$[NiCl_4]^{2-}$ $[PdCl_4]^{2-}$ $[PtCl_4]^{2-}$

$[NiCl_4]^{2-}$: sp^3, tetrahedral

para, $\sqrt{8}$ BM

$[PdCl_4]^{2-}$, $[PtCl_4]^{2-}$: dsp^2, sq. planar

$\mu = 0$ (dia)

Acc to VBT, all of three complexes should have same hybridisation because ligands are same, charge on metal is same but they have different hybridisation. This is drawback of VBT.

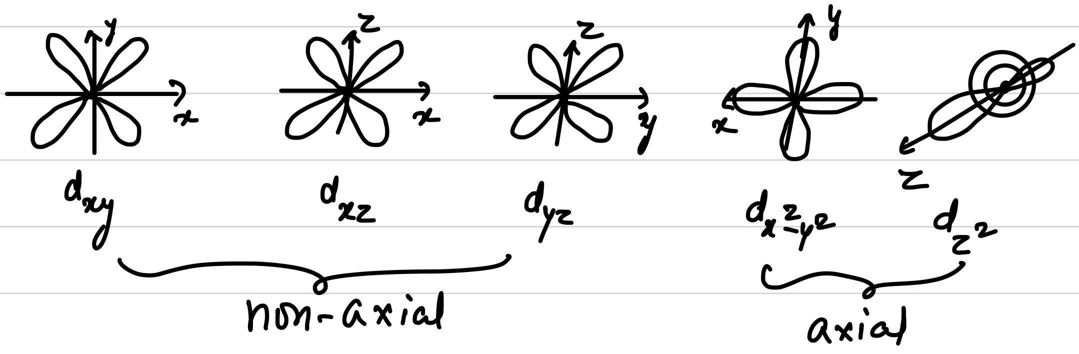
Drawbacks of VBT

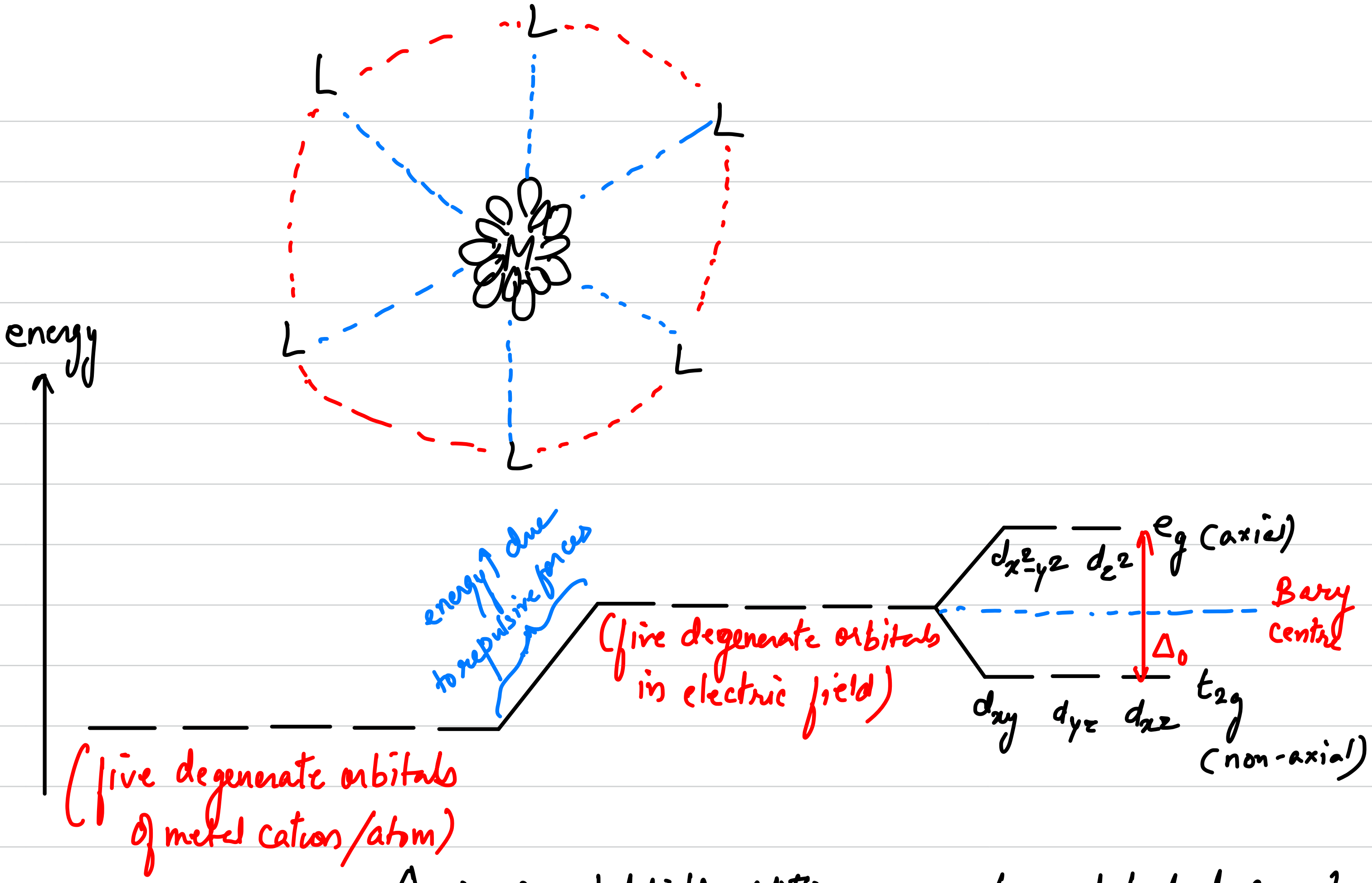
1) VBT can't explain magnetic behaviour in complex compound regularly.

2) VBT can't explain colour in complex compound properly.

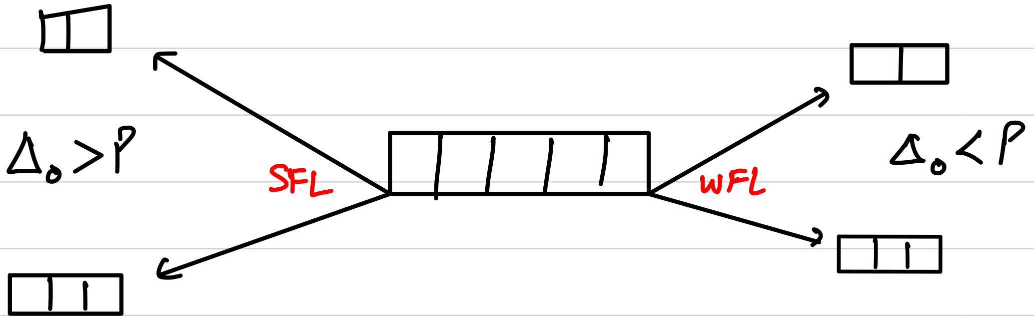
3) VBT can't explain high spin and low spin compounds.

CRYSTAL FIELD THEORY (CFT)





$\Delta_o \Rightarrow$ crystal field splitting energy for octahedral complex

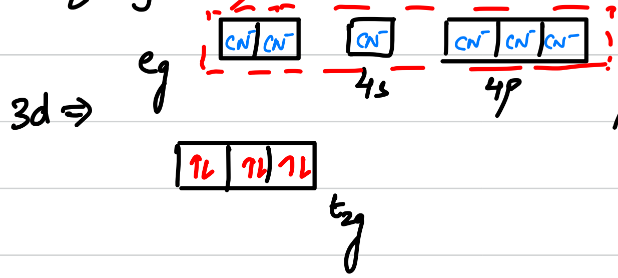


d^7 config

1) $K_4[Fe(CN)_6]$ $4K^+$ Fe^{2+} $6CN^\ominus$

SFL

$Fe^{2+} \Rightarrow [Ar]\,3d^6\,\cancel{4s^2}$



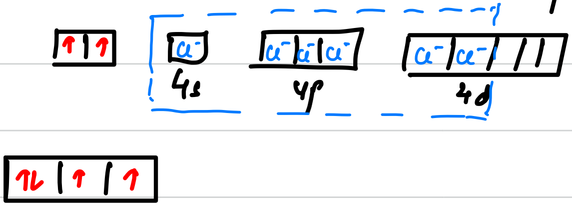
d^2sp^3, inner octa, $\mu = 0$, dia, low spin

2) $K_4[Fe(Cl)_6]$ $4K^+$ Fe^{2+} $6Cl^-$

WFL

⇓

$Fe^{2+} \Rightarrow [Ar]\,3d^6$



sp^3d^2, outer octa, para, $\sqrt{24}$ BM, high spin

$K_3[Fe(CN)_6]$

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

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

$[CoF_3(H_2O)_3]$

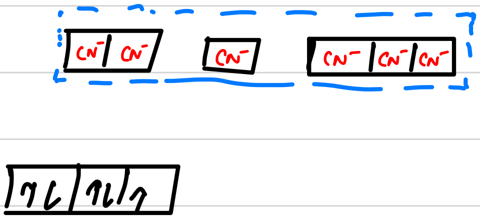
$[Co(H_2O)_6]^{2+}$

$K_3[Fe(CN)_6]$

$3K^+$ Fe^{3+} $6CN^-$

SFL

$Fe^{3+} \Rightarrow [Ar]\, 3d^5$



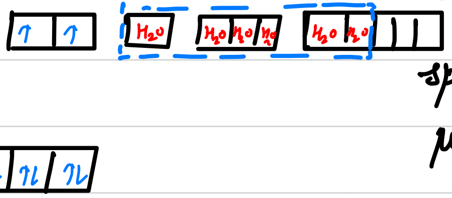
d^2sp^3, inner octa,
para, $\mu = \sqrt{3}$ BM
low spin

