Theories of Bonding in Coordination Compounds

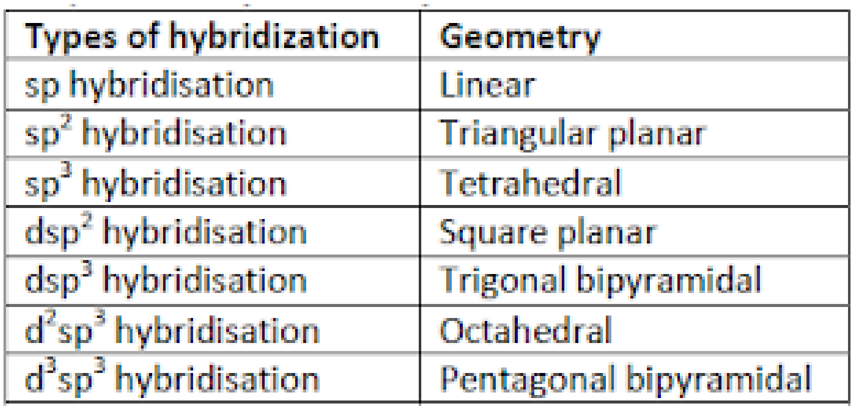
There are mainly three theories which are used to describe the nature the nature of metal-ligand bonding in coordination compounds.

1. **Valence Bond Theory (VBT):** VBT was developed by **Linus Pauling** and Others in 1930.
2. **Crystal Field Theory (CFT):** CFT was proposed by **Hans Bethe in 1929.**
3. **Ligand Field Theory (LFT) or Molecular Orbital Theory (MOT):** Developed by **J.H.Van Vleck in 1935.**

Valence Bond Theory (VBT)

VBT was the first theory used to explain the geometry and magnetic property of many to coordination compounds. The basic idea of the theory is that the formation of a complex is a reaction between a ***Lewis*** base (ligand; electron donor) and a ***Lewis*** acid (metal or metal ion; electron acceptor) with the formation of a coordinate-covalent bond (dative bond) between the ligand and the metal. This is based on following assumptions:

1. The central **metal atom or ion** provides number of **vacant s,p** & **d orbitals equal to its coordination number** to form coordinate bond with the ligand orbitals.
2. Each ligands has at least one б-orbital containing a lone pair of electrons
3. The empty orbitals of the **metal atom or ion** undergo **hybridisation** to form same number of hybrid orbitals. These hybrid orbitals overlap with the filled б-orbitals of the ligands to form ligand to metal coordinate б-bond.
4. The **geometry** of complex ion depends on **hybridisation** of metal orbitals.

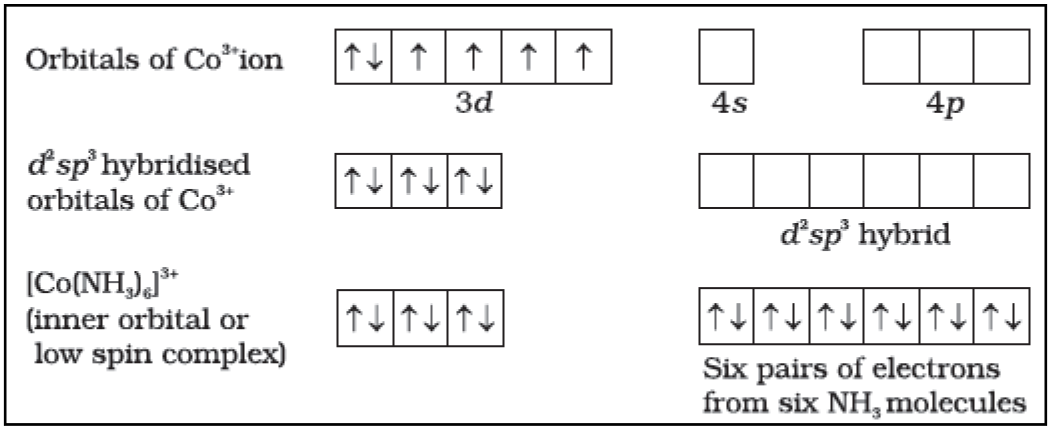


Types of hybridization	Geometry
sp hybridisation	Linear
sp^2 hybridisation	Triangular planar
sp^3 hybridisation	Tetrahedral
dsp^2 hybridisation	Square planar
dsp^3 hybridisation	Trigonal bipyramidal
d^2sp^3 hybridisation	Octahedral
d^3sp^3 hybridisation	Pentagonal bipyramidal

