Q.1 $[MnBr_4]^{2-}$ and $[Mn(H_2O)_6]^{2+}$. Which complex do you think more colourfull and have higher molar absorption coefficient?

Q.2 $[Cu(Phen)_2]^+$ and $[Cu(MeCN)_4]^+$. The first one is of dark orange colour, while second one is colourless. Why.

Q.3. What are oxidation states of Metal present in oxyhemoglobin and deoxyhemoglobin. Oxyhemoglobin is of bright-Red colour, while deoxyhemoglobin is purple blue. Why? predict the magnetic moments also.

Q.4 In $[Cu(en)_2(H_2O)_2]^{2+}$, the trans complex has lower ε value than cis one. Why?

Q.5. An unlabelled solution of $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_4]^{2+}$ is given for labelling. How you will distinguish with and without collecting the spectra.

Q.6. In $[CoCl_4]^{2-}$ → deep blue and $[Co(H_2O)_6]^{2+}$ → pink, which complex do you think will have orbital contribution in their magnetic moments?

Q.7 Why MnO_4^-, CrO_4^-, VO_4^{3-} have colours (dark)? Arrange LMCT energy order in MnO_4^-, CrO_4^- and VO_4^{3-}.

Q.8 Explain the origin of colour in $Fe_4[Fe(CN)_6]_3$

Q.9 Magnetic moment of $[Fe(Phen)_2(NCS)_2]$ varies with temperature. The magnet moment at 200k and 50k are 4.9BM and 0 BM. Give the suitable reason.

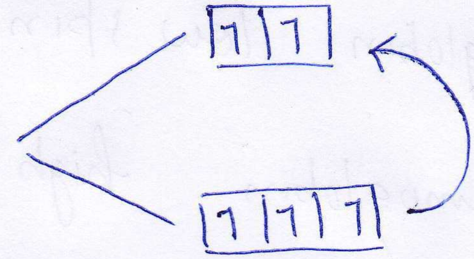
Q.10 $K_2[NiF_6]$ & ~~$K_3[Ni$~~ $K_3[CoF_6]$ are diamagnetic and paramagnetic respectively why? In which case μ_{eff} is greater than $\mu_{spin only}$ value why?

Solutions for Assignment-4

1) $[MnBr_4]^{2-}$ d^5

$[Mn(H_2O)_6]^{2+}$ d^5

$Mn(+2)$ - $3d^5$



spin forbidden transition as $\Delta S \neq 0$

→ Both complexes will have spin forbidden transition, and therefore they will have <u>weak colours</u>.

BUT $[MnBr_4]^{2-}$ will be more coloured and higher ε value than $[Mn(H_2O)_6]^{2+}$

Because

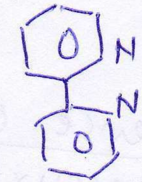
$[MnBr_4]^{2-}$ is Tetrahedral and have no centre of symmetry. This will lead to d-p Mixing.

While $[Mn(H_2O)_6]^{2+}$ will have small d-p mixing as a result of Mn−L bond vibrations.