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

$Ni^{2+} \Rightarrow [Ar]\, 3d^8$

$6H_2O$

WFL

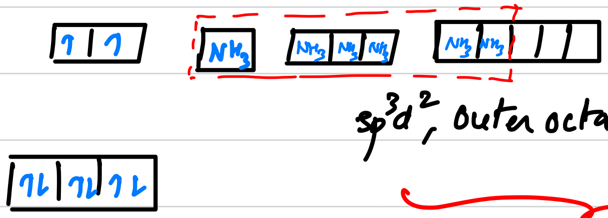


sp^3d^2, outer octa, para,
$\mu = \sqrt{8}$ BM

$[Ni(NH_3)_6]^{2+}$ ⇒ $Ni^{2+} \Rightarrow [Ar]\, 3d^8$ ~~$4s^2$~~

$6NH_3$

SFL

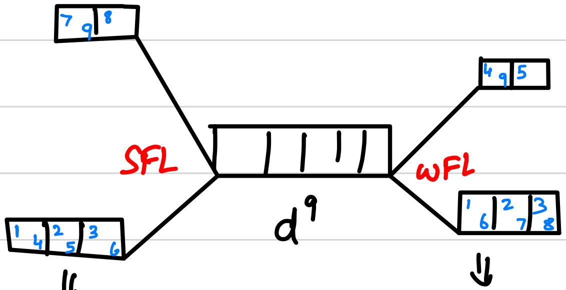


$\underbrace{sp^3d^2\text{, outer octa, para, } \sqrt{8}\text{ BM}}_{\text{no high or low spin defined}}$

d^1, d^2, d^3 } No high spin

d^8, d^9, d^{10} } No low spin

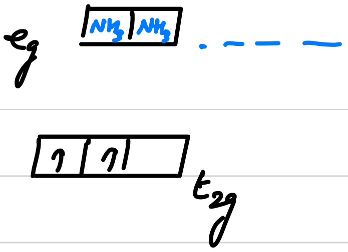
$d^4 \longrightarrow d^7$ — SFL → low spin
— WFL → high spin



⇓
1 upe

⇓
1 upe

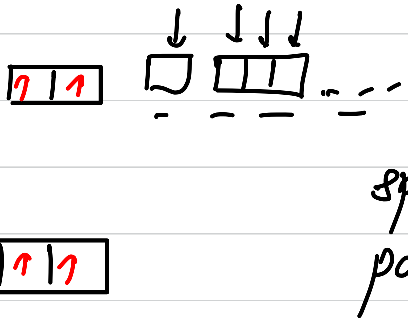
$[V(NH_3)_6]^{3+}$ ⇒ V^{3+} ⇒ $[Ar]\,3d^{\cancel{3}\,2}\,\cancel{4s^2}$



d^2sp^3, inner octa, para,
$\mu = \sqrt{8}$ BM
(no high/low spin defined)

$[CoF_3(H_2O)_3]$ Co^{3+} ⇒ $[Ar]\,3d^{\cancel{7}\,6}\,\cancel{4s^2}$

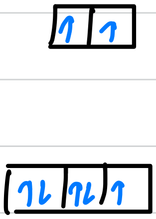
$\underbrace{3F^-, 3H_2O}_{WFL}$



sp^3d^2, outer octa,
para, $\sqrt{24}$ BM, high spin

$[Co(H_2O)_6]^{2+}$ ⇒ Co^{2+} ⇒ $[Ar]3d^7\,\cancel{4s^2}$

$\underbrace{6H_2O}$ WFL

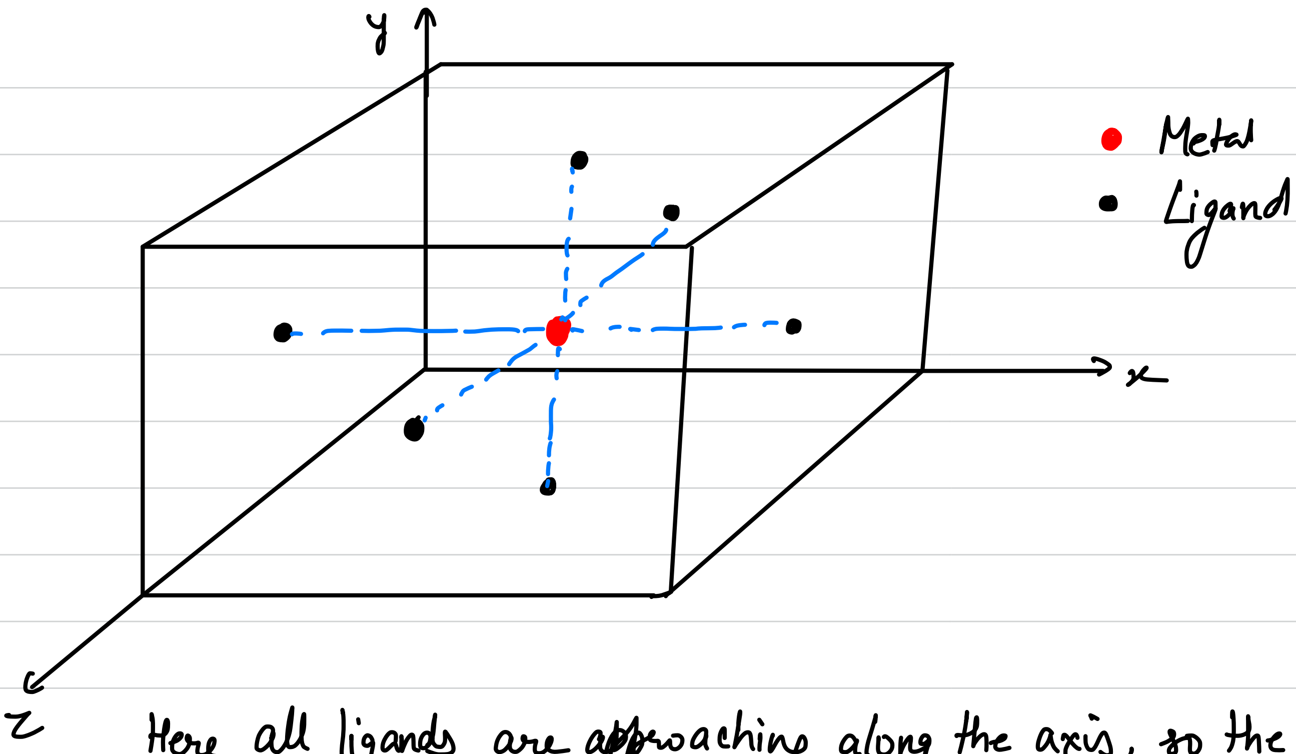


sp^3d^2, outer octa, $\mu = \sqrt{15}$ BM,
para, high spin.

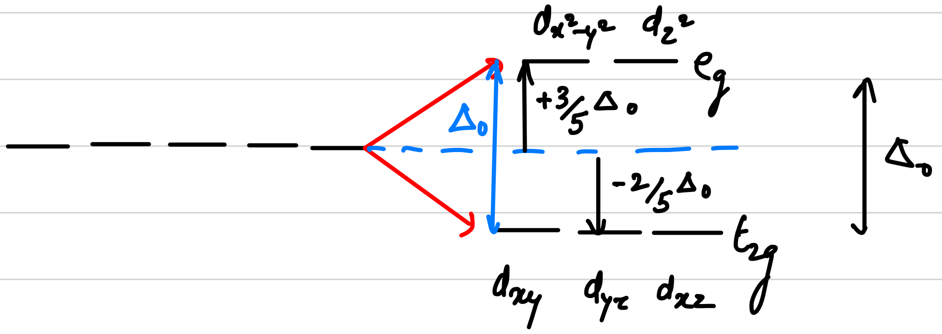
$[Sc(H_2O)_6]^{3+}$, $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$
$[Cr(gly)_3]$

All have d^2sp^3 hybridisation

Sc^{3+}, Ti^{3+}, V^{2+}, V^{3+}, Cr^{3+} ⇒ All have $d^1 \rightarrow d^3$ config
d^0



Here all ligands are approaching along the axis, so the energy of axial orbitals will be higher than that of of non-axial orbitals.



Tetrahedral splitting (CN = 4)

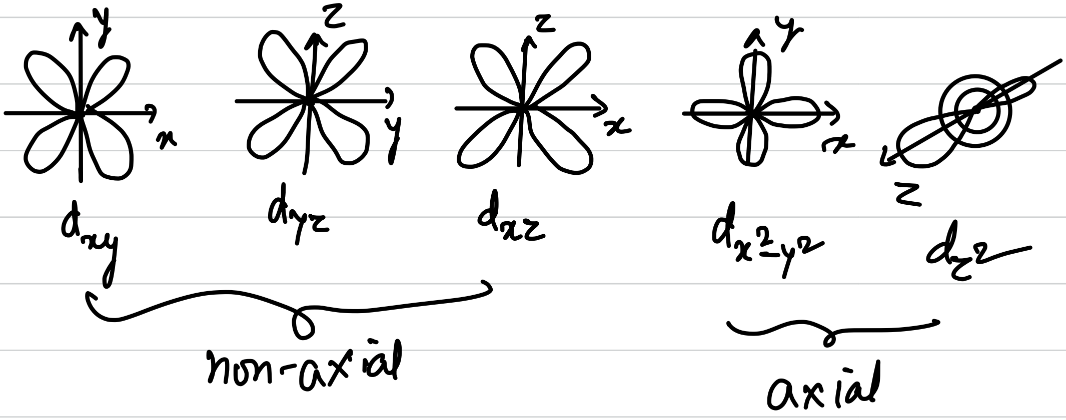
Drawbacks of V.B.T.

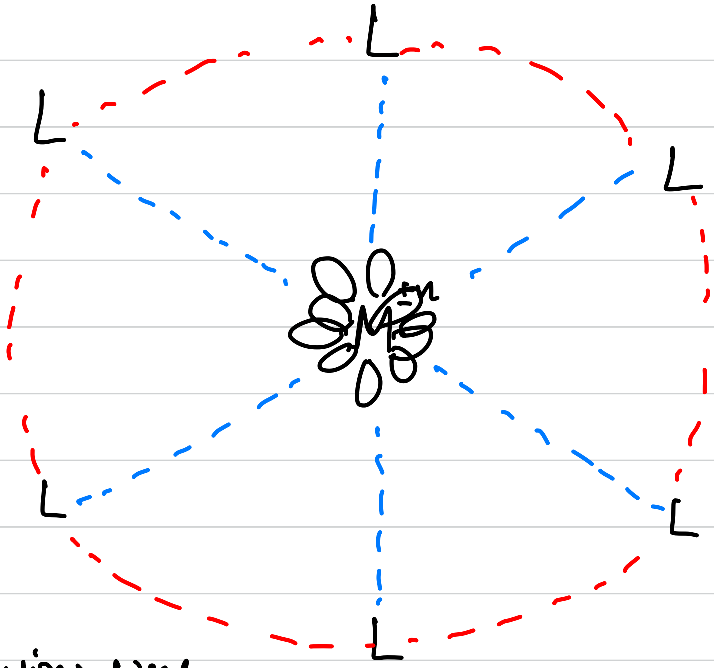
1) VBT can't explain magnetic behaviour in complex compound regularly

2) VBT can't explain colour in complex compound properly.

