

Chapter

1

PTI

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METAL-LIGAND BONDING IN TRANSITION METAL COMPLEXES

Transition metals have very good tendency to form coordination compounds or complexes. Though many attempts were made by different workers to explain the bonding and structure of coordination compounds, the main credit goes to the brilliant work of Werner. In 1893, Werner proposed a theory, which is commonly known as **Werner's coordination theory**. This was the first successful attempt to explain the bonding in coordination complexes. In recognition of his work in this field, Werner was awarded **Noble Prize in 1913**. He explained the bonding in these complexes on the basis of two types of valencies of the metal viz., *the primary valency* corresponding to *oxidation state* and the *secondary valency* corresponding to *coordination number*. The secondary valency or coordination number determined the stereochemistry of the complexes. However, the Werner's assumptions were not based on theoretical justification and the scientists started making attempts to find basis of bonding in these complexes. The first attempt in this regard was made by Sidgwick who extended the Lewis theory of electron pair bond formation to explain the bonding in transition metal complexes. He suggested that *metal ion/ atom accepts electron pairs from ligands until it achieves the next noble gas configuration and gave a term effective atomic number (EAN)*.

EAN is the total number of electrons possessed by the central metal ion and the electrons gained by it from ligands. However, this theory lacked fundamental basis and simply gave emphasis on the stability of inert gas configuration in coordination compounds.

With the advances in theories of chemical bonding, three modern theories of bonding in transition metal complexes have been developed. These are :

1. Valence bond theory VBT
2. Crystal field theory CFT
3. Molecular orbital theory MOT

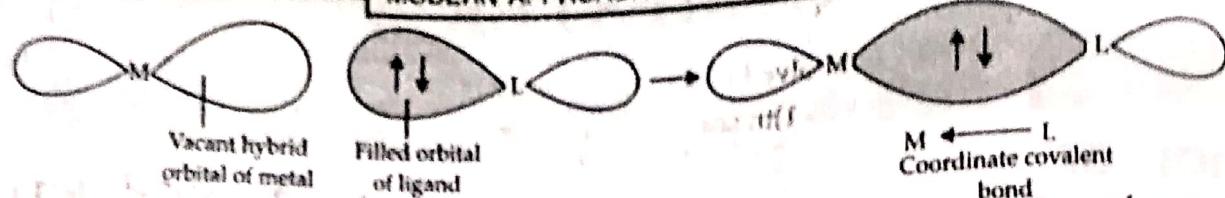
In the present text, we shall discuss mainly crystal field theory of bonding. The valence bond theory has already been discussed in the previous classes. We shall briefly recall valence bond theory before discussing the main crystal field theory.

VALENCE BOND THEORY (VBT)*

This theory was developed by Linus Pauling. It describes bonding between metal and ligands using hybrid orbitals of the metals and electron pairs of the ligands. 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 atom or ion forming a coordinate covalent bond.

The valence bond theory assumes the bonding between the metal atom/ion and ligands to be purely covalent.

* Only Limitations of valence bond theory is in the Syllabus.



This is the simplest of the three theories and is easy to apply. It gives accurate explanation for the structures and magnetic properties of coordination compounds.

Basis of Valence Bond Theory

The main assumptions of this theory are :

1. The central metal atom or ion in the complex makes available a number of empty orbitals for the formation of coordinate bonds with suitable ligands. The number of empty orbitals made available for this purpose is equal to coordination number of the central metal ion.

For example, if coordination number is 6, six empty orbitals are made available and if coordination number is 4, four empty orbitals are made available in the central metal ion.

2. The appropriate atomic orbitals (*s*, *p* and *d*) of the metal hybridise to give a set of new orbitals of equivalent energy, called hybrid orbitals. These hybrid orbitals are directed towards the ligands according to definite geometry of the complex such as square planar, tetrahedral, octahedral and so on.

3. The *d*-orbitals involved in the hybridisation may be either inner (*n* - 1) *d*-orbitals or outer (*nd*) orbitals. For example, in case of octahedral hybridisation, the orbitals may be one *ns*, three *np* and two *nd* (i.e. sp^3d^2 hybridisation) or one *ns*, three *np* and two (*n* - 1) *d* (i.e. d^2sp^3 hybridisation).

4. Each ligand has at least one orbital (of donor atom) containing a lone pair of electrons.

5. The empty hybrid orbitals of metal ion overlap with the filled orbitals of the ligand to form a covalent sigma bond ($L \rightarrow M$). The bond is also called a coordinate bond.

6. In addition to a sigma bond, there is also a possibility of π bond provided suitable orbitals are available on the metal atom and the ligands.

Some common types of hybridisation of atomic orbitals and their geometries are given in Table 1.

Table 1. Some common types of hybridisations.

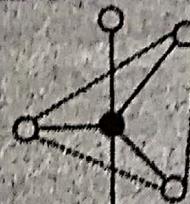
Coordination number	Hybridisation	Shape	Geometry
2	sp	Linear	
3	sp^2	Trigonal planar	
4	sp^3	Tetrahedral	
4	dsp^2 The <i>d</i> -orbital involved is $d_{x^2-y^2}$ of the inner i.e. (<i>n</i> - 1)th shell.	Square planar	

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 dsp^3

The d -orbital involved is d_{z^2} of the inner i.e., $(n - 1)$ th shell.

Trigonal bipyramidal

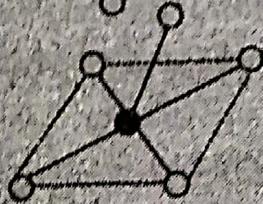


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 sp^3d

The d -orbital involved is $d_{x^2-y^2}$ of the outer, i.e., the n th shell.

Square pyramidal

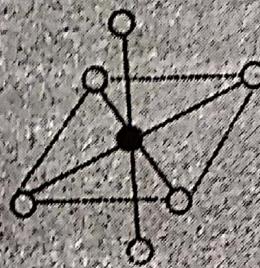


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 d^2sp^3 or sp^3d^2

The d -orbitals involved are d_{z^2} and $d_{x^2-y^2}$ of the inner, i.e., $(n - 1)$ th shell in the first case and of the outer, i.e., n th shell in the second case

Octahedral



APPLICATIONS OF VALENCE BOND THEORY

The valence bond theory was used to explain many stereochemical and magnetic properties of coordination compounds. We have learnt that a substance which does not contain any unpaired electron is not attracted by magnetic field and is called **diamagnetic**. On the other hand, a substance which contains one or more unpaired electrons is attracted by the magnetic field and is called **paramagnetic**. If we know the magnetic properties of a compound, we can predict the type of hybridisation used in the formation of the complex and hence its geometry can be predicted. Alternatively, if we know the geometry of the complex, its magnetic properties i.e. diamagnetic or paramagnetic character can be predicted.

Let us take some examples to illustrate the valence bond theory.

Examples of Complexes of Coordination Number 6

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

The chromium ($Z = 24$) has the electronic configuration $3d^5 4s^1$ as shown in Fig. 1(a). The chromium in this complex is in +3 oxidation state and the ion is formed by the loss of one $4s$ and two of the $3d$ electrons as shown in Fig. 1(b). The inner d -orbitals are already vacant and two vacant $3d$, one $4s$ and three $4p$ orbitals are hybridised to form six d^2sp^3 hybrid orbitals. Six pairs of electrons one from each NH_3 molecule, occupy the six hybrid orbitals. The molecule has octahedral geometry.

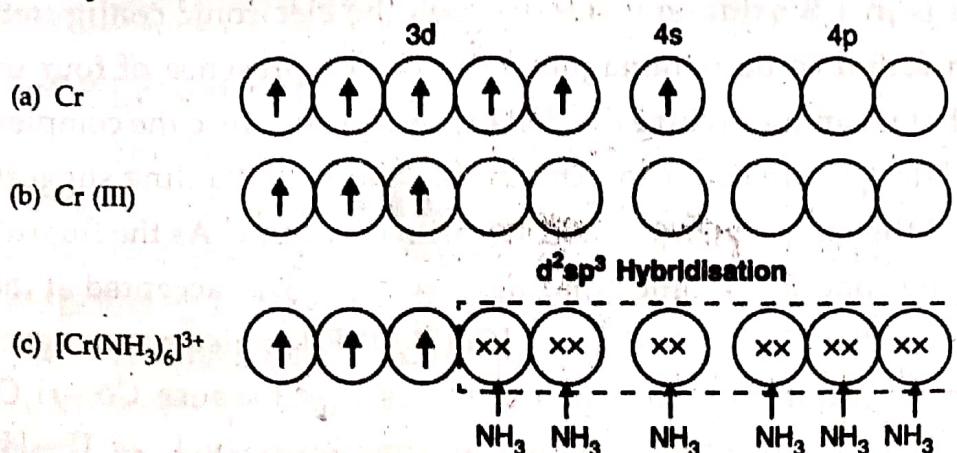


Fig. 1. Formation of $[\text{Cr}(\text{NH}_3)_6]^{3+}$ complex involving d^2sp^3 hybridisation.
xx represents electron pairs from ligands.

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

Cobalt atom ($Z = 27$) has the electronic configuration $3d^7 4s^2$. In this complex, cobalt is in +3 oxidation state and has the electronic configuration $3d^6 4s^1$ as shown in Fig. 2(b). According to Hund's rule, four of the $3d$ orbitals are singly filled and one $3d$ orbital has a pair of electrons. Octahedral complexes are formed by involving d^2sp^3 hybridisation. This requires that the metal atom must have two of its $3d$ orbitals empty. To achieve this, two electrons in the $3d$ orbitals are paired up with electrons in other $3d$ orbitals leaving two $3d$ orbitals empty. Therefore, we expect that $[\text{Co}(\text{NH}_3)_6]^{3+}$ complex ion will be diamagnetic and this has been experimentally observed. Then, these six vacant orbitals (two $3d$, one $4s$ and three $4p$) hybridise to form six vacant d^2sp^3 hybrid orbitals. Six pairs of electrons one from each NH_3 molecule are donated to these vacant hybrid orbitals. Six pairs of electrons one from each NH_3 molecule are donated to these vacant hybrid orbitals. Thus, the complex has octahedral geometry and is diamagnetic.

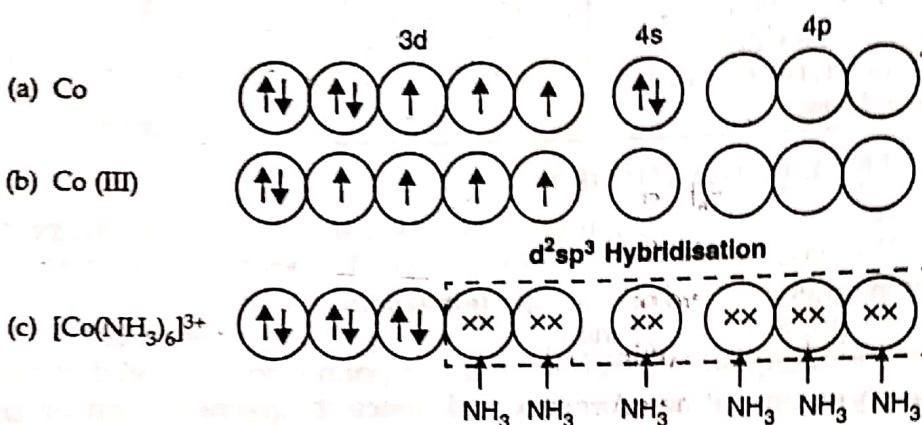


Fig. 2. Formation of $[\text{Co}(\text{NH}_3)_6]^{3+}$ complex ion involving d^2sp^3 hybridisation.

From the above discussion, we may conclude that all the octahedral complexes of Co^{3+} should be diamagnetic. But, this is not true. It has been observed that the complexes of Co^{3+} such as $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{H}_2\text{O})_3\text{F}_3]$ are paramagnetic and have four unpaired electrons. To solve this problem, the theory was modified as described below.

3. $[\text{CoF}_6]^{3-}$ complex ion

In this case cobalt is in +3 oxidation state and has the electronic configuration $3d^6$. This complex has been found to be paramagnetic due to the presence of four unpaired electrons. This means that it cannot involve d^2sp^3 hybridisation because the complex would be diamagnetic as $[\text{Co}(\text{NH}_3)_6]^{3+}$. In order to explain this anomaly, Pauling suggested that this complex is ionic and the metal ligand bonds are primarily ionic. As the fluoride ion is highly electronegative the concept of ionic bonding in $[\text{CoF}_6]^{3-}$ was accepted at that time. However, it was observed that the Co^{3+} complex $[\text{Co}(\text{H}_2\text{O})_3\text{F}_3]$ is also paramagnetic. But the Pauling suggestion does not look convincing in this case because $\text{Co}-\text{H}_2\text{O}$ bonds cannot be ionic. Similarly, many other octahedral complexes such as $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Ni}(\text{H}_2\text{O})_6]^{3+}$, etc. were prepared which were found to be paramagnetic. However, these complexes cannot be ionic.

To solve this anomaly Huggins (in 1937) suggested that the metal can also use outer d -orbitals for hybridisation. Therefore, in the complex ion $[\text{CoF}_6]^{3-}$, the $3d$ orbitals are not disturbed and the outer $4d$ orbitals are used for hybridisation. The six orbitals (one $4s$, three $4p$ and two $4d$) are hybridised forming six sp^3d^2 hybrid orbitals. Six pairs of electrons, one each from F^- ion are donated to the vacant hybrid orbitals forming $\text{Co}-\text{F}$ bonds.

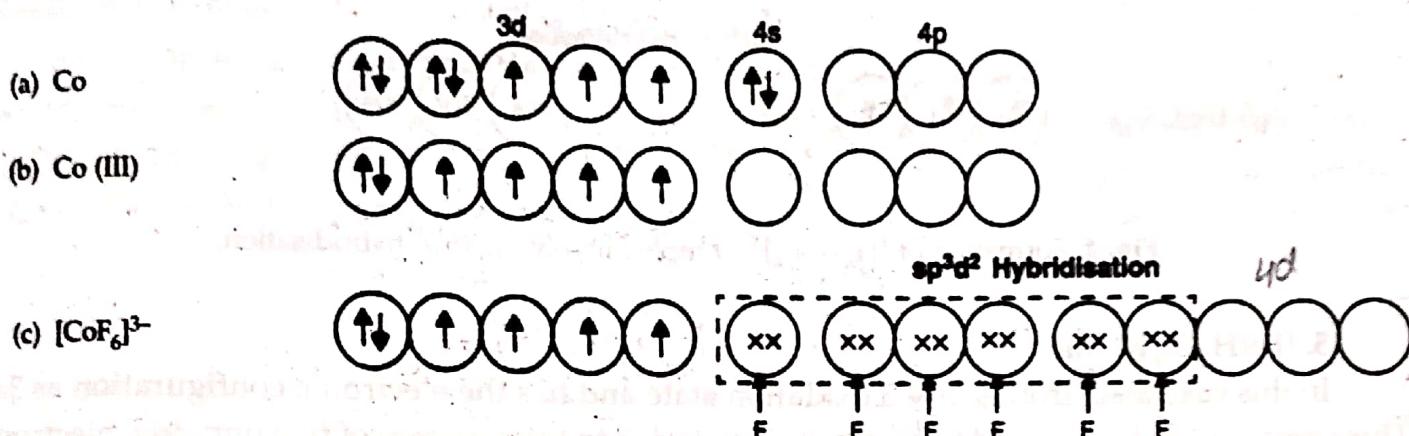


Fig. 3. Formation of $[\text{CoF}_6]^{3-}$ complex ion involving sp^3d^2 hybridisation.

