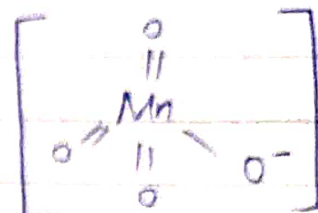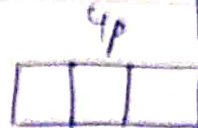NAME: ANKUR KUMAR.
BRANCH: IT
ROLL NO: 22IT3007.
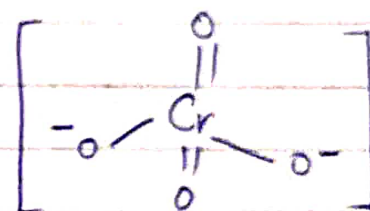
(1) Predict the hybridisation of following:

• MnO_4^-

$\{Mn^{+7}\}$ _____ : $3d^0 \, 4s^0 \, 4p^1$

3d   4s   4p

$\therefore$ sd^3 or d^3s hybridisation.

• CrO_4^{2-}

$\{Cr^{+6}\}$ = $4s^0 \, 3d^0$

4s   3d

$\therefore$ d^3s hybridisation.

• $Cr_2O_7^{2-}$

$\{Cr^{+6}\}$ = $4s^0 \, 3d^0$

4s   3d

$\therefore$ d^3s hybridisation.

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

  $\{Cr^{+3}\} = 3d^3 \; 4s^0$

  $\{Octahedral\}$

  $\underbrace{}_{d^2sp^3}$ hybridisation.

  $\therefore$ CN^- is a strong field ligand, but due to rule for filling of $e^\ominus$ in t_{2g} orbital, all 3 $e^\ominus$ will remain unpaired.

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

  $\{V^{3+}\} \longrightarrow d^2$ $\overbrace{\qquad\qquad}^{d^2sp^3 \; hyb^n}$

  $3+$ $\{Octahedral\}$

- $[Cr(H_2O)_6]^{2+}$

  $\{Cr^{2+}\} = 3d^4$

  $3d \qquad 4s \qquad 4p \qquad 4d$

  $\{Octahedral\}$ $\qquad sp^3d^2$ hybridisation.

- $[Fe(CN)_6]^{3-}$ $\{Fe^{+3}\} = 3d^5$.

  $\{Octahedral\}$ $\qquad d^2sp^3 \; hyb^n$

- $[Ni(CN)_4]^{2-}$ $\{Ni^{+2}\} = 3d^8$.

$$\boxed{\begin{array}{|c|c|c|c|c|}\hline 1L & 1L & 1L & 1L & \mathbf{1} \\\hline\end{array}}\quad \boxed{}\quad \boxed{\begin{array}{|c|c|c|}\hline & & \\\hline\end{array}}$$

$$\left[\begin{array}{c} CN^- \\ CN^+ \diagdown \; Ni \; \diagup CN^- \\ | \\ CN^- \end{array}\right]^{2-}$$

