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Internal Assessment - I (Set-1)

Part-A :-

1. CFSE of $[CoCl_6]^{2-}$ = 21000 cm^{-1}
CFSE of $[CoCl_4]^{2-}$ = $\frac{4}{9} \times 21000$ $\left[\because \Delta_t = \frac{4}{9}\Delta_o\right.$
= 9333 cm^{-1}
$[CoCl_6]^{2-} \rightarrow O_h$ complex
$[CoCl_4]^{2-} \rightarrow T_d$ complex $\left.\right]$

2. $K_3[Cr(C_2O_4)_3] \longrightarrow 3K^+ + [\underset{x}{Cr}(C_2O_4)_3]^{3-}$
bidentate ligand (ox)
Here, $C_2O_4^{2-}$:- No. of ligands here = 2x3
= 6
$\therefore$ Coordination no. (CN) = 6

$x + (-2)\times 3 = -3 \Rightarrow x = -3+6$
$= +3$
$\therefore$ Oxidation no. (ON) = +3

4. $[Co(NH_3)_5(NO_2)]^{2+}$ & $[Co(NH_3)_5(ONO)]^{2+}$ $\Rightarrow$ Linkage isomerism
Here, NO_2 is an Ambidentate ligand

$\therefore$ $NO_2 \rightarrow$ N donor group
ONO $\rightarrow$ O donor group

3. In $Na_2[Pt(CN)_4]$, lewis acid is Pt^{2+} [$\because$ CMA $\rightarrow Pt^{2+}$]

5. In 1s e^- of N :- $1s^2 2s^2 2p^3$
* S = 0.3 [For 1s of any atom/ion]

$\therefore Z_{eff} = Z - S$
$= 7 - 0.3$
$= 6.70$

Part-B:-

6a) (i) **Hard Acid v/s Soft Acid**

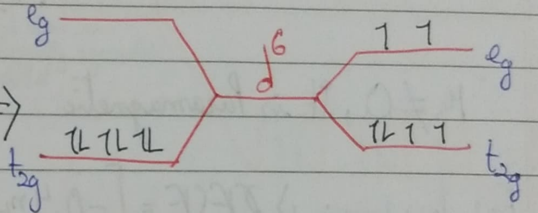
Hard Acid	Soft Acid
• Small ionic radius	• Large ionic radius
• Low electron affinity & high electronegativity	• High electron affinity & low electronegativity
• High +ve charge	• Low +ve charge
• Low Polarizability	• High Polarizability
• High Ionization Potential	• Low Ionization Potential
Eg:- H^+, Na^+, K^+, Ca^{2+}	Eg:- Cu^+, Ag^+, Pt^{2+}

(ii) For Fe(II):-

Fe :- [↑↓ | ↑ | ↑ | ↑ | ↑] [↑↓]

Fe^{2+} :- [↑↓ | ↑ | ↑ | ↑ | ↑] [ ]

$\Rightarrow$



For high spin:- 1) CFSE $= [-0.4 n_{t_{2g}} + 0.6 n_{e_g}]\Delta_o + 3P$

$= [-0.4(4) + 0.6(2)]\Delta_o + 3P$

$= [-1.6 + 1.2]\Delta_o + P$

$\Rightarrow$ CFSE $= -0.4\Delta_o + P$

2) Magnetic nature :- $\mu_s = \sqrt{n(n+2)}$

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

$\because \mu_s \neq 0$, It is Paramagnetic $\quad = \sqrt{4(6)}$

$\Rightarrow \mu_s = \sqrt{24} = 4.89$

For low spin:- 1) CFSE $= [-0.4 n_{t_{2g}} + 0.6 n_{e_g}]\Delta_o + P$

$= [-0.4(6) + 0.6(0)]\Delta_o + P$

$\Rightarrow$ CFSE $= -2.4\Delta_o + P$

2) Magnetic nature :- $\mu_s = \sqrt{n(n+2)}$

$= \sqrt{0(0+2)}$

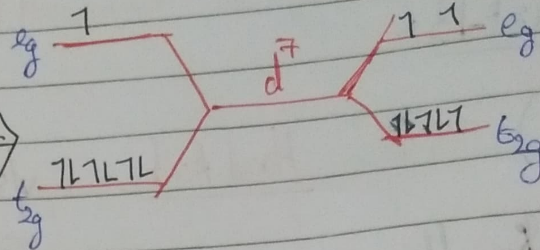
$\Rightarrow \mu_s = 0$

$\because \mu_s = 0$, It is Diamagnetic

For Co(II) :-

Co :- [↑↓|↑↓|↑↓|↑|↑] [↑↓]

Co^{2+} :- [↑↓|↑↓|↑|↑|↑] [ ]