Application of VBT to Coordination Compounds

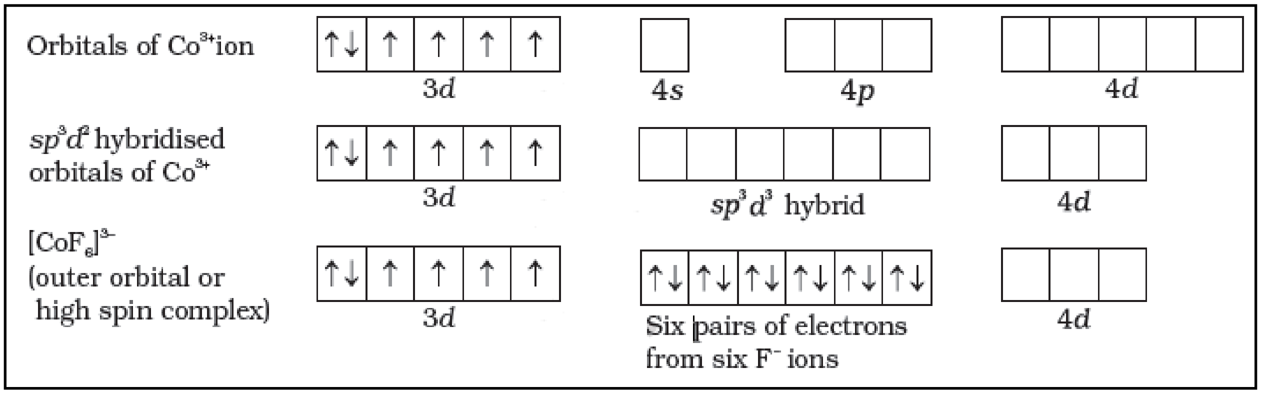
It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory.

In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration $3d^6$. The hybridisation scheme is as shown in diagram.

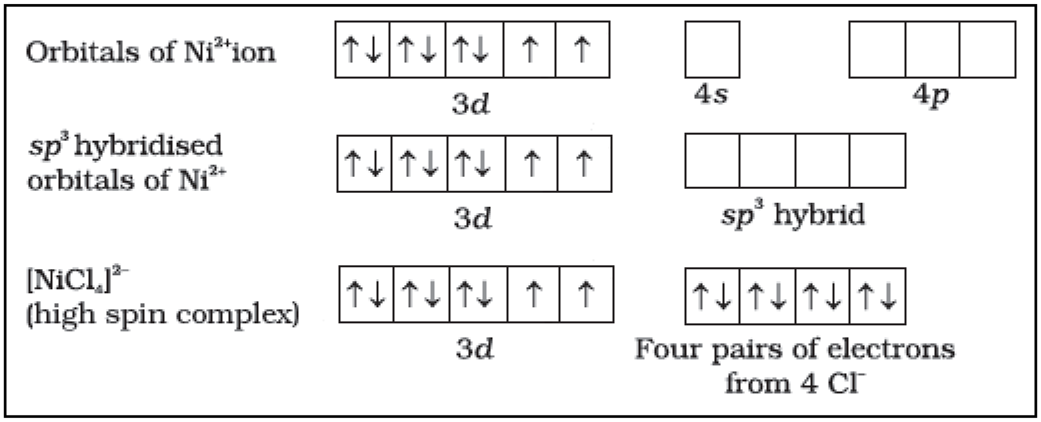


Six pairs of electrons, one from each NH_3 molecule, occupy the six hybrid orbitals. Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron. In the formation of this complex, since the inner *d* orbital (3*d*) is used in hybridisation, the complex, $[Co(NH_3)_6]^{3+}$ is called an **inner orbital** or **low spin** or **spin paired complex**.

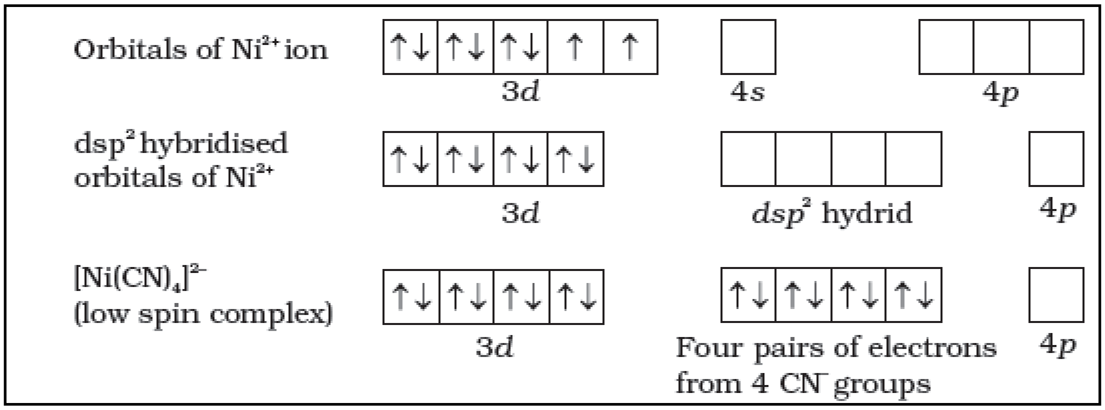
The paramagnetic octahedral complex, $[CoF_6]^{3-}$ uses outer orbital (4*d*) in hybridisation (sp^3d^2). It is thus called **outer orbital** or **high spin** or **spin free complex**. Thus:



In tetrahedral complexes one *s* and three *p* orbitals are hybridised to form four equivalent orbitals oriented tetrahedrally. This is illustrated below for $[NiCl^{4}]^{2-}$. Here nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridisation scheme is as shown in diagram. Each Cl^- ion donates a pair of electrons. The compound is paramagnetic since it contains two unpaired electrons. Similarly, $[Ni(CO)_4]$ has tetrahedral geometry but is diamagnetic since nickel is in zero oxidation state and contains no unpaired electron.