3d   4s   4p
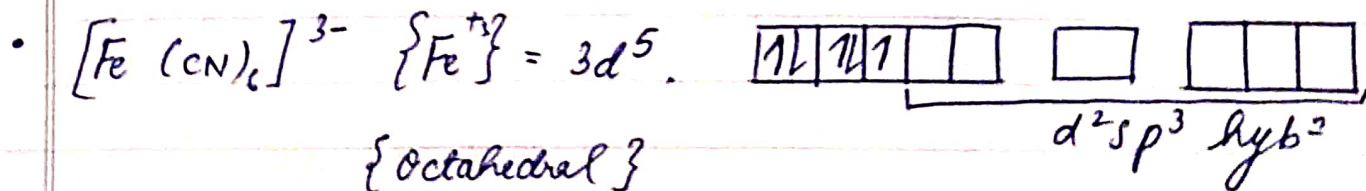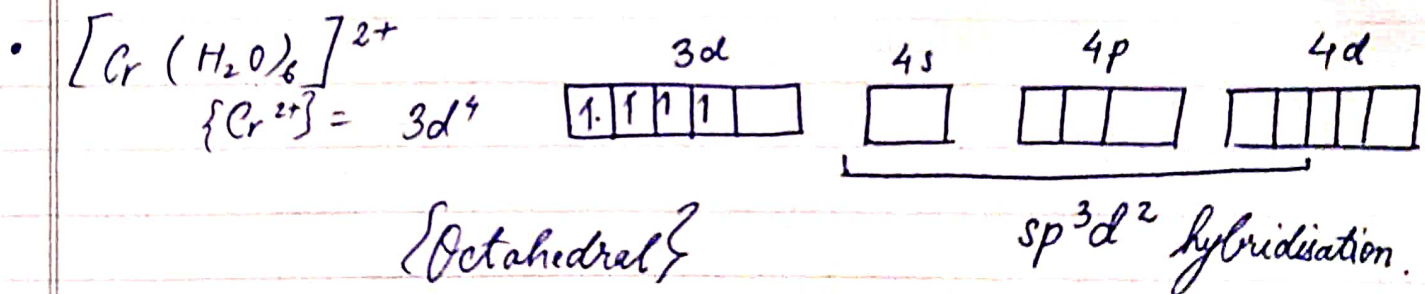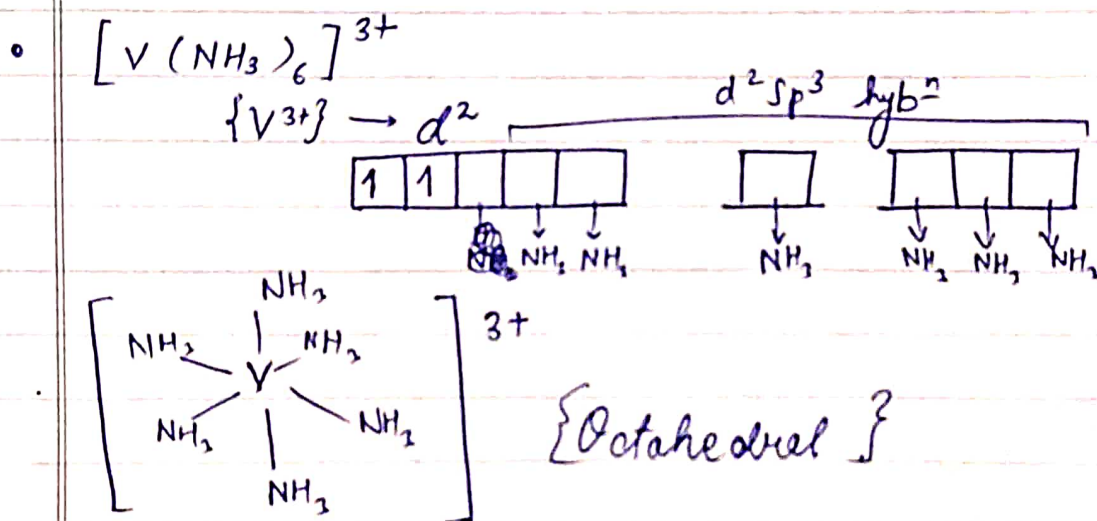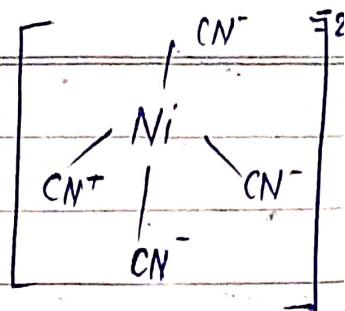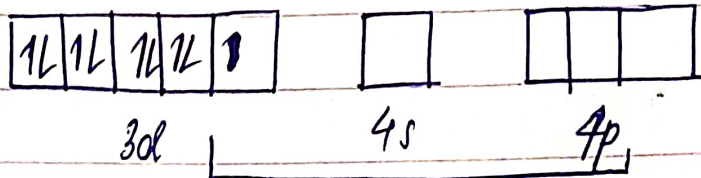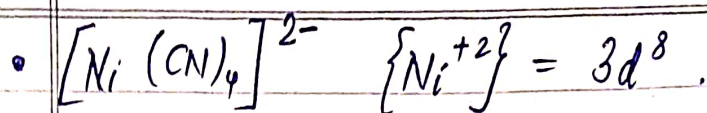
dsp^2 hybridisation.
{Tetrahedral}

- $[Cu(NH_3)_4]^{2+}$ $\{Cu^{2+}\} = 3d^9$.

3d   4s   4p

$$\boxed{\begin{array}{|c|c|c|c|c|}\hline 1L & 1f & 1L & 1L & 1 \\\hline\end{array}}\quad \boxed{}\quad \boxed{\begin{array}{|c|c|c|}\hline & & \\\hline\end{array}}$$

sp^3 hybridiation
{Tetrahedral}

- $[Fe(CO)_5]$ $\{Fe^0\} = 3d^6\,4s^2$

3d   4s   4p

$$\boxed{\begin{array}{|c|c|c|c|c|}\hline 1L & 1L & 1L & 1L & \\\hline\end{array}}\quad \boxed{}\quad \boxed{\begin{array}{|c|c|c|}\hline & & \\\hline\end{array}}$$

$$\left[\begin{array}{c} CO \\ | \\ CO - Fe - CO \\ | \\ CO \end{array} \quad CO\right]$$
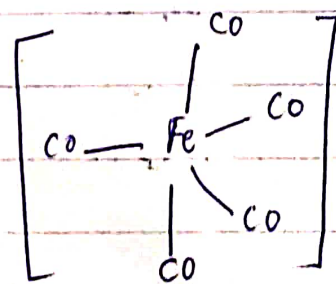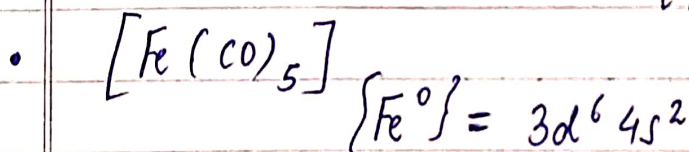
dsp^3 hybridisation   {Trigonal Bipyramidal}