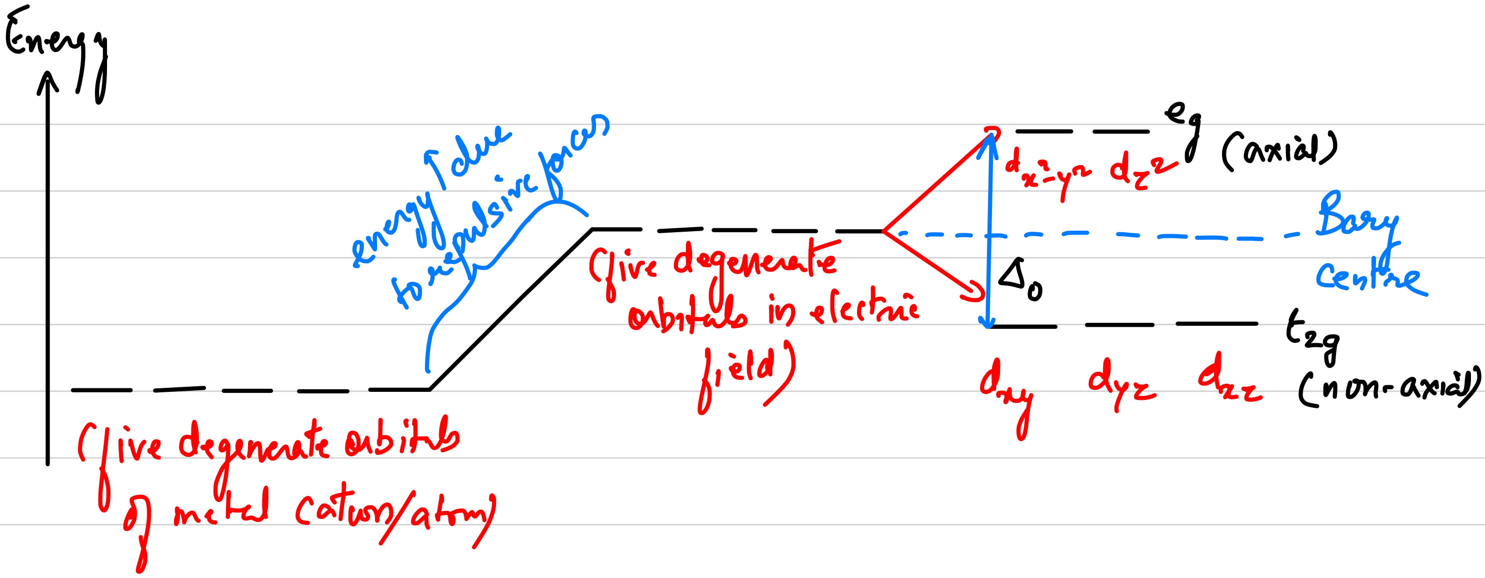
3) VBT can't explain high spin and low spin compounds.

CRYSTAL FIELD THEORY (CFT)

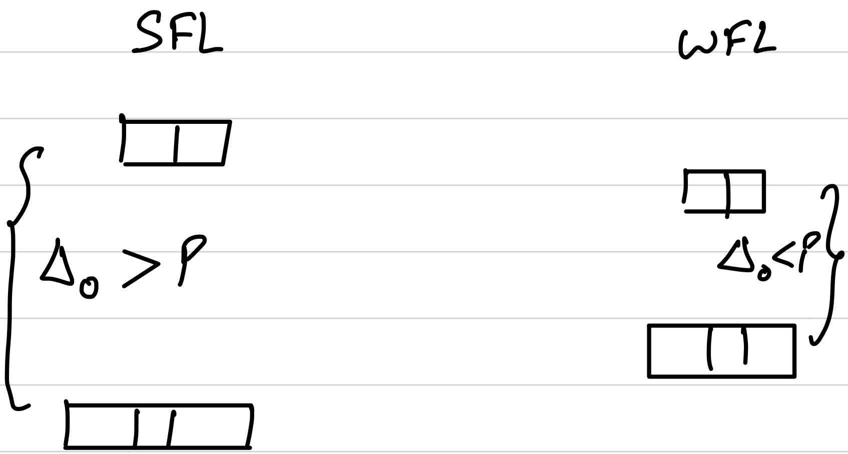




Initially Repulsions were same because all ligands were at infinite distances

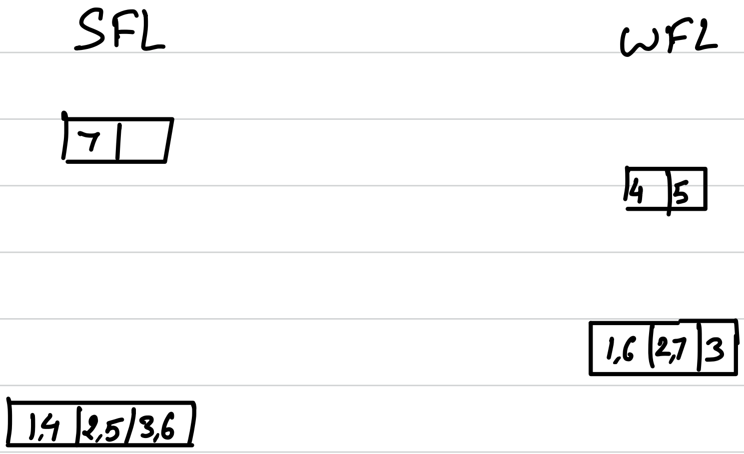


$\Delta_o \Rightarrow$ Crystal field splitting energy for octahedral



$\Downarrow$

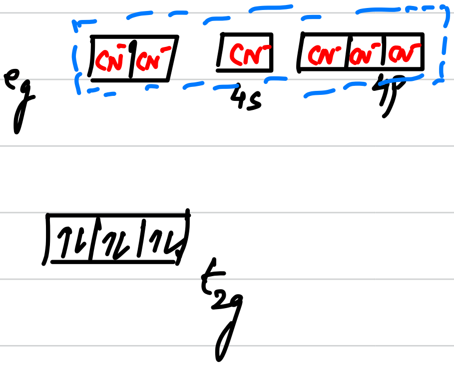
d^7 config



$K_4[Fe(CN)_6]$ $6CN^-$, $Fe^{2+} \Rightarrow [Ar]\, 3d^6\, \cancel{4s^2}$

SFL

$3d \Rightarrow$



d^2sp^3, inner octa.

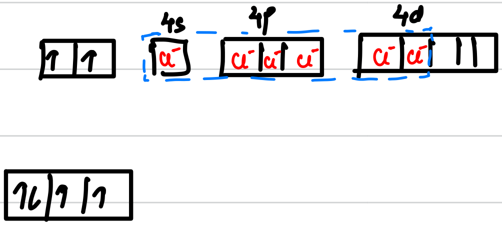
dia $\mu = 0$ BM

low spin

$K_4[Fe(Cl)_6]$ Fe^{2+} $6Cl^-$

WFL

$Fe^{2+} \Rightarrow [Ar]\, 3d^6\, \cancel{4s^2}$



$\Rightarrow sp^3d^2$ outer octa.

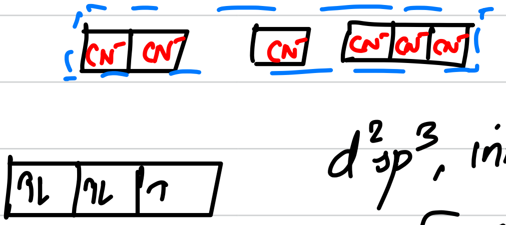
para $\mu = \sqrt{24}$ BM

high spin

$K_3[Fe(CN)_6]$

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

$K_3[Fe(CN)_6]$ $Fe^{3+} \Rightarrow 3d^{\overset{5}{\cancel{6}}}\, \cancel{4s^2}$



d^2sp^3, inner octa.

$\mu = \sqrt{3}$ BM para

low spin

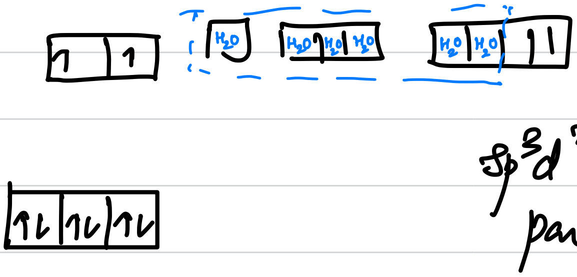
More examples

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

$[CoF_3(H_2O)_3]$

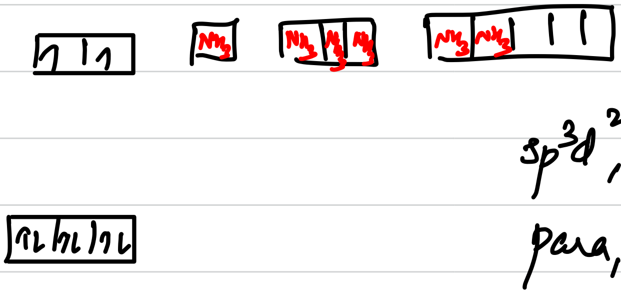
$[Co(H_2O)_6]^{2+}$

⇒ $[Ni(H_2O)_6]^{2+}$ $Ni^{2+} \Rightarrow [Ar]3d^8 \cancel{4s^0}$ $6H_2O$ WFL



sp^3d^2, outer octa., para, $\mu = \sqrt{8}$ BM

$[Ni(NH_3)_6]^{2+}$



sp^3d^2, outer octa

para, $\mu = \sqrt{8}$ BM

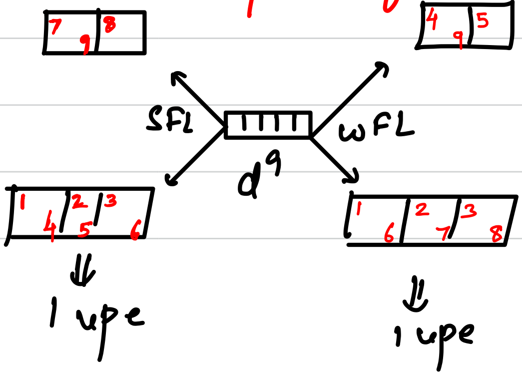
No high spin or low spin defined

d^1, d^2, d^3 } No high spin

d^8, d^9, d^{10} } No low spin

$d^4 \rightarrow d^7$ — $\xrightarrow{SFL}$ low spin

$\xrightarrow{WFL}$ high spin



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

$[CoF_3(H_2O)_3]$

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

$\Rightarrow$ $V^{3+} \Rightarrow [Ar]\,3d^{\overset{2}{\cancel{2}}}\ \cancel{4s^{2}}$

d^2sp^3, inner octa, para,

$\mu = \sqrt{8}$ BM

$\boxed{NH_3 \,|\, NH_3}$ e_g

$\boxed{\uparrow \,|\, \uparrow \,|\, \quad}$ t_{2g}

$\overset{3+\ (-1)}{[CoF_3(H_2O)_3]}$ $Co^{3+} \Rightarrow [Ar]\,3d^{\overset{6}{\cancel{7}}}\ \cancel{4s^{2}}$ $\underbrace{3F^-,\ 3H_2O}_{WFL}$

$\boxed{\uparrow \,|\, \uparrow}$

sp^3d^2, outer octahedral

$\mu = \sqrt{24}$ BM, para

high spin

$\boxed{\uparrow\downarrow \,|\, \uparrow \,|\, \uparrow}$

$[Co(H_2O)_6]^{2+}$ $Co^{2+} \Rightarrow [Ar]\,3d^{7}\ \cancel{4s^{2}}$ $\underbrace{6H_2O}_{WFL}$

$\boxed{\uparrow \,|\, \uparrow}$

sp^3d^2, outer octa.

