Metal Ligand Bonding in Transition Metal complexes

Valence Bond Theory (VBT):

Developed by Linus Pauling
According to VBT, the bonding in metal complexes arise when a filled ligand orbital containing a lone pair of electrons overlaps with a vacant hybrid orbital on the metal (ion) to give a coordinate covalent bond.

vacant metal hybrid atomic orbital

occupied ligand atomic orbital

coordinate covalent bond

- VBT assumes the bonding between the metal (ion) and the ligands to be purely covalent.
- The hybrid orbitals that a metal (ion) uses in accepting the pair of electrons from the ligands are those that point in the directions of the ligands.

Salient features of VBT:

1. The central metal (ion) in the coordination compounds offers a number of vacant orbitals which is equal to the coordination number of the metal (ion) for the formation of coordinate bonds with the ligands.

2. The approximate atomic orbitals (s, p and d) of the metal hybridise to give a new set of orbitals of equivalent energy called the hybrid orbitals.

- These hybrid orbitals are directed towards the ligands depending upon the geometry of the coordination complex.

3. The d-orbitals involved in the hybridization may be either inner $(n-1)d$ orbitals or outer nd orbitals. Thus, hybridisation in case of octahedral complex may involve d^2sp^3 or sp^3d^2 depending upon whether inner or outer d-orbitals are used for hybridization.

d^2sp^3 : Inner orbital complex : Low spin complex
sp^3d^2 : Outer orbital complex   High spin complex
stability Order : $d^2sp^3 > sp^3d^2$

d-orbital involved for hybridization in octahedral complex = $d_{x^2-y^2}$ and d_{z^2}
for tetrahedral Complex : sp^3 or sd^3 hybridization.
d-orbitals involved in sd^3 are d_{xy}, d_{yz} and d_{zx}.
for Square Planar Complexes : dsp^2 hybridization

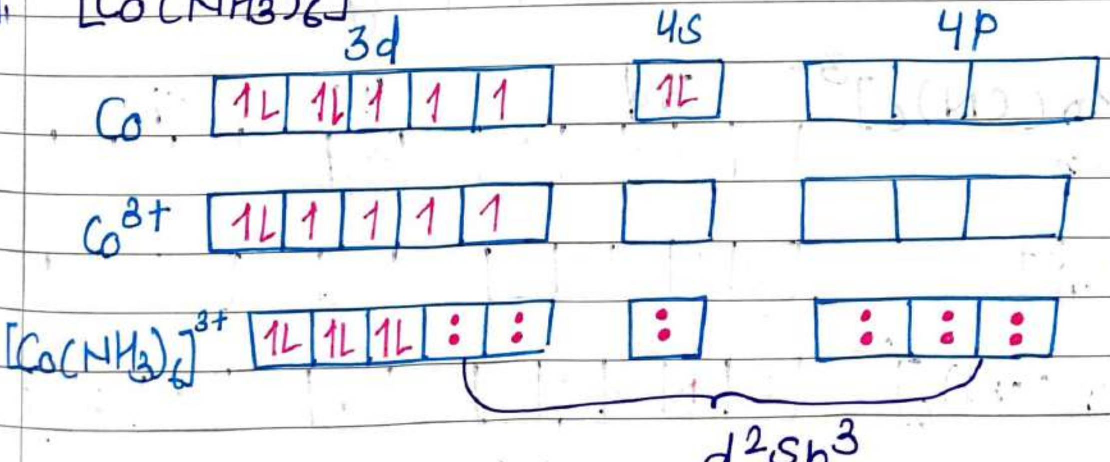
$p \to p_x$
$p \to p_y$

$d \to d_{x^2-y^2}$

4. The vacant hybrid orbitals of the metal (ion) overlap with the filled (or occupied) orbitals of the ligands and forms a coordinate bond.

