## Valence Bond Theory:

The valence bond theory is based on covalent interactions between the central metal and the ligands. According to VBT there is a direct covalent coordinate bond between a ligand and the CMA/CMI. (Remember a coordinate bond can be σ or π)

- The central metal loses a fixed number of electrons thus creating vacant orbitals and increasing the Zeff (force of attraction exerted by nucleus) of CMA/CMI.
- This facilitates the gain of electron pairs by the CMA from various ligands since a greater force of attraction of the nucleus pulls the ligands towards itself.
- The vacant orbitals hybridize to form new hybrid orbitals equal to the number of electron pairs to be accepted i.e. coordination number or rightfully called steric number.
- Thus coordination number is one of the major factors deciding the geometry of a complex along with the nature of the ligand.
- A strong ligand can alter the configuration of the core or the central metal ion by causing forced pairing against Hund's rule of maximum multiplicity whereas a weak ligand cannot alter the configuration of the central metal atom or ion e.g. CN^- will alter the configuration of Co^{+2} ion as under:

Co^{+3}: $3d^6$
4 unpaired electrons

$\xrightarrow[\text{forced pairing}]{\substack{CN^- \\ \text{SFL causing}}}$

Co^{+3}: $3d^6$
0 unpaired electrons
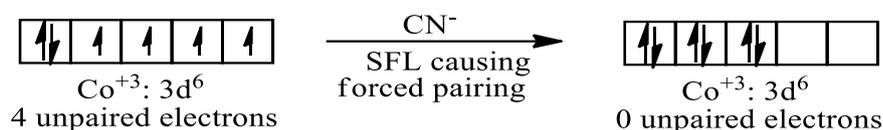
Thus it can be seen that the presence of a strong field can reduce the number of unpaired electrons by forcefully pairing them against Hund's rule. This may also result in the creation of vacant orbitals in the other filled inner d orbitals.

- The ligand with C and N donor atoms are generally strong ligands whereas the ones with O and halide donor atoms are weak ligands. **Order of strength of ligands with donor atoms C > N > O > X.**
- The exact order of the strength of the ligand depends on various other factors other than the donor atom, such as its ability to act as σ donor and π acceptor, donating ability etc. Based on all these factors various ligands can be arranged in increasing or decreasing order of their strength. This series of ligands arranged in decreasing order of their strength is determined experimentally and is called the spectrochemical series. The spectrochemical series is as under:

## (A). COORDINATION NUMBER 6 OR OCTAHEDRAL GEOMETRY:

In complexes with coordination number six, the total number of electron pairs accepted by the central metal atom or ion will be equal to 6. Thus six atomic orbitals of the central atom will mix or hybridize to form six new hybrid orbitals. Depending on the d orbitals participating (inner d or outer d), the hybridization will be d^2sp^3 or sp^3d^2. In both cases the geometry obtained will be octahedral.

The exact hybridization of the central atom (sp^3d^2 or d^2sp^3) in various octahedral complexes can be found on the basis of counting six vacant orbitals of lowest energy e.g. in the complex ion $[FeF_6]^{-3}$,

if the oxidation number of Fe is x, then using charge balance: $x + 6(-1) = -3$; $x = +3$. So, Fe ($3d^64s^2$) is present as Fe^{+3} ion ($3d^54s^0$).

3d   4s   4p   4d
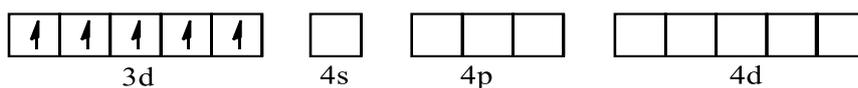
Here the ligand is F^- & it is a weak ligand (since the donor atom is halide) thus no forced pairing will occur, and the electron pairs will be accepted as under:

4s   4p   4d

F^- F^- F^- F^- F^- F^-
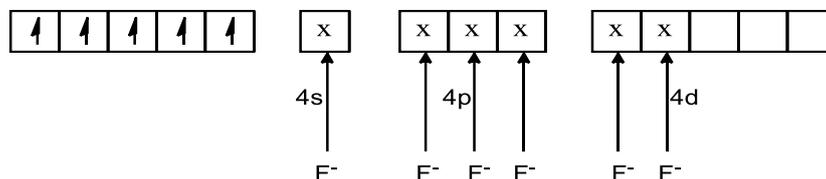
It can be seen that the d orbitals used in the hybridization and accepting electron pairs from the ligands are the outer d orbitals (4d), thus the hybridization is sp^3d^2 and therefore the geometry of the complex will be octahedral. Since the outer d orbitals are involved in hybridization (sp^3d^2) such complexes are called outer orbital complexes. Some other important aspects are:

- Number of unpaired electron(n) = 5;
- Magnetic moment (μ) = $\sqrt{n(n+2)}$ BM = $\sqrt{35}$ BM

Since the number of unpaired electrons in Fe^{+3} ion is not reduced by the presence of a weak field ligand, a high value of magnetic moment is observed. Such complexes are called high spin complexes.