- $[Ni(CN)_5]^{3-}$ $\{Ni^{2+}\} = 3d^8$

3d   4s   4p

$$\boxed{\begin{array}{|c|c|c|c|}\hline 1L & 1L & 1L & 1L \\\hline\end{array}}\quad \boxed{}\quad \boxed{\begin{array}{|c|c|}\hline & \\\hline\end{array}}$$

dsp^3 hybridiation

- $[Co(NO_2)_6]^{4-}$, $\{Co^{2+}\} = 3d^7$

3d					4s	4p			4d				
⇅	⇅	⇅							1				
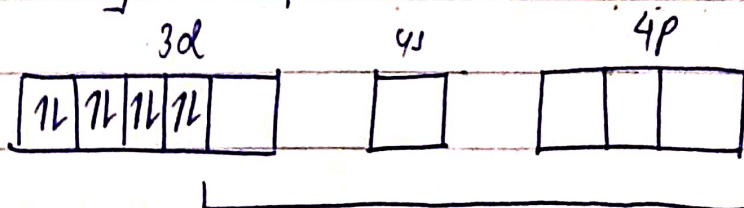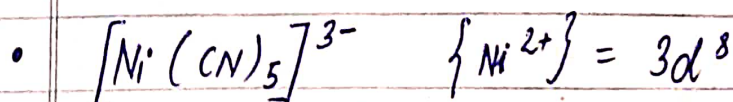
d^2sp^3 hybridisation

$-NO_2$ is a strong field ligand which favours pairing of electron.

- $[Cu(NH_3)_4]^{2+}$ $\{Cu^{2+}\} = 3d^9$.
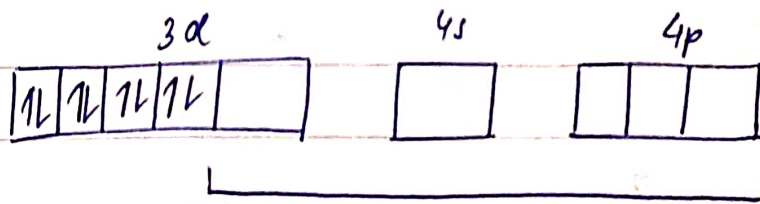
↿	⇅	⇅	⇅				1
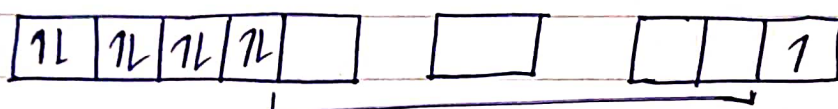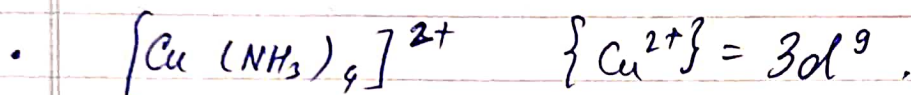
{Tetrahedral} dsp^2 hybridisation

- $[Mn_2(CO)_{10}]$.

$\{Mn^\circ\} = 3d^5 4s^2$.

