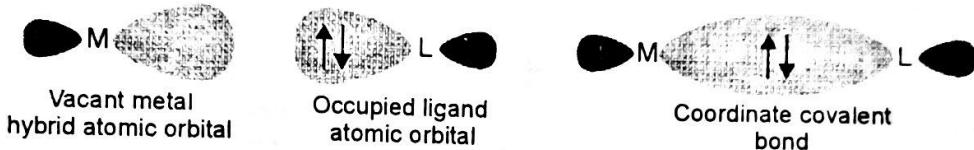


METAL-LIGAND BONDING IN TRANSITION METAL COMPLEXES

1.1. VALENCE BOND THEORY

Valence bond theory was developed by Linus Pauling. According to valence bond theory, the bonding in metal complexes arises when a filled ligand orbital containing a pair of electrons overlaps with a vacant hybrid orbital on the metal/metal ion to give a coordinate covalent bond.



Thus, *valence bond theory assumes the bonding between the metal/metal ion and the ligands to be purely covalent*. The hybrid orbitals that a metal atom/ion uses in accepting the pair of electrons from the ligands are those that point in the directions of the ligands.

Valence bond theory successfully explains the structures and magnetic properties of coordination compounds. The salient features of the theory are recapitulated below :

1. The central metal atom or ion in the coordination compounds offers a number of vacant orbitals which is equal to the coordination number of the metal atom/ion for the formation of coordinate bonds with the ligands.
2. The approximate atomic orbitals (*s*, *p* and *d*) of the metal hybridise to give a new set of orbitals of equivalent energy called the *hybrid orbitals*. These hybrid orbitals are directed towards the ligands depending upon the geometry of the coordination complex.
3. The *d*-orbitals involved in the hybridisation may be either inner ($n - 1$) *d*-orbitals or outer (*nd*) orbitals. Thus, hybridisation in case of octahedral complex may involve d^2sp^3 or sp^3d^2 depending upon whether inner or outer *d*-orbitals are used for hybridisation.
4. The vacant hybrid orbitals of the metal/metal ion overlap with the filled (or occupied) orbitals of the ligands and form a coordinate bond *i.e.*, ($L \rightarrow M$) bond.

Let us take some examples to highlight the features of valence bond theory to complexes with coordination number 4 and 6.

Complexes with Coordination number 4

Coordination compounds with coordination number 4 are well known. Complexes with coordination number 4 can be either tetrahedral or square planar depending upon whether the hybridisation is sp^3 or dsp^2 respectively. Some of the most commonly found examples are described below :

1. Formation of $[\text{Ni}(\text{CN})_4]^{2-}$ ion

The oxidation state of nickel in the complex ion, $[\text{Ni}(\text{CN})_4]^{2-}$ is +2. We can represent the electronic configuration of Ni^{2+} ion by losing two electrons from the outermost 4s orbital. Electronic configuration of Ni ($Z = 28$) is $_{18}[\text{Ar}] 3d^8 4s^2$

Thus, the electronic configuration of Ni^{2+} ion is $_{18}[\text{Ar}] 3d^8$

Eight electrons present in the d -orbitals of Ni^{2+} will occupy in such a way that we shall have three of the 3d orbitals occupied by two electrons while the remaining two 3d-orbitals are singly occupied as shown in Fig. 1.1. There are two ways in which the coordination complexes of nickel with coordination number 4 can be formed. If the complex involves sp^3 hybridisation, it will have tetrahedral structure. On the other hand, if the complex involves dsp^2 hybridisation it will have a square planar structure.

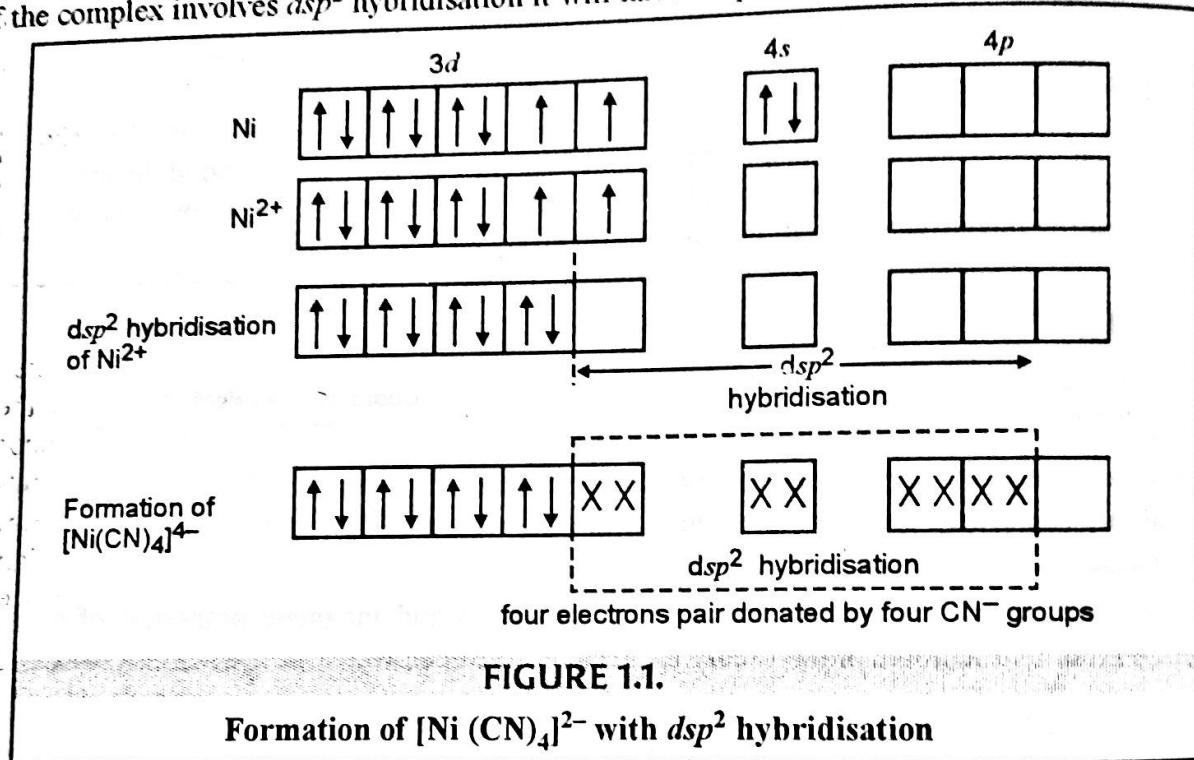


FIGURE 1.1.

Formation of $[\text{Ni}(\text{CN})_4]^{2-}$ with dsp^2 hybridisation

In case the complex ion acquires tetrahedral structure the hybridisation is sp^3 . It means that the two unpaired 3d electrons are not affected. As a result, the coordination compound with sp^3 hybridisation will be paramagnetic (as is the case with Ni^{2+} ions itself).

However, the square planar structure, which involves dsp^2 hybridisation, requires one of the 3d-orbital vacant for hybridisation. This is possible only if the two unpaired 3d-electrons are paired up. Pairing makes one of the 3d-orbitals empty. During this exercise, no unpaired electrons are left and the complex should be diamagnetic.

It has been experimentally observed that the complex $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic which conclusively indicates that the hybridisation is dsp^2 and secondly it has no unpaired electrons as shown in the Fig. 1.1.

2. Formation of $[\text{NiCl}_4]^{2-}$

The oxidation number of nickel in $[\text{NiCl}_4]^{2-}$ is +2. This is obtained by the loss of two electrons from the 4s-orbital of nickel as shown in the Fig. 1.2.

Experimentally, the complex has been found to be paramagnetic corresponding to two unpaired electrons. It implies that the 3d orbitals are not disturbed and the complex involves sp^3 hybridisation. As a result, the structure of the complex is *tetrahedral* as shown in the scheme below.

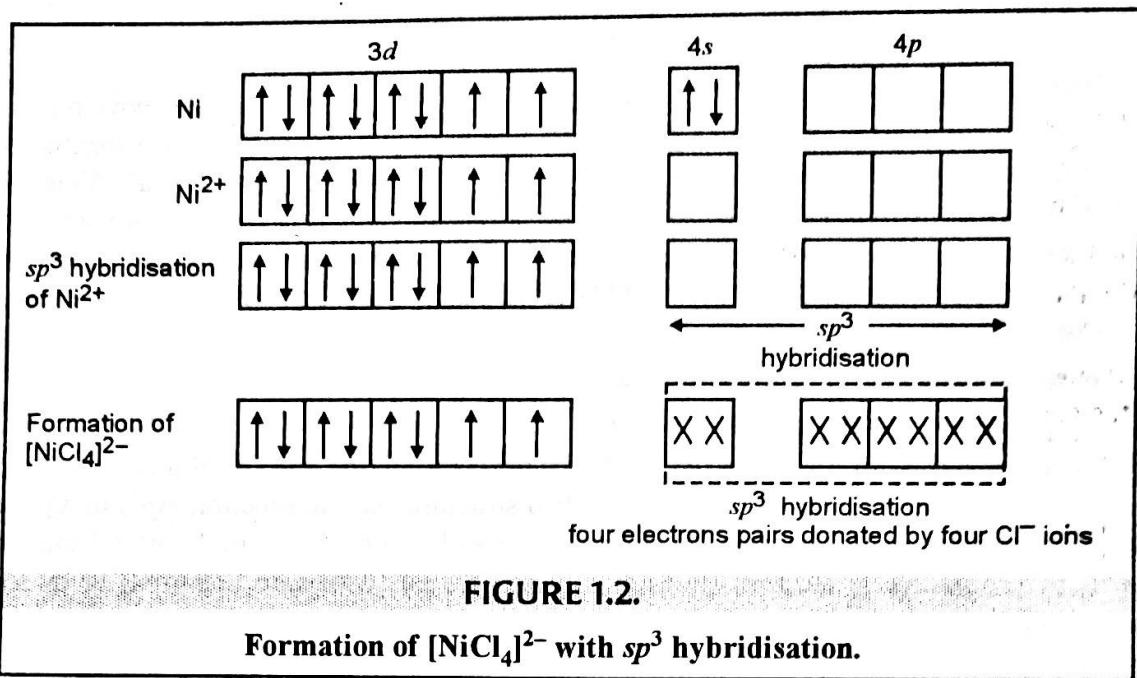


FIGURE 1.2.

Formation of $[\text{NiCl}_4]^{2-}$ with sp^3 hybridisation.

3. Formation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$

An inspection at the complex, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ reveals that the oxidation state of copper in the complex is +2. The resulting electronic configuration of Cu²⁺ is $_{18}[\text{Ar}] 3d^9$. According to Hund's rule, the nine d -electrons occupy the five $3d$ -orbitals and only one orbital is singly occupied. In order to accommodate four ammonia molecules around Cu²⁺, the metal ion exhibit two possible geometrical arrangements for the complex. If the complex is tetrahedral, it will involve sp^3 hybridisation and the complex will be *paramagnetic*. On the other hand, if the complex happens to be square planar, it will involve dsp^2 hybridisation and the complex will be *paramagnetic* again. Now a natural question arises which of the two structures of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is true i.e., tetrahedral or square planar.

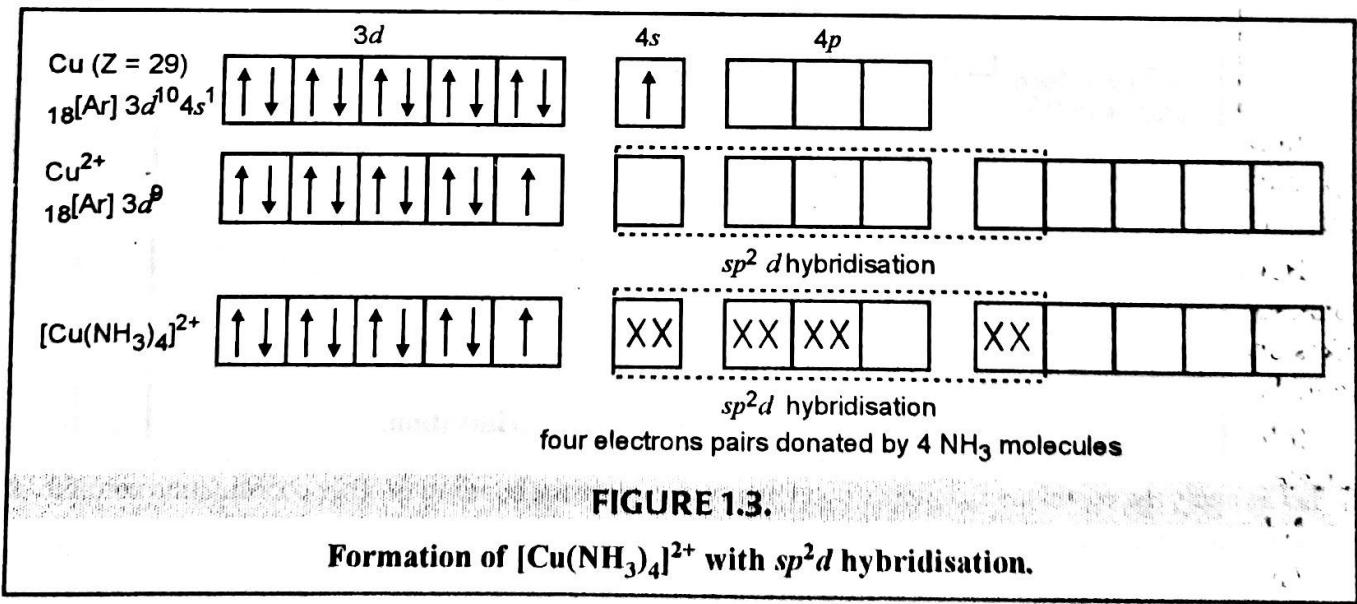


FIGURE 1.3.

Formation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ with sp^2d hybridisation.

