Q. Predict the hybridisation of :-

1) Brown Ring Complex $[Fe(H_2O)_5NO]SO_4$ (Fe: +1, NO: +1, SO_4: 2−; whole: 2+)

$Fe^{+1} \Rightarrow [Ar]\,3d^6\,4s^{\cancel{2}\,1}$ $\xrightarrow{\text{excitation}}$ $3d^7\,4s^0$

$5H_2O$ = WFL, $1\,NO^+$ = SFL

(Splitting acc to WFL)

sp^3d^2, outer octa, para

upe = 3, $\sqrt{15}$ BM

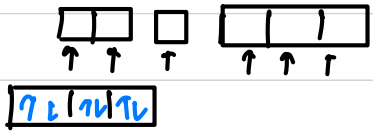
high spin

2) Sodium nitroprusside

$Na_2[Fe(CN)_5NO] \Rightarrow 2Na^+ + [Fe(CN)_5NO]^{2-}$

(Fe: +2, CN^-: −1, NO^+: +1)

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



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

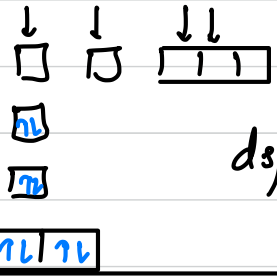
$5CN^-, 1NO^+$ — SFL

3) $[Ni(dmg)_2]$ (Ni: +2, dmg: −1) Rosy Red ppt

CN = 4

dmg^- ⇒ both N atoms donor ⇒ chelation (4 Rings) hence 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^- ⇒ due to chelation, will act as SFL

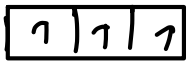
⇓

unsymmetrical bidentate

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

CN = 6 Octahedral

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

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

$\boxed{\text{Ope} = 3}$

(no low/high spin defined)

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

CN = 6 Octahedral

$Co^{3+} \Rightarrow [Ar]\,3d^6\,4s^0$

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

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

(+2) (-1) (-2) ✗ — then

SFL — Superoxido

CN = 6 octahedral

Fe O_2 ✓✓

(+2) (-1) — then

$Fe^{2+} \Rightarrow [Ar]\ 3d^6\ 4s^0$

O upe, dia, d^2sp^3, inner octa, low spin

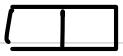
✗ ✗

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

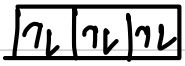
Correct ⇒ 1 upe, para, d^2sp^3, inner octa, low spin

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

$Ni^{+4} \Rightarrow [Ar]\ 3d^8\ 4s^0$ → $3d^6$ [high +ve charge hence large splitting]



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



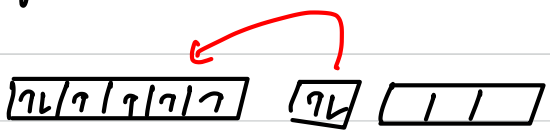
10) $[AuCl_4]^{\ominus} \Rightarrow Au^{3+} \quad 4Cl^-$ CN = 4 square planar

$Au^{3+} \Rightarrow [Xe]\ 4f^{14}\ 5d^{10}\ 6s^0$ → $5d^8$

dsp^2, square planar, dia, 0 BM

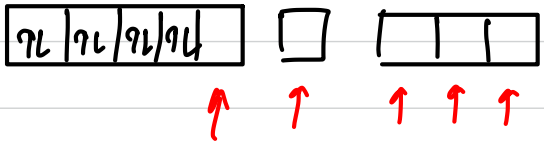
11) $[Fe(CO)_5]$ Fe^0 5CO (SFL) CN = 5

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



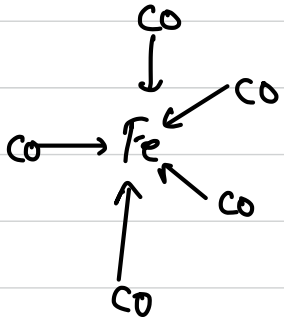
due to SFL, pairing of e^- and excitation of 4s e^-

3d 4s 4p



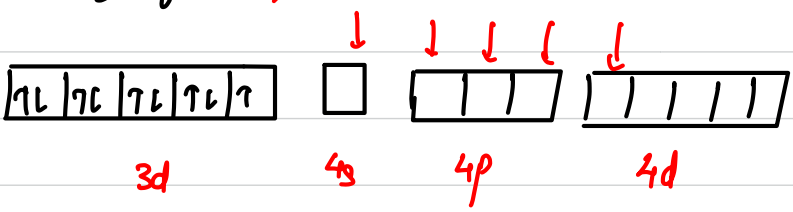
dsp^3, dia, $\mu = 0$ Trigonal bipyramidal

d_{z^2}



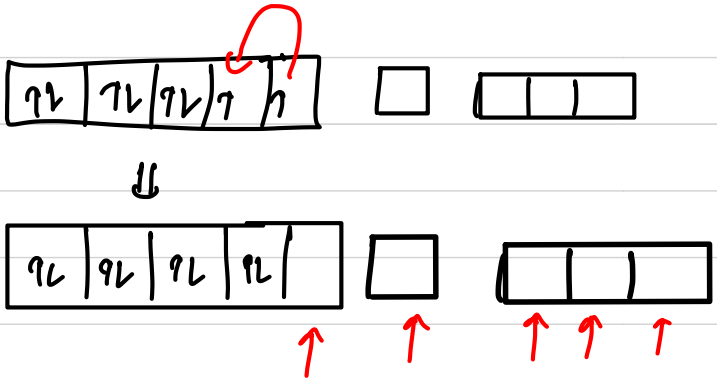
12) $[CuCl_5]^{3-}$ Cu^{2+}, 5Cl^- (WFL)

