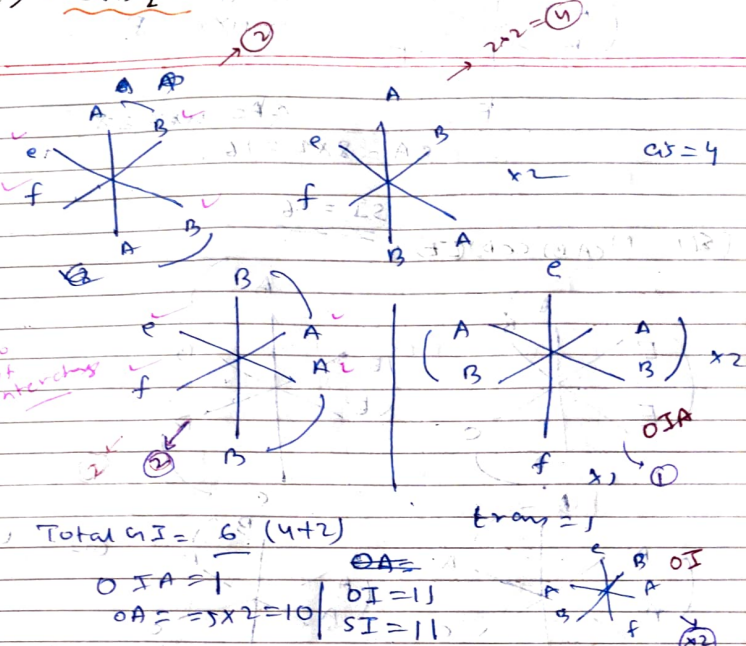
OI = 3

SI = 3

mI = 2

(OA) (OIA)

(a) M(AB)$_2$ ef.



cis = 4

Total mI = 6 (4+2)

OIA = 1

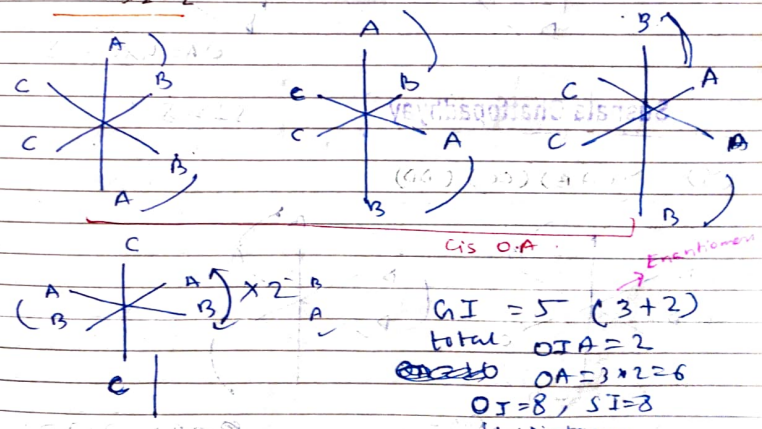
OA = 5×2 = 10

OI = 11

SI = 11

trans = 1

(b) M(AB)$_2$ C_2



cis OA

mI = 5 (3+2)

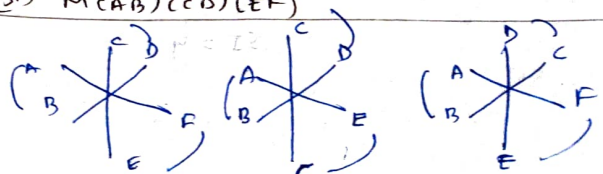
total OIA = 2

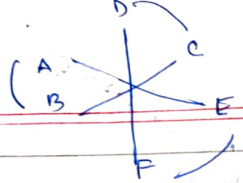
OA = 3×2 = 6

OI = 8, SI = 8

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(c) M(AB)(CD)(EF)





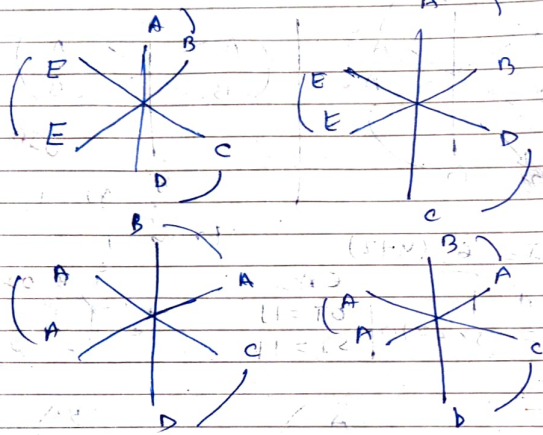
Total
$= 4 \times 2 = 8$.