Crystal structure determination of the compound has revealed that the complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ has the square planar structure. It implies that dsp^2 hybridisation must be involved with one of the $3d$ orbital made available for hybridisation. This can be done by promoting one electron of the $3d$ -orbital to a higher energy vacant $4p$ orbital. Once the electron is promoted into the higher energy orbital, it becomes unstable and can be lost easily. It means that Cu²⁺ complex can be easily oxidised to Cu⁺³ complex.



However, it is not true because Cu^{3+} ions are practically unknown. In brief, the above representation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion is inadequate. Although it explains the square planar geometry together with the magnetic moment of the complex, it fails to explain that Cu^{2+} can be easily oxidised to Cu^{3+} . This anomalous behaviour can be easily answered if it is considered that the electrons in the $3d$ orbitals are not perturbed at all and the hybridisation involves outer $4d$ orbitals. This model explains not only the square planar geometry together with magnetic moment but also the stability of Cu^{2+} ions (which do not undergo easy oxidation to Cu^{3+} by loss of electron).

4. Formation of $[\text{Ni}(\text{CO})_4]$

$[\text{Ni}(\text{CO})_4]$ is a *unique* compound in which the oxidation state of nickel is zero. The electronic configuration of nickel ($Z = 28$) is $_{18}[\text{Ar}] 3d^8 4s^2$. Since the coordination number of nickel in tetracarbonyl nickel is 4, the compound can acquire either of the two structures *i.e.*, tetrahedral (sp^3) or square planar (dsp^2). Since in both the cases, $4s$ orbitals are used in hybridisation, therefore $4s$ orbital must be made vacant either by promoting $4s$ electrons to higher energy orbital (with spin unpaired) or by forcing $4s$ electrons to occupy the vacant $3d$ orbital with spin paired.

In the first case where the $3d$ electrons are promoted to occupy higher energy $4d$ orbitals, the compound $[\text{Ni}(\text{CO})_4]$ will be paramagnetic as the electrons are not spin paired. On the other hand, when the electrons are forced to occupy the $3d$ -orbitals, the compound $\text{Ni}(\text{CO})_4$ will be *diamagnetic* because the forced $4s$ electrons have no other option but to pair with the two unpaired electrons sitting in the $3d$ orbitals. Since the compound, $[\text{Ni}(\text{CO})_4]$ has experimentally been found to be diamagnetic (no-unpaired electrons) the nickel atom prefers to involve sp^3 hybridisation as shown.

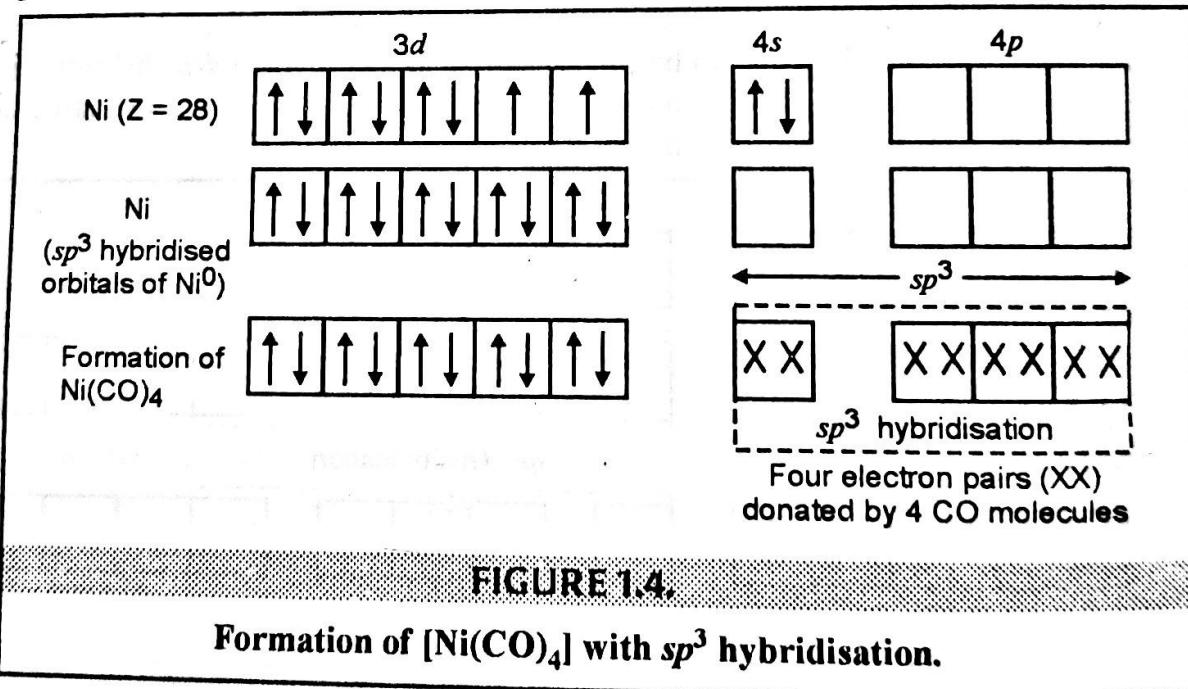


FIGURE 1.4.
Formation of $[\text{Ni}(\text{CO})_4]$ with sp^3 hybridisation.

Let us apply the postulates of valence bond theory to explain the bonding in other coordination complexes with coordination number 6.

Examples of Complexes with Coordination number 6

1. Formation of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ complex ion

The oxidation state of chromium in $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ion is +3. The electronic configuration of chromium ($Z = 24$) is $_{18}[\text{Ar}] 3d^5 4s^1$. Thus, chromium in +3 oxidation state is formed by the loss of one $4s$ and two $3d$ electrons as shown.

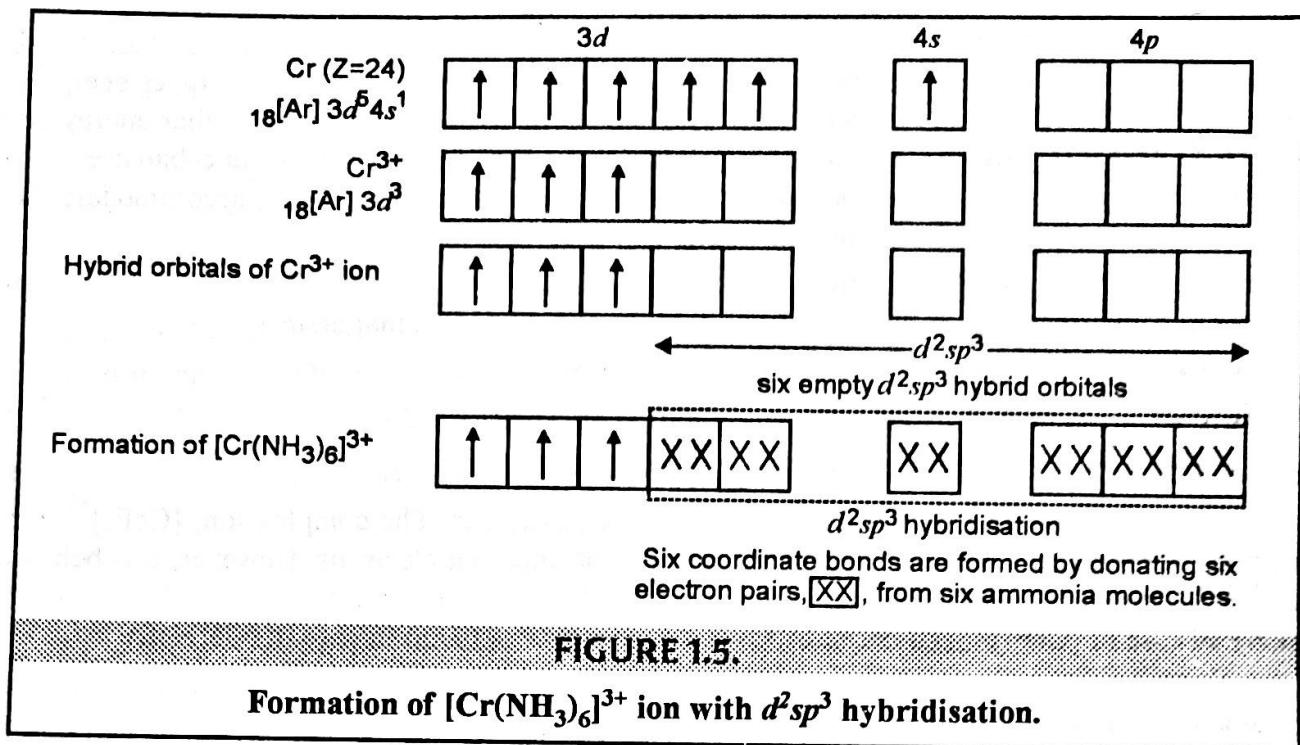


FIGURE 1.5.

Formation of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ion with d^2sp^3 hybridisation.

Two vacant $3d$ orbitals, one $4s$ and three $4p$ orbitals of chromium are hybridised to give six d^2sp^3 hybrid orbitals. In other words, Cr^{3+} provides six empty orbitals to accommodate six pairs of electrons from six molecules of ammonia. The resulting complex, $[\text{Cr}(\text{NH}_3)_6]^{3+}$ involves d^2sp^3 hybridisation and is octahedral. The presence of three unpaired electrons in the complex makes it paramagnetic.

2. Formation of $[\text{Co}(\text{NH}_3)_6]^{3+}$

The electronic configuration of cobalt ($Z = 27$) is $18[\text{Ar}] 3d^7 4s^2$. The oxidation state of cobalt in the complex is +3, which is obtained by the loss by two $4s$ and one $3d$ electron. Thus, the electronic configuration of Co^{3+} is $18[\text{Ar}] 3d^6$ as shown below

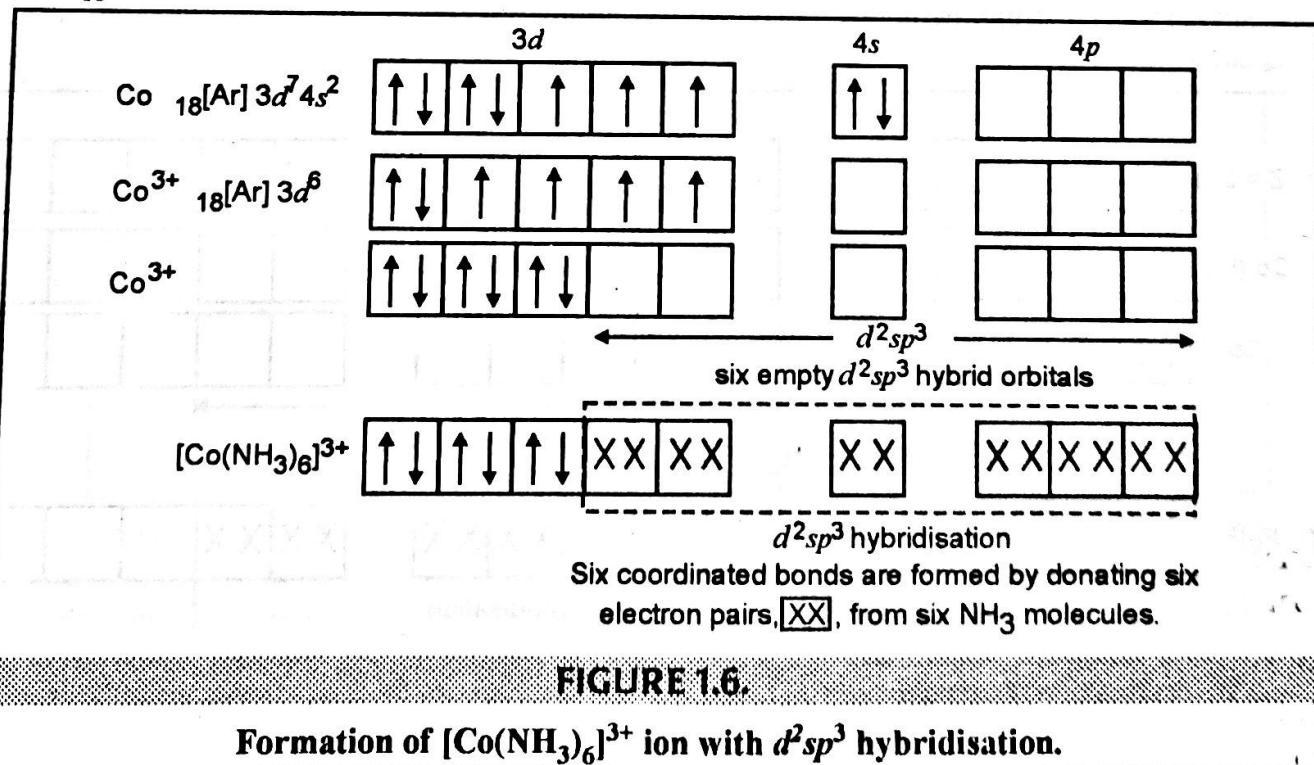


FIGURE 1.6.

Formation of $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion with d^2sp^3 hybridisation.

In this arrangement, there are four unpaired electrons and one paired electrons in the $3d$ orbitals. In order to acquire octahedral geometry, the complex should have d^2sp^3 hybridisation. This can be achieved in

two ways. The two electrons in the $3d$ orbitals are either paired up with electrons in the other $3d$ orbitals, thus leaving the other $3d$ orbitals empty. Or the two $3d$ electrons can be pushed into higher energy vacant $4d$ or $5s$ orbitals. Since pairing of electrons require less energy than promoting to higher energy orbitals, the electrons prefer to pair up. Two vacant $3d$ orbitals, one $4s$ and three $4p$ orbitals of cobalt are hybridised to give six d^2sp^3 hybrid orbitals. In other words, Co^{3+} provides six empty orbitals to accommodate six pairs of electrons from six molecules of ammonia as shown in Fig. 1.6.

