Valence Bond Theory (VBT)

Introduction

We have already said that Werner was the first to explain the nature of bonding in complex compounds. However, with the advancement of theories of valence, modern theories have been proposed to explain the nature of metal-ligand bonding in complexes. These theories can also explain the colour, geometry and magnetic properties of the complex compounds. These mode theories are:
(i) Valence Bond Theory: VBT (due to L. Pauling and JL Slater, 1935)
(ii) Crystal Field Theory: CFT (due to H. Bethe. 1929 and Van Vleck, 1932) (iii) Ligand Field Theory LFT or Molecular Orbital Theory, MOT (due to J. Van Vleck, 1935). Here we shall discuss only valence bond theory.

Valence Bond Theory (VBT)

This theory is mainly due to Pauling. It deals with the electronic structure of the central metal ion in its ground state, kind of bonding, geometry and magnetic properties of the complexes.

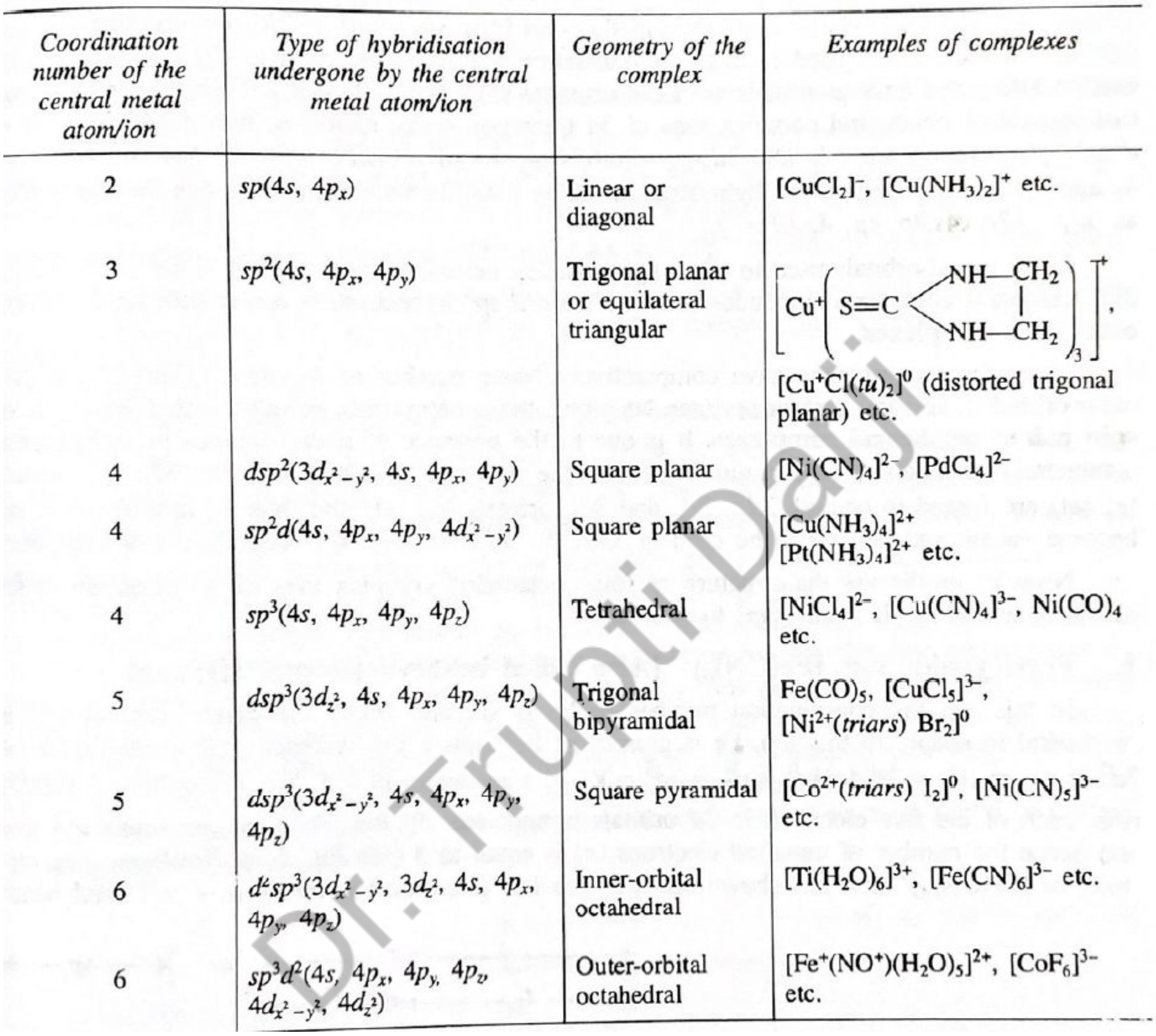
Assumptions of valence bond theory :

