Basics of Co-ordination Compounds

Introduction:-

* Addition Compounds:-

→ Compounds formed by combination of two or more stable compounds in a fixed stoichiometry is called as addition compounds or molecular compounds.

$KCl + MgCl_2 + 6H_2O \xrightarrow{Cool} KCl \cdot MgCl_2 \cdot 6H_2O$ (Carnalite)
→ in $MgCl_2$ production
→ source of Potash for fertilizer

$4KCN + Fe(CN)_2 \longrightarrow 4KCN\,Fe(CN)_2$ (Light yellow)
Percussor in Prussian blue pigments, anticaking agent in food Ind.
Potassium ferro cyanide $\longrightarrow K_4[Fe(CN)_6]$

$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
(Potash Alum फिटकरी)

$2NH_4 + Fe(SO_4)_2 + 6H_2O \longrightarrow (NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$
Mohr salt
Used in titration of oxidizing Agents & as a stable source of ferrous ions.

Types of addition Compounds:-

① Double Salt

→ The Compounds which are stable in solid state but dissociate into simple ions completely when dissolved in water, are known as double salt

e.g $KCl\,MgCl_2 \cdot 6H_2O(aq)$

$K^+ + Cl^- + Mg^{2+} + 2Cl^- + 6H_2O$

Loose identity when dissolved in water completely.
Gives test of all ions. etc
e.g. Potash alum etc.

② Complex Salt / Complex / Co-ordination Compounds

→ The addition compounds which do not dissociates completely in to constituent ions, are known as co-ordination or complex compounds.

→ Some of the ions or molecules Lose their identity on Solution.

e.g. $4KCN + Fe(CN)_2 \rightarrow 4KCN\,Fe(CN)_2$

$\longrightarrow K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$ complex anion

(Fe^{2+} but $+ 6CN^-$) Not possible here.

iin₂ → one ionic bond.

→ Here, $K_4[Fe(CN)_6]$, does not give CN^- Test.

e.g. $[Cu[NH_3]_4]SO_4 \rightarrow [Cu(NH_3)_4]^{2+} + SO_4^{2-}$

does not give Cu^{2+} test. → Complex cation.

* Terms used in Co-ordination Compounds:-

(i) Central Atom/Ion:- In a Co-ordination entity, the atom/ion to which a fixed no. of ions/groups are bound in a definite geometrical arrangement around it, is called central atom or ion.

e.g. $K_4[Fe(CN)_6] \longrightarrow 4K^+ [Fe(CN)_6]^{4-}$

Here O.S of Fe = +2

So, Fe^{+2}, C.N. = 6

So $[Fe^{2+}(CN^-)_6]^{4-}$, Here Fe^{2+} acts as Central atom/ion.

e.g. $[Cu(NH_3)_4]SO_4 \rightarrow$ Cu Centre atom.

$[Cr(H_2O)_6]Cl_3 \rightarrow$ Cr "

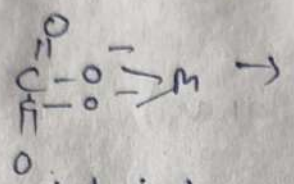
(ii) Ligands:- The ions or molecules bound to the central atom/ion in the co-ordination entity are called ligands. e.g. CN^-, $\ddot{N}H_3$, $H_2\ddot{O}$ → are ligands in above examples.

(iii) Co-ordination Number:- The no. of co-ordinate bonds formed by the central metal atom/ion, with ligands e.g. 6 in all above cases.

CN^- & H_2O & 4 NH_3.

e.g. $(Cu(NH_3)_4)SO_4$ – C.N. = 04 , $NH_3 \rightarrow$ one Co-ordinate bond.

$[Co(C_2O_4)_3]^{3-}$



$\rightarrow$ CN = 3 × 2 = 06 , One $C_2O_4 \rightarrow$ 2 Co-ordinate bond makes

Here CN = 6.

(Oxalate ion)

Imp: So C.N. depends on ligand also.

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* 3d series elements in +3 state $\rightarrow$ C.N. $\Rightarrow$ 6
* 3d series elements in +2 " $\rightarrow$ 4/5/6
  $Ni^{2+} \rightarrow Cl^-, CN^-$ = CN $\Rightarrow$ 4
  $[Ni(H_2O)_6]^{2+} \Rightarrow$ C.N $\Rightarrow$ 6.
* $Ag^+ / Au^+ \Rightarrow$ C.N. $\rightarrow$ 2
* Imp: $Pt^{2+} / Pd^{2+} / Ag^{3+} / Au^{3+} \Rightarrow$ C.N = 4
* $Pt^{4+} / Pd^{+4} \Rightarrow$ C.N $\Rightarrow$ 6
* $Zn^{2+} / Cd^{2+} / Hg^{2+} \Rightarrow$ C.N $\Rightarrow$ 4.

learn & do fast Questions & also learn e^- Configuration.

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* Co-ordination Sphere :-

→ The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the Co-ordination sphere.

→ The ionisable groups are written outside the bracket and are called Counter ions.

$K_4[Fe(CN)_6]$

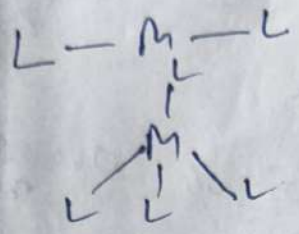
K^+, Counter ions

Co-ordination sphere.

* Co-ordination polyhedron :-

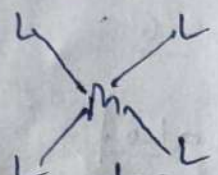
→ The spatial arrangement of the ligand's atoms which are directly attached to the central atom/ion defines a co-ordination polyhedron about the central atom.

e.g.



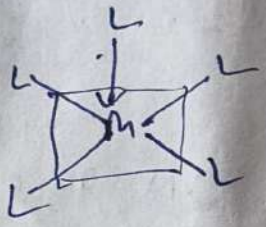
(linear)

(Tetrahedral)



(square planar)

(octahedral)



(Square pyramidal)
↓ Polyhedron.

* Oxidation No. →
→ The charge on central atom/ion if the all ligands are removed along with the e^- pairs that are shared with the central atom.

e.g. $K_4[Fe(CN)_6] \longrightarrow 4K^+ + [\underset{x}{Fe}(CN)_6]^{4-}$

CN^{-1}

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

$x = -4+6 = 2$, Fe^{2+}

e.g. $[Cu(NH_3)_4]SO_4 \longrightarrow \underset{O.N.}{Cu} = x + 0 = +2$, As SO_4^{2-}, $[Cu(NH_3)_4]^{2+}$, Cu^{2+}

$[Cr(H_2O)_6]Cl_3 \longrightarrow x + 0 = +3$, Cr^{3+}

$[Co(NH_3)_6]^{3+} \longrightarrow Co \rightarrow O.No \rightarrow x = 3$, Co^{3+}

$[Pt(NH_3)_2(Cl)_2] \longrightarrow x + 0 \times 2 + 2(-1) = 0$

$x = +2$, Pt^{2+}

* Homoleptic and Heteroleptic Complexes:-

→ Complexes in which a metal is bound to only one kind of donor groups, are known as homoleptic.

e.g. $K_4[Fe(CN)_6]$

→ Complexes in which a metal is bound to more than one kind of donor groups, are known as heteroleptic.

e.g. $[Pt(NH_3)_2(Cl_2)]$

* Classification of ligands:-

(A) On the basis of charge:-

* Neutral ligands:-

H_2O - Aqua

NH_3 - Ammine

Co - Carbonyl

No - Nitrosyl

CH_2-NH_2
CH_2-NH_2 — Ethylene diamine (Ethane-1,2-diamine) en.

donor atom

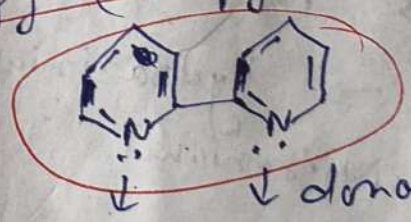
C_6H_6 - Benzene

$P(Ph)_3$ - Triphenyl phosphine

Py - Pyridine

* bpy (Bipyridine) ↓ donor atom

dpy (dipyridine)



↓ donor atom.

* Anionic ligands:-

Cl^- → Chloride / Chloro

Br^- → Bromide / Bromo

I^- → Iodide / Iodo

OH^- → Hydroxide / Hydroxo

H^- → Hydrido

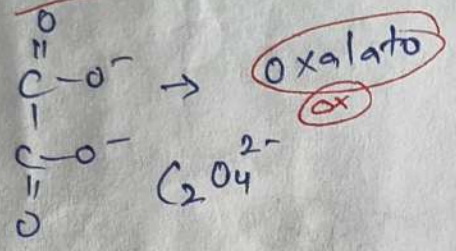
$CH_3-\underset{O}{C}-O^-$ → Acetato

NH_2^- → Amido

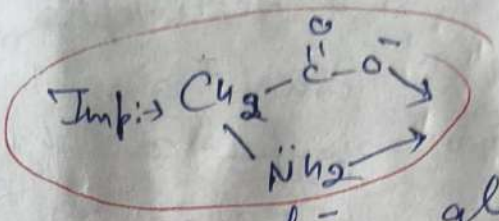
NH^{2-} → Imido

SO_4^{2-} → Sulphato

CO_3^{2-} → Carbonato

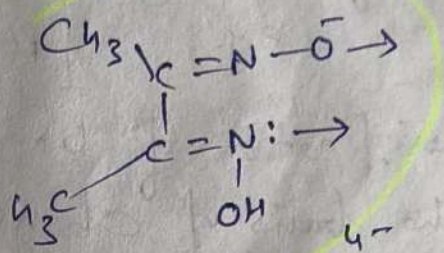


→ Oxalato (ox)

Imp:→ 

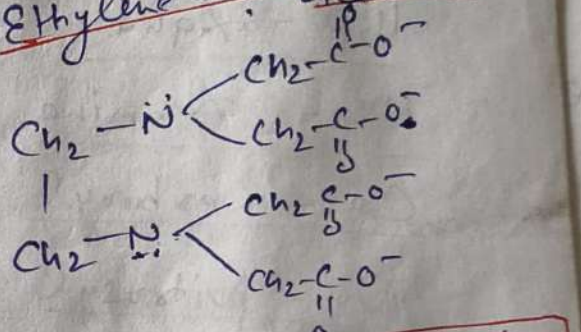
gly⁻ – glycinato

Imp:→ dmg → dimethyl glyoxamato



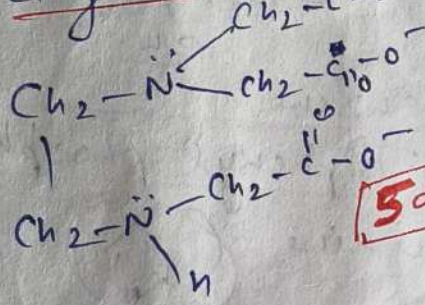
$EDTA^{4-}$

Ethylene diamine tetra acetato



6 donar sites

$EDTA^{3-}$ → Ethylene diamine triacetato)



5 donar sites

* Cationic ligands:- (ium) last π

NO^+ → Nitrosylium | nitrosonium

$NH_2-NH_3^{\oplus}$ → Hydrazinium

$NO_2^{\oplus}$ – Nitronium

Cl^+ → Chloronium

Br^+ → Bromonium.

(B) On the basis of denticity:-

→ No. of co-ordination bonds formed by one molecule of ligand, is known as denticity of that ligand.

a) Monodentate ligands:-

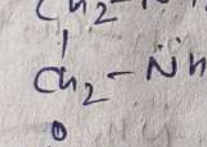
↳ one donor atom

e.g. H^-, OH^-, Cl^-, Br^-, NH_2^-, N^-H, N^-H_3, $H_2\ddot{O}$ etc.

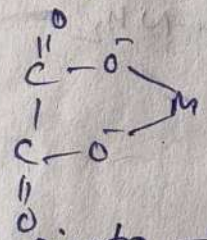
b) Bidentate ligands:-

↳ 2 donor atoms.

↳ 5/6/7 membered ring.

e.g. 

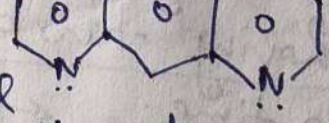
(en) — Bidentate ligand symmetrical also.

e.g. 

→ Symmetrical bidentate (chelate) (5-membered ring stable)

e.g. glycinato → Unsymmetrical bidentate ligand.

e.g. NH_2-NH_2 → Hydrazine (monodentate due to formation of unstable 3-membered ring) → may be neutral. acts as a bridging agent.

e.g. Phenanthroline →  is bidentate.

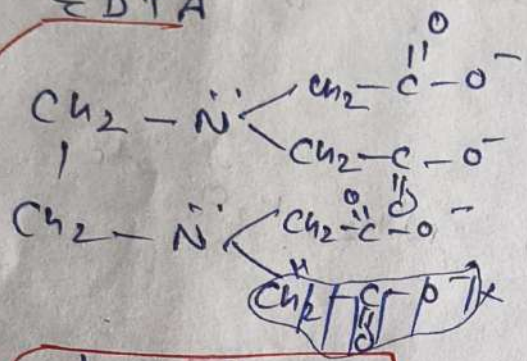
e.g. dmg. — unsymmetrical bidentate ligand. or didentate ,, .

e.g. bpy → symmetrical bidentate ligand.

(c) Polydentate ligand:-

e.g. more than two donor atoms, denticity > 2.

$EDTA^{3-}$



denticity = 5

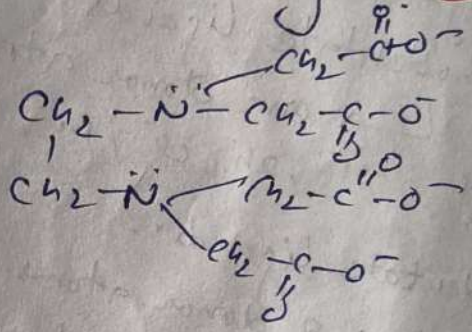
5 donor atom

5 Co-ordinate bond.

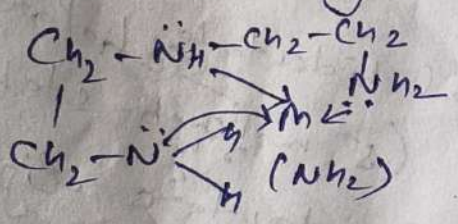
Similarly

Tell - $EDTA^{4-}$

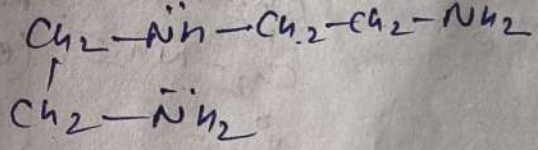
denticity = ? 6



e.g. dien (diethylenetriamine)



or



denticity = 3

e.g. $EDTA^{3-}$ / $EDTA^{4-}$

denticity = 5 denticity = 06.

d) Ambidentate ligands:-

→ ligands having two donor atoms but only one is used at a time. ← C≡N →

^{-}CN ← $\ddot{N}C^{-}$ ← $:NO_2^{-}$ ← ^{-}ONO

cyanido/cyano — Isocyanido/Isocyano — Nitrito-N (Nitro) — (Nitrito-O) (Nitrito).

(cyanido-C) [cyanido-N]

e.g. $\leftarrow SCN^{\ominus}$ Thiocyanato-S $\leftarrow NCS^{\ominus}$ Thiocyanato-N

$\leftarrow SO_3^{2-}$ Sulphito-S $\leftarrow OSO_2^{2-}$ Sulphito-O

$\leftarrow S_2O_3^{2-}$ Thiosulphato-S $\leftarrow OS_2O_2^{2-}$ Thiosulphato-O.

