UNIT II (*Answer any four*)
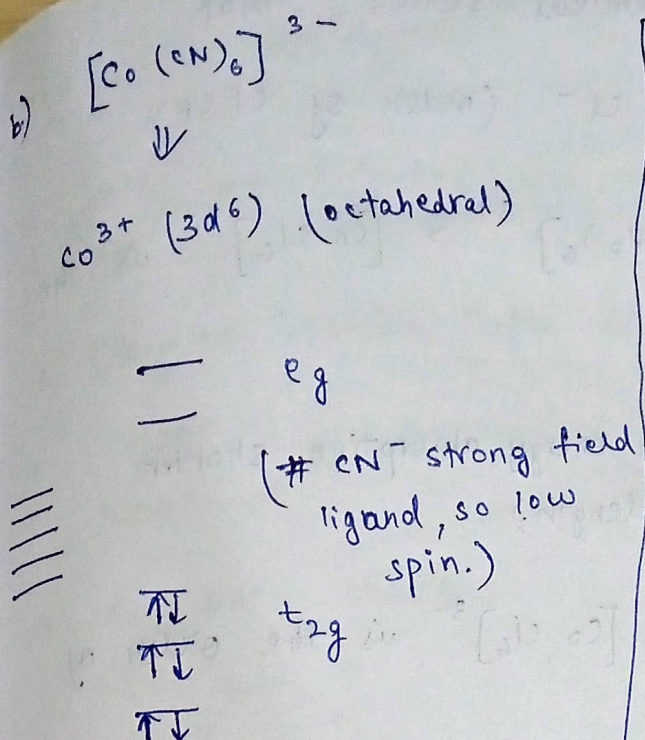
2. (a) Fe(phen)$_2$(NCS)$_2$ is found to be diamagnetic at low temperatures and paramagnetic at high temperatures. Explain

(b) Among these two compounds *viz.* Co(CN)$_6^{3-}$ and Ni(CO)$_4$ which one has a larger CFSE?

(c) Why do M(II) metal ions generally prefer tetrahedral geometry whereas M(III) metal ions prefer octahedral holes in spinel structures?

(d) What will be the correct order of absorption wavelength in the visible region, for these complexes, CoCl$_6^{3-}$, Co(CN)$_6^{3-}$, and Co(NH$_3$)$_6^{3+}$? Explain your answer.

(e) Calculate CFSE for Ti(H$_2$O)$_6^{3+}$ in kJmol^{-1} (Given absorption maxima is at 20300 cm^{-1} and 1 kJmol^{-1} = 83.7 cm^{-1}).

[2½ x 4]
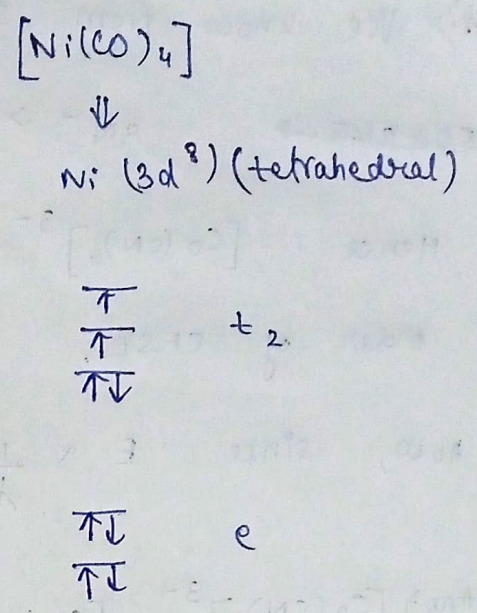
2> a) $[Fe(phen)_2(NCS)_2]$ exhibits spin crossover behaviour.

Co-ordination compounds of transition metal ions like Fe exhibit a switching phenomenon whereby central metal ion changes the spin state (high spin to low spin) upon change in temperature, pressure, magnetic field, etc. This phenomenon is called spin crossover (SCO). Therefore, $[Fe(phen)_2(NCS)_2]$ shows diamagnetic behaviour at low temperature (due to low-spin configuration $t_{2g}^6 e_g^0$) and paramagnetic behaviour at high temperature.

b) $[Co(CN)_6]^{3-}$

$\Downarrow$

Co^{3+} $(3d^6)$ (octahedral)

$\equiv\ e_g$

$\overline{}\ \overline{}$

(# CN^- strong field ligand, so low spin.)

