

EAN:

$A \cdot NO + 2(C \cdot NO) - a \cdot \text{No. of metal}$

except

"NO"

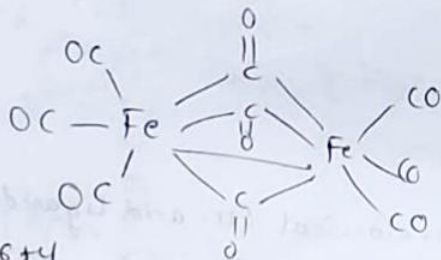
* $+1_x [Mn(CO)_5]$ find x value?

A) $Mn(CO)_5$ for EAN stable; for charge = -1

$\therefore H \rightarrow +1$

$\rightarrow \boxed{x=1}$

* $Fe_2(CO)_9$



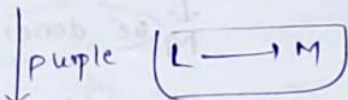
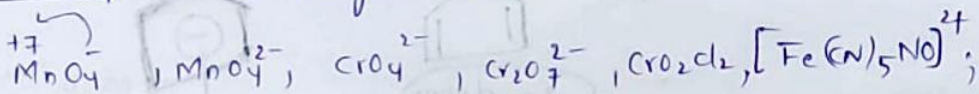
$EAN = 26 + 6 + 4 = 36$

* $Co_2(CO)_x$

$x=8$

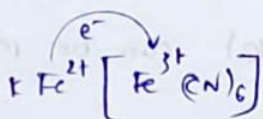
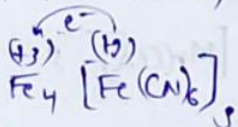
$Mn_2(CO)_{10}$

Colour depends on charge transfers:



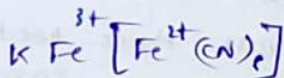
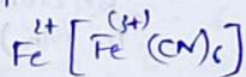
$Mn^{+6} \rightarrow e^-$ transfer from Ligand to metal; colour come

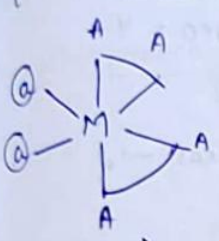
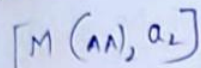
2019 prev. (main)



prussian blue colour

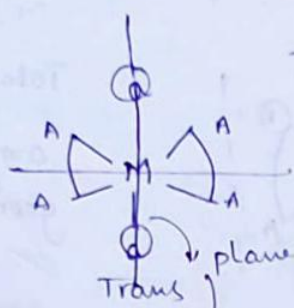
Turnable blue





no plane of symmetry

so, optically active

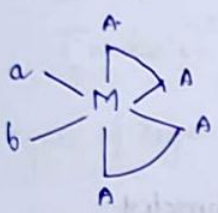
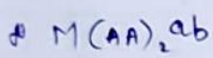


plane of symmetry

pos. d.o.s.

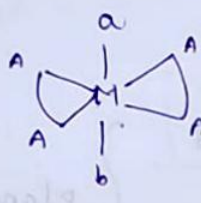
Totally stereo - 3

Geometrical - 2
optical - 1

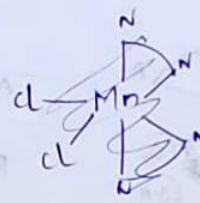


no plane of symmetry

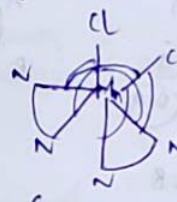
(0-0)



Trans

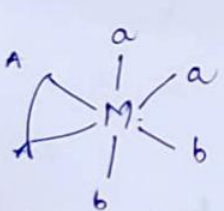
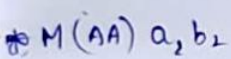


No of cis in d types?

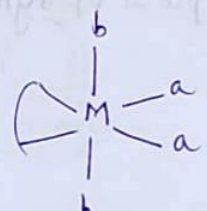
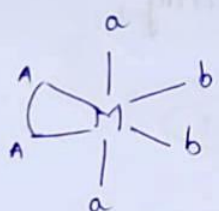


Totally dMnN cis angles?