1. The central metal atom or ion makes available a number empty s, p and d atomic orbitals equal to its coordination number. These vacant orbitals hybridized together to form hybrid orbitals which are the same in number as the atomic orbitals hybridized together. These hybrid orbitals are vacant, equivalent in energy and have definite geometry: Important types of hybridisation occuring in the first row transition metal (3d) complexes and the geometry of the complex are given in Table.

2. The ligands have at least one σ-orbital containing a lone pair of electrons.

3. Vacant hybrid orbitals of the metal atom or ion overlap with the filled (containing lone pair of electrons) σ-orbitals of the ligands to form ligand→ metal σ-bond. This bond is known as coordinate bond is a special type of covalent bond and shows the characteristics of both the

overlapping orbitals. However, it also possesses a considerable amount of polarity because of the mode of its formation.



Coordination number of the central metal atom/ion	*Type of hybridisation undergone by the central metal atom/ion*	*Geometry of the complex*	*Examples of complexes*
2	$sp(4s, 4p_x)$	Linear or diagonal	$[CuCl_2]^-$, $[Cu(NH_3)_2]^+$ etc.
3	$sp^2(4s, 4p_x, 4p_y)$	Trigonal planar or equilateral triangular	$\left[Cu^+\left(S{=}C<\begin{smallmatrix}NH-CH_2\\ NH-CH_2\end{smallmatrix}\right)_3\right]^+$, $[Cu^+Cl(tu)_2]^0$ (distorted trigonal planar) etc.
4	$dsp^2(3d_{x^2-y^2}, 4s, 4p_x, 4p_y)$	Square planar	$[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$
4	$sp^2d(4s, 4p_x, 4p_y, 4d_{x^2-y^2})$	Square planar	$[Cu(NH_3)_4]^{2+}$ $[Pt(NH_3)_4]^{2+}$ etc.
4	$sp^3(4s, 4p_x, 4p_y, 4p_z)$	Tetrahedral	$[NiCl_4]^{2-}$, $[Cu(CN)_4]^{3-}$, $Ni(CO)_4$ etc.
5	$dsp^3(3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z)$	Trigonal bipyramidal	$Fe(CO)_5$, $[CuCl_5]^{3-}$, $[Ni^{2+}(triars)\ Br_2]^0$
5	$dsp^3(3d_{x^2-y^2}, 4s, 4p_x, 4p_y, 4p_z)$	Square pyramidal	$[Co^{2+}(triars)\ I_2]^0$, $[Ni(CN)_5]^{3-}$ etc.
6	$d^2sp^3(3d_{x^2-y^2}, 3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z)$	Inner-orbital octahedral	$[Ti(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$ etc.
6	$sp^3d^2(4s, 4p_x, 4p_y, 4p_z, 4d_{x^2-y^2}, 4d_{z^2})$	Outer-orbital octahedral	$[Fe^+(NO^+)(H_2O)_5]^{2+}$, $[CoF_6]^{3-}$ etc.

Table: Important types of hybridisation found in the first row transition metal complexes and the geometry of the complexes

4. The non-bonding electrons of the metal atom or ion are rearranged in the metal orbitals (viz. pure d, s or p orbitals as the case may be) which do not participate in forming the hybrid orbitals. The rearrangement of non-bonding electrons takes place according to Hund's rule.

Geometry of 6-coordinated complex ions:

In all the complex ions the coordination number of the central metal atom or ion is six the complex ions have octahedral geometry.

This octahedral geometry arises due to d^2sp^3 or sp^3d^2 hybridisation of the central metal atom or ion. What type of hybridisation will occur depends on the number of unpaired or paired electrons present in the complex ion. d^2sp^3 or sp^3d^2 hybridisation is also called octahedral hybridisation.