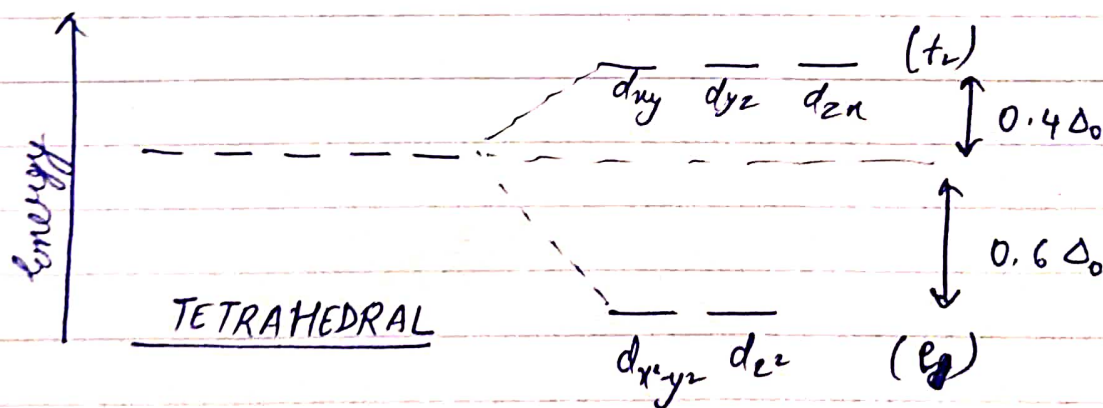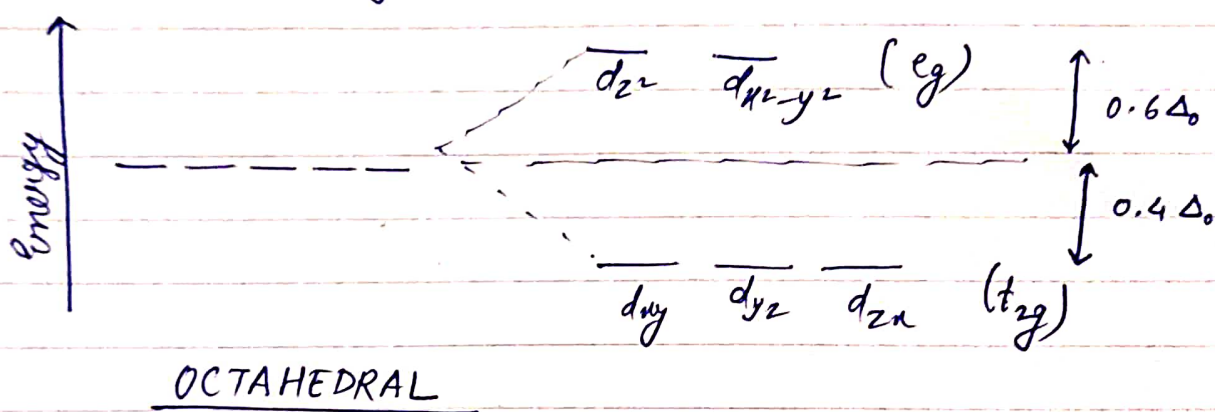|							
⇅	⇅	⇅	⇅				
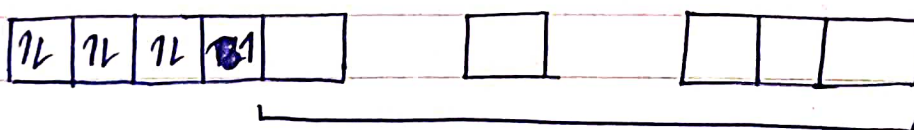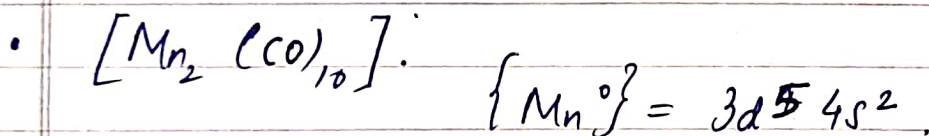
{Trigonal Bipyramidal} dsp^3 hybridisation.

(2) In octahedral crystal field splitting, ligands approach the central atom ~~thr~~ along the axes while in tetrahedral splitting, ligands approach between the axes.

In tetrahedral, ligands attack through d_{xy}, d_{yz} and d_{zx} axis while in octahedral they attack from d_{z^2} and $d_{x^2-y^2}$.

Also, $\Delta_t = \dfrac{4}{9} \Delta_0$.

Energy

$$\overline{d_{z^2}} \quad \overline{d_{x^2-y^2}} \quad (e_g)$$

$\updownarrow$ $0.6\,\Delta_0$

$\updownarrow$ $0.4\,\Delta_0$

$$\overline{d_{xy}} \quad \overline{d_{yz}} \quad \overline{d_{zx}} \quad (t_{2g})$$

OCTAHEDRAL

Energy

$$\overline{d_{xy}} \quad \overline{d_{yz}} \quad \overline{d_{zx}} \quad (t_2)$$

$\updownarrow$ $0.4\,\Delta_0$

$\updownarrow$ $0.6\,\Delta_0$

TETRAHEDRAL

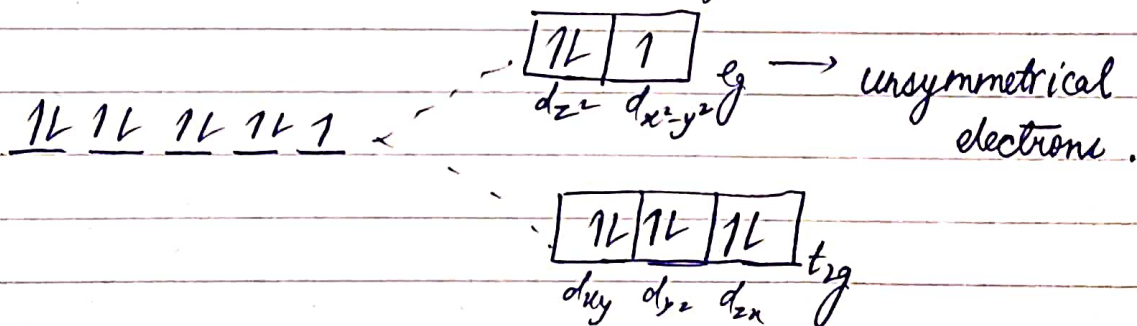$$\overline{d_{x^2-y^2}} \quad \overline{d_{z^2}} \quad (e_g)$$

(3) F-orbital has smaller crystal field splitting due to f-orbital having the lowest shielding effect and thus, electrons are present more in inner sides of atom. Thus, it has smaller crystal field splitting.