Since there are no unpaired electrons in the $3d$ orbitals in the complex ion, $[\text{Co}(\text{NH}_3)_6]^{3+}$, it should be diamagnetic. Experimentally, it has been found that the complex is diamagnetic.

3. Formation of $[\text{CoF}_6]^{3-}$

As already discussed, the electronic configuration of cobalt ($Z = 27$) is $_{18}[\text{Ar}] 3d^7 4s^2$. The oxidation state of cobalt in CoF_6^{3-} is +3, which is easily achieved by losing two electrons from $4s$ and one electron from $3d$ orbital. The electronic configuration of Co^{3+} is $_{18}[\text{Ar}] 3d^6$. The complex ion, $[\text{CoF}_6]^{3-}$ has been found to be *paramagnetic* which suggests the presence of unpaired electrons. However, this behaviour is altogether different from what we observed in case of $[\text{Co}(\text{NH}_3)_6]^{3+}$. It amounts to saying that the octahedral geometry in case of $[\text{CoF}_6]^{3-}$ can not be attributed to $d^2 sp^3$ as is found in case of $[\text{Co}(\text{NH}_3)_6]^{2+}$.

In an effort to explain this distinct behaviour, Lewis Pauling suggested that the complex $[\text{CoF}_6]^{3-}$ is ionic and the metal-ligand bonds are ionic. This appeared justified *at that time* in view of the highly electronegative character of F^- , fluoride ion. However, it was soon discovered that other complexes like $[\text{Co}(\text{H}_2\text{O})_3 \text{F}_3]$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Ni}(\text{H}_2\text{O})_6]^{3+}$ were found to be paramagnetic. Since the bonding between metal and water ($M = \text{Co, Fe and Ni}$) in these compounds can not be ionic, it suggests that Pauling's formulation of ionic bond between metal and the ligand is not correct.

An alternative explanation was proposed by Huggins in 1937 to explain the anomalous magnetic behaviour of $[\text{CoF}_6]^{3-}$ by suggesting that the metal can use outer d -orbitals for hybridisation in place of inner d -orbitals. This formulation keeps the inner d -orbitals undisturbed and uses the outer $4d$ orbitals for hybridisation as shown below. Thus, six $sp^3 d^2$ hybrid orbitals are formed from one $4s$, three $4p$ and two $4d$ orbitals. Six pairs of electrons are donated to the six vacant hybrid orbitals of the metal forming six $\text{Co}-\text{F}$ bonds as shown in Fig. 1.7.

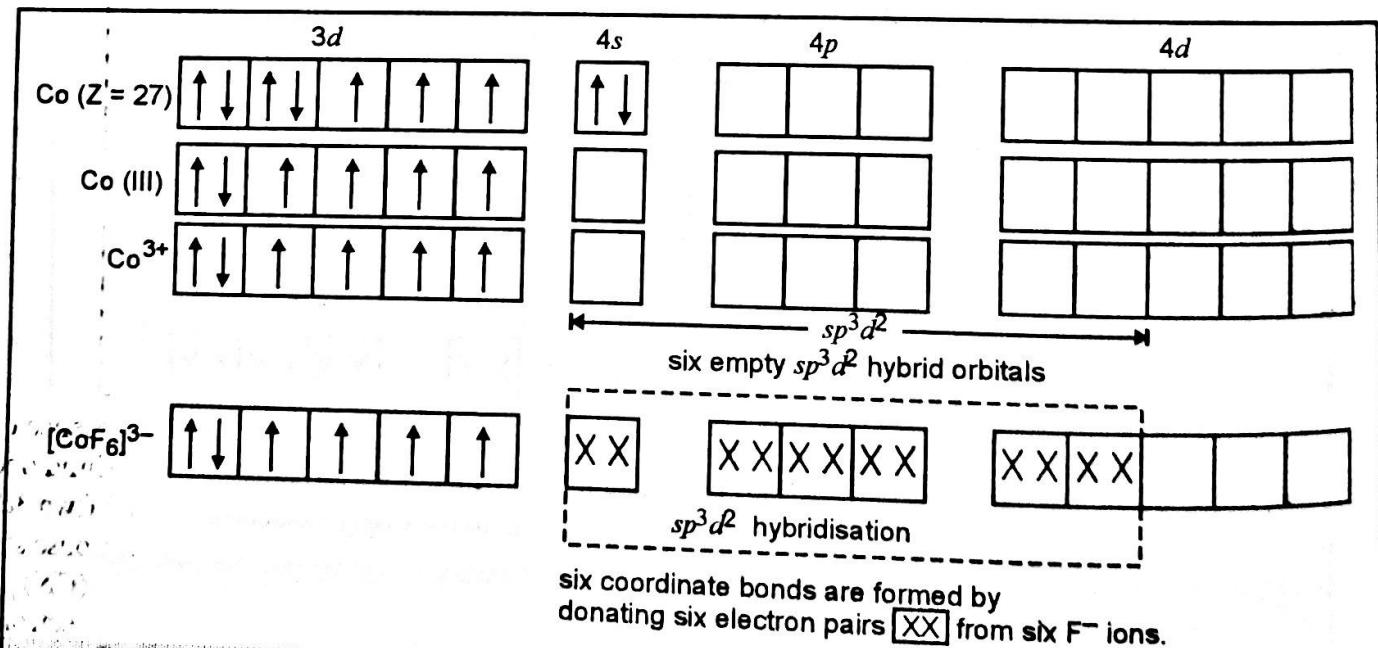


FIGURE 1.7.
Formation of $[\text{CoF}_6]^{3-}$ ion with sp^3d^2 hybridisation.

It is clear from the above discussion, that the central metal atom/ion has the ability to use either inner $(n - 1)d$ -orbitals or outer nd orbitals for hybridisation depending upon the ligand and the magnetic property of the complex.

In case the coordination complex uses the inner $(n - 1)d$ -orbitals for hybridisation (d^2sp^3), it is called the **inner orbital complex**. On the other hand, if the coordination complex uses the outer nd -orbitals for hybridisation (sp^3d^2), it is called the **outer orbital complex**.

In case of inner orbital complex, the metal electrons prefer to pair up. As a result, the complex will be either completely paired or will have lesser number of unpaired electrons. This type of complex formed is called **low spin complex**. On the other hand, in case of outer orbital complex, the electrons of the metal prefer to remain unpaired. As a result the complex will have more number of unpaired electrons. This type of complex formed is called **high spin complex**.

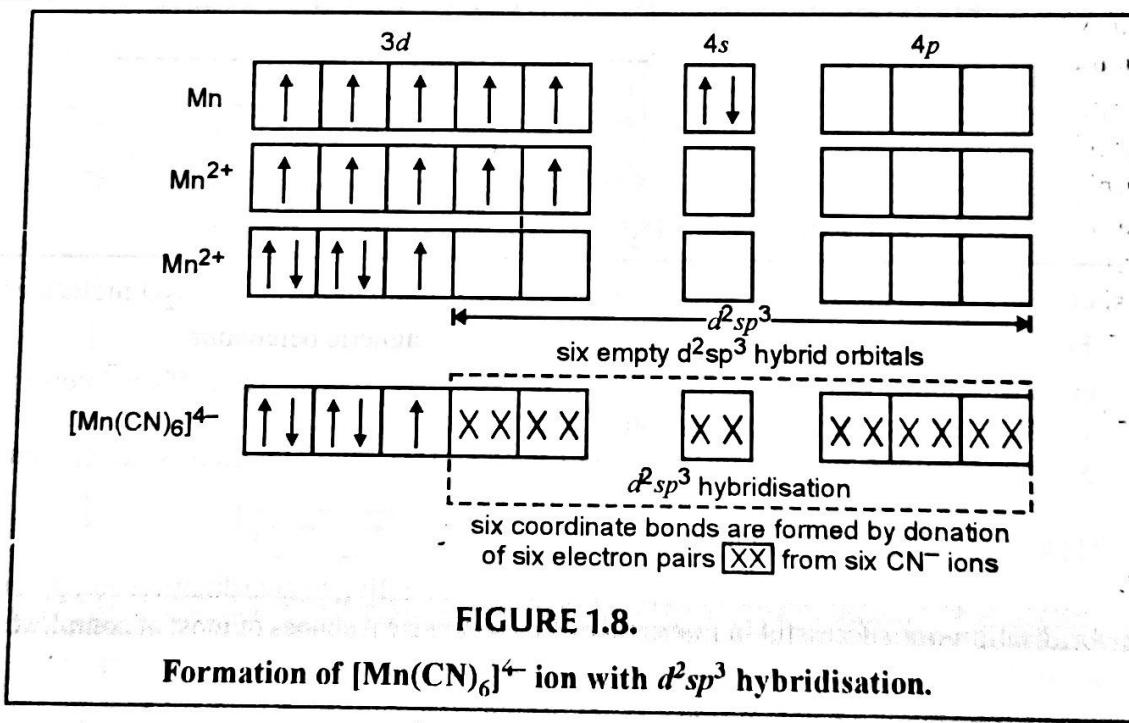
In brief

Outer orbital complexes (sp^3d^2) \Rightarrow High spin complexes

Inner orbital complexes (d^2sp^3) \Rightarrow Low spin complexes

(d) Formation of $[\text{Mn}(\text{CN})_6]^{4-}$

The electronic configuration of manganese ($Z = 25$) is ${}_{18}[\text{Ar}] 3d^5 4s^2$. The oxidation state in the complex is +2 which is obtained by the loss of 4s electrons. Therefore the electronic configuration of Mn^{2+} is ${}_{18}[\text{Ar}] 3d^5$.



The magnetic moment of $[\text{Mn}(\text{CN})_6]^{4-}$ has experimentally been found to correspond to the presence of a single electron. This can be easily accounted for if the four 3d electrons are paired up leaving behind one unpaired electron along with two unoccupied 3d orbitals as shown above. Now six vacant orbitals (two 3d, one 4s and three 4p) intermix together to give six sp^3d^2 hybrid orbitals. These hybrid orbitals can house six pairs of electrons from the six cyanide ions to give an octahedral geometry. The complex, $[\text{Mn}(\text{CN})_6]^{4-}$ shows **reduced paramagnetic** behaviour corresponding to the presence of only one unpaired electron. What would you like to call this complex, an inner orbital (or low spin) or outer orbital (or high spin) complex? This is an example of low spin complex because of reduced magnetic moment value.

5. Formation of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion

The oxidation state of iron in the complex is +3.

Electronic configuration of $\text{Fe}^0 = {}_{18}\text{[Ar]} \ 3d^6 \ 4s^2$.

Electronic configuration of $\text{Fe}^{3+} = {}_{18}\text{[Ar]} \ 3d^5$.

The complex $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ has been found to be paramagnetic and the magnetic moment corresponds to the presence of five unpaired electrons. It clearly indicates that the $3d$ -electrons are not disturbed at all. In addition, the outer $4d$ orbitals are used up for hybridisation. It means one $4s$, three $4p$ and two $4d$ orbitals are hybridised to afford six sp^3d^2 hybrid orbitals which are occupied by six pairs of electrons, one from each water molecule.

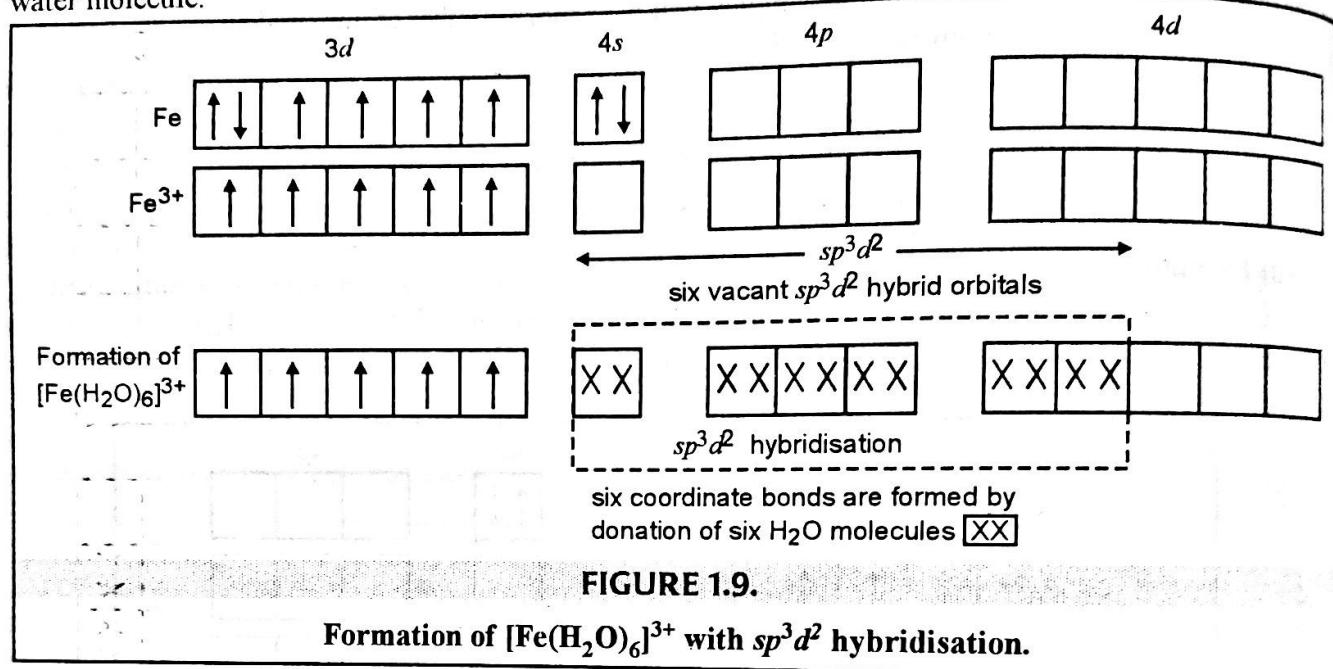


FIGURE 1.9.

Formation of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ with sp^3d^2 hybridisation.