~~QA = 4×2 = 8~~

$OA = 8 \times 2 = 16$.

$SI = 16$

(5) $M_{(AB)(CD)(EE)}$



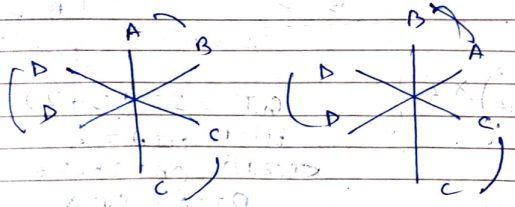
GI = 4

$OA = 4 \times 2 = 8$

$SI = 8$

Susnata Chattopadhyay

(3) $M_{(AB)(CC)(DD)}$

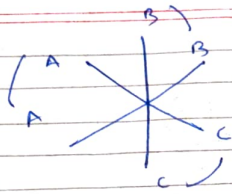


GI = 2

$OA = 2 \times 2 = 4$

$SI = 4$

(6) $M_{(AA)(BB)(CC)}$

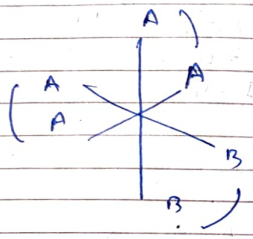


GI = 1

DI = 2

SI = 2

(2) $M_{(AA)_2(BB)}$

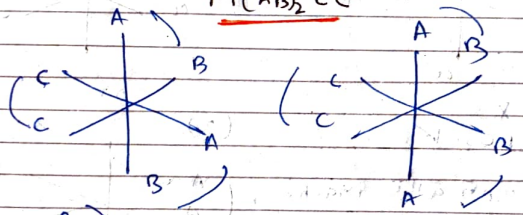


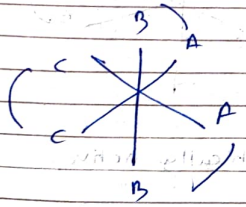
GI = 1.

OA = 2

SI = 2

(·) $M_{(AB)_2CC}$





GI = 3

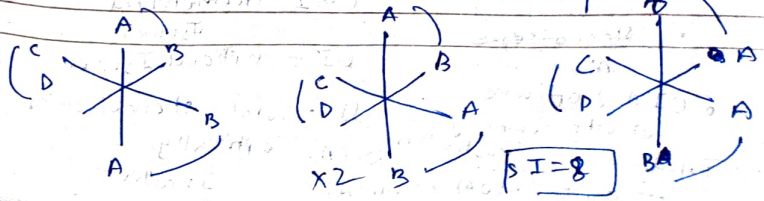
$OA = 3 \times 2 = 6$

$SI = 6$

(··) $M_{(AB)_2(CD)}$

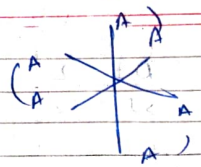
Total GI = 4

$OA = 4 \times 2 = 8$



SI = 8

(∴) $M(AA)_3$.



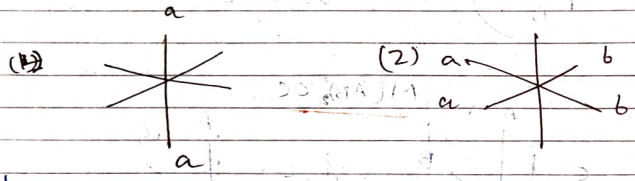
GI = 1.
OI = 2
SI = 2

(∴) $M(AB)_3$ as like Ma_3b_3.

fac-Mer GI = 2
OA = 2×2 = 4
= OI
SI = 4

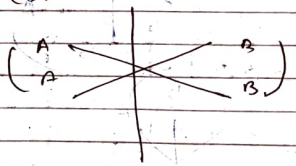
Optical Isomerism.