From the above discussion, we note that in octahedral complexes, the central metal atom/ion may use inner $(n-1)d$ orbitals or outer nd orbitals for hybridisation.

If the complex is formed by the use of inner d -orbitals for hybridisation (written as d^2sp^3), it is called an **inner orbital complex**. If on the other hand, the complex is formed by the use of outer d -orbitals for hybridisation (written as sp^3d^2), it is called an **outer orbital complex**. In the formation of inner orbital complex, the electrons of the metal are forced to pair up and hence the complex will be either diamagnetic or will have lesser number of unpaired electrons. Such a complex is also called **low spin complex**. On the other hand, the outer orbital complex will have a larger number of unpaired electrons since the configuration of the metal ion remains undisturbed. Such a complex is also called **high spin complex**. Thus,

Outer orbital complex (uses outer nd orbitals) = high spin

Inner orbital complex (uses inner $(n-1)d$ orbitals) = low spin

4. $[\text{Fe}(\text{CN})_6]^{3-}$ complex

Iron atom ($Z = 26$) has the electronic configuration $3d^64s^2$. In this complex, iron is in +3 oxidation state and has the electronic configuration $3d^5$ as shown in Fig. 4(a). It has been experimentally observed that the complex has one unpaired electron. To account for this, the two electrons in $3d$ orbitals are paired up leaving two $3d$ orbitals empty as shown in Fig. 4(c). These six vacant orbitals (two $3d$, one $4s$ and three $4p$) hybridise to form d^2sp^3 hybrid orbitals. Six pairs of electrons one from each CN^- ion occupy the six vacant hybrid orbitals. The molecule has octahedral geometry and is paramagnetic due to the presence of one unpaired electron.

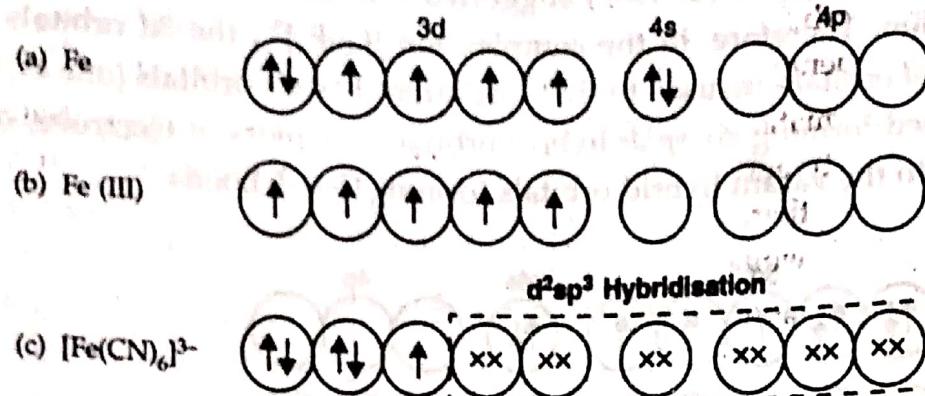


Fig. 4. Formation of $[\text{Fe}(\text{CN})_6]^{3-}$ complex involving $d^2\text{sp}^3$ hybridisation.

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

In this case also, iron is in + 3 oxidation state and has the electronic configuration as $3d^5$. This complex has been found to be paramagnetic due to the presence of five unpaired electrons. To account for this, the electrons in $3d$ -orbitals are not disturbed and the outer $4d$ orbitals are used for hybridisation. The six orbitals (one $4s$, three $4p$ and two $4d$) are hybridised resulting sp^3d^2 hybridisation. Six pairs of electrons, one from each water molecule occupy the six hybrid orbitals. The molecule is octahedral and is paramagnetic.

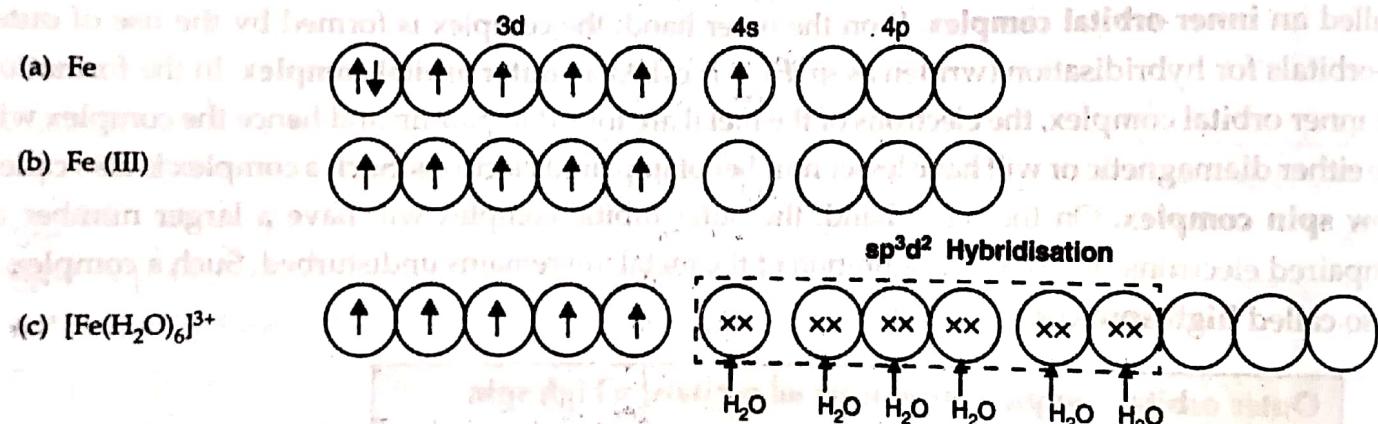


Fig. 5. Formation of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ complex involving sp^3d^2 hybridisation.

Examples of Complexes of Coordination Number 4

The complexes of coordination number 4 may have **tetrahedral** or **square planar geometry**. As already discussed tetrahedral geometry involves sp^3 hybridisation while square planar complexes involve dsp^2 hybridisation. Some common examples are discussed below :

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

The nickel atom has the ground state electronic configuration as $3d^8 4s^2$. In this case nickel is in + 2 oxidation state and its electronic configuration is $3d^8$. Depending upon the type of hybridisation, there are two possible ways in which the complexes of nickel with coordination number 4 may be formed. If the complex involves sp^3 hybridisation, it would have **tetrahedral structure**. If, on the other

hand, the complex involves dsp^2 hybridisation, it would have *square planar structure*. For the formation of tetrahedral structure, the $3d$ -orbitals remain unaffected and, therefore, the two unpaired d -electrons remain as such. Consequently, the complex would be *paramagnetic* like the Ni^{2+} ion itself.

On the other hand, for the formation of square planar structure through dsp^2 hybridisation, one of the $3d$ -orbitals should be empty and available for hybridisation. This is possible, if the two unpaired d -electrons are paired up thereby making one of the $3d$ -orbitals empty. There is thus no unpaired electron and the complex would be *diamagnetic*.

We know from experiments that the complex $[\text{Ni}(\text{CN})_4]^{2-}$ is *diamagnetic* indicating that the hybridisation involved in this case is dsp^2 as represented in Fig. 6. Consequently, the structure of the complex would be *square planar*. The empty hybrid orbitals of the metal overlap with the orbitals of cyanide ions, to form metal-ligand coordinate bonds, as shown in the figure.

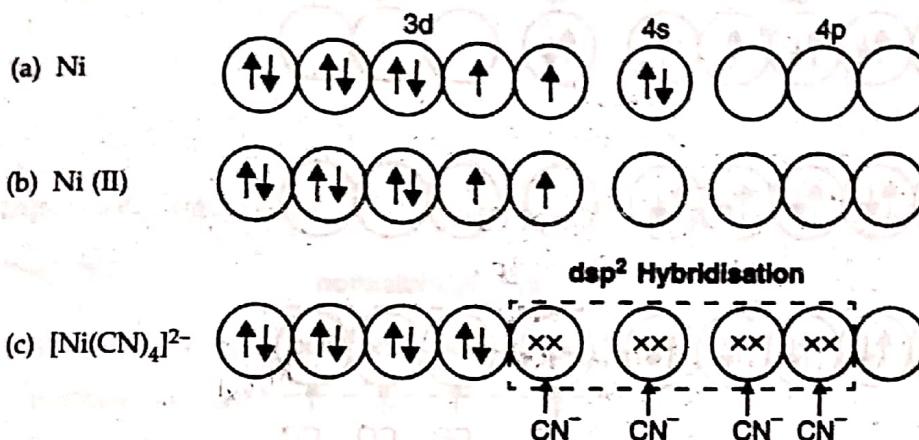


Fig. 6. Formation of square planar complex $[\text{Ni}(\text{CN})_4]^{2-}$ involving dsp^2 hybridisation.

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

The nickel(II) ion has two unpaired electrons, as shown in Fig. 7. As discussed above, if the complex of nickel with coordination number 4, is *paramagnetic*, it would involve sp^3 hybridisation and its structure should be *tetrahedral*. If the complex is *diamagnetic*, it would involve dsp^2 hybridisation and it would have *square planar structure*. The magnetic measurements of the complex $[\text{NiCl}_4]^{2-}$ show that it is *paramagnetic* and has two unpaired electrons. Therefore, in this case the $3d$ -orbitals remain undisturbed and sp^3 hybridisation occurs resulting in *tetrahedral structure* of the complex. As is evident from Fig. 7, there are two unpaired electrons in the complex.

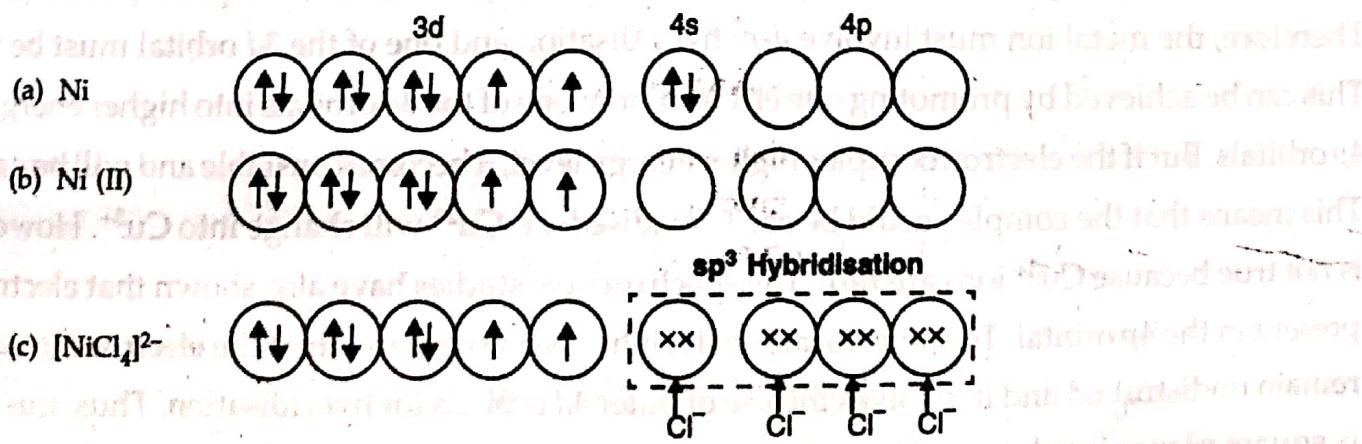


Fig. 7. Formation of tetrahedral $[\text{NiCl}_4]^{2-}$ complex involving sp^3 hybridisation.

3. $[\text{Ni}(\text{CO})_4]$

The nickel (0) has $3d^84s^2$ as its outer electronic configuration. For complexes with coordination number 4, the central atom may involve sp^3 or dsp^2 type of hybridisation, for each of which the $4s$ orbital must be empty. The electrons of $4s$ orbitals may either be promoted to higher $4d$ -orbitals or be forced into the $3d$ -orbitals to pair up with the two unpaired d -electrons. In the first case, the complex will be *paramagnetic* while in the second case, it will be *diamagnetic*. The magnetic studies of the complex $[\text{Ni}(\text{CO})_4]$ show that the complex is *diamagnetic* indicating that the two electrons in the $4s$ -orbital are forced to pair up with the $3d$ -orbitals. This results in sp^3 hybridisation and the complex has *tetrahedral structure* as shown in Fig. 8.