(e) Flexidentate ligands:- ligands having flexible denticity, which depends upon the nature of metal.

e.g. CH_3COO^-, NO_3^-, SO_3^{2-}, $S_2O_3^{2-}$ etc

Ex:- $EDTA^{4-}$

donor 2 N, 4 O-donor

denticity → 6

If 4 needed, 4 donor atoms can be used

6 " , 6 donor atoms can be used

e.g. CO_3^{2-} $\overset{O}{\overset{\|}{C}}-O^- \rightarrow$, $O^- \rightarrow$ — can donate one & two a/c to requirement

e.g. SO_4^{2-} $O^- - \overset{O}{\overset{\|}{S}} - O^-$, $\overset{O}{\overset{\|}{O}}$ → one and two donor a/c to requirement

monodentate ligand

e.g. $[Cr(NH_3)_5(SO_4)]Br$

O.S of Cr = $x + 0\times5 + (-2) = +1$

$x = +1+2$

$x = +3$, SO_4 → monodentate ligand.

$[Cr(NH_3)_4(SO_4)]Br$ Bidentate

$x + 0\times4 - 2 = +1$

$x = +3$

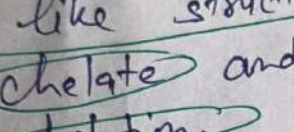
SO_4 → Bidentate ligand

* Chelating ligands / Chelation:-

→ Bidentate or polydentate ligands forms a ring like structure with central metal, called chelate and the phenomenon is known as chelation.

Provide extra stability.

chelate / chelating ligands.



(en)

effect ↑ (chelation effect)

5, 6, 7 - stable

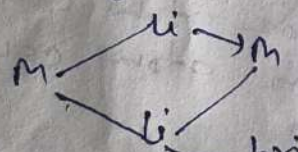
3-member - unstable.
↳ angle strain

e.g. $C_2O_4^{2-}$, dmg, gly, $EDTA^{4-}$ etc. no need to be symmetrical for chelation.

generally polydentate ligands are in this category

* Bridging ligands:-

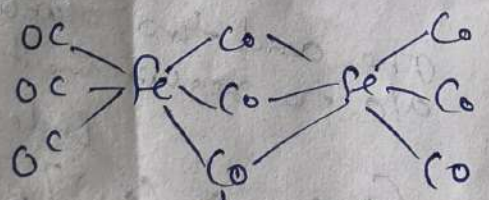
→ M_2L_2 → metal



bridging ligands.

monomuclear Co-ordination compounds is in JEE-Advanced. ✓

e.g.



Fe_2Co_9

↓ Bridging ligands

* Classical & Non-Classical ligands:-

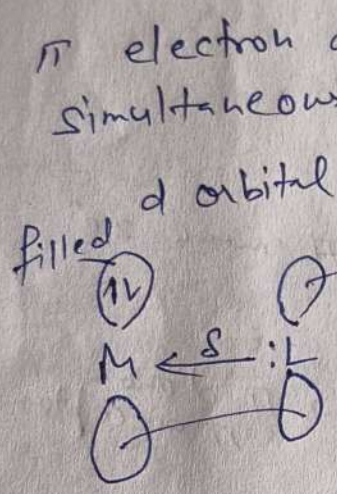
(i) Donate lone pair to the central metal and do not do any back bonding due to the absence of vacant d orbital or π^* MO in their valence shell.

$HO^- \xrightarrow{\sigma} M$

$H_3\ddot{N} \xrightarrow{\sigma} M$

$H_2\ddot{O} \xrightarrow{\sigma} M$ – Co-ordinate bond

→ Non-classical ligands: Donate either lone pair or π electron density to the central metal and simultaneously form π back bond from fully filled d orbital of central atom.



Sometimes π-donor, π-acceptor

σ-donor, π-acceptor

* π-acid ligands (σ-donor π-acceptor)

Reason –:–

like Back-bonding.

↳ Synergic bonding also

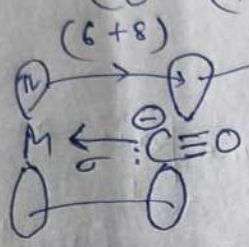
→ Non-Classical ligands

- σ-donor (lone pair → Metal)
  - Accepts ē in
    - P-orbital
    - d-orbital — PF_3, AsH_3 etc
    - π* orbital — σ donor, π-acceptor — CO, NO, N_2 etc. — anti bonding — Imp. π* orbital
    - σ* orbital
- π-donor (accepts ē pair in π* orbital)

Non-classical ligands:-

→ CO (No of e^- - 14)

(6+8)



→ π^* orbital.

(MOT, N_2) → energy level dia.

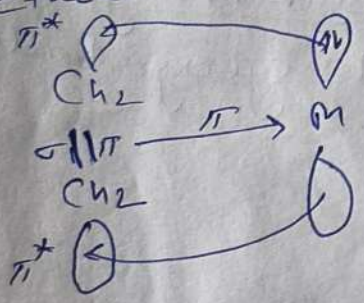
$B.O = \frac{1}{2}(N_b - N_a)$

(13)

→ π-donor ligands (η^*) eta

(π-donor, π-acceptor)

* e.g. Ethene:-

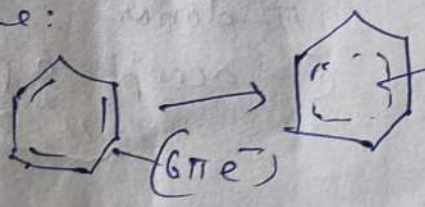


Here ethene, π mean $2e^-$ donor.

$[\eta^2 - C_2H_4]$ means π donor, π acceptor

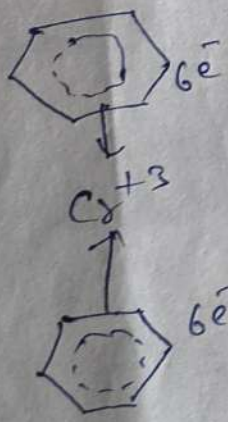
$[\pi - C_2H_4]$ π donor, π acceptor.

e.g Benzene:



Resonance hybrid

3π bond = 6π e^-

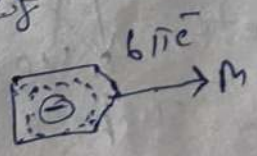


$[\eta^6 - C_6H_6]_2$

e.g $C_5H_5^{\ominus}$ (cyclopenta dienyl ion) or diene

$(\sigma - C_5H_5)$ or $(\eta^1 - C_5H_5)$

e.g



$[\eta^6 - C_5H_5)$
$\pi - C_5H_5)$

e.g. butal,3diene.

$CH_2 = CH - CH = CH_2$

$4\pi e^-$

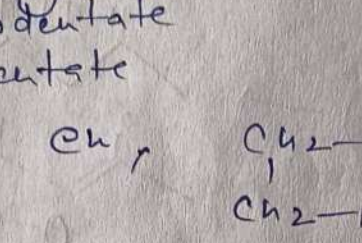
$[\eta^4 - C_4H_6]$

Quest: Ethylene diamine is an example of a _____ ligand.

a) Monodentate c) tridentate

b) bidentate d) hexadentate.

Ans:- (b) bidentate



Quest: The co-ordination no. and oxidation no. of X in the given compound $[X(NH_3)_5(SO_4)]Cl$ will be :-

a) 10 & 3 b) 2 & 6 c) 6 & 3 d) 6 & 4

Ans:-

$[X(NH_3)_5(SO_4)]^{+1}$

0 — 1 or 2 — co-ordinate bond may be.

5 coordinate bond

So, CN = 6

$X + 0 \times 5 - 2 = +1$

$X = +1 + 2 = +3$ Ans: (c)

Quest: A complex compound in which the oxidation no. of a metal is zero.

a) $[Ni(CO)_4]$ (b) $[Pt(NH_3)_4]Cl_2$ (c) $K_4[Fe(CN)_6]$

d) $K_3[Fe(CN)_6]$.

Ans:- $[Ni(CO)_4]$ (a)

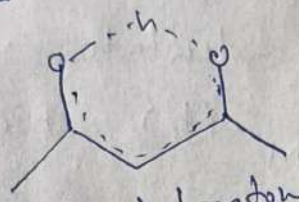
↓ neutral ligand

Quest: Which of the following ligands does not form metal-nitrogen bond when bonded with metal?

a) $EDTA^{4-}$ b) en c) Gly^- d) $acac^{1-}$ ✓

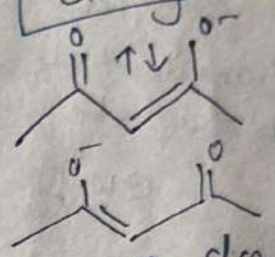
~~CH_3COO^-~~

Ans:- $EDTA^{4-}$ N-donor, en N-donor, Gly^- N-donor, $\boxed{\text{acetylacetonate}}$



acetylacetone (enol form)

(HACAC) ⟶



or

O-donor.

Quest: Which of the following is not an ambidentate ligand?

a) NO_2^- b) SCN^- c) CN^- d) NH_3

Ans:- $\ddot{N}H_3$ (d) → Neutral

Quest:- Glycinato ligand is

a) CH_2-CH_2 (N, O) b) Bidentate ligand c) Two donor sites N & O^-

d) All of there.

Ans:- b) & c).

Quest:- Among the following, which is not the π-bonded Complex organo-metallic compound?

a) $(CH_3)_4Sn$ b) $Cr(\eta^6-C_6H_6)_2$ c) $Fe(\eta^3-C_5H_5)_2$

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

Ans:- (A) Ans.

Quest: The ligand called π-acid is

A) CO B) NH_3 C) $C_2O_4^{2-}$ D) CH_4

Ans:- CO — σ- donor, π- acceptor (A)

Quest:→ Out of following which ligand is a π acid ligand?

a) CO b) CN^- c) NO d) All of there.

Ans:- All of there - (d)

* Classification of complexes:-

(1) On the basis of nature of ion:→

(i) Simple cation complex anion:-

e.g $K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$

$4K^+$ → simple cation; $[Fe(CN)_6]^{4-}$ → complex anion.

(ii) Complex cation simple anion:-

$[Cu(NH_3)_4]^{2+} SO_4^{2-} \longrightarrow [Cu(NH_3)_4]^{2+} + SO_4^{2-}$

$[Cu(NH_3)_4]^{2+}$ → complex cation; SO_4^{2-} → simple anion.

(iii) Complex cation & complex anion:-

$[Cr(NH_3)_6]^{-3} [Co(CN)_6]^{+3}$ ✓

(iv) Neutral complex - $[Pt(NH_3)_2(Cl_2)]$ — no charge -

$[Ni(CO)_4]$ — no charge.

ii) $K_3[Co(NO_2)_6]$ — fisher salt (yellow ppt)
Simple cation complex anion

→ $Na_2[Fe(CN)_5NO]$ — Sodium nitro pruside
SCCA

$[Fe(H_2O)_5NO]SO_4$ — Brown ring complex
CCSA

Cis-$[Pt(NH_3)_2Cl_2]$ — Cis-Platin — Cancer treatment
Neutral Complex

$[Rh(PPh_3)_3Cl]$ — Wilkinson Catalyst.
Neutral Complex

Quest:- $[Pt(NH_3)_3Cl]$, $[PtCl_4]$, $[Pt(NH_3)_4][PtCl_6]$

Ans, CCCA, $[Fe(H_2O)_6]_3[Fe(CN)_6]_2$ CCCA, CCCA ✓

---

*(2) On the basis of stability of complex ion:-

e.g. (ML_4)

$M + 4L \rightleftharpoons ML_4$ Let this Rxn is in equilibrium

$K_{stability}$, K_f or $K_{formation}$ → equilibrium constant

$$\frac{[ML_4]}{[M][L]^4}$$

If $K_f \uparrow$ → stability ↑

$K_f \downarrow$ → Complex stability ↓

(i) Perfect or penetrating complexes:-

→ In such complexes, the complex ions is either completely stable or very feebly dissociates in a Solution

e.g. $Cu^{2+} + K^+CN^- \rightarrow Cu^{+1}CN + (CN)_2$

$CuCN + KCN \rightarrow K_3[Cu^{+1}(CN)_4]$ ✓

$K_3[Cu(CN)_4] + H_2S \rightarrow$ No ppt.
perfect complex.

ii) Imperfect Complex:-

→ In such Complexes, the complex ions is less stable or dissociates appreciably in a solution.

$Cd^{2+} + KCN \rightarrow Cd(CN)_2$

$Cd(CN)_2 + KCN \rightarrow K_2[Cd(CN)_4]$

$K_2[Cd(CN)_4] + H_2S \longrightarrow CdS$ (Yellow ppt) ✓

↓ (K_f ↓) less stable

(3) (i) Sigma Complexes: → In these complexes, all the ligands are lone pair donors.

$K_4[Fe(CN)_6]$

$[Pt(NH_3)_2Cl_2]$ – Cis-platin ✓ – cancer

$[Cu(NH_3)_4]SO_4$

(ii) π-Complexes. In these complexes, at least one ligand is pi-donor

ferrocene – $[Fe(\eta^6-C_5H_5)_2]$ → Sandwich Complex

total 12 π e⁻

Zeise's salt – $K[PtCl_3(\eta^2-C_2H_4)]$ ✓ $CH_2=CH_2$ (2e⁻)

Quest: π-bonding is not involved in
a) ferrocene. b) dibenzene chromium c) Zeise's Salt
d) Grignard Reagent (R-Mg-X).

Ans:- Grignard Reagent.

* Naming of Co-ordination Compounds:- (Nomenclature)

(i) The cation is named first in both positively & negatively charged co-ordination entities.

(ii) The ligands are named in an alphabetical order before the name of the central atom/ion.

(iii) Names of the anionic ligands end in 'o', cationic ligands end with 'ium'. ido

(iv) Prefixes mono, di, tri etc. (tetra, penta) are used to indicate the no. of ligands, Prefixes bis, tris, tetrakis are used for Complex ligands including a numerical prefix.

e.g. $K_4[Fe(CN)_6] \rightarrow 6\ CN$, hexa-cyano / hexa cyanido

$[Cr(en)_3]^{3+} \rightarrow$ Tris diamine

(v) Oxidation state of the metal in cation, anion or neutral Co-ordination entity is indicated by Roman numeral in parenthesis/bracket.

e.g. $K_4[\overset{+2}{Fe}(CN)_6]^{-4} \rightarrow (II)$

$[\overset{III}{Cr}(en)_3]^{3+} \rightarrow (III)$

↓ neutral ligand.

(vi) If the complex ion is an anion, the name of the metal ends with the suffix ate. e.g. $K_4[Fe(CN)_6]^{4-}$ → ferrate.

for Zn → zincate, Ag - Argentate, Ni - Nickelate, Al - Aluminate.

Au - Aurate.
Pb - Plumbate.
Sn - Stenate.
Pt - Platinate
Cr - Chromate,

(e.g.)