1) POS



All OI ✗
POS ✓
optically inactive,

(3)

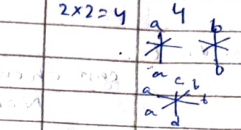
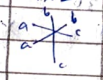
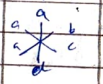


Note :-

- 3 bidentate is always optically active.
- 2 bidentate, CIS isomer is always optically active.

GI - Geometrical Isomer
OI = Optical Isomer
SI : Total stereoisomer
OIA : optically Inactive

- OIA & OA are diastereomer of each other.
∴ Total OI = n(OA) + n(OIA)

Type	GI	OA	OIA	OI	SI
$Mabcdef$	15	15×2	0	30	30
Ma_2bcde	6+3=9	6×2	3 (a a trans)	15	15
Ma_2b_2cd	6	2×2=4	4 	8	8
$Ma_2b_2c_2$	5	1×2 	4	6	6
Ma_3b_2c	3	0	3	0	3
Ma_3bcd	4	1×2 	3	5	5
Ma_3b_3	2	0	12	0	2
Ma_nb_2	2	0	2	0	2
Ma_nbc	2	0	2	0	2
$M(AA)bcde$	6	6×2	0	12	12
Notrans of Ma_2bcde					
$M(AB)cdef$	12	12×2	0	24	24
$M(AA)b_2cd$	4	2×2	2 	6 	6
$M(AA)c_2d_2$	3	1×2=2	2	4	4
$M(AA)c_3d$	2	0	2	0	2
$M(AA)c_4$	1	0	1	0	1
$M(AB)c_2d_2$	7	5×2=10	2	12	12
$M(AB)c_2d_2$	4	2×2=4	2	6	6
$M(AB)c_3d$	3	1×2=2	2	4	4
$M(AB)c_4$	1	0	1	0	1

CN = 4

- Square planar → POS ✓ around CMI.

but If ligand is OA, it can show OI.

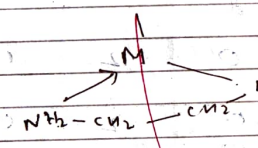
- Tetrahedral.

can show OI.

Non planar.

	Ma4	Ma3b	Ma2b2	Ma2bc	Mabcd
OI	X	X	X	X	✓

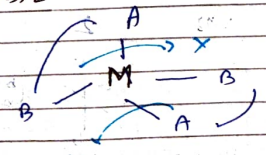
	M(AA)b2	M(AA)bc	M(AA)2	M(AA)(BC)	M(AA)(BB)
OI	X	X	X	X	X



POS ✓

When sym. bidentate present in CN = 4 (irrespective of geometry) it does not show SI.

M(AB)2



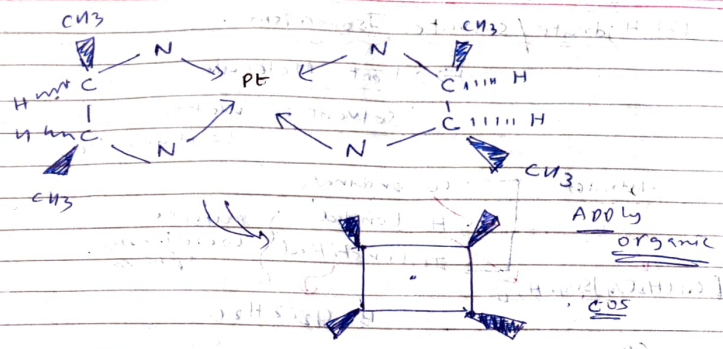
POS X

OA ✓

M(AB)CD	M(AB)Cd	M(AB)2
POS X	POS X	POS ✓
OA	OA	OI X



SHOT 11



STRUCTURAL ISOMERISM

1) Ionization Isomerism:

$[ML_x]A \leftrightarrow [ML_{x-1}A]L$

Complex having same molecular formula but furnishes different different ions, in aq. medium, are ionization isomer of each other. In such case ligand act as counter ion and counter ion act as ligand

They can be distinguished by

(I) Qualitative Analysis

(II) Conductivity Measurement

(III) ~~[Cr(NH3)6]~~

Now.