$\mu = \sqrt{15}$ BM, para

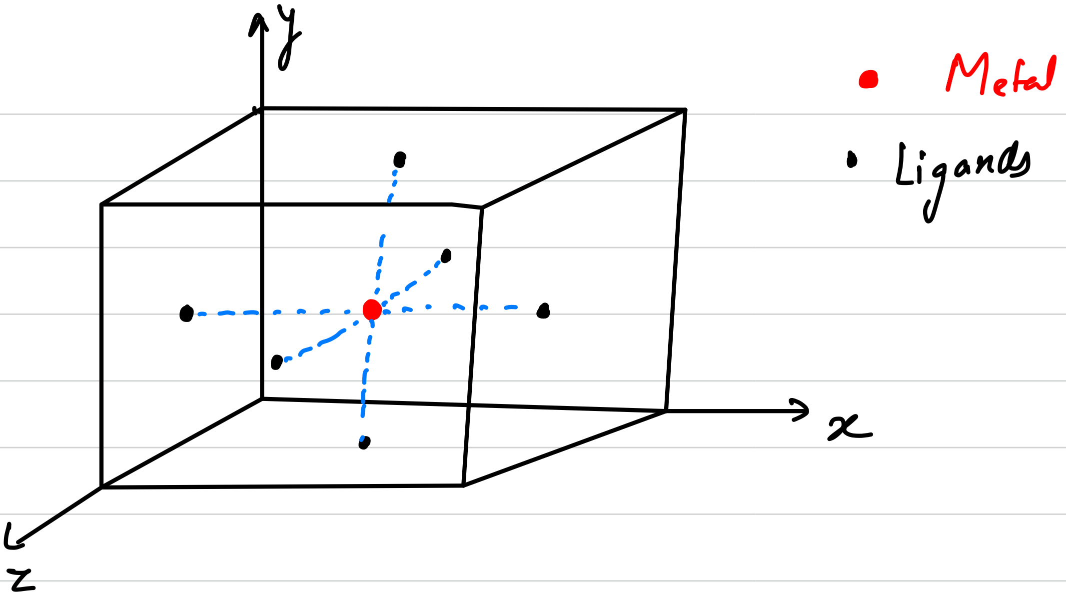
high spin

$\boxed{\uparrow\downarrow \,|\, \uparrow\downarrow \,|\, \uparrow}$

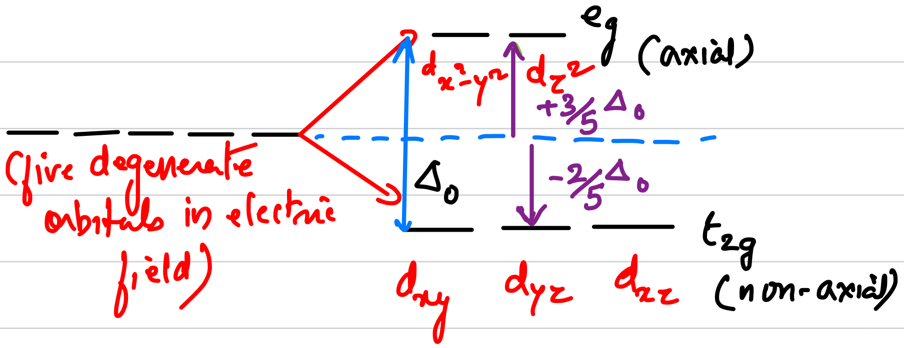
$\underbrace{[Sc(H_2O)_6]^{3+},\ [Ti(H_2O)_6]^{3+},\ [V(H_2O)_6]^{2+},\ [V(H_2O)_6]^{3+},\ [Cr(H_2O)_6]^{3+}\ \ [Cr(NH_3)_6]^{3+}\ \ [Cr(gly)_3]}$

All have d^2sp^3 hybridisation

$\underset{d^0}{Sc^{3+}}$, Ti^{3+}, V^{2+}, V^{3+}, Cr^{3+} $\Rightarrow$ have $d^1 \rightarrow d^3$ config



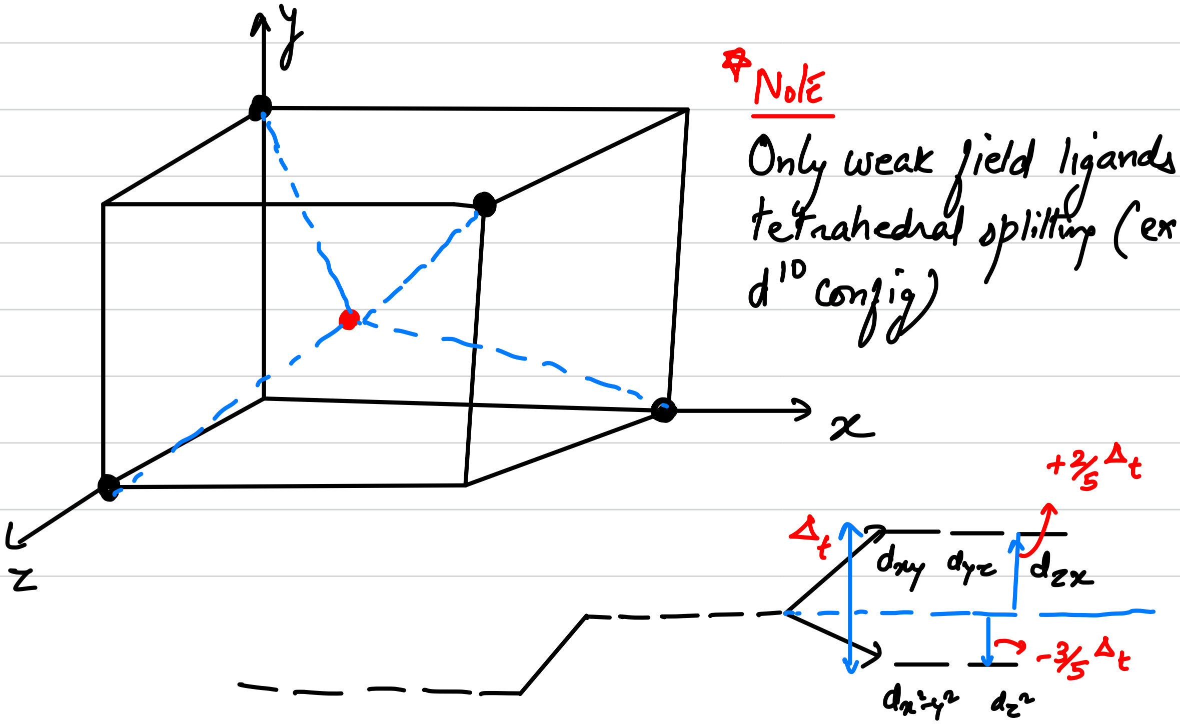
Here all ligands are approaching along the axis, so the energy of axial orbitals will be higher than that of non-axial orbitals.



Tetrahedral Splitting (CN=4)

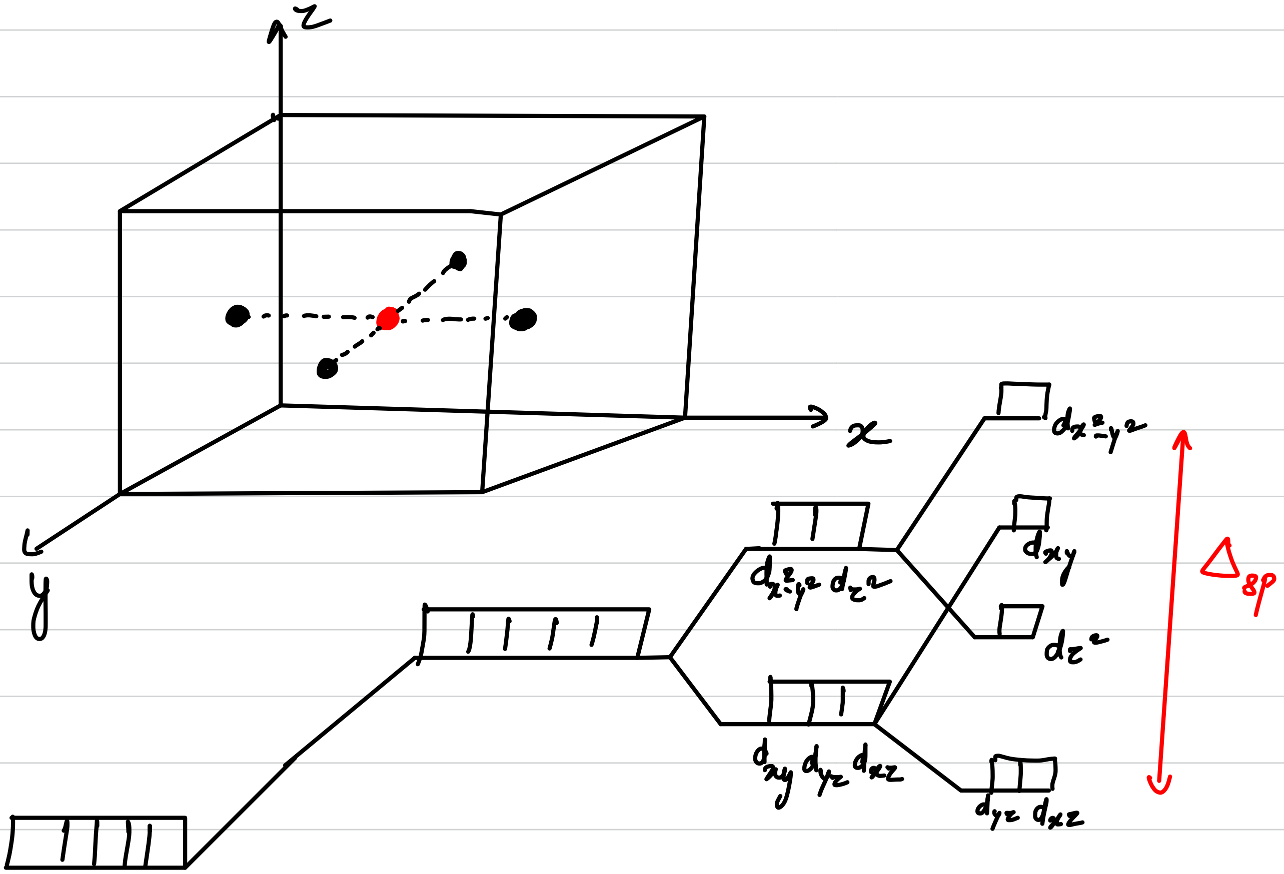
*Note

Only weak field ligands shows tetrahedral splitting (except d^{10} config)