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

$\Rightarrow$ CFSE $= 6 \times (-0.4\Delta_0) + 3P$

$= -2.4\Delta_0 + 3P$

(# now, $\Delta_t = \frac{4}{9}\Delta_0$)

$\therefore \boxed{|CFSE(Co^{3+})| > |CFSE(Ni)|}$

$[Ni(CO)_4]$

$\Downarrow$

Ni $(3d^8)$ (tetrahedral)

$\overline{\uparrow}$
$\overline{\uparrow}$ t_2
$\overline{\uparrow\downarrow}$

$\equiv$

$\uparrow\downarrow$ e
$\uparrow\downarrow$

(# although CO^- is strong field ligand, tetrahedral fields are always high spin)

$\Rightarrow$ CFSE $= 4 \times (-0.6\Delta t) +$
$\qquad\qquad 4 \times (0.4\Delta t) + 3P$

$= -0.8\Delta_t + 3P$

$= -0.8\left(\frac{4}{9}\Delta_0\right) + 3P$

$\approx -0.356\Delta_0 + 3P$

---

c) The CFSE (Δ_t) is smaller $(= \frac{4}{9}\Delta_0)$. This means that for $M(II)$ ions, CFSE might be lower in tetrahedral co-ordination. $M(III)$ ions have higher CFSE in octahedral co-ordination due to greater field splitting (Δ_0). Also, $M(II)$ ions are larger than $M(III)$ ions, so they experience less distortion in tetrahedral sites.

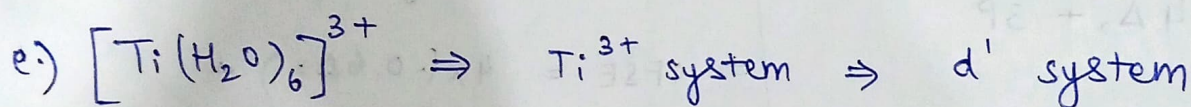d.) We know from spectrochemical series, that

$CN^- > NH_3 > Cl^-$ (order of CFSE)
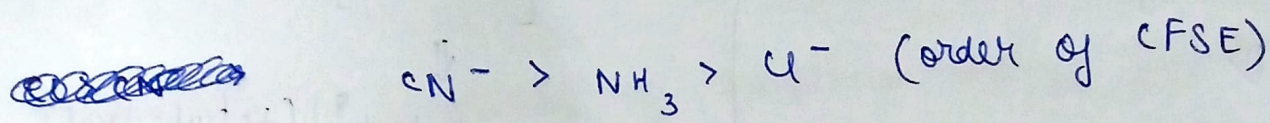
Hence, $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co\,Cl_6]^{3-}$ is the

order of CFSE.

now, since $E \propto \dfrac{1}{\lambda}$ (higher energy absorption; shorter wavelength)

Ans.) $[Co(CN)_6]^{3-} < [Co(NH_3)_6]^{3+} < [Co\,Cl_6]^{3-}$ is the order of

absorption wavelength.

e.) $[Ti(H_2O)_6]^{3+} \Rightarrow Ti^{3+}$ system $\Rightarrow d^1$ system

$\Rightarrow$ CFSE $= -0.4 \Delta_o \times 1 = -0.4 \Delta_o$

now, $\Delta_o = \dfrac{20\,300 \; cm^{-1}}{83.7 \; cm^{-1}/KJ\,mol^{-1}} = 242.53 \; kJ/mol$

$\therefore$ CFSE $= -0.4 \times 242.53 = \boxed{-97.012 \; kJ/mol}$

2. (a) (i) How is the crystal field splitting energy for octahedral (Δ_o) and tetrahedral (Δ_t) complexes related?
(ii) Calculate the CFSE for d^7 metal ion for octahedral high spin and low spin complexes.

(b) Answer *any two*:
(i) Explain the violet colour of $[Ti(H_2O)_6]^{3+}$ complex on the basis of the crystal field theory?
(ii) Comment on the colour and magnetic moment of $[Mn(H_2O)_6]^{2+}$ and $MnCl_4^{2-}$ and explain the facts.
(iii) What differences do you expect between the molecular structures of *trans*-$[Co(en)_2F_2]^+$ and *trans*-$[Co(en)_2(CN)_2]^+$ ions?

(c) (i) Discuss the position of halides in spectrochemical series. (ii) Explain why Mn_3O_4 is a normal spinel whereas Fe_3O_4 is an inverse one.

(d) Give an example of these drugs (*any two*) with structures (i) Vanadium-based insulin mimic (ii) Platinum-based anti-cancer (iii) Gold-based medicine for treatment of rheumatoid arthritis.

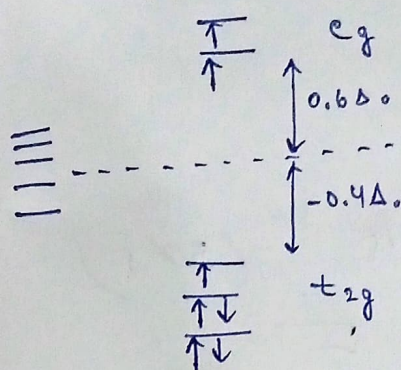(e) Discuss the role of following metal ions (*any one*) in human body (i) Ca (ii) Na

$$[(2+2)+(2+2)+(2+2)+(1\frac{1}{2}+1\frac{1}{2})+2]$$

2.) a.) i.) $\Delta_t = \frac{4}{9} \Delta_o$ $\Delta_t =$ crystal field splitting energy for tetrahedral complexes