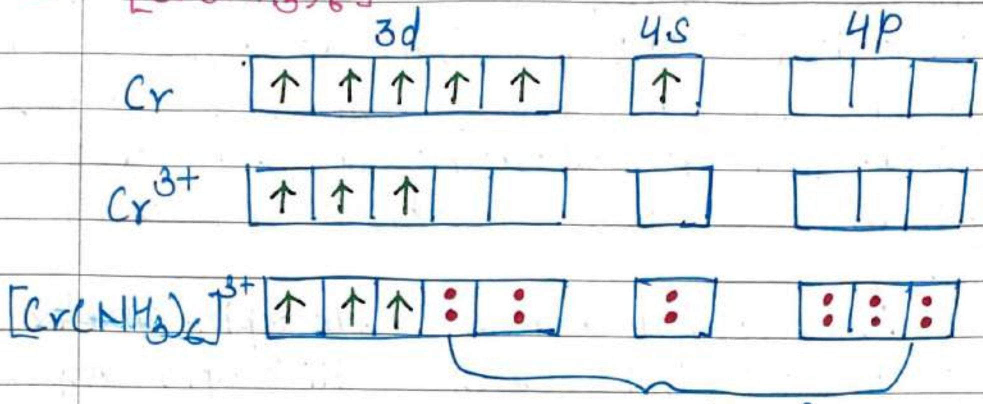
Examples of Complexes with C.N. 6 :

1. $[Co(NH_3)_6]^{3+}$



d^2sp^3
Octahedral
Inner orbital Complex
Diamagnetic

2. $[Cr(NH_3)_6]^{3+}$



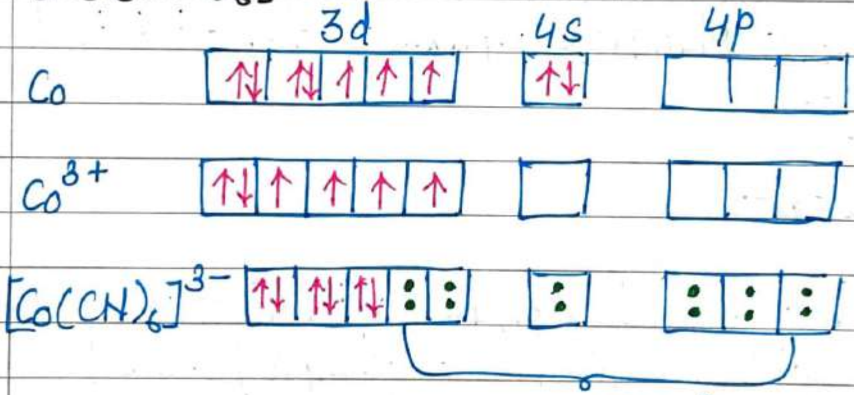
d^2sp^3

Octahedral

Inner orbital complex

Paramagnetic

3. $[Co(CN)_6]^{3-}$:



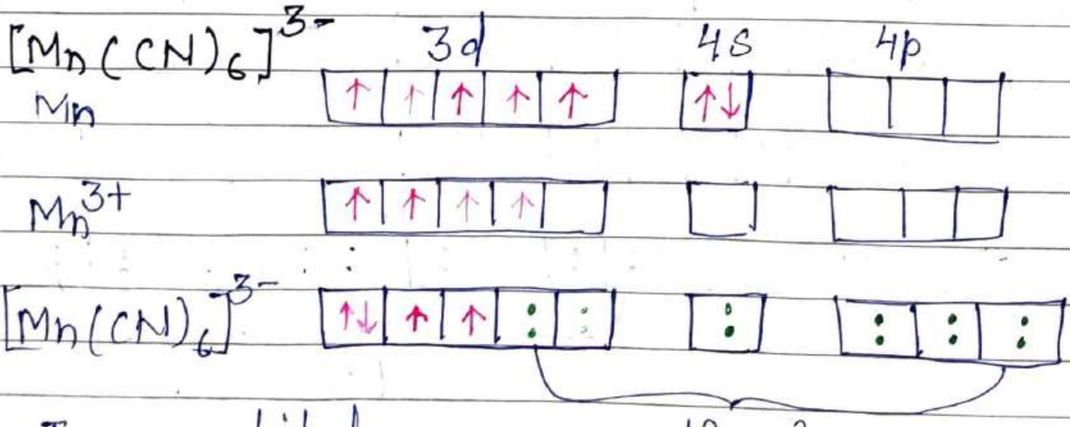
d^2sp^3

Octahedral

Inner orbital complex

Diamagnetic

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

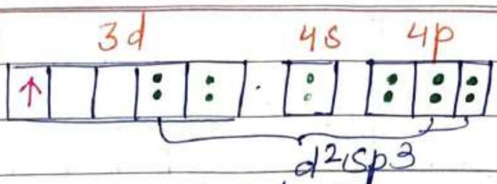
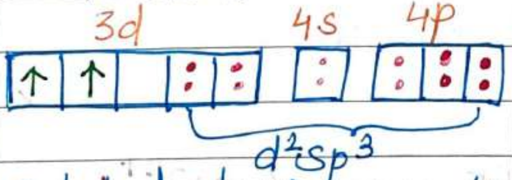
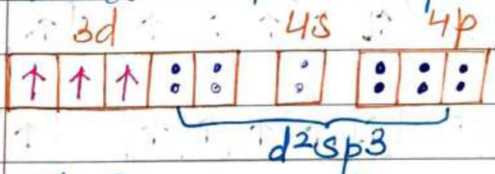
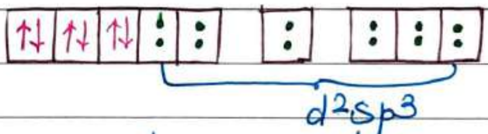
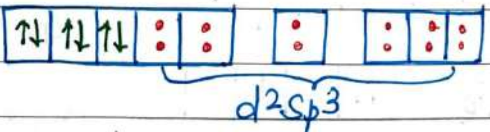
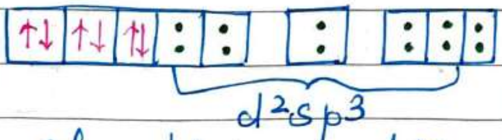