(4)
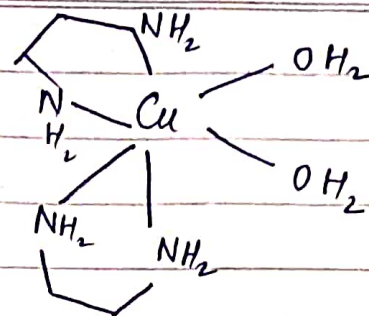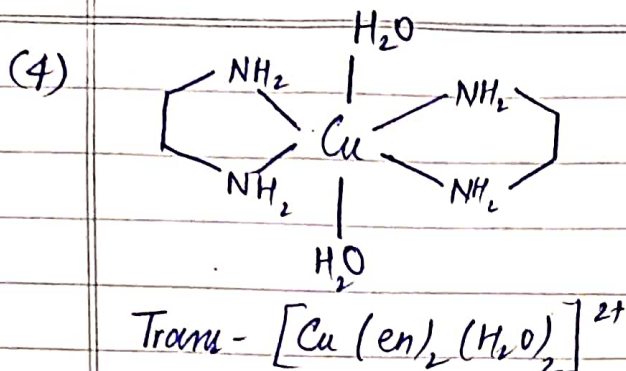
Trans - $\left[Cu(en)_2(H_2O)_2\right]^{2+}$

cis - form

Trans - $\left[Cu(en)_2(H_2O)_2\right]^{2+}$ is more stable due to less repulsion and less steric hinderance in the complex.

(5) $KCuF_3$
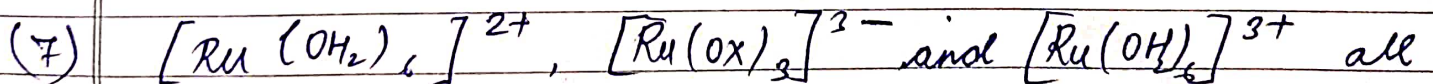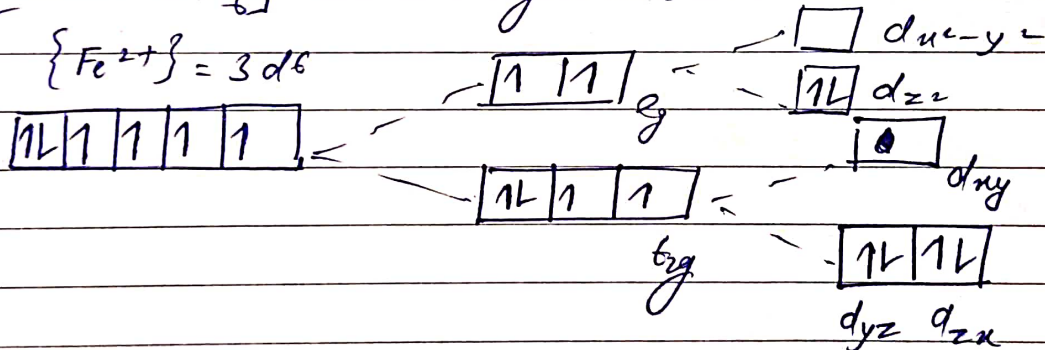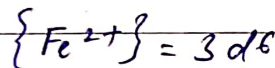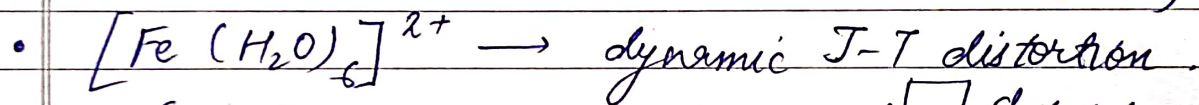
Cu has $3d^9$ electronic configuration.

$$1L \quad 1L \quad 1L \quad 1L \quad 1$$

$1L$	1	$e_g \longrightarrow$ unsymmetrical
d_{z^2}	$d_{x^2-y^2}$	electrons.

$1L$	$1L$	$1L$	t_{2g}
d_{xy}	d_{yz}	d_{zx}

As e_g has unsymmetrical electrons, it will have very strong Jahn-Teller distortion which will lead to formation of distorted tetragonal structure (elongated).
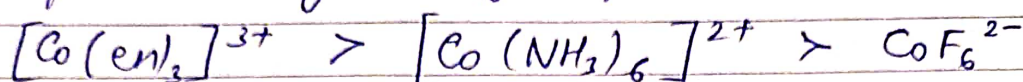
(6) Dynamic J-T distortion is temperature dependent (occurs at low temp.) and in presence of weak ligand form equilibrium of elongated and compressed

J-T distortion of octahedral shape. (z-in and z-out are in equilibrium).

- $[Ti(H_2O)_6]^{3+} \longrightarrow$ dynamic J-T distortion.

$\{Ti^{3+}\} = 3d^2$

d_{xy}

d_{xy}, d_{zy}

- $[Fe(H_2O)_6]^{2+} \longrightarrow$ dynamic J-T distortion.