In the square planar complexes, the hybridisation involved is dsp^2. An example is $[Ni(CN)_4]^{2-}$. Here nickel is in +2 oxidation state and has the electronic configuration $3d^8$. The hybridisation scheme is as shown in diagram:



Each of the hybridised orbitals receives a pair of electrons from a cyanide ion. The compound is diamagnetic as evident from the absence of unpaired electron.

It is important to note that the hybrid orbitals do not actually exist. In fact, hybridisation is a mathematical manipulation of wave equation for the atomic orbitals involved.

Magnetic property of coordination compounds:

The magnetic moment of coordination compounds can be measured by the magnetic susceptibility experiments. The results can be used to obtain information about the structures adopted by metal complexes. A critical study of the magnetic data of coordination compounds of metals of the first transition series reveals some complications. For metal ions with upto three electrons in the *d* orbitals, like Ti^{3+} (d^1); V^{3+} (d^2); Cr^{3+} (d^3); two vacant *d* orbitals are available for octahedral hybridisation with 4*s* and 4*p* orbitals. The magnetic behaviour of these free ions and their coordination entities is similar. When more than three 3*d* electrons are present, the required pair of 3*d* orbitals for octahedral hybridisation is not directly available (as a consequence of Hund's rule). Thus, for d^4 (Cr^{2+}, Mn^{3+}), d^5 (Mn^{2+}, Fe^{3+}), d^6 (Fe^{2+}, Co^{3+}) cases, a vacant pair of *d* orbitals results only by pairing of 3*d* electrons which leaves two, one and zero unpaired electrons, respectively.

The magnetic data agree with maximum spin pairing in many cases, especially with coordination compounds containing *d*6 ions. However, with species containing *d*4 and *d*5 ions there are complications. $[Mn(CN)^6]^{3–}$ has magnetic moment of two unpaired electrons while $[MnCl_6]^{3–}$ has a paramagnetic moment of four unpaired electrons. $[Fe(CN)^6]^{3–}$ has magnetic moment of a single unpaired electron while $[FeF^6]^{3–}$ has a paramagnetic moment of five unpaired electrons. [CoF6]3– is paramagnetic with four unpaired electrons while [Co(C2O4)3]3– is diamagnetic. This apparent anomaly is explained by valence bond theory in terms of formation of inner orbital and outer orbital coordination entities. $[Mn(CN)_6]^3$, $[Fe(CN)_6]^{3–}$ and $[Co(C_2O_4)_3]^{3–}$ are inner orbital complexes involving d^2sp^3 hybridisation, the former two complexes are paramagnetic and the latter diamagnetic. On the other hand, $[MnCl_6]^{3–}$, $[FeF_6]^{3–}$ and $[CoF_6]^{3–}$ are outer orbital complexes involving sp^3d^2 hybridisation and are paramagnetic corresponding to four, five and four unpaired electrons.

Problem: The spin only magnetic moment of $[MnBr_4]^{2–}$ is 5.9 BM. Predict the geometry of the complex ion?

Solution: Since the coordination number of Mn^{2+} ion in the complex ion is 4, it will be either tetrahedral (sp^3 hybridisation) or square planar (dsp^2 hybridisation). But the fact that the magnetic moment of the complex ion is 5.9 BM, it should be tetrahedral in shape rather than square planar because of the presence of five unpaired electrons in the *d* orbitals.

Limitations of VBT

The VBT reigned for a period of two decades in the realm of coordination chemistry because of its simplicity and ease in explaining structural and magnetic properties. It could adequately explain low-spin square-planar, high-spin tetrahedral and both low- and high-spin octahedral complexes.

But with the progress of time following shortcomings were noticed with the VBT and it is now largely abandoned.

Disadvatages:

1. It fails to predict whether a 4-coordinate complex will be tetrahedral or square-planar and whether an octahedral complex will be low-spin or high-spin.
2. It fails to distinguish certain geometries like tetragonal or distorted octahedral.
3. It completely neglects excited states in a complex and can not explain absorption spectrum.
4. It doesn't have scope for quantitative calculation of bopd energy and stability of complexes.
5. It does not adequately explain the magnetic data beyond specifying the number of unpaired electrons .
6. Too much stress has been given on metal ion while the importants of ligands is not properly addressed.