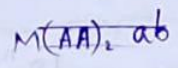
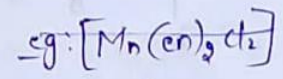
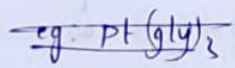
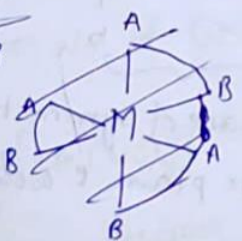
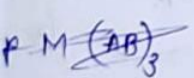
=> 6.

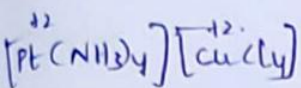


optically active

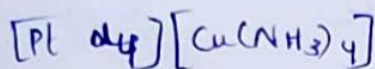
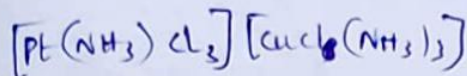
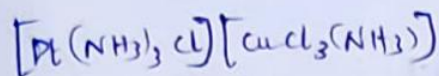
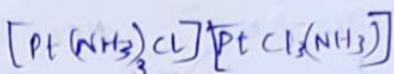
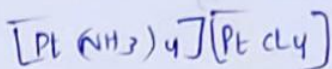


Total stereo - 4
Geometrical - 3
optical - 1





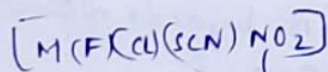
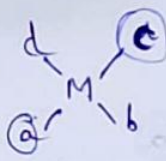
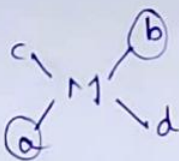
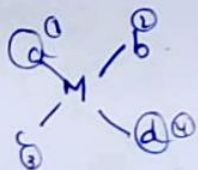
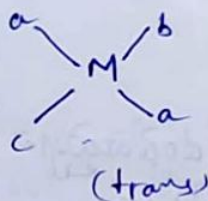
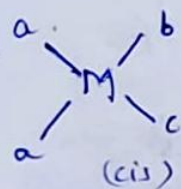
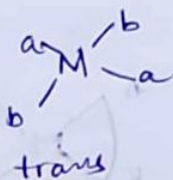
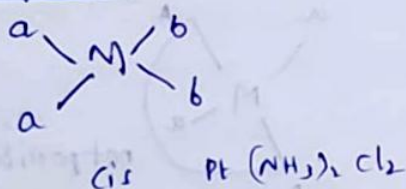
-if same metal



Stereo isomerism:

Geometrical: (cis trans isomerism):

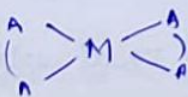
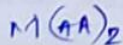
square planar:



3 → initial ↘ ambidentate

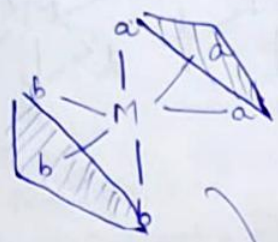
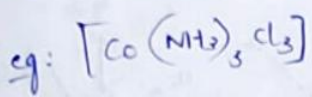
i.e. $2 \times 2 \times 3 = 12$ possible

for bidentate

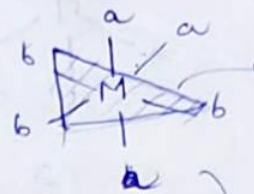


both cis and trans are present in some structure so; No Geometrical isomerism

Ma₃b₃:



facial face isomer



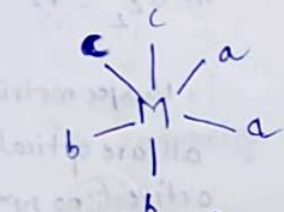
meridional isomer

plane of symmetry there

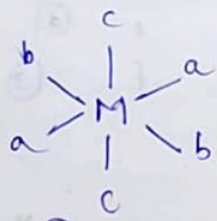
square plane pass every plane

a, axial; b equatorial plane

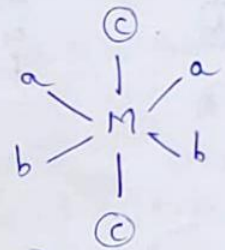
Ma₂b₂c₂:



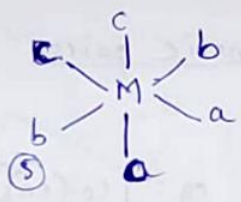
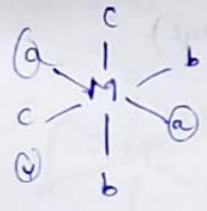
① cis no POS



② Trans

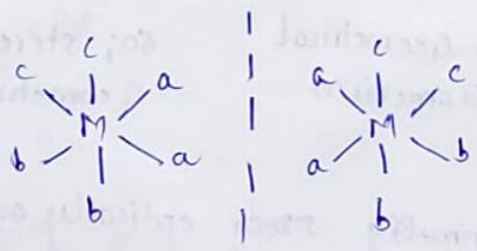


③ cis

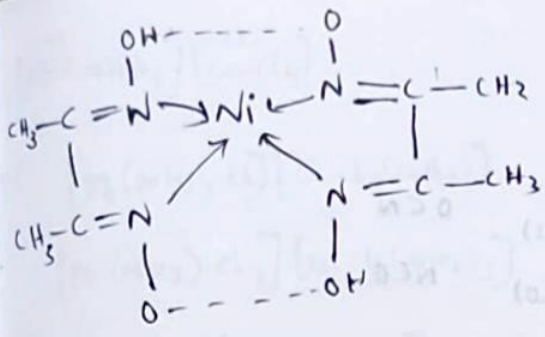


2, 3, 4, 5 → POS

① → optically active

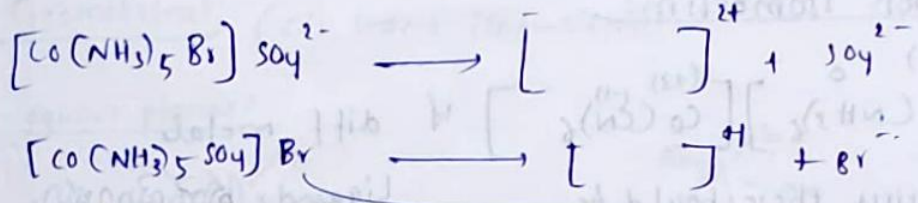


∴ optically active isomers are 2.

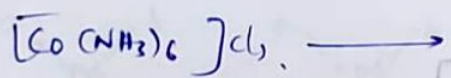


Structural isomerism:

1) Ionisation isomerism:



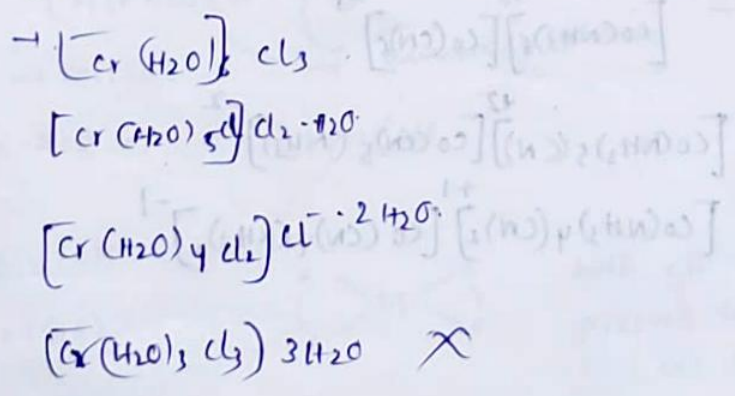
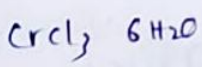
Co-ordination sphere ~~isomerism~~ ionic sphere



only ions should be exchanged but not neutral molecules during exchange co-ordination number

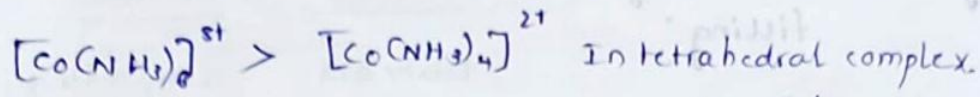
2) Solvate isomerism:

H₂O, NH₃, ROH.