MeCN ≡ CH_3-CN

2) $[Cu(Phen)_2]^+$ } Phen

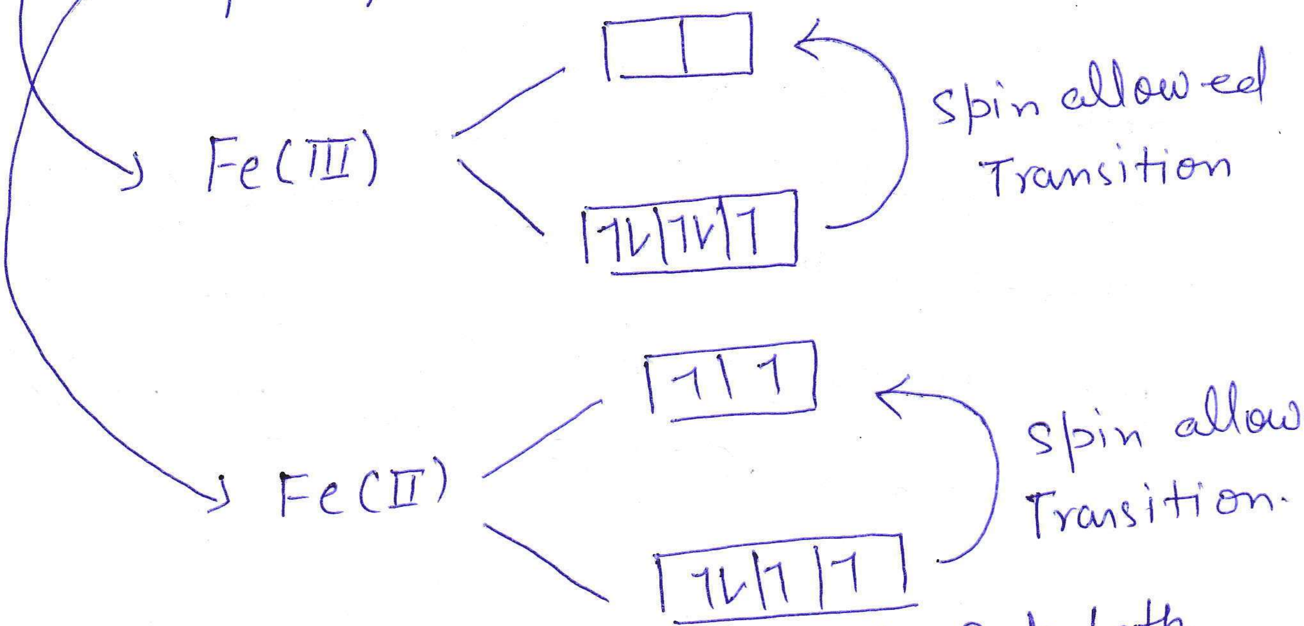
$\boxed{3d^{10}}$



$[Cu(Phen)_2]^+$ has Ligand → Metal Charge transfer transition and that's why colourful.

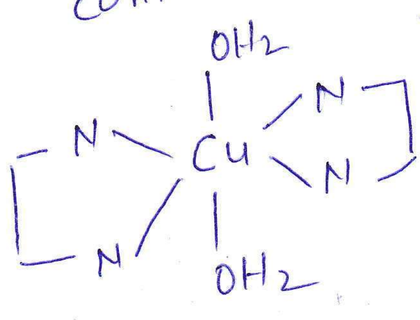
(3) Oxyhemoglobin low spin Fe(III)

deoxyhemoglobin high spin ~~Fe(III)~~ Fe(II)

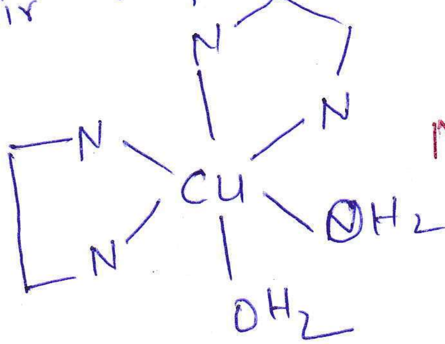


Therefore both are colourful. But both transitions are different and therefore complementary colours are different. Both complex will have orbital contribution in their magnetic moment.

(4)



trans



cis

More colourful

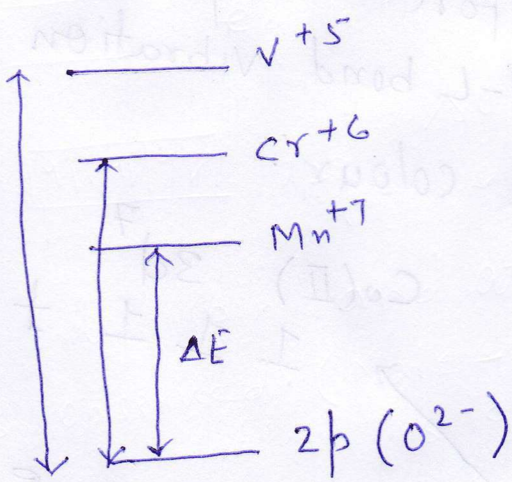
cis has absence of centre of symmetry so d-p mixing occur and will be more colourful and small