Inner orbital

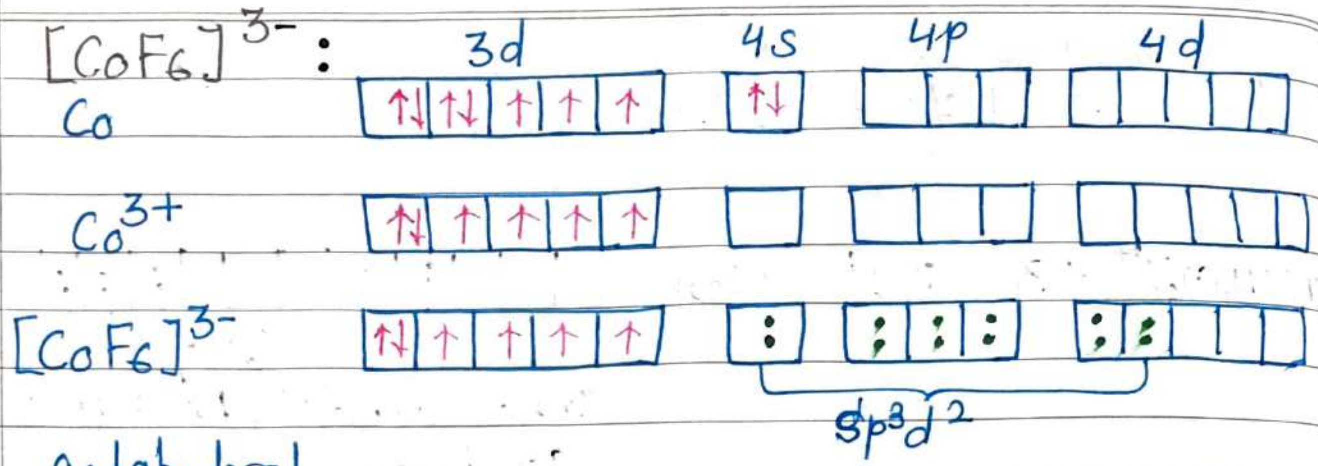
Paramagnetic

d^2sp^3

octahedral

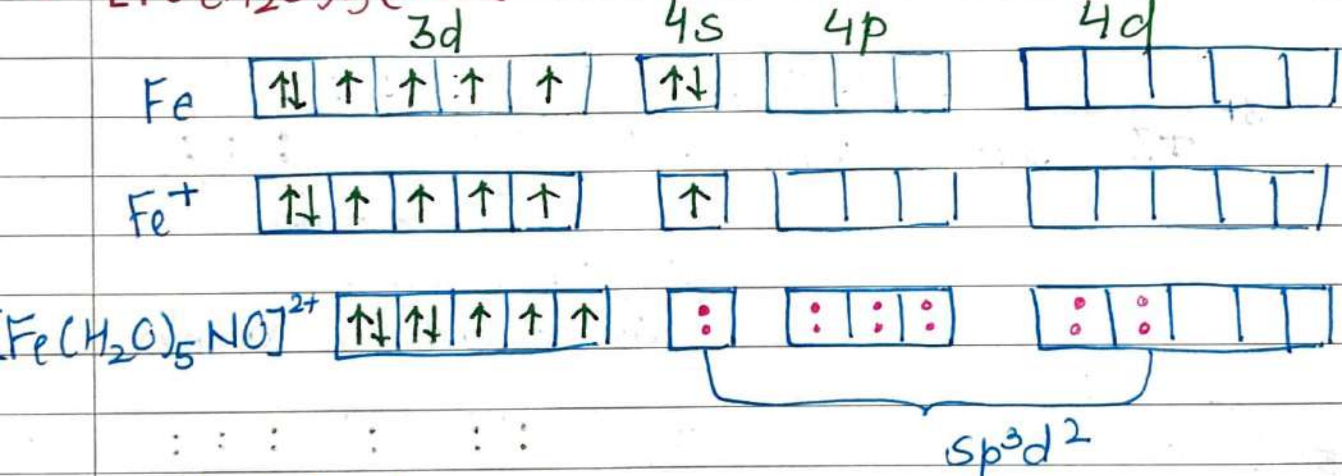
Complex Ion	O.S. of Metal	V.S.E.C of Metal (ion)	Nature of Ligands	Valence Bond Electron Description	No. of unpaired electrons
$[Ti(H_2O)_6]^{3+}$	+3	$3d^1$	Weak	 Inner orbital, Paramagnetic Octahedral	1
$[V(H_2O)_6]^{3+}$	+3	$3d^2$	Weak	 Octahedral, Paramagnetic Inner Orbital Complex	2
$[Cr(H_2O)_6]^{3+}$	+3	$3d^3$	Weak	 Oh, Paramagnetic Inner orbital complex	3
$[Fe(CN)_5NO]^{2-}$	+2	$3d^6$	Strong	 Oh, diamagnetic Inner Orbital Complex	0
$[Fe(CN)_6]^{4-}$	+2	$3d^6$	Strong	 Oh, diamagnetic Inner Orbital Complex	0
$[PtCl_6]^{2-}$	+4	$5d^6$	Weak	 Oh, diamagnetic Inner orbital Complex	

5. $[CoF_6]^{3-}$:



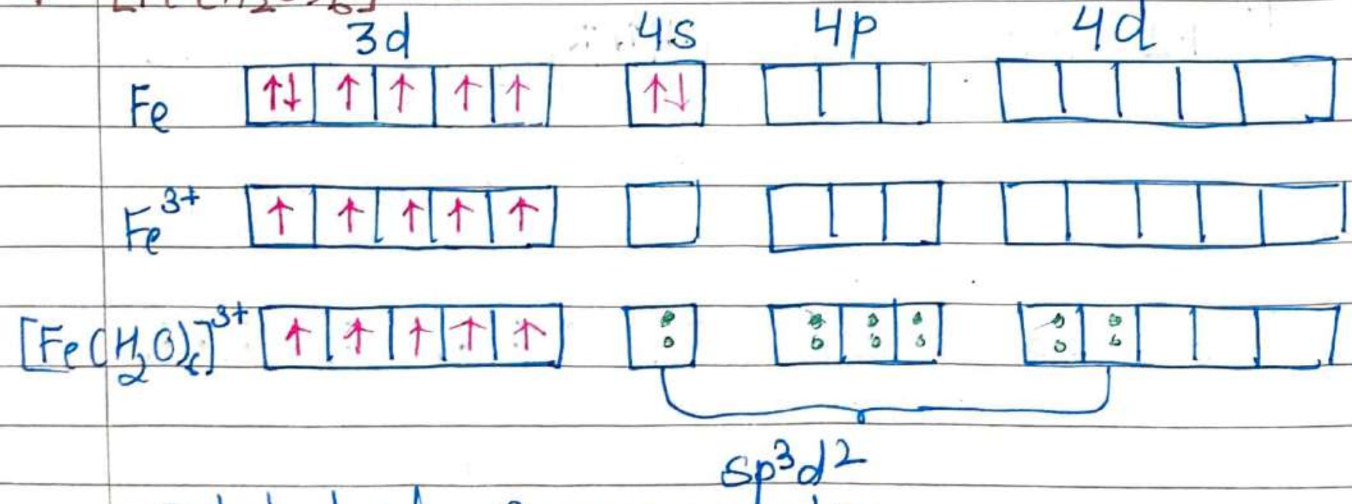
- Octahedral
- Paramagnetic
- Outer orbital complex