Octahedral complexes in which the central atom is d^2sp^3 hybridised are called inner-orbital octahedral complexes while the octahedral complexes in which the central atom is sp^3d^2 hybridised are called outer-orbital octahedral complexes.

d^2sp^3 Hybridisation in Inner Orbital Octahedral Complexes:

This type of hybridisation takes place in those octahedral complexes which contain strong ligands. On the basis of the orientation of the lobes of d-orbitals in space, these orbitals have been classified into two sets viz. t_{2g} (d_{xy}, d_{yz} and d_{xz}) and e_g ($d_{z2}$and d_{x2-y2}) orbitals. In the formation of six d^2sp^3 hybrid orbitals, two (n-1) d-orbitals of e_g set, one ns and three np (np_x, np_y, and np_z) orbitals combine together and form six d^2sp^3 hybrid orbitals.

Thus we see that the two d-orbitals used in d^2sp^3 hybridisation are from penultimate shells [ie. (n-1)th shell] while s and three p-orbitals are from ultimate shell (ie. nth shell). This discussion shows that in case of octahedral complex ions of 3d transition series elements, two d-orbitals used in d^2sp^3 hybridisation are $3d_{z2}$ and $3d_{x2-y2}$ orbitals while s- and p-orbitals are 4s and 4p orbitals. Thus d^2sp^3 hybridization taking place in such complexes can be represented as: $d_{x2-y2}.d_{z2}.4s.4p_x.4p_y.4p_z(d^2sp^3)$.

Since two d-orbitals used in d^2sp^3 hybridisation belong to the inner shell [i.e. (n-1)th shell], the octahedral complex compounds resulting from d^2sp^3 hybridisation are called **inner orbital octahedral complexes**.

Ferrocyanide ion OR hexacyanoferrate (II) ion $[Fe(CN)_6]^{4-}$:

In this ion, since the coordination number of Fe is six, the given complex ion has octahedral geometry. In this ion, Fe is present as Fe^{2+} ion whose valence-shell configuration is $3d^6\ 4s^0\ 4p^0$ or , $t_{2g}{}^4\ e_g{}^2 4s^0\ 4p^0$ which shows that Fe^{2+} ion has 4 unpaired electrons. Magnetic studies have, however, shown that the given complex ion is diamagnetic and hence it has no unpaired electrons (n = 0). Hence in order to get all the electrons in the paired state, two electrons of e_g orbitals are sent to t_{2g} orbitals so that n becomes equal to zero.

Since CN^- ions (ligands) are strong ligands, they are capable of forcing the two electrons of e_g orbitals to occupy t_{2g} orbitals and thus make all the electrons paired. Now for the formation of $[Fe(CN)_6]^{4-}$ ion, two 3d orbitals of e_g set, 4s orbital (one orbital) and three 4p orbitals (all these six orbitals are vacant orbitals) undergo d^2sp^3 hybridisation (see Figure). It is due to d^2sp^3 hybridisation that $[Fe(CN)_6]^{4-}$ ion is an inner orbital octahedral complex ion. The electron pair donated by CN^- ion (ligand) is accommodated in each of the six d^2sp^3 hybrid orbitals as shown in Figure.