(7) Because of L → M charg transfer trans^n.

$$\boxed{\overset{2-}{O} \xrightarrow{e^-} Mn}$$

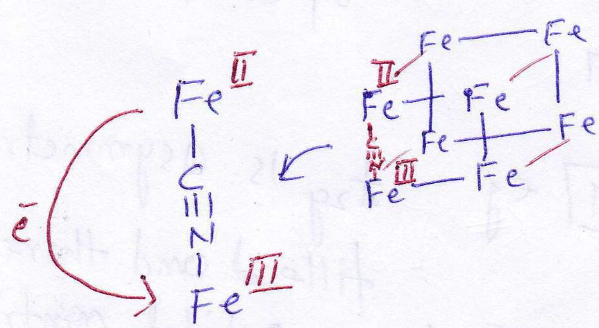
$\overset{+7}{Mn}O_4$ $\quad$ $\overset{+6}{Cr}O_4^{2-}$ $\quad$ $\overset{+5}{V}O_4^{3-}$

Higher the oxidation state of the metal, higher the nuclear charge and smaller the size of the metal & lower will the LMCT energy.



so order will be $MnO_4^- < CrO_4^{2-} < VO_4^{3-}$

(8) $Fe_4^{III}[Fe^{II}(CN)_6]_3$ $\quad$ pigment Prussian Blue



A Kind of Polymer structure
or
you can say a "coordination polymer"

colours appear because of $Fe(II) \longrightarrow Fe(III)$ charge transfer.

(5) $[Cu(H_2O)_6]^{2+}$

$[Cu(NH_3)_4]^{2+}$

→ absence of centre of symmetry will ~~d~~ lead to d-p mixing and therefore more colorful.

→ presence of centre of symmetry and therefore very small d-p mixing because of M-L bond vibration leads to very weak colour.

(6) $[CoCl_4]^{2-}$ Co(II) $3d^7$

$$3d^7 \begin{cases} \uparrow \ \uparrow \ \uparrow & t \\ \uparrow\downarrow \ \uparrow\downarrow & e \end{cases}$$

t-orbitals are symmetrically filled and therefore No orbital contribution in the magnetic Moment of complex.

$$\boxed{\mu_{eff} \cong \mu_{spin\,only}}$$

$[Co(H_2O)_6]^{2+}$ Co(II) $3d^7$

$$3d^7 \begin{cases} \boxed{\uparrow \mid \uparrow} & e_g \\ \boxed{\uparrow\downarrow \mid \uparrow\downarrow \mid \uparrow} & t_{2g} \end{cases}$$

t_{2g} is asymmetrically filled and therefore Orbital contribu^n

(9) ~~Fe(CN)~~.

$[Fe(Phen)_2(NCS)_2]$ Here, high spin - low spin equilibrium is shown.

At high temp ($\approx$ 200K)

d^6: e_g [↑|↑], t_{2g} [↑↓|↑|↑]

$\mu = \sqrt{n(n+2)}$

$= \sqrt{4(4+2)} = 4.9$ BM

At low temp (50 K)

d: e_g [|], t_{2g} [↑↓|↑↓|↑↓]

so $\boxed{\mu = 0}$ B.M.

At high temp high spin and at low temp low spin behaviour is observed. (Note - orbital contribution is ignored here in value).

(10) $[NiF_6]^{2-} \Rightarrow Ni^{4+} \Rightarrow 3d^6$: e_g [|], t_{2g} [↑↓|↑↓|↑↓]

low-spin complex

No unpaired electron $\boxed{\mu_{eff} \cong \mu_{spin only}}$

so Diamagnetic

$K_3[CoF_6] \Rightarrow Co^{3+} \Rightarrow 3d^6$: e_g [↑|↑], t_{2g} [↑↓|↑|↑]

high spin complex

so paramagnetic