1. $[Cr(NH_3)_3(H_2O)_3]\overset{+3}{Cl_3}^{-3}$

Name:- Triamminetriaqua chromium(III) chloride

2. $[Co(en)_3]_2^{+6}(SO_4)_3^{-6}$

→ Tris(en) Cobalt (III) Sulphate

3. $[Pt(NH_3)_2Cl(NO_2)]$

Diammine chloro nitrito-N platinum(II)

chloro → chloride, nitro

4. $K_3[Cr(C_2O_4)_3]^{-3}$

Potassium trioxalato chromate(III)

e.g. $[Cu(NH_3)_4]^{2+} SO_4^{2-}$

O.S. of Cu, central atom = Cu^{2+}

So Tetra ammine copper (II) sulphate

e.g. $[Pt(NH_3)_2(Cl_2)]$ alphatical order not for di, tri etc.

diammine di chloro ~~plati~~ platinum (II).
or chlorido

O.S. of Pt = +2
$x + 0 \times 2 + 2 \times -1 = 0$
$x = 2 - 0.S.$

e.g. $[Cr(H_2O)_6]^{+3} Cl_3^{-3}$

Hexaaqua chromium (III) chloride.

e.g. $[Ni(CO)_4]$ → Tetracarbonyl nickel (0).

e.g. $[Co(H_2O)_6]^{3+}$ → hexaaqua cobalt (III) ion — due to charge here complex.

e.g. $[Cr^{+3}(en)_3]^{+3} Cl_3$ → Tris ethane 1,2, diamine chromium (III) chloride.
(en)

e.g. $K_4[Fe(CN)_6]^{4-}$ → Pot. Hexacyanido-C ferrate (II).
or cyanido
or cyano

no. of counter ion (+3)

e.g. $[Cr(NH_3)_3(H_2O)_3]Cl_3$

Triammine Triaqua chromium (III) chloride

e.g. $[Co^{+3}(en)_3]^{+}_2 (SO_4)_3$ → Tris (ethane 1,2-diamine cobalt (III) sulphate
or ethylene

$(2 \times 3 = 6)$ $2- \times 3 = -6$

e.g. $[Pt(NH_3)_2Cl(NO_2)]$ → diammine chlorido nitrito-N platinum (II)
chloro nitro

e.g. $K_3[\overset{+3}{Cr}(C_2O_4)_3]^{(-3)}$ → potassium trioxalato chromate (III)

$x + (-2 \times 3) = -3$
$x = +6 - 3 = +3$

e.g. $[\overset{+2}{Pt}(NH_3)_4Cl_2]\,[\overset{+2}{Pt}\overset{+2}{Cl_4}]^{-2}$ → Select cation & given for $Pt^{+2} \rightarrow CN = 4$

→ Tetra ammine dichloro platinum (IV) tetra chloro platinate (II).

e.g. $[Pt(Py)_4]^{+2}\,[\overset{+2}{Pt}Cl_4]^{-2}$ →

→ Tetra pyridine platinum (II) tetra chloro platinate (II)

But $Pt^{+4} \rightarrow C.N. = 6$.

Quest:- The formula of the complex tris (ethylene diamine) chromium (III) sulphate:-

Ans. $[\overset{+3}{Cr}(\underset{0}{en})_3]_2(\overset{-6}{SO_4})_3$.

Quest:- The complex cis $[CoCl(NH_3)_3(NH_2CH_2CH_2NH_2)_2]^{2+}$ has an octahedral geometry, Name of this complex ion

Ans:- O.S. of Cobalt = $x + (-1) + 0 + (0 \times 2) = 2$

$x - 1 + 0 = 2$
$x = +1 + 2 = 3$

Cis - ammine chloro bis (en) Cobalt (III) ion Ans.

Quest:- As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]^{+3}Cl_3^{-3}$ is.

Ans:- Diammine tetra aqua Cobalt (III) chloride

Quest:- The IUPAC name of $\overset{+0}{Xe}[\overset{+5}{Pt}F_6]^{-}$ → Pt^{+4} generally CN = 6 but here Xe inert gas 0, charge

Xenon hexa fluoro platinate (V)

$[Xe]^{+}[PtF_6]^{-}$, Pt, O.S = +5

e Quest:- Which of the following pair of the name or formula of the complex is not correct?

a) Tetraammine copper(II) sulphate – $[Cu(NH_3)_4]^{+2}SO_4^{-2}$ ✓

b) Diammine silver(I) chloride – $[Ag(NH_3)_2Cl]^{+1}Cl^{-}$ ✓

c) Potassium ammine penta chloridoplatinate(IV) – $K^{+}[Pt^{+4}(NH_3)Cl_5]^{-1}$ ✓

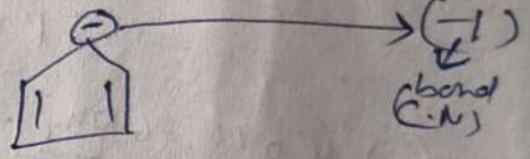
d) Tetrapotassium hexa cyanido ferrate(III) – $K_4^{+4}Fe^{+2}(CN)_6^{-4}$ ✗

here O.S., Fe = +2.

Ans:- (d)

Quest: The correct IUPAC name of the complex $Fe^{+2}(C_5H_5^{-})_2$.

Ans: Bis (cyclopentadienyl) iron-II.



Quest: The IUPAC name of $[Cr(NH_3)_6]^{3+}$

Ans:- Hexaammine Chromium(III) ion

Quest: formula of hydrido trimethoxido borate(III) ion:-

Ans:- $[\overset{+3}{B}H(OCH_3)_3]^{-}$ O.S. of B → +3.

(from $CH_3\bar{O}H^{+}$ methoxide) $OCH_3 = 3 \times -1 = -3$

$H = -1$

$x + (-1) + (-1 \times 3) = -1$

$x - 4 = -1$

$x = -1 + 4 = 3$

* Werner's Theory:-

Postulate / Points: 1 In co-ordination compounds metals show two types of linkages (valences) – primary & secondary.

2. The primary valences are normally ionisable and satisfied by negative ions. (Corresponds to oxidation state of metal).

3. The secondary valences are non-ionisable. These are satisfied by neutral molecules or negative ions.

4. The secondary valences are equal to co-ordination no. and is fixed for a metal.

5. Primary valency is non directional but secondary valency is directional.

6. Geometry of a complex compound is determined by secondary valency.

7. Electrical conductance of an electrolyte depends on the no. of ions per formula unit and the charges present on ions.

We Denote:- ——— → S.V.
- - - - → P.V

e.g. (a) $[CoCl_3 \cdot 6NH_3]$ + Excess of $AgNO_3$ → 3 mol $AgCl\downarrow$ (ppt) white Then

Write formula of this

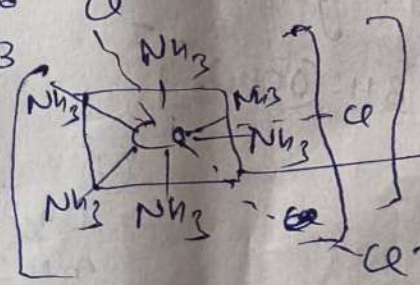
$[Co(NH_3)_6]^{+3}Cl_3$ → $[Co(NH_3)_6]^{3+}$ + $3Cl^-$ ↓ due to $3AgCl$

Produce → 4 ions

S.V. = 6

P.V. = 3

Representation:-



e.g. (b) $CoCl_3 \cdot 5NH_3$ + Excess $AgNO_3$ → 2 mol $AgCl\downarrow$

formula

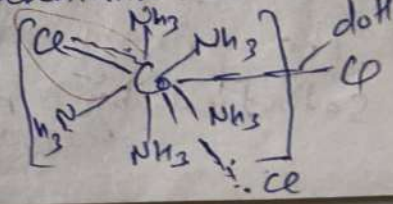
$[Co(NH_3)_5Cl]Cl_2$ → $[Co(NH_3)_5Cl]^{2+}$ + $2Cl^-$

Total ions - 3

S.V, C.N = 6

O.S or P.V → 3,

Representation:-



eg $CoCl_3 \cdot 4NH_3$ + Excess $AgNO_3$ → 1 mol $AgCl$ ↓

formula $[Co(NH_3)_4Cl_2]Cl$ → $[Co(NH_3)_4Cl_2]^+ + Cl^-$

S.V = 6
P.V = 3

(∝ No. of ions ∝ charge of ions.)

2 ions

* electrical conductance → a > b > c
* Colligative Properties → a > b > c
  ↳ depend on no. of particles.

Quest:- Select complex which have all following characteristics:-
→ 1:1 type electrolyte (no. of cation to no. of anion ratio)
→ Heteroleptic complex
→ Does not give AgCl with $AgNO_3$ (solution).

a) $[Pt(NH_3)_3Cl_3]Cl$ ✓ b) $K^+[Pt(NH_3)Cl_5]^{-1}$ ✓
c) $K_2^{+2}[PtCl_6]^{-2}$ ✗ d) $[Pt(NH_3)_2Cl_4]^0$ ✗

Ans:→ (B) $K[Pt(NH_3)Cl_5]$ → more than one ligand - Heteroleptic
K → does not give AgCl.
Cation : anion
1 : 1 ✓

Quest:- Select correct about $PtCl_4 \cdot 4NH_3$ complex salt:-
1. ✗ All the chlorides are bonded by primary valency.
2. ✗ All the chlorides are bonded by secondary valency.
3. All the NH_3 are bonded by secondary valency.
4. Half of the ~~chloride~~ chlorides are bonded by with secondary valency.

a) I, III b) III, IV c) II, III d) only III.

Ans:- $Pt^{+4}Cl_4$ - So, C.N = 6 So, 2 Cl^- are bonded with secondary valency.

$[Pt(NH_3)_4Cl_2]Cl_2$

Ans:- (b) III, IV.

Quest:- Which one of the following complexes will consume more equivalents of aqueous solution of $Ag(NO_3)$?

a) $[Cr(H_2O)_6]Cl_3$ (b) $Na_2[CrCl_5(H_2O)]$

c) $[Na_3(CrCl_6)]$ (d) $[Cr(H_2O)_5Cl]Cl_2$

Ans:- (A) $3Cl^-$ - out of sphere.

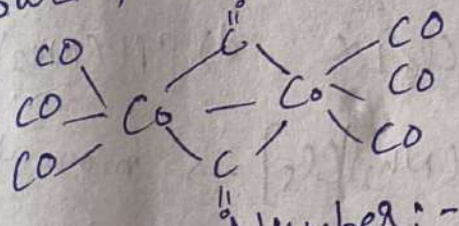
Quest:- $[Co_2(CO)_8]$ displays:-

a) no Co-Co bond, four terminal CO & four bridging CO.

b) one Co-Co bond, six terminal CO and two bridging CO.

c) no Co-Co bond, six terminal CO and two bridging CO.

d) one Co-Co bond, four terminal CO and four bridging CO.



Ans:- (B)

* EAN -> Effective Atomic Number:- The no. of electrons present around the central metal, is called as effective atomic number.

EAN = $Z - O.S. + 2(C.N.)$ formula.

no of given by ligand to C. metal

e.g $K_4[Fe(CN)_6]$

$EAN_{Fe} = 26 - 2 + 2(6) = 36.$

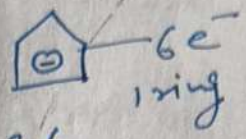
e.g $[Cu(NH_3)_4]SO_4$, EAN = $29 - 2 + 2(4) = 35.$

$[Cr(H_2O)_6]^{3+}$, " = $24 - 3 + 2(6) = \underline{33}$. Ans

$[RhCl(PPh_3)_3]$

$= 45 - 1 + 2(4) = 52.$

* $Fe(\eta^5 - C_5H_5)_2$

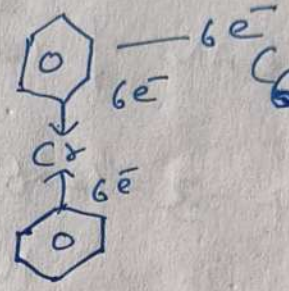


cyclopentadienyl ion

$EAN = 26 - 2 + (2 \times 6) = 36$

* $[Cr^0(\eta^6 - C_6H_6)_2]$

$EAN = 24 - 0 + 2 \times 6$
$= 36$



$C_6H_6 \rightarrow$ Neutral ligand.

* Sidgwick Rule of EAN :-

→ Every central atom tries to gain the $\bar{e}$ configuration of succeeding noble gas. So a complex with EAN equal to the atomic no. of an inert gas is more stable.

→ This rule is applicable for the metal carbonyl and pi complexes (with an exception of $[V(CO)_6]$ (σ bond)

→ The stability, reducing and oxidising nature can be determined by this rule.

e.g $[Co(CO)_4]^{2-}$

CO → neutral compound.

$EAN \rightarrow 27 - (-2) + 2 \times 4$
$= 37$

Z - atomic No.

nearby noble gas $|Kr| - 36$

$37 \rightarrow 36 -$ $1e^-$ donate (oxidation)

it behaves as reducing agent.

e.g. $[Mn(CO)_5^-]$

EAN = 25 − 0 + 2×5 = 35

So, to gain 2 = 36, it gains one e^-

So reduction occurs.

& it acts as an oxidising agent.

Quest: The EAN of cobalt in the complex ion $(Co(en)_2Cl_2)^+$ is

(en → bidentate)

Ans: 27 − 3 + (2×6) = 36

Here, O.S. of Co = +3

Then C.N

$2\times2+2 = 6$
en Cl

Quest: The complex that violates the EAN rule:-

a) Potassium ferrocyanide b) Potassium ferricyanide, C_6

c) Tetra carbonyl Nickel $Ni(CO)_4$

d) Hexamine cobalt (III) chloride → $[Co(NH_3)_6]Cl_3$

$K_3[Fe(CN)_6]^{3-}$ – ferricyanide ion (Fe^{+3})

$K_4[Fe(CN)_6]^{4-}$ – ferrocyanide ion (Fe^{+2})

Fe_2O_3 / III ferric, Ferrous II

EAN (a) → 26 − 3 + 2×6 = 35 – n of follow EAN rule. (Sidgwick) not equal to noble gas

EAN (b) → 26 − 2 + 2×6 = 36

EAN (c) → 28 − 0 + 2×4 = 36

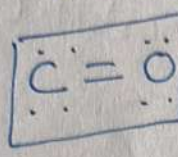
EAN (d) → 27 − 3 + 2×6 = 36

Ans = (a)

* → Nitrosyl group (NO) is 3 e^- donor.

$[Cr(CO)_6] + 4NO \longrightarrow [Cr(NO)_4] + 6CO$

Co - $2e^-$ donor



EAN of $[Cr(CO)_6]$ = 24 - 0 + 2×6 = 36

Here $(NO)_4$ replaces = $(CO)_6$

$x \times 4$ = 2×6 (e^-)

x = 3 e^- - so, NO is $3e^-$ donor

then EAN of $[Cr(NO)_4]$

= 24 - 0 + 3×4 = 36.

EAN = Z - O.S + (2×(C.N)) generally

EAN = Z - O.S + 3×(C.N) in NO case

So in case of NO, EAN = Z - O.S. + 3×(C.N.)

NO
↙
neutral ligand

e.g. $[Fe(CO)_5] + 2NO \rightarrow [Fe(CO)_2(NO)_2] + 3CO$.

& $NO^+ \rightarrow 2e^-$ donor also.

* Valence Bond theory (VBT):— (i) The central atom/ion makes available a number of vacant orbitals equal to its co-ordination number.

(ii) Empty atomic orbitals undergo hybridisation and equal number of hybrid orbitals are obtained having specific geometry.

(iii) A covalent bond is formed by the overlap of a vacant metal orbital and filled ligand orbitals. This complete overlap leads to the formation of a metal ligand σ-bond.