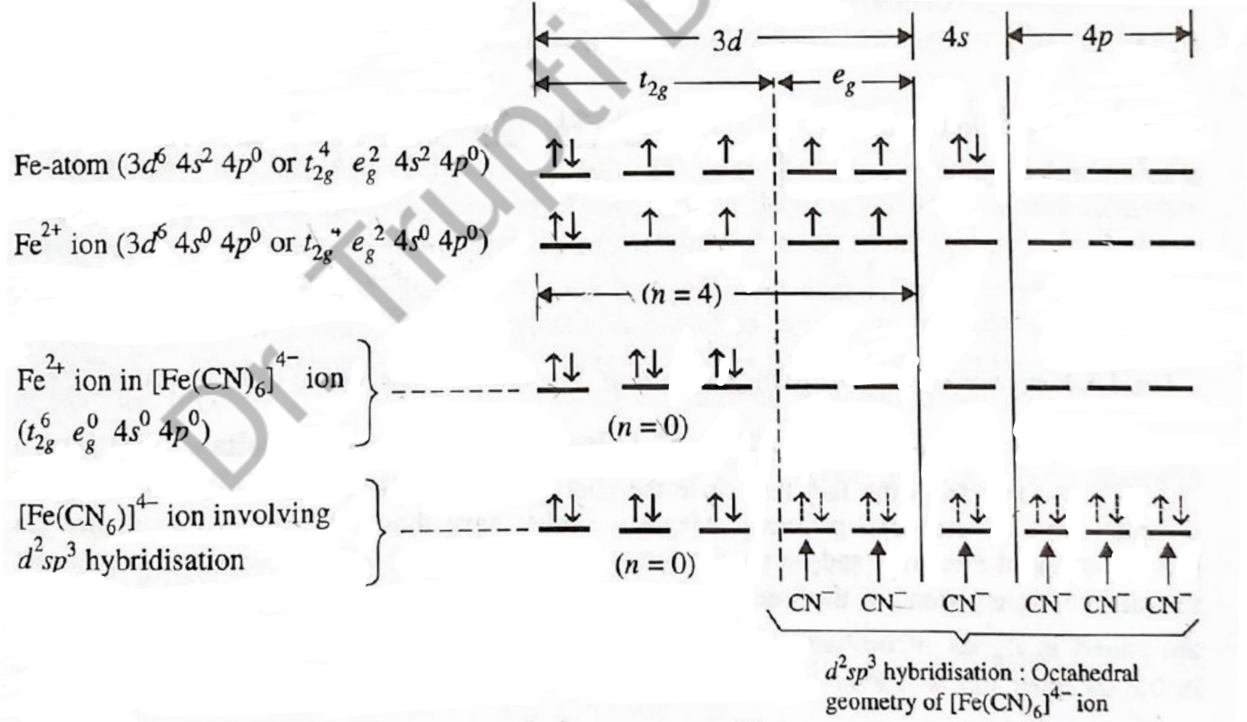


Fig. Formation of $[Fe(CN)6]^{4-}$ ion by d^2sp^3 hybridisation. ↑↓ indicates electron pair donated by each CN^- ion (ligand) (Inner-orbital octahedral complex ion).

sp^3d^2 Hybridisation in Outer Orbital Octahedral Complexes

This type of hybridisation takes place in those octahedral complex ions which contain weak ligands. Weak ligands are those which cannot force the electrons of d_{z2} and d_{x2-y2} orbitals of the inner shell to occupy d_{xy}, d_{yz} and d_{xz} orbitals of the same shell. Thus in this hybridisation. $(n-1)d_{z2}$ and $(n-1)d_{x2-y2}$ orbitals are not available for hybridisation. In place of these orbitals, we use nd_{z2} and nd_{x2-y2} orbitals (These d-orbitals belong to the outer shell) and hence sp^3d^2 hybridisation can be represented as ns, np_x, np_y, np_z, nd^2, nd_{x2-y2} .

This hybridisation shows that all the six orbitals involved in hybridisation belong to the higher energy level (outer shell). This discussion shows that in the case of octahedral ions of 3d transition series, d-orbitals used in hybridisation are $4d_{z2}$ and $4d_{x2-y2}$ orbitals. Since two d-orbitals are from the outer shell (i.e., nth shell), the octahedral complexes resulting from sp^3d^2 hybridisation are called **outer orbital octahedral complexes**. Since these complexes have a comparatively greater number of unpaired electrons than the inner orbital octahedral complexes, these are also called **high spin or spin free octahedral** complexes. Now let us discuss the structure of some octahedral complex ions of 3d transition series elements which are formed by sp^3d^2 hybridisation.

Hexafluroferrate (III) ion $[FeF_6]^{3-}$:

In this ion, the coordination number of Fe is six and hence the given complex ion has octahedral geometry. Here iron is present as Fe^{3+} whose valence shell electronic configuration is $3d^5\ 4s^0\ 4p^0$ or $t_{2g}^{\ 3}\ e_g^{\ 2}$. Each of the five electrons is unpaired and hence n = 5. Magnetic properties of the given ion have also shown that the ion has five unpaired electrons and hence is paramagnetic corresponding to the presence of five unpaired electrons. Thus two electrons residing in orbitals cannot be forced to occupy t_{2g} orbitals as we have done in case of $[Fe(CN)_6]^{3-}$ ion, otherwise the number of electrons would become equal to one.

Thus we find that in case of the given ion, the two d-orbitals used in hybridisation are $4d_{z2}$ and $4d_{x2-y2}$, (and not $3d_{z2}$ and $3d_{x2-y2}$ as in case of

$[Fe(CN)_6]^{3-}$ ion) and s and p orbitals are 4s and 4p. Thus the given ion results from (4s) ($4p^3$) ($4d_{z2}$) ($4d_{x2-y2}$) hybridisation as shown in Figure. This discussion shows that in the formation of $[FeF_6]^{3-}$ in the original valence-shell configuration of Fe^{3+} ion is not disturbed.