NOTE

Strong field ligands show square planar splitting.



$$\boxed{\Delta_{sp} > \Delta_o > \Delta_t}$$

$$\boxed{\begin{aligned} \Delta_{sp} &= 1.3\,\Delta_o \\ \Delta_t &= \tfrac{4}{9}\,\Delta_o \end{aligned}}$$

HW

Q. If Δ_o for $[CoCl_6]^{4-}$ is 18000, then calculate the value of Δ for $[CoCl_4]^{2-}$

HW

1) $[Ni(CN)_4]^{2-}$

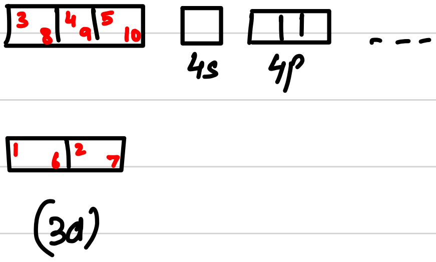
2) $[NiCl_4]^{2-}$

3) $[Cu(CN)_4]^{3-}$

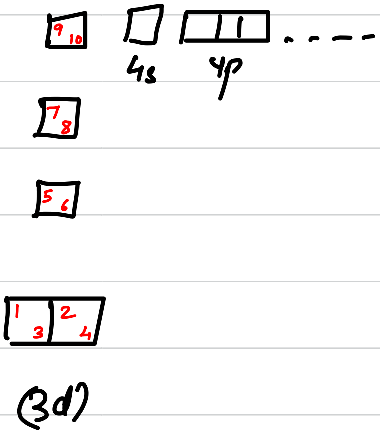
4) $[Cu(Cl)_4]^{3-}$

e^- filling order in square planar and tetrahedral splitting

tetrahedral (always)

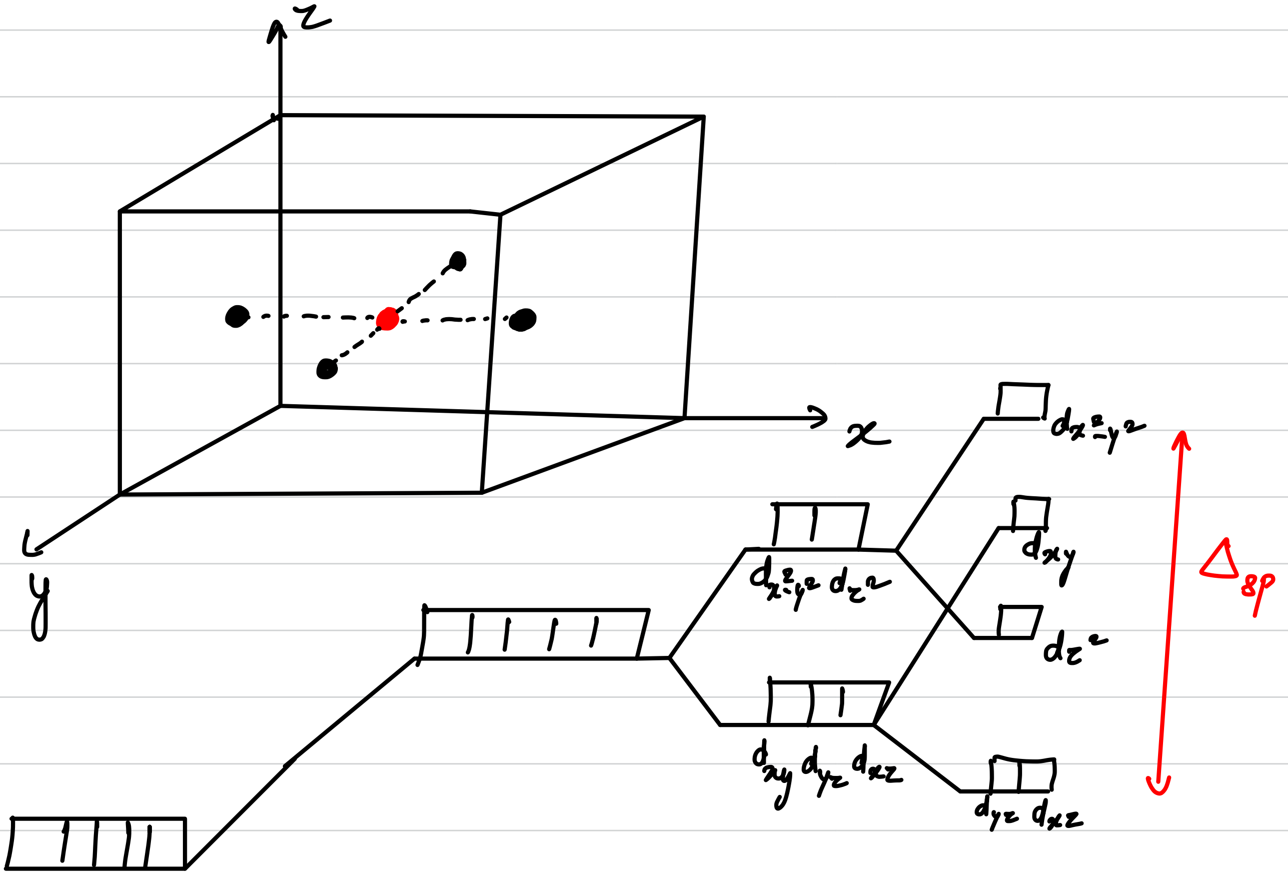


square planar (always)



NOTE

Strong field ligands show square planar splitting.



$$\boxed{\Delta_{sp} > \Delta_o > \Delta_t}$$

$$\boxed{\begin{aligned}\Delta_{sp} &= 1.3\,\Delta_o \\ \Delta_t &= \tfrac{4}{9}\,\Delta_o\end{aligned}}$$

HW

Q. If Δ_o for $[CoCl_6]^{4-}$ is 18000, then calculate the value of Δ for $[CoCl_4]^{2-}$

$[CoCl_4]^{2-} \Rightarrow \underset{\Downarrow}{Co^{2+}}$ $4Cl^-$

3d^7 WFL

Δ_t needs to be calculated as splitting will be tetrahedral

$\Delta_t = \frac{4}{9}\Delta_o = \frac{4}{9} \times 18000 = \boxed{8000}$ Ans

HW

1) $[Ni(CN)_4]^{2-}$

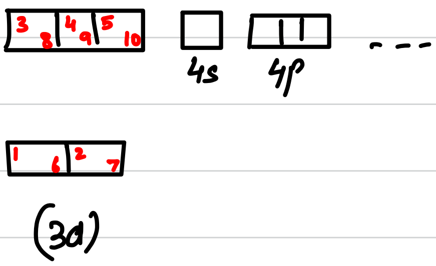
2) $[NiCl_4]^{2-}$

3) $[Cu(CN)_4]^{3-}$

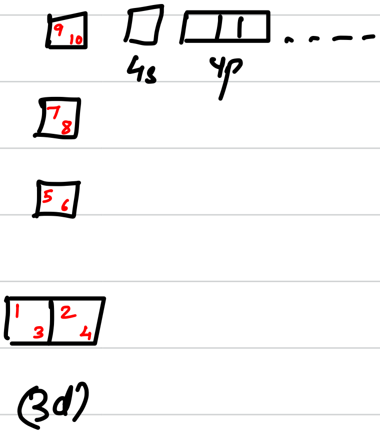
4) $[Cu(Cl)_4]^{3-}$

e^- filling order in square planar and tetrahedral splitting

tetrahedral (always)



square planar (always)

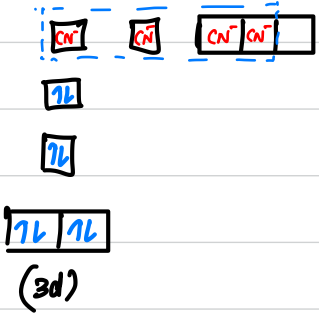


1) $[Ni(CN)_4]^{2-}$ ⇒ Ni^{2+} $\quad 4\underset{\sim}{CN^-}$ $\quad CN=4$

SFL

(square planar)

$[Ar]\,3d^8$

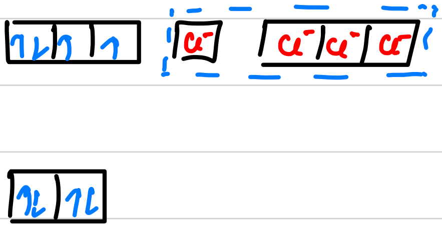


⇒ dsp^2

dia, $\mu=0$

2) $[NiCl_4]^{2-}$ ⇒ Ni^{2+} ⇒ $[Ar]3d^8$ $\underset{\sim}{4Cl^-}$ tetrahedral

WFL



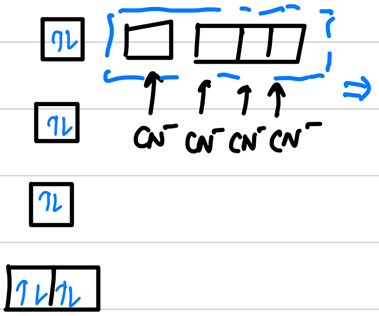
sp^3

tetrahedral

para, $\sqrt{8}$ BM

3) $[Cu(CN)_4]^{3-}$ ⇒ Cu^+ ⇒ $[Ar]3d^{10}$ $\cancel{4s^1}$ $\underset{\sim}{4CN^-}$ square planar