splitting is more for octahedral complex.

because more ligands more splitting $\Rightarrow \Delta_o > \Delta_t$



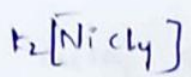
$\Delta_o > \Delta_t$

follow Hund's rule (Δ_t low)
(Ligands at 109.5°)

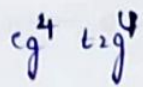
$\Delta_t = \frac{2}{3} \times \frac{2}{3} \Delta_o$ ratio of ligands

$\Delta_t = \frac{4}{9} \Delta_o$

ratio due to on axis, in two axis. splitting energies



$N_i + 2$

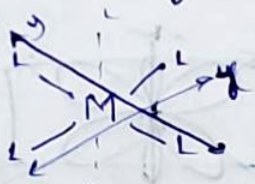


$4(-\frac{3}{5} \Delta_t) + 4(\frac{2}{5} \Delta_t)$

$\rightarrow -\frac{4}{5} \Delta_t \Rightarrow \bullet$

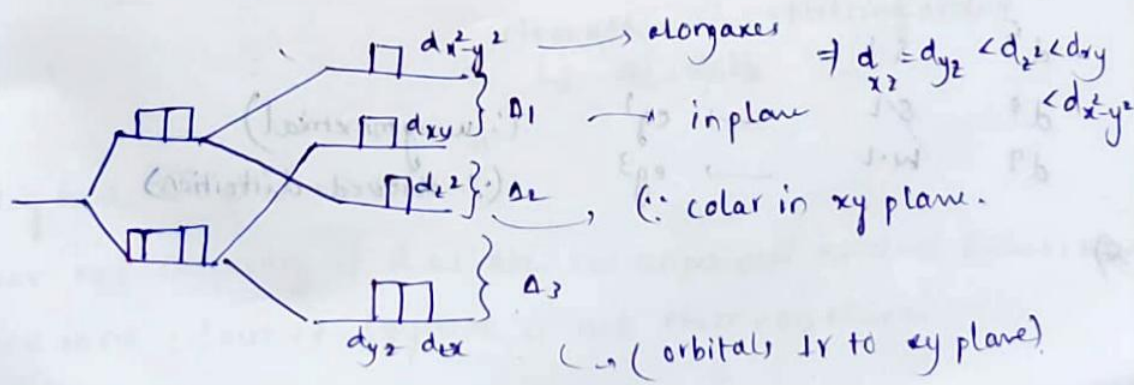
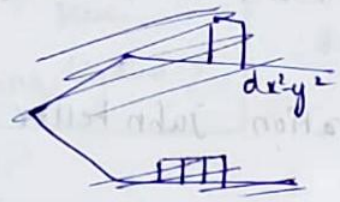


Crystal field theory in square planar complex.



Ligands present along axis
similar to octahedral

$\therefore d_{x^2-y^2}$ is along \rightarrow axis

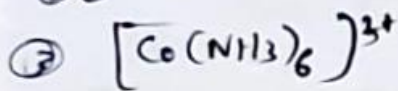
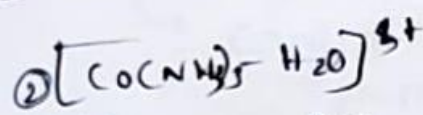
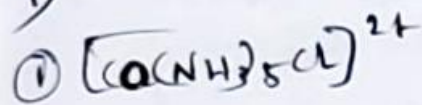


Colours:

<u>observed</u>	<u>absorbed</u>
yellow green	Red violet
Orange	blue
red	blue green
Yellow	Indigo
purple	Green

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow$ emit blue ; absorb \rightarrow orange

1)

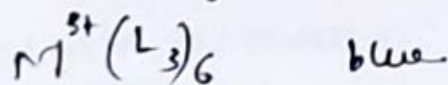
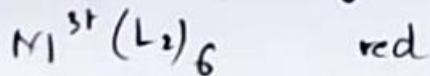
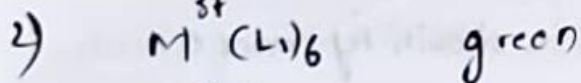


} order of observed wavelength

\rightarrow ③ \rightarrow ② \rightarrow ①

absorbed wavelength

① $>$ ② $>$ ③



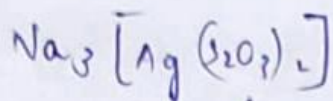
which is strong ligand ?