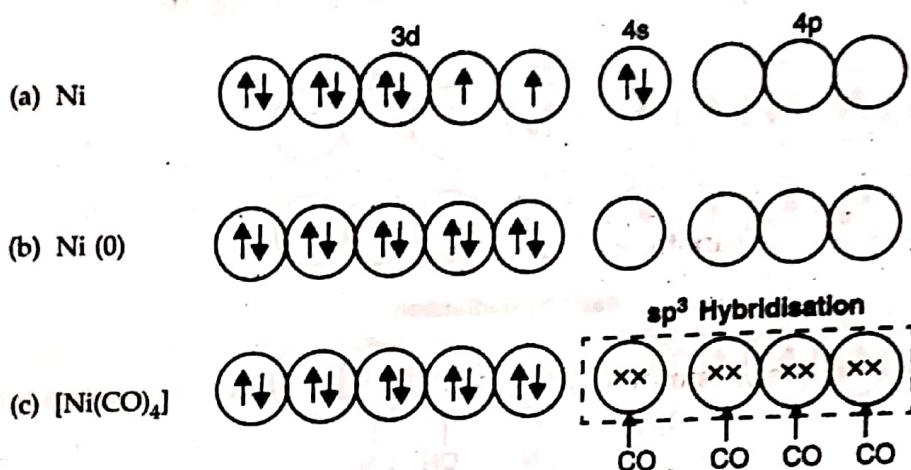
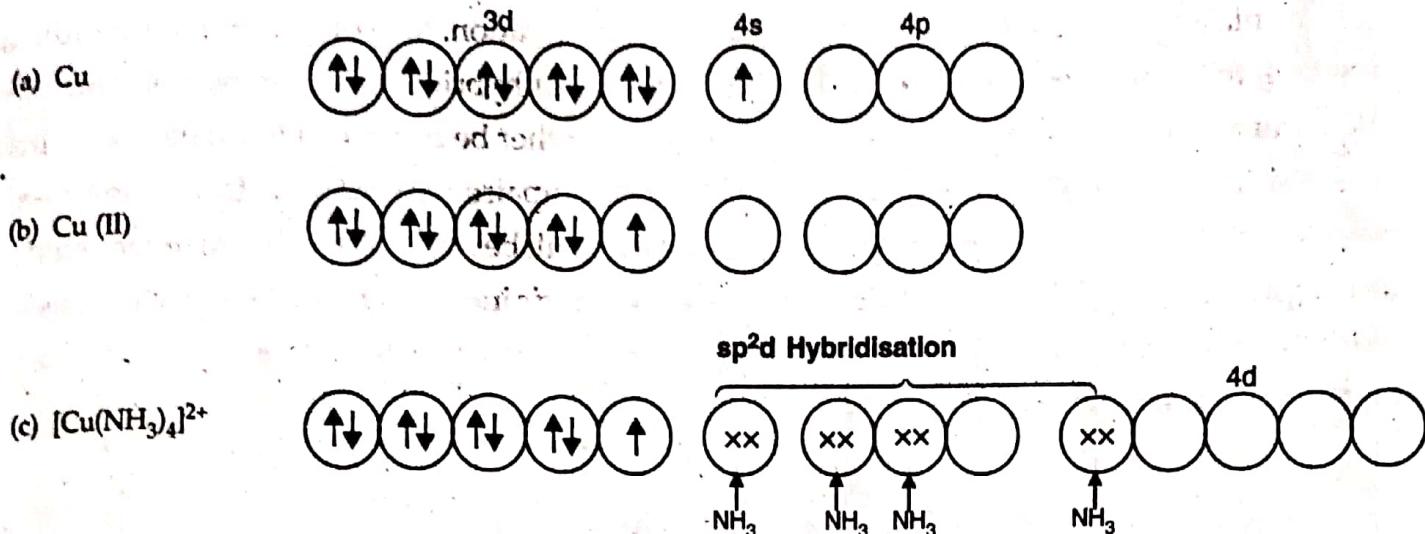


Fig. 8. Formation of tetrahedral $[\text{Ni}(\text{CO})_4]$ complex.

4. $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion

The oxidation state of copper in this complex ion is + 2. Therefore, it has $3d^9$ outer configuration. In accordance with Hund's rule, only one $3d$ orbital will be singly filled. We know that there are two possible geometries for this complex as tetrahedral or square planar. If the complex is tetrahedral, it involves sp^3 hybridisation. The complex will be paramagnetic due to the presence of one unpaired electron. Thus, the tetrahedral geometry can explain the magnetic behaviour of the complex ion.

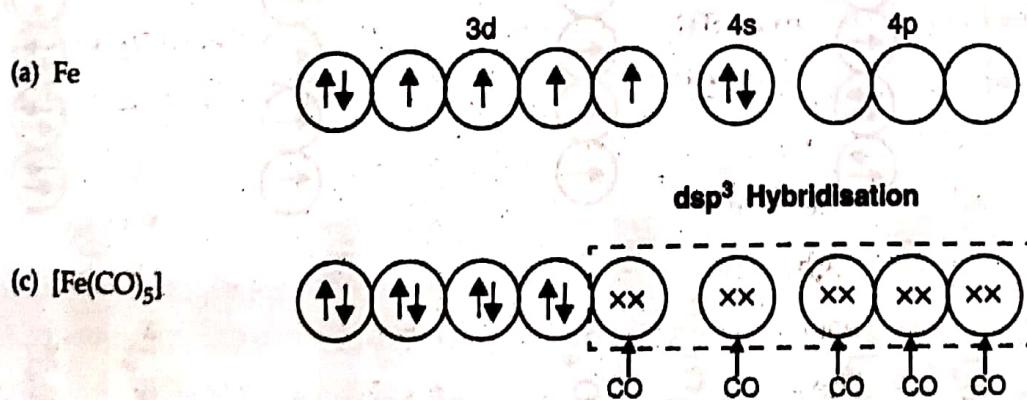
However, X-ray studies have shown that this complex ion has a square planar geometry. Therefore, the metal ion must involve dsp^2 hybridisation and one of the $3d$ orbital must be vacated. This can be achieved by promoting one electron from one of the $3d$ orbitals into higher energy vacant $4p$ orbitals. But if the electron occupies higher energy level, it becomes unstable and will be easily lost. This means that the complex could be easily oxidised, i.e. Cu^{2+} will change into Cu^{3+} . However, this is not true because Cu^{3+} ions are rare. The spectroscopic studies have also shown that electron is not present in the $4p$ orbital. To solve the anomaly, it has been suggested that the electrons in $3d$ orbitals remain undisturbed and it involves the use of outer $4d$ orbitals for hybridisation. Thus, this complex is square planar involving sp^2d hybrid orbitals as shown in Fig. 9.

Fig. 9. Formation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex.

Examples of Complexes of Coordination Number 5

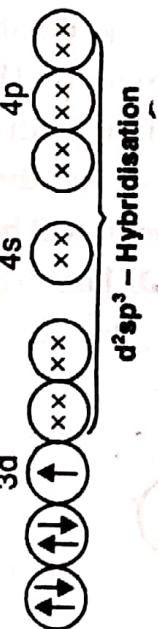
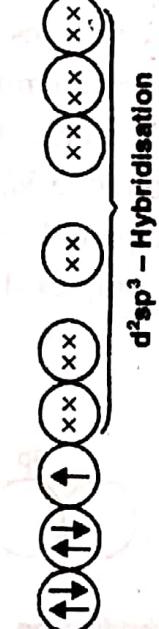
1. $\text{Fe}(\text{CO})_5$

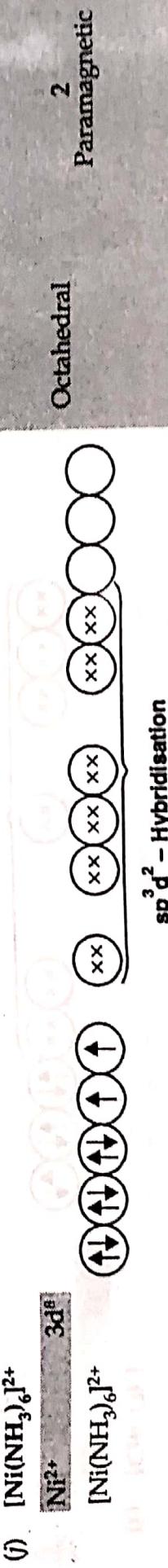
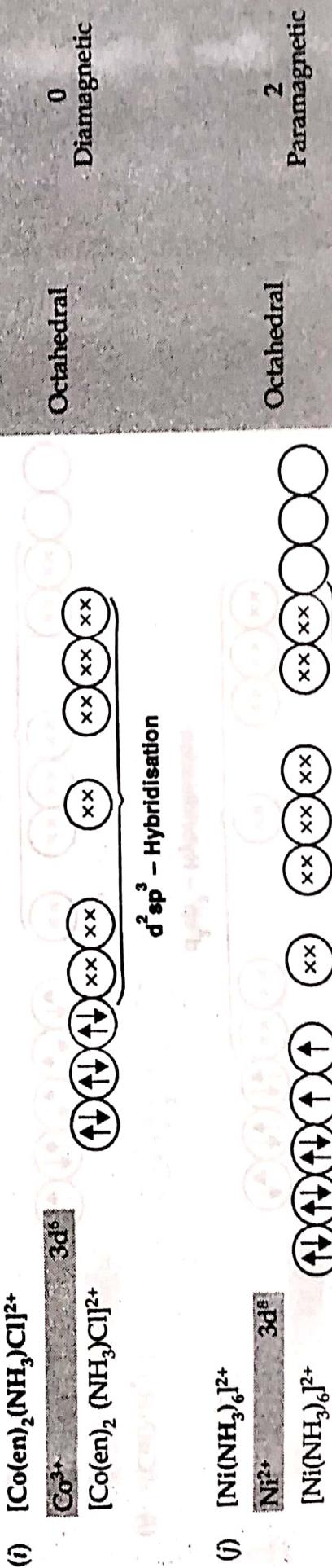
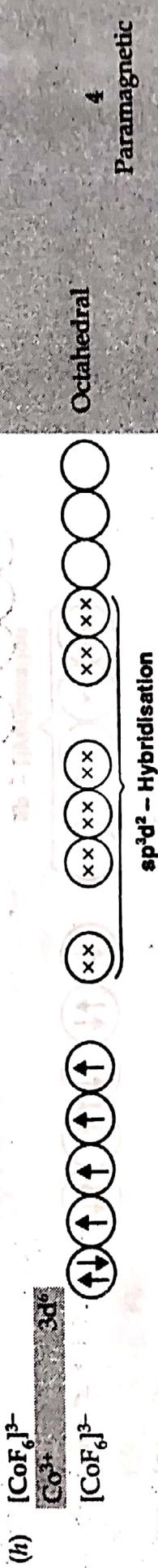
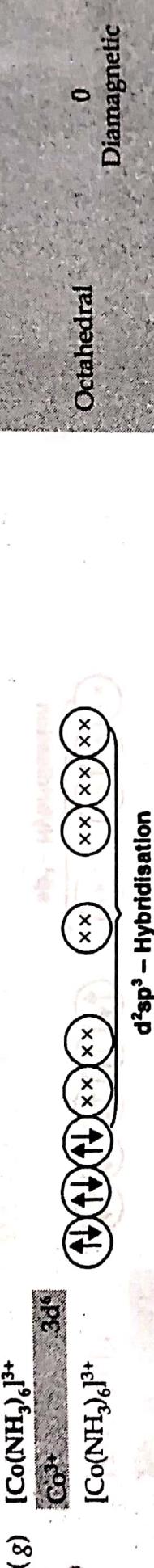
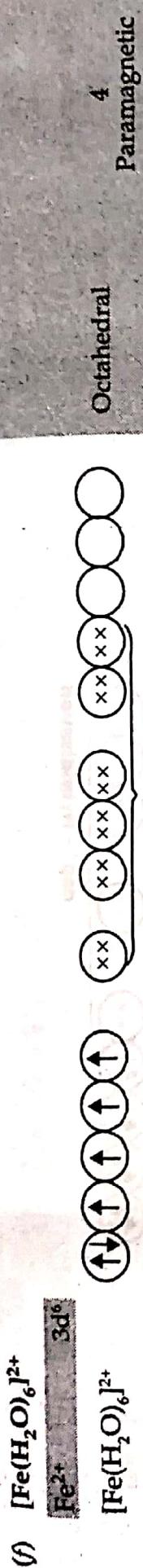
The oxidation state of iron in this complex is zero and it has the outer electronic configuration as $3d^6 4s^2$. In accordance with the Hund's rule, the six electrons shall occupy the five $3d$ orbitals in such a way that there are four unpaired electrons. For the complexes with coordination number 5, the central atom may involve dsp^3 hybridisation, and the $4s$ orbital must be empty. The two electrons of $4s$ orbital and one electron of $3d$ orbital are pushed into $3d$ orbitals to pair up with the three unpaired $3d$ electrons. The metal atom involves dsp^3 hybridisation (one $3d$, one $4s$ and three $4p$) to give five vacant dsp^3 hybrid orbitals. Since the complex has no unpaired electron, it will be diamagnetic and it is in agreement with experimental results. Thus, the complex $[\text{Fe}(\text{CO})_5]$ has trigonal bipyramidal geometry and is diamagnetic.

Fig. 10. Formation of $\text{Fe}(\text{CO})_5$ complex.

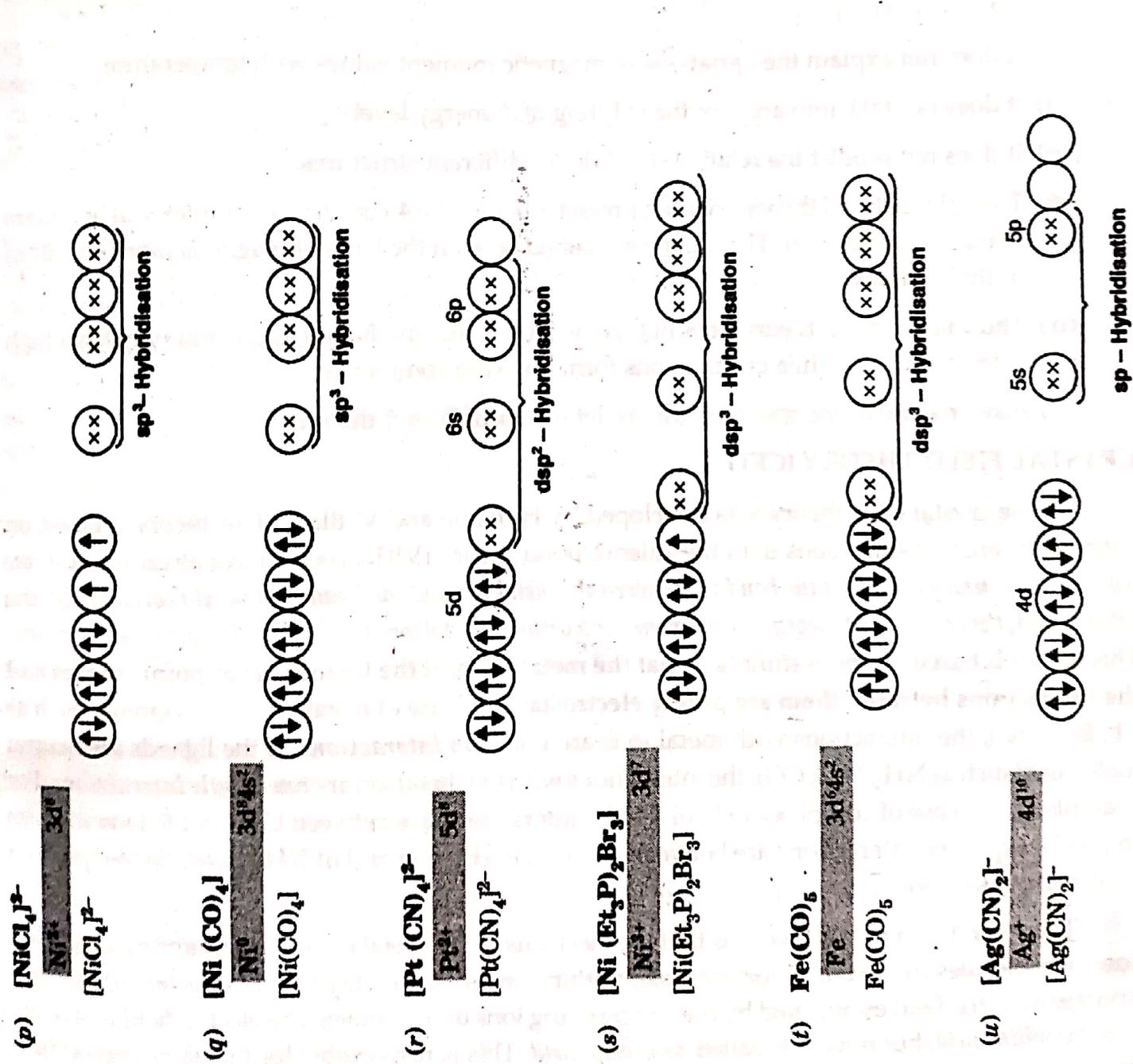
The valence bond descriptions for some important complexes are given in Table 2.