SFL

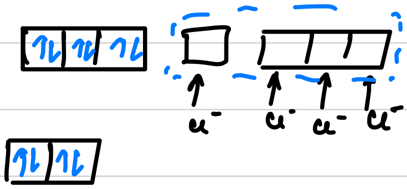


sp^3, tetrahedral

dià, $\mu = 0$ BM

4) $[CuCl_4]^{3-}$ ⇒ Cu^+ ⇒ $[Ar]3d^{10}$ $\cancel{4s^1}$ $\underset{\sim}{4Cl^-}$ tetrahedral

WFL



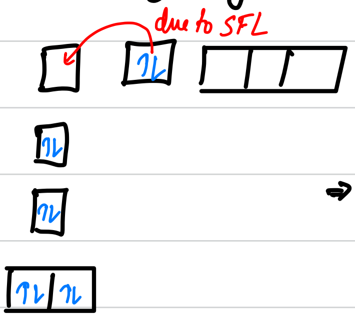
sp^3, tetrahedral

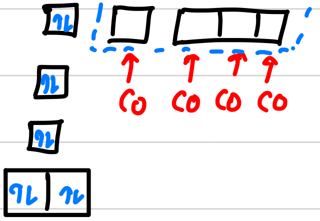
$\mu = 0$ BM

(dia)

5) $[Ni(CO)_4]^0$ Ni^0 ⇒ $[Ar]3d^8 4s^2$ $\underset{\sim}{4CO}$ square planar splitting

SFL





sp^3, tetrahedral

$\mu = 0$

dià

Orbitals used in hybridisation

$sp \Rightarrow s +$ any one p out of p_x, p_y, p_z

$sp^2 \Rightarrow s +$ any two p out of p_x, p_y, p_z

$sp^3 \Rightarrow s + p_x + p_y + p_z$

$sp^3d \Rightarrow s + p_x + p_y + p_z + d_{z^2}$

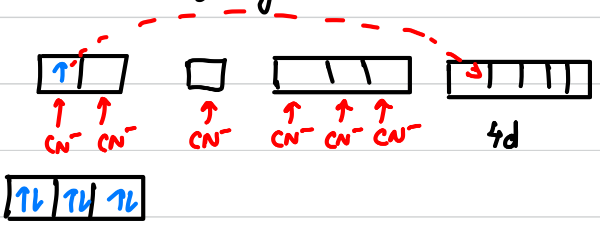
$sp^3d^2 \Rightarrow s + p_x + p_y + p_z + d_{z^2} + d_{x^2-y^2}$

$dsp^2 \Rightarrow d_{x^2-y^2} + s + p_x + p_y$

6) $[Co(CN)_6]^{4-} \Rightarrow Co^{2+}$ $\quad$ $6\ \underbrace{CN^-}_{SFL}$ $\Rightarrow$ octahedral

$\Downarrow$

$[Ar]\ 3d^7$



$\Rightarrow d^2sp^3$, inner octa.

para, 1 upe, $\sqrt{3}$ BM

low spin

Transference

When Co^{2+} is surrounded by 6 S.F.L., then it always form inner orbital complex compound with the hybridisation d^2sp^3. In such type of complex compounds, unpaired e^- is present in 4d orbital rather than 3d orbital due to transference. These compounds acts as strong reducing agent.

$$\underset{\text{(Reducing agent)}}{M} \longrightarrow M^+ + e^- \ \text{(Oxidation)}$$

Conditions for transference

1) Complex should contain only SFL

2) Complex should have only one unpaired electron

3) Complex should have possibility of inner orbital complex compound

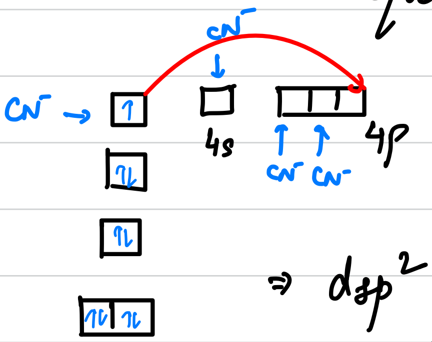
All three conditions should be simultaneously satisfied.

7) $[Cu(CN)_4]^{2-}$

⇓

$Cu^{2+} \Rightarrow [Ar]3d^9$ $4CN^-$ SFL

square planar



⇒ dsp^2 hybridisation

upe = 1, para, $\sqrt{3}$ BM

1) presence of SFL ✓

2) only one upe ✓

3) possible of dsp^2 ✓

⇓

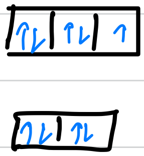
transference ✓

$[CuCl_4]^{2-}$

⇓

$Cu^{2+} \Rightarrow [Ar]3d^9$ $4Cl^-$ WFL

tetrahedral



As no SFL, no transference

Exception

bidented

CN=6

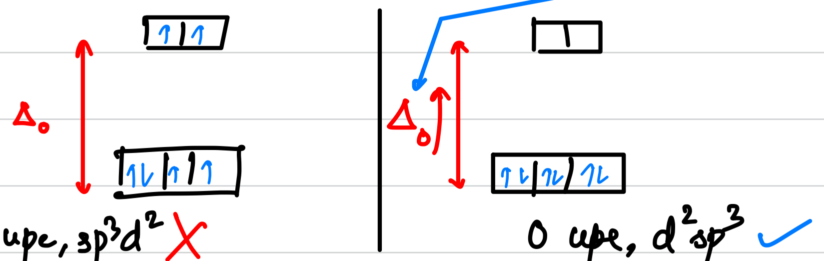
$[Co(C_2O_4)_3]^{3-} \Rightarrow Co^{3+} \quad 3\, C_2O_4^{2-}$

octahedral

WFL ⇒ chelation

$\Downarrow$

$[Ar]\, 3d^6$



4 upe, sp^3d^2 ✗ $\qquad$ 0 upe, d^2sp^3 ✓

Co^{3+} $\qquad$ Co^{3+}

FACTORS AFFECTING CFSE VALUE

1) Nature of ligands

As the metal and ligand come close together, the $e^- - e^-$ repulsion will be higher and the splitting will be very much higher which in turn increases the stability of the compound

i) No of ligands same
ii) charge on cation same
iii) type of cation same

order of stability : $[\overset{(+3)}{Fe}(CN)_6]^{3-} > [\overset{(+3)}{Fe}(NO_2)_6]^{3-} > [\overset{(+3)}{Fe}(NH_3)_6]^{3+}$

$\boxed{SFL \uparrow \ \text{stability} \uparrow}$

2) Charge on cation :-

i) Nature of ligand same
ii) No of ligand same
iii) type of cation same

then $\boxed{\text{Charge on cation} \uparrow \text{ stability} \uparrow}$

$[Fe(CN)_6]^{3-}$ $[Fe(CN)_6]^{4-}$

As the charge increases, more attraction is there in between metal cation and ligand, hence more stability.

3) No. of ligands :-

(i) Charge on cation same
(ii) Nature of ligand same
(iii) type of cation same

$[Ni(H_2O)_4]^{2+}$ Δ_t $[Ni(H_2O)_6]^{2+}$ Δ_o

$[Ni(CN)_4]^{2-}$ Δ_{sp} $[Ni(CN)_6]^{2-}$ Δ_o

④ Z_{eff} of metal cation :-

poor shielding orbitals and e^-

3d - - - - - - - Ni Cu Zn ⇒ $3d^{10}$
4d - - - - - - - Pd Ag Cd ⇒ $3d^{10}\ 4d^{10}$
5d - - - - - - - Pt Au Hg ⇒ $3d^{10}\ 4d^{10}\ 4f^{14}\ 5d^{10}$

$[NiCl_4]^{2-}$ $[PdCl_4]^{2-}$ $[PtCl_4]^{2-}$

{ leave space }

5) Chelation :-

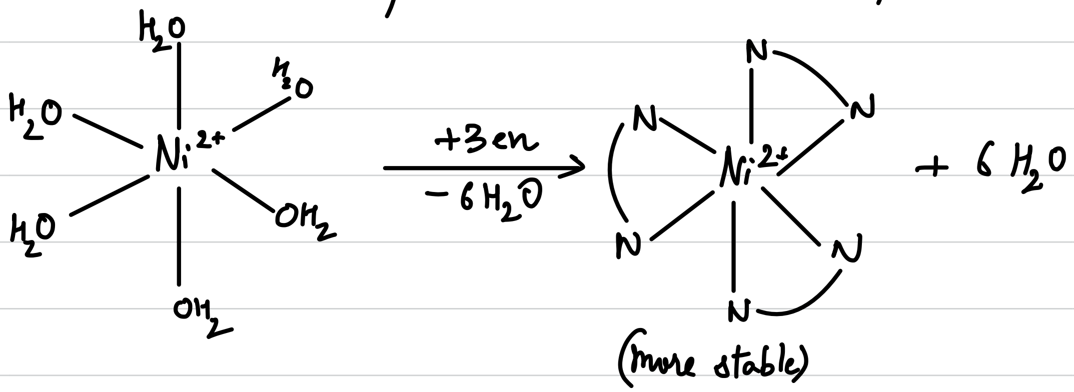
$[Ni(H_2O)_6]^{2+} + 3en \longrightarrow [Ni(en)_3]^{2+} + 6H_2O$

$\Delta S > 0$ chelate ring is formed

$\Delta H = -ve$

$\Delta G = -ve$

processor reaction is spontaneous so reaction is possible.



It is more stable due to ring formation, more the no. of rings is the stability.