$[Cr(NH_3)_5Br]^{+2}SO_4^{-2}$ (A) $\xrightarrow{H_2O}$ SO_4^{-2}

$[Cr(NH_3)_5SO_4]^{+1}Br^{-1}$ (B) $\xrightarrow{H_2O}$ Br^{-1}

	$BaCl_2$	$AgNO_3$
(A)	White $BaSO_4\downarrow$	No ppt
(B)	No ppt	$AgBr\downarrow$ Pale Yellow

Conductivity

A > B

(2) Hydrate / Solvate Isomerism.

↳ Solvent Molecule

Solvent = water

↳ Hydrate.

Hydrates → Co-ordinate.
→ H-bonded
→ Interstitial
} outside coordination sphere

$[Cu(H_2O)_4]SO_4 \cdot H_2O$

$BaCl_2 \cdot 2H_2O$

Complexes having same Molecular formula but diff no. of water molecules inside or outside of coordination sphere. (H_2O is ligand) exchanged with counter ion.

$Cr \cdot 6H_2O \cdot Cl_3$

- $[Cr(H_2O)_6]Cl_3$ (A)
- $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (B)
- $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (C)
- ~~$[Cr(H_2O)_3Cl_3] \cdot 3H_2O$~~ ✗ Not isomer

complex should be ionic, for water to exist outside sphere.

can be distinguished by

(I) Conductivity measurement A > B > C

(II) Quantitative measurement.

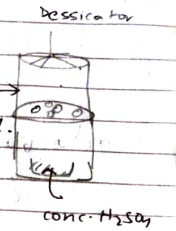
↳ when react with excess $AgNO_3$

A →	3 AgCl
B →	2 AgCl
C →	1 AgCl
D →	No ppt.

(3) Weight Loss measurement

or ~~Rxn~~ with conc. H_2SO_4.

Removal of non-coordinate water take place.



A → No weight loss

B & C → weight loss

$BaCl_2$

(3) Linkage Isomerism.

Requirement of Ambidentate ligand because it can be linked with CMI by diff. donor sites.

CN⁻, NO₂⁻

Eg. $[Pt(NH_3)_3(NCS)]^+ \leftrightarrow [Pt(NH_3)_3(SCN)]^+$

Ambidentate →

$CN^-, NO_2^-, NOS^-, SCN^-, OCN^-, SO_3^{2-}, S_2O_3^{2-}, C_2O_2S_2^{2-}$

Q) No. of linkage isomers of $[Pt(CN)_4]^{2-}$

donor site	C	N
	4	0
	3	1
	2	2
	1	3
	0	4

A) 5

Q) $[Pt(CN)_2(NCS)_2]^{2-}$

A) $3 \times 3 = 9$ linkage

Total No. of CI = $8 \times 2 + 1 \times 3 = 19$

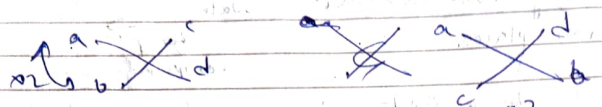
CN	NS
2	0
1	1
0	2

(1) Ma_2b_2 (3) (1) Ma_2bc (3)

(1) $Mabcd$

Q) Find total isomers of

$[Pt(NH_3)(H_2O)(CN)(Cl)]$



CI = 3.

linkage NC + CN → ②

OI = 0.

Total = 3 × 2 = 6

Q) Coordination Isomerism

This type of isomerism arises in complex contain complex cation + complex anion (2 diff coordination sphere).

When ligand or group of ligand present in diff-diff coordination sphere Complex are coordination isomers of each other.

[ ][ ] ← This type.