$\{Fe^{2+}\} = 3d^6$

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

d_{z^2}

d_{xy}

t_{2g}

$d_{yz}\ d_{zx}$

(7) $[Ru(OH_2)_6]^{2+}$, $[Ru(ox)_3]^{3-}$ and $[Ru(OH_2)_6]^{3+}$ all
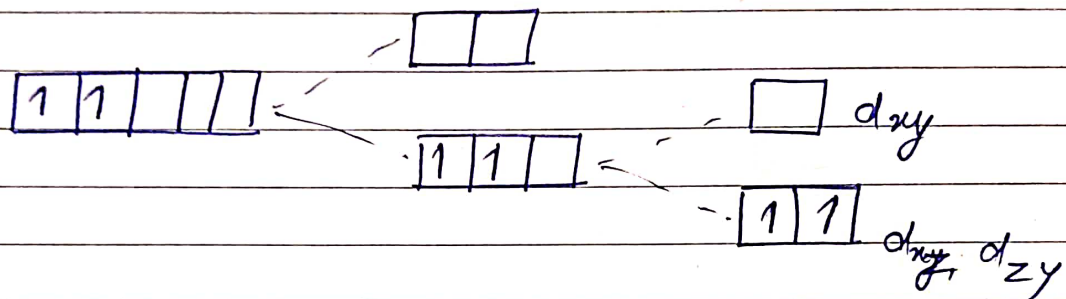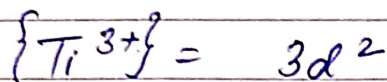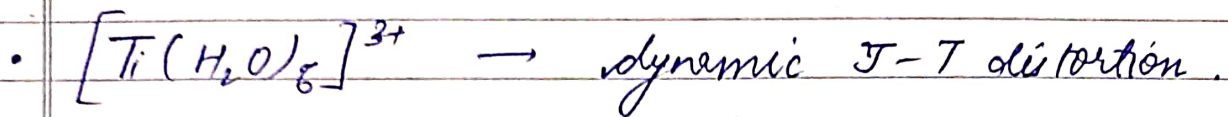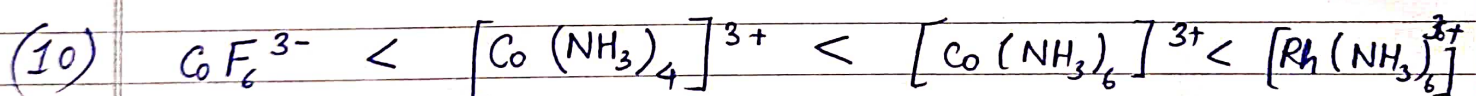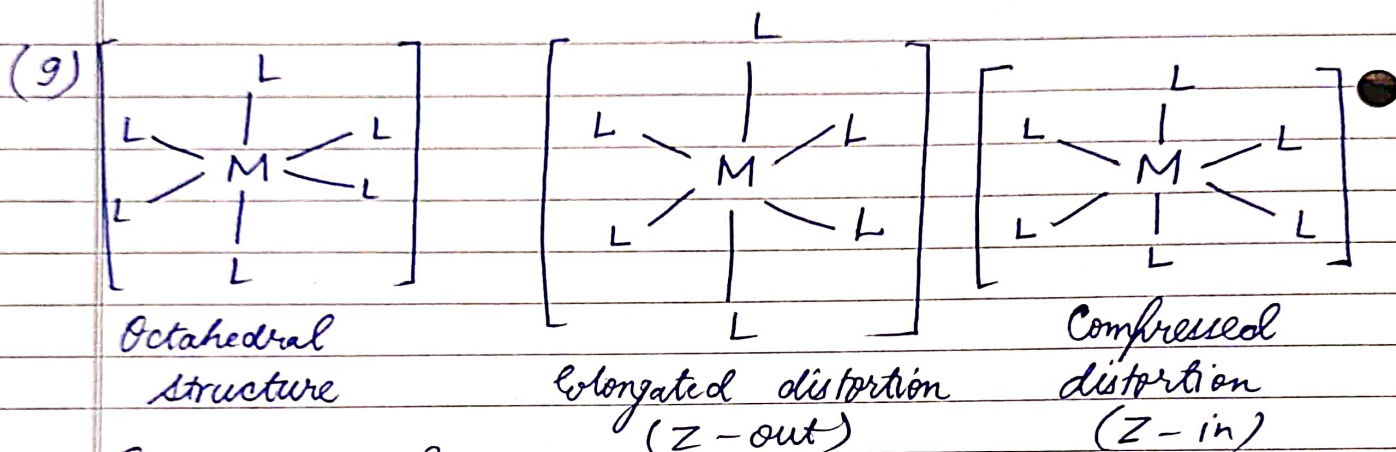
are considered as strong field ligand due to present in ~~group~~ period 5, so it will have $p \gg \Delta_o$, therefore it will lead to pairing of electrons in t_{2g} ~~and~~ only.
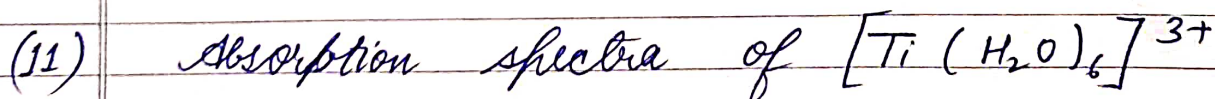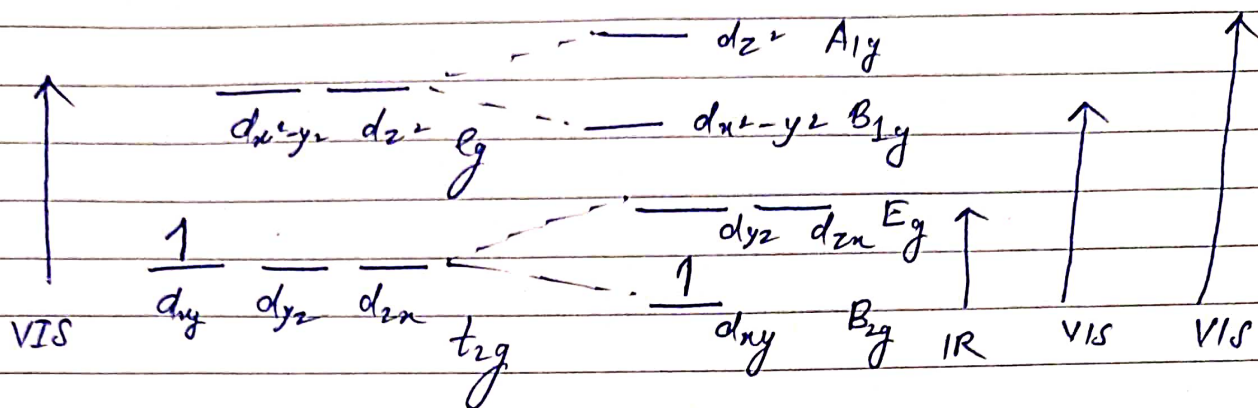
(8) Crystal field splitting energy of cobalt :