Q. Compare stability :-

a) $[Ni(H_2O)_6]^{2+}$ $[Ni(en)_3]^{2+}$

b) $[Ni(NO_2)_6]^{4-}$ $[Ni(en)_3]^{2+}$

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

d) $[Fe(en)_3]^{3+}$ $[Fe(EDTA)]^{\ominus}$

e) $[Fe(NH_3)_6]^{3+}$ $[Fe(C_2O_4)_3]^{3-}$

Key point :-

$CN = 4$ → WFL tetrahedral

$CN = 4$ → SFL square planar

$d^1 \longrightarrow d^9$ SFL dsp^2

$d^{10} \longrightarrow$ SFL/WFL sp^3

$d^1 \longrightarrow d^9 \Rightarrow$ WFL sp^3 tetrahedral

Electronic Configuration and CFSE in octahedral complex

CFSE ⇒ crystal field stabilisation energy

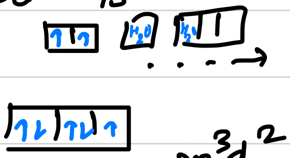
Configuration	Δ_o (WFL)	Configuration	Δ_o (SFL)
d^1 t_{2g}^1	-0.4×1	d^1 t_{2g}^1	-0.4×1
d^2 t_{2g}^2	-0.4×2	d^2 t_{2g}^2	-0.4×2
d^3 t_{2g}^3	-0.4×3	d^3 t_{2g}^3	-0.4×3
d^4 t_{2g}^3 e_g^1	$-0.4\times3+0.6\times1$	d^4 t_{2g}^4	-0.4×4
d^5 t_{2g}^3 e_g^2	$-0.4\times3+0.6\times2$	d^5 t_{2g}^5	-0.4×5
d^6 t_{2g}^4 e_g^2	$-0.4\times4+0.6\times2$	d^6 t_{2g}^6	-0.4×6
d^7 t_{2g}^5 e_g^2	$-0.4\times5+0.6\times2$	d^7 t_{2g}^6 e_g^1	$-0.4\times6+0.6\times1$
d^8 t_{2g}^6 e_g^2	$-0.4\times6+0.6\times2$	d^8 t_{2g}^6 e_g^2	$-0.4\times6+0.6\times2$
d^9 t_{2g}^6 e_g^3	$-0.4\times6+0.6\times3$	d^9 t_{2g}^6 e_g^3	$-0.4\times6+0.6\times3$
d^{10} t_{2g}^6 e_g^4	$-0.4\times6+0.6\times4$	d^{10} t_{2g}^6 e_g^4	$-0.4\times6+0.6\times4$

Q. Predict the hybridisation of :-

1) Brown Ring Complex $[\underset{(+1)}{Fe}(H_2O)_5\underset{(+1)}{NO}]^{2+}SO_4^{2-}$

$Fe^{+1} \Rightarrow [Ar]\,3d^6\,4s^{\cancel{2}\,1} \xrightarrow{\text{excitation}} 3d^7\,4s^0$ $\underbrace{5H_2O}_{WFL}$ $\underbrace{1\,NO^+}_{SFL}$

(splitting acc to WFL)

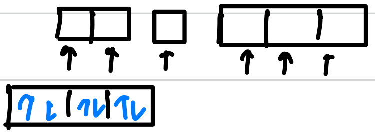


sp^3d^2, outer octa, para
upe = 3, $\sqrt{15}$ BM
high spin

2) Sodium nitroprusside

$Na_2[Fe(CN)_5NO] \Rightarrow 2Na^+ \quad [\underset{(2+)}{Fe}(\underset{(-1)}{CN})_5\underset{(+1)}{NO}]^{2-} \Rightarrow \underbrace{5CN^-, 1NO^+}_{SFL}$

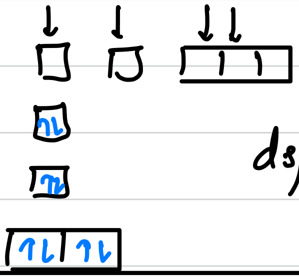
$Fe^{2+} \Rightarrow [Ar]\,3d^6$



⇒ d^2sp^3, inner octa,
dia, $\mu = 0$ low spin

3) $[\underset{(+2)}{Ni}(\underset{(-1)}{dmg})_2]$ Rosy Red ppt CN=4 $dmg^- \Rightarrow$ both N atoms donor
⇒ chelation (4 Rings)
hence $\underline{\underline{SFL}}$

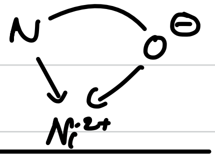
$Ni^{2+} \Rightarrow [Ar]\,3d^8$



dsp^2, square planar,
$\mu = 0$, dia

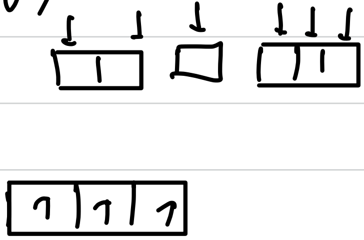
4) $[Ni(gly)_2]$ (CN=4) As same as $[Ni(dmg)_2]$ $gly^- \Rightarrow$ due to chelation, will act as SFL

gly
‖
unsymmetrical bidented



5) $[Cr(gly)_3]$ (CN=6) $gly^- \Rightarrow SFL$

$Cr^{3+} \Rightarrow [Ar]\,3d^3$



d^2sp^3, inner octa,
para, $\sqrt{15}$ BM

H.W.

6) $[Cr(C_2O_4)_3]^{3-}$

H.W.

7) $[Co(C_2O_4)_3]^{3-}$

HW

8) $K_4[Fe(CN)_5O_2]$

HW

9) $[NiF_6]^{2-}$

HW

10) $[AuCl_4]^{\ominus}$

6) $[Cr(C_2O_4)_3]^{3-} \Rightarrow Cr^{3+} \quad 3\,C_2O_4^{2-}$ (large splitting due to chelation)

CN=6 Octahedral

$Cr^{3+} \Rightarrow [Ar]\,3d^3$

d^2sp^3, inner octa, $\sqrt{15}$ BM, para.

$\boxed{upe = 3}$

(no low/high spin defined)

7) $[Co(C_2O_4)_3]^{3-} \rightarrow Co^{3+} \quad 3\,C_2O_4^{2-}$ (large splitting)

CN=6 octahedral

$Co^{3+} \Rightarrow [Ar]\,3d^{\overset{6}{\cancel{7}}}\,\cancel{4s^2}$

d^2sp^3 inner Octa, dia, $\mu = 0$ BM, low spin

8) $\underset{(+3)\quad(-1)\quad(-2)}{K_4[Fe(CN)_5O_2]^{4-}}$ ✗ then $\Rightarrow$ $4K^+$ Fe^{2+} $\underset{SFL}{5CN^-}$ O_2^- (large splitting)

superoxido

CN=6 octahedral

$\underset{(+2)}{Fe}$ $\underset{(-1)}{O_2}$ ✓ then

$Fe^{2+} \Rightarrow [Ar]\,3d^6\,\cancel{4s^2}$

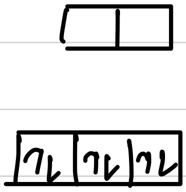
$\underset{✗}{0}$ upe, $\underset{✗}{dia}$, d^2sp^3, inner octa, low spin

Here O_2^- (acc. to MOT) has unpaired e^- so paramagnetic

Correct $\Rightarrow$ 1 upe, para, d^2sp^3, inner octa, low spin

9) $[NiF_6]^{2-}$ $\Rightarrow$ Ni^{4+} $6F^-$ CN = 6 octahedral

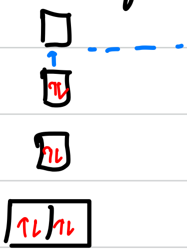
$Ni^{+4} \Rightarrow [Ar]\,\overset{3d^6}{\cancel{3d^8}}\,\cancel{4s^2}$ [high +ve charge hence large splitting]



d^2sp^3 inner octa, 0 upe, 0 BM, dia

10) $[AuCl_4]^{\ominus}$ $\Rightarrow$ Au^{3+} $4Cl^-$ CN = 4 square planar

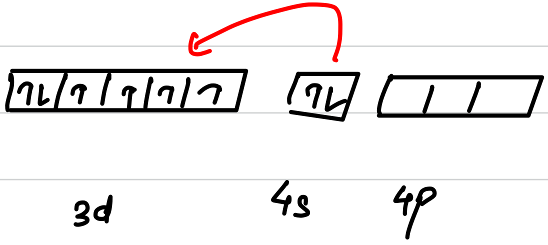
$Au^{3+} \Rightarrow [Xe]\,4f^{14}\,5d^{\overset{8}{\cancel{10}}}\,\cancel{6s^1} \Rightarrow 5d^8$



dsp^2, square planar, dia, 0 BM

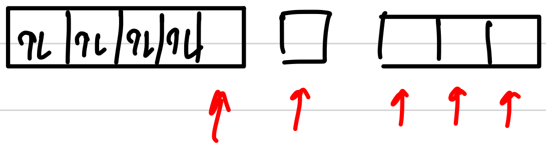
11) $[Fe(CO)_5]$ Fe^0 $\underbrace{5CO}_{SFL}$ CN = 5

$Fe \Rightarrow [Ar]\,3d^6 4s^2$



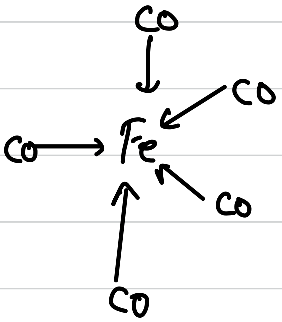
due to SFL, pairing of e⁻ and excitation of 4s e⁻

⇓



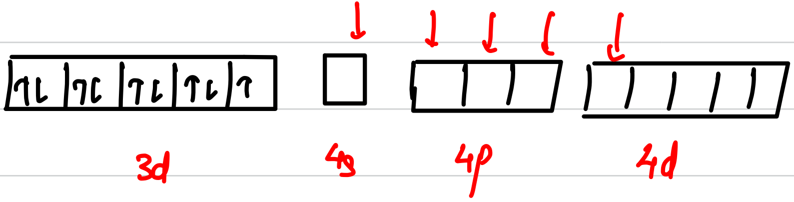
dsp^3, dia, $\mu = 0$ Trigonal bipyramidal

d_{z^2}



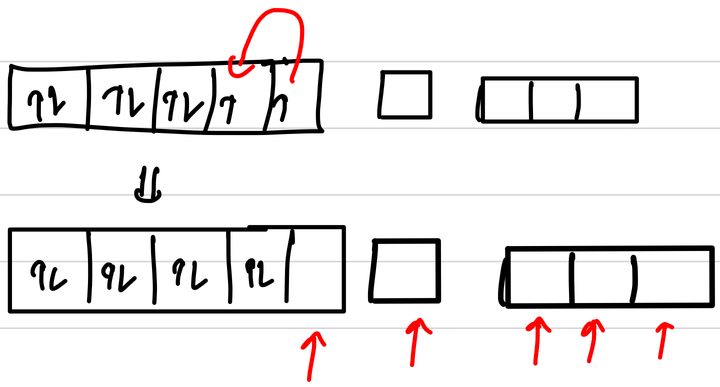
12) $[CuCl_5]^{3-}$ Cu^{2+}, $\underbrace{5Cl^-}_{WFL}$

$Cu^{2+} \Rightarrow [Ar]\,3d^{\cancel{10}\,9}\,\cancel{4s^1}$

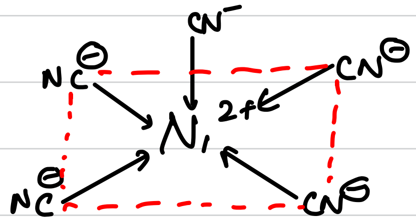


sp^3d, trigonal bipyramidal, para, $\sqrt{3}$ BM

13) $[Ni(CN)_5]^{3-}$ $Ni^{2+} \rightarrow [Ar]3d^8$ $5\,\underbrace{CN^-}_{SFL}$



dsp^3, $d_{x^2-y^2}$, square pyramidal, 0 BM, dia



Colour Nature of Compound

1) Polarisation

$\xrightarrow{\hspace{3cm}}$ Polarisation ↑

$\underbrace{AgF \quad AgCl}_{\text{white}} \quad \underbrace{AgBr}_{\text{pale yellow}} \quad \underbrace{AgI}_{\text{yellow}}$