Table 2. Valence bond treatment for some complexes.

Complex/ion	Electronic configuration and hybridisation	Geometry	No. of unpaired electrons/magnetic character
(a) $[\text{Mn}(\text{CN})_6]^{4-}$ Mn^{2+} $3d^5$	$3d$ 	Octahedral	1 Paramagnetic
(b) $[\text{Fe}(\text{CN})_6]^{3-}$ Fe^{3+} $3d^5$	$3d$ 	Octahedral	1 Paramagnetic
(c) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ Fe^{3+} $3d^5$	$3d$ 	Octahedral	5 Paramagnetic
(d) $[\text{FeF}_6]^{3-}$ Fe^{3+} $3d^5$	$3d$ 	Octahedral	5 Paramagnetic
(e) $[\text{Fe}(\text{CN})_6]^{4-}$ Fe^{2+} $3d^6$	$3d$ 	Octahedral	0 Diamagnetic



Tetrahedral	2	Paramagnetic
Tetrahedral	0	Diamagnetic
Square planar	0	Diamagnetic
Trigonal bipyramidal	1	Paramagnetic
Trigonal bipyramidal	0	Diamagnetic
Linear	0	Diamagnetic



LIMITATIONS OF VALENCE BOND THEORY

We have seen that valence bond theory has satisfactorily explained many stereochemical and magnetic properties. But it has many limitations. The main limitations of valence bond theory are :

- (i) It provides only qualitative explanations for complexes.
- (ii) It does not explain the colour and electronic spectra of complexes.
- (iii) The theory fails to explain why some metal complexes in a particular oxidation state are low spin (i.e., inner orbital) complexes while some other complexes of the same metal ion in the same oxidation state are high spin (i.e., outer orbital) complexes.
- (iv) It does not predict the relative stabilities of different complexes. We know that certain complexes are **labile** in which the displacement of ligand takes place rapidly, while some are **inert** in which ligand displacement by another ligand is very slow. Valence bond theory does not explain the kinetic inertness of complexes such as Cr(III) and low spin Co(III) octahedral complexes.
- (v) It does not explain the variations of magnetic moment values with temperature.
- (vi) It does not take into account the splitting of d -energy levels.
- (vii) It does not predict the relative stabilities of different structures.
- (viii) The valence bond theory does not predict whether the 4-coordinate complex will be square planar or tetrahedral. This can be explained only on the basis of magnetic moment values of the complex.
- (ix) The valence bond theory does not tell us why water and halide ions commonly form high spin complexes while cyanide ions form low spin complexes.

To answer some of the above problems, let us discuss other theories.

CRYSTAL FIELD THEORY (CFT)

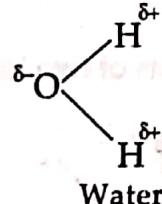
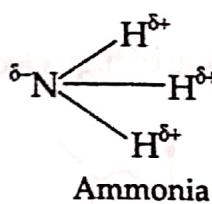
The crystal field theory was developed by H. Bethe and V. Bleck. This theory is based on entirely different assumptions than the valence bond theory (VBT). As we have already learnt, *the valence bond theory considers the bonding between the metal ion and the ligands as purely covalent*. On the other hand, *the crystal field theory considers the bond between metal ion and the ligand as purely electrostatic*. This theory is based on the assumption that the metal ion and the ligands act as point charges and **the interactions between them are purely electrostatic**. In case of negative ligands (anions such as Cl^- , Br^- , CN^-), the interactions with metal ions are ***ion - ion interactions***. If the ligands are neutral molecules (such as NH_3 , H_2O , CO), the interactions with the metal ion are ***ion-dipole interactions***. For example, in the case of complex ion $[\text{CoF}_6]^{3-}$ the interactions are between Co^{3+} and F^- ions whereas in $[\text{Co}(\text{NH}_3)_6]^{3+}$, the interactions are between negatively charged end of NH_3 molecule (δ -charge on N atom) and Co^{3+} ion.

The central idea of this theory is that the electrons of the metal ion in the environment of other ions or molecules (ligands), as for example, within the lattice of a crystal are affected by the non-spherical electric field established by the surrounding ions or molecules. The electric field was called the *crystalline field*, but now, it is called as *crystal field*. This is responsible for the name *crystal field theory*.

Basis of Crystal Field Theory

The basic assumptions of crystal field theory are :

- The transition metal ion is surrounded by the ligands with lone pairs of electrons.
- All types of ligands are regarded as point charges. The ligands may be either ionic (F^- , Cl^- , CN^- , etc.) or molecules (such as H_2O , NH_3 , CO , etc.). If the ligand is a neutral molecule, then the negative end of the dipole is oriented towards the metal ion. For example, ammonia, NH_3 , is polar molecule having $\delta-$ negative charge on N and $\delta+$ charges on H atoms. Similarly, water is also polar with $\delta-$ charge on O and $\delta+$ charges on H atoms.



- The interactions between the metal ion and the negative ends of anion (or ion dipoles) is purely electrostatic, i.e. the bond between the metal and ligand is considered 100% ionic.

- The ligands surrounding the metal ion produce electrical field and this electrical field influences the energies of the orbitals of central metal ion, particularly d -orbitals.

- In the case of free metal ion, all the five d -orbitals have the same energy. These orbitals having the same energies are called **degenerate orbitals**. This means that an electron can occupy any one of these five d -orbitals with equal ease. However, on the approach of the ligands, the orbital electrons will be repelled by the lone pairs of the ligands. The repulsion will raise the energy of the d -orbitals. If all the ligands approaching the central metal ion are at equal distance from each of the d -orbitals, the energy of each orbital will increase by the same amount. Therefore, these orbitals will still remain degenerate, but they will have higher energy than before. But we know that d -orbitals have different orientations and, therefore, these orbitals will experience different interactions from the ligands. The orbitals lying in the direction of the ligands, will experience greater repulsion and their energies will be raised to greater extent. On the other hand, the orbitals lying away from the approach of the ligands will have lesser interactions and therefore, their energies will be raised to lesser extent. Therefore, due to the electrical field of the ligands, the energies of the five d -orbitals will split up. **This conversion of five degenerate d -orbitals of the metal ion into different sets of orbitals having different energies in the presence of electrical field of ligands** is called **crystal field splitting**. This concept forms the basis of crystal field theory.

- The number of ligands (coordination number) and their arrangement (geometry) around the central metal ion will have different effect on the relative energies of the five d -orbitals. In other words, **the crystal field splitting will be different in different structures with different coordination numbers**.

- The magnetic properties, spectra and preference for particular geometry can be explained in terms of splitting of d -orbitals in different crystal fields.

Thus, to understand the crystal field theory, it is essential to have a clear picture of the disposition of the five d -orbitals in space and the geometrical arrangement of the ligands around the central metal ion. We may illustrate this concept by considering the complexes with coordination number 6 and 4, which are very common.

Shapes of d -orbitals

There are five d -orbitals. These are designated as d_{xy} , d_{yz} , d_{zx} , $d_{x^2-y^2}$ and d_{z^2} . The shapes of these orbitals are described below :

(i) The three orbitals d_{xy} , d_{yz} and d_{zx} are similar and each consists of four lobes of high electron density lying in xy , yz and zx planes respectively. These lobes lie in between the principal axes. For example, in case of d_{xy} orbital, the four lobes lie in xy plane in between the x and y -axes.

(ii) The $d_{x^2-y^2}$ orbital has also four lobes of high electron density along the principal axes x and y . It may be noted that this orbital is exactly like d_{xy} orbital except that it is rotated through 45° around the z -axis.

(iii) The d_{z^2} orbital consists of two lobes along the z -axis with a ring of high electron density in the xy plane.

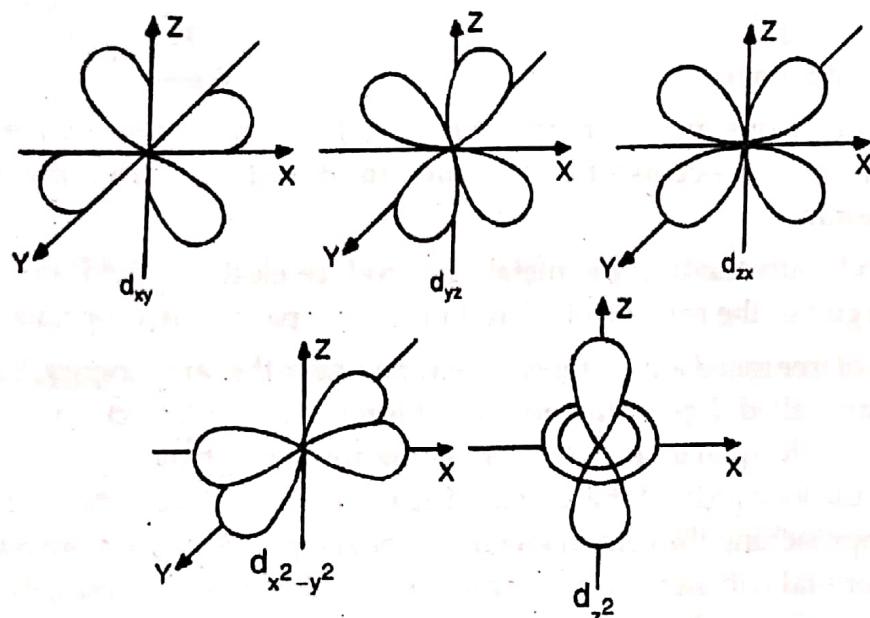


Fig. 11. Shapes of five 3d orbitals.

It may be noted that although d_{z^2} and $d_{x^2-y^2}$ orbitals do not look to be similar yet they are equivalent so far as interactions with the metal ions are concerned. The d_{z^2} orbital can be regarded as a linear combination of two orbitals $d_{z^2-x^2}$ and $d_{z^2-y^2}$, each of which is equivalent to the $d_{x^2-y^2}$ orbital as shown below :

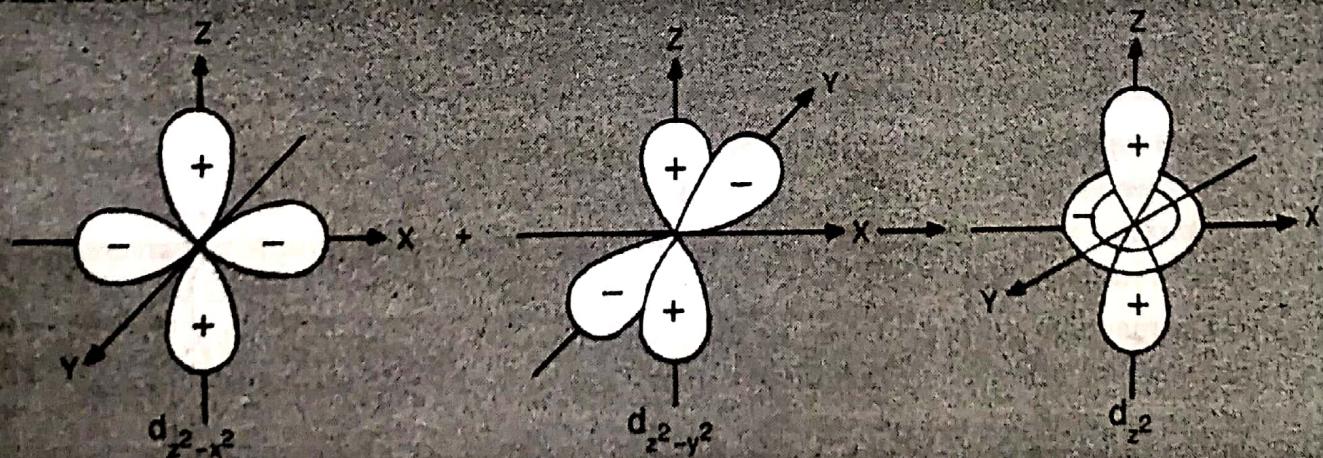


Fig. 12. Representation of d_{z^2} orbital as a linear combination of $d_{z^2-x^2}$ and $d_{z^2-y^2}$ orbitals.

However, it may be noted that these two orbitals ($d_{z^2-x^2}$ and $d_{z^2-y^2}$) do not have independent existence but the d_{z^2} orbital can be thought of as having the average properties of the two.

Crystal Field Splitting in Octahedral Complexes

In an octahedral complex (coordination number 6), the metal ion is at the centre of the octahedron and the ligands are at the six corners as shown in Fig. 13. The three axes X, Y and Z point along the corners of the octahedron and are also shown. Let us suppose that the metal ion, M^{n+} , has a single d -electron (d^1 configuration, e.g., Ti^{3+} in $[TiF_6]^{3-}$). In the free ion, when there are no ligands the electron can occupy any one of the five d -orbitals because all are of the same energy, and are called degenerate orbitals.

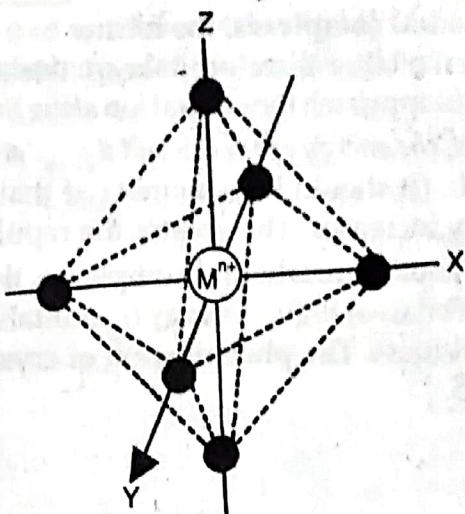


Fig. 13. Six ligands at the corners of an octahedron surrounding the metal ion, M^{n+} .