$$[Co(en)_3]^{3+} > [Co(NH_3)_6]^{2+} > CoF_6^{2-}$$

because of ligand strength $(en) > NH_3 > F^-$.

(9)

Octahedral structure   Elongated distortion   Compressed distortion

                         (Z – out)   (Z – in)

{ All bonds are of same length }   { Axial bonds are longer then equitorial bonds }   { eq. bonds are longer than axial }

(10) $CoF_6^{3-} < [Co(NH_3)_4]^{3+} < [Co(NH_3)_6]^{3+} < [Rh(NH_3)_6]^{3+}$

Splitting energy from low to high.

(11) Absorption spectra of $[Ti(H_2O)_6]^{3+}$

$$[Ti(H_2O)_6]^{3+} \qquad \{Ti^{\oplus 3+}\} = 3d^2\,4s^0$$

$$\begin{array}{l}
\text{---- } d_{z^2}\ A_{1g}\\[4pt]
\overline{d_{x^2-y^2}\ d_{z^2}}\ e_g \quad \text{---- } d_{x^2-y^2}\ B_{1g}\\[4pt]
\text{---- } d_{yz}\ d_{zx}\ E_g\\[4pt]
\underline{1}\ \underline{}\ \underline{}\\
d_{xy}\ d_{yz}\ d_{zx}\ t_{2g} \qquad \underline{1}\ d_{xy}\ B_{2g}
\end{array}$$

VIS   IR   VIS   VIS
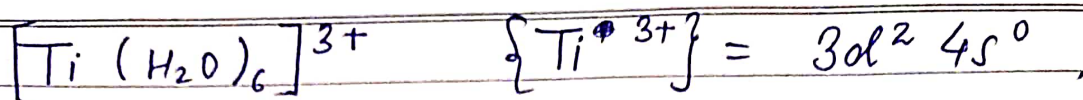
So, $[Ti(H_2O)_6]^{3+}$ has square planar geometry

and has two electronic transitions in visible
region and one in infrared.

Absorption

Visible absorption spectrum of $[Ti(H_2O)_6]^{3+}$

(12) $[Ni(CN)_6]^{4-}$ $\{Ni^{2+} = 3d^8\,4s^0\}$ ☐☐ e_g

$3d^8$ ☐☐☐☐☐   ☐☐☐ t_{2g}

strong field ligand.
~~Strong J-T distortion~~

$$\left[Ni \ (H_2O)_6 \right]^{2+}$$

$$\boxed{1 \ | \ 1} \quad e_g$$

$$Ni^{2+} \Rightarrow 3d^8 \quad \boxed{1L \ | \ 1L \ | \ 1L \ | \ 1 \ | \ 1} \ < $$

\# Weak field ligand.