$Cu^{2+} \Rightarrow [Ar]\, 3d^9 4s^0$

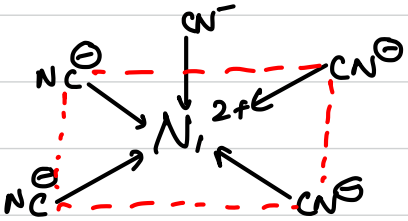


sp^3d, trigonal bipyramidal, para, $\sqrt{3}$ BM

13) $[Ni(CN)_5]^{3-}$ $\quad Ni^{2+} \Rightarrow [Ar]3d^8$ $\quad 5\,\underset{SFL}{CN^-}$



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



Colour Nature of Compound

1) Polarisation

$\longrightarrow$ Polarisation ↑

AgF	AgCl	AgBr	AgI
white		pale yellow	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)

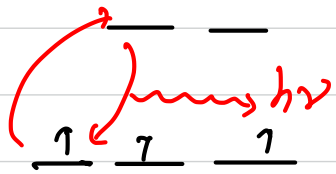
3) d-d transition

(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 $e^- = 0$ compounds are diamagnetic and colourless (yes) (it is not always true)



ex

$K_4[Fe(CN)_6]$

$Fe^{2+} \Rightarrow [Ar]3d^6$ $6CN^- \Rightarrow SFL$

0 upe, dia

colourless

$K_4[FeF_6]$

$Fe^{2+} \Rightarrow [Ar]3d^6$ $6F^{\ominus} \Rightarrow WFL$

4 upe, para

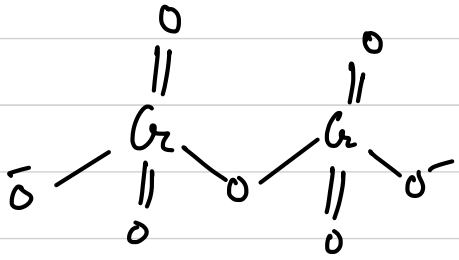
coloured

4) Charge Transfer Spectrum (CTS)

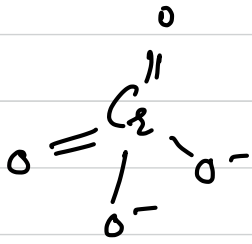
CTS	O.S.	upe⁻
1) $Cr_2O_7^{2-}$	+6	0
2) CrO_4^{2-}	+6	0
3) MnO_4^-	+7	0
4) VO_4^{3-}	+5	0
5) CrO_2Cl_2	+6	0
6) CrO_2F_2	+6	0

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

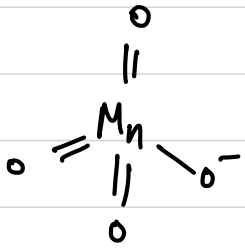
1) $Cr_2O_7^{2-}$



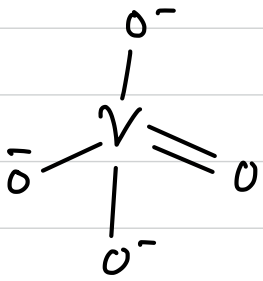
2) CrO_4^{2-}



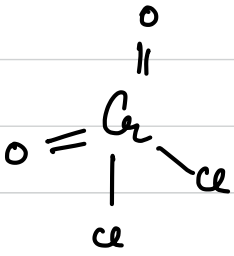
3) MnO_4^-



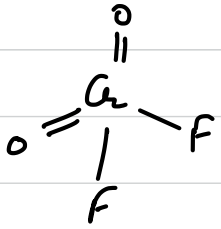
4) VO_4^{3-}



5) CrO_2Cl_2

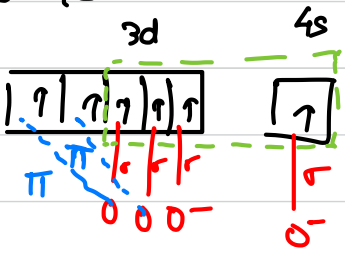


6) CrO_2F_2

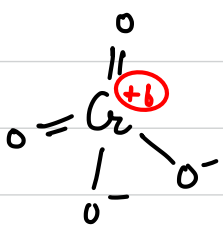


CrO_4^{2-}

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



$\Rightarrow d^3s$, tetrahedral



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.

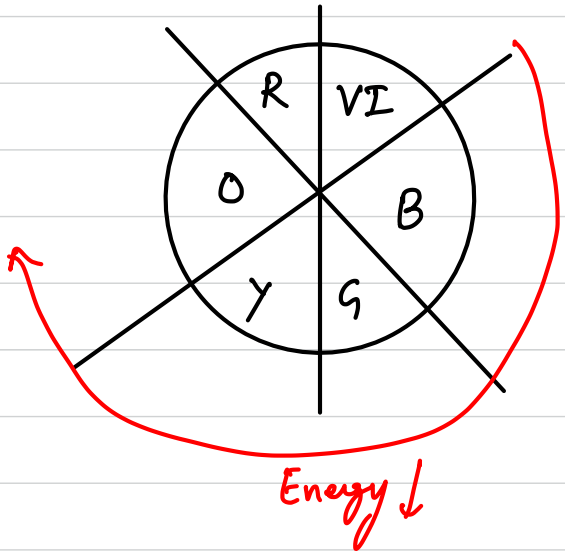
$$d^2s \Rightarrow d_{xy}, d_{yz}, d_{xz}, s$$

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

V I B G Y O R

λ_{min} ↓ ν_{max} ↑ E_{max} ↑

λ_{max} ↑ ν_{min} ↓ E_{min} ↓



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