$Pt^{2+} \rightarrow [Xe]\, 4f^{14}\, 5d^{8} \rightarrow$ C.N-4, d^8 – highly favourable for square planar geometries

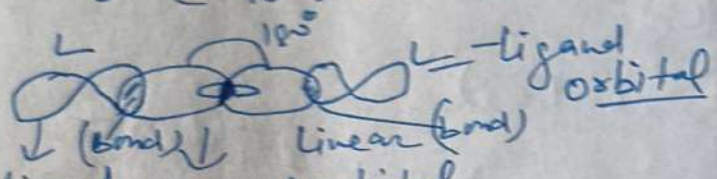
$Pt^{4+} \rightarrow [Xe]\, 4f^{14}\, 5d^{6} \rightarrow$ C.N-6,

↓ octahedral geometry.

← CFSE → makes splitting of d-orbital

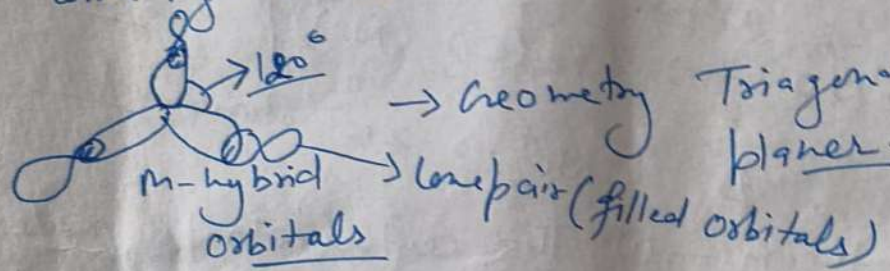
e.g. If C.N. of Central atom

C.N → 2



If C.N. → 3

3 vacant orbital intermix with each other to form 3 new hybrid orbitals & makes bond with ligand orbitals.



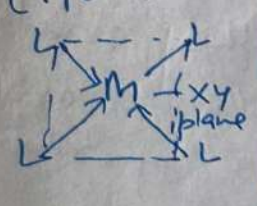
In our syllabus. C.N = 4

C.N = 6

If C.N – 2 → sp linear geometry

C.N → 3 – sp^2 – Triagonal planar

Central metal C.N → 4 – → sp^3 → Tetrahedral



dsp^2 → Square planar [d-orbital ↓ $d_{x^2-y^2}$ + P_x + P_y] ↓ orbital on x-y axis.

d^2s → x not in syllabus

If C.N. = 6

- $sp^3d^2 \rightarrow s + p_x + p_y + p_z + d_{z^2} + d_{x^2-y^2}$ (octahedral)
- d^2sp^3
  - ↳ $(n-1)d_{x^2-y^2} + (n-1)d_{z^2} + s + p_x + p_y + p_z$ (octahedral)
    - ↓
    - $(n-1)d$ → Inner orbital complex: (e.g. dsp^2, d^2sp^2, dsp^3)
    - nd = outer orbital complex (e.g. sp^3d, sp^3d^2)

Ligands

- Strong field ligands
  - ↳ donor atom
    - ↳ C, N
  - e.g. CO, NH_3, CN
- Weak field ligands
  - ↳ O, X → halogen

Note → VBT does not give any information about strong & weak field ligands
→ CFT tells about this Crystal field theory.

* Spectrochemical Series:-
When ligands are arranged in increasing order or their strength, the obtained series is known as spectrochemical series.

→ Weak ligands ← Weak

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < NO_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O <$
$NCS < edta^{4-} < NH_3 = Py < en < dipy < NO_2^- < CN^- < CO.$

→ Strong ligands ←

donar C, N – strong ligand
donar X, O – weak "

* Check hybridisation :→

$[CoF_6]^{3-}$ → Hybridisation of Co - central metal.

C.N - 6

So, octahedral , O.S. of Co = +3

So, hybridisation → sp^3d^2

$Co_{27} = |Ar|\ 4s^2\ 3d^7$

Ground state of Co^{3+} → $Co^{3+} = |Ar|\ 3d^6$ ($4s^2, 3d^1$ ↑ higher energy level → ↓ निकल जाते)

t_{2g}	e_g
↑↓ ↑ ↑ ↑ ↑	

3d 4s 4p 4d

Incase of strong ligand (pairing up is done) like ↑↓ ↑↓ ↑↓ | | vacant orbitals

F^- → Weak ligand

So, 6 vacant orbital required → 1 from 4s 3 from 4p & 2 from 4d.

Outer orbital complex

→ 4 - unpaired - e^-

→ $\mu_s = \sqrt{n(n+2)}$ B.M. & paramagnetic.

e.g. Ground state of any element :-

Sn_{50} → $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^2$

→ $|Kr|\ 5s^2\ 4d^{10}\ 5p^2$.

e.g. C → $1s^2\ 2s^2\ 2p^2$ or $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^0$

Carbon

1s	2s	2p		
↑↓	↑↓	↑	↑	

Carbon excited state :-

↑↓	↑	↑	↑	↑

Complex → High spin or outer orbital for sp^3d^2

& inner spin or low-spin d^2sp^3.

1s
2s 2p
3s 3p 3d
4s 4p 4d 4f
5s 5p 5d 5f
6s 6p 6d
7s 7p
8s

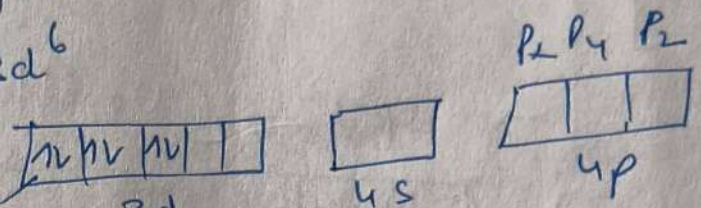
e.g. $[Co(NH_3)_6]^{3+}$

→ Ans. - d^2sp^3 C.N = 6

NH_3 - strong field ligand

Co^{3+} = |Ar| $3d^6$

Ground state: after pairing



6 vacant orbitals

$d^2 s p^3$

→ Inner orbital complex

→ n = 0, no unpaired e^-.

→ Diamagnetic [low spin Complex].

e.g. $[NiCl_4]^{2-}$

hybridisation of Nickel ?

Here, Oxidation No. of Nickel = $x + (-1) \times 4 = -2$

$x = -2 + 4 = +2$

e.c. of $(Ni)^{2+}$ → |Ar| $3d^8$

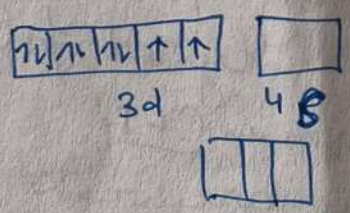
$(Ni)_{28}$ → |Ar| $4s^2 3d^8$

here, C.N = 4

Cl^- → weak ligand

Ground state:-

Ni^{2+} →



So Ans: sp^3

→ outer-orbital Complex

n = 2

→ paramagnetic, $\mu_s = \sqrt{2(2+2)}$ B.M.

→ High spin complex.

→ Tetrahedral.

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

hybridisation of Ni ?

O.S. of Ni = +2

but due to CN (pairing is done) strong ligand.

the hybridisation should be → dsp^2 Ans.

→ inner-orbital complex (~~high~~ low spin complex)

→ Diamagnetic as n = 0

→ Square planar

(i) Trick for C.N = 6 → for hybridisation only.

if e⁻ configuration

d^0, d^1, d^2, d^3 — hybridisation is d^2sp^3 (no effect of ligand)

(ii) d^8, d^9, d^{10} → sp^3d^2 — (No effect of ligand)

(iii) d^4, d^5, d^6, d^7 → Weak field ligand → sp^3d^2 — hybridisation.
Strong field ligand → d^2sp^3 — hybridisation (pairing is done)

(iv) e.g. $[Fe(H_2O)_6]^{3+}$
C.N = 6, Fe^{3+} = |Ar| $3d^5$
H_2O → Weak field ligand → sp^3d^2 hybridisation.

(v) e.g. $[Fe(CN)_6]^{4-}$ C.N = 6, Fe^{2+} = |Ar| $3d^6$ → d^2sp^3
CN → strong field ligand.

e.g. $[Cr(NH_3)_6]^{3+}$ C.N = 6, Cr^{3+} → |Ar| $3d^3$ → d^2sp^3
NH_3 → strong field ligand

e.g. $[Ni(NH_3)_6]^{3+}$, C.N = 6, Ni^{3+} – |Ar| $3d^7$ → d^2sp^3 ✓
NH_3 – SFL

* Exceptions of VBT:- (i) All ligands behave as strong field ligands for 4d & 5d series and +4 ions. e.g. Pt^{2+}, Pd^{2+} & C.N = 4 → dsp^2 (d^8 configuration)

(ii) Generally NH_3 is a strong field ligand but behaves as weak field ligand for Cr^{2+}, Mn^{2+}, Fe^{2+} and Co^{2+}. Reason in CFT.

(iii) Generally oxygen donors are weak field ligands but act as strong field ligand for Cu^{2+} & Co^{3+}.

(iv) for $Pt^{+4,2}$, Pd^{+4} (Pt = 78, Pd = 46) CN - 6 → d^2sp^3 for All ligands

* limitations of VBT:-

(i) It does not give quantitative interpretation of magnetic data.

(ii) It does not explain the colour exhibited by Co-ordination compounds.

(iii) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of Co-ordination compounds.

(iv) It does not make exact predictions regarding the tetrahedral and square planar structures of 4- Co-ordinate complexes.

(v) It does not distinguish b/w weak and strong ligands.

Quest:- Match List-I with List-II

Complexes – List-I		Hybridisation – List II
A) $[Ni(CO)_4]$	$Ni_{28}^{0} \rightarrow [Ar]\,4s^2\,3d^8$ (Pairing)	(I) sp^3
B) $[Cu(NH_3)_4]^{2+}$	$Cu_{27}^{2+} \rightarrow [Ar]\,4s^0\,3d^9$	(II) dsp^2
C) $[Fe(NH_3)_6]^{2+}$ (strong)	$Fe_{24}^{2+} \rightarrow [Ar]\,3d^6$	(III) sp^3d^2
D) $[Fe(H_2O)_6]^{2+}$ (weak)	$Fe_{24}^{2+} = [Ar]\,3d^6$	(IV) d^2sp^3

Ans: a – I or I, B – II, C – IV, d – III

Quest:- Given below are two statements: one is labelled as "Assertion A" and other is labelled as Reason (R)".

Assertion – A → In the complex $Ni(CO)_4$, $Fe(CO)_5$, the metals have zero oxidation state.

Reason – R → Low oxidation states are found when a complex has ligands capable of π-donor character in addition to σ-bonding.

Ans:- A is true R is incorrect.

Quest:- Match list I and II

A) $[PtCl_4]^{2-} \rightarrow Pt^{2+}$, C.N → 4 — (I) sp^3d

B) BrF_5 — (II) d^2sp^3

C) PCl_5 — (III) dsp^2

D) $[Co(NH_3)_6]^{3+} \rightarrow Co^{3+}_{24} - |Ar|\,3d^6 \rightarrow (NH_3)$ SFL → C.N → 6 → d^2sp^3 — (IV) sp^3d^2

Ans:-

A – III B – IV C – I D – II

Quest:- Spin only magnetic moment of an octahedral complex of Fe^{2+} in the presence of a strong field ligand in BM is:

Ans: $n = 4$, $Fe^{2+}_{24} = |Ar|\,3d^6$

$\mu_s = \sqrt{4(4+2)}$

$= \sqrt{24}$

$= \sqrt{4 \times 4 \times 1.5}$

$= 4\sqrt{1.5} = 4.89$ BM

unpaired e^-

Quest:- The species that has a spin-only magnetic moment of 5.9, (tetrahedral = Td)

a) $[MnBr_4]^{2-}$ [Td] b) $[NiCl_4]^{2-}$ Td

c) $Ni(Cl)_4$ (Td) d) $(Ni(CN)_4)^{2-}$, Square planar

Ans: $n = 5$, for $\sqrt{n(n+2)}$ B.M should be $= \sqrt{5 \times 7} = 5.9$

a) $Mn^{+2}_{23} = |Ar|\,3d^5$ ✓

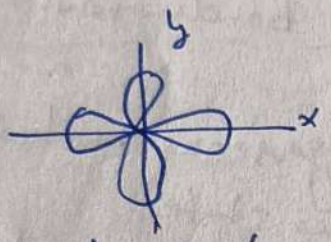
b) $Ni^{2+}_{26} = |Ar|\,3d^8$ ×

(C) $Ni^{+4}_{24} = |Ar|\,3d^6$ ×

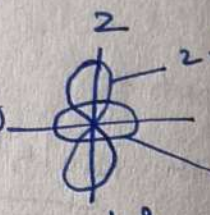
(d) $Ni^{+2}_{26} = |Ar|\,3d^8$.

CFT → Crystal field theory

d-orbital → 5 no.
$d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{yz}, d_{zx}.

(i) 

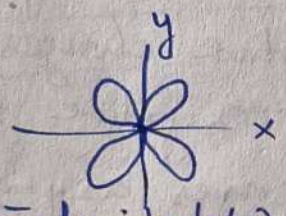
$d_{x^2-y^2}$ (e^- density presence on x & y axis)

(ii) 

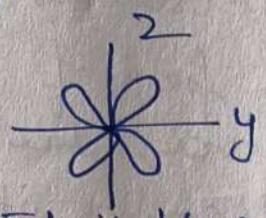
z axis (e^- density presence)

xy plane (e^- density presence)

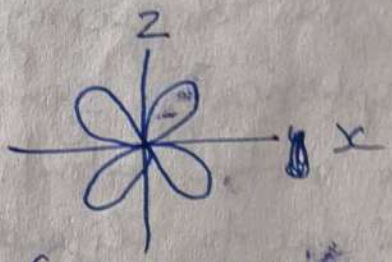
d_{z^2}

(iii) 

(e^- density b/w x & y axis)

(iv) 

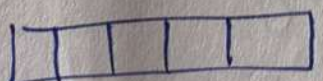
(e^- density b/w z & y axis)

(v) 

(e^- density b/w z & x axis)

($d_{x^2-y^2}$, d_{z^2}) → axial orbitals, eg (orbitals)

(d_{xy}, d_{yz}, d_{zx}) → Non axial orbitals, (t_{2g} orbitals)

In free state :-  → energy same of all 5 orbitals

(degenerate orbitals)

during bonding there will be splitting of energy, metal-ligand co-ordinate bonding leads to splitting of energy, which is known as CFT. (Crystal field splitting Theory)

→ The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions b/w the metal & the ligand.

$d_{x^2-y^2}, d_{z^2}$ (e_g) orbitals

→ ligands are treated as point charges in case of anions or pointdipoles in case of neutral molecules.

e.g. $H_2\overset{\delta-}{\ddot{O}} \rightarrow \overset{\delta+}{M}$

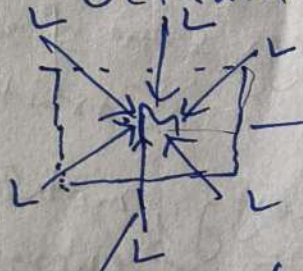
partial negative

(bonding ionic type)

→ The five d-orbitals in an isolated gaseous metal atom/ion have same energy, in free state
ie. they are degenerate orbitals.

→ This degeneracy of d-orbitals is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. However, when this negative field is due to ligands in a complex, it becomes asymmetrical and the degeneracy of the d-orbitals is lifted. It results in splitting of the d-orbitals and known as crystal field splitting.

* Octahedral Geometry (splitting)

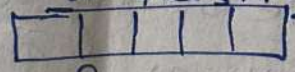


ligands in same plane

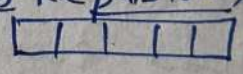
z axis (ligands presence)

Ligand Approaches direction along ligands → +x, −x, +y, −y, +z, −z

if e^- in orbitals in free state, due to e^--Repulsion energy increases



In free state orbitals



So, along the axis repulsion increases → energy ↑
orbitals, not along the axis repulsion decreases.
energy ↓

So,

Δ_0 - in octahedral complex.