6. $[Fe(H_2O)_5(NO)]^{2+}$:



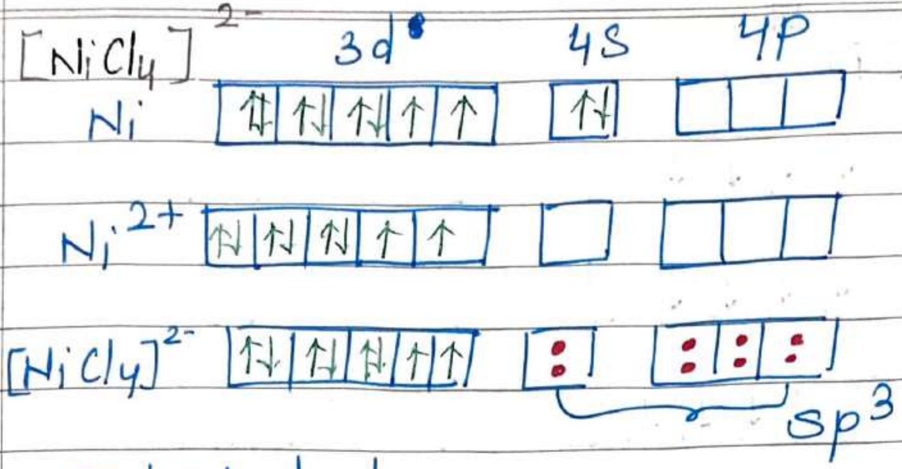
Octahedral
Paramagnetic
Outer orbital complex

7. $[Fe(H_2O)_6]^{3+}$:



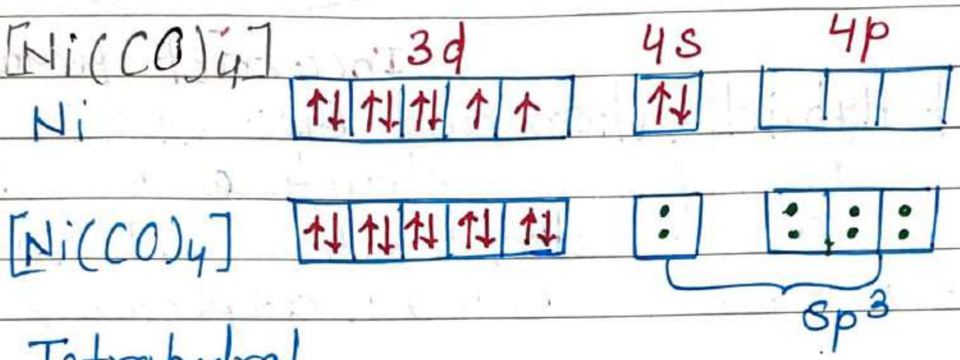
Octahedral, Paramagnetic
Outer orbital complex