For high spin :- 1) CFSE $= [-0.4 n_{t_{2g}} + 0.6 n_{e_g}]\Delta_o + P$

$= [-0.4(5) + 0.6(2)]\Delta_o + P$

$= [-2 + 1.2]\Delta_o + P$

$\Rightarrow$ CFSE $= \cancel{-0.6}\ -0.8\Delta_o + P$

2) Magnetic nature :- $\mu_s = \sqrt{n(n+2)}$

$= \sqrt{3(3+2)}$

$= \sqrt{15}$

$\Rightarrow \mu_s = 3.87$

$\because \mu_s \neq 0$, It is Paramagnetic

For low spin :- 1) CFSE $= [-0.4 n_{t_{2g}} + 0.6 n_{e_g}]\Delta_o + P$

$= [-0.4(6) + 0.6(1)]\Delta_o + P$

$= [-2.4 + 0.6]\Delta_o + P$

$\Rightarrow$ CFSE $= -1.8\Delta_o + P$

2) Magnetic nature :- $\mu_s = \sqrt{n(n+2)}$

$= \sqrt{1(1+2)}$

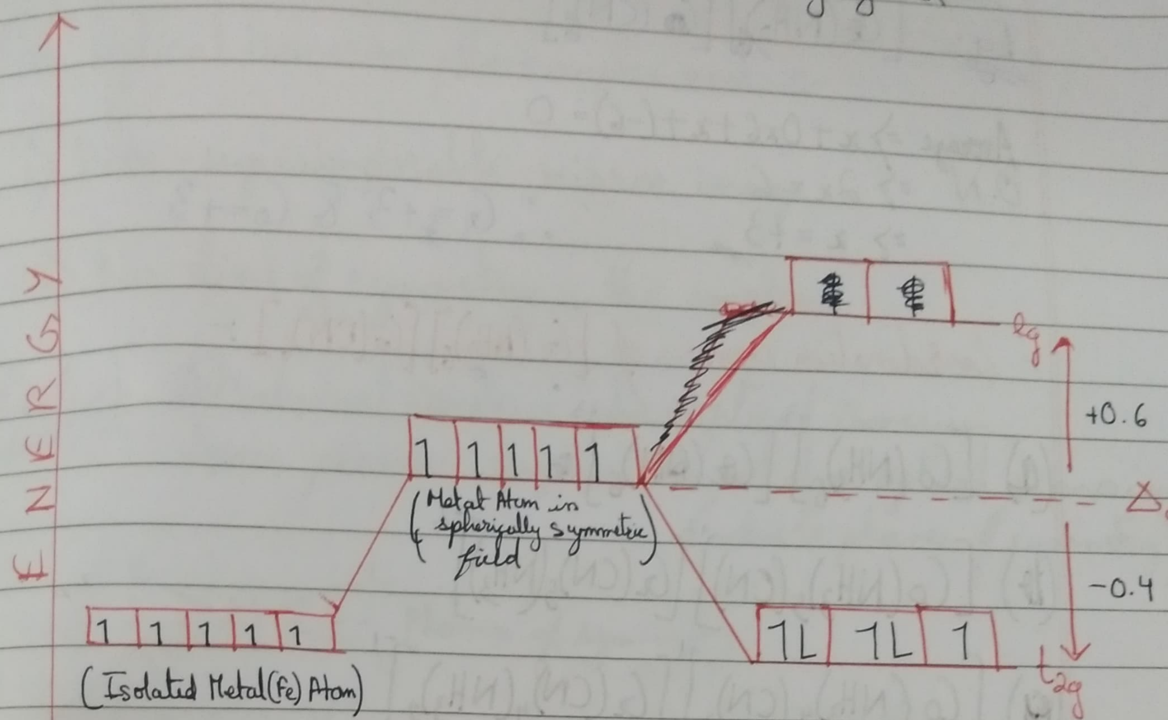
$= \sqrt{3}$

$\Rightarrow \mu_s = 1.73$

$\because \mu_s \neq 0$, It is Diamagnetic

6b) $[Fe(CN)_6]^{3-}$:-

Fe^{3+} :- [1|1|1|1|1] [ ] & CN → strong ligand



<u>For CFSE</u> :- $CFSE = [-0.4\, n_{t_{2g}} + 0.6\, n_{e_g}]\Delta_o$
$= [-0.4(5) + 0.6(0)]\Delta_o$
$= -2.0\Delta_o$

<u>For Magnetic Moment</u> :- $\mu_s = \sqrt{n(n+2)}$
$= \sqrt{1(1+2)}$
$= \sqrt{3}$
$= 1.73$

$\because \mu_s \neq 0$, It is <u>Paramagnetic</u>

7a) (i) Coordination isomerism :- Occurs when there is exchange of ligands in cationic-antonic complex

Eg:- $\left[\overset{+3}{Cr}(NH_3)_6\right]\left[Co(CN)_6\right]^{-3}$

Average O.N $\Rightarrow x + 0\times 6 + x + (-6) = 0$

$\Rightarrow 2x = 6$

$\Rightarrow x = +3$ $\therefore Cr = +3$ & $Co = +3$

$\therefore$ Coordination isomers of $[Cr(NH_3)_6][Co(CN)_6]$:-

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

(b) $[Co(NH_3)_5(CN)]^{+2}[Cr(CN)_5(NH_3)]^{-2}$

(c) $[Co(NH_3)_4(CN)_2]^{+1}[Cr(CN)_4(NH_3)_2]^{-1}$

(d) $[Co(NH_3)_3(CN)_3][Cr(CN)_3(NH_3)_3]$ → neutral complex

(ii) Hydrate isomerism :- Occurs when there is exchange ~~of water~~ between water (H_2O) in complex and anionic ligand