* Tetrahedral Geometry :-

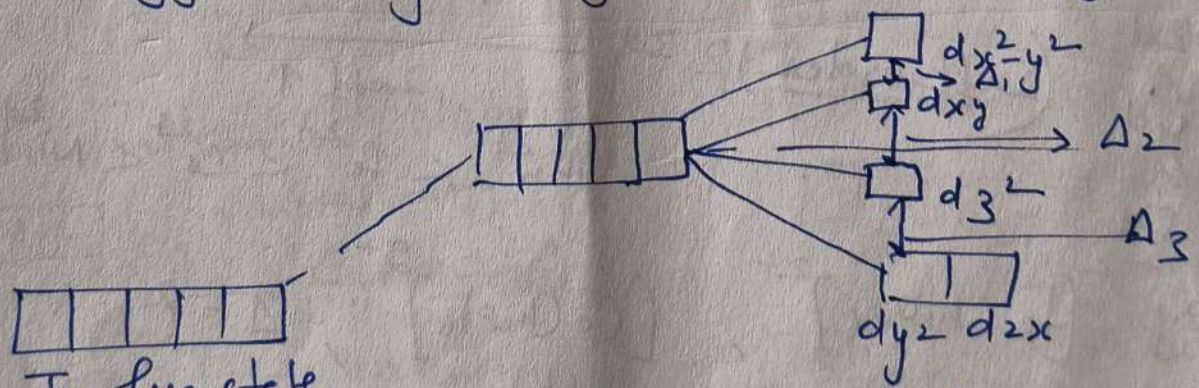
* Square planar geometry :-

e_g → evenally generated

t_{2g} → triply generated.

ligand, $+x, -x, +y, -y$

Energy :- $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{zx} > d_{yz}$.



$\Delta_{sp} = \Delta_1 + \Delta_2 + \Delta_3$

Δ_1 → max

$\Delta_1 > \Delta_2 > \Delta_3$

(f) Positive oxidation state of central metal:-

* Relationship b/w splitting Energies:-

$\boxed{\Delta_t = 4/9\, \Delta_o}$

$\Delta_{sp} = 1.3\Delta_o$ — 1.2 (may be)

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

Quest:- Why $\Delta_o > \Delta_t$

→ In octahedral molecule/ligands along the axis, comes & no. of ligand are high.

* factors affecting splitting Energy:-

1 Distance b/w ligand and central metal:→

M ← L , Distance ↓, Repulsion ↑, CFSE ↑

2. Effective nuclear charge (Z_{eff}) of central metal:-

$\boxed{\Delta_{CFSE} \propto Z_{eff}}$ of central metal

more attraction of nucleus on outermost e^-, more tendency to take e^- from ligands & Δ (CFSE) ↑.

In period

3d
↑
4d
↑
5d

(Z_{eff} order) 3d ⟶ Z_{eff} ↑

$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+}$

e.g. $[Fe(H_2O)_6]^{2+}$ (a), $[Co(H_2O)_6]^{2+}$ (b), $\Delta = ?$

So $a < b$. Ans.

③ Positive oxidation state of central metal:-

$\Delta \propto$ +ve oxidation state.

e.g. $[\overset{2+}{Fe}(CN)_6]^{4-} < [\overset{+3}{Fe}(CN)_6]^{3+}$, Δ order

$[\overset{2+}{Co}(H_2O)_6]^{2+} < [\overset{3+}{Co}(H_2O)_6]^{3+}$, Δ order

④ Strength of ligand:-

$\Delta \propto$ strong of ligand

↓ strength (more tendency to give e^-)

↙

Spectrochemical series:

e.g. $[Fe(H_2O)_6]^{3+} < [Fe(CN)_6]^{3-}$, Δ order.

strength $CN^- > H_2O$

SfL WfL

⑤ Geometry of co-ordination entity:-

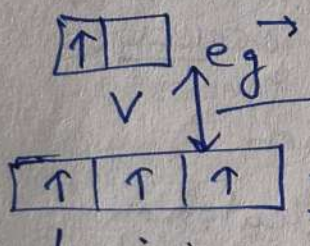
$\Delta_{sp} > \Delta_o > \Delta_t$.

* formation of low spin & high spin complexes:-

i.e. (pairing reasm)

WfL

In octahedral complex (No pairing)



→ more energy

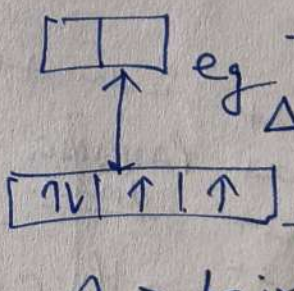
Δ order → less SE (difference)

→ less energy

↓ pairing energy; $\Delta <$ pairing energy

SfL (pairing occurs)

In Octahedral complex:-



→ more energy

Δ → more, SE splitting

→ less energy

$\Delta >$ pairing energy

Pairing dine-

Consists

* CFS

... ilization Energy :-

In Oc
As we

* exceptions of VBT- NH_3 acts as weak field ligand for Cr^{2+}, Mn^{2+}, Fe^{2+} & Co^{2+}

We can understand

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

(less 2eff.) 2eff - increases → Nalayak cation

CFSE (splitting) is low here.

Cr^{2+} upto Co^{2+} → So NH_3 strong ligand bhi weak ki tarah behave karega.

& Pairing energy > Δ - So, no pairing occurs.

(C

* Oxygen donor are generally WFL but they act as SFL for Co^{3+} and Cu^{2+}.

Reason:-

Co^{3+}, Cu^{2+} 2eff ↑, Δ ↑, P.E < Δ.

ache. So pairing occurs. So, oxygen donor behaves as SFL.

bache

* All ligand are SFL ligand for 4d & 5d elements & +4 ions.

(i) If.

3d
4d 2eff ↑, Δ ↑
5d

In 4d & 5d

So, All ligands SFL, pairing occurs.

in +4, Δ ↑, 2eff ↑, so, ligand SFL, pairing occurs

* Pt^{2+}
Pd^{2+}
Au^{3+}
Ag^{3+}
Rh^{+1}

PAIRING done. → dsp^2 hybridisation.

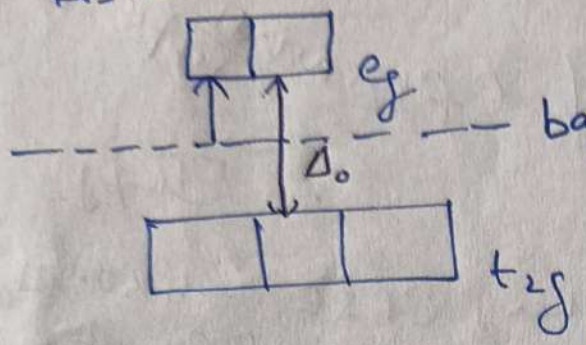
If C.N = 4] Trick → no calculation required.

* CfSE → Crystal field stablisation Energy :-

→ not same as (splitting)

In Octahedral complex :-

As we know :-



If $\bar{e}$ goes to e_g orbital, its energy increased by $0.6\Delta_o$

If $\bar{e}$ goes to t_{2g}, It decreases energy by $(-0.4\Delta_o)$

$$(CfSE)_{\Delta_o} = n_{e_g}[0.6\Delta_o] - n_{t_{2g}}(0.4\Delta_o) + x \times P.E.$$

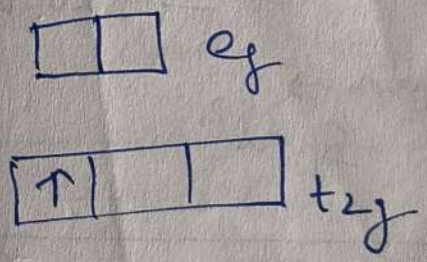
n_{e_g} → no. of e^- in e_g orbital

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

x → no. of extra $\bar{e}$ pair formed.

e.g. for WFL :→

(i) If metal – d^1 configuration →



CfSE = ?
stablisation energy

$CfSE = -0.4\Delta_o$ ← splitting energy.

(ii) In d^2 → $CfSE = -2 \times 0.4\Delta_o$

(iii) In d^3 → $CfSE = -3 \times 0.4\Delta_o$

C.N. = (octahedral) | C.N = 4 [square planar]

In d^7 co

(iv) In d^4 configuration → Lim:-

[↑|] eg

[↑|↑|↑] t_{2g}

(i) In SFL:- CFSE → $1 \times 0.6\Delta_0 - 3 \times 0.4\Delta_0$.

d^1, (ii) d^2, (iii) d^3 → Same value of CFSE as WFL respectively.

but in (iv) d^4 configuration:-

[|]

then, CFSE = $-4 \times 0.4\Delta_0 + 1 \times$ P.E. Ans

Imp.

(v) & so on we can calculate. [↑↓|↑|↑]

In d^5 configuration

WFL

[↑|↑]

— — — Barycentre

[↑|↑|↑]

CFSE = $2 \times 0.6\Delta_0 - 3 \times 0.4\Delta_0$

hybridisation → sp^3d^2

In d^5 Configuration:-

SFL

[|] eg.

— — — Barycentre

[↑↓|↑↓|↑]

CFSE = $-(0.4) \times 5 + 2 \times$ P.E. Ans.

Hybridisation → d^2sp^3

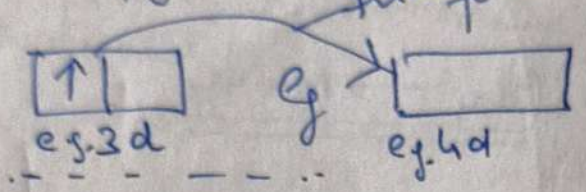
---

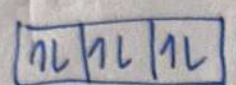
* Transference:- Conditions:-

1. Strong ligand should be present
2. Only one $\bar{e}$ should be in highest energy $(n-1)d$ orbital.

C.N. = 6 (octahedral)
→ SFL

In d^7 configuration:-





that's why d^2sp^3 (hybridisation)

→ SFL
→ d^7

Reason

e.g. $[Co(CN)_6]^{4-}$ ($\Delta > P.E$)

$Co \rightarrow |Ar|\, 3d^7 4s^2$

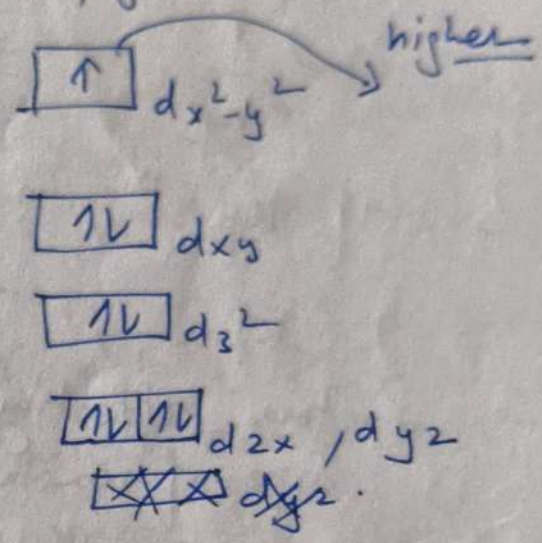
$Co^{2+} \rightarrow |Ar|\, 3d^7$

So, transference occurs so d^2sp^3 hybridization

* but in case of WFL, this will not happen

C.N = 4 [square planar]

In d^9 configuration:-



→ d^9 → Configuration

transference occurs

hybridisation: dsp^2

d^8 → No transference.

d^8 also favourable for square planar geometry and show, +4 → octahedral - C.N. = 6

C.N. = 4, Pt

e.g. $[Cu^{2+}(NH_3)_4]SO_4$

$Cu^{2+} = |Ar|\, 3d^9$

NH_3 → SFL so, dsp^2 hybridisation.

* Application of CFT:-

* ① Stability of Complex Compounds:-

$M + 4L \rightleftharpoons ML_4$, K_f

$K_f = \dfrac{[ML_4]}{[M][L]^4}$,

formation constant

$M + L \rightleftharpoons ML$, K_1

$ML + L \rightleftharpoons ML_2$, K_2

$ML_2 \rightleftharpoons ML_3$, K_3

$ML_3 \rightleftharpoons ML_4$, K_4

If we add all 4 equations :-

then, $K_f = K_1 \times K_2 \times K_3 \times K_4$ (from equilibrium)

and $\frac{1}{K_f}$ = Instability Constant or dissociation Constant.

$ML_4 \longrightarrow M + 4L$

So, if $K_f \uparrow$, stability $\uparrow$.

$K_f \downarrow$, Instability $\uparrow$

So, factors affecting stability :-

i) Size of metal :- bond length $\uparrow$ b/w ligand & metal.

& Stability $\propto \frac{1}{\text{size of metal}}$] in a series

So in series $\xrightarrow{\text{left to right}}$ stability increases

size decreases ($Z_{eff} \uparrow$)

electronegativity $\uparrow$

ii) Charge of the central metal :-

Stability $\propto$ +ve O.S. of metal.

charge of metal..

(iii) Strength of ligand :-

stability $\propto$ strength of ligand.

(iv) Present of chelate Rings :-

Stability $\propto$ No. of chelate rings.

(v) formation Constant :-

Stability $\propto K_f$

(vi) Z_{eff} :→ Stability $\propto Z_{eff}$

of central metal

Quest: Compare stability:-

1. $K_4[Fe^{+2}(CN)_6]^{-4} \underset{0.5}{<} K_3[Fe^{+3}(CN)_6]^{-3}$

2. $Ni^{+2}[Cl_4]^{2-} < \cancel{Ni[(CN)_4]^{2-}}$ $Ni^{+2}[(CN)_4]^{2-}$
   WFL — 2 chelate ring — SFL — 3 chelate ring

3. $[Co(NH_3)_6]^{3+} < [Co(en)_2(NH_3)_2]^{3+} < [Co(en)_3]^{3+}$

4. $[Co^{+3}(CN)_6]^{3-} > [Co^{3+}(NH_3)_6]^{3+} > [Co^{3+}(H_2O)_6]^{3+} > [Co^{+3}F_6]^{3-}$

learn spectrochemical series.

Advanced

Quest: The crystal field stablization energy (CFSE) of $[CoF_3(H_2O)_3]$ $(\Delta_0 < P)$ is

V.V Imp

Ans:- here, Co^{+3}_{24}, $= |Ar|\,3d^6$

$|H_2O| \rightarrow$ WFL

$F \rightarrow$ WFL, no pairing

$P.E > \Delta_0$

$\boxed{\uparrow|\uparrow}$ eg

$\boxed{\uparrow\downarrow|\uparrow|\uparrow}$ t_{2g}

$CFSE = 4 \times (-0.4\Delta_0) + 2 \times (0.6\Delta_0) + 0 \cdot P.E.$

$= -1.6 + 1.2 = -0.4\Delta_0$ Ans

Trick. check stability here.

Quest: Arrange the following Cobalt complexes in the order of increasing Crystal field stablisation (CSFE) value:-

$[Co^{+3}F_6]^{3-}$ (a), $[Co^{2+}(H_2O)_6]^{2+}$ (b), $[Co^{3+}(NH_3)_6]^{3+}$ (c) & $[Co(en)_3]^{3+}$ (d)

Ans: $d > c > a > b$ Ans.