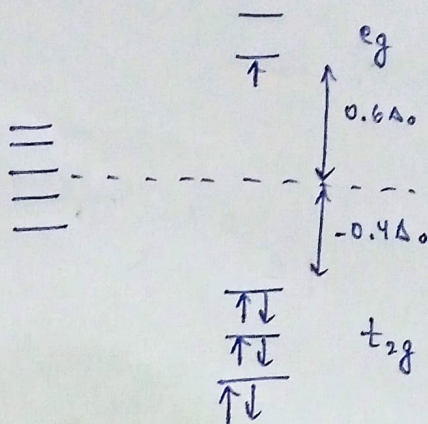$\Delta_o =$ crystal field splitting energy for octahedral complexes

ii) d^7 (high spin)

$$\frac{\uparrow}{\uparrow} \quad e_g$$

$$\equiv \;-----\begin{array}{c} \downarrow \\ \uparrow \end{array} \Big\} 0.6\Delta_o \\ ----$$

$$\Big\downarrow -0.4\Delta_o$$

$$\frac{\uparrow}{\frac{\uparrow\downarrow}{\uparrow\downarrow}} \quad t_{2g}$$

$\Rightarrow$ CFSE $= 5 \times (-0.4\Delta_o) +$

$2 \times (0.6\Delta_o) +$

$2P$

$= \boxed{-0.8\Delta_o + 2P.}$

d^7 (low spin)

$$\frac{\overline{}}{\uparrow} \quad e_g$$

$$\equiv \;----- \begin{array}{c} \downarrow \\ \uparrow \end{array} \Big\} 0.6\Delta_o \\ ----$$

$$\Big\downarrow -0.4\Delta_o$$

$$\frac{\uparrow\downarrow}{\frac{\uparrow\downarrow}{\uparrow\downarrow}} \quad t_{2g}$$

$\Rightarrow$ CFSE $= 6 \times (-0.4\Delta_o) +$

$1 \times (0.6\Delta_o) + 3P$

$= \boxed{-1.8\Delta_o + 3P}$

b) i) The violet colour of $[Ti(H_2O)_6]^{3+}$ is due to d-d transition of the single d-electron $(Ti^{3+} = 4s^0 3d^1)$ from t_{2g} to e_g level in octahedral crystal field. The complex absorbs light in yellow-green region (500-550nm) and hence, reflects violet light.

ii)
$[Mn(H_2O)_6]^{2+}$

$\Downarrow$

Mn^{2+}

(weak field ligand)

$\Rightarrow 3d^5$ system

$\Rightarrow \mu = \sqrt{n(n+2)} = \sqrt{5 \times 7} = \boxed{5.92\,BM}$
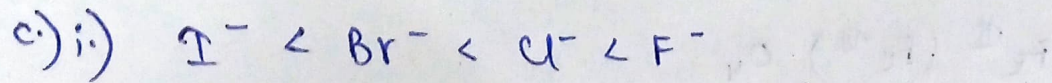
$[MnCl_4]^{2-}$

$\Downarrow$

Mn^{2+}
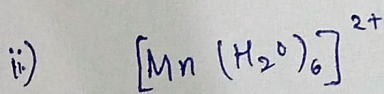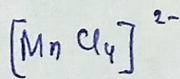
(weak field ligand)

$\Rightarrow 3d^5$ system

$\Rightarrow \mu = \sqrt{n(n+2)} = \sqrt{5 \times 7}$

$= \boxed{5.92\,BM}$

Both complexes are light pink coloured due to weak spin forbidden d-d transitions.
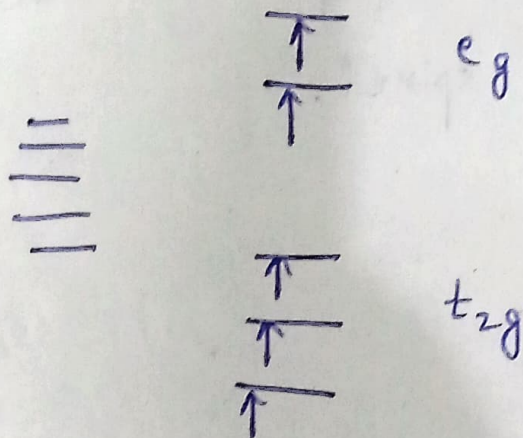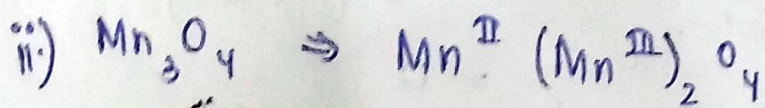
c) i) $I^- < Br^- < Cl^- < F^-$