However, in the octahedral complex MX_6 , all the five d -orbitals will not remain of equal energy. This can be easily understood by considering the shapes of these orbitals. The comparison of arrangement of d -orbitals in Fig. 14 shows that the two lobes of d_{z^2} orbital and four lobes of $d_{x^2-y^2}$ orbital point directly towards the corners of the octahedron, where the negative charges of the ligands are concentrated. The remaining three orbitals are oriented in between the axes. In the case of

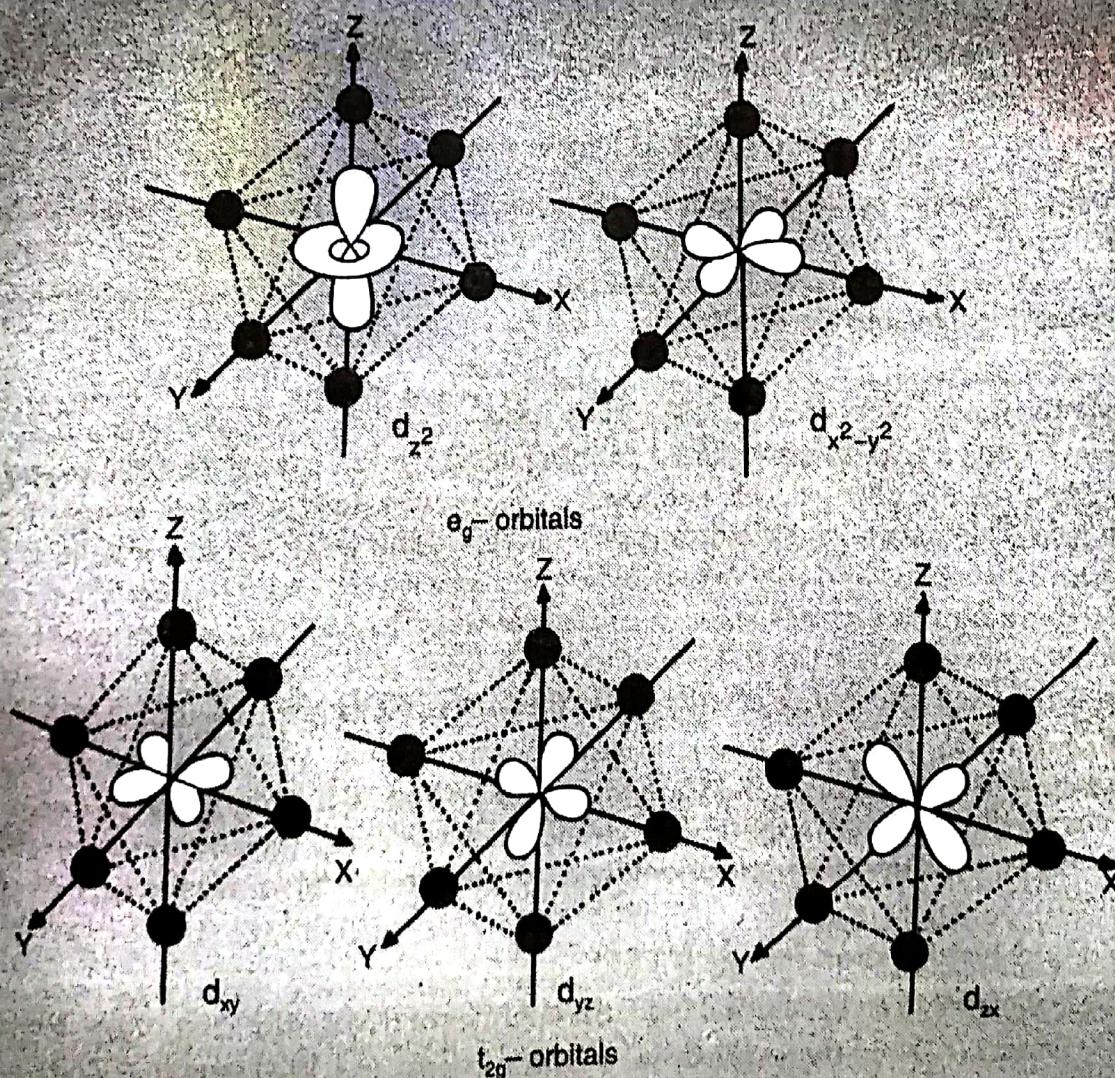


Fig. 14. Orientations of different d -orbitals in an octahedral field of six ligands.

octahedral complexes, the former two orbitals are designated as e_g (pronounced as "e- g") orbitals while the latter three orbitals are designated as t_{2g} (pronounced as "t-two-g") orbitals. As the two ligands approach the central ion along the axes, the e_g orbitals are repelled more than the t_{2g} orbitals. In other words, the energy of the d_{z^2} and $d_{x^2-y^2}$ orbitals increases much more than the energy of the d_{xy} , d_{yz} and d_{zx} orbitals. (It should be remembered that when a charge is repelled by a similar charge, its potential energy increases. The greater the repulsion, the greater is the increase in energy).

Thus, in octahedral complexes, the five d-orbitals split up into two sets : one set consisting of two orbitals of higher energy (e_g orbitals) and the other set consisting of three orbitals of lower energy (t_{2g} orbitals). The phenomenon of crystal field splitting in an octahedral complex is illustrated in Fig. 15.

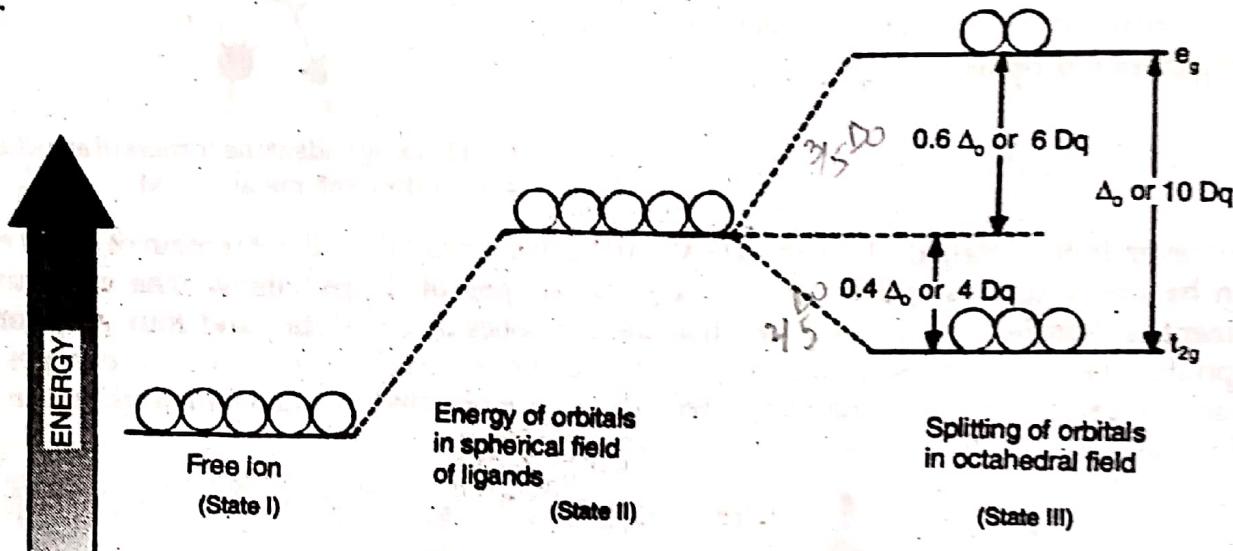


Fig. 15. Crystal field splitting in an octahedral complex.

The energy difference between two sets of d-orbitals; t_{2g} and e_g is called crystal field splitting energy and is symbolically represented as Δ_o (the subscript (o) stands for octahedral). The magnitude of Δ_o varies for different complexes. The crystal field splitting is also measured in terms of another parameter called Dq. The two are related as :

$$\Delta_o = 10 \text{ Dq}$$

These two parameters are very commonly used.

It may be noted that the crystal field splitting occurs in such a way that the average energy of the d-orbitals does not change. This is known as barycentre rule, which is similar to 'centre of gravity' type rule. This 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. Therefore, in terms of total energy 10 Dq, the energy of each of the two e_g orbitals is raised by 6 Dq and the energy of each of the three t_{2g} orbitals is lowered by 4 Dq. In terms of Δ_o , the energy of each of the two e_g orbitals is raised by $3/5 \Delta_o$ (or $0.6 \Delta_o$) and the energy of each of the three t_{2g} orbitals is lowered by $2/5 \Delta_o$ (or $0.4 \Delta_o$).

The value of 10 Dq or Δ_o is measured spectroscopically. In Fig. 15, we observe that initially the energies of all the five d-orbitals are raised equally as shown in state II. This would be observed if the field created by the ligands were spherically symmetrical. However, the energies of d-orbitals split into two sets because of the different orientation of the orbitals towards the ligands as shown in state III.

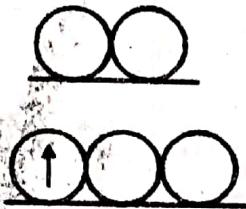
Crystal Field Stabilization Energy (CFSE)

We have learnt that in an octahedral field, the energies of five d-orbitals split-up. Three orbitals are lowered in energy (t_{2g}) and two orbitals are raised in energy (e_g). We know that electrons always prefer to occupy an orbital of lower energy. For example, in the case of d^1 system (e.g., Ti^{3+} in $[\text{TiF}_6]^{3-}$),

the d -electron will prefer to occupy a t_{2g} orbital and is, therefore, stabilized by an amount equal to $0.4 \Delta_o$ or $4 Dq$. The amount of stabilization provided by splitting of the d -orbitals into two levels is called crystal field stabilization energy. It is abbreviated as CFSE. Thus, in octahedral field for each electron entering into the t_{2g} orbital, the crystal field stabilization is $-4 Dq$ and for each electron entering into the e_g orbital the crystal field destabilization energy is $+6 Dq$. Thus, the CFSE is calculated as the algebraic sum of $-4Dq$ per electron in t_{2g} level and $+6 Dq$ for each electron in e_g orbital.

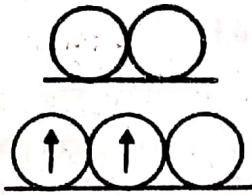
CFSE for various Octahedral Complexes

(i) For a d^1 system (e.g., Ti^{3+} ion) electron will be present in any one of the three t_{2g} orbitals. The electronic configuration may be written as t_{2g}^1 . The **crystal field stabilization energy** is $-4Dq$:



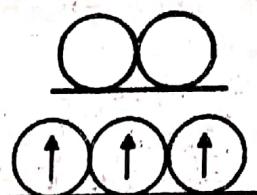
$$CFSE = 1(-4Dq) = -4Dq$$

(ii) For a d^2 system (e.g., V^{3+} ion) the electrons will occupy t_{2g} orbitals with their spins parallel in accordance with Hund's rule. The electronic configuration is t_{2g}^2 and **crystal field stabilization energy** is $-8Dq$:



$$CFSE = 2(-4Dq) = -8Dq$$

(iii) Similarly, for a d^3 system (e.g., Cr^{3+}), the electronic configuration is t_{2g}^3 . The **crystal field stabilization energy** is $-12 Dq$:



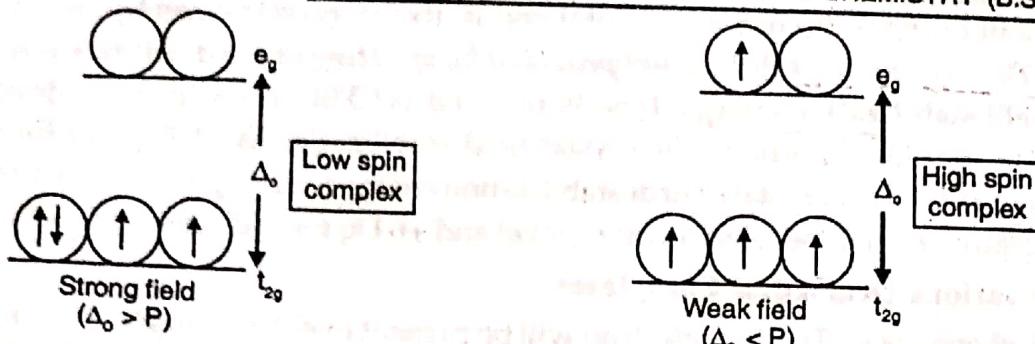
$$CFSE = 3(-4Dq) = -12Dq$$

(iv) For a d^4 system (e.g., Mn^{3+} ion), there are two possibilities :

- (a) All the four electrons may occupy t_{2g} orbitals with one electron gets paired. The electronic configuration may be written as t_{2g}^4 .
- (b) Three electrons occupy t_{2g} orbitals and the fourth electron goes to one of the e_g orbitals. The configuration may be written as $t_{2g}^3 e_g^1$.

The actual configuration may be decided on the basis of Δ_o and the pairing energy (P), i.e. the energy required to pair the electrons with one another.

The configuration (a) is possible if $\Delta_o > P$. These complexes are called **strong field complexes** because Δ_o is large. In this case, the complex has less number of unpaired electrons and is called **low spin complex**. The configuration (b) is possible if $\Delta_o < P$. It is called **weak field** and the complexes are called **weak field complexes**. In that case, the maximum number of electrons remain unpaired and the complex is called **high spin complex**.



Thus, we may generalize that if

$$\Delta_o > P \text{ (strong field)} : \text{ Low spin complex}$$

$$\Delta_o < P \text{ (weak field)} : \text{ High spin complex}$$

As shown above, for a low spin complex having $t_{2g}^4 e_g^1$ configuration,

$$\text{CFSE} = 4(-4Dq) = -16Dq$$

However, if we take into account pairing energy (P) also, the net CFSE becomes :

$$\text{Net CFSE} = -16Dq + P$$

On the other hand, for a high spin complex, having the configuration $t_{2g}^3 e_g^1$:

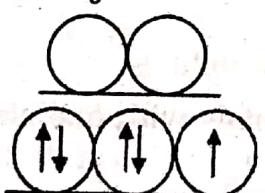
$$\text{CFSE} = 3(-4Dq) + 1(6Dq) = -6Dq.$$

(v) Similarly, for a d^5 system (e.g., Fe^{3+} ion), there are two possibilities :

- (a) All the five electrons may occupy t_{2g} orbitals with two orbitals get paired. The electronic configuration may be written as t_{2g}^5 . This is possible if $\Delta_o > P$ and the complex will be called **strong field or low spin complex**.
- (b) The three electrons occupy t_{2g} orbitals and two electrons occupy e_g orbitals. The electronic configuration may be written as $t_{2g}^3 e_g^2$. This will be possible if $\Delta_o < P$ and the complex is called **weak field or high spin complex**.

