

CHEMISTRY STUDY MATERIALS FOR CLASS 12

(NCERT BASED NOTES OF CHAPTER - 09)

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Co-ordination Compounds

Bonding in Coordination Compounds Werner's Theory

Metals exhibit two types of valencies in the formation of complexes. These are primary valencies and secondary valencies.

1. Primary valencies correspond to oxidation number (ON) of the metal and are satisfied by anions. These are ionisable and non-directional.
2. Secondary valencies correspond to coordination number (CN) of the metal atom and are satisfied by ligands. These are non-ionisable and directional. Hence, geometry is decided by these valencies.

Valence Bond Theory (VBT)

This theory was proposed by L. Pauling in 1930 s. According to this theory, when a complex is formed, the metal ion/atom provides empty orbitals to the surrounding ligands. Coordination number shows the number of such empty orbitals, i.e., number of empty orbitals is equal to the coordination number. These empty orbitals hybridized before participation in bonding and the nature of hybridisation depends on the nature of metal and on the nature of approaching ligand.

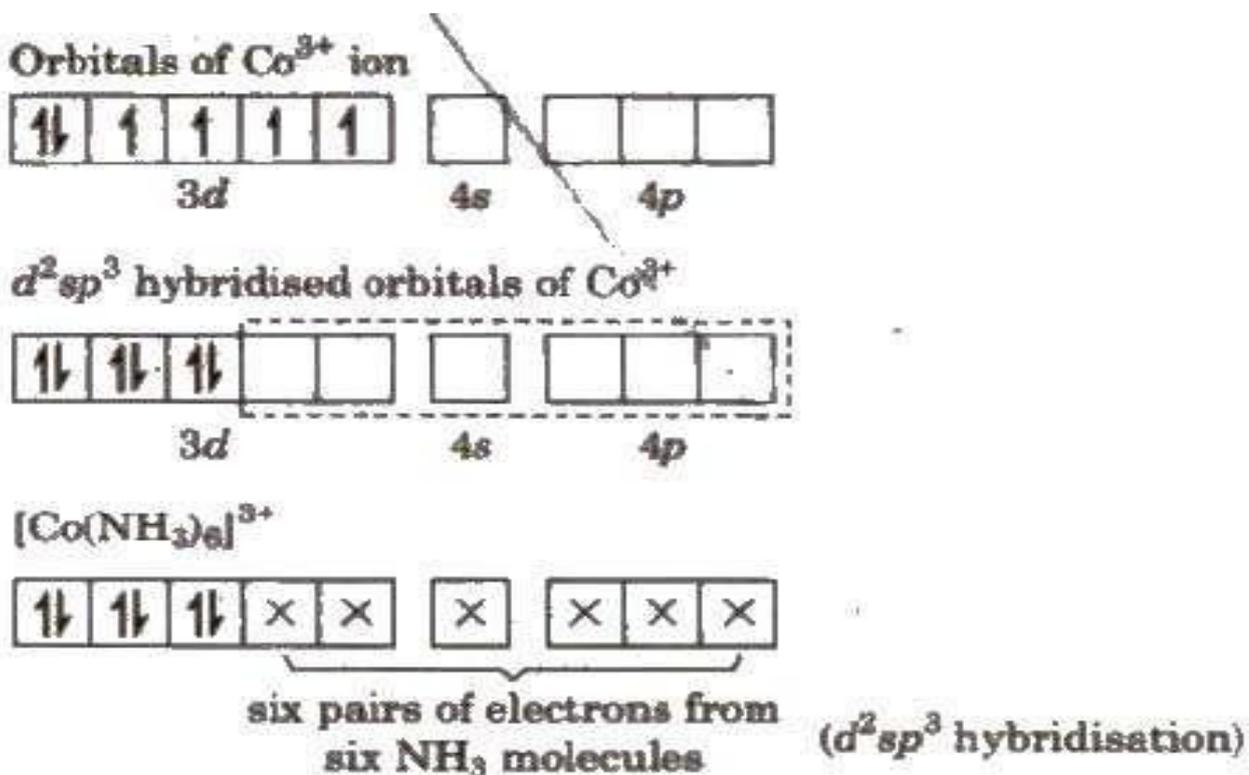
Inner orbital complexes or outer orbital complexes

When outer d-orbitals are used in bonding, the complexes are called outer orbital complexes. They are formed due to weak field ligands or high spin ligands and hybridisation is sp^3d^2 . They have octahedral shape.

When d-orbitals of $(n - 1)$ shell are used, these are known as inner orbital complex, they are formed due to strong field ligands or low spin ligands and hybridisation is d^2sp^3 . They are also octahedral in shape.

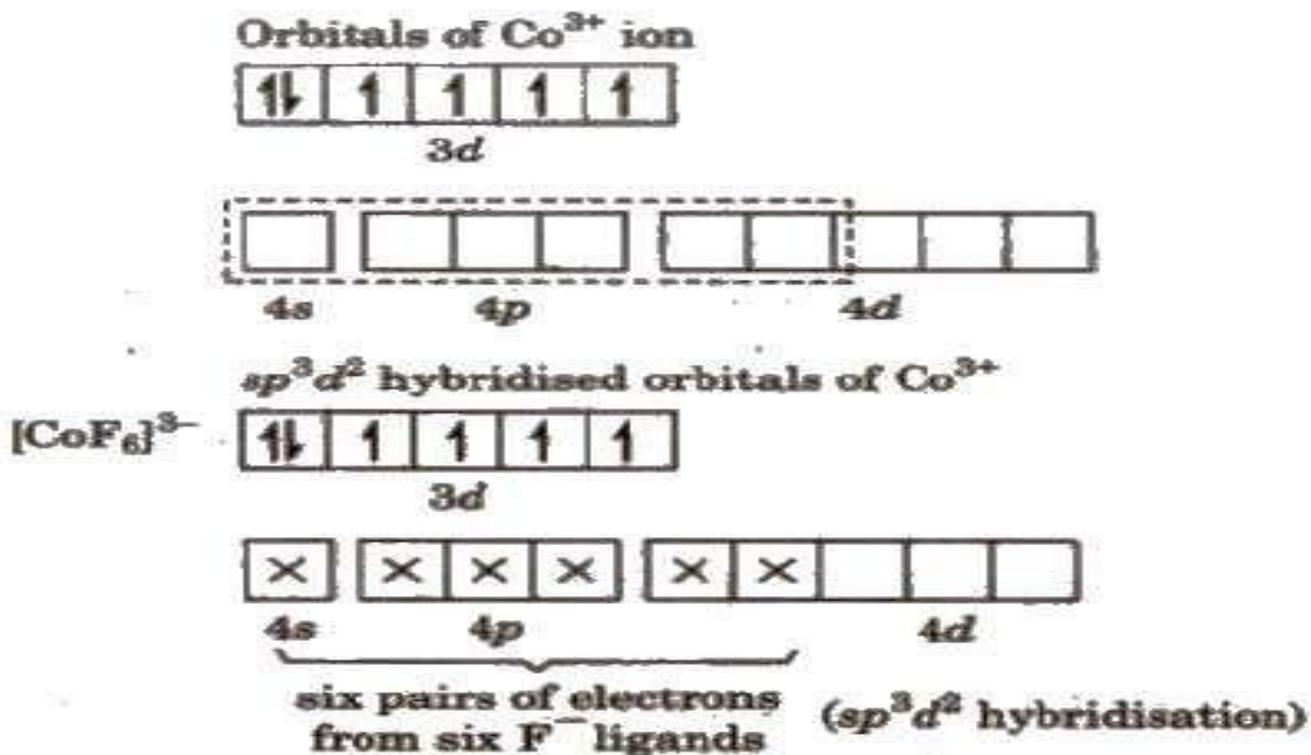
1.6 – Ligands (unidentate), octahedral entity.

(i) Inner orbital complex $[\text{Co}(\text{NH}_3)_6]^{3+}$



All electrons are paired; therefore complex will be diamagnetic in nature.

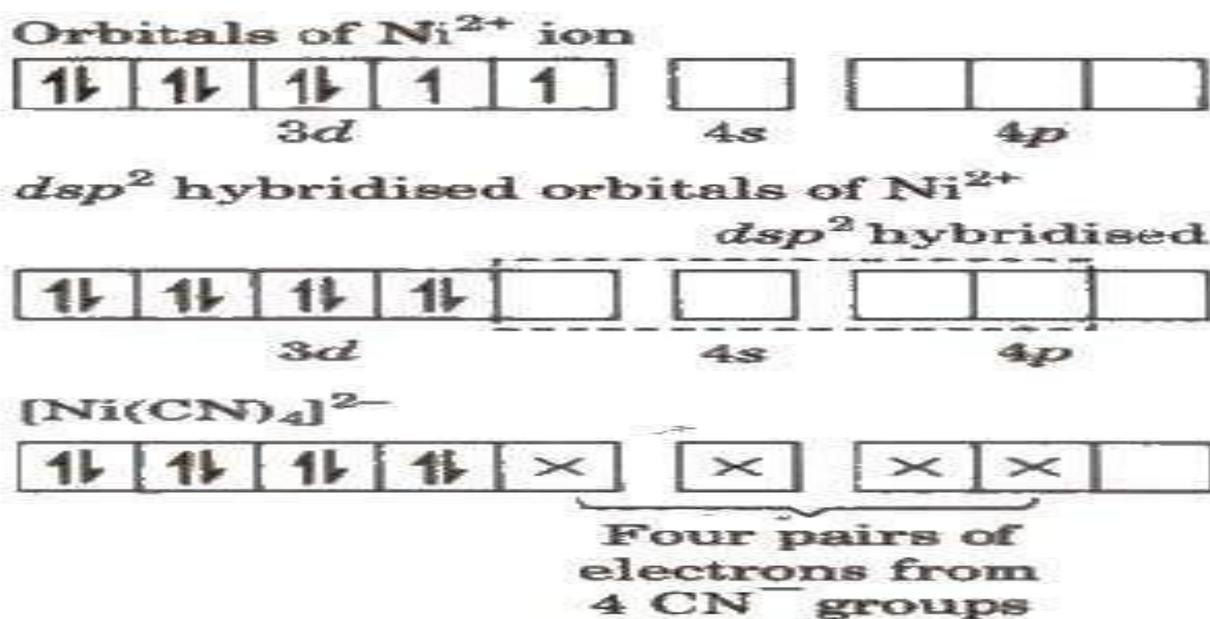
(ii) Outer orbital complex, $[\text{CoF}_6]^{3-}$



Complex has unpaired electrons; therefore, it will be paramagnetic in nature.

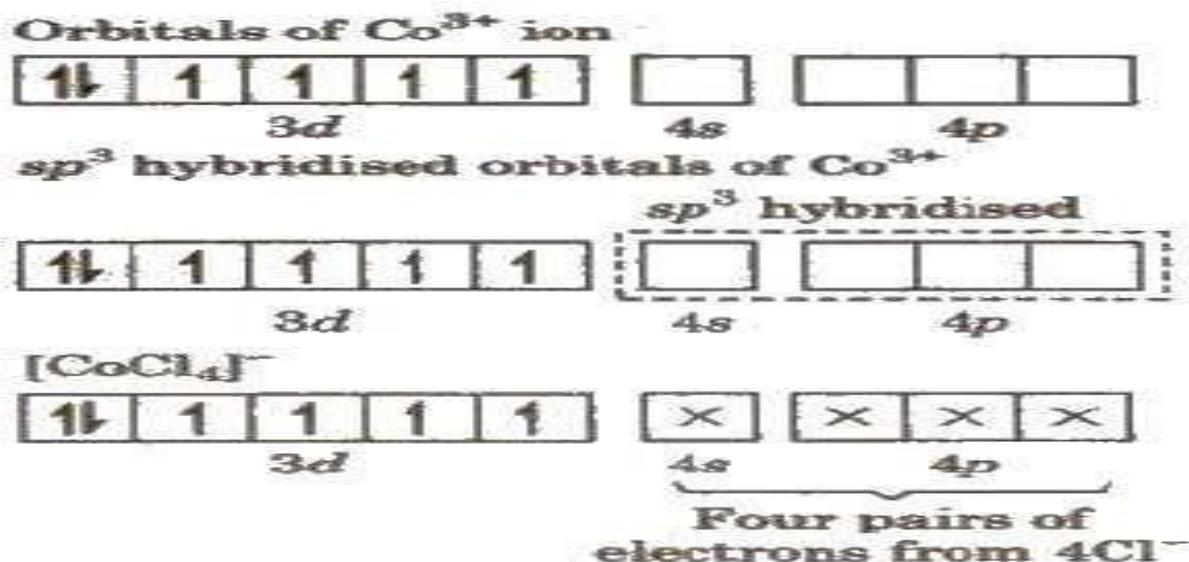
4-ligands (unidentate) tetrahedral entity.

(i) Inner orbital complex, $[\text{Ni}(\text{CN})_4]^{2-}$



All electrons are paired so complex will be diamagnetic in nature.

(ii) Outer orbital complex, $[\text{CoCl}_4]^-$



Since, complex has unpaired electrons. So it will be paramagnetic in nature.

S. No.	Inner orbital complexes	Outer orbital complexes
1.	Strong field or low spin ligands	Weak field or high spin ligands
2.	Hybridization is dsp^2 (where one orbital of 3d, one orbital of 4s and two orbitals of 4p)	Hybridization is sp^3 (where orbital of 4s and three orbitals of 4p)
3.	Square planar shape	Tetrahedral shape

Limitations of VBT

This theory could not explain the quantization of the magnetic data, existence of inner orbital and outer orbital complex, change of magnetic moment with temperature and colour of complexes.

Crystal Field Theory (CFT)

This theory was proposed by H. Bethe and van Vleck. Orgel in 1952 applied this theory to coordination compounds. In this theory, ligands are treated as point charges in case of anions and dipoles in case of neutral molecules.

The five d-orbitals are classified as

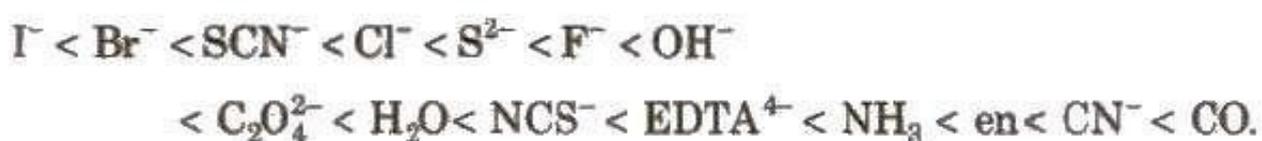
- (i) Three d-orbitals i.e., d_{xy} , d_{yz} and d_{zx} are oriented in between the coordinate axes and are called t_{2g} – orbitals.
- (ii) The other two d-orbitals, i.e., $dx^2 - y^2$ and dz^2 oriented along the x – y % axes are called e_g – orbitals.

Due to approach of ligands, the five degenerate d-orbitals split. Splitting of d-orbitals depends on the nature of the crystal field.

[The energy difference between t_{2g} and e_g level is designated by Δ and is called crystal field splitting energy.]

By using spectroscopic data for a number of coordination compounds, having the same metal ions but different ligand, the crystal field splitting for each ligand has been calculated. A series in which ligand are arranged in order of increasing magnitude of crystal field splitting, is called **spectrochemical series**.

Spectrochemical series



Crystal field splitting in octahedral complexes

In case of octahedral complexes, energy separation is denoted by Δ_o (where subscript 0 is for octahedral).

In octahedral complexes, the six-ligands approach the central metal ion along the axis of $d_{x^2 - y^2}$ and d_{z^2} orbitals.

Energy of e_g set of orbitals > energy of t_{2g} set of orbitals.

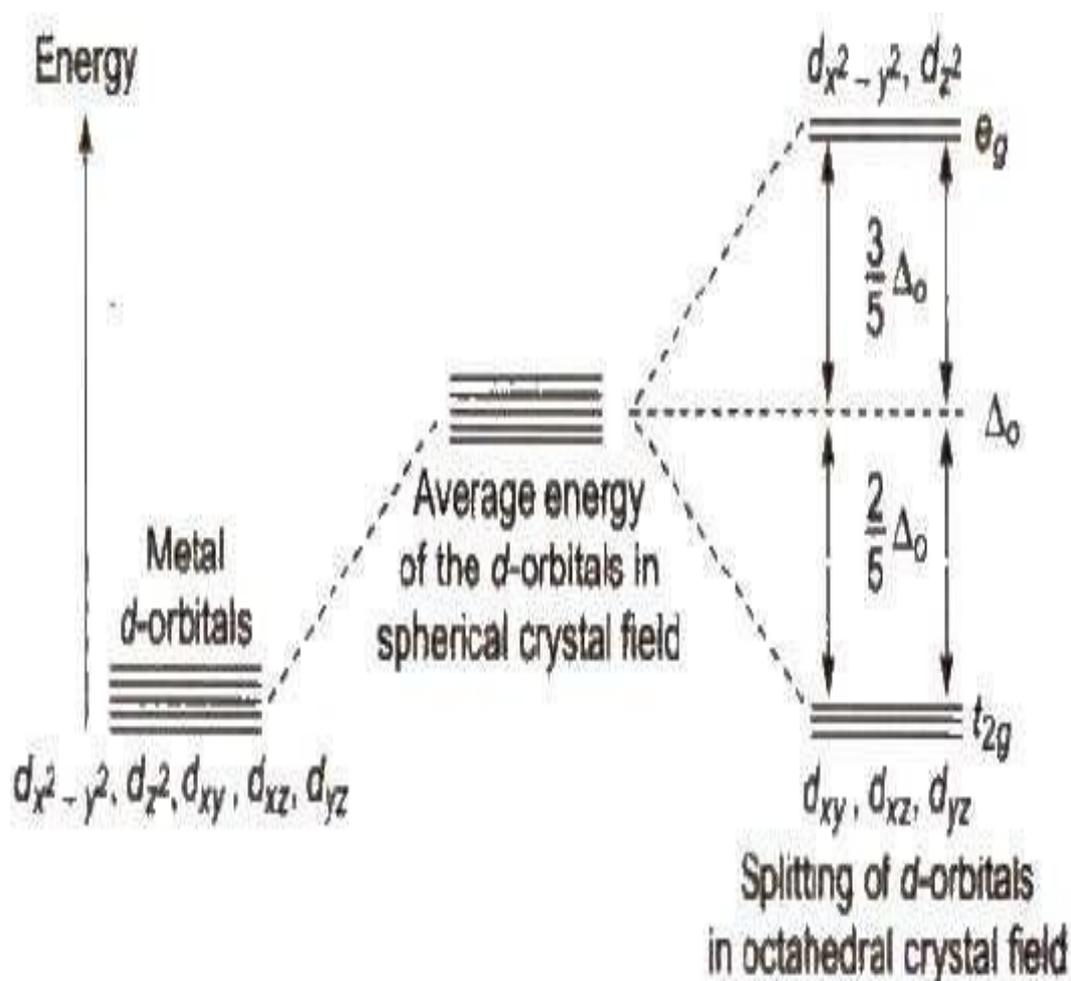
The energy of e_g orbitals will increase by $(3/5) \Delta_o$ and t_{2g} will decrease by $(2/5) \Delta_o$.

If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$. Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.

If $\Delta_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$.

(where, P = energy required for e^- pairing in an orbital).

Ligands which produce this effect are known as strong field ligands and form low spin complexes.



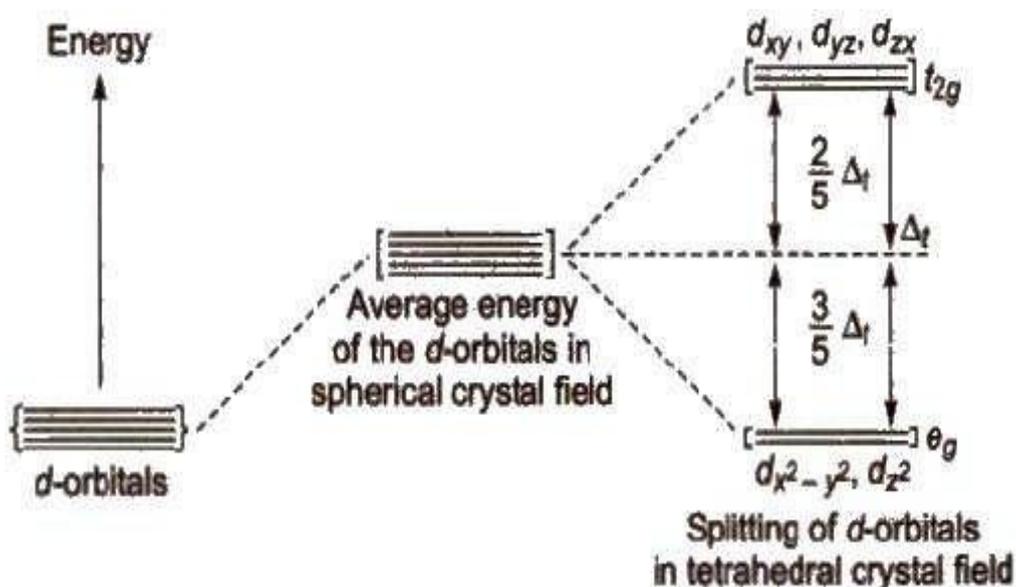
Crystal field splitting in tetrahedral complexes

In tetrahedral complexes, four ligands may be imagined to occupy the alternate corners of the cube and the metal ion at the center of the cube.

Energy of t_{2g} set of orbitals $>$ Energy of e_g set of orbitals.

In such complexes d – orbital splitting is inverted and is smaller as compared to the octahedral field splitting.

Orbital splitting energies are so low that pairing of electrons are not possible so these are high spin complexes.



Colour in Coordination Compounds

The crystal field theory attributes the colour of the coordination compounds to $d-d$ transition of the electron, i.e., electron jump from t_{2g} level to higher e_g level.

In the absence of ligands, crystal field splitting does not occur and hence the substance is colourless.