Six coordinate bonds are formed by donation of six electron pairs from six H_2O molecules.

Thus $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is an octahedral molecule with paramagnetic behaviour.

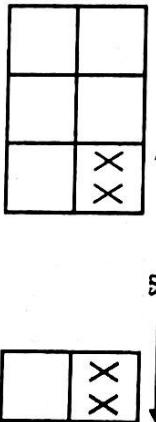
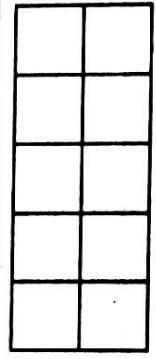
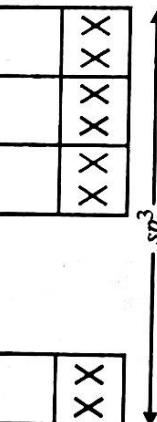
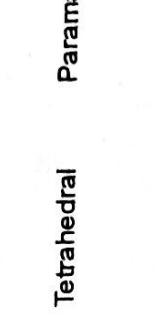
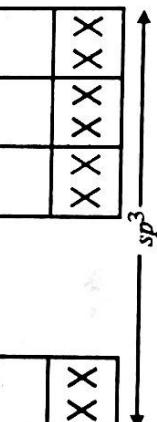
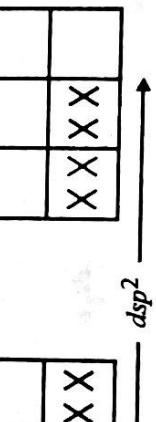
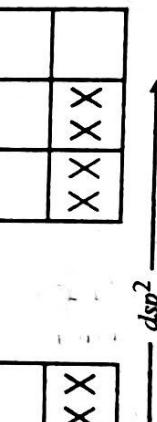
It is important to remember that geometry and hybridisation go hand in hand. If you know the geometry of a complex, you can easily know which hybrid orbitals the metal atom/ion uses. The relationship between the geometry of the complex and the hybrid orbitals used by the metal atom/ion is nicely summarized in Table 1.1.

1.2. LIMITATIONS OF VALENCE BOND THEORY

The valence (or directed bond) theory extended by Linus Pauling to coordination compounds in terms of orbital hybridisation was successful in interpreting the geometrical shapes of most of complexes. However, the theory failed to account for several properties associated with the complexes. For example,

- It fails to explain the colour and spectra of the complexes.
- It fails to explain the differences between the measured and calculated magnetic moments, although the theory is successful in predicting the number of unpaired electrons in the complex.
- It also fails to explain why the magnetic moment values varies with temperature.
- The theory fails to explain (or offer any concrete explanation) to the relative stabilities of the complexes.
- It fails to explain why some complexes are labile while others are inert. Labile complexes are those in which one of the ligand can be easily displaced by another ligand. On the other hand, inert complexes are those in which the displacement of ligands is slow.

TABLE 1.1. Valence bond approach to some complexes showing different hybridisations and stereochemistry along with magnetic behaviour.

Complex/ion (Species)	Electronic Configuration		Spatial arrangement of bonds	Number of unpaired electrons (magnetic behaviour)
	4s	4p		
Ag ⁺			Linear	Diamagnetic
[Ag(CN) ₂] ⁻			Tetrahedral	Paramagnetic
Cu ²⁺			Tetrahedral	Diamagnetic
[CuCl ₄] ²⁻			Square planar	Diamagnetic
Zn ²⁺			Square planar	Diamagnetic
[Zn(NH ₃) ₄] ²⁺			Square planar	Diamagnetic
Ni ²⁺			Square planar	Diamagnetic
[Ni(CN) ₄] ²⁻			Square planar	Diamagnetic
Pt ²⁺			Square planar	Diamagnetic
[PtCl ₄] ²⁻			Square planar	Diamagnetic

Fe^{3+}	$[\text{FeF}_6]^{3-}$	Octahedral	Paramagnetic
Mn^{2+}	$[\text{Mn}(\text{CN})_6]^{4-}$	Octahedral	Paramagnetic
Fe^{3+}	$[\text{Fe}(\text{CN})_6]^{3-}$	Octahedral	Paramagnetic
Fe^{2+}	$[\text{Fe}(\text{CN})_6]^{4-}$	Octahedral	Diamagnetic
Cu^{+}	$[\text{Cu}(\text{NH}_3)_6]^{+}$	Octahedral	Diamagnetic
Ni^{2+}	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	Octahedral	Paramagnetic
Co^{3+}	$[\text{Co}(\text{en})_2(\text{NH}_3)(\text{Cl})]^2+$	Octahedral	diamagnetic
Cr^0	$[\text{Cr}(\text{CO})_6]$	Octahedral	diamagnetic

Diagram illustrating the electronic configurations and magnetic properties of transition metal complexes in octahedral and tetrahedral fields.

The diagram shows the filling of atomic orbitals (AOs) for different complexes:

- Octahedral Field:**
 - Fe^{3+} : All AOs filled with 1 electron each.
 - Mn^{2+} : All AOs filled with 1 electron each.
 - Fe^{3+} : All AOs filled with 1 electron each.
 - Fe^{2+} : All AOs filled with 1 electron each.
 - Cu^{+} : All AOs filled with 1 electron each.
 - Ni^{2+} : All AOs filled with 1 electron each.
 - Co^{3+} : All AOs filled with 1 electron each.
 - Cr^0 : All AOs filled with 1 electron each.
- Tetrahedral Field:**
 - $[\text{FeF}_6]^{3-}$: All AOs filled with 1 electron each.
 - $[\text{Mn}(\text{CN})_6]^{4-}$: All AOs filled with 1 electron each.
 - $[\text{Fe}(\text{CN})_6]^{3-}$: All AOs filled with 1 electron each.
 - $[\text{Fe}(\text{CN})_6]^{4-}$: All AOs filled with 1 electron each.
 - $[\text{Cu}(\text{NH}_3)_6]^{+}$: All AOs filled with 1 electron each.
 - $[\text{Ni}(\text{NH}_3)_6]^{2+}$: All AOs filled with 1 electron each.
 - $[\text{Co}(\text{en})_2(\text{NH}_3)(\text{Cl})]^2+$: All AOs filled with 1 electron each.
 - $[\text{Cr}(\text{CO})_6]$: All AOs filled with 1 electron each.

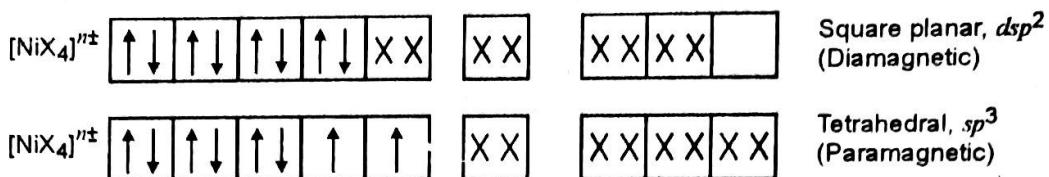
Magnetic properties are indicated by the presence of 'X' marks in the AOs:

- Paramagnetic:** Fe^{3+} , Mn^{2+} , Fe^{3+} , Fe^{2+} , Cu^{+} , Ni^{2+} , Co^{3+} , $[\text{Cr}(\text{CO})_6]$.
- Diamagnetic:** $[\text{FeF}_6]^{3-}$, $[\text{Mn}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Cu}(\text{NH}_3)_6]^{+}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, $[\text{Co}(\text{en})_2(\text{NH}_3)(\text{Cl})]^2+$.

Electron configuration arrows indicate the filling of AOs from left to right across the row of complexes.

(vi) It does not predict whether the 4-coordinate complex specie will be square planar or tetrahedral.

For example, the decision about the geometry of nickel (II) specie depends upon the value of magnetic moments.



(vii) It considers $\text{Ni}(\text{acac})_2$ to be tetrahedral whereas in fact it has octahedral geometry.

(viii) The theory fails to explain why some metal complexes in a particular oxidation state are **low spin** (i.e., *inner orbital complex*) while some other complexes of the same metal ion in the same oxidation state are **high spin** (i.e., *outer orbital complexes*).

For example, $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{CoF}_6]^{3-}$ in which cobalt is in +3 oxidation state, the former is **low spin** (inner orbital complex) while the later is **high spin** (outer orbital complex).

1.3. CRYSTAL FIELD THEORY

Valence bond theory helps us to understand the bonding in coordination compound. However, the theory suffers because it neither accounts for the colour of the coordination compounds nor explains why some complexes are high-spin whereas others are low spin.

Crystal field theory, on the other hand, explains successfully the colours of the complexes as well as their magnetic properties. This theory was developed by the Physicists named H. Bethe and V. Bleck to account for the colour and magnetic properties of hydrated salts of transition metals. Originally, crystal field theory was applied to transition metal ions in ionic crystals. That is why, the theory is called **crystal field theory**. Chemists began to apply the crystal field theory to transition metal complexes in the 1950's and since that time, inorganic chemistry has become an excited field of research.

Crystal field theory considers the central metal ion and the surrounding ligands as point charges. Point charges are electric charges that exist at a single point. It is important to note that point charge has neither an area nor a volume. According to **crystal field theory**, *it is the electrostatic attraction between the positive charge on the central metal ion and the negative charge on the ligand that holds the ligands to the metal ion.*

In brief, *crystal field theory assumes the bond between the metal ion and the ligand as purely electrostatic*. In case the ligand happens to be negatively charged ions (such as CN^- , Br^- , I^- etc.), the interaction between the metal and the ligand is referred as *ion-ion interaction*. In case the ligand happens to be neutral molecule it can be considered to have a dipole moment, as in ammonia, NH_3 . The nitrogen in NH_3 acquires a negative charge, δ^- and the hydrogen acquires a positive charge, δ^+ . In such cases the interaction of the metal ion with the ligand is referred as *ion-dipole interactions*.

The *d*-orbitals and crystal field theory

Since *d*-orbitals are frequently used in coordination compounds, it is more important to study their shape and distribution in space.

In order to understand crystal field theory, it is necessary to look again at the spatial orientation of all the five *d*-orbital relative to the position of ligands in the metal complex.

There are five *d*-orbitals and are designated as d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$ and d_{z^2} . The boundary surface of these orbitals are given :

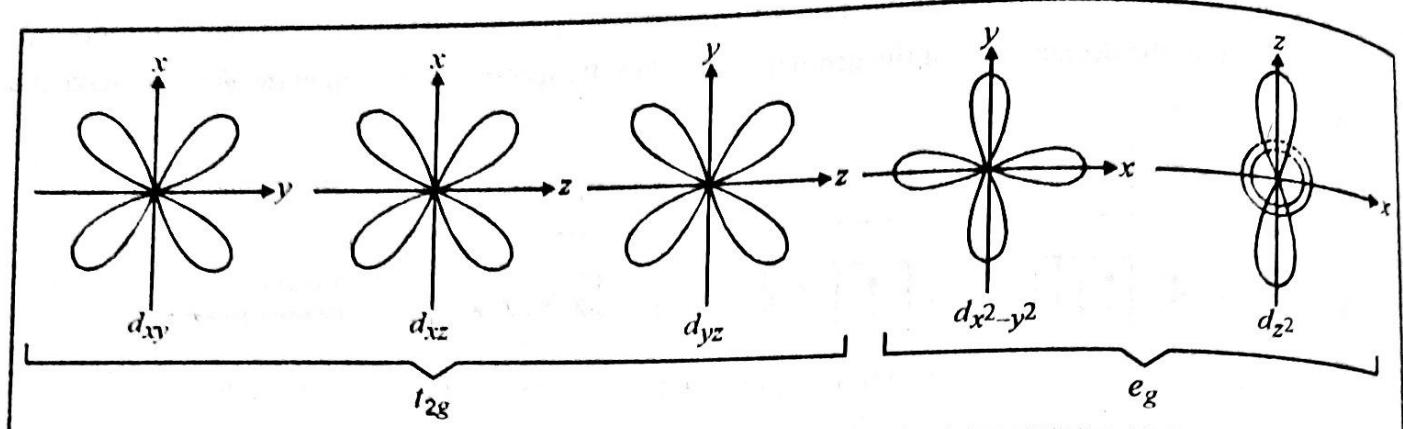


FIGURE 1.10.
Boundary surface of d -orbitals

One subset of three orbitals viz., d_{xy} , d_{yz} , d_{zx} are similar in shape and each consists of four lobes of high electron density lying between the xy , yz and zx plane respectively. The lobes of these orbitals lie in between the principal axes.

There is another subset of two orbitals viz., $d_{x^2-y^2}$ and d_{z^2} . The orbital $d_{x^2-y^2}$ consists of four lobes that lie along the x and y axes ; the orbital d_{z^2} consists of two lobes that lie along the z -axis and a dough-nut (called a torus) in the xy plane. It is important to point out that although d_{z^2} and $d_{x^2-y^2}$ orbitals do not look alike in shape, yet they are equivalent as far as their interaction with the metal ions are concerned.

The unique shape of d_{z^2} orbital can be regarded as a linear combination of two orbitals viz., $d_{z^2-x^2}$ and $d_{z^2-y^2}$, each of which is equivalent to $d_{x^2-y^2}$ orbital as shown in Figure 1.11.