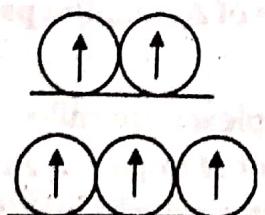
The CFSE in these two types of complexes will be :

(a) **Strong field : $\Delta_o > P$**



$$\begin{aligned}\text{CFSE} &= 5(-4Dq) + 2P \\ &= -20Dq + 2P\end{aligned}$$

(b) **Weak field : $\Delta_o < P$**

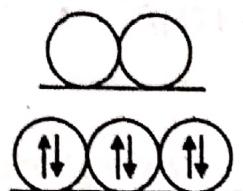


$$\begin{aligned}\text{CFSE} &= 3(-4Dq) + 2(6Dq) \\ &= 0\end{aligned}$$

Similarly, d^6 and d^7 systems have two possibilities depending upon the relative magnitudes of crystal field splitting energy (Δ_o) and the pairing energy of the electrons (P).

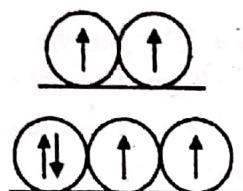
For a d^6 system (Co^{3+})

(a) Strong field : $\Delta_o > P$



$$\begin{aligned}\text{CFSE} &= 6(-4 \text{ Dq}) + 2 \text{ P} \\ &= -24 \text{ Dq} + 2 \text{ P}\end{aligned}$$

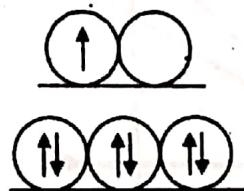
(b) Weak field : $\Delta_o < P$



$$\begin{aligned}\text{CFSE} &= 4(-4 \text{ Dq}) + 2(6 \text{ Dq}) \\ &= -4 \text{ Dq.}\end{aligned}$$

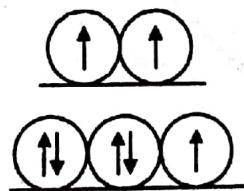
For a d^7 system (Co^{2+})

(a) Strong field : $\Delta_o > P$



$$\begin{aligned}\text{CFSE} &= 6(-4 \text{ Dq}) + 1(6 \text{ Dq}) \\ &= -18 \text{ Dq} + \text{P}\end{aligned}$$

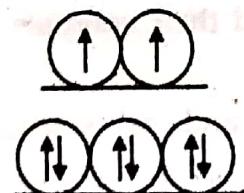
(b) Weak field : $\Delta_o < P$



$$\begin{aligned}\text{CFSE} &= 5(-4 \text{ Dq}) + 2(6 \text{ Dq}) \\ &= -8 \text{ Dq.}\end{aligned}$$

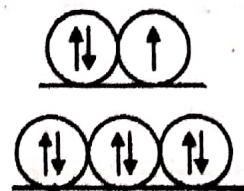
The d^8 , d^9 and d^{10} systems have only one possible configuration. This is because if we assume the complex to be high spin, the first five electrons would go one each into the five d -orbitals and remaining (3, 4 or 5) electrons would fill the t_{2g} and e_g orbitals. But if we assume the complex to be low spin, the first six electrons would fill the t_{2g} orbitals and the remaining (2, 3 or 4) electrons would go into the t_{2g} orbitals. In both cases the configurations will be the same. Therefore, there is only one possible electronic configuration for d^8 , d^9 and d^{10} systems.

For a d^8 system (Ni^{2+})



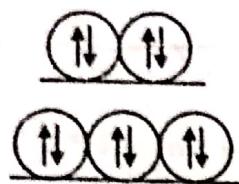
$$\begin{aligned}\text{CFSE} &= 6(-4 \text{ Dq}) + 2(6 \text{ Dq}) \\ &= -12 \text{ Dq}\end{aligned}$$

For a d^9 system (Cu^{2+})



$$\begin{aligned}\text{CFSE} &= 6(-4 \text{ Dq}) + 3(6 \text{ Dq}) \\ &= -6 \text{ Dq}\end{aligned}$$

For a d^{10} system (Zn^{2+})



$$\begin{aligned} \text{CFSE} &= 6(-4 \text{ Dq}) + 4(6 \text{ Dq}) \\ &= 0 \end{aligned}$$

Crystal field stabilization energies (CFSE) for metal ions having different configurations are given in Table 3.

Crystal Field Splitting in Tetrahedral Complexes

The coordination number for tetrahedral complexes is 4. The tetrahedral arrangement of four ligands surrounding a metal ion may be visualized by placing ligands on the four of the eight corners of the cube. The directions X, Y and Z point to the centre of the faces of the cube. From Fig. 16, it is clear that the orbitals d_{xy} , d_{yz} and d_{zx} point between X, Y and Z-axis (i.e. towards the centre of the

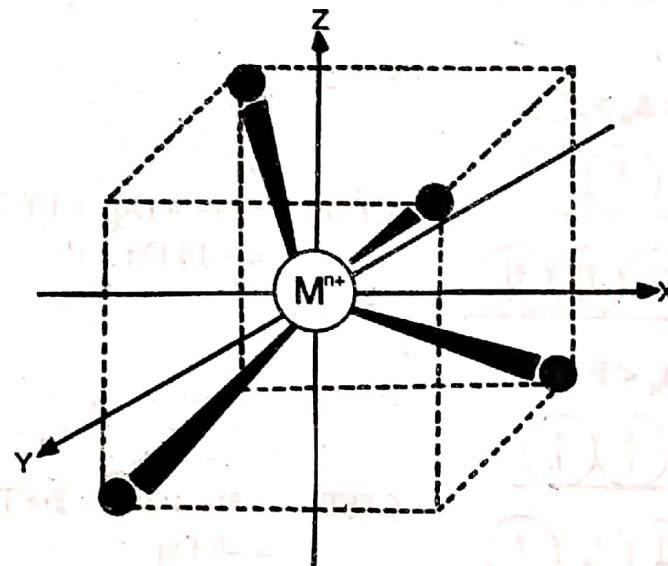


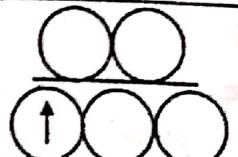
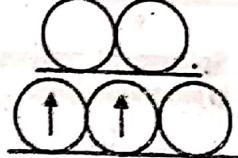
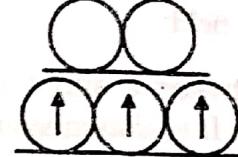
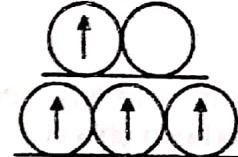
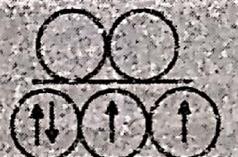
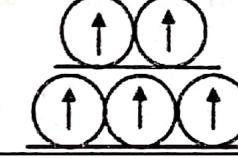
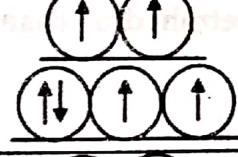
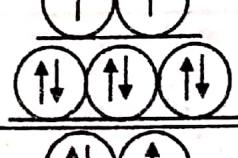
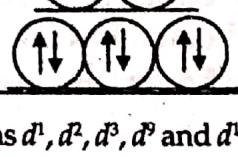
Fig. 16. Tetrahedral field of four ligands around the central metal ion.

edges of the cube) whereas the orbitals $d_{x^2-y^2}$ and d_z^2 point along X, Y and Z axis (i.e. to the centres of the faces). It is clear that in tetrahedral field, *none of the d-orbitals point exactly towards the ligands and therefore, the splitting of energy will be less than that in octahedral field*. The three d-orbitals d_{xy} , d_{yz} and d_{zx} are pointing close to the direction in which the ligands are approaching while the two orbitals $d_{x^2-y^2}$ and d_z^2 are lying in between the ligands. Therefore, the energies of the three orbitals will be raised while the energies of the two orbitals will be lowered. Thus, in the presence of tetrahedral field, the degeneracy of five d-orbitals split-up as :

- (i) The two orbitals, $d_{x^2-y^2}$ and d_z^2 become stable and their energies are lowered. These are designated as 'e' orbitals.
- (ii) The three orbitals d_{xy} , d_{yz} and d_{zx} become unstable and their energies are raised. These are designated as ' t_2 ' orbitals.

* It may be noted that for the splitting of d-orbitals in tetrahedral field, the subscript 'g' is not used. For example, the orbitals $d_{x^2-y^2}$ and d_z^2 are designated as 'e' orbitals whereas the other three orbitals d_{xy} , d_{yz} and d_{zx} are designated as t_2 . This is because a tetrahedral geometry has no centre of symmetry. The symbols 'g' and 'u' have meaning only for fields which have centre of symmetry.

Table 3. Crystal field stabilization energies for metal ions having different numbers of d -electrons in octahedral complexes.

Number of d electrons	Weak field	CFSE	Strong field*	CFSE
d^1		$-4Dq$ or $-0.4\Delta_o$		
d^2		$-8Dq$ or $-0.8\Delta_o$		
d^3		$-12Dq$ or $-1.2\Delta_o$		
d^4		$-6Dq$ or $-0.6\Delta_o$		$-16Dq + P$ or $-1.6\Delta_o + P$
d^5		0		$-20Dq + 2P$ or $-2.0\Delta_o + 2P$
d^6		$-4Dq$ or $-0.4\Delta_o$		$-24Dq + 2P$ or $-2.4\Delta_o + 2P$
d^7		$-8Dq$ or $-0.8\Delta_o$		$-18Dq + P$ or $-1.8\Delta_o + P$
d^8		$-12Dq$ or $-1.2\Delta_o$		$-12Dq$ or $-1.2\Delta_o$
d^9		$-6Dq$ or $-0.6\Delta_o$		
d^{10}		0		

*The systems d^1 , d^2 , d^3 , d^9 and d^{10} have same configuration in weak field and strong field and, therefore, have same CFSE values.

This is diagrammatically shown in Fig. 17.

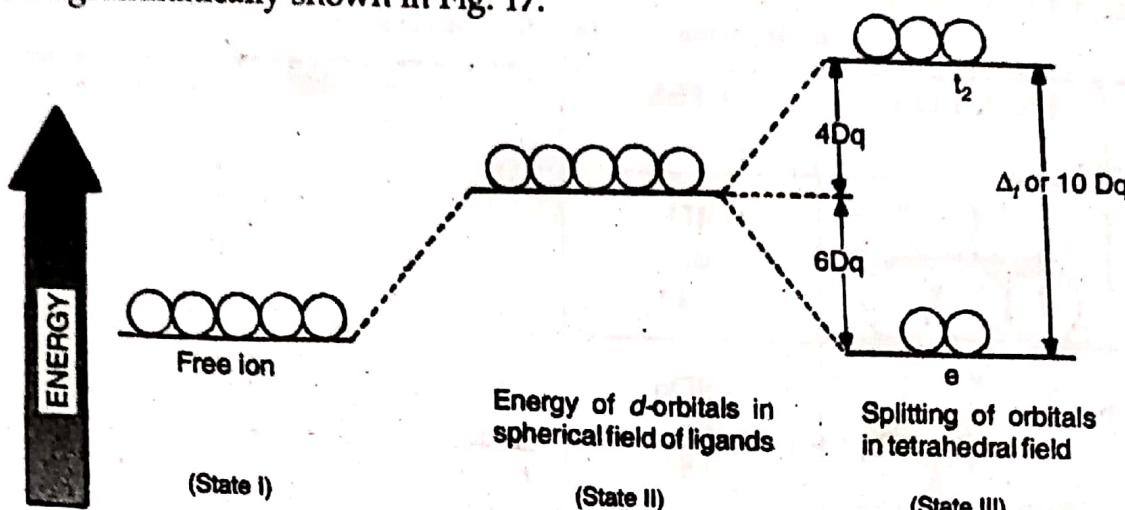


Fig. 17. Crystal field splitting in a tetrahedral field.

The magnitude of crystal field splitting is the difference between e and t_2 orbitals and is designated as Δ_t (the subscript (t) indicating tetrahedral complexes). It is also measured in terms of Dq and

$$\Delta_t = 10 \text{ Dq}$$

If we compare the magnitude of crystal field splitting in octahedral and tetrahedral complexes (having same metal ion, ligands and metal ion-ligand distances), it has been observed that the crystal field splitting in tetrahedral complexes (Δ_t) is considerably less than in octahedral complexes (Δ_o). It has been found to be

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

Reasons for the smaller value of crystal field splitting in tetrahedral than in octahedral complexes.

There are two main reasons for this :

- (i) In tetrahedral complexes there are four ligands while there are six ligands in octahedral complexes. Therefore, lesser ligands produce less crystal field splitting. The crystal field splitting in tetrahedral field is about two third of the octahedral field.
- (ii) In tetrahedral field, none of the orbitals is pointing directly towards the ligands and, therefore, splitting is less.

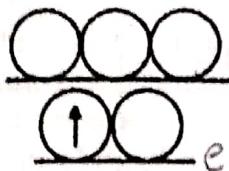
Since the magnitude of crystal field splitting in tetrahedral field is quite small and is always less than the pairing energy, therefore, the pairing of electrons will never be energetically favourable. Thus, all the tetrahedral complexes are high spin complexes. No tetrahedral complex with low spin has been found to exist.

CFSE for Tetrahedral Complexes

As we know that an electron always prefers to occupy an orbital of lower energy. Since average energy of the d -orbitals does not change (barycentre rule), therefore, in terms of 10 Dq the energy of each of the e orbital is lowered by 6 Dq and the energy of each of the t_2 orbital is raised by 4 Dq . CFSE is therefore, calculated as the algebraic sum of -6 Dq per electron in e orbital and $+4 \text{ Dq}$ for each electron in t_2 orbital. In terms of Δ_t , the energy of each e orbital is lowered by $3/5 \Delta_t$ (or $0.6 \Delta_t$) while each of the t_2 orbital is raised by $2/5 \Delta_t$ (or $0.4 \Delta_t$).