→ Now let us analyze a similar complex compound of Fe^{+3} ion but with a strong field ligand instead of a weak field ligand having a coordination number of six e.g. in the complex ion $[Fe(CN)_6]^{-3}$, the oxidation number of iron is +3 using charge balance. Thus the Fe^{+3} ion is present having an electronic configuration of $3d^54s^0$.

3d   4s   4p   4d
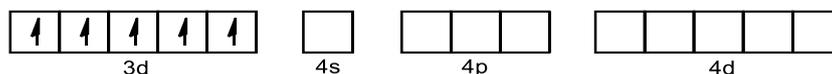
Here the ligand is CN^- and it is a strong field ligand (since the donor atom is C). The presence of the strong field ligand will cause forced pairing against Hund's rule as under:

Fe^{+3}: $3d^5$ $\xrightarrow[\text{SFL causing forced pairing}]{CN^-}$ Fe^{+3}: $3d^5$
5 unpaired electrons   1 unpaired electrons
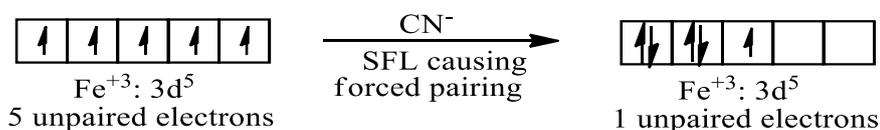
Now since due to forced pairing the two inner d orbitals are available to participate in hybridization and consequently accept electron pairs from the ligands as under:

3d   4s   4p
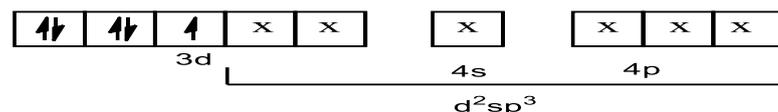
d^2sp^3

It can be seen that the d orbitals used in the hybridization are the inner d orbitals (3d) instead of the outer d orbitals (4d), thus the hybridization is d^2sp^3 and the geometry will be octahedral. Since the inner d orbitals are involved in hybridization (d^2sp^3) such complexes are called inner orbital complexes. Some other important aspects are:

- Number of unpaired electron(n) = 1;
- Magnetic moment (μ) = $\sqrt{n(n + 2)}$ BM = $\sqrt{3}$ BM

Since the number of unpaired electrons in Fe^{+3} ion is reduced (from 5 to 1) by the presence of a strong field ligand, a low value of magnetic moment ($\sqrt{3}$ BM instead of $\sqrt{35}$ BM) is observed. So these type of complexes are called Low spin complexes.

$\rightarrow$ It must not be misunderstood that the presence of a strong field ligand will always cause forced pairing or will lead to the formation of an inner orbital or low spin complex. In many cases forced pairing in not observed even in the presence of a strong field ligand. Generally, a strong field ligand causes forced pairing if there is the possibility of the formation of an inner orbital complex after forced pairing. Some important examples of complexes with coordination number 6 are explained below and one must try to understand the procedure of analyzing a complex:

(1). *$[Ti(CN)_6]^{-4}$*

$x + 6(-1) = -4;$ $\qquad$ $x = +2;$ $\qquad$ $Ti^{+2}: 3d^2 4s^0$
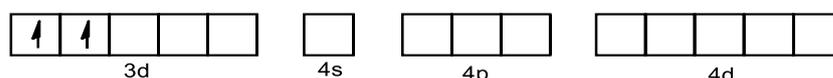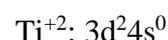
- Here CN^- is the ligand and is a SFL which can force pair but for inner orbital complex formation force pairing is not required since two inner d orbitals are already vacant and available for participating in hybridization. Thus no force pairing will occur.


d^2sp^3, octahedral geometry
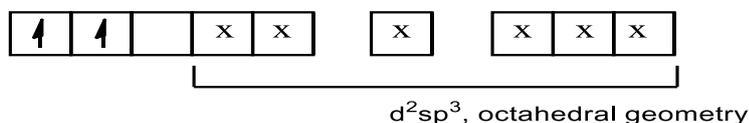
- Hybridization: d^2sp^3 – Inner orbital complex – Geometry: Octahedral
- Unpaired electrons (n) = 2; $\mu = \sqrt{2 \times (2 + 3)} = \sqrt{8}$ BM; Paramagnetic.