Eg - $[Ag(NH_3)_2][Ag(CN)_2]$

↳ $[Ag(NH_3)(CN)][Ag(NH_3)(CN)]$

diff + diff exist.

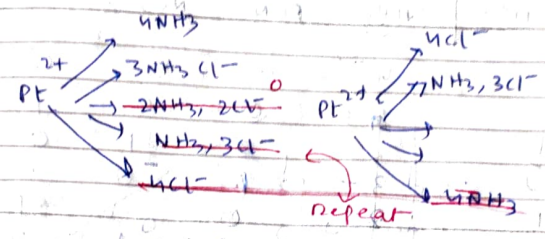
but $[Ag(NH_3)_2][Au(CN)_2]$

$[Ag(CN)_2][Au(NH_3)_2]$

CI = 2

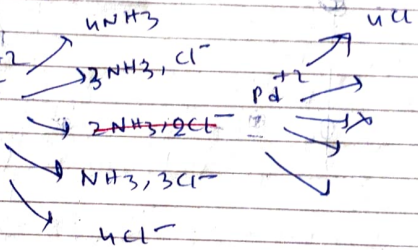
Reject the complex where '0' charge is forming one each.

3) $[Pt(NH_3)_4][PtCl_4]$



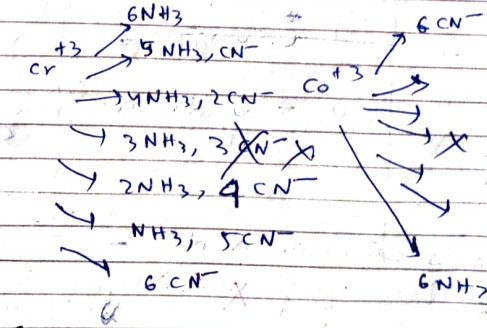
CI = 2

But, 4) $[Pt(NH_3)_4][PdCl_4]$



CI = 4

5) $[Cr^{+3}(NH_3)_6][Co(CN)_6]^{-3}$



CI = 6

~~$[Cr(NH_3)_6][Co(CN)_6]$~~

$[Cr(NH_3)_6][Cr(CN)_6]$

only 1st 3, rest repeat

CI = 3

only Cl ● Given SCN⁻, not take NCS⁻

⑦ $[Pt(NH_3)_4][Pt(SCN)_4Cl_2]$ 10 isomers count ✓

$+2 \quad +2$

$4NH_3$

$Pt^{2+} \rightarrow 3NH_3 \; 1Cl^- \; 1SCN^-$

$\rightarrow 2NH_3$ ✗

$\rightarrow 1NH_3 \rightarrow 3SCN^- \; 2Cl^-, 1SC$

$1Cl^-, 2SCN$

$0NH_3 \rightarrow 2Cl^-, 2SC$

$\rightarrow 1Cl^-, 3SCN$

$\rightarrow 0Cl^-, 4SC$

3+3+3 = 9

Total structural

1) $[Cr(NH_3)_6][Cr(CN)_6]$ ⑦

$+3 \quad +3$

$1 \times \quad 4$

$[Cr(NH_3)_5(CN)]$ ② $[Cr(NH_3)(CN)_5]$ ⑥ = 6×2 = 12

$[Cr(NH_3)_2(CN)_4]$ ⑤ $[Cr(NH_3)_4(CN)_2]$ ③ 5×3 = 15

15+12+7 = 34 ✓

N	
6	0
5	1
4	2
3	3
2	4
1	5
0	6

2021 Adv) a) Total No. of possible isomers for $[Pt(NH_3)_4Cl_2]Br_2$

① $[Pt(NH_3)_4Cl_2]Br_2$ ×2

② $[Pt(NH_3)_4ClBr]ClBr$ ×2

③ $[Pt(NH_3)_4Br_2]Cl_2$ ×2

Total = 6.00

[Ma₂b₂]

cis ① trans ②

[Ma₂bc]

① ②

Stability of complex

$M + nL \xrightarrow{K_f} ML_n$

$M + L \xrightarrow{K_1} ML$

$ML + L \xrightarrow{K_2} ML_2$

$\vdots$

$ML_{n-1} + L \xrightarrow{K_n} ML_n$

$K_f = K_1 \times K_2 \times K_3 \times \dots K_n$

Now for any rxn,

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

↑ Bond Formation. (Δ, CFSE)

↑ due to chelation.