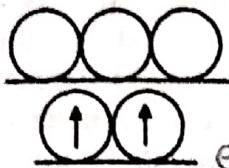
For example,

- (i) For d^1 system, the electronic configuration is e^1 . Therefore,



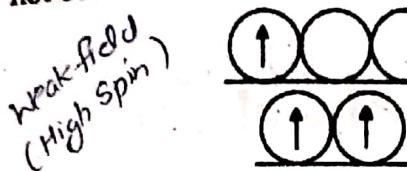
$$CFSE = 1(-6Dq) = -6Dq$$

(ii) For d^2 system, the electronic configuration is e^2 . Therefore,



$$CFSE = 2(-6Dq) = -12Dq$$

(iii) For d^3 system, the electronic configuration is $e^2 t_2^1$. As already discussed, crystal field splitting in tetrahedral field is quite small and is always less than the pairing energy. Therefore, pairing does not occur and most of the complexes are high spin complexes. Therefore,



$$CFSE = 2(-6Dq) + 1(4Dq) = -8Dq$$

The CFSE for complexes with metal ions having different configurations of d -orbitals in tetrahedral field are given in Table 4.

Table 4. Crystal field stabilization energies for tetrahedral complexes with metal ions having different numbers of d -orbitals.*

$t_2 \quad d^1$		$CFSE = -6Dq$	d^2		$CFSE = -12Dq$
e					$2(-6Dq) + 2(4Dq)$ $CFSE = -4Dq$
d^3		$CFSE = -8Dq$	d^4		$-12 + 8$
					$CFSE = -6Dq$
d^5		$CFSE = 0$	d^6		
					$CFSE = -8Dq$
d^7		$CFSE = -12Dq$	d^8		$CFSE = 0$
d^9		$CFSE = -4Dq$	d^{10}		$CFSE = 0$

*For simplicity, the pairing energies are not given.

Crystal Field Splitting in Tetragonal and Square Planar Complexes

The splitting of d -orbitals in *tetragonal* and *square planar* complexes can be easily understood from the known splitting of d -orbitals in octahedral complexes. This is because tetragonal and square planar geometries can be understood by *removing two trans ligands from an octahedral complex*. This process is called **elongation**. Generally, we consider the removal of trans ligands along the Z-axis.

As the ligands lying on the Z-axis are moved away, the ligands in the XY plane tend to approach the central ion more closely. As a result of increase in metal-ligand bond along Z-axis, the repulsions from the ligands to electrons in d_{z^2} orbital decreases and therefore, the energy of d_{z^2} orbital is decreased relative to that in octahedral field. At the same time, the metal-ligand bond along X and Y are shortened so that the d -orbital in XY plane, $d_{x^2-y^2}$ experiences greater repulsion from the ligands and therefore, its energy is raised. Similarly, the d_{xy} and d_{z^2} orbitals are lowered in energy because of decrease in repulsion effects along the Z-axis while the energy of d_{xy} orbital is raised. The resulting splitting pattern is shown in Fig. 18. This state represents **tetragonally distorted octahedral structure**.

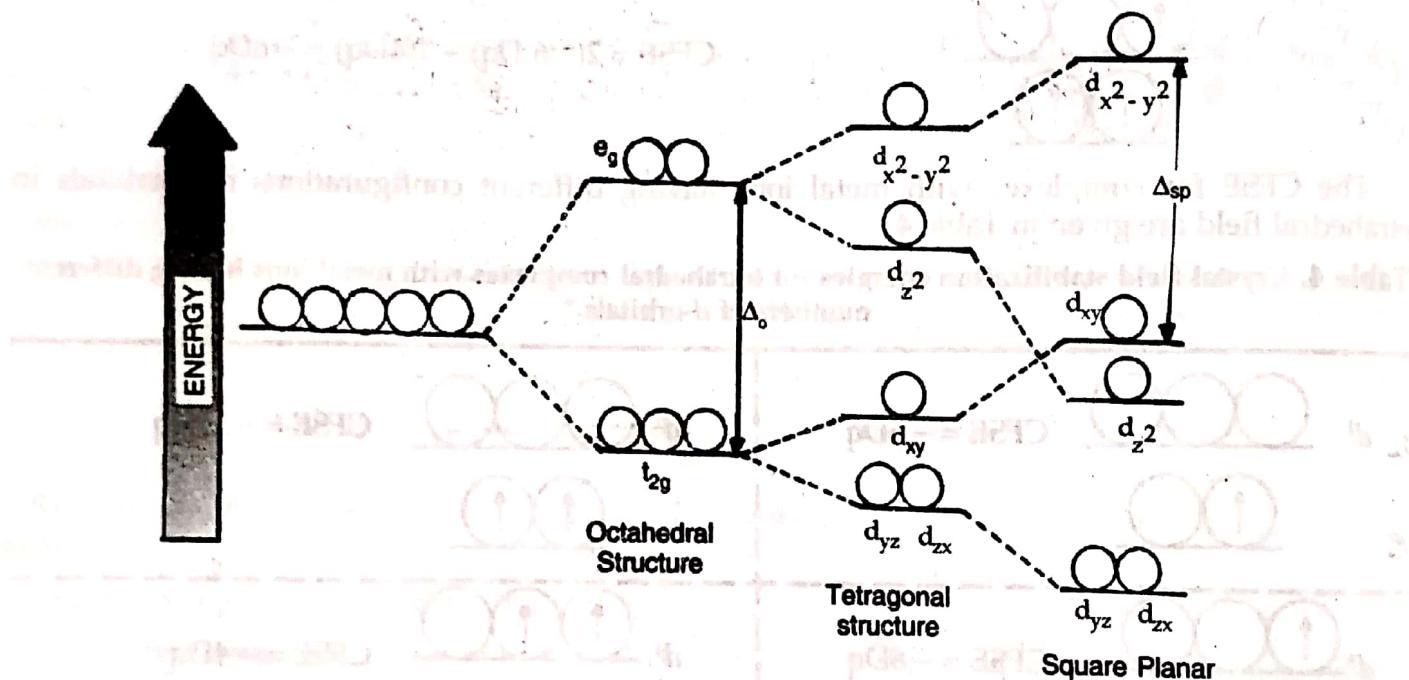


Fig. 18. Crystal field splitting in octahedral, tetragonal and square planar complexes.

As the trans ligands lying along Z-axis are completely removed, a **square planar complex** is formed. In the square planar complex, there is further rise in the energies of $d_{x^2-y^2}$

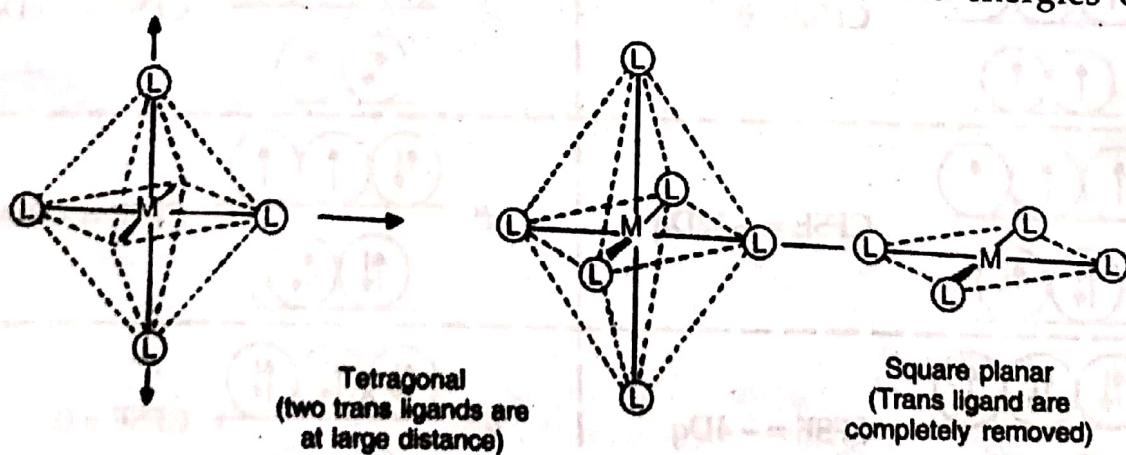


Fig. 19. Change of octahedral geometry to tetragonal and finally to square planar geometry by removing two trans ligands.

and d_{xy} orbitals and a further fall in the energies of d_{z^2} , d_{x^2} and d_{yz} orbital as shown in Fig. 18. It has been observed that in square planar complex, the energy of d_{z^2} orbital falls even below the d_{xy} orbital. The change of an octahedral complex to tetragonally distorted octahedron and finally to square planar arrangement is shown in Fig. 19.

It may be remembered that tetragonally distorted structure can also be obtained when the two *trans* ligands are brought closer to the metal ion. This is called flattening of an octahedron. This is shown in Fig. 20 where Fig. 20(a) shows elongation of octahedron. In flattening of octahedron, the two *trans* M—L bonds are shortened while other four M-L bonds become large. The splitting of energies of *d*-orbitals will be reverse of what has been observed in the case of elongation (Fig. 18).

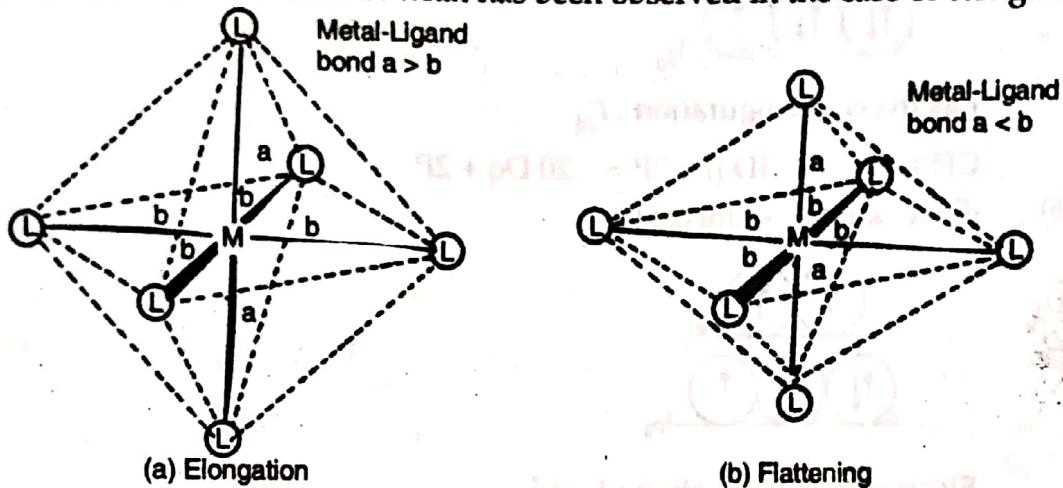


Fig. 20. Tetragonally distorted octahedron (a) elongation (b) flattening.

Example 1

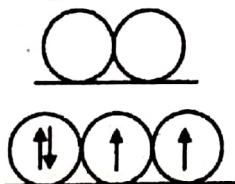
Calculate CFSE for the following ions in octahedral complexes :

- (i) d^4 strong field octahedral (ii) d^6 weak field (iii) d^7 strong field

(Pb. U. 2010)

Solution :

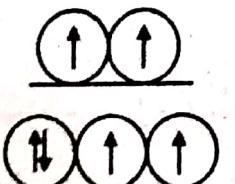
- (i) d^4 strong field



Electronic configuration : t_{2g}^4

$$\text{CFSE} = 4 \times (-4 \text{Dq}) + P = -16 \text{Dq} + P$$

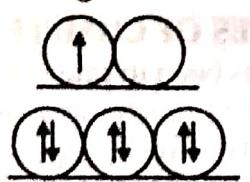
- (ii) d^6 weak field



Electronic configuration : $t_{2g}^4 e_g^2$

$$\text{CFSE} = 4 \times (-4 \text{ Dq}) + 2 \times (6 \text{ Dq}) = -4 \text{ Dq}$$

- (iii) d^7 strong field



Electronic configuration : $t_{2g}^6 e_g^1$

$$\text{CFSE} = 6 \times (-4 \text{ Dq}) + 1 \times (6 \text{ Dq}) + P = -18 \text{ Dq} + P$$

Example Calculate crystal field stabilization energies for the following :

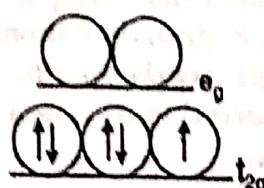
2 (a) d^5 strong field octahedral (b) d^7 weak field octahedral

(c) d^6 tetrahedral (d) d^4 tetrahedral

(H.P.U. 2012)

Solution :

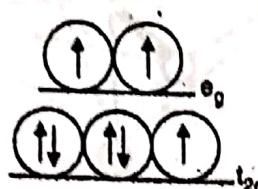
(a) d^5 system strong field octahedral



Electronic configuration : $t_{2g}^5 e_g^2$

$$\text{CFSE} = 5 \times (-4Dq) + 2P = -20Dq + 2P$$

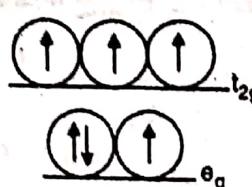
(b) d^7 weak field octahedral



Electronic configuration : $t_{2g}^5 e_g^2$

$$\text{CFSE} = 5(-4Dq) + 2(6Dq) = -8Dq$$

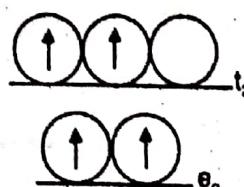
(c) d^6 tetrahedral



Electronic configuration : $e^3 t_2^3$

$$\text{CFSE} = 3(-6Dq) + 3(4Dq) = -6Dq$$

(d) d^4 : tetrahedral



Electronic configuration : $e^2 t_2^2$

$$\text{CFSE} = 2(-6Dq) + 2(4Dq) = -4Dq$$

CRYSTAL FIELD THEORY AND MAGNETIC PROPERTIES OF COMPLEXES

One of the important applications of crystal field theory has been in understanding the magnetic properties of coordination compounds. The primary object of studying magnetism is to know whether a particular complex is *paramagnetic* or *diamagnetic*. The substances which have all paired electrons are called diamagnetic while the substances which contain unpaired electrons are called paramagnetic substances. The number of unpaired electrons, in a given complex of known geometry

can be easily predicted provided we know whether the complex is low spin or high spin. This will also depend upon the magnitude of Δ_o and pairing energy P. For example,

- If $P > \Delta_o$, the electrons will not pair up and the complex will be **high spin complex**.
- If $\Delta_o > P$, the electrons will prefer to pair up and the complex will be **low spin complex**.

Thus, the complexes with **weak ligand field** are **high spin complexes** (paramagnetic) and those with **strong ligand field** are **low spin complexes** (diamagnetic or low magnetic character).

Let us illustrate this by considering the complexes of cobalt (III). From experiments, it has been observed that the complex $[\text{Co}(\text{NH}_3)_6]^{3+}$ is **diamagnetic** while the complex $[\text{CoF}_6]^{3-}$ is **paramagnetic**.