VIBGYOR

λ order: Red $>$ Green $>$ Blue

observed \rightarrow $\text{L}_2 > \text{L}_1 > \text{L}_3$

$\text{L}_3 > \text{L}_1 > \text{L}_2$

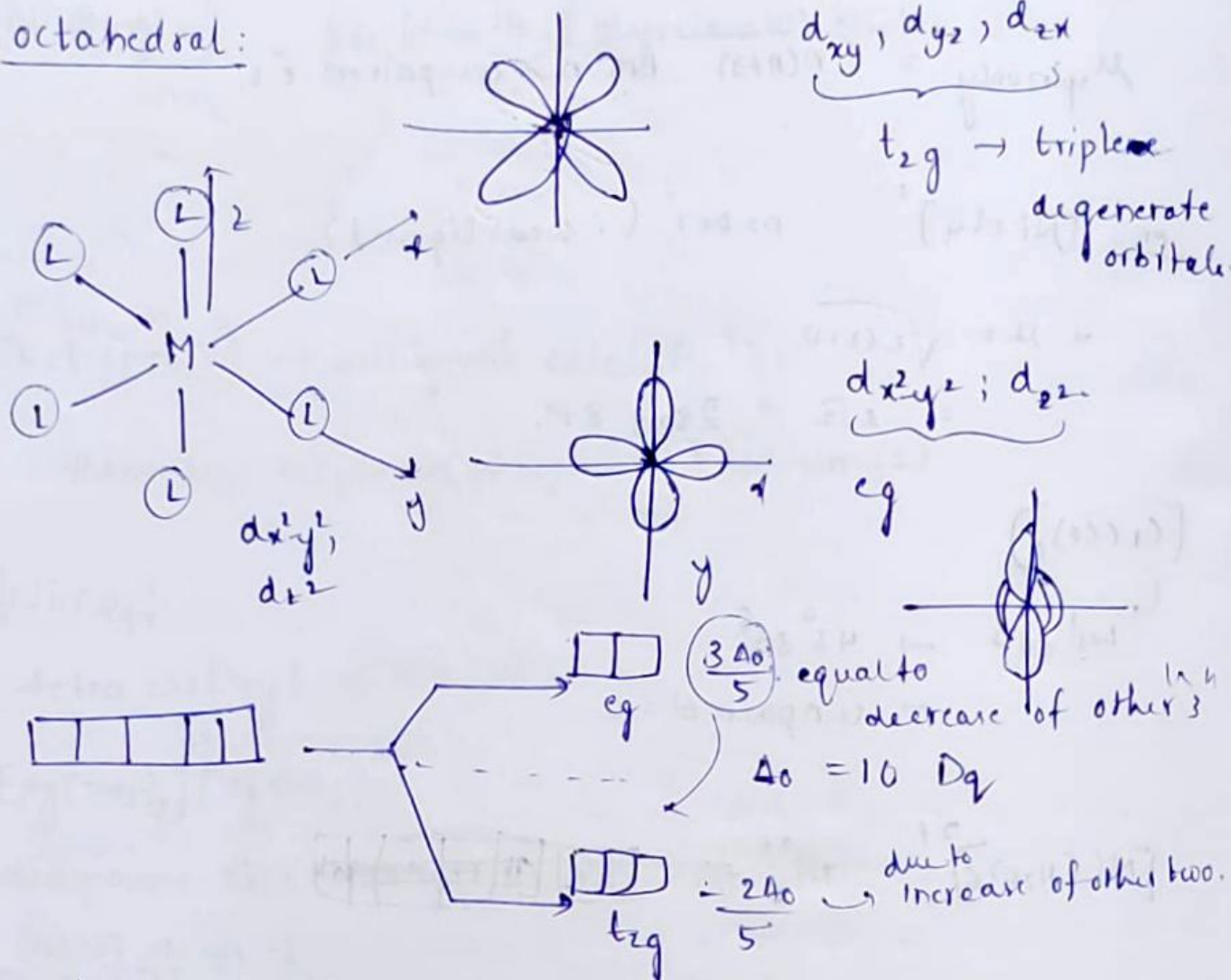


Thiosulphato

sodium dithiosulphato Argentate (I)