Stability α Δ

α chelation.

$Ni(H_2O)_6^{2+}$

en → $[Ni(en)(H_2O)_4]^{2+} + 2H_2O$ (1)

2en → $[Ni(en)_2(H_2O)_2]^{2+} + 4H_2O$ (2)

3en → $[Ni(en)_3]^{2+} + 6H_2O$ (3) ↑ Most stable.

Δ S α Δ (moles) α No. of rings.

No. of ring 1 < 2 < 3

Δn 1 < 2 < 3

Eg:- $NiCl_4^{2-} < PdCl_4^{2-} < PtCl_4^{2-}$ (down the group)

∴ stability α Δ.

→ $[Fe(NH_3)_6]^{2+} < [Fe(NH_3)_6]^{3+}$

α charge.

→ $Co(CN)_6^{3-}$ (A) $Co(NO_2)_6^{3-}$ (B) $Co(en)_3^{3+}$ (C) $Co(C_2O_4)_3^{3-}$ (D)

$[Co(NH_3)_6]^{3+}$ (E) $[Co(H_2O)_6]^{3+}$ (F)

A > C > D > B > E > F stability.

↑ C-donor ↑ chelation ↑ strength of ligand α Δ α stab.

Note

For same (MI, C- donor > chelation > for same no. of ring strength of ligand.

- $[Co(edta)]^-$ < $[Co(en)_3]^{3+}$

Δ stability 5-ring > 3-ring.

But stability of $[Fe(ox)_3]^{3-} > [Fe(CN)_6]^{3-}$

↑ As ring ↑, chelation

Stability of Metal carbonyls is explained by EAN rule.

EAN Rule (18 e⁻ like octet)

Acc. to Sidgwick (MLI tries to complete its valence shell ((n-1)d, ns, np) with 18e⁻ to gain stability (e⁻ equal to next inert gas config.)
This rule is also known 18e⁻ rule.

3d → Kr → 36e⁻
4d → Xe → 54e⁻
5d → Rn → 86e⁻.

Q) Which of them follow EAN rule?
A) $Cr(CO)_5$ B) $Ni(CO)_4$ C) $Co(CO)_4$ D) $Mn(CO)_5$
24+10 = 34 | 28+8 = 36 | 27+8 = 35

This rule is applicable for metal carbonyls.

Q) For $x M(CO)_z$ for Make 36e⁻

Sc Ti V Cr
2 2 2 2 2 3 ½ 4
f → 6×2
+12

$Cr(CO)_x$, $Fe(CO)_y$, $Ni(CO)_z$

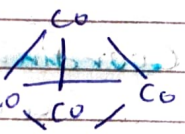
$x = 6$

$24 + 10 = 36$ | $y = 5$ | $z = 4$
$10 = 5 \times 2$

Now Diff. Properties of Mono nuclear Metal Carbonyl.

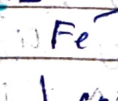
Tetramer

+e⁻
33 → 1 → 0 / Trimerise
34 / oxidising Agent
35 → Dimerisation (1-1 pair)
36 → Stable
37 / Reducing Agent.
-e⁻



Eg:- 33 • $Co(CO)_3$ → $Co_4(CO)_{12}$ (stable)
6 M-M bond.

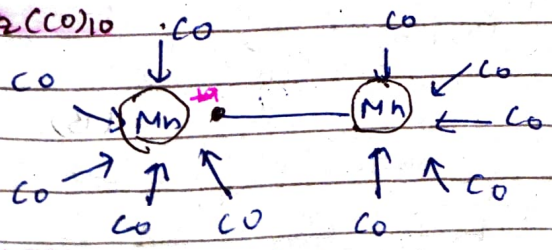
34 • $Fe(CO)_4$ → $Fe_3(CO)_{12}$



35 { $Co(CO)_4 \rightarrow Co_2(CO)_8$ | Co–Co
$Mn(CO)_5 \rightarrow Mn_2(CO)_{10}$ | Mn–Mn.

