Internal Assessment-I (Set 2)
[CCA1-T1]

Part-A :-

1. high spin → weak field ligand Iron(II) octahedral complex

Fe^{2+} :- $3d^6 4s^0$ d^6 ↑↑ / ↑↓↑↑ ∴ No. of unpaired e^- = 4

2. $\mu_B = \sqrt{n(n+2)} \Rightarrow 1.73 = \sqrt{n(n+2)}$

Here, for $n = 1$ (1 unpaired), $\mu_B = 1.73$

$[Ni(CN)_4]^{2-}$:- d^8 ↑↑ → 2 / ↑↓↑↓↑↓

$[Ti(Cl)_4]$:- d^2 ↑↑ → 2

$[Cu[NH_3]_4]^{2+}$:- d^9 ↑↓↑↓↑ → 1 / ↑↓↑↓

$[Co(Cl)_6]^{4-}$:- d^5 ↑↑ / ↑↑↑ → 5

3. e_g ↑↑ / t_{2g} ↑↓↑↓↑ d^7 ↑ e_g / ↑↓↑↓↑↓ t_{2g}

$CFSE = (-0.4 n_{t_{2g}} + 0.6 n_{e_g}) + n_p P$

For weak :- $CFSE = [-0.4(5) + 0.6(2)]\Delta_o = -0.8\Delta_o + 2P$ (+2P)

For strong :- $CFSE = [-0.4(6) + 0.6(1)]\Delta_{ov} = +1.8\Delta_o + 3P$ (+3P)

4. $[CoCl_2(en)_2]$ → In the form of $[MA_2B_2]$ ∴ Geometrical Isomerism

5. Ca^{2+}

Part-B :-

6a) (i)

Ionization Energy	Electron Affinity
Energy required to remove outermost electron from gaseous isolated atom	Energy released when a gaseous isolated atom gains an e^-
For metals :- Along period, IE ↑ (due to rise in nuclear charge)	For metals :- Along period, E.A ↓ (non-metallic character increases)
Along group, IE ↓ (no. of shells increase)	Along group, E.A ↑ (metal character decreases)
For non-metal :- Along period, IE ↑ (same reason as previous)	For non-metal :- Along period, E.A ↑ (non-metallic character ↑)
Along group, IE ↓ (metallic character ↑, non-m ↓)	Along group, E.A ↓ (non-metallic character ↓)

6 a) (ii) $Ca^{2+} < Ca$

Ca^{2+} has $2e^-$ less than Ca $\therefore$ Nuclear pull increase,
$\therefore$ Size of Ca^{2+} decrease

$F^- > F$

F^- has $1e^-$ more than F and attains noble gas configuration
$\therefore$ Effective nuclear pull decrease, $\rightarrow$ Size of F^- increase

6 b) (i) Factors affecting Δ_o are:-

1. Strong/Weak Field ligands:- [Nature of ligand]
   In case of strong, splitting of d-orbitals is high
   In case of weak, splitting of d-orbitals is low

2. Nature of metal/CMA:- Weather the metal belongs to 1^{st} (3d), 2^{nd} (4d), 3^{rd} (5d) transition series

3. Charge on CMA:-
   Charge on CMA (transition metals) have variable valencies
   More the charge, greater the Δ_o value and vise versa

4. Electronic configuration of CMA:-
   The distribution of e^- in t_{2g} & e_g orbitals directly impacts CFSE

(ii) For $[MnCl_4]^{2-}$:- $x + (-4) = -2 \Rightarrow x = +2$ $[Mn^{2+}]$

~~Here, Cl → weak ligand~~

Mn^{2+}:- $3d^5 4s^0$ $\longrightarrow$ d^5

$\uparrow\uparrow\uparrow$ t_{2g} $\uparrow +0.4$

$\uparrow\uparrow$ e_g $\downarrow -0.6$

Here, $[MnCl_4]^{2-} \rightarrow$ tetrahedral (4 ligands)