Coordination Compounds:-

Quest:- The stepwise formation of $[Cu(NH_3)_4]^{2+}$ is given below:-

$$Cu^{2+} + NH_3 \overset{K_1}{\rightleftharpoons} [Cu(NH_3)]^{2+}$$

$$[Cu(NH_3)]^{2+} + NH_3 \overset{K_2}{\rightleftharpoons} [Cu(NH_3)_2]^{2+}$$

$$[Cu(NH_3)_2]^{2+} + NH_3 \overset{K_3}{\rightleftharpoons} [Cu(NH_3)_3]^{2+}$$

$$[Cu(NH_3)_3]^{2+} + NH_3 \overset{K_4}{\rightleftharpoons} [Cu(NH_3)_4]^{2+}$$

The value of stability constants K_1, K_2, K_3, K_4 are 10^4, 1.58×10^3, 5×10^2 and 10^2 respectively.

The overall equilibrium constants for dissociation of $[Cu(NH_3)_4]^{2+}$ is $x \times 10^{-12}$, find $x = ?$

Ans:-

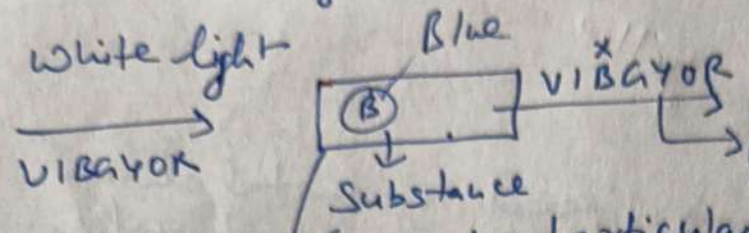
$$K_f = K_1 \times K_2 \times K_3 \times K_4$$

$$\frac{1}{x \times 10^{-12}} = 10^4 \times 1.58 \times 10^3 \times 5 \times 10^2 \times 10^2$$

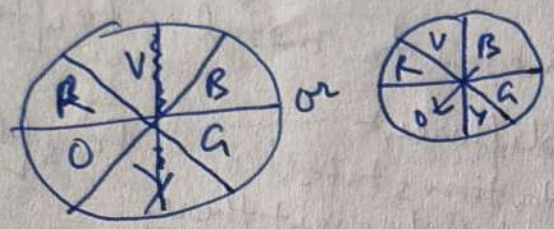
$$10^{12} = \frac{10^{11} \times 7.90}{x}$$

$$x = \frac{10}{7.90} = \frac{1000}{790} = 1.26 \simeq 1 \text{ Ans.}$$

* Colour of Co-ordination Compounds:-

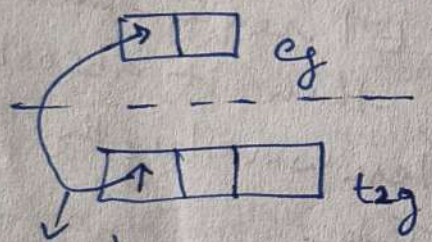


Colour wheel:-



Colour Absorbed	Complementary Colour
i) blue -	orange
ii) Green -	Red
iii) Yellow -	Violet & vice versa

In complexes:-
there will be splitting in d-orbitals.



by absorb a particular colour wavelength.

This phenomenon is d-d transition.
↓
Reason of colour in complex compounds

d^0, d^{10} → generally colourless.

e.g. $[Ti(H_2O)_6]Cl_3$ Coloured complex:-
$\xrightarrow{\Delta, heat}$ Colourless:- On heating water evaporates

e.g $CuSO_4 \cdot 5H_2O \xrightarrow{\Delta, Heat}$ Colourless.
water evaporates.
no ligand.
no d-d-transition

In the absence of ligand substance, will be colourless.

Exceptions:-

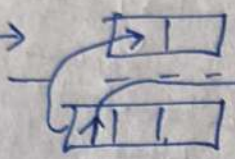
$MnO_4^{\ominus}$ (+7), $Cr_2O_7^{2-}$ (+6), CrO_4^{2-} (+6), CrO_2Cl_2

[d^0] [d^0] yellow

violet orange.

Reason:- Colour due to LMCT → ligand to metal charge transfer.

d^0 →



ligand give e^- (charge)

$Ni(CO)_4$, e.g. $Fe(\eta^6-C_5H_5)_2$ Not in syllabus

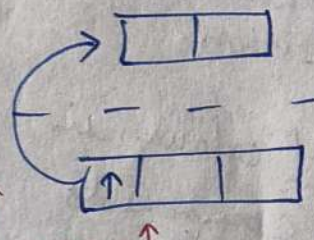
$Cr(\eta^6-C_6H_6)_2$

* Charge transfer from metal to ligand:-

* Charge transfer from metal to metal:- $Fe_4[Fe(CN)_6]_3$

↓ two different oxidation state of metal present there.

e.g. $Fe_3[Fe(CN)_6]$



e_g

Δ

t_{2g}

$\lambda\uparrow f\downarrow, \nu\uparrow$

Trick

SFL → more splitting is done $\Delta\uparrow$, then $E\uparrow$ requirement is more, then it absorbs light of less wavelength.

Imp.

because $\boxed{E \propto \frac{1}{\lambda}}$ $\propto f$

e.g. $[AlF_6]^{3-}$ → Red, Red blue Orange, which colour is absorbed

$[A(H_2O)_6]^{3+}$ → Orange

$[A(CN)_6]^{3-}$ → blue. SFL order

VIBGYOR → Max. Wavelength

(min λ) ↓ less wavelength

$CN > H_2O > A$

then, $\Delta\uparrow, E\uparrow, \lambda\downarrow$, then $\Delta\downarrow, E\downarrow, \lambda\uparrow$

Quest:- The correct order of energy of absorption for the following metal complexes is

A: $[Ni(en)_3]^{2+}$, B: $[Ni(NH_3)_6]^{2+}$, C: $[Ni(H_2O)_6]^{2+}$

a) C < B < A ✓ Ans.

SFL - strong, $\Delta\uparrow$, $\Delta E\uparrow$, $\lambda\downarrow$

(Stability $\propto \frac{1}{\lambda}$)

b) B < C < A

en > NH_3 > H_2O.

c) C < A < B

Spectrochemical series.

d) A < C < B

---

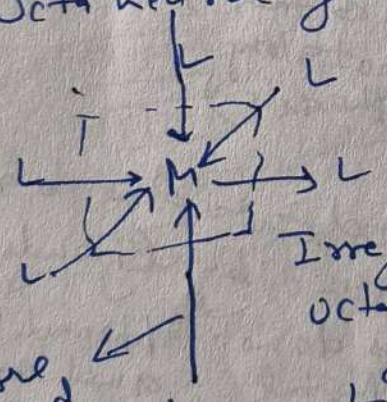
* Jahn Teller Distortion:-

→ In octahedral complexes when the t_{2g} or e_g are unsymmetrically field, they will repel Some ligands in the complex more then other. Thus the octahedral structure is distorted. This is known as jahn teller distortion.

triply generate gerade orbital

doubly generate gerade orbitals.

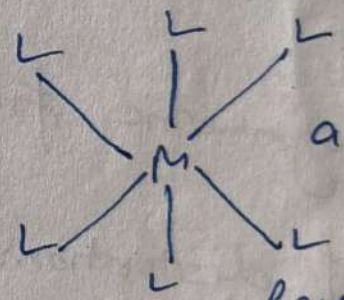
In Octahedral geometry:



more bond length (distortion)

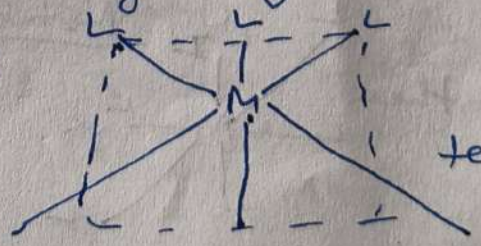
Tetragonal elongation

Irregular octahedral geometry



all bond angles & lengths are same.

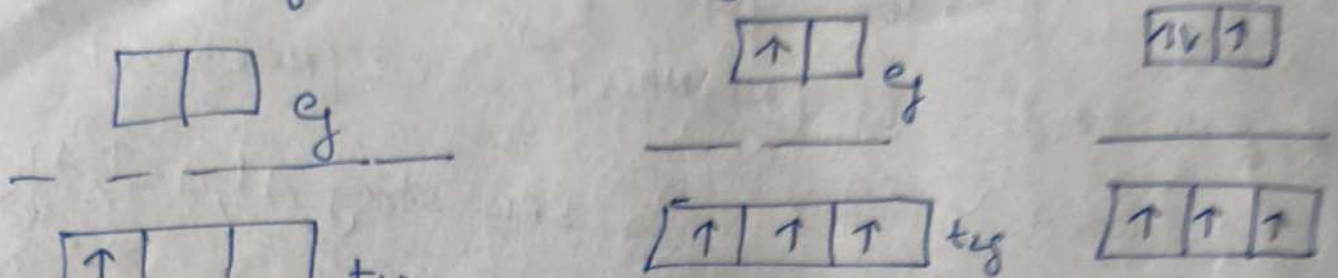
Regular octahedral geometry



tetragonal compression

there both are JTD.

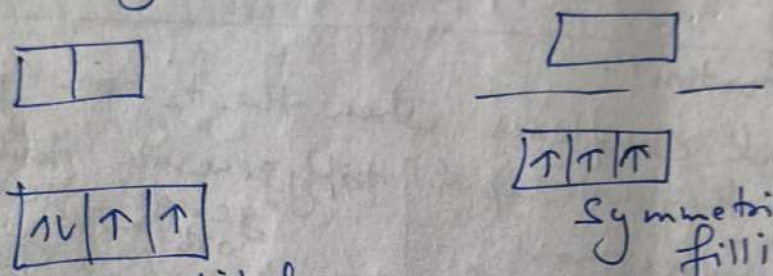
* Reason of distortion - unsymmetrical filling of distortion



Unsymmetrical filling of t_{2g} orbital

Unsymmetrical filling of e_g orbital

" e_g orbital



" t_2 orbital

Symmetrical filling.

ii) * Unsymmetrical filling of e_g orbital → strong JTD (lobes along the axis) more repulsion due to ligands

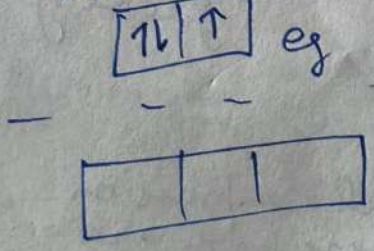
iii)

iv) * Unsymmetric filling of t_{2g} orbital → Weak JTD (not along the axis)

v)

* Reason of distortion:-

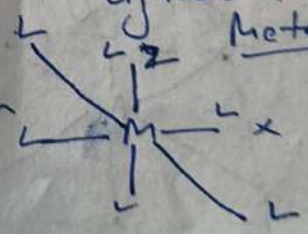
$d_{x^2-y^2}$ & d_{z^2}



more repulsion on $d_{x^2-y^2}$ due to more e^- along the axis by ligands of x, y axis

Ligands do not approach Metal and more easy for d_{z^2}.

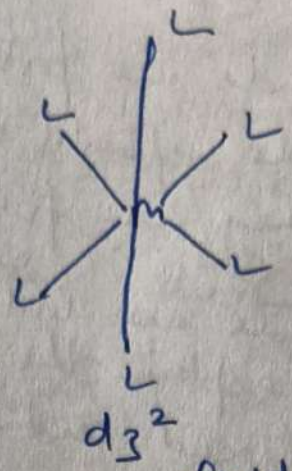
then



(compression) occurs

If [↑|↑↓] $d_{x^2-y^2}$ d_{z^2}

or [| ↑] $d_{x^2-y^2}$ d_{z^2} → then



Tetragonal elongation occurs

e.g

Let i) d^1 configuration, WFL → weak field ligand. then weak JTD.

[↑| |] t_{2g} → JTD of d^1 is weak. (t_{2g}) → unsymmetrical filling of t_{2g}.

Unsymmetrical filling of t_{2g}

JTD, e_g > JTD t_{2g}.

ii) d^2, $t_{2g}^{1,1,0}$, [↑|↑|] $\xrightarrow{WFL}$ weak JTD

iii) d^3, [↑|↑|↑] ^{1,1,1} $\xrightarrow{WFL}$ No JTD

iv) d^4, [↑|] $\xrightarrow{WFL}$ Strong JTD

v) d^5, [↑|↑|↑] [↑|↑] [↑|↑|↑] $\xrightarrow{WFL}$ No JTD

Note:-
for dsp^2 → square planar
sp^3 – tetrahedral

But in case of SFL:
(JTD) d^1, d^2, d^3, is same.

d^4 $\xrightarrow{SFL}$ ~~WFL~~ Weak JTD

d^5 SFL → weak JTD & so on.

* limitations of CFT:-

1. Assuming ligands as point charges, it follows that anionic ligands should exert the greater splitting effect. But they are found at the low end of the spectrochemical series. Why negatively charged ligands are WFL, doesn't not explain.

2. It does not explain the covalent character of bonding b/w ligand and metal.

Quest: Which of the following cannot be explained by CFT.?

A. The order of spectrochemical series. ✓

B. Magnetic properties of transition metal complexes.

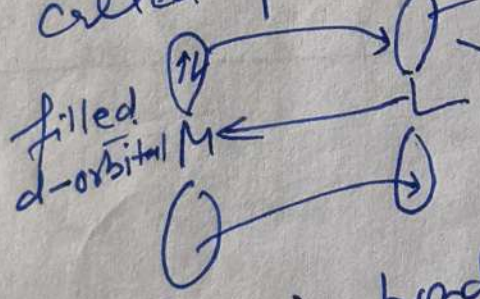
C. Colour of metal complexes.

D. Stability of metal complexes.

Ans:- (A) Ans.

* Synergic Bonding:→

→ If a ligand donates e^- pair to central metal and accepts e^- pair from d-orbital of central metal, then it is called synergic bonding and the ligands are called pi-acid ligands.



Synergic bonding.

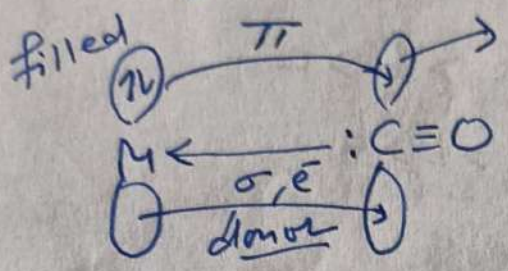
→ p, d, π^*, σ^* etc.

* Synergic bonding in metal Carbonyls:- formed

→ The metal-carbon sigma bond is by the donation of lone pair of carbonyl carbon into vacant orbitals of metal.

→ Metal-carbon pi bond is formed by donation of e^- pair from a filled d-orbital of metal into vacant antibonding orbital of CO (carbonyl).

e.g. $Ni(CO)_4$, $Fe(CO)_5$ etc.



, σ donor
, π acceptor

So

Extent of Metal −ve O.S. ∝ Synergic Bond

" ∝ Bond order metal-carbon increases (bond-strong)

" ∝ $\frac{1}{\text{Bond length of M-C}}$

" ∝ Bond-energy of M-C ↑

→ Effect on C≡O, bond length and bond-order,

" ∝ $\frac{1}{\text{Bond order of CO bond}}$

" ∝ $\frac{\text{Bond length of CO bond}}{}$

BO b/w CO decreases on synergic bonding :→

Reason :- In MOT

Bond order formula $= \frac{N_b - N_a}{2}$ ← e^- increases here So, bond order decreases b/w CO.

So, bond length b/w CO increases.

Quest. $[V(CO)_6]^-$ (a), $[Cr(CO)_6]$ (b), $[Mn(CO)_6]^{+x}$ (c)

Synergic bonding order:-

$a > b > c$

Metal-carbon bond order: $a > b > c$.

C-O " " : $c > b > a$.

etc. as on back page.

* Isomerism:-

→ Compounds having same chemical formula but different structural arrangement due to which they differ in one or more physical or chemical properties, are called as isomers and this phenomenon is called isomerism.

Two types:- 1) Structural 2) Stereoisomerism.
Geometrical Optical

→ Compounds having same chemical formula but different structures (different connectivity of ligand) are known as structural isomers. / Structural isomerism. - Type:-

* Ionisation Isomerism:-

→ This isomerism is shown by those ionic compounds in which a simple anion outside the co-ordination sphere can be replaced by anionic ligand and the complex will give different ions.

→ Co-ordination number and oxidation state of central metal should remain same.

e.g. $Cr(NH_3)_5(SO_4)Br$

$[Cr(NH_3)_5(SO_4)]Br$ $\qquad$ $[Cr(NH_3)_5(Br)]SO_4$

Br replaces SO_4, no C.N change, no O.S "
so there are ionisation isomers.

Quest: Which of the following complexes does not exhibit ionisation isomerism?

1 $[Co(Br)(NH_3)_5]Br$ × same

2. $[Cr(NH_3)_6]Cl_3$ ×

3. $[Ir(SO_4)(H_2O)]^+$ ×

4. $Na_2[Fe(CN)_5(NO)]$ ×

5. None of these

Ans:- None of there.

Quest. Which of following compound does not exhibit ionisation isomerism?

1. × $[Ir(CO)_2(en)_2]Br$ — 2 C.N, 1 C.N.

2. $[Cr(CN)_2(H_2O)_4][Ag(CN)_2]$ × no simplication

3. ✓ $[Cr(NO_2)(en)_2]^{+3}$ ox $^{+2}$ $^{-2}$ — C.N. = 6, C.N 2, C.N 4 (2 C.N.)

then C.N. change

No change in O.S & C.N.

4. ✓ $[Co(Br)(NH_3)_5]SO_4^{+3}$ — C.N = 6, monodentate

No change in O.S & C.N.

*. Linkage Isomerism:-

→ In this type of isomerism, metal has different linkages with the ambidentate ligand.

e.g. $[Cr(NH_3)_5(NO_2)]Cl_2$ — Nitrogen linkage $\qquad$ $[Cr(NH_3)_5(ONO)]Cl_2$ — oxygen linkages

Quest: find out all possible linkage isomers of

$[Co(NO_2)(SCN)(H_2O)(NH_3)_3]Br$

—ONO ——— , —(NCS)— , —(ONO)(NCS)—

Ans:- four.

* Hydrate Isomerism or Solvate Isomerism:-

→ In this isomerism, the isomers differ in number of water molecule as a ligand and free solvent molecules.

→ Co-ordination number and oxidation state should remain constant and the complex should remain ionic.

e.g. $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

6 H_2O ligand — 5 H_2O ligand — 1 solvent H_2O

$[Cr(H_2O)_4(Cl_2)]Cl \cdot 2H_2O$

4 H_2O ligand — 2 H_2O solvent

like ionisation isomerism.

* Co-ordination Isomerism:-

→ This isomerism arises due to the exchange of ligands b/w positive and negative co-ordination sphere such that co-ordination number and oxidation state remains same.

$[Pt(NH_3)_4]^{+2}[PtCl_4]^{-2}$ → Kaise pata laga. Pt^{+2} → C.N = 4 dekh liya.

$[Pt(NH_3)_3Cl]^{+1}[PtNH_3Cl_3]^{-1}$, $[Pt(NH_3)_2Cl_2]^{0}$

So there are co-ordination isomers. $[Pt(NH_3)_2Cl_2]^{0}$ → this is not Co-ordination isomer (no charge)

$[Pt(NH_3)Cl_3]$ $[Pt(Cl)(NH_3)_3]$ &

$[Pt(NH_3)_4]^{+2}[PtCl_4]^{-2}$

are two isomers of this Compound only.

Quest. How many no. of co-ordination isomers of

$[\overset{+2}{Pt}(NH_3)_4]^{+2}[\overset{+2}{Cu}Cl_4]^{-2}$

Ans: $[Pt(NH_3)_3Cl]^{+1}[\overset{+2}{Cu}Cl_3(NH_3)]^{-1}$

$[Pt(NH_3)_2Cl_2]^{0}[Cu\,Cl_2(NH_3)_2]^{0} \rightarrow \underline{X}$

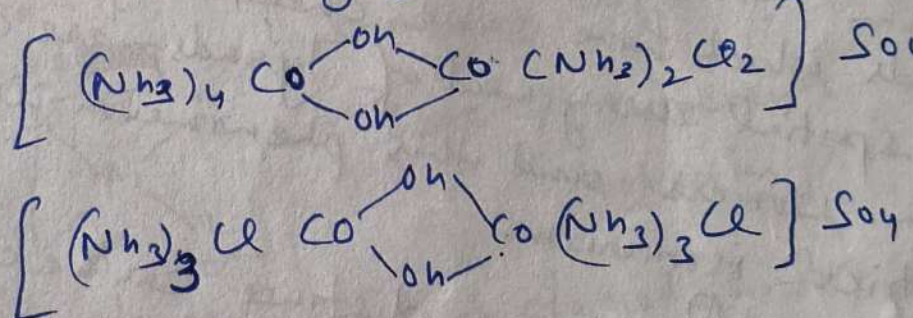
So Ans: 2 possibilities.

* Co-ordination - Position Isomerism:-

→ This isomerism is shown by polynuclear complexes.

→ This isomerism arises due to the different arrangement of ligands in bridging complexes.

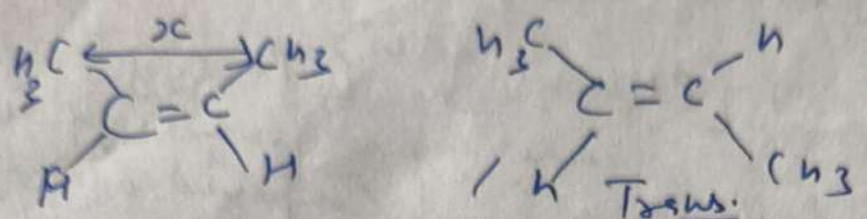
e.g.



* Stereoisomerism:-

→ Compounds having same chemical formula but different arrangement of atoms in space, are called as stereoisomers and this phenomenon is known as Stereoisomerism.

In Geometrical isomerism:-



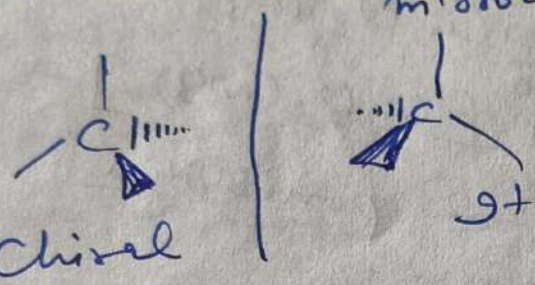
Cis- Trans.

in organic chemistry.

distance b/w CH_3-CH_3 changes.

There are geometrical isomers of other.

Optical Isomer:→



Chiral

It does not superimpose on its mirror image

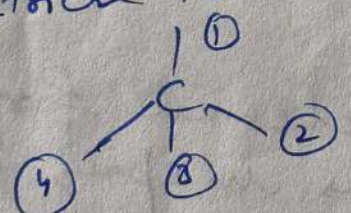
So it shows optical isomerism.

shows optical

So, Tetrahedral complexes does not show geometrical isomerism

→ Compounds which have same chemical formula but different spatial arrangement of ligands, are called as geometrical isomers and this phenomenon is known as geometrical isomerism.

* e.g.



→ distance can be changed So, does not show geometrical isomerism. (G.I.)

* Optical Isomerism conditions:-

↳ Complex should be chiral.

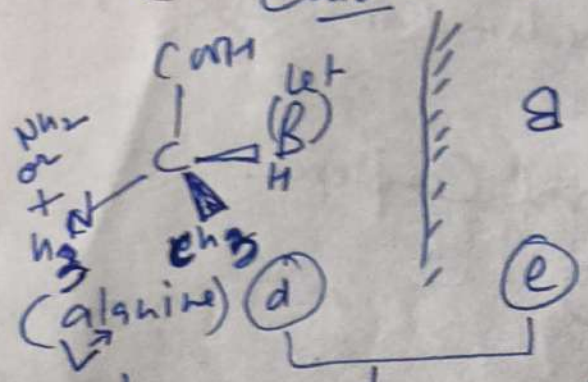
↳ Does not superimpose on its mirror image

↳ Symmetry elements [POS] should not be present.

Plane of symmetry.

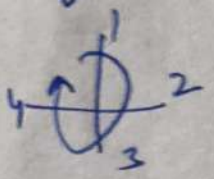
dextrorotatory (clockwise) 'd' or (+) Chiral e.g. alanine sign.

Levorotatory (Anti-clockwise) 'l' or (−) e.g.- alanine sign.



a → does not superimpose on its mirror image.

they can rotate plane polarised light in clockwise & anti-clockwise dirn.



enantiomers (enantiomeric pair)

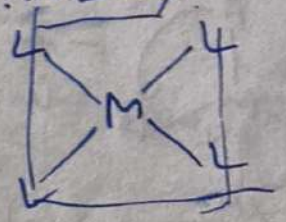
Dextroismers - rotate plane polarized light clockwise,

(+) dextro rotatory (−) Levorotatory levoismers - rotate plane polarized light anticlockwise.

R- enantiomer S- enantiomer

Quest: Can square planar complex show optical isomerism?

Ans: No [redacted] L should be different.



& here POS presents (Molecular plane of symmetry)

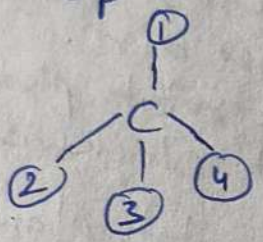
→ Square planar complexes do not show optical isomerism because of the presence of POS but they can show G.I (molecular POS)

→ Tetrahedral complexes do not show G.I. but can show O.I.

→ Octahedral complexes can show both G.I & O.I.

Notations:-

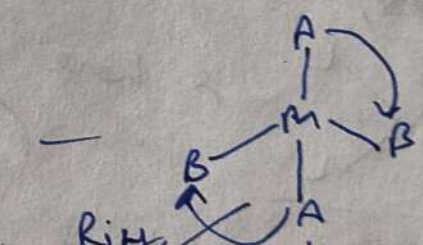
* Monodentate ligands:- a, b, c, d, e, f - - -
* Symmetrical Bidentate ligands - (AA) (BB) (CC) (DD) - - -
  (en, Edta^{4-}) जो E-Polydentate हो।
* Unsymmetrical Bidentate ligands - (AB) (CD) (Ef) - - -
  (gly, dmg etc)
* Optical isomerism in tetrahedral Complexes:-



① ≠ ② ≠ ③ ≠ ④
Condition:- ↑

e.g. Ma_4 — does not show O.I
Ma_3b — "
Ma_2b_2 — "
Ma_2bc — "
$Mabcd$ — show (✓) 2 stereoisomers. (enantiomer) S & R type.

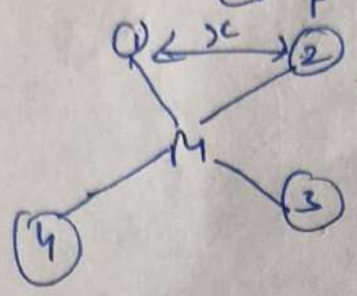
e.g. $M(AA)a_2$ — ×
$M(AA)bc$ — ×
$M(AB)_2$ — ✓ —



- 2 O.I. Ring (in plane)
Ring (out of plane) does not show POS. no-mirror image.

Trick :→ (i) Tetrahedral complexes having only monodentate ligands show O.I if ligands are different.
(ii) Tetrahedral complexes having two bidentate ligands show O.I. if both ligands are unsymmetrical.

* Geometrical Isomerism in square planar Complexes:-



(Ligands) all in same plane

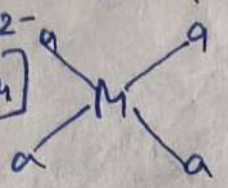
Cis → (1,2), (2,3), (3,4), (4,1)

Trans → (1,3), (2,4) ∠180°

(x - increases)

	O.I.	G.I
e.g. Ma_4 →	×	×

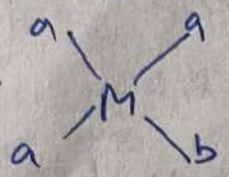
e.g. $[PtCl_4]^{2-}$



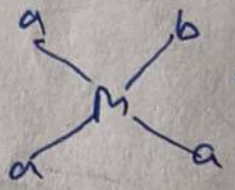
⟷ same in trans.

Ma_3b

e.g.



⟷

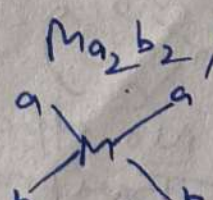


→ × × (e.g. $[Pt(NH_3)_3Br]$)

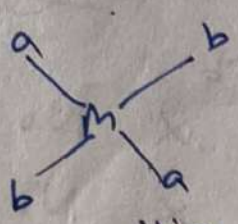
(a,a) (a,b) transposition

(a,a) (a,b) same transposition

e.g. Ma_2b_2, e.g. $[Pt(NH_3)_2Cl_2]$



⟷



→ No. O.I
2 G.I
Total stereoisomer = 2 Ans.

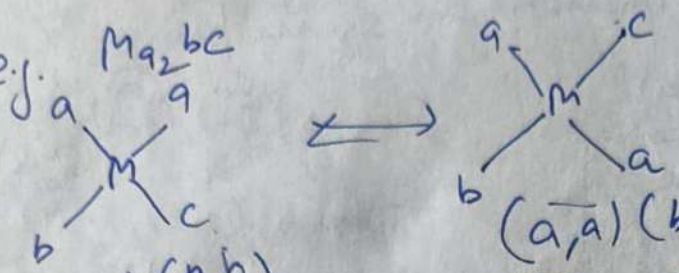
Trans-position (a,b) (a,b)

~~trans~~-position changed.
(a,a) (b,b)

(Cis-platin) Used in cancer therapy

Trans

e.g. Ma_2bc



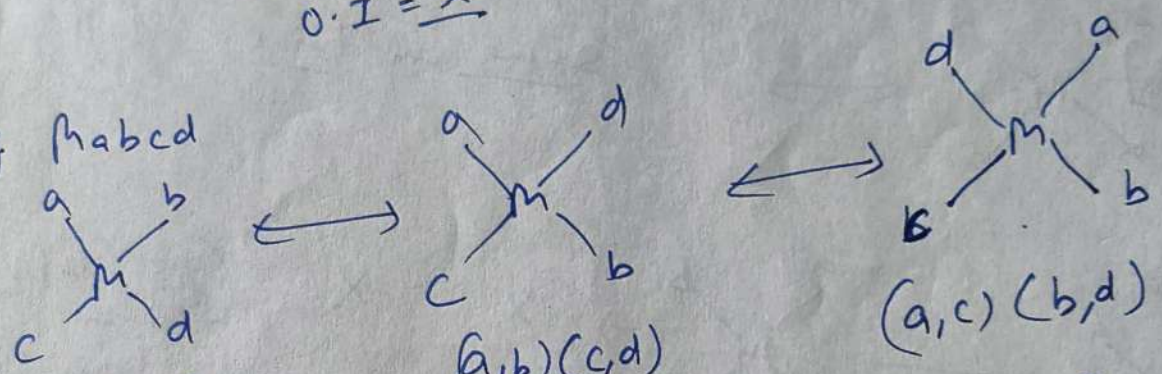
(a,c) (a,b)
Trans position

(a,a) (b,c)
Trans position

G.I = 2
O.I = x

Total S.I = 2.

e.g. Mabcd



(a,d) (c,b)

(a,b)(c,d)

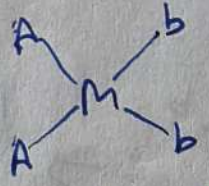
(a,c) (b,d)

Total G-I - 3
O-I - x

Total S.I = 3

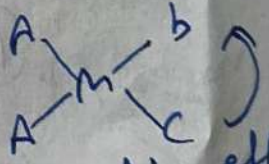
Note: Bidentate always attach to cis position:-

e.g. $M(AA)b_2 \rightarrow$ [Pt(en)Cl_2]



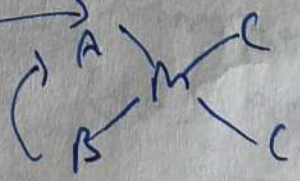
— No. G.I

e.g. $M(AA)bc \longrightarrow$ × No G.I.