Crystal field theory:

1) octahedral:



each e_g orbital energy is increased by $\frac{3}{5} \Delta_0$

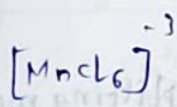
$\Delta_0 \rightarrow$ crystal field splitting energy.

$$\Delta_0 = \frac{hc}{\lambda}$$

$Dq \rightarrow$ energy unit.

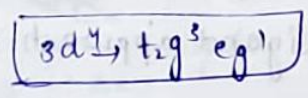
Spectrochemical series: (strength of ligands):

	S.L ($\Delta_0 > P$)	W.L ($\Delta_0 < P$)
d^1	t_{2g}^1	t_{2g}^1
d^2	t_{2g}^2 ↑↓	t_{2g}^2
d^3	t_{2g}^3	t_{2g}^3
d^4	t_{2g}^4	$t_{2g}^3 e_g^1$
d^5	t_{2g}^5	$t_{2g}^3 e_g^2$
d^6	t_{2g}^6	$t_{2g}^4 e_g^2$
d^7	$t_{2g}^6 e_g^1$	$t_{2g}^5 e_g^2$
d^8	$t_{2g}^6 e_g^2$	$t_{2g}^6 e_g^2$
d^9	$t_{2g}^6 e_g^3$	$t_{2g}^6 e_g^3$
d^{10}	$t_{2g}^6 e_g^4$	$t_{2g}^6 e_g^4$



$Mn \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

$Mn^{3+} \rightarrow 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0 3d^4$



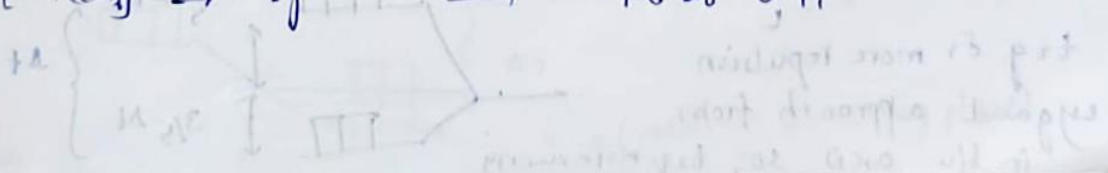
CFSE (crystal field stabilisation energy):

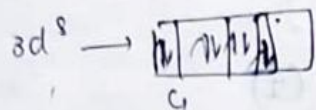
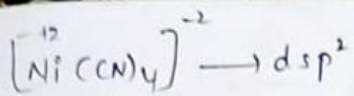
$(n_{t_{2g}}) [-0.4 \Delta_0] + n_{e_g} \times (0.6 \Delta_0) + \frac{1}{2} n_p P$
 $n_{t_{2g}}$ → no. of e pairs, P → pairing energy

→ It is formula to calculate s.e in octahedral complex.

$[MnCl_6]^{3-} \rightarrow t_{2g}^3 e_g^1 \rightarrow -0.6 \Delta_0$

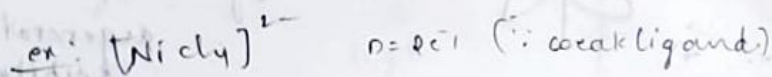
$[Mn(CN)_6]^{3-} \rightarrow t_{2g}^4 \rightarrow -1.6 \Delta_0 + 0.4 P$



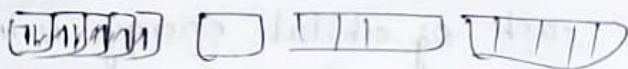
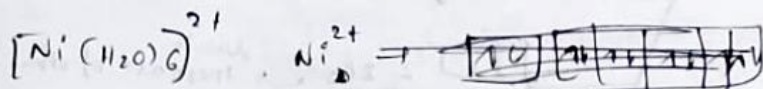
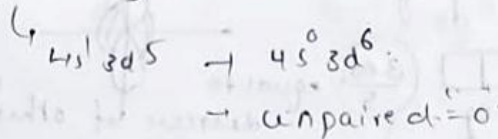
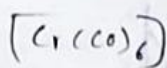