$\therefore$ CFSE $= [-0.6\, n_{e_g} + 0.4\, n_{t_{2g}}]\Delta_t + n_p P$

~~$= -0.6(2) + (0)P$ [$n_p = 0$, no paired e^-]~~

$= [-0.6(2) + 0.4(3)]\Delta_t + (0)P$

$= 0\Delta_t + 0P$

$\Rightarrow$ CFSE $= 0$

$\therefore \mu_s = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35}$
$= 5.92$

For $[CoCl_4]^{2-}$:- $x+(-4)=-2 \Rightarrow x=+2$ $[Co^{2+}]$

~~Here,~~

All ligands in tetrahedral complexes are WFL $\left[\Delta_t = \frac{4}{9}\Delta_o\right]$

Co^{2+} :- $3d^7 4s^0 \longrightarrow d^7$: $\uparrow\uparrow\uparrow$ t_{2g} ; $\uparrow\downarrow\ \uparrow\downarrow$ e_g

$\therefore$ $CFSE = [-0.6\, n_{e_g} + 0.4\, n_{t_{2g}}]\Delta_t + n_p P$

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

$= -1.2\Delta_t + 2P$

$\mu_s = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15}$

$= 3.87$

For $[CuCl_4]^{2-}$:- $x+(-4)=-2 \Rightarrow x=+2$ $[Cu^{2+}]$

Cu^{2+} :- $3d^9 4s^0 \longrightarrow d^9$: $\uparrow\downarrow\ \uparrow\downarrow\ \uparrow$ t_{2g} ; $\uparrow\downarrow\ \uparrow\downarrow$ e_g

$\therefore$ $CFSE = [-0.6(4) + 0.4(5)]\Delta_t + 4P$

$= -0.4\Delta_t + 4P$

$\mu_s = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3}$

$= 1.73$

7a) (i) $[Pt(NH_3)_4(OH)_2]SO_4$ & $[Pt(NH_3)_4SO_4](OH)_2$

The type of Isomerism shown here → Ionisation Isomerism

In this type of Isomerism, there is exchange of coordination and ionization spheres of the coordinate complex

When compounds give different ions in solution, even though they have ~~same~~ same composition

Here ① $[Pt(NH_3)_4(OH)_2]SO_4 \longrightarrow [Pt(NH_3)_4(OH)_2]^{2+} + SO_4^{2-}$

② $[Pt(NH_3)_4SO_4](OH)_2 \longrightarrow [Pt(NH_3)_4SO_4]^{2+} + 2OH^-$

In ① we get SO_4^{2-} & ② we get OH^-

$\therefore$ The counter ions (anion) are different

(ii) $[Co(NH_3)_5SCN]$ & $[Co(NH_3)_5NCS]$

The type of isomerism shown here → Linkage Isomerism

In this type of isomerism, the ambidentate ligand in the complex changes their orientation and hence different donor atom.

When there is ambidentate ligands in a complex, linkage isomerism can take place.

Here, the ambidentate ligand is SCN (S donor atom) $:\ddot{S}-C\equiv N:$

SCN changes its orientation ⟶ NCS (N donor atom) $:N\equiv C-\ddot{S}:$

~~(iii) $[Pt(Py)_2(NH_3)_2Cl_2]^{2+}$~~

~~The type of isomerism shown here → Ligand Isomerism~~

~~In this type of isomerism, ligands adopt different isomeric form within the complex itself~~

~~When ligands itself shows isomerism, ligand Isomerism takes place~~

(iii) $[Pt(Py)_2(NH_3)_2Cl_2]^{2+}$

The type of isomerism shown here → Geometrical Isomerism

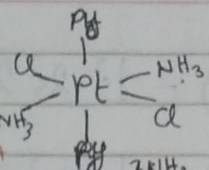
In this type of isomerism, the complex have same structural formula, chemical ~~formula~~ bonds but different spacial arrangements of ligands

In $[MA_2B_2C_2]$ form →
- M(aa)(bb)(cc)
- M(ab)(ab)(cc)
- M(aa)(bc)(bc)
- M(ac)(bb)(ac)
- M(ac)(ab)(bc)

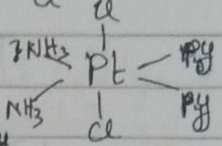
} 5 G.I

* Cis & trans form also possible for each case

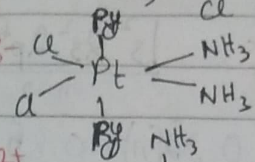
Here, 1) $[Pt(Py)_2(NH_3)_2Cl_2]^{2+}$:-



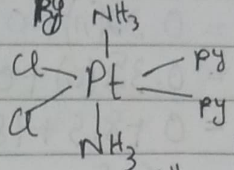
2) $[Pt(Py\,NH_3)(Py\,NH_3)Cl_2]^{2+}$:-



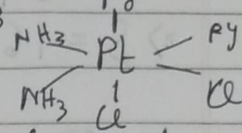
3) $[Pt(Py)_2(NH_3Cl)(NH_3Cl)]^{2+}$:-



4) $[Pt(py)(Cl)(NH_3)_2(py)(Cl)]^{2+}$:-



5) $[Pt(py)(Cl)(py\,NH_3)(NH_3Cl)]^{2+}$:-



7b) (i) In $[CrF_6]^{3-}$ $\rightarrow$ F is a halogenic ligand (weak ligand)

In $[Cr(CN)_6]^{3-}$ $\rightarrow$ CN is a carbon donar ligand (streng ligand)

In $[Cr(H_2O)_6]^{3+}$ $\rightarrow$ H_2O is a oxygen donar ligand (weak ligand)

A/c to Spectrochemical series, $F < H_2O < CN$

We know, CFSE $\propto$ Nature of ligand & $CFSE = E = \frac{hc}{\lambda}$ $\therefore CFSE \propto \frac{1}{\lambda}$

Based on nature of ligand :- 1) Streng ligand $\rightarrow$ CFSE $\uparrow$ $\rightarrow$ $\lambda \downarrow$

2) Weak ligand $\rightarrow$ CFSE $\downarrow$ $\rightarrow$ $\lambda \uparrow$

$\therefore$ In order of wavelength of light :-

$$[CrF_6]^{3-} > [Cr(H_2O)_6]^{3+} > [Cr(CN)_6]^{3-}$$

Here, $[CrF_6]^{3-}$ has the ~~lowest~~ lowest CFSE = highest λ

$[Cr(CN)_6]^{3-}$ has the highest CFSE = lowest λ

(ii) $Cu(29)$:- $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^9\, 4s^2$

$\Downarrow$

$1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^{10}\, 4s^1$ (Maintain stable configuration)

For 4s :- $\underbrace{1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6}_{n-2=18}\ \underbrace{3d^{10}}_{n-1=10}\ \underbrace{4s^{1}}_{n=0}$

$\therefore S = 0.35(n) + 0.85(n-1) + 1(n-2)$

$= 0.35(0) + 0.85(10) + 1(18)$

$= 0 + 8.5 + 18$

$\Rightarrow S = 16.5$

$\therefore Z_{eff} = Z - S$

$= 29 - 16.5$

$= 12.5$

For 3d :- $\underbrace{1s^2\, 2s^2\, 2p^6}_{n-2}\ \underbrace{3s^2\, 3p^6}_{n-1}\ \underbrace{3d^{10}}_{n=9}\ 4s^1$ no contribution here

$\therefore S = 0.35(n) + 0.85(n-1) + 1(n-2)$

$= 0.35(9) + 0.85(8) + 1(10)$

$= 3.15 + 6.8 + 10$

$\Rightarrow S = 19.95$

$\therefore Z_{eff} = Z - S$

$= 29 - 19.95$

$= 9.05$