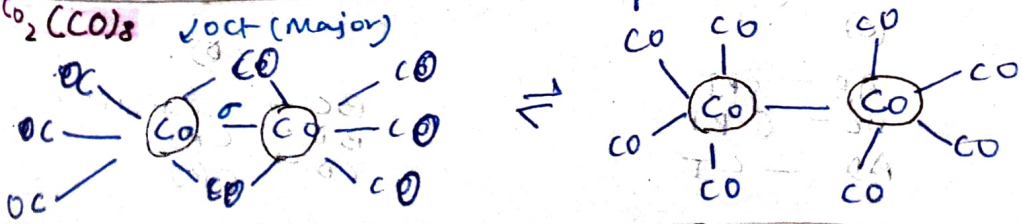
$Mn_2(CO)_{10}$

Oct =



Collectively 70e's are present in both Mn
Individually → 36e⁻ in a Mn.

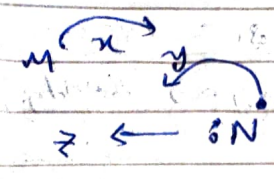
$Co_2(CO)_8$ ↓ oct (Major)



NO = 3e⁻ donor.

NO⁺ 2e⁻ donor

15eT



14e⁻

i.e., 3 CO can be replaced by 2 NO

3 CO = 3×2 = 6e⁻

2 NO = 2×3 = 6e⁻

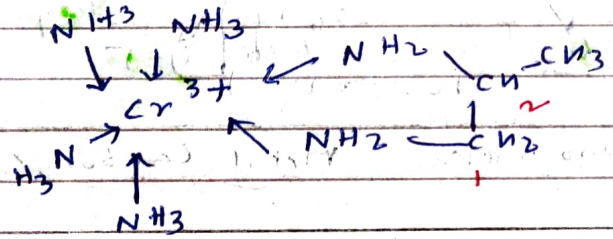
$Fe(CO)_5 \xrightarrow{-3CO} Fe(CO)_2(NO)_2$ (+2NO)

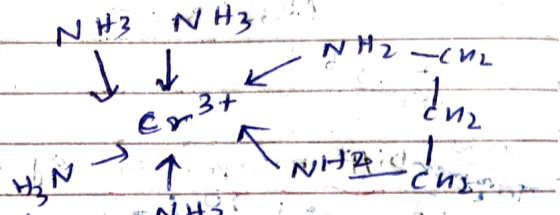
$Cr(CO)_6 \xrightarrow{-3CO} Cr(CO)_3(NO)_2$ (+2NO) → $Cr(NO)_4$

out of syllabus

Ligand Isomerism.

When ligand itself can show position isomerism. compound containing such ligand can show ligand isomerism.





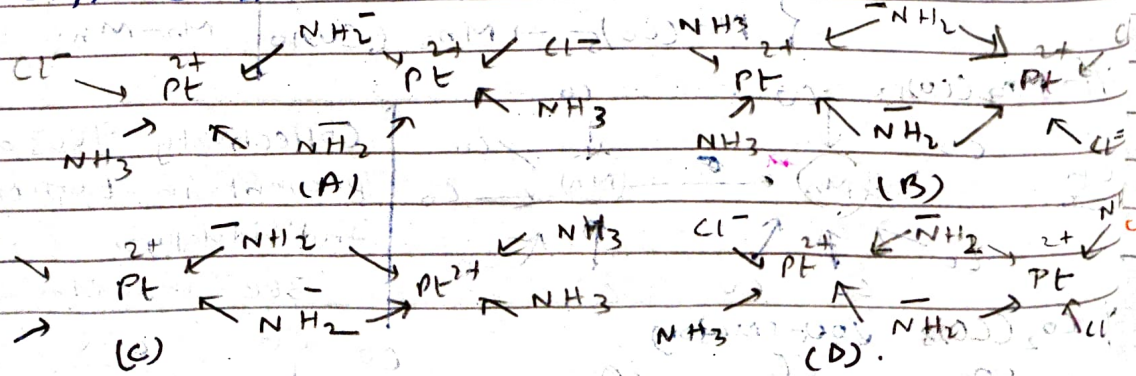
Coordination Position Isomerism (CPI)

coordination sphere → 1 CMI

2 Mononuclear → 2 CMI

Polynuclear.

This type of isomerism arises in polynuclear complexes, ligand or group of ligands are coordinated with diff-diff CMI in a co-ordination sphere.



(A) (B) (C) (D)

AB - CPI

AC - CPI

AD - CPI

BC - Identical

BD - CPI

CD - CPI

Polymerisation Isomerisation. → Not a true Isomerisation

diff Molecular formula but same empirical formula.

$[Pt(NH_3)_2Cl_2]$ → 1:2:2

$[Pt(NH_3)_4][PtCl_4]$ → 2:4:4

$[Pt(NH_3)_3Cl]_2[PtCl_4]$ → 3:6:6

$M L_x' L_y''$

↑ Neutral ↑ Anionic

Naming of Polynuclear complex. >/2 CMI

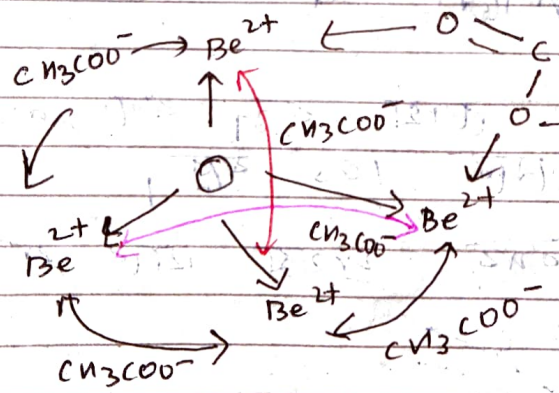
Ligands which join two or more CMI are represent with prefix — μ_n (where n = No. of CMI) are called bridging ligand.

(A) Ammine chloro platinum(II) : n=2 → μ_2/μ

prev pg. di-μ-amido ammine chloro platinum(II) : n=4 → μ_4

- di μ-amido (ammine chloro platinum(II))
- Bis (μ-amido ammine chloro platinum(II))

$[Be_4O(CH_3COO)_6]$ Hexa-μ-acetato-μ_4-oxo-tetra beryllium (II)



Type of complexes.

1) On the basis of variety of ligands.

Homoleptic → Same type of ligands.

Heteroleptic → diff type of Ligand.

σ complex

- Brown Ring complex → $[Fe(H_2O)_5NO]SO_4$ (+1, +1)
- Sodium Nitro prusside $Na_2[Fe(CN)_5NO]$
- Cis Platin (Anti cancer) → cis $[Pt(NH_3)_2Cl_2]$
- Wilkinson ~~Catty~~ Catalyst → $[Rh(PPh_3)Cl]$
- Fischers, salt → $K_3[Co(NO_2)_6]$

2) on the basis of donor type.

1) σ complex → only lp donor present

2) π-complex — Atleast one π-donor present
Eg- ferrocene, Zeise's salt.

3) on basis of stability.

1) Perfect Complex — Stable wrt particular reagent.

2) Imperfect Complex — Unstable wrt particular reagent.

$CuSO_4 + KCN \longrightarrow CuCN + CCN_2 \uparrow$ (perfect wrt to H_2S)
$\xrightarrow{KCN} K_3[Cu(CN)_4] \xrightarrow{H_2S}$ No ppt.

$CdSO_4 + KCN \rightarrow Cd(CN)_2 \downarrow$ Imperfect wrt to H_2S.
$\xrightarrow{KCN} K_2[Cd(CN)_4] \xrightarrow{H_2S} CdS \downarrow$
Yellow.

যদি সবটা দিয়ে
কোনো Question আসে
যদি
চেষ্টা করবে, লক্ষ্য
সমাধান করে 10s বসে।
অবশ্যই প্রথম থেকে পড়বে।

Susnata Chattopadhyay