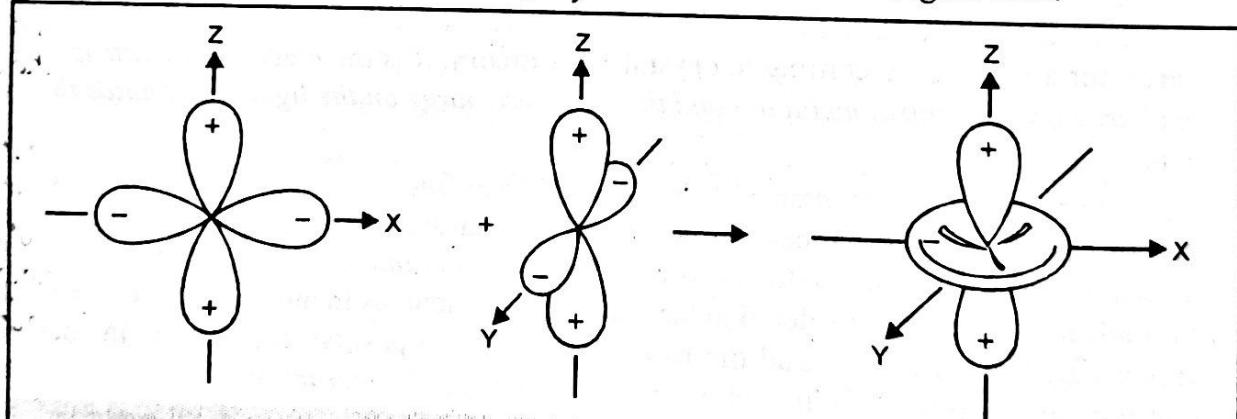


FIGURE 1.11.

Representation of d_{z^2} orbital as a linear combination of $d_{z^2-x^2}$ and $d_{z^2-y^2}$.

Since both the orbitals $d_{z^2-x^2}$ and $d_{z^2-y^2}$ have high electron density along the z -axis, the d_{z^2} orbital has a large amount of electron density concentrated along the z -axis. Since one of the component wave functions is maximized along the x -axis, $d_{z^2-x^2}$ and the other along the y -axis, $d_{z^2-y^2}$ the resultant d_{z^2} has a torus of electron density in the xy plane.

However, both the orbitals $d_{z^2-x^2}$ and $d_{z^2-y^2}$ do not have independent existence.

1.4. ASSUMPTIONS OF CRYSTAL FIELD THEORY, CFT

Crystal field theory is now more widely used than the valence bond theory. It considers the attraction between the central metal and the ligands in the complex as *purely electrostatic*. The basic assumptions of CFT are the following :

1. *The transition metal ion is surrounded by a number of ligands with lone pair of electrons.*
2. *The ligands are treated as point charges.* Point charges are electric charges that exist at a single point. It is important to remark that point charge has neither an area nor a volume.
3. *The ligands may be neutral or negatively charged species.* In case the ligands are neutral (such as NH_3 , H_2O , en), it is the negative end of the dipole that is oriented towards the metal ion that accounts for the electrostatic interaction. In case of negatively charged ligands (such as Cl^- , $\text{C}_2\text{O}_4^{2-}$, CN^-), the interaction between the central metal ion and the ligands is purely i.e., 100% ionic.
4. All the five *d*-orbitals of the isolated, gaseous metal atom have the same energy. These five *d*-orbitals of the gaseous atom possessing the same energies are called **degenerate orbitals**. If a spherically symmetric field of negative charges is placed around the metal ion, all the five *d*-orbitals of the metal will be raised in energy as a repulsion between the negative field and the negatively charged electrons of the orbitals. In brief, the energy of the orbitals is raised because of the repulsion between the field and the electrons on the metal. However, the energy of the five *d*-orbitals will still remain degenerate.

If the electric field results from the influence of real ligands (either from negatively charged anionic ligands or the negative end of the dipolar ligand such as NH_3) the electric field is not spherical symmetrical because of finite number (usually 4 and 6) of ligands involved. In such a case, the *d*-orbitals are not affected equally by the electric field of the ligands. We have also noted that the *d*-orbitals have different orientations in space and therefore, these orbitals will experience different interactions from the ligands. The orbitals lying in the directions of the ligands will experience greater respulsive interactions and consequently their energies will be raised. On the other hand, the metal orbitals lying away from the ligands will experience lesser respulsive interactions. As a result, their energies will be raised to a smaller extent. In summary, the energies of the five *d*-orbitals of the metal are split up due to the electric field generated by the ligands surrounding the metal.

*The splitting of energy of the five degenerate *d*-orbitals of the metal ion into two different sets of orbitals into different energies in the presence of electrical field of ligands is called crystal field splitting.*

5. The number of ligands (coordination number) surrounding the metal affects the energies of the five *d*-orbitals. It means that the crystal field splitting will be different with different coordination numbers.
6. The properties of the coordination compounds such as magnetic properties and colour of the compounds can be easily explained in terms of splitting of *d*-orbitals in different crystal fields.

1.5. CRYSTAL FIELD SPLITTING IN OCTAHEDRAL COMPLEXES

In an octahedral complex, the metal ion is at the centre of the octahedron whereas the surrounding ligands are at the six corners of the octahedron as shown in the Fig. 1.12.

Let us consider first a metal ion without any ligand surrounding it. In this case, all the five *d*-orbitals possess the same energy and are called *degenerate orbitals*. This is represented by five lines at the same level on the left in Fig. 1.13 marked state I. Let us now place this metal ion in a spherically symmetrical electric field consisting of six negative charges. Electrons present in the metal *d*-orbitals will interact repulsively with the electric field of the six negative charges. This repulsion between the like charges raises the energy of the *d*-orbitals equally by some amount as shown in the figure 1.13 marked state II.

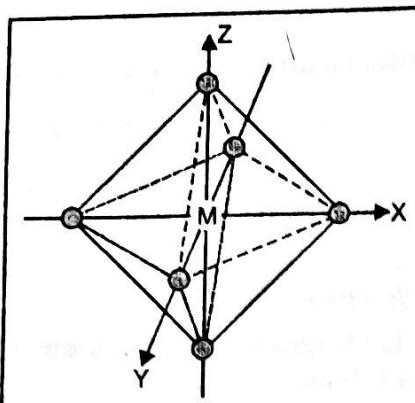
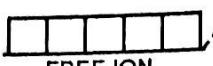


FIGURE 1.12.

Six ligands at the corners of an octahedron surrounding the metal ion.



FREE ION
STATE I

ENERGY OF ORBITALS
IN SPHERICAL FIELD
OF LIGANDS
STATE II

SPLITTING OF ORBITALS
IN OCTAHEDRAL FIELD
STATE III

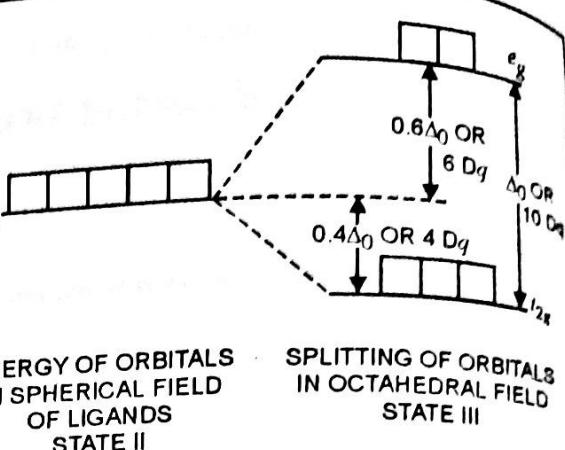


FIGURE 1.13.

Crystal field splitting in an octahedral complex.

Let us now consider the electric field generated by six charges placed at the vertices of an octahedron on the x , y and z -axes. It is important to recall that the total charge around the metal ion is the same but its distribution is different and hence the surrounding charge is not spherically symmetrical. An inspection of Fig. 1.14. shows that d_{z^2} and $d_{x^2-y^2}$ orbitals point directly towards the six point charges representing the ligands. These two orbitals interact *directly and strongly* with the ligand charges. As a result of strong repulsive interactions, their energies are raised (Fig. 1.14). The other three orbitals *viz.*, d_{xy} , d_{yz} and d_{zx} are not affected as much compared to d_{z^2} and $d_{x^2-y^2}$. As a result the energies of d_{xy} , d_{yz} and d_{zx} are lowered as shown in Fig. 1.14 (relative to the energy of five orbitals in a spherically symmetrical field).

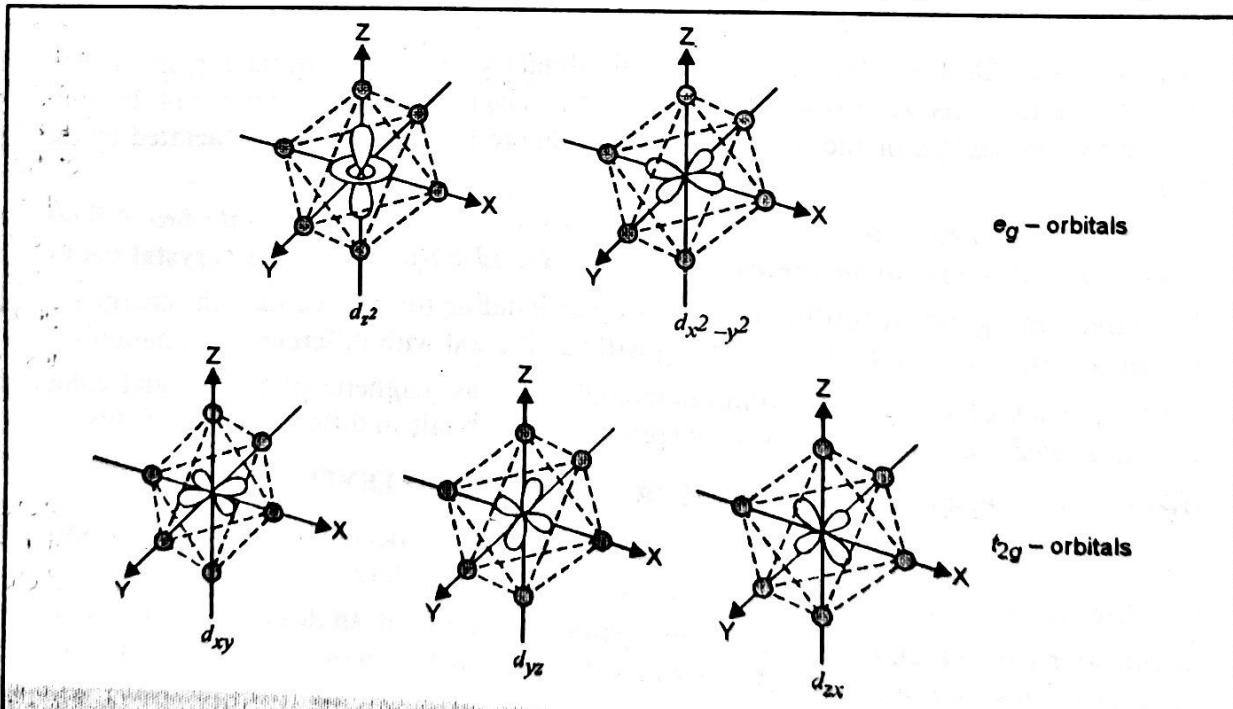


FIGURE 1.14.

Orientations of different d -orbitals in an octahedral field of six ligands.

It is important to note that the energies of d_{z^2} and $d_{x^2-y^2}$ orbitals are precisely equal. It means that these two orbitals are degenerate. Similarly, the three orbitals d_{xy} , d_{yz} and d_{zx} are also degenerate. A close inspection of Fig. 1.14 reveals that d_{xy} , d_{yz} and d_{zx} orbitals are in equivalent environments in the octahedral geometry.

It may appear that as $d_{x^2-y^2}$ orbital is being repelled more (by four ligands) and d_{z^2} is being repelled less (by two ligands). It is important to recall that d_{z^2} orbital is a linear combination of $d_{z^2-x^2}$ and $d_{z^2-y^2}$ and has also electron density in the xy plane. As a result, both the $d_{x^2-y^2}$ and d_{z^2} orbitals are equally affected and are degenerate.

The pattern of one doubly degenerate and one triply degenerate orbital set shown in Fig. 1.13 is characteristic of all the octahedral complexes. The set of three degenerate orbitals is named as t_{2g} (read as "t- two -g"). The origin of this name comes from a branch of mathematics called group theory. The other set of two degenerate orbitals is named as e_g (read as "e-g") and the origin of this name comes from group theory.

We have noted so far that in octahedral complexes, the five d -orbitals are split up into two sets. One set consisting of three orbitals of lower energy (t_{2g} orbitals) and the other set consisting of two orbitals of higher energy (e_g orbitals). The energy difference between two sets of d -orbitals is called crystal field splitting energy and is abbreviated as CFSE. It is symbolically designated as Δ_o . The subscript '0' indicate that the complex is Octahedral. The actual value of Δ_o depends upon a particular compound and varies with the metal ion, the ligands and the charge on the complex. Some of these factors will be discussed later.

Sometimes another parameter D_q is used instead of Δ_o . These two parameters are related as

$$\Delta_o = 10 D_q$$

Let us consider the approach of ligands as a two-step process. In the first step, the ligands approach the metal ions and produce a hypothetical spherically symmetrical field which repels all the orbitals to the same extent. In the second step, the ligands approach the metal ion and splits the orbital degeneracy (due to repulsions to different extents). It is important to note that the crystal field occurs in such a way that the average energy of the d -orbitals remains the same. In other words, the barycenter or "center of gravity" of the orbitals remains constant during the second step. It means that the decrease in energy of the set of orbitals that lie at the lower energy level must be balanced by the corresponding increase in other set of orbitals. Therefore, if the t_{2g} set drops by two units, a balance is achieved if the e_g set rises by three units. If the difference between t_{2g} and e_g level is defined as Δ_0^{**} , then it is clear that the energy of t_{2g} level changes by $-0.6 \Delta_0$ while the energy of e_g set changes by $+0.4 \Delta_0$ (relative to spherical field reference point).

In terms of $10 D_q$, in octahedral case, the t_{2g} level is stabilized by $6 D_q$ while the e_g level is destabilized by $4 D_q$ (relative to spherical field reference point).

1.6. VARIOUS d^n CONFIGURATIONS OF OCTAHEDRAL COMPLEXES

We have discussed in Section 1.5. that in an octahedral complex, the energies of the five d -orbitals are split up into two sets of degenerate orbitals viz. t_{2g} and e_g . The energy of the t_{2g} set is lowered whereas that of e_g set is raised due to repulsive interactions with ligands to different extents. The number of d -electrons present in the metal ion are to be arranged in the t_{2g} and e_g energy levels of d -orbitals.