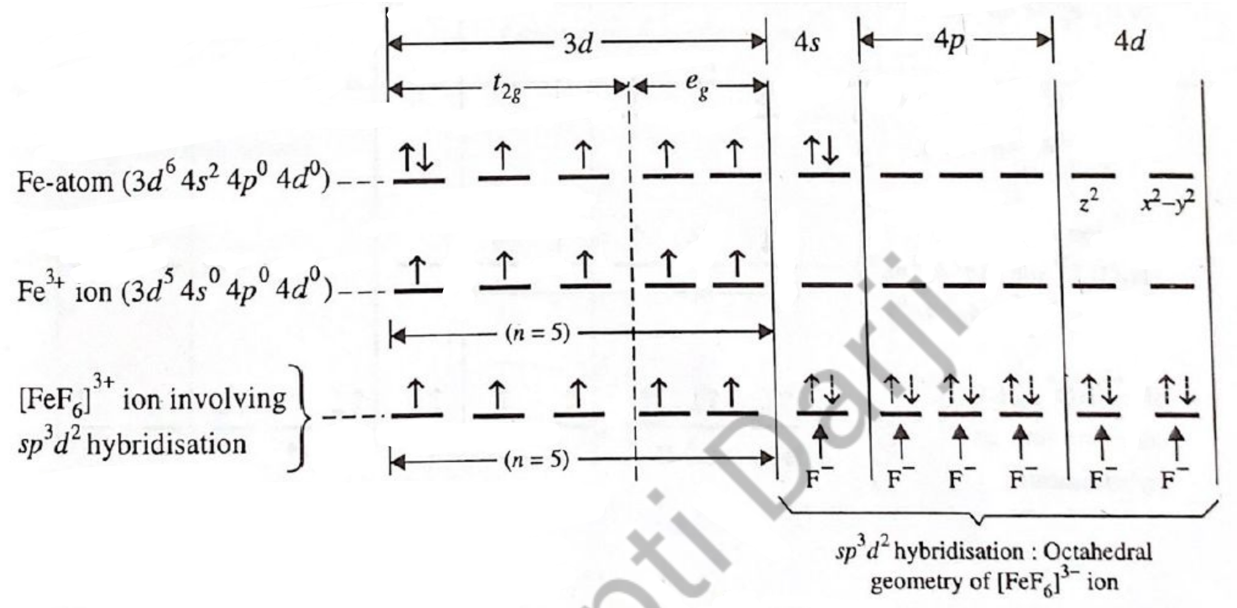


Fig. Formation of $[FeF_6]^{3-}$ ion by sp^3d^2 hybridisation. (Outer-orbital octahedral complex ion).

Differences between inner orbital and outer orbital octahedral complexes

Inner orbital octahedral complexes	Outer orbital octahedral complexes
(i) These are formed by d^2sp^3 hybridisation i.e.in the formation of six d^2sp^3 hybrid orbitals, two (n-1)d orbitals of e_g set, one ns and three np orbitals are used. (n-1)d orbitals belong to the inner (penultimate) shell while ns and np orbitals belong to the outer (ultimate) shell.	(i) These are formed by sp^3d^2 hybridisation i.e.in the formation of six sp^3d^2 hybrid orbitals, two nd orbitals of e_g set, one ns and three np orbitals are used. Thus all the orbitals belong to the outer (ultimate) shell.
(ii) These complexes have comparatively lesser number of unpaired electrons and hence are also called low spin or spin paired complexes.	(ii) These complexes have a comparatively greater number of unpaired electrons and hence are also called high spin or spin free complexes.
(iii) These are given by strong ligands.	(iii) These are given by weak ligands.

Geometry of 4-coordinate complex ions :

Examples of 4-coordinated complex ions formed by some transition metals. In these complex ions the coordination number of the central metal atom or ion is four. Such complex ions may have either square planar or tetrahedral geometry, depending on whether the central atom or ion is dsp^2 or sp^3 hybridised. What type of hybridisation (ie.. whether dsp^2 or sp^3) the central metal atom or ion of a 4-coordinated complex ion undergoes depends on the number of unpaired or paired electrons present in the complex ion.