Polarisation ↑ cov. ch ↑ intensity of colour ↑

2) HOMO-LUMO transition

F_2, Cl_2, Br_2, I_2 they are coloured due to this concept
(all are diamagnetic)

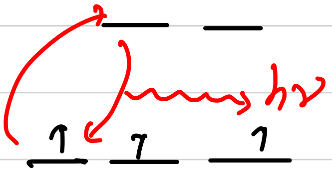
3) d-d transition

(i) d-orbital must have atleast one electron

ii) d-orbital must have atleast one vacant orbital

iii) Generally unpaired electron compound are paramagnetic and have coloured nature.

iv) Generally, unpaired $e^- = 0$ (zero) compounds are diamagnetic and colourless (it is not always true)



ex

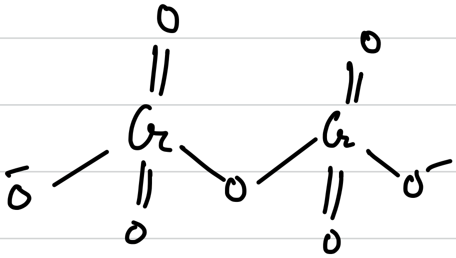
$K_4[Fe(CN)_6]$	$K_4[FeF_6]$
$Fe^{2+} \Rightarrow [Ar]3d^6$ $\quad 6CN^- \Rightarrow SFL$	$Fe^{2+} \Rightarrow [Ar]3d^6$ $\quad 6F^- \Rightarrow WFL$
0 upe, dia colourless	4 upe, para coloured

4) Charge Transfer Spectrum (CTS)

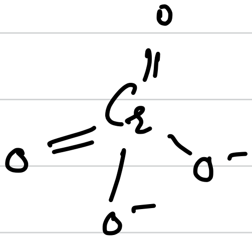
CTS	O.S.	upe^-
1) $Cr_2O_7^{2-}$	+6	0
2) CrO_4^{2-}	+6	0
3) MnO_4^-	+7	0
4) VO_4^{3-}	+5	0
5) CrO_2Cl_2	+6	0
6) CrO_2F_2	+6	0

All these compounds are diamagnetic and coloured, tetrahedral and hybridisation is d^3s instead of sp^3

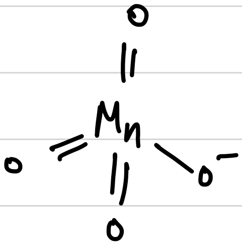
1) $Cr_2O_7^{2-}$



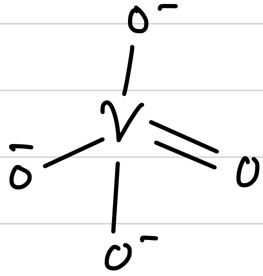
2) CrO_4^{2-}



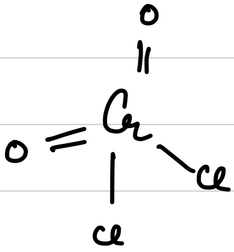
3) MnO_4^-



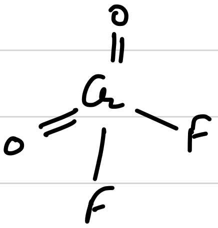
4) VO_4^{3-}



5) CrO_2Cl_2

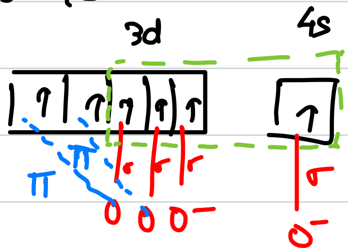


6) CrO_2F_2



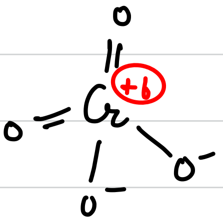
<u>CrO_4^{2-}</u>

$Cr = [Ar]\,3d^5 4s^1$



$\Rightarrow d^3s$, tetrahedral

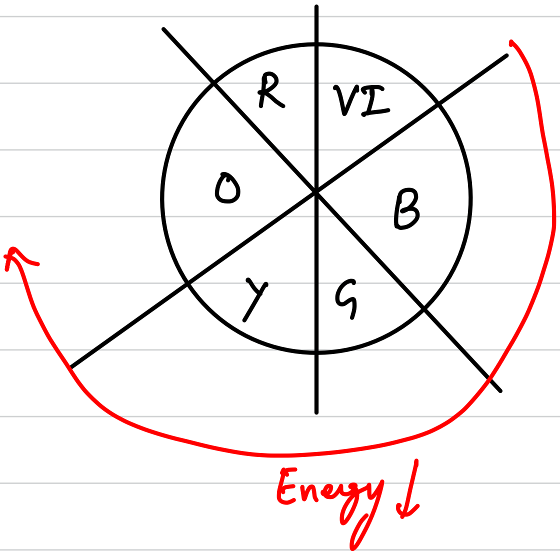
$\Downarrow$



Here O.S. of Cr is +6, that is its max charge hence Z_{eff} ↑↑. This causes to attract shared pair of e^- towards Cr and now, the O.S. changes to +5 which is unstable and oxygen and fluorine are also highly EN so e^- returns to them. This transition of e^- releases energy whose wavelength is in the visible range. That is why, they all are coloured.

$$d^3s \Rightarrow d_{xy}, d_{yz}, d_{xz}, s$$

5) <u>By complimentary colour wheel</u>



V I B G Y O R

$\lambda_{min}\downarrow$ $\lambda_{max}\uparrow$

$\nu_{max}\uparrow$ $\nu_{min}\downarrow$

$E_{max}\uparrow$ $E_{min}\downarrow$

$$\text{Absorbed energy } (E) \Rightarrow E = \frac{hc}{\lambda} = h\nu$$

Energy: $[M(CN)_6]^{4-} > [M(NO_2)_6]^{4-} > [M(H_2O)_6]^{2+}$

$\lambda_{absorbed}$: $[M(CN)_6]^{4-} < [M(NO_2)_6]^{4-} < [M(H_2O)_6]^{2+}$

Q Three complexes give red, blue and green colour in aq. solution $[M(en)_3]^{+n}$, $[M(H_2O)_6]^{+n}$, $[M(Br)_6]^{-6+n}$. Identify the colour of each complex with appropriate reason.

Q. Match the proper colour with the following compounds

1) $[M(NO_2)_6]$	P) Yellow
2) $[M(H_2O)_6]$	Q) Red
3) $[MF_6]$	R) Blue

$M^{+n} \Rightarrow$ same oxidation state

Here O.S. of Cr is +6, that is its max charge hence Z_{eff} ↑↑. This Causes to attract shared pair of e^- towards Cr and now, the O.S. changes to +5 which is unstable and oxygen and fluorine are also highly EN so e^- returns to them. This transition of e^- releases energy whose wavelength is in the visible range. That is why, they all are coloured.

$$d^3s \Rightarrow d_{xy}, d_{yz}, d_{xz}, s$$

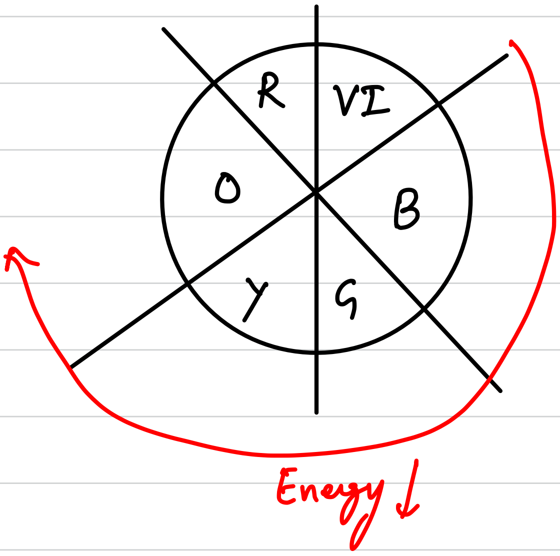
5) **By complimentary colour wheel**

V I B G Y O R

$\lambda_{min}\downarrow$ $\lambda_{max}\uparrow$

$\nu_{max}\uparrow$ $\nu_{min}\downarrow$

$E_{max}\uparrow$ $E_{min}\downarrow$



Absorbed energy (E) $\Rightarrow E = \frac{hc}{\lambda} = h\nu$

Energy: $[M(CN)_6]^{4-} > [M(NO_2)_6]^{4-} > [M(H_2O)_6]^{2+}$

$\lambda_{absorbed}$: $[M(CN)_6]^{4-} < [M(NO_2)_6]^{4-} < [M(H_2O)_6]^{2+}$

Q Three complexes give red, blue and green colour in aq. solution $[M(en)_3]^{+n}$, $[M(H_2O)_6]^{+n}$, $[M(Br)_6]^{-6+n}$. Identify the colour of each complex with appropriate reason.

Q. Match the proper colour with the following compounds

1) $[M(NO_2)_6]$ P) Yellow

2) $[M(H_2O)_6]$ Q) Red

3) $[MF_6]$ R) Blue

M^{+n} ⇒ same oxidation state

		Released		Absorbed
Ans. 1.	$[M(en)_3]^{n+}$	⇒ Red	$\longrightarrow$	Green
	$[M(H_2O)_6]^{n+}$	→ blue	$\longrightarrow$	Orange
	$[M(Br)_6]^{-6+n}$	⇒ green	$\longrightarrow$	Red

Ans.2.

1) $[M(NO_2)_6]$	P) Yellow
2) $[M(H_2O)_6]$	Q) Red
3) $[MF_6]$	R) Blue

Released Absorbed E_{abs}

$$\text{Yellow} \longrightarrow \underset{\lambda\downarrow\downarrow}{\text{Violet}} \longrightarrow \uparrow\uparrow \quad [M(\overset{\text{SFL}}{NO_2})_6]$$

$$\text{Red} \longrightarrow \underset{\lambda\downarrow}{\text{green}} \longrightarrow \uparrow \quad [M(H_2O)_6]$$

$$\text{Blue} \longrightarrow \underset{\lambda\uparrow}{\text{Orange}} \longrightarrow \downarrow \quad [MF_6]$$