*The constancy of the barycenter of the d -orbitals is similar to conservation of energy of the orbitals.

**The unit Δ_0 is preferred to $10 D_q$ as it states the geometry of the complex and avoids confusion while discussing the other geometries for which a different value of crystal field splitting energy is used.

The $d^0 - d^3$ configuration

The electronic configurations for the $d^0 - d^3$ cases are shown below in Fig. 1.15. If the electronic configuration of the metal is d^0 , then there is no electron in the d -orbitals of the complex. In case of d^1 system (e.g., Ti^{3+}) the d -electron occupies the lowest available orbital. This can be placed in any one of the t_{2g} set. Since the electron occupies one of the t_{2g} set, it is stabilized by an amount equal to $0.4 \Delta_0$ (or $4 Dq$) relative to the energy of the five d -orbitals in the electric field shown by dotted lines. Since positive values go upwards the dotted lines, the d^1 configuration is stabilized by $-0.4 \Delta_0$ relative to the reference point. This stabilization is called *crystal field stabilization energy (CFSE)*.

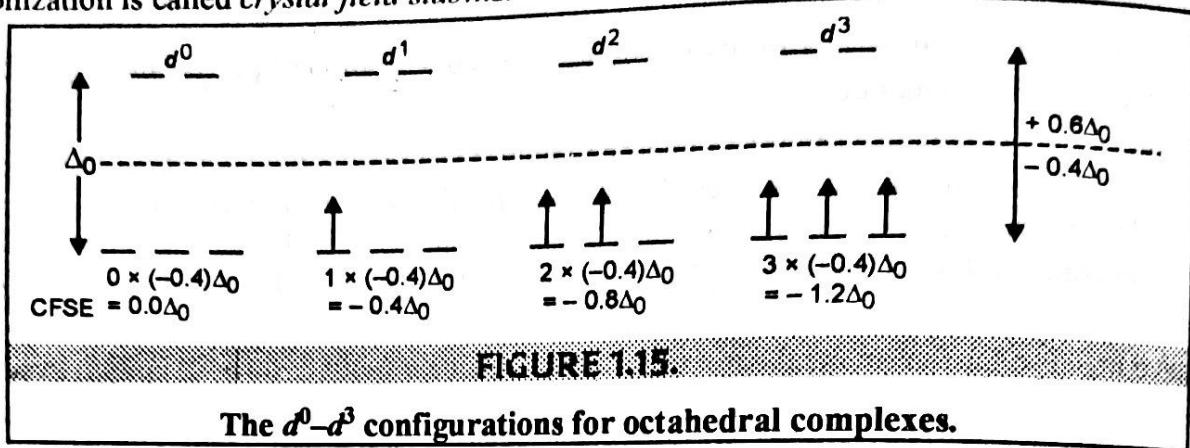


FIGURE 1.15.

The $d^0 - d^3$ configurations for octahedral complexes.

In the d^2 configuration (e.g., V^{3+} ion), there are two electrons. These two electrons will occupy the t_{2g} orbitals with their spins parallel in accordance with Hund's rule. Each of the electron is stabilized by $-0.4 \Delta_0$, so the total crystal field stabilization energy is $2 \times (-0.4 \Delta_0) = -0.8 \Delta_0$.

In the d^3 configuration (e.g., Cr^{3+} ion), there are three electron to be put into the t_{2g} set. These go one into each orbital with their spins parallel. The crystal field stabilization energy is, therefore, given by $3 \times (-0.4 \Delta_0) = -1.2 \Delta_0$.

The $d^4 - d^7$ configurations

The filling of one to three electrons in the d -orbital in case of octahedral complexes is simple and straight forward. However, in case of d^4 configuration, there are two possibilities :

(i) All the four electrons may occupy t_{2g} orbital. Three electrons will occupy t_{2g} orbitals while the fourth electron have to spin pair with any one of the three electrons occupied in the orbitals. In such a case, the electronic configuration will be t_{2g}^4 .

In this case, there is an energy penalty to pay for pairing up two electrons. This is called *pairing energy*.

(ii) Three electrons may occupy t_{2g} orbital while the fourth electron may go to either of the e_g orbital. In such a case, the electronic configuration will be $t_{2g}^3 e_g^1$.

In this case, extra energy is required to push the electron into the e_g orbital over the dotted line as shown in Fig. 1.16, the reference point in energy terms.

In the first case, the contribution to CFSE for the fourth electron is given by $-0.4 \Delta_0 + P$, where P is the pairing energy. In the second case, the contribution to the CFSE for the fourth electron is given by $+0.6 \Delta_0$ (a destabilization). The actual configuration can be decided on the basis of Δ_0 .

There are two *unpaired* electrons in the first case as shown in the resulting energy level diagram (Fig. 1.16). There are *four* unpaired electrons in the second case. Since there are fewer unpaired electrons in the first configuration than in the second (where there are four unpaired electrons), the first configuration is called *low spin* and the latter is called *high spin*.

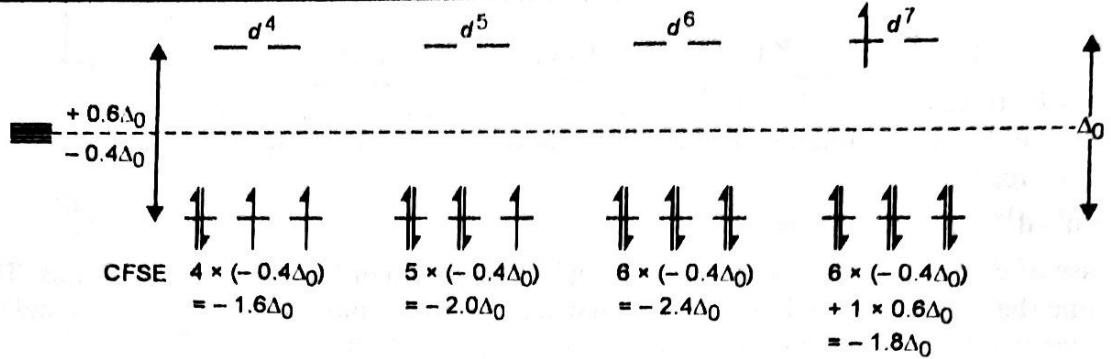


FIGURE 1.16.

The electronic configuration of octahedral low spin d^4-d^7 complexes.

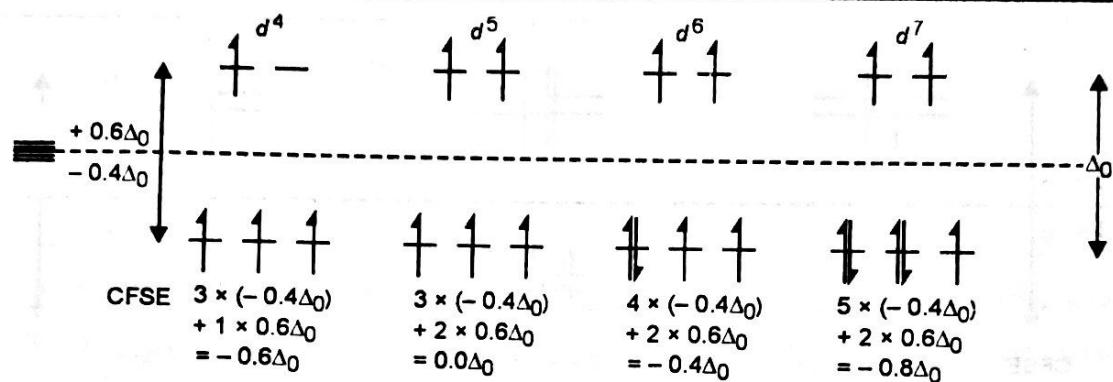


FIGURE 1.17.

The electronic configuration of octahedral high spin d^4-d^7 complexes.

The CFSE values for the d^4 configurations are shown in Fig. 1.16 and 1.17. In the low spin case, the overall CFSE is $-1.6\Delta_0 + P$ and in the high spin case, the CFSE is $-0.6\Delta_0$. Assuming that the fourth electron has to occupy another orbital, it is clear that if $\Delta_0 > P$ the complex will prefer to have low spin configuration. In case $P > \Delta_0$, the complex will prefer to have high spin configuration. This is shown in Fig. 1.17. The centre part of the diagram represents the five degenerate d -orbitals in a spherically symmetrical field. The situation on the left is the low spin case for which Δ_0 is greater than the pairing energy. The situation on the right is the high spin for which Δ_0 is less than the pairing energy. It is important to realize that for d^4 case in spherically symmetrical field, there are no unpaired electrons. In the octahedral field in the low spin case two of the electrons are paired, hence the value P must be included in the CFSE calculations. In case of high spin, there are no unpaired electrons, so no value of P has to be included.

Further if Δ_0 is large, the complexes are called strong field complexes. On the other hand, if Δ_0 is small, the complexes are called weak field complexes. Strong field complexes encourage pairing, whenever possible and are, therefore, low spin complexes. On the other hand, weak field complexes do not encourage pairing and are, therefore, high spin complexes.

In summary

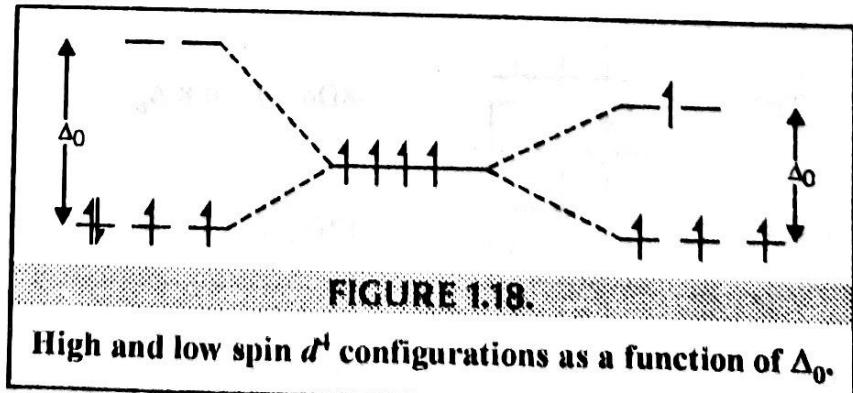


FIGURE 1.18.

High and low spin d^4 configurations as a function of Δ_0 .

If, $\Delta_0 > P$ (Strong Field Complexes) \Rightarrow Low Spin Complexes
 $\Delta_0 < P$ (Weak Field Complexes) \Rightarrow High Spin Complexes

Similarly, in case of d^5 , d^6 and d^7 octahedral complexes, there are two possibilities corresponding to low spin and high spin complexes. The CFSE in these cases can be easily calculated as shown in Fig. 1.16 and Fig. 1.17 respectively.

The d^8-d^{10} configurations

In case of d^8 configuration, there is nothing like high spin or low spin configurations. This is because if we assume the complex to be low spin, the first six electrons would fill the t_{2g} orbitals and the remaining two electrons would go into the e_g orbitals, one electron to each. If we assume the complex to be high spin, the first five electrons will go one each into the five d -orbitals and the remaining three would fill the t_{2g} set. In both cases, the result is the same.

Thus, there is only one possible electronic configuration in d^8 case. Similarly, there is only electronic configuration in case of d^9 and d^{10} case.

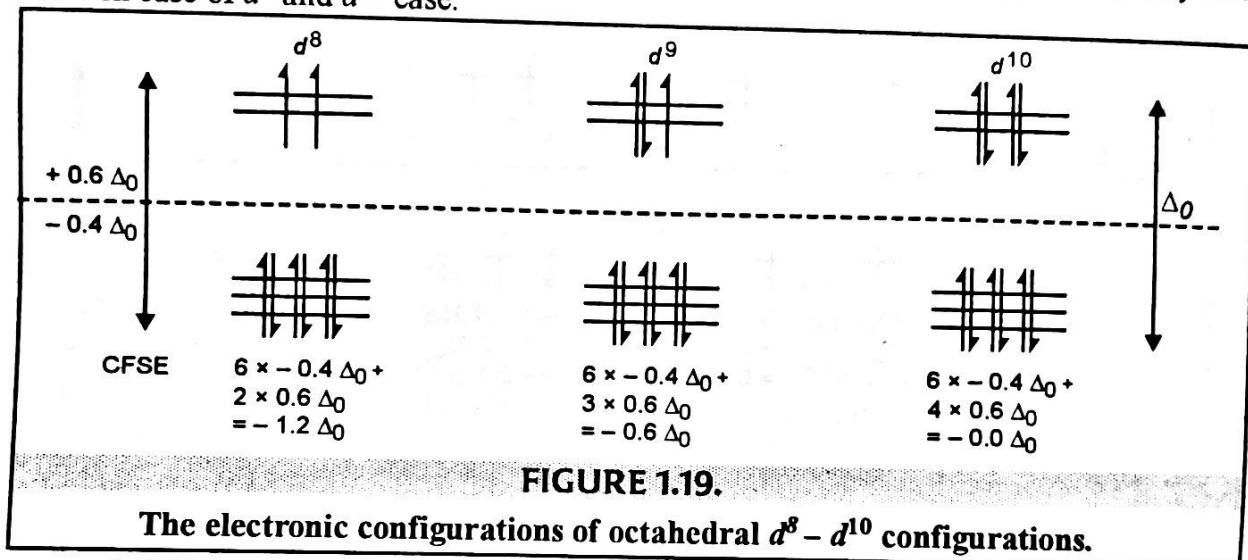


FIGURE 1.19.

The electronic configurations of octahedral d^8-d^{10} configurations.

The crystal field stabilization energy for metal ions with d^1 to d^{10} electronic configuration in weak and strong fields are summarized in Table 1.2.