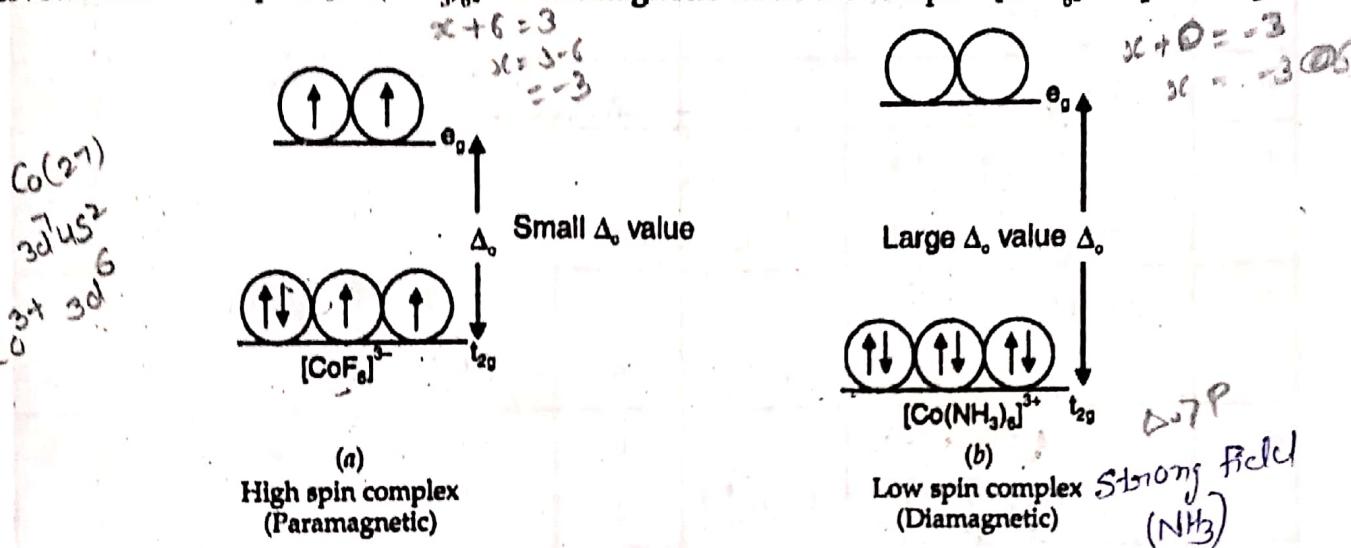


Fig. 21. Crystal field splitting and explanation for $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ complexes.

Cobalt in $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{CoF}_6]^{3-}$ is in +3 oxidation state and it has six d electrons. It has been observed that F⁻ ion is a weak field ligand and therefore Δ_o is small. Therefore, Δ_o will be less than P and the electron will remain unpaired as far as possible. The complex will be high spin. As clear from Fig. 21. (a), the complex is paramagnetic due to the presence of four unpaired electrons. On the other hand, NH₃ is a strong field ligand and therefore, Δ_o will be greater than P. As a result, the electrons pair up and this results in a *low spin* complex. This happens in the case of $[\text{Co}(\text{NH}_3)_6]^{3+}$, as represented in Fig. 21.(b). It may be noted that in Fig. 21., Δ_o is shown to be much higher in the case of $[\text{Co}(\text{NH}_3)_6]^{3+}$ than that in the case of $[\text{CoF}_6]^{3-}$. The crystal field splitting energies (Δ_o) and pairing energies for some complexes are given in Table 5.

Table 5. CFSE (Δ_o) and pairing energies (P) for some complexes.

Complex	Configuration	Δ_o (cm ⁻¹)	P (cm ⁻¹)	High spin/low spin
$[\text{CoF}_6]^{3-}$	d^6	13000	21000	param high spin W.F.
$[\text{Co}(\text{NH}_3)_6]^{3+}$	d^6	23000	21000	Dia. low spin S.F.D.P
$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	d^6	10400	17600	param high spin W.F.
$[\text{Fe}(\text{CN})_6]^{4-}$	d^6	32850	17600	Dia. low spin S.F.D.P

Thus, the number of unpaired electrons in a given complex can be easily predicted if we know whether the complex is a high spin or a low spin complex. The number of unpaired electrons for octahedral and tetrahedral complexes having different configurations are given in Table 6. For tetrahedral complexes, only high spin configurations are discussed (because Δ_t is always less than P and low spin complexes are not known).

Table 6. Number of unpaired electrons for octahedral and tetrahedral complexes.

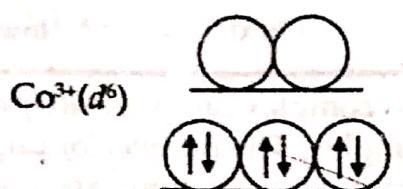
Electronic configuration	Octahedral*		No. of unpaired electrons	Tetrahedral		No. of unpaired electrons	
	t_{2g}	e_g		e	t_2		
d^1	(1)		1	(1)		1	
d^2	(2)		2	(2)		2	
d^3	(3)		3	(3)		3	
d^4	(a) (4)		2	(2)		4	(b) (4)
		(1)	4	(1)	(1)		
d^5	(a) (5)		1	(1)	(1)	5	(b) (5)
		(1)	5	(1)	(1)		
d^6	(a) (6)		0	(1)	(1)	4	(b) (4)
		(1)	4	(1)	(1)		
d^7	(a) (7)		1	(1)	(1)	3	(b) (3)
		(1)	3	(1)	(1)		
d^8	(8)		2	(1)	(1)	2	(2)
		(1)	2	(1)	(1)		
d^9	(9)		1	(1)	(1)	1	(1)
		(1)	1	(1)	(1)		
d^{10}	(10)		0	(1)	(1)	0	(0)
		(1)	0	(1)	(1)		

*(a) is the configuration for low spin and (b) is the configuration for high spin.

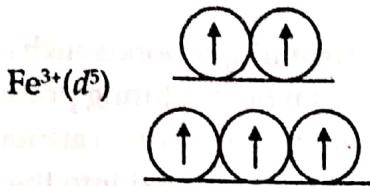
Example Calculate the number of unpaired electrons in the following :

- 3 (i) Co^{3+} (octahedral strong field)
(ii) Fe^{3+} (octahedral weak field)
(iii) Cr^{3+} (octahedral strong field)

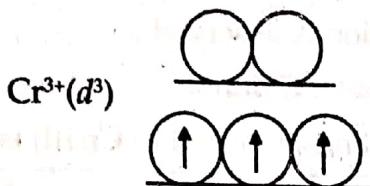
Solution : (i) Co^{3+} : Octahedral strong field



No. of unpaired electrons = 0

(ii) Fe^{3+} : Octahedral weak field

No. of unpaired electrons = 5

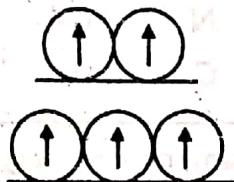
(iii) Cr^{3+} : Octahedral strong field

No. of unpaired electrons = 3

Example Determine the number of unpaired electrons and CFSE for the following :

- 4 (i) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (K.U. 2010)
(ii) $[\text{Cr}(\text{NH}_3)_6]^{3+}$

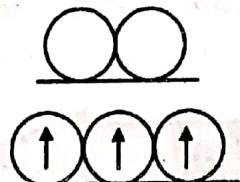
Solution: (i) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$: In this complex ion, Fe(III) has the electronic configuration $3d^5$. Water is a weak field ligand so that its configuration is $t_{2g}^3 e_g^2$.



No. of unpaired electrons = 5

CFSE = $3(-4 \text{ Dq}) + 2(-6 \text{ Dq}) = 0$

(ii) $[\text{Cr}(\text{NH}_3)_6]^{3+}$: In this complex ion, Cr(III) has the electronic configuration : d^3 . NH_3 is a strong field ligand so that its configuration in t_{2g}^3 .



No. of unpaired electrons = 3

CFSE = $3(-4 \text{ Dq}) = -12 \text{ Dq}$

FACTORS DETERMINING THE MAGNITUDE OF CRYSTAL FIELD SPLITTING

The following factors influence the magnitude of crystal field splitting :

1. Nature of the ligand (spectrochemical series)

The crystal field theory depends upon the nature of the ligands. The greater the ease with which the ligands can approach the metal ion, the greater will be the crystal field splitting caused by it. The ligands which cause only a small degree of crystal field splitting are called **weak field ligands** while those which cause a large splitting are called **strong field ligands**. The spectrochemical series is an experimentally determined series. It is very difficult to explain, the order because it incorporates the effects of both σ and π bonding. In general, the variation in the splitting is caused by a number of factors such as :

- (a) Small ligands can cause greater crystal field splitting because they can approach the metal ion closely. For example, F^- ion produces more Δ_0 value than large Cl^- and Br^- ions.

- (b) The ligands containing easily polarizable electron pair will be drawn more closely to the metal ion.
- (c) The ligands which have greater tendency to form multiple bonds such as CN^- and NO_2^- cause greater crystal field splitting. The very high crystal field splitting produced by CN^- ligand is about double that for weak field ligands like halide ions. This is attributed to the π bonding in metal. The metal donates electrons from a filled t_{2g} orbital into the vacant orbital on the ligand.
- (d) The following pattern of increasing σ donation is observed :

halide donors < O donors < N donors < C donors

The effect of crystal field splitting (Δ_o) on the ligands attached to Cr(III) is shown below :

Complex	Ligand	Donor atom	$\Delta_o (\text{cm}^{-1})$
$[\text{CrCl}_6]^{3-}$	Cl^-	Cl	13640
$[\text{CrF}_6]^{3-}$	F^-	F	15260
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	H_2O	O	17830
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	NH_3	N	21680
$[\text{Cr}(\text{en})_3]^{3+}$	en	N	21900
$[\text{Cr}(\text{CN})_6]^{3-}$	CN^-	C	26280

The common ligands can be arranged in an increasing order of crystal field splitting Δ . This regular order is called spectrochemical series. The order remains almost same for different metal ions.

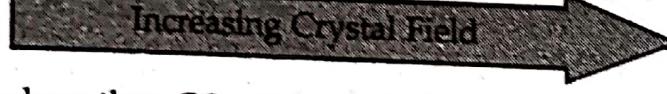
The spectrochemical series in the increasing order of crystal field splitting is given below :

Weak field ligands

$\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{ox}^{2-} < \text{H}_2\text{O} < \text{EDTA} < \text{py} \approx \text{NH}_3 < \text{en} < \text{dipy} < \text{o-phen}$
 $< \text{NO}_2^- < \text{CN}^- < \text{CO}$

Strong field ligands

Increasing Crystal Field



From the series, it is clear that CO, CN⁻ and NO₂⁻ are strong field ligands whereas I⁻, Br⁻ and Cl⁻ are weak field ligands.

In general, the ligands upto NH₃ are called **weak field ligands** while those on the right of NH₃ are called **strong field ligands**. The order of the spectrochemical series remains practically same irrespective of the transition metal ions.

2. Oxidation state of the metal ion

The magnitude of the crystal field splitting depends upon the oxidation state of the transition metal ion. The metal ion with higher oxidation state causes larger crystal field splitting than is done by the ion with lower oxidation state. For example, the crystal field splitting energy Δ_o for $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ complex in which the oxidation state of cobalt is +3, is 18600 cm^{-1} , whereas for the complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ in which the oxidation state of Co is +2, $\Delta_o = 9300 \text{ cm}^{-1}$. Similarly, for the complexes $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ in which iron has oxidation state +3 and +2, respectively, the values of Δ_o are 13700 cm^{-1} and 10400 cm^{-1} , respectively.

This is clear from the following data in which crystal field splitting energies (Δ_o) for hexaaqua complexes of M²⁺ and M³⁺ ions of the first transition series are given :

Metal ion	Oxidation state	Electronic configuration	Δ_o (cm ⁻¹)	Oxidation state	Electronic configuration	Δ_o (cm ⁻¹)
V	II	d ³	11800	III	d ²	18000
Cr	II	d ⁴	13900	III	d ³	17830
Mn	II	d ⁵	7800	III	d ⁴	21000
Fe	II	d ⁶	10400	III	d ⁵	13700
Co	II	d ⁷	9300	III	d ⁶	18600

3. Type of d-orbitals (transition series)

The extent of crystal field splitting for similar complexes of a metal in the same oxidation state increases by about 30 to 50% on going from 3d-series (first transition series) to 4d series (second transition series). The increase is almost of the same amount (30—50%) on going from 4d-series (second transition series) to 5d-series (third transition series).

This may be explained on the basis that 4d-orbitals in comparison to 3d-orbitals are bigger in size and extend farther into space. As a result, the 4d-orbitals can interact more strongly with the ligands and, therefore, the crystal field splitting is more. Similarly, 5d-orbitals are bigger than 4d-orbitals and Δ_o for the third transition series is more than that for second transition series. This is evident from the following data :

Complex ion	Electronic configuration	Δ_o (cm ⁻¹)
[Co(NH ₃) ₆] ³⁺	3d ⁶	23000
[Rh(NH ₃) ₆] ³⁺	4d ⁶	34000
[Ir(NH ₃) ₆] ³⁺	5d ⁶	41000

4. Geometry of the complex

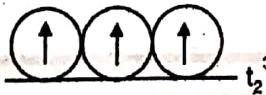
As mentioned earlier, the crystal field splitting energy of tetrahedral complexes (Δ_t) is nearly half the value (Δ_o) for octahedral complexes ($\Delta_t \approx 4/9 \Delta_o$). In other words, the value of splitting energy for tetrahedral complexes, in general, is small as compared to the pairing energy P. **The tetrahedral complexes are, therefore, mostly high spin complexes.**

Example Show the d-electron configuration in the following complexes :

5 (i) [Co(NCS)₄]²⁻ tetrahedral

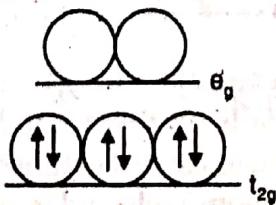
(ii) [Fe(CN)₆]⁴⁻ low spin octahedral.

Solution : (i) [Co(NCS)₄]²⁻. In this complex ion Co is in +2 oxidation state and is d⁷ system. Its electronic configuration is :



Electronic configuration : e⁴t_{2g}³

(ii) [Fe(CN)₆]⁴⁻. In this complex ion, Fe is in +2 oxidation state and is d⁶ system. Its electronic configuration is :



Electronic configuration : t_{2g}⁶e_g⁰