(1) Square Planar geometry (dsp^2)

$[Ni(CN)_4]^{2-}$ Tetracyanonickelate(II) ion:

When $[NI(CN)_4]^{2-}$ion is square planar geometry, Ni^{2+} ion should be dsp^2 hybridised. In this hybridisation, due to the energy made available by the approach of four CN^- ions (ligands), the two unpaired 3d-electrons are paired up, thereby, making one of the 3d orbitals empty. This empty 3d orbital (which is $3d_{x2-y2}$ orbital) is used in dsp^2 hybridisation. This hybridisation makes all the electrons paired (n = 0) and hence is diamagnetic, as shown in Figure.

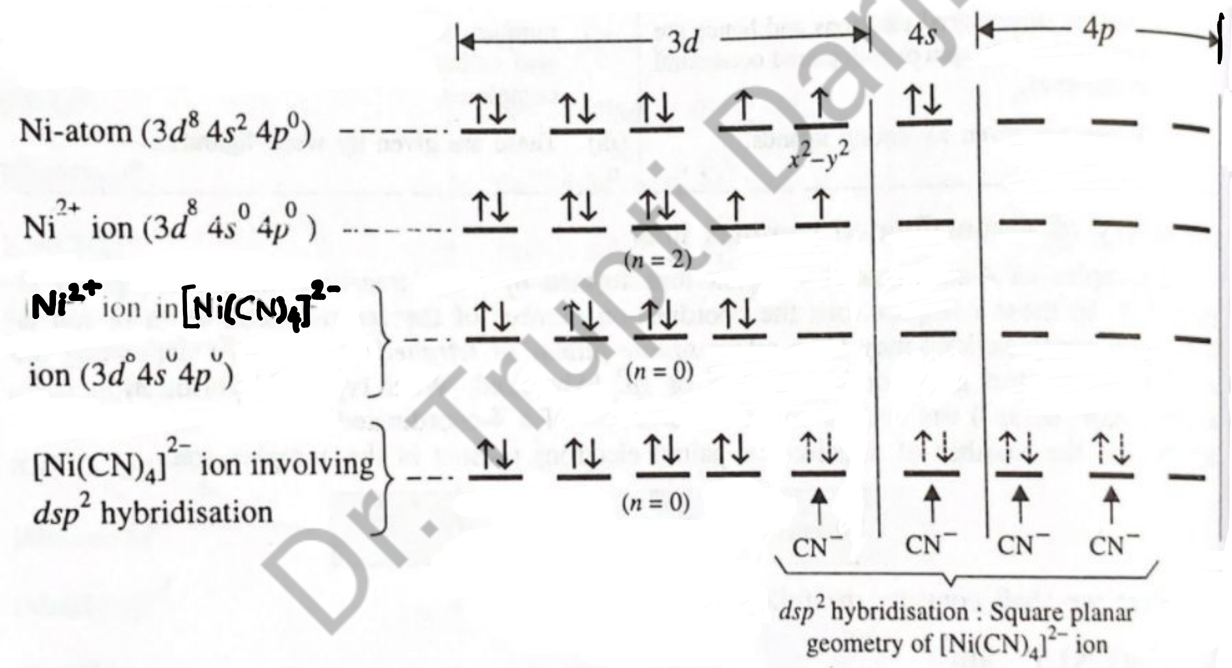
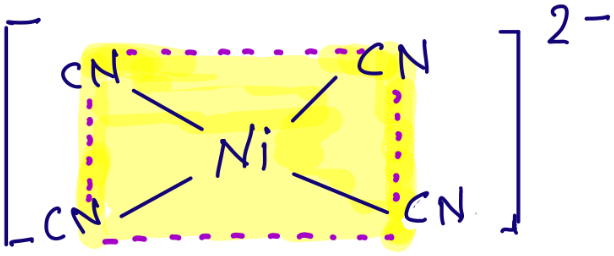


Fig. Formation of $[Ni(CN)_4]^{2-}$ ion by dsp^2 hybridisation (Square planar complex ion with n = 0)



(2) Tetrahedral geometry (sp^3)

A. [Ni(CO)$_4$] molecule (Tetracarbonylnickel) :

In this complex compound Ni is in zero oxidation state and has its valence-shell configuration as $3d^8 4s^2$. This compound has tetrahedral geometry which arises due to sp^3 hybridisation of Ni atom.

The magnetic studies of [Ni(CO)$_4$] have indicated that this molecule is diamagnetic (n = 0), showing that the two 4s electrons are forced to pair up with 3d orbitals. This results in sp^3 hybridisation and the [Ni(CO)$_4$] molecule has a tetrahedral structure in the figure.

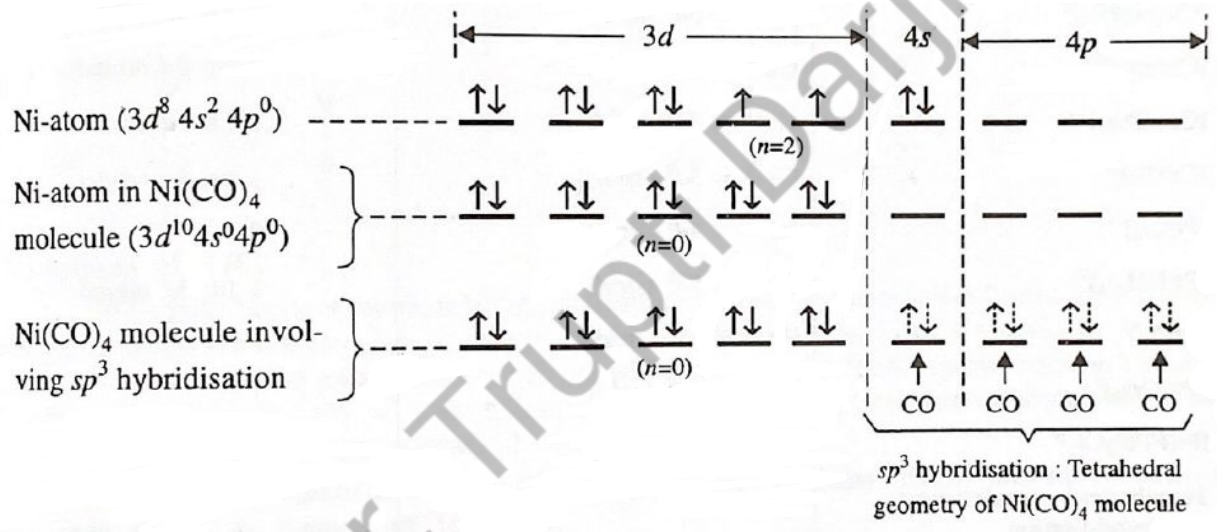
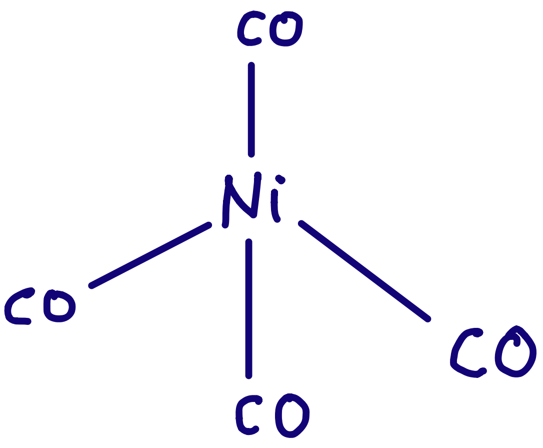
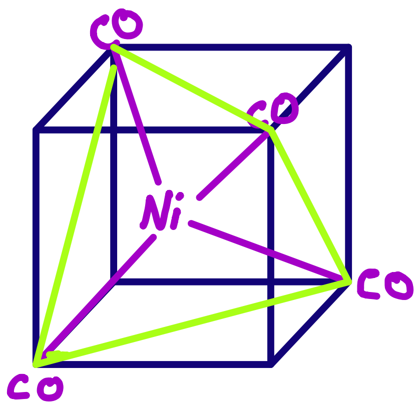


Fig. sp^3 hybridisation of Ni-atom in Ni(CO)4 molecule which has tetrahedral shape.





B. $[NICl_4]^{2-}$ ion (Tetrachloronickelate(II) ion) :

This complex ion has Ni^{2+} ion whose valence-shell configuration is $3d^8 4s^0$. Magnetic measurements reveal that the given ion is paramagnetic and has two unpaired electrons (n = 2). This is possible only when this ion is formed by sp^3 hybridisation and has tetrahedral geometry in the figure.

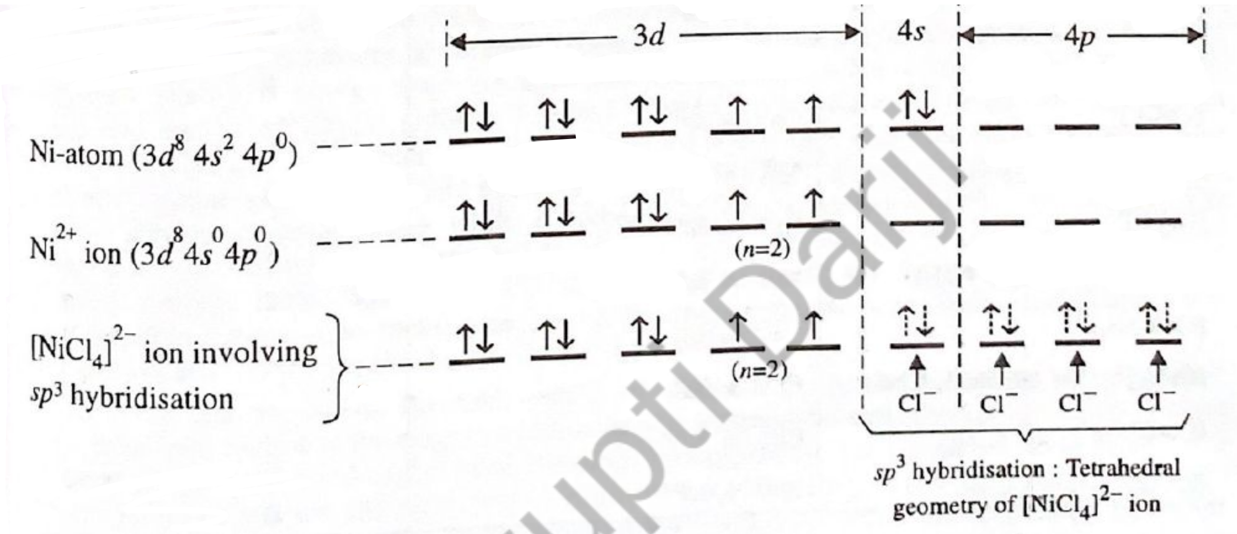


Fig. sp^3 hybridisation of Ni^{2+} ion in $[NiCl_4]^{2-}$ ion which has tetrahedral geometry.

Limitations of Valence bond theory :

(1) VBT cannot account for the relative stabilities of different shapes and different coordination numbers in metal complexes, e.g., it cannot explain satisfactorily as to why Co(+2) (d^8 system) forms both octahedral and tetrahedral complexes while Ni(+2) (d^7 system) rarely forms tetrahedral complexes.

(2) VBT cannot explain as to why Cu(+2) forms only one distorted octahedral complex even when all the six ligands are identical.

(3) This theory cannot account for the relative rates of reactions of analogous metal complexes. e.g. $[Mn(phen)_3]^{2+}$ dissociates instantaneously in acidic aqueous solution while $[Fe(phen)_3]^{2+}$dissociates at a slow rate.

(4) The classification of metal complexes on the basis of their magnetic behaviour into covalent (inner-orbital) and ionic (outer-orbital) complexes is not satisfactory and is often misleading.

(5) VBT fails to explain the finer details of magnetic properties including the magnitude of the orbital contribution to the magnetic moments, i.e. although both tetrahedral (sp^3 hybridisation) and outer-orbital octahedral (sp^2d^2 hybridisation) complexes of Co(+2) (d^7 system) have three unpaired electrons and are, therefore, expected to have μ value equal to 3.87 B.M.; the tetrahedral complexes generally have μ value in the range of 4.4 - 4.8 B.M., while the octahedral complexes have still higher value of μ in the range of 4.7 - 5.2 B.M. The increase in the value of μ is due to the orbital contribution. Similar is the case with tetrahedral and octahedral complexes of Ni(+2) (d^8 system). VBT cannot explain the increase in the value of μ.

(6) VBT cannot interpret the spectra (colour) of the complexes.

(7) This theory does not predict or explain the magnetic behaviours of complexes. This theory only predicts the number of unpaired electrons. Its prediction even for the number of unpaired electrons and their correlation with stereochemistry is misleading. VBT cannot explain the temperature dependent paramagnetism of the complexes.

(8) VBT cannot give any explanation for the order of reactivities of inner-orbital inert complexes of d^3, d^4, d^5 and d^6 ions of the observed differences in the energies of activation in a series of similar complexes.

(9) The magnetic moment values of the complexes of certain ions (e.g., Co^{2+}, Ni^{2+} etc.) are much higher than those expected by spin-only formula. VBT can not explain the enhanced values of magnetic moments.