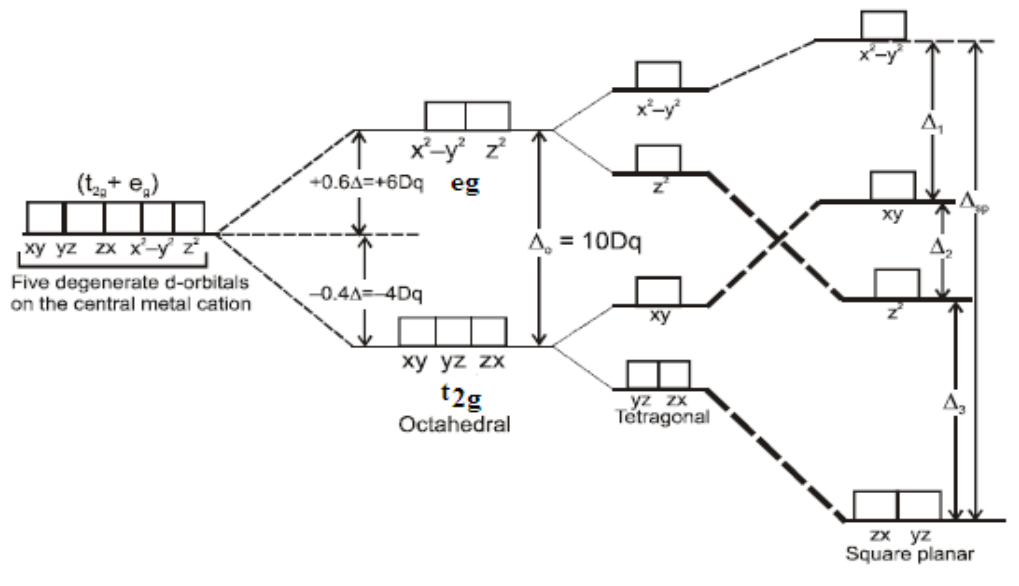
Metal-Ligand Bonding in Transition Metal Complexes

(Lecture-1)

B.Sc. 5th Semester (Pass Course)

INORGANIC CHEMISTRY

(As per MDU, Rohtak Syllabus)



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CONTENT

- Limitation of VBT
- Introduction of CFT
- Shapes of d-orbitals

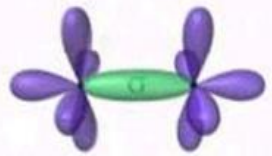
Valence Bond Theory

- Covalent bonds form between atoms as a result of the overlap of atomic orbitals (s and p orbitals).
- Explains the electron domain geometry