This order reflects the increasing ligand field strength among the halides.
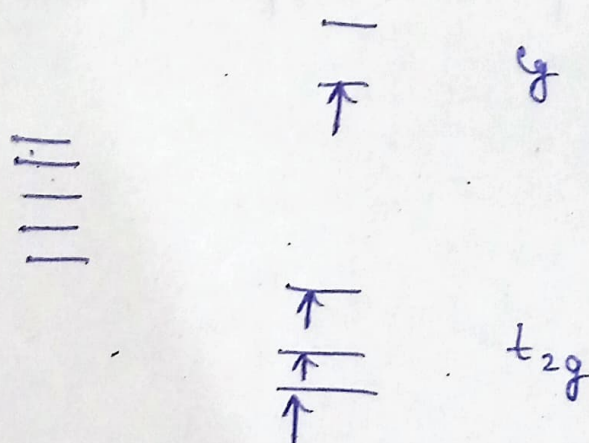
As we move from I^- to F^- :

size decreases $\Rightarrow$ charge density increases

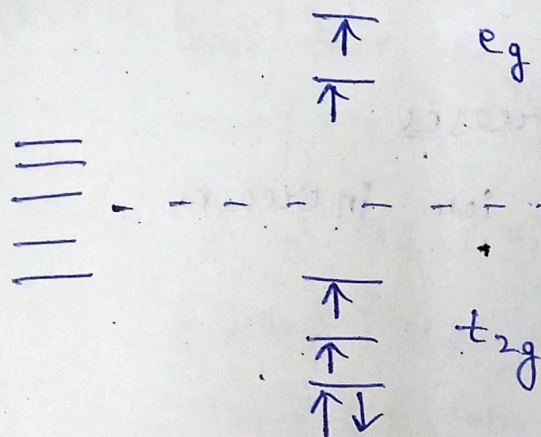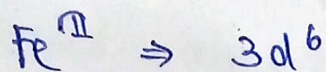$\Rightarrow$ bonding with metal ion increases.

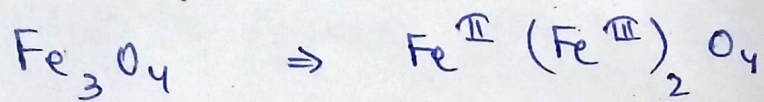ii) $Mn_3O_4 \Rightarrow Mn^{II}(Mn^{III})_2 O_4$

$Mn^{II} \Rightarrow 3d^5$

$$e_g \quad \uparrow\downarrow \quad \uparrow$$

$$t_{2g} \quad \uparrow\uparrow \quad \uparrow\uparrow \quad \uparrow$$

$$CFSE = 3\times(-0.4\Delta_o) +$$
$$2\times(0.6\Delta_o)$$
$$= 0$$

$Mn^{III} \Rightarrow 3d^4$

$$e_g \quad - \quad \uparrow$$

$$t_{2g} \quad \uparrow \quad \uparrow\uparrow \quad \uparrow$$
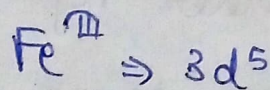
$$CFSE = 3\times(-0.4\Delta_o) + 1\times(0.6\Delta_o)$$
$$= -0.6\Delta_o.$$

Since $|CFSE(Mn^{III})| > |CFSE(Mn^{II})| \Rightarrow Mn_3O_4$ is normal spinel.

$Fe_3O_4 \Rightarrow Fe^{II}(Fe^{III})_2 O_4$

$Fe^{II} \Rightarrow 3d^6$

$$\frac{\uparrow}{\uparrow} \quad e_g$$

$$\equiv \quad - - - - - - - - -$$

$$\frac{\uparrow}{\uparrow\uparrow\downarrow} \quad t_{2g}$$

$\Rightarrow CFSE = 4 \times (-0.4\Delta_o) +$

$\quad\quad 2 \times (0.6\Delta_o) + P$

$\quad = -0.4\Delta_o + P$

$Fe^{III} \Rightarrow 3d^5$

$$\frac{\uparrow}{\uparrow} \quad e_g$$

$$\equiv \quad \Leftarrow - - - - - - -$$

$$\frac{\uparrow}{\uparrow\uparrow} \quad t_{2g}$$

$\Rightarrow CFSE = 3 \times (-0.4\Delta_o) +$

$\quad\quad 2 \times (0.6\Delta_o)$

$\quad = 0$
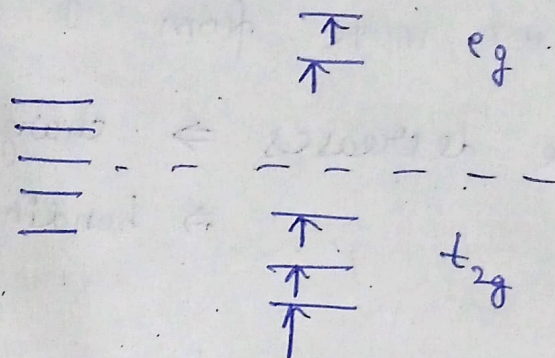
Since $|CFSE(Fe^{II})| > |CFSE(Fe^{III})| \Rightarrow Fe_3O_4$ is inverse spinel.

2. (a) Write down the criteria for a radioelement to be chosen for use as a radiodiagonostic agent or a radiotherapeutic agent. Give examples of radionucleotides used as radiodiagonostic agents and radiotherapeutic agents.

(b) Draw the crystal field splitting diagrams for a d^5 metal ion in octahedral high spin and low spin environments and then calculate their Crystal Field Stabilization Energies (CFSE).

(c) Predict which of the following compounds will undergo Jahn-Teller distortion:
$[Ni(H_2O)_6]^{2+}$, $[MnF_6]^{3-}$ and $[CoF_6]^{3-}$.