Table 1.2. Crystal Field Stabilization Energies (CFSE) for Metal Ions with d^1 to d^{10} Electrons in Octahedral Complexes.

Number of d electrons	Weak Field	CFSE	Strong field	CFSE
1, Ti^{3+}		$-4Dq$. or $-0.4 \Delta_0$	—	—
2, Ti^{2+}		$-8Dq$ or $-0.8 \Delta_0$	—	—
3, V^{2+}		$-12Dq$ or $-1.2 \Delta_0$	—	—
4, Cr^{2+}		$-6Dq$ or $-0.6 \Delta_0$		$-16Dq + P$ or $1.6 \Delta_0 + P$

5, Fe ³⁺		0		-20Dq + 2P or -2.0 Δ₀ + 2P
6, Co ³⁺		-4Dq or -0.4 Δ₀		-24Dq + 2P or -2.4 Δ₀ + 2P
7, Co ²⁺		-8Dq or -0.8 Δ₀		-18Dq + P or -1.8 Δ₀ + P
8, Ni ²⁺		-12Dq or -1.2 Δ₀		-12Dq or -1.2 Δ₀
9, Cu ²⁺		-6Dq or -0.6 Δ₀		—
10, Zn ²⁺		0		—

1.7. CRYSTAL FIELD STABILISATION ENERGY, CFSE FOR TETRAHEDRAL COMPLEXES

Imagine a metal ion which is not surrounded by ligands. All the five *d*-orbitals of the metal ion in such a case have the same energy and this is represented by five lines lying at the same level on the left in Fig. 1.17. In the presence of a tetrahedral field, the degeneracy of the five *d*-orbitals is lifted up as :

- (i) the two orbitals $d_{x^2-y^2}$ and d_{z^2} become stable and their energies are lowered by $6 D_q$.
- (ii) the three orbitals d_{xy} , d_{yz} and d_{zx} become unstable and their energies are raised by $4 D_q$.

The crystal field stabilization energy in tetrahedral complexes can be calculated in terms of the algebraic sum of $-6 D_q$ per electron in *e* orbitals and $+4 D_q$ for each electron in *t*₂ orbital. The CFSE for tetrahedral complexes with different number of metal *d*-electrons in terms of D_q and Δ_t are shown in figure 1.20.

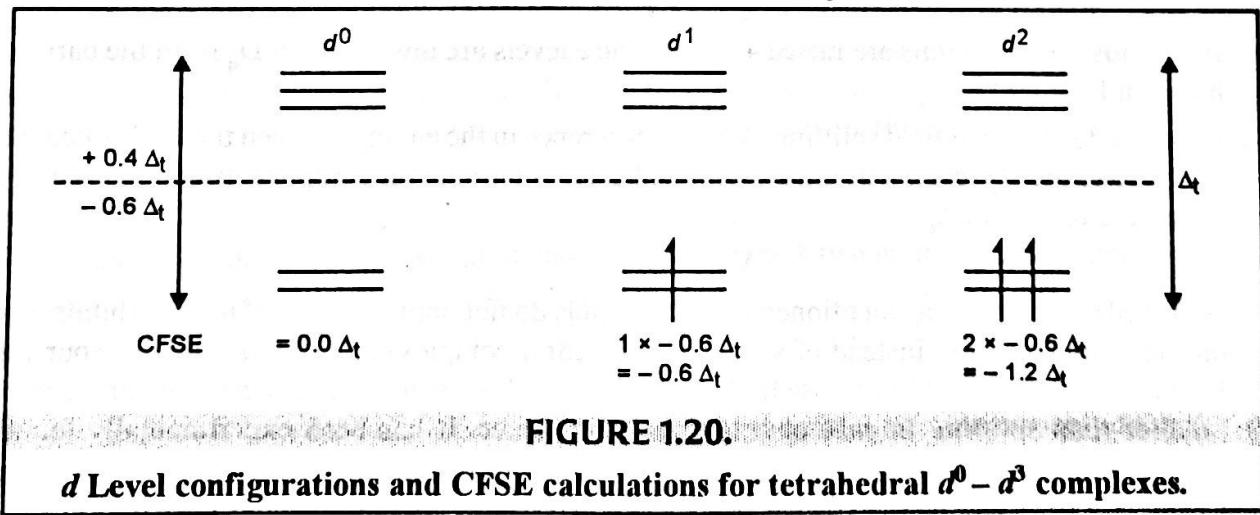


FIGURE 1.20.

d Level configurations and CFSE calculations for tetrahedral *d*⁰ – *d*³ complexes.

The splitting of *d*-orbitals in case of tetrahedral complexes are designated as *e* and *t*₂ instead of *e*_g and *t*_{2g}. The subscript 'g' is dropped because the tetrahedral geometry has no centre of symmetry. The symbol 'g' is only used for electric fields which has a centre of symmetry.

TETRAHEDRAL COMPLEXES

Two of the most common geometries for 4-coordinate complexes are the tetrahedral and square planar arrangements. A tetrahedral arrangement of four ligands surrounding a metal ion can be imagined by placing four ligands on the alternate corners of a cube (or by placing four ligands on the opposite corners of a cube). A tetrahedral complex can also be imagined by removing four of the eight ligands from opposite corners of a cube (Fig. 1.21). The three coordinate axes are defined as those passing through the centres of the cube and the centres of each cube face. In this arrangement, the ligands do not directly approach any of the metal d -orbitals. However, the ligands come closer to the d_{xy} , d_{yz} and d_{zx} orbitals that are directed towards the edges of the cube compared to the $d_{x^2-y^2}$ and d_{z^2} orbitals that are directed to the centres of the faces of the cube. As a result, the energy of three orbitals (namely d_{xy} , d_{yz} and d_{zx}) labelled t_2 will be raised whereas the energies of two orbitals (*viz.*, $d_{x^2-y^2}$ and d_{z^2}) (labelled as e) will be lowered.

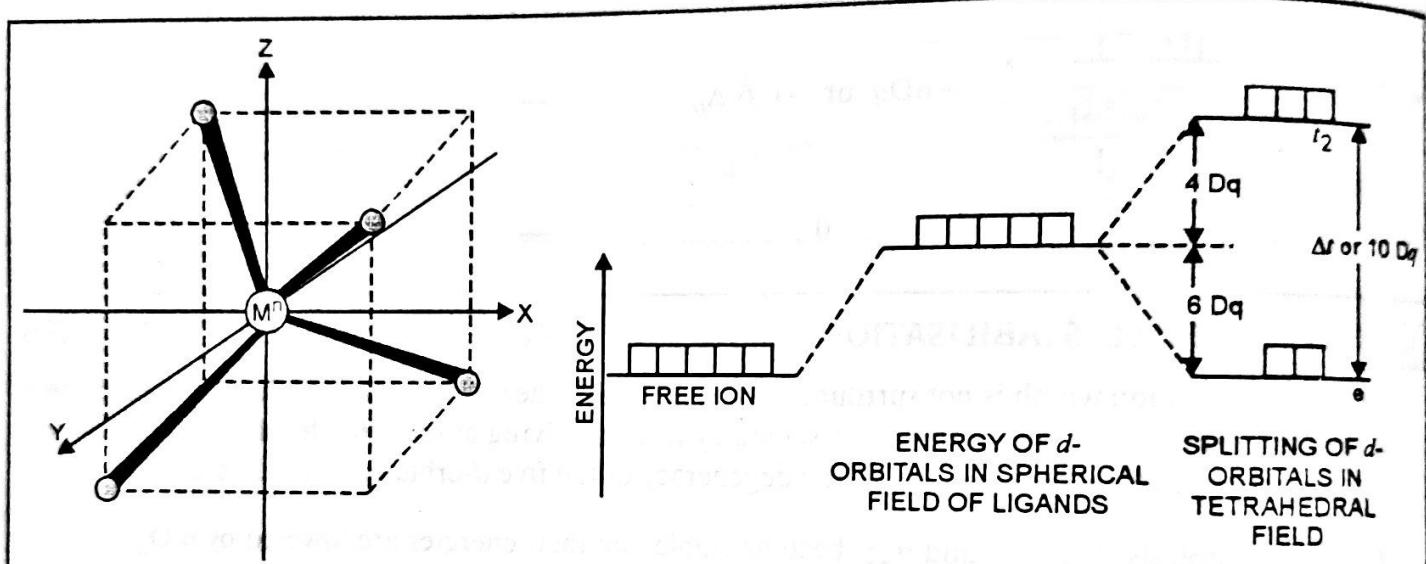


FIGURE 1.21.

Tetrahedral field of four ligands around the central metal ion.

FIGURE 1.22.

Crystal field splitting in a tetrahedral field.

Thus, the t_2 orbitals are destabilized whereas the e orbitals are stabilized. Further, since the "centre of gravity" rule holds, the t_2 orbitals are raised $4 D_q$ and the e levels are lowered by $6 D_q$ from the bary centre. This is shown in Fig. 1.22.

The magnitude of crystal field splitting, Δ_t , is the difference in the energy between the doubly degenerate, e and triply degenerate, t_2 level. The subscript, t indicates a tetrahedral complex. It is also measured in terms of D_q and is related to Δ_o ,

$$\Delta_t = 10 D_q$$

In a tetrahedral complex, as mentioned earlier, ligands do not approach any of metal orbitals directly. In addition, only four ligands (instead of six of an octahedral complex) split the d -orbitals. Four ligands instead of six would result in 33% decrease in the field. Thus, splitting of d -orbitals in tetrahedral complexes is much smaller than splitting in case of octahedral complexes. It has been experimentally found that crystal field splitting in octahedral field is nearly more than twice as strong for a tetrahedral field for the same metal ion and the same ligands. It has been found for a point-charge model

$$\Delta_t = \frac{4}{9} \Delta_o$$

$$\text{i.e., } 10D_{q(Td)} = \frac{4}{9} \cdot 10D_{q(O_h)}$$

Since the crystal field splitting in tetrahedral field is quite small, it means that pairing of electrons is not energetically favoured. It amounts to saying that pairing energy P is virtually always greater than the splitting between e and t_g energy levels. As a result, virtually all the tetrahedral complexes are **high spin** complexes.

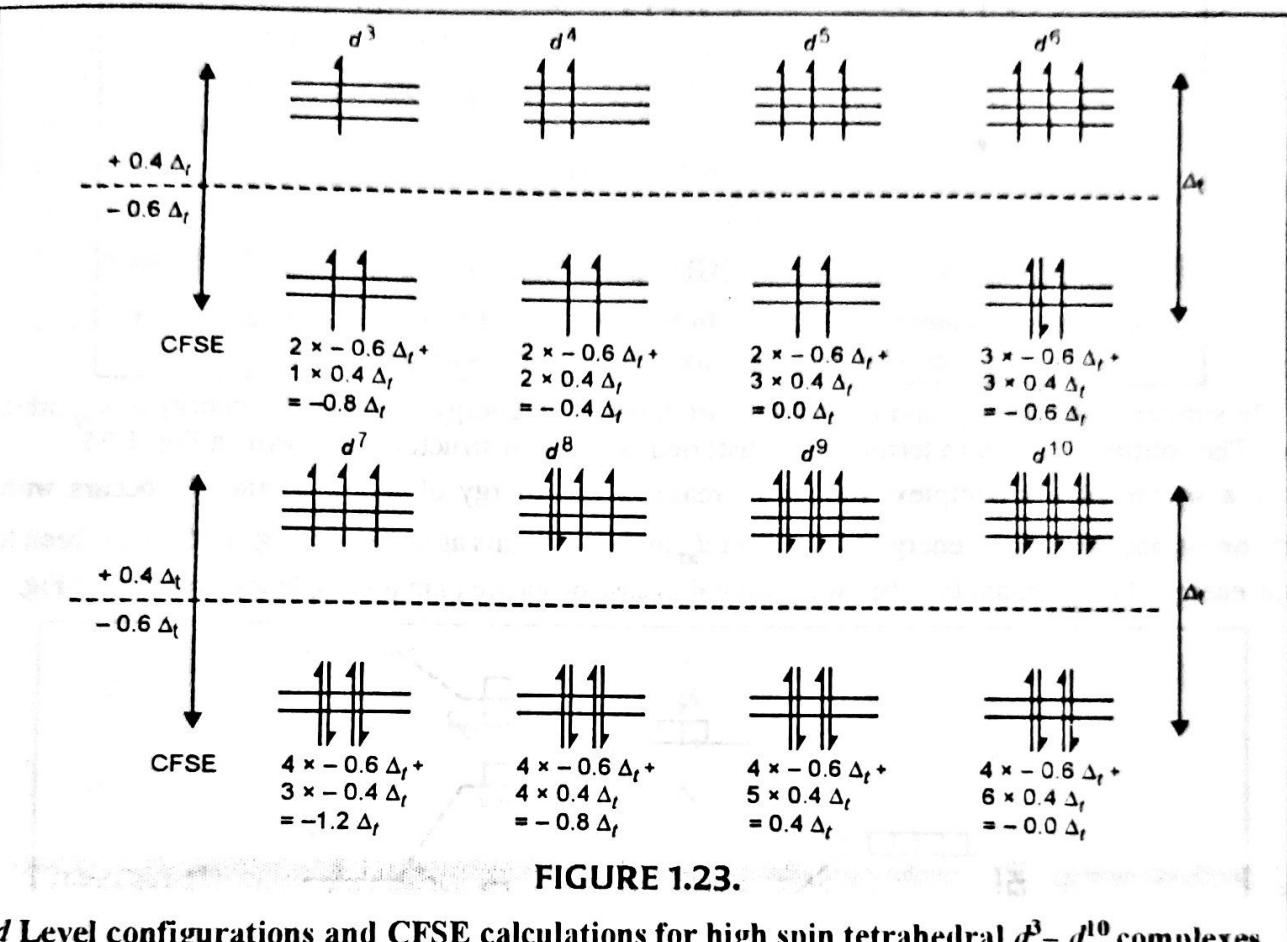


FIGURE 1.23.

d Level configurations and CFSE calculations for high spin tetrahedral d^3-d^{10} complexes.