Two type of overlap

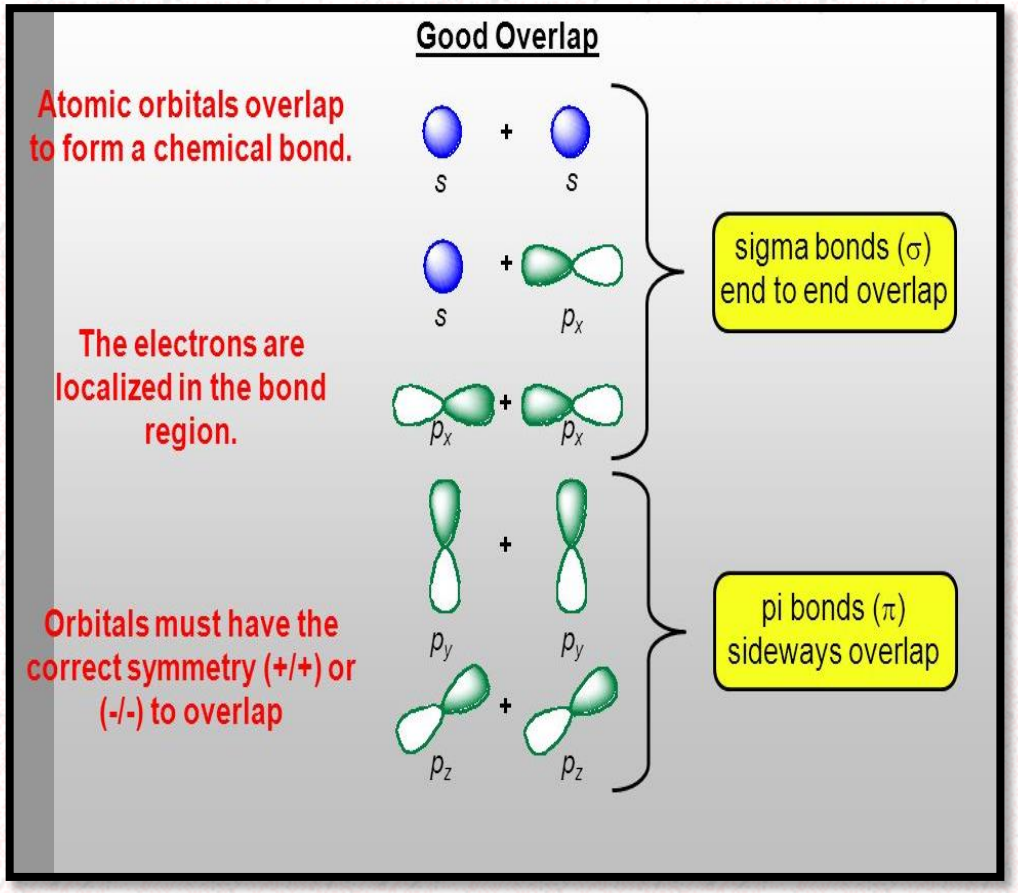
<u>sigma (σ) bond</u>

- Formed by the direct end on end overlap of atomic orbitals. This results in the electron density concentrated between the nuclei of the bonded atoms.



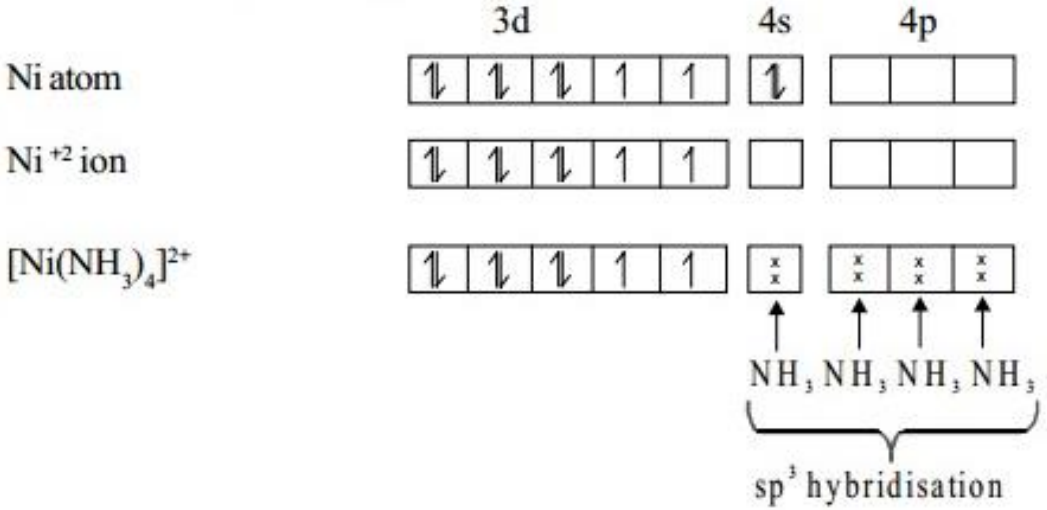
<u>pi (π) bond</u>

- Formed by the sideways overlap of atomic orbitals . This results in the electron density above and below the plane of nuclei of the bonding atoms



1) Nickel atom

Outer electronic configuration $3d^8\ 4s^2$



Number of unpaired electrons = 2

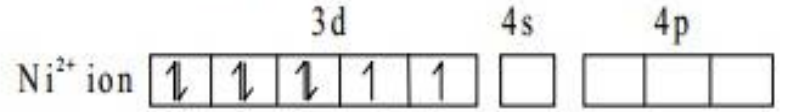
$$\therefore \quad \mu_s = \sqrt{2(2+2)} = 2.83\,BM$$

Since the hybridisation is sp^3, the geometry of the molecule is tetrahedral.

Outer-orbital Complex

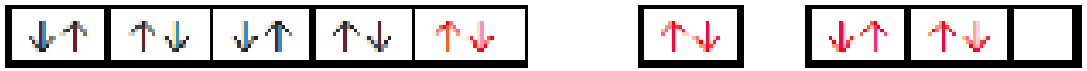
2) $[Ni(CN)_4]^{2-}$

Another possible geometry for the 4 coordinated complex is the square planar configuration involving dsp^2 hybridisation.



The ligand CN^- is a powerful ligand. Hence it forces the unpaired electrons to pair up in d orbitals. Hence this complex ion does not contain unpaired electrons. It is diamagnetic.

Electron distribution in $Ni(CN)_4^{2-}$ (dsp^2 hybridization)

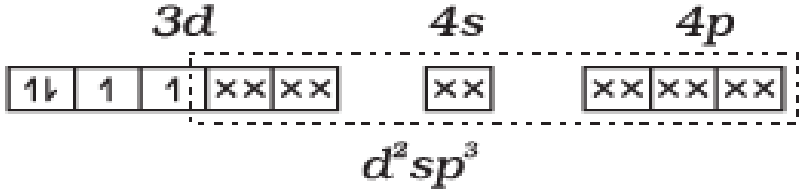


(metal 3d electrons in four 3d orbitals) (ligand electrons in one 3d, one 4s and in two 4p orbitals)

Inner-orbital Complex

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

$Mn^{3+} = 3d^4$

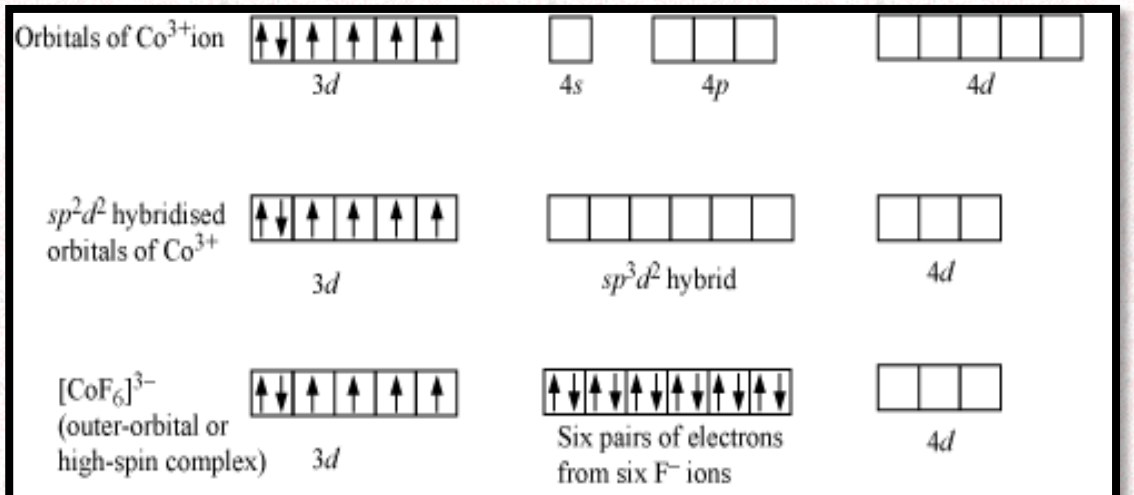


(i) d^2sp^3

(ii) Inner orbital complex

(iii) Paramagnetic

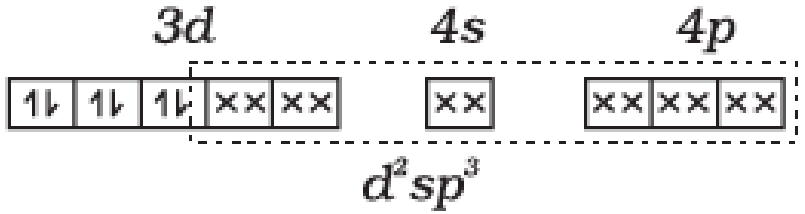
(iv) $\sqrt{2(2+2)} = \sqrt{8} = 2.87$ BM



Complexes hybridisation according to valence bond theory

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

$Co^{3+} = 3d^6$



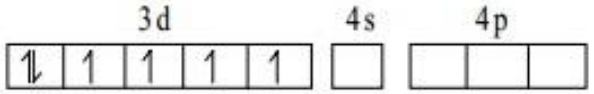
(i) d^2sp^3

(ii) Inner orbital complex

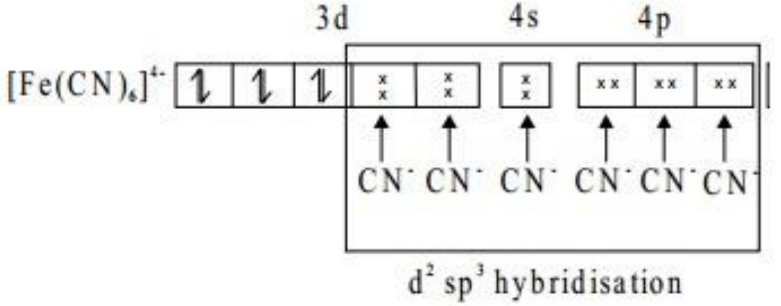
(iii) Diamagnetic

(iv) Zero

2) Fe^{+2} ion



In $[Fe(CN)_6]^{4-}$ complex the CN^- ligand is a powerful ligand, it forces the unpaired electrons in 3d level to pair up inside. Hence the species has no unpaired electron. The molecule is diamagnetic.



Limitation of Valence Bond Theory (VBT):

(i) It involves a number of assumptions.

(ii) It does not give quantitative interpretation of magnetic data.

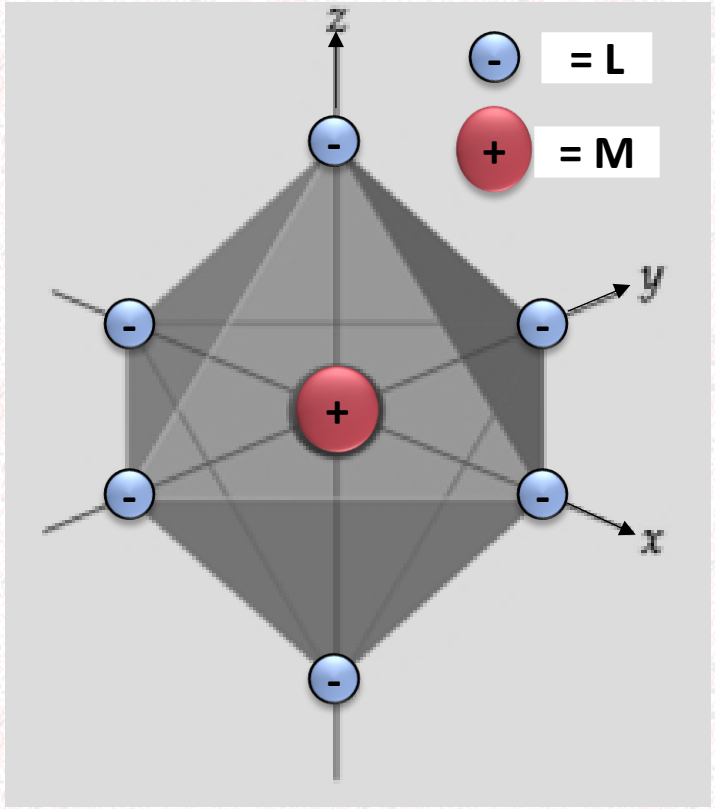
(iii) It does not explain the color exhibited by coordination compounds.

(iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.

(v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.

(vi) It does not distinguish between weak and strong ligands.

Introduction of Crystal Field Theory (CFT):



ML_6 Octahedral Complex

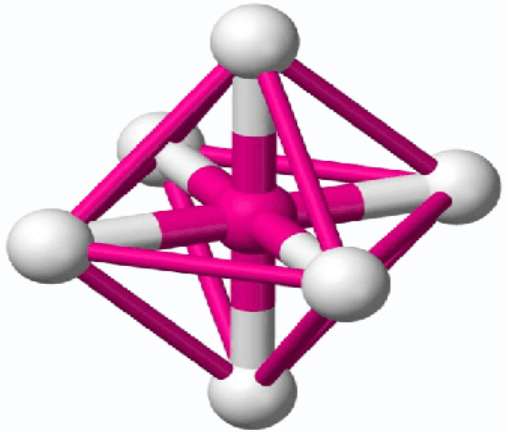
Electrostatic approach to bonding.
First Applied to ionic crystalline substances.

Assumptions:

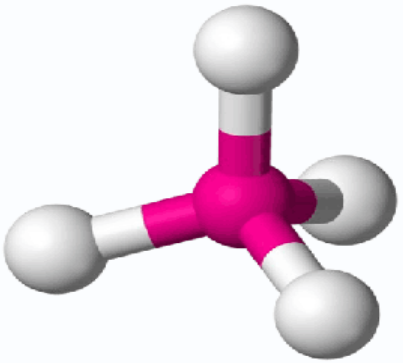
1) Metal ion at the center.
2) Ligands are treated as point charges.
3) Bonding occurs through M+ and L- electrostatic attraction.
4) Bonding is purely ionic.
5) M and L electrons repel each other.
6) d orbital degeneracy is broken as ligands approach.

Crystal Field Model

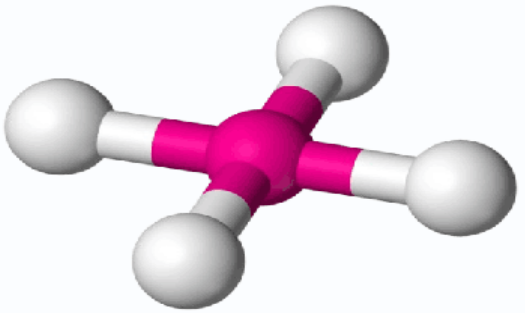
1. **A purely *ionic* model for transition metal complexes. In its simplest treatment CFT does not consider covalent bonding in complexes.**
2. **Ligands are considered as point charge.**
3. **The CFT does not provide for electrons to enter the metal orbitals, i.e. it does not consider any orbital overlap.**
4. **Predicts the pattern of splitting of d-orbitals.**
5. **Used to rationalize spectroscopic and magnetic properties.**



Octahedral complex (O_h)

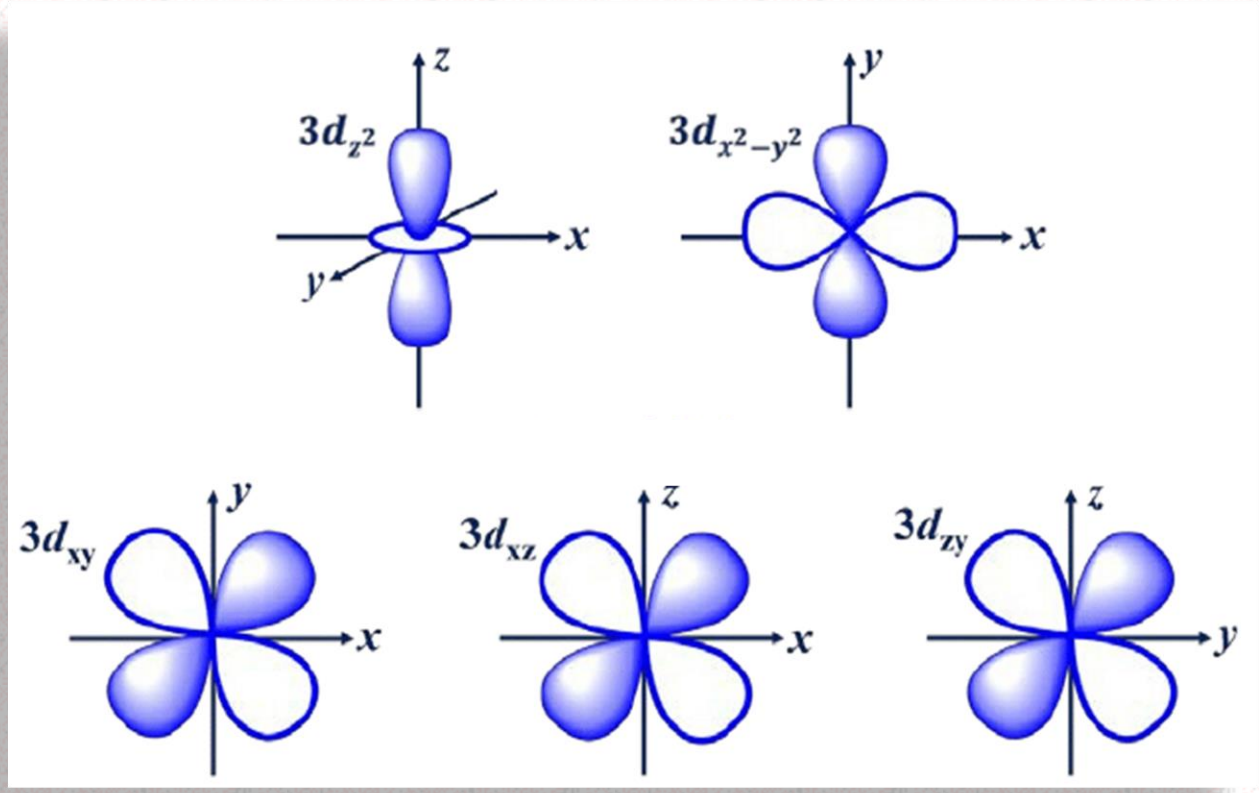


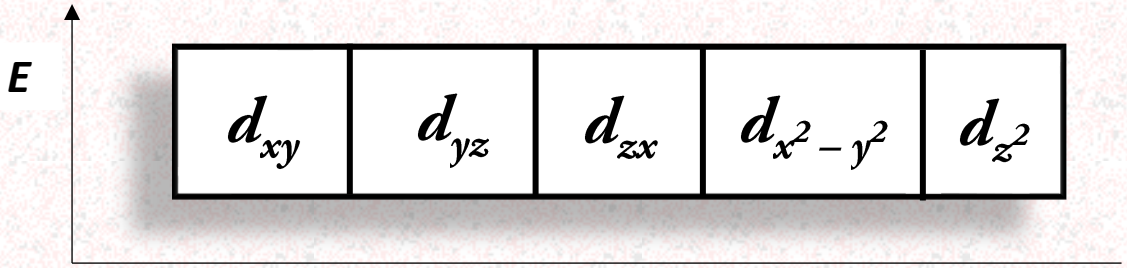
Tetrahedral complex (T_d)



Square planer complex (Sp)

Shapes of d-orbitals





1. There is a set of five degenerate orbitals in a d-subshell.
2. Out of these, shapes of 4 orbitals are alike i.e. double-dumbell shape.
3. Lobes of 3 orbitals (d_{xy} d_{yz} d_{zx}) lie in between the axes.
4. Lobes of 2 orbitals ($d_{x^2-y^2}$ and d_{z^2}) lie along the axes.


THANK YOU