Eg:- $[Co(H_2O)_6]Cl_3$

Average O.N $\Rightarrow x + 0\times 6 + (-3) = 0$

$\Rightarrow x = +3$ $\therefore Co = +3$

$\therefore$ Hydrate isomers of $[Co(H_2O)_6]Cl_3$:-

(a) $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$

(b) $[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$

(c) $[Co(H_2O)_3Cl_3] \cdot 3H_2O$

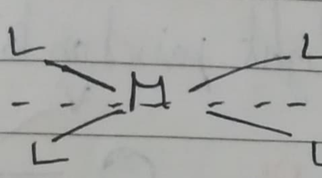
(iii) Optical isomerism:- When a compound/complex is able to rotate plane polarized light, then such compounds whose ~~sup~~ mirror image is the optical isomer of that compound/complex.

For optical isomerism, ~~the complex must~~ :-

1) Non-superimposable mirror image

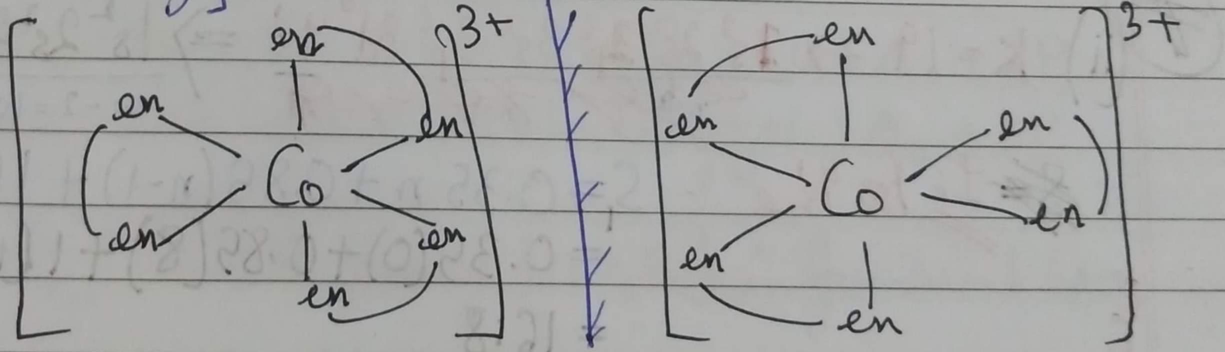
2) No line of symmetry in the complex

Eg:- { Tetrahedral complexes shows optical isomerism
Square planer complexes do not show optical isomerism
(due to plane of symmetry)



Plaine of symmetry

Eg:- $[Co(en)_3]^{3+}$



Non-supperimposable M.I formed

$\therefore$ $[Co(en)_3]^{3+}$ is opticaally active

b) (i) Given,

$\lambda_{max} = 600nm$

- $C.F.S.E = E = h\nu = h\frac{c}{\lambda_{max}}$

$= 6.626 \times 10^{-34} \times \frac{3 \times 10^{8}}{600 \times 10^{-9}}$

$= 3.313 \times 10^{-17}\ J$

E (in kJ) → Avogadro no (molecule/mol)

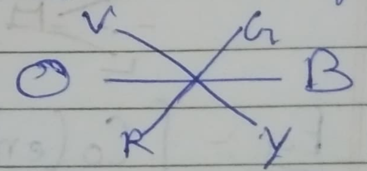
- $\Delta_0 = \frac{3.313 \times 10^{-17}}{10^{3}} \times (6.626 \times 10^{23})$

$= 21.95 \times 10^{3}\ kJ/mol$

(ii) • $\lambda_{max} = 600nm$:→ Orange light passed on to this complex

~~VBGYOR~~

∴ Complementary colour is ~~Orange~~ Blue



(ii) $K = 19 \rightarrow 1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^0\, 4s^1$

1. For 4s :- $\underbrace{1s^2\, 2s^2\, 2p^6}_{n-2=10}\ \underbrace{3s^2\, 3p^6}_{n-1=8}\ 3d^0\ \underbrace{4s^{\cancel{1}\to 0}}_{n=0}$ not contributing

$\therefore S = 0.35(n) + 0.85(n-1) + 1(10)$
$= 0.35(0) + 0.85(8) + 10$
$= 16.8$

$Z_{eff} = 19 - 16.8$
$= 2.2$

2. For 3d :- $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^0\, 4s^1$ → not contributing

In 3d orbital of K, there is zero electrons.

$\therefore Z_{eff}$ is not possible → negligible

Hence, by slater's rules, we have Z_{eff} for 4s > 3d

Hence, the 4s e^- is filled first and then 3d