1.8. CRYSTAL FIELD SPLITTING IN TETRAHEDRAL AND SQUARE PLANAR COMPLEXES

If two *trans* ligands in an octahedral complex are moved either towards or away from the metal ion, the resulting complex is called *tetragonally distorted*. If the two *trans* ligands are brought closer to the metal ion, the octahedron tends to flatten. This is called **flattening of the octahedron** in which two *trans* M-L bonds are shortened while other four M-L becomes longer. If the two mutually *trans* ligands are completely removed, it results in the formation of a square planar complex as shown in Fig. 1.24.

Since the octahedron is symmetrical, it does not matter which two mutually *trans* ligands are removed, but the axis from which these ligands are removed is conventionally defined as the z -axis. A partial removal of the ligands along the z -axis gives a distorted octahedron. As the ligands on the z -axis are moved away, there is an increase in the metal-ligand bond length along the z -axis. The increase in the length of metal-ligand bond decreases the repulsion between the ligands and the metal electron present in the d_{z^2} orbital. As a result, energy of d -orbital is decreased relative to that in octahedral field.

On the other hand, if the metal-ligand bond along the X and Y axes are shortened, the d -orbital in the XY plane viz., $d_{x^2-y^2}$ feels greater repulsion from the ligands and, therefore, its energy is increased.

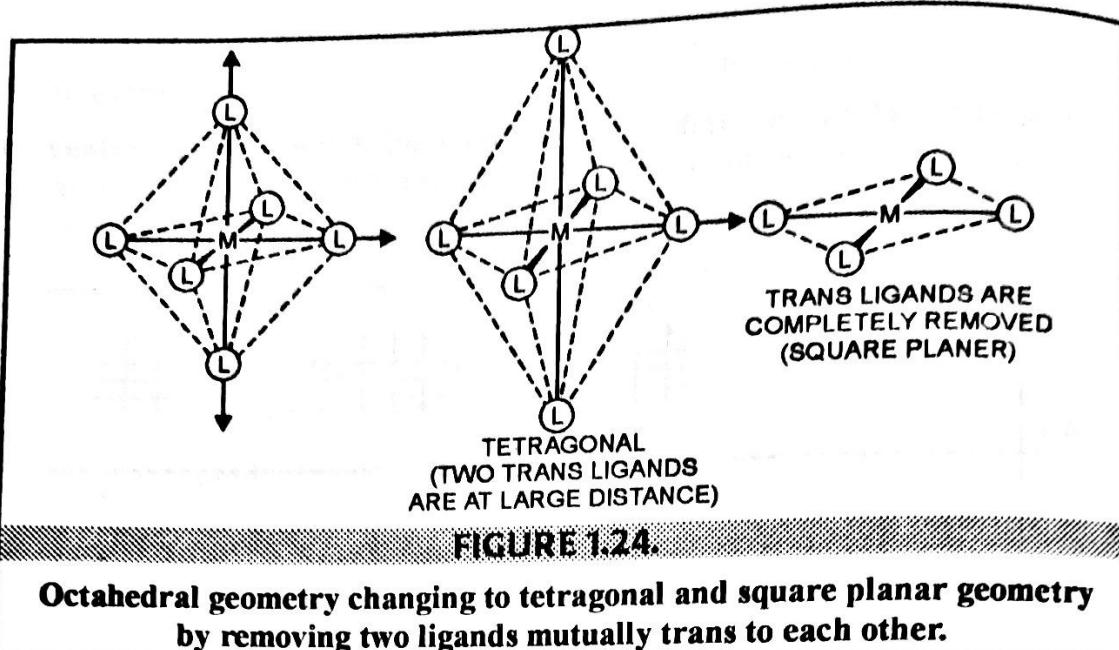


FIGURE 1.24.

Octahedral geometry changing to tetrahedral and square planar geometry by removing two ligands mutually trans to each other.

On similar lines, the d_{xz} and d_{yz} orbitals are lowered in energy whereas the energy of d_{xy} orbital is raised. The splitting pattern in tetragonally distorted octahedral structure is shown in Fig. 1.25.

In a square planar complex, further increase in the energy of $d_{x^2-y^2}$ and d_{xy} occurs with the simultaneous decrease in the energy of d_{z^2} and d_{xz} and d_{yz} orbitals as shown in Fig. 1.25. It has been found that the energy of d_{z^2} orbital falls below d_{xy} orbital in case of square planar complexes as shown in Fig. 1.25.

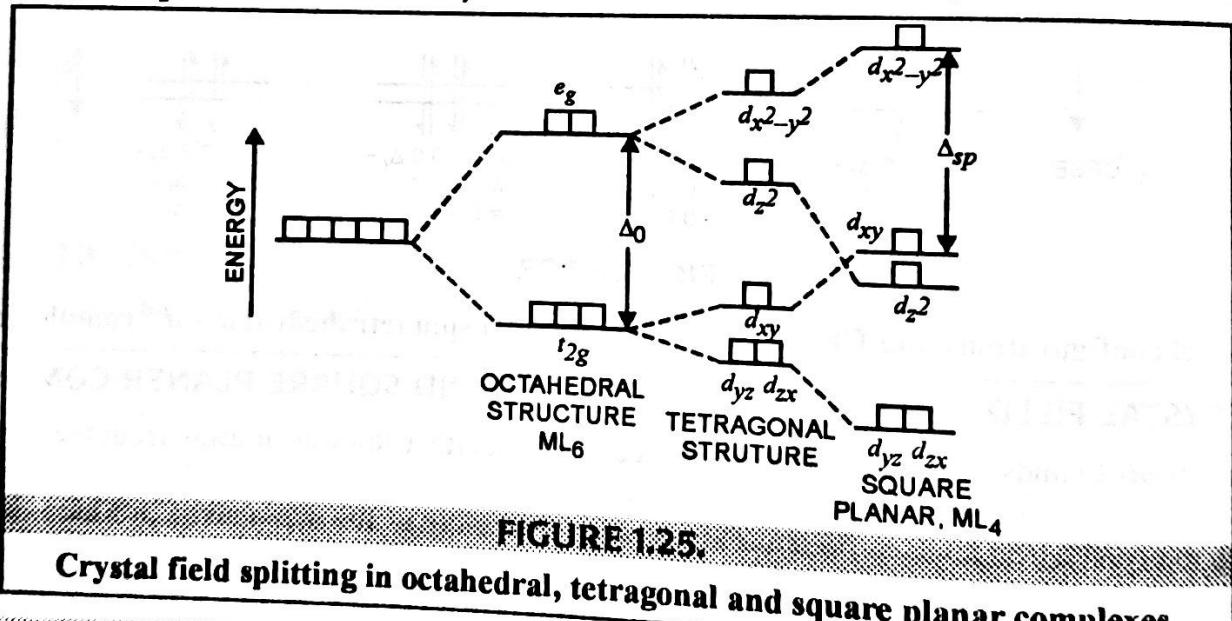


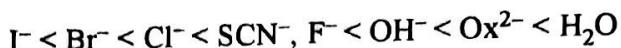
FIGURE 1.25.

Crystal field splitting in octahedral, tetrahedral and square planar complexes.

1.9. FACTORS AFFECTING THE CRYSTAL FIELD PARAMETERS

There are a number of factors that affect the extent of splitting of the d-orbitals by the ligands. These are discussed below :

1. Nature of the ligands. The crystal field splitting depends primarily on the nature of the ligands surrounding the metal ion. The greater the ease with which the ligands can approach the metal ion, the greater will be the crystal field splitting. The ligands which cause smaller crystal field splitting are called weak field ligands and ligands which cause larger crystal field splitting are called strong field. Ligands can be arranged in a series called spectrochemical series according to the increasing magnitude of the crystal field splitting as shown below.



→ **Increasing field strength** →
 → **Increasing value of Δ_0** →

Those on the left of $\boxed{\text{NH}_3}$ are called **weak-field ligands** and those on the right of $\boxed{\text{NH}_3}$ are called **strong-field ligands**. The order of the spectrochemical series remains practically same irrespective of the transition metal ions.

The effect of crystal field splitting (Δ_0) on the ligands attached to chromium (III) and cobalt (III) are shown below in the Table 1.3. A close inspection of the Table 1.3 reveals that the order of the ligands remains same irrespective of the metal.

TABLE 1.3. CFSE of various metal complexes.

Complex	Ligand	Donor atom	Δ_0 (cm ⁻¹)
$[\text{CrCl}_6]^{3-}$	Cl^-	Cl	13,200
$[\text{CrF}_6]^{3-}$	F^-	F	15,200
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	H_2O	O	17,400
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	NH_3	N	21,600
$[\text{Cr}(\text{en})_3]^{3+}$	en	N	21,900
$[\text{Cr}(\text{CN})_6]^{3-}$	CN^-	C	26,200
$[\text{CoCl}_6]^{2-}$	Cl^-	Cl	—
$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	H_2O	O	18,600
$[\text{Co}(\text{NH}_3)_6]^{3+}$	NH_3	N	22,900
$[\text{Co}(\text{en})_3]^{3+}$	en	N	23,200
$[\text{Co}(\text{CN})_6]^{3-}$	CN^-	C	33,500

2. Oxidation state of the metal ion. The magnitude of the crystal field splitting depends upon the oxidation state (or valency) of the central metal ion. Trivalent metal ions causes larger crystal field splitting than the divalent metal ions. For example, the crystal field splitting in trivalent cobalt complex, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ is $18,600 \text{ cm}^{-1}$ whereas in the corresponding divalent cobalt complex viz. $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ the CFSE is only $9,400 \text{ cm}^{-1}$. This increase in the crystal field splitting is due to the increased charge on the metal ion that tends to pull the negatively charged ligands more effectively towards itself. An inspection of the Table 1.4 reveals that trivalent metal ions displays greater crystal field splitting than the divalent metal ions.

TABLE 1.4. Crystal field splitting for hexaaquo complexes of M^{2+} and M^{3+} ions of first transition series.

Metal ion	Oxidation state	Δ_0 (cm ⁻¹)	Metal ion	Oxidation state	Δ (cm ⁻¹)
V^{2+}	II	11,800	V^{3+}	III	18,000
Cr^{2+}	II	14,000	Cr^{3+}	III	17,400
Mn^{2+}	II	7,500	Mn^{3+}	III	21,000
Fe^{2+}	II	10,400	Fe^{3+}	III	14,000
Co^{2+}	II	9,400	Co^{3+}	III	18,600

3. Type of d -orbitals. The magnitude of crystal field splitting within the same transition series as shown in Table 1.4 do not vary greatly. However, appreciable changes (30-50%) in the crystal field splitting occur on moving from $3d$ (first transition series) to $4d$ (second transition series). An almost similar increase in the crystal field splitting is observed on moving from $4d$ (second transition series) to $5d$ (third transition series). This can be readily seen from the values in Table 1.5.

Table 1.5. Crystal field splitting values for transition metal complexes.

Complex ion	$10 Dq \text{ (cm}^{-1}\text{)}$	Complex ion	$10 Dq$	Complex ion	$10 Dq$
$[\text{CrCl}_6]^{3-}$	13,200	$[\text{MoCl}_6]^{3-}$	19,200	$[\text{CoCl}_6]^{3-}$	—
$[\text{CoCl}_6]^{3-}$	—	$[\text{RhCl}_6]^{3-}$	20,300	$[\text{IrCl}_6]^{3-}$	25,000
$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	18,600	$[\text{Rh}(\text{H}_2\text{O})_6]^{3+}$	27,000	$[\text{Ir}(\text{H}_2\text{O})_6]^{3+}$	—
$[\text{Co}(\text{NH}_3)_6]^{3+}$	22,900	$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34,100	$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41,000

4. Geometry of the complex. The crystal field splitting energy in case of tetrahedral complex (Δ_t) is less than that for an octahedral complex (Δ_0). This is because there are only four ligands in the tetrahedral field as compared to six ligands in case of octahedral field. In addition, there is a ligand along each axis on the octahedral field whereas no ligand lies directly along any axis in tetrahedral field.

The splitting in an octahedral field has been found somewhat more than twice as strong as for a tetrahedral field for the same metal and the same ligands.

i.e.,

$$\Delta_t \approx 4/9 \Delta_0$$

The splitting energy for tetrahedral complexes is small as compared to the pairing energy, P. This explains as to why most of the tetrahedral complexes are high spin-complexes.

SUMMARY FOR REVIEW

Valence bond theory considers the bonding between the metal ion and the ligand as purely **covalent**.

Crystal field theory considers the bonding between the metal ion and the ligand as purely **electrostatic**.

In crystal-field theory, there are no covalent bonds, no shared electrons and no hybrid-orbitals.

Crystal field splitting. The splitting of five degenerate d -orbitals of the metal into different sets of orbitals having different energies in the presence of electric field of the ligand is called **crystal field splitting**.

Ligands differ in their abilities to produce splitting of the d -energy levels.

The arrangement of ligands in order of their increasing abilities to produce a splitting of the d -energy level is called **spectrochemical series**.

TYPICAL QUESTIONS WITH ANSWERS

Q. 1. Why the magnitude of crystal field splitting, Δ_t in tetrahedral complexes is smaller than in the octahedral fields.

Ans. The magnitude of crystal field splitting, Δ_t in tetrahedral complexes is smaller primarily due to :

(i) There are only four ligands instead of six ligands in a tetrahedral complex, so the ligand field is only two third. As a result, the ligand field splitting is also two thirds (compared to octahedral field).

(ii) The direction of the metal d -orbitals does not coincide with the direction of the ligands. This reduces the crystal field splitting further by roughly two thirds.

Thus, the tetrahedral crystal field splitting Δ_t is roughly $2/3 \times 2/3 = 4/9$ of the octahedral crystal field splitting, Δ_0 .