8. $[NiCl_4]^{2-}$



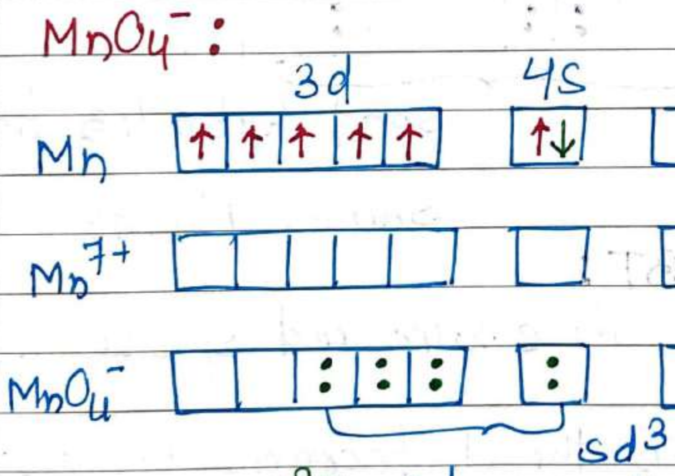
Tetrahedral
Paramagnetic

9 $[Ni(CO)_4]$



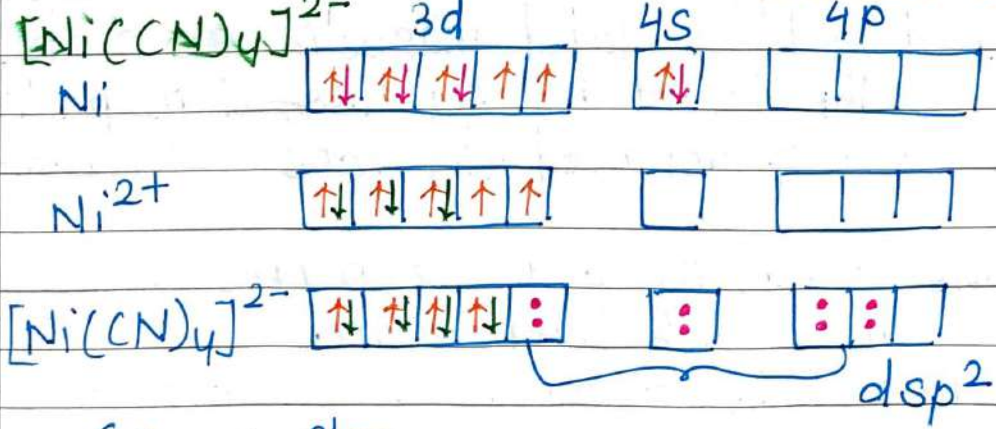
Tetrahedral
Diamagnetic

10. MnO_4^- :



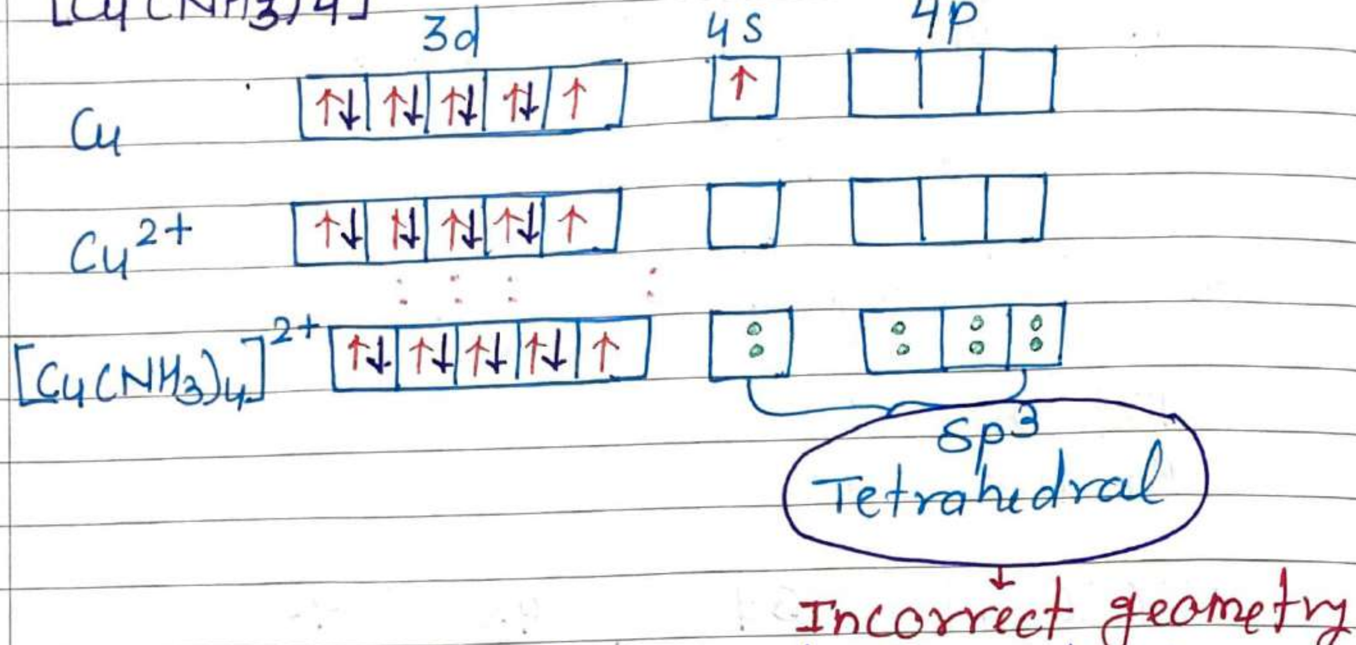
Tetrahedral

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



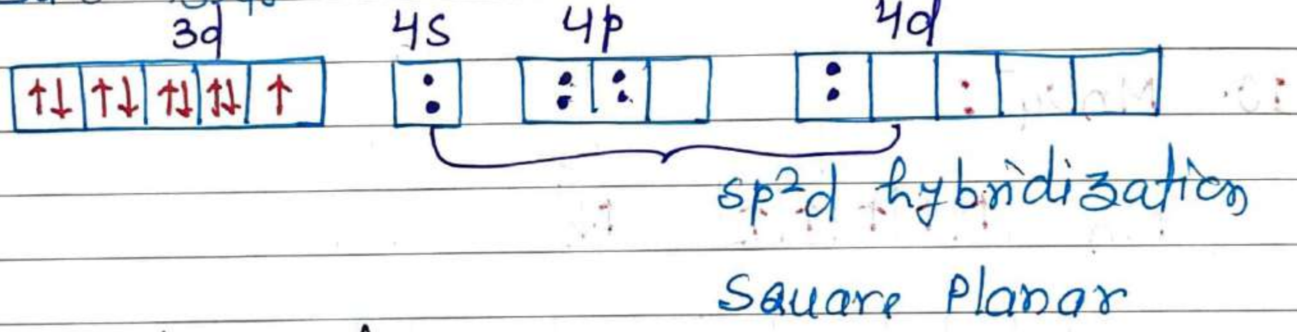
Square Planar
Diamagnetic

12 $[Cu(NH_3)_4]^{2+}$



Correct Hybridization and Geometry:
Based ESR and X-ray structure determination studies correct hybridization and geometry dsp^2 and square planar, respectively.

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



Limitations of VBT:

1. It fails to explain the colour and spectra of the complexes.
2. It fails to explain the differences between the measured and calculated magnetic moments, although the theory is successful in predicting the number of unpaired electrons in the complex.
3. It fails to explain why the magnetic moment values varies with temperature.
4. The theory fails to explain to the relative stabilities of the complexes.

5. It fails to explain why some complexes are labile while others are inert.

Labile Complexes: Those complexes in which one of the ligand can be easily displaced by another ligand.

Inert Complexes: Those complexes in which the displacement of ligands is slow.

6. It does not predict whether the 4-coordinate complex species will be square planar or tetrahedral.
e.g. $[Cu(NH_3)_4]^{2+}$

7. It considers $Ni(acac)_2$ to be tetrahedral whereas in fact it has octahedral geometry.

8. The theory fails to explain why some metal complexes in a particular oxidation state are low spin (i.e. inner orbital complex) while some other complexes of the same metal (ion) in the same oxidation state are high spin (i.e. outer orbital complexes).

e.g. $[CoF_6]^{3-}$ High spin complex
$[Co(NH_3)_6]^{3+}$ Low spin complex