(d) $[NiCl_4]^{2-}$ is paramagnetic, $[Ni(CN)_4]^{2-}$ is diamagnetic – explain in the light of crystal field theory.

(e) Δ_o value for $[Ru(H_2O)_6]^{3+}$ is greater than $[Ru(H_2O)_6]^{2+}$ – give reason.

$[(4+1+1)+3+3+3+2]$

2) b) d^5 (high spin) d^5 (low spin)
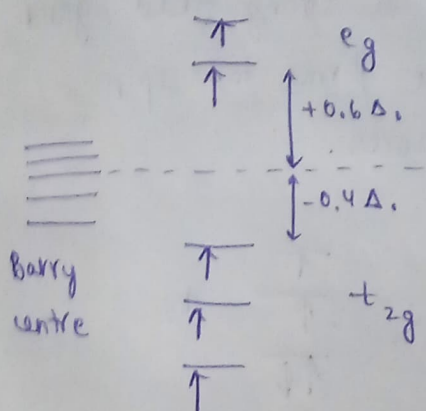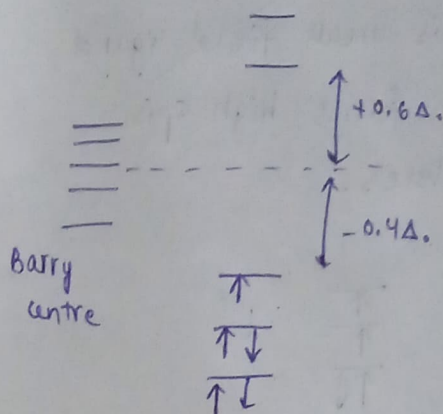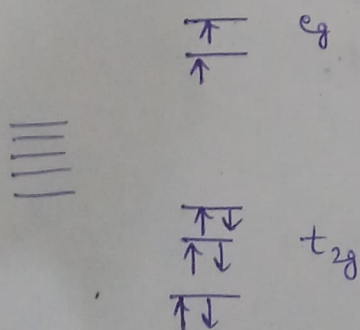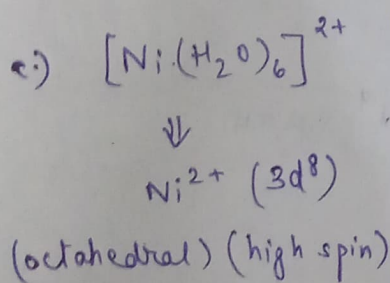
eg
↑
↑ | +0.6Δ.

| -0.4Δ.

Barry centre
↑
↑ t_{2g}
↑

$\Rightarrow$ CFSE $= 3 \times (0.4Δ.) +$

$2 \times (0.6Δ.)$

| CFSE $=$ 0 |

Barry centre

↑
↑↓
↑↓

↑ | +0.6Δ.

↑ | -0.4Δ.

$\Rightarrow$ CFSE $= 5 \times (-0.4Δ.) + 2P$

| CFSE $= -2Δ. + 2P$ |

c) $[Ni(H_2O)_6]^{2+}$

$\Downarrow$

Ni^{2+} $(3d^8)$

(octahedral) (high spin)

↑ eg
↑

↑↓
↑↓ t_{2g}
↑↓

Since electron distribution is symmetrical, no Jahn-Teller is observed.

$[Mn F_6]^{3-}$

$\Downarrow$

Mn^{3+} $(3d^4)$

(octahedral)(high spin)

— | eg
↑

↑
↑ t_{2g}
↑
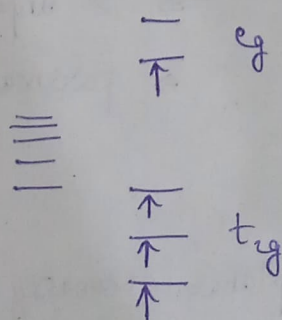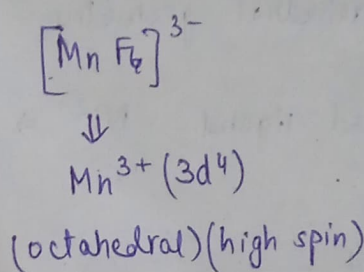
Since electron distribution is unsymmetrical, Jahn-Teller is observed.

$[CoF_6]^{3-}$

$\Downarrow$

Co^{3+} $(3d^6)$

(octahedral) (high spin)

↑ eg
↑

↑
↑ t_{2g}
↑↓
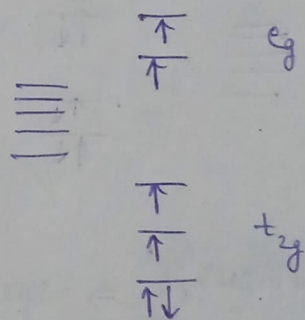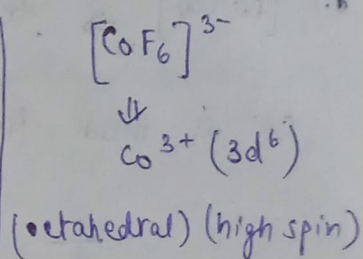
Since electron distribution is symmetrical, no Jahn-Teller is observed.

d.) $[NiCl_4]^{2-}$ ⟹ tetrahedral geometry

Cl^- is weak field ligand, Ni^{2+} ⟹ d^8 system

t_2 : ↑ / ↑ / ↑↓

e : ↑↓ / ↑↓

⟹ 2 unpaired e^-

⟹ paramagnetic
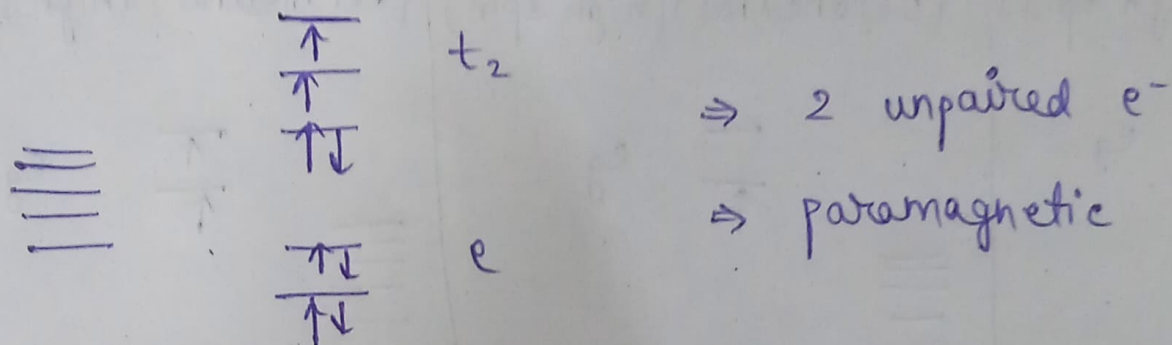
$[Ni(CN)_4]^{2-}$ ⟹ square planar geometry

CN^- is strong field ligand, $Ni^{2+} = d^8$ system

$d_{x^2-y^2}$: —

d_{xy} : ↑↓

d_{z^2} : ↑↓

d_{yz} : ↑↓

d_{xz} : ↑↓

⟹ diamagnetic

e.) $[Ru(H_2O)_6]^{3+}$ > $[Ru(H_2O)_6]^{2+}$ (CFSE)
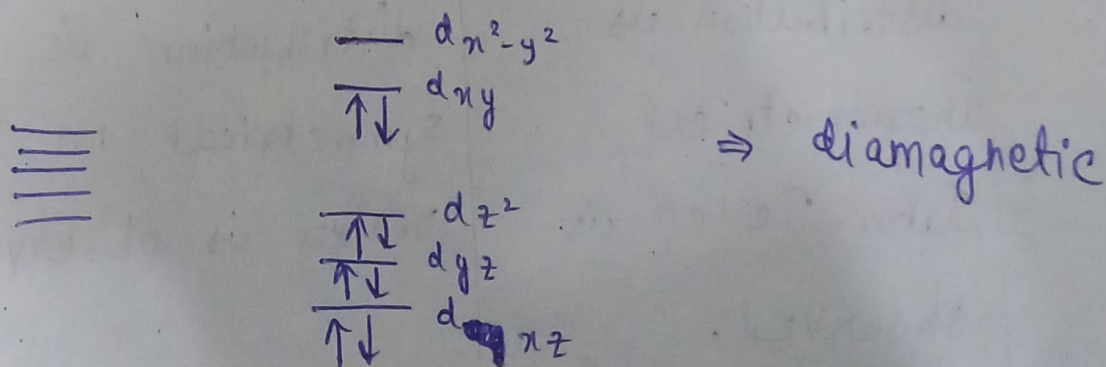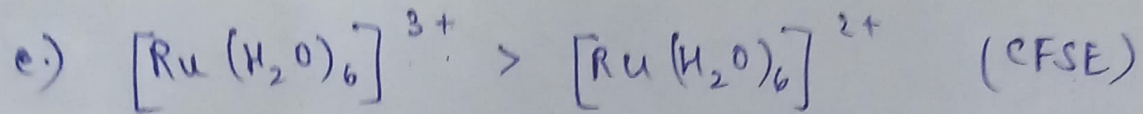
This is because, higher the oxidation state of metal cation, greater will be magnitude of Δ_0. Higher the oxidation state, the ligand approaches more closely to it & hence higher splitting of d-orbitals is expected due to greater repulsion.

∴ $\Delta_0 [Ru(H_2O)_6]^{3+}$ > $\Delta_0 [Ru(H_2O)_6]^{2+}$
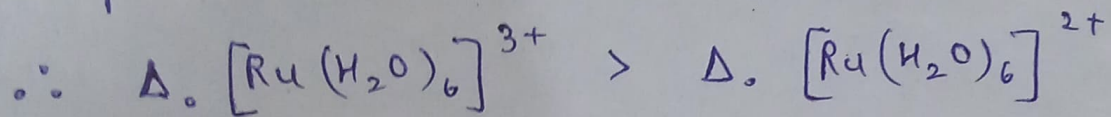
2. a) Mention the diseases that will occur due to both deficiency and excessive accumulation of copper in the body.
    b) Give a reaction scheme to show how Lewisite attacks free enzymes in the body and then demonstrate how British anti-Lewisite removes Lewisite from the body.

or

Draw a graph showing the dependence of metabolic activity on the concentration of essential elements and explain the different segments of the graph.
    c) Give the full names and structures of the two chelating agents DMSA and DPA used in chelation therapy.

d) Why does *cis*-Platin remains almost passive in blood but becomes active after reaching the cytoplasm?
e) Why ^{99m}Tc is considered most desirable to be used as a radio-diagnostic agent? Which Tc-complexes are selectively taken up by heart tissues?
f) How thyroid gland cancer cells are destroyed by radio-therapeutic technique?
g) Define CFSE and OSSE? Calculate CFSE values for an octahedral Co(II)-complex in both high-spin and low-spin electronic configuration.

[2+3+2+2+2+2+4]

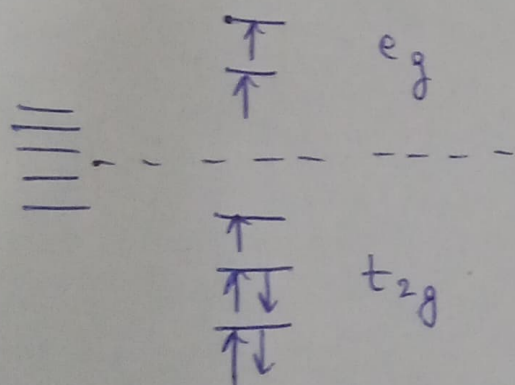g) The extra stabilisation energy that is gained by a co-ordination complex due to crystal field splitting is called Crystal field Stabilisation Energy (CFSE).

OSSE (Octahedral Site Selection Energy) is a determing factor which decides whether a transition metal spinel would adopt regular or inverse structure.
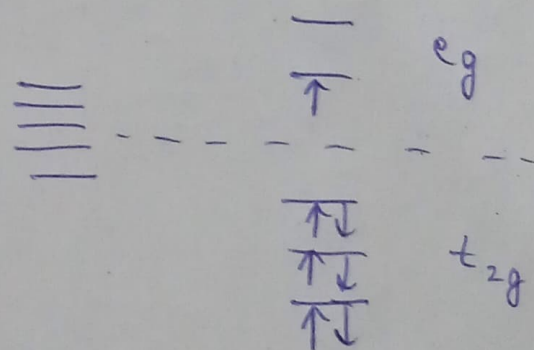
Co^{2+} (high spin)   (3d^7 system) Co^{2+} (low spin)

$$CFSE = 5 \times (-0.4 \Delta_o) + 2 \times (0.6 \Delta_o) + 2P$$

$$\Rightarrow \boxed{CFSE = -0.8 \Delta_o + 2P}$$

$$CFSE = 6 \times (-0.4\Delta_o) + 1 \times (0.6\Delta_o) + 3P$$

$$\Rightarrow \boxed{CFSE = -1.8 \Delta_o + 3P}$$

1 (a) Draw the structures of Lewisite and British anti-Lewisite (BAL). Show how Lewisite attacks a free enzyme in the body and then show how anti-Lewisite breaks the complex to regenerate the free enzyme. Draw structure of one water soluble chelating ligand for the removal of arsenic.

(b) Write down the name and structure of two platinum based anticancer drugs. *Cis*-platin shows anti cancer activity whereas its *trans* analogue does not - explain.

OR

What are the essential criteria that a radioisotope must satisfy to be considered for the radiodiagnosis? Give example of a radionucleotide widely used for diagonstic purpose.
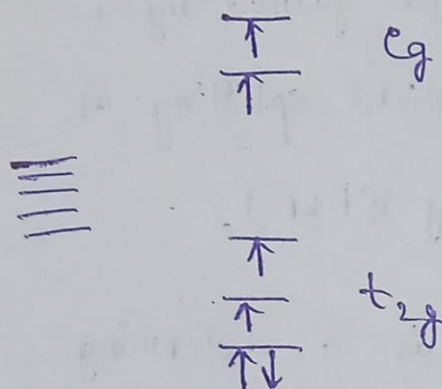
(c) Explain the following:
(i) $K_3[CoF_6]$ is paramagnetic, whereas $K_3[Co(CN)_6]$ is diamagnetic.
(ii) $K_3[CoF_6]$ is paramagnetic, whereas $K_2[NiF_6]$ is diamagnetic.
(iii) H_2O shows higher Crystal Field splitting than OH^-.
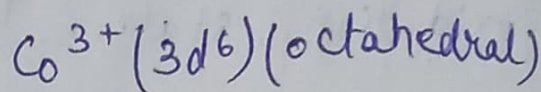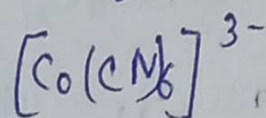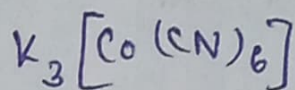
$$[(1+1+4+1)+(4)+(2+2+2)]$$

1.) c) i) $K_3[CoF_6]$

$$\Downarrow$$

$$[CoF_6]^{3-}$$

$$\Downarrow$$

Co^{3+} $(3d^6)$ (octahedral)
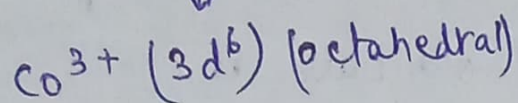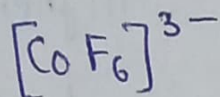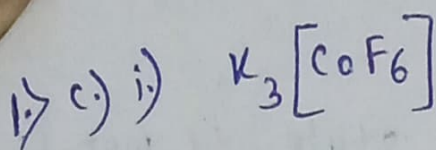
F^- is weak field ligand, hence forms high spin complex.

$$\overline{\uparrow} \quad \overline{\uparrow} \quad e_g$$

$$\underline{\underline{\underline{\qquad}}}$$

$$\begin{array}{l} \overline{\uparrow} \\ \overline{\uparrow} \quad t_{2g} \\ \overline{\uparrow\downarrow} \end{array}$$

$\Rightarrow$ 4 unpaired e^-

$\therefore$ paramagnetic

$K_3[Co(CN)_6]$

$$\Downarrow$$

$$[Co(CN)_6]^{3-}$$

$$\Downarrow$$

Co^{3+} $(3d6)$ (octahedral)

CN^- is strong field ligand hence forms low spin complex.

$$\underline{\qquad} \quad \underline{\qquad} \quad e_g$$

$$\underline{\underline{\underline{\qquad}}}$$

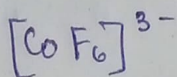$$\begin{array}{l} \overline{\uparrow\downarrow} \\ \overline{\uparrow\downarrow} \quad t_{2g} \\ \overline{\uparrow\downarrow} \end{array}$$
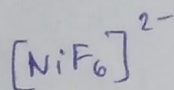
$\Rightarrow$ 0 unpaired e^-

$\therefore$ diamagnetic

ii) $K_3[CoF_6]$

$\Downarrow$

$[CoF_6]^{3-}$

$\Downarrow$

Co^{3+} $(3d^6)$ (octahedral)

$\uparrow$ | $\uparrow$ e_g

$\equiv$

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

$\Rightarrow$ 4 unpaired e^-

∴ paramagnetic

$K_2[NiF_6]$

$\Downarrow$

$[NiF_6]^{2-}$

$\Downarrow$

Ni^{4+} $(3d^6)$ (octahedral)
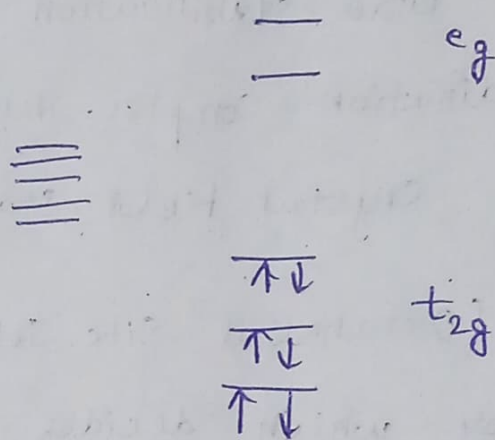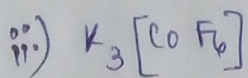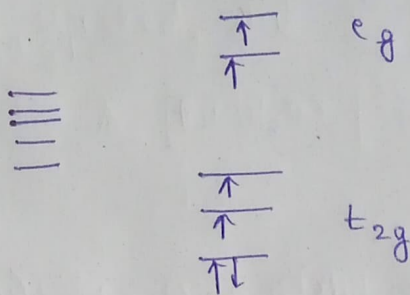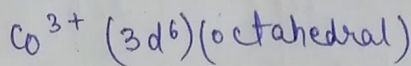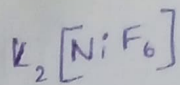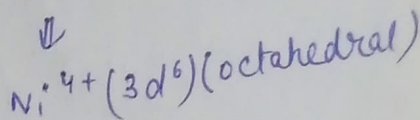
Since Ni^{4+} has higher oxidation state, crystal field splitting increases & causes pairing of e^-.

$-$ | $-$ e_g

$\equiv$

$\uparrow\downarrow$
$\uparrow\downarrow$ t_{2g}
$\uparrow\downarrow$
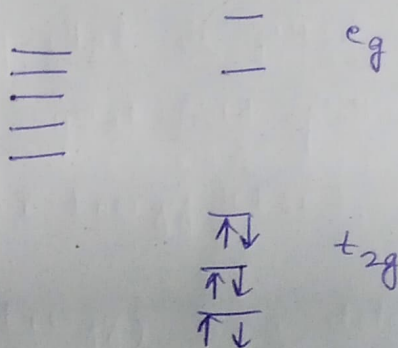
$\Rightarrow$ 0 unpaired e^-

∴ diamagnetic

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iii) H_2O is only σ-donor ligand, whereas OH^- are σ-donor & ~~π-donor~~ π-donor type ligands. The ligands having better π-donation character act as weak field ligand more. Also, H_2O forms more effective overlap with metal d-orbitals due to lone pairs on oxygen.