$$\boxed{1L \ | \ 1L \ | \ 1L} \ t_{2g}$$

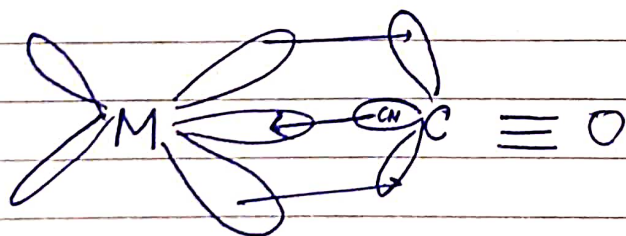So, in $\left[Ni \ (CN)_6 \right]^{4-}$ and $\left[Ni \ (H_2O)_6 \right]^{2+}$
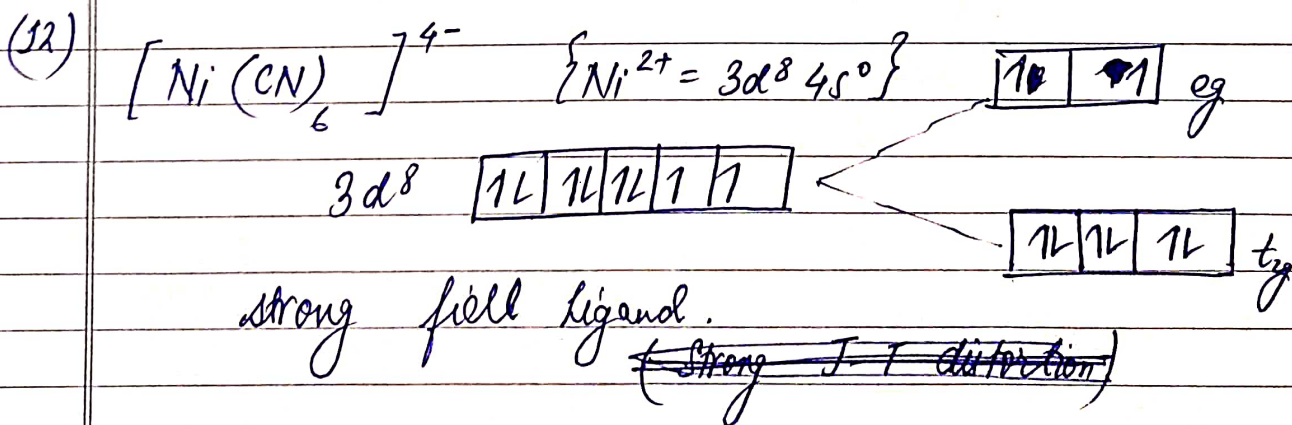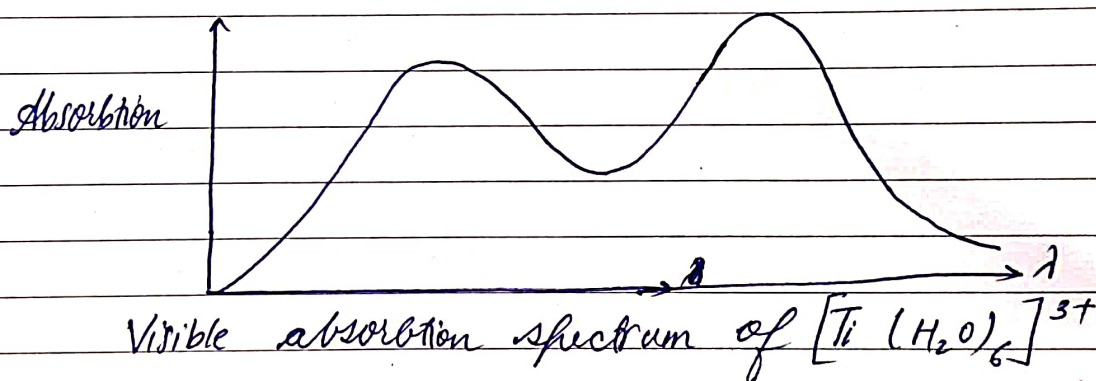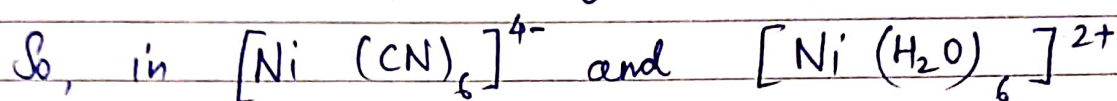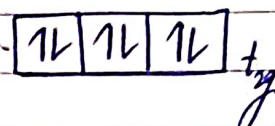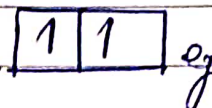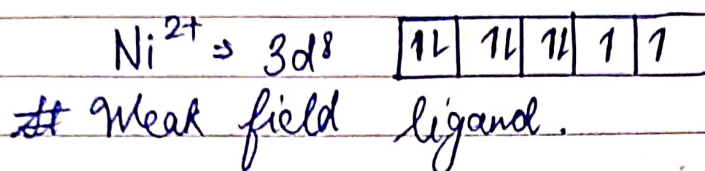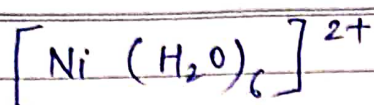
there will be no distortion and it will have perfect octahedral geometry.

(13) CO is a neutral molecule and CFSE is based on ~~point ch~~ considering ligands as point charges interacting with central atom. So, it can't be explained by CFT.

But, 'CO' is a strong field ligand because of formation of special type of 'synergic' bond and back bonding.

'CO' is a π- acceptor and therefore, a strong field ligand.