$\rightarrow$ **Thus in octahedral complex with configuration of CMA/CMI as d^1, d^2 and d^3, always inner orbital complex is formed with d^2sp^3 hybridization regardless of the nature of ligand. i.e.**

$[Ti(H_2O)_6]^{+2}, [Ti(CO)_6]^{+2}, [Ti(ox)_3]^{-4}$

$[Sc(H_2O)_6]^{+2}, [Sc(CO)_6]^{+4,} [Sc(NH_3)_6]^{+2}, [Sc(ox)_3]^{-4}$ $\qquad d^2sp^3$

$[V(CO)_6]^{+2}, [V(CN)_6]^{-2}, [V(H_2O)_6]^{+3}$

(2). *$[Ni (H_2O)_6]^{+2}$*

$x + 6(0) = +2 ;$ $\qquad$ $x = +2 ;$ $\qquad$ $Ni^{+2} : 3d^8 4s^0$
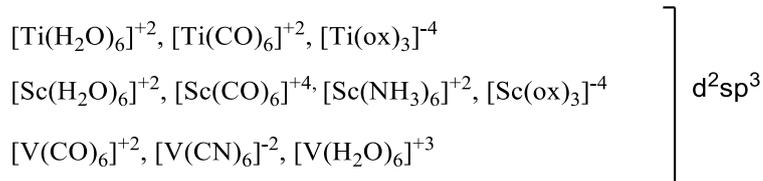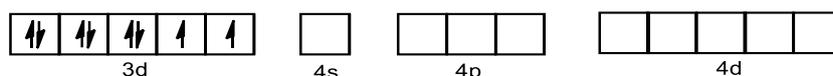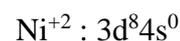
- H_2O is a weak ligand so no forced pairing will occur.
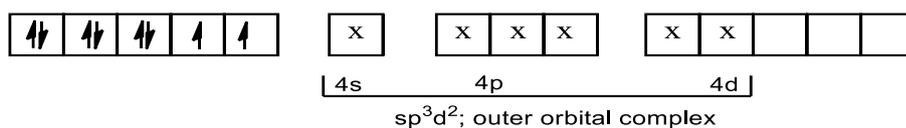
↑↓	↑↓	↑↓	↑	↑		x		x	x	x		x	x			

|← 4s →|← 4p →|← 4d →|

sp^3d^2; outer orbital complex

- Hybridization: sp^3d – Outer orbital complex   – Geometry: Octahedral
- Unpaired electrons (n) = 2;   – Magnetic moment (μ) = $\sqrt{8}$ BM;
- Paramagnetic nature.

(3).   *$[Ni(CN)_6]^{-4}$*

$x + 6(-1) = -4;$ $x = +2;$ $Ni^{+2}: 3d^8\ 4s^0$

↑↓	↑↓	↑↓	↑	↑											

    3d   4s   4p   4d
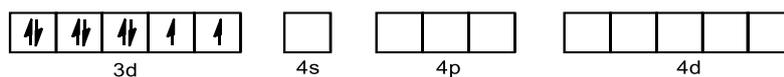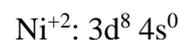
CN^- is a strong field ligand and can cause forced pairing but inner orbital complex cannot be formed even after forced pairing since only one inner d orbital will be available and the formation of an octahedral complex requires two vacant orbitals either inner or outer. Thus no purpose or necessity of forced pairing thus it will not occur so.
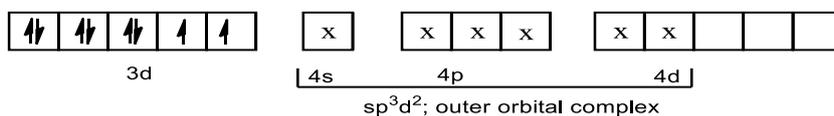
↑↓	↑↓	↑↓	↑	↑		x		x	x	x		x	x			

    3d |← 4s →|← 4p →|← 4d →|

sp^3d^2; outer orbital complex

- Hybridization: sp^3d – Outer orbital complex   – Geometry: Octahedral

- Unpaired electrons (n) = 2; Magnetic moment (μ) = $\sqrt{8}$ B; Paramagnetic.

→ **Thus, in octahedral complexes with configuration of CMA/CMI as d^8, d^9 and d^{10} always outer orbital complex is formed with sp^3d^2 hybridization regardless of nature of ligand i.e.**

sp^3d^2 outer orbital complexes $\begin{cases} [Ni(H_2O)_6]^{+2},\ [Ni(CN)_6]^{-4},\ [Ni(CO)_6]^{+2} \\ [Cu(NH_3)_6]^{+2},\ [Cu(H_2O)_6]^{+2},\ [Zn(NH_3)_6]^{+3} \\ [Zn(H_2O)_6]^{+2},\ [Zn(CN)_6]^{-4} \end{cases}$
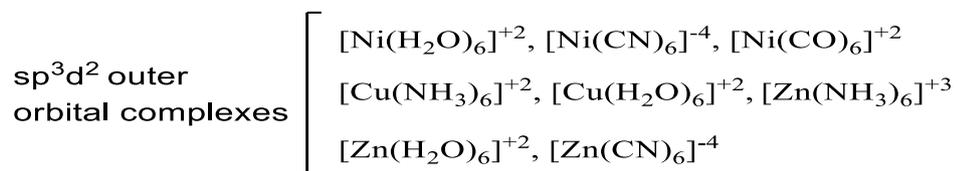
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