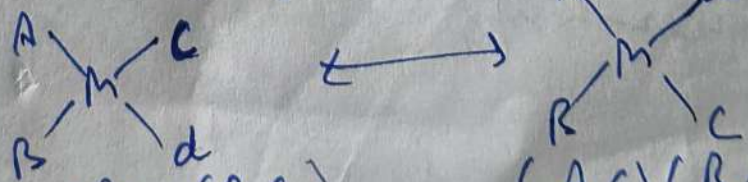
No effect on Trans position

e.g. $M(AB)C_2 \longrightarrow$ × No G.I.



No effect on trans-position.

e.g. $M(AB)Cd \longrightarrow$ yes



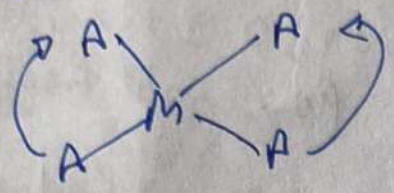
(A,d) (B,C)

(A,C) (B,d).

2 G.I.

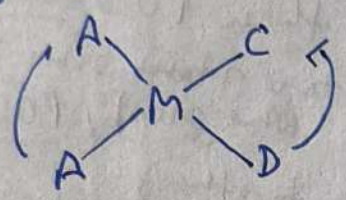
e.g. $M(AA)_2$

$[Pt(en)_2]^{2+}$



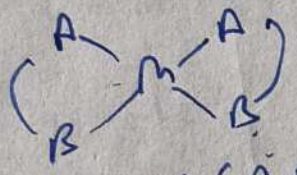
→ × G.I.

e.g. $M(AA)(CD)$



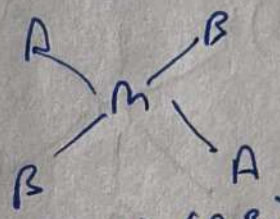
⟷ × No. G.I

e.g. $M(AB)_2$



Trans position (A,B) (A,B)

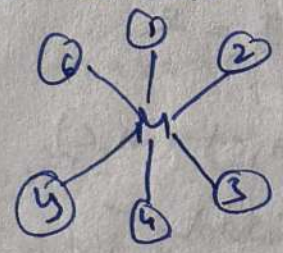
→



(AA) (BB)

→ 2 G.I.

* Stereo Isomerism in Octahedral Complexes:-



Trans-position:- At 180°, (1,4) (2,5) (3,6)

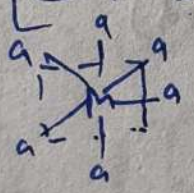
Cis → Rest of all.

Dealing is easy here.

If different trans-position occurs then isomer exists otherwise not.

e.g. Ma_6 →

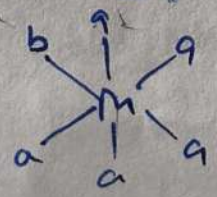
$[Cr(NH_3)_6]^{3+}$



Pos exist so, no O.I.

transpositions are same, no G.I. So → S.I = 1

e.g. Ma_5b

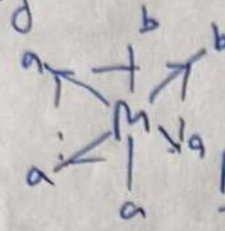


G.I = ×

Pos exist, So D.I = ×

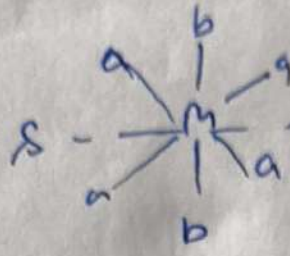
So, S.I = 1

e.g Ma_4b_2



POS

(a,b) (a,b) (a,a)



POS

(b,b) (a,a), (a,a)

So G.I = 2

No O.I = ×, So, S.I = 2

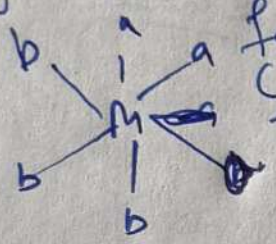
POS exists here

Trick: – (i) In case of Monodentate ligands, if two transpositions are same, then POS exists: (POS)

(ii) (a,a) (a,b), two atoms same in one group, POS ✓

e.g. Ma_3b_3 (Imp.)

fac (facial) (3a) together &

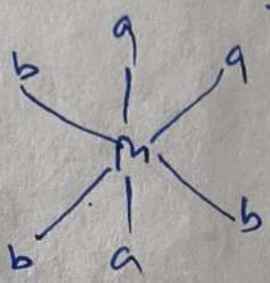


(a,b) (a,b) (a,b)

POS ✓

So, No O.I.

mer (meridia) (2 a together) 3a, separated



(a,a) (a,b) (b,b) POS ✓

2 G.I., No O.I.

So, S.I = 2

e.g. $[Ma_2b_2c_2]$

× (a,a) (b,b) (c,c), (a,a) (b,c) (b,c), × (b,b) (a,c) (a,c),

(c,c) (a,b), (a,b), (a,b) (b,c) (c,a) ✓ (Important) → 2 enantiomer

× Total G.I = 5

O.I = 2 − 1 = 1 (already considered)

O.I. = 2.

then, stereoisomer = 6 (S.I)

Quest: Which of the following [illegible]

* Table for Symmetrical bidentate & monodentate (Mix).

Complex-Octahedral

Complex	G. I.	Enantiomeric pair O. I. pair optically active	Total S. I
① $M(AA)_3$	0	1	2
② $M(AA)_2b_2$	2	1	3
③ $M(AA)_2bc$	2	1	3
④ $M(AA)b_4$	0	0	1
⑤ $M(AA)b_3c$	2	0	2
⑥ $M(AA)b_2c_2$	3	1	4
⑦ $M(AA)b_2cd$	4	2	6
⑧ $M(AA)bcde$	6	6	12

Imp:

---

* Stereo Isomerism in octahedral Complexes:-

* $M(AB)_3$ — Table

Complex	G. I	Enantiomeric pair Optically active	Total S. I.
① $M(AB)_3$ — Imp	2	2	4
② $M(AB)_2c_2$	5	3	8
③ $M(AB)_2cd$	6	5	11
④ $M(AB)c_4$	—	—	1
⑤ $M(AB)c_3d$	3	1	4
⑥ $M(AB)c_2d_2$	4	2	6
⑦ $M(AB)c_2de$	7	5	12
⑧ $M(AB)cdef$	12	12	24

Quest:- The ionization isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is:-

exchange

a) $[Cr(H_2O)_4(O_2N)]Cl_2$

b) $[Cr(H_2O)_4Cl_2][NO_2]$

c) $[Cr(H_2O)_4Cl(ONO)]Cl$

d) $[Cr(H_2O)_4Cl_2(NO_2)]H_2O$

Ans:→ (b)

Quest:→ Which of the following pairs represent linkage isomer?

A) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

B) $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$

C) $[Co(NH_3)_5(NO_3)]SO_4$ and $[Co(NH_3)_5(SO_4)]NO_3$

D) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

Ans:- for linkage ismer, ambidentate ligand must.

(B)

Quest:- Among (I) - (IV), the complexes that can display geometrical ismerism are

1. $[Pt(NH_3)_3Cl]^+$, Ma_3bx 2. $[Pt(NH_3)Cl_5]^-$, Ma_5b X

Ma_2bc 3. $[Pt(NH_3)_2Cl(NO_2)]$ 4. $[Pt(NH_3)_4ClBr]^{2+}$, Ma_4bc

a) I & II b) II & III c) IV & I d) III & IV

Ans:- (d) ✓

(67)

somerism

105 exist
No O.I

3.I = 2
ol already
Considered,

Quest:- Indicate the complex/complex ion which did not show any geometrical isomerism:-

A) $[Co(NH_3)_3(NO_2)_3]$ (Ma_3b_2), B) $[CoCl_2(en)_2]$

c) $[Co(NH_3)_4Cl_2]^+$ (Ma_4b_2) d) $[Co(CN)_5(NC)]^{3-}$ (Ma_5b)

Ans: So, Ma_5b does not show G.I.

Quest:- The complex that can show fac and mer isomeris→

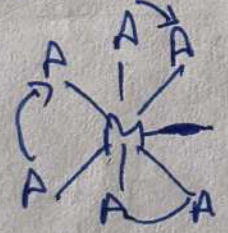
A) $[CoCl_2(en)_2]$ B) $[Pt(NH_3)_2Cl_2]$

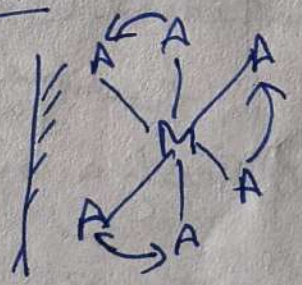
c) $[Co(NH_3)_4Cl_2]$ D) $[Co(NH_3)_3(NO_2)_3]$

Ans:- Ma_3b_3 → So, (d) Ans.

Quest: $[M(AA)_3]$ → Imp. e.g. $[Cr(en)_3]^{3+}$

Ans:- G.I. O.I



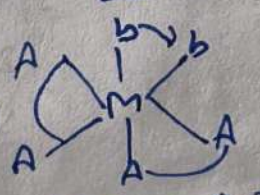


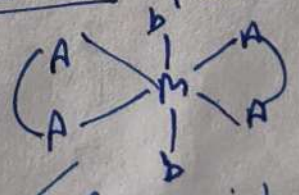
It will show O.I because it does not superimpose on its mirror image.

2 O.I, So S.I = 2

01 enantiomeric pair.

Quest:- $[M(AA)_2b_2]$





Enantiomeric Pair = 01

O.I = 2

Total → S.I → 3

Pos ×, O.I ×

Pos exist / No O.I

2 G.I

O.I — ×

S.I = 2

01 already considered.

* for octahedral complexes:-

	Complex	G.I	Enantiomeric pair	S.I.
1	Ma_6	0	0	1
2	Ma_5b	0	0	1
3	Ma_4b_2	2	0	2
4	Ma_4bc	2	0	2
5	Ma_3b_3	2	0	2
6	Ma_3b_2c	3	0	3
7	Ma_3bcd	4	1	5
8	$Ma_2b_2c_2$	5	1	6
9	Ma_2b_2cd	6	2	8
10	Ma_2bcde	9	6	15
11	$Mabcdef$	15	15	30

Quest:- The no. of geometrical isomers that can exist for square planar $[Pt(Cl)(py)(NH_3)(NH_2OH)]^+$ is [py = pyridine]:

Ans:- $[Mabcd] \rightarrow$ square planar - pos exists.

G.I = 3

O.I $\rightarrow$ X

Quest: $[Cr(H_2O)_6]Cl_3$ & $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ represent:-

Ans:- Hydrate isomerism.

Quest. Which complex ion has cis (G.I.) and trans isomer:-

a) $[PtCl_3NH_3]^-$ b) $[Pd(CN)_5NH_3]^-$ c) $[PtCl_2(CN)_2]^{2-}$

Ans:- (d) $[Pt(C_2O_4)_2]^{2-}$ $Pt^{+2} \rightarrow$ square planar

$\rightarrow Ma_2b_2 \rightarrow$ (c) Ans.

Quest: Which of the following Complexes shows optical isomerism?

A) $[Co(NH_3)_4Cl_2]Cl$

B) $[Co(NH_3)_3Cl_3]$

C) Cis $(Co(en)_2Cl_2)Cl$

D) trans $[Co(en)_2Cl_2]Cl$

Ans:- Cis $[M((AA)_2b_2)]$

2.G.I → 1- common
one show O.I pair

S.I. → 3

Cis $(Co(en)_2Cl_2)Cl$ — (C)

Quest. Which one of the following has an optical isomer?

A) $[Zn(en)_2]^{2+}$ B) $[Zn(en)(NH_3)_2]^{2+}$

C) $[Co(en)_3]^{3+}$ d) $[Co(H_2O)(en)]^{3+}$

Ans:- $M(AA)_3$ → (C) GI ✗, O.I ✓

Quest:- Which of the following does not show optical isomerism?

A) $[Co(NH_3)_3Cl_3]$ B) $[Co(en)Cl_2(NH_3)_2]^+$

C) $[Co(en)_3]^{3+}$ d) $[Co(en)_2Cl_2]^+$

Ans:- Ma_3b_3 → O.I — ✗ (A)

Quest:- Chiral complex from the following is:

A) Cis $[PtCl_2(en)_2]^{2+}$ B) trans $[PtCl_2(en)_2]^{2+}$

C) Cis- $[PtCl_2(NH_3)_2]$ D) trans $[Co(NH_3)_4Cl_2]^+$

Ans:- A - shows O.I. → It is chiral.

Quest:- The complex(es), which can exhibit the type of isomerism shown by $[Pt(NH_3)_2Br_2]$, is (are)

$[en = H_2N\,CH_2CH_2NH_2]$

C.N = 4

$Pt^{+2} \rightarrow$ Square planar

A) $[Pt(en)(SCN)_2]X$ $M(AA)b_2$

B) $[Zn(NH_3)_2Cl_2]X$ $\rightarrow sp^3 \rightarrow$ tetrahedral (Zn+2) G.I ✓ O.I ✗

C) $[Pt(NH_3)_2Cl_4]$ Ma_2b_4 ✓

D) $[Cr(en)_2(H_2O)(SO_4)]^+$ $M(AA)bc$ ✓

Ans: C & D.

Quest: Total no. of cis N-Mn-Cl bond angles (that is, Mn-N and Mn-Cl bonds is cis positions) present in a molecule of cis-$(Mn(en)_2Cl_2)$ complex is

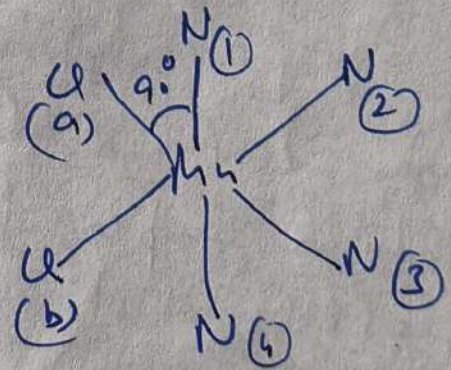
6.

Ans. octahedral geometry. cis positions are at 90° to each other, 2 Cl ligands

Total N-Mn-Cl bond angles = 2×4 = 8 Ans

In Cis → 6

Cl_a - Mn - N(1)
Cl_a - Mn - N(2)
Cl_a - Mn - N(4)
Cl_b - Mn - N(1)
Cl_b - Mn - N(3)
Cl_b - Mn - N(4)



Cis (Cl-Mn-N)