Magnetic character:

$$\mu_{\text{spin only}} = \sqrt{n(n+2)} \text{ B.M. } n \rightarrow \text{unpaired } e^-s$$



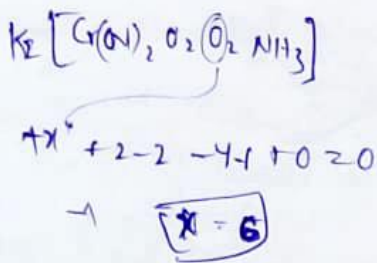
$$\begin{aligned} \mu &= \sqrt{2(2+2)} \\ &= 2\sqrt{2} \approx 2.828 \text{ B.M.} \end{aligned}$$



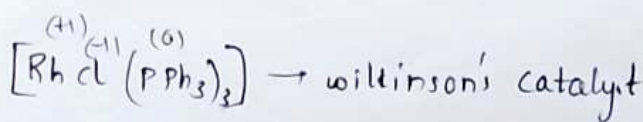
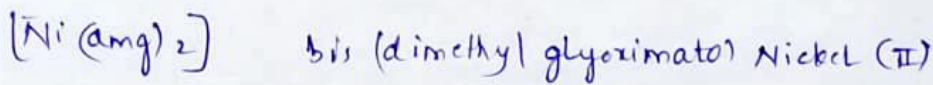
$sp^3d^2 \rightarrow$ outer-orbital complex high spin.

$d^2sp^3 \rightarrow$ inner-orbital complex; low spin.

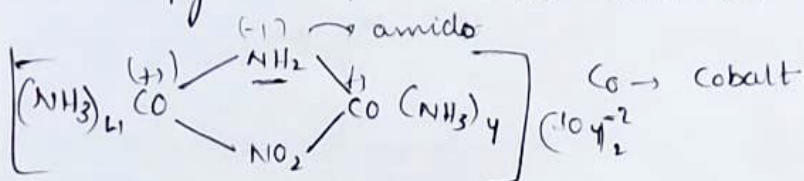
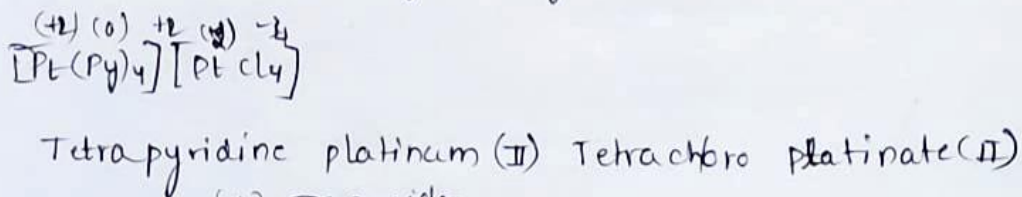
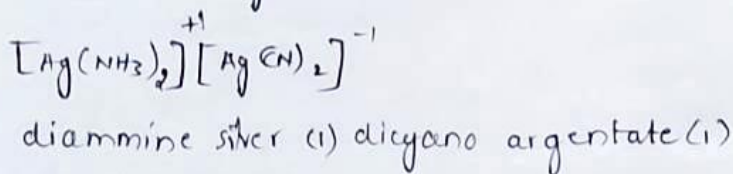
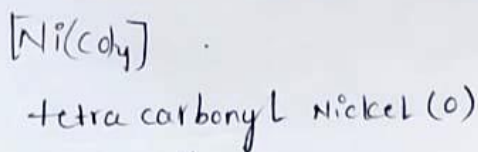
in brownring $Fe + O.S \rightarrow [Fe(H_2O)_6]^{2+}$



potassium ammine dicyano oxo
peroxo chromate(V)



dichloro tris triphenyl phosphine Rhodium(I)



octaamine - μ-amido-μ Nitro dicobalt(III) sulphate

VBT:

