WERNER'S COORDINATION THEORY

- In 1892, Werner put forward his famous theory of coordination to explain the formation and structure of complex compounds.
- The main postulates of Werner's theory are
 - Every element exhibits two types of valencies, viz., primary valency and secondary valency. The primary valency is ionisable and non-directional, represented by dotted lines (.....). It corresponds to the oxidation state of the metal atom or ion. The secondary valency is non-ionisable and directional, represented by solid lines (----). It corresponds to the coordination number of the metal atom or ion.
 - Every metal atom has a fixed number of secondary valencies, *i e.*, its coordination number.
 - Every element wants to satisfy both its primary and secondary valencies.
 - The secondary valencies are always directed towards fixed positions in space. The stereo chemistry of a complex is determined by the number and arrangement of such ligands.

Example :



Structure of CoCl₃·5NH₃ complex Number of Cl⁻ ions precipitated = 2 Total number of ions = 3 Coordination number = 6 Oxidation number = 3

VBT (VALENCE BOND THEORY)

- Main postulates of this theory are
 - The central metal ion makes available as many number of empty orbitals as its coordination number in compound formation.
 - Appropriate vacant orbitals of metal undergoes hybridisation to give a definite geometry such as square planar(dsp²), tetrahedral(sp³), octahedral(d²sp³), etc.
 - Empty hybrid orbital of metal overlap with filled orbital of ligands containing lone pair to form M <-- L coordinate bond.</p>

Octahedral Complexes



Shape – Octahedral ; Hybridisation – d^2sp^3

Magnetic behaviour – Paramagnetic because of unpaired electrons.

Tetrahedral Complexes



Magnetic behaviour – Diamagnetic due to absence of unpaired electrons.

Inner and Outer Orbital Complexes

- During octahedral compound formation, two type of complexes are possible:
 - Inner orbital complexes : If the complex formation involves inner *d*-orbital *i.e.*, [(n-1)], the complex is called inner orbital complex. These are also known as *low spin complex* since they have none or lesser number of unpaired electrons. *e.g.*, [Co(NH₃)₆]³⁺, [Co(CN)₆]⁴⁻, etc.
 - Outer orbital complexes : If complex formation involves outer *d*-orbitals, the complex is called outer orbital complex. These are also called *high spin complex* since they have large number of unpaired electrons.
 - $e.g., [MnF_6]^{3-}, [Ni(NH_3)_6]^{2+}$

CFT (CRYSTAL FIELD THEORY)

- Main postulates of crystal field theory are
 - In a coordination compound there are electrostatic interaction between metal atom/ion and ligands.
 - In an isolated metal atom or ion all five *d*-orbitals have equal energy *i.e.* they are degenerate.
 - When metal atom/ion gets surrounded by ligands, there occur interaction between *d*-electron cloud of metal atom/ion and ligands.
 - ▶ If the field due to ligand around metal atom is spherically symmetrical, the *d*-orbitals of metal remain degenerate.
 - If the field due to ligand surrounding metal is unsymmetrical (as in octahedral and tetrahedral complexes) the degeneracy of *d*-orbitals is splitted into two sets of orbitals.
 - Orbitals lying in the direction of ligands (point charges) are raised to higher energy state than those orbitals lying between the ligands (point charges).
 - The energy difference between two sets of orbitals is denoted by Δ_o and Δ_t for octahedral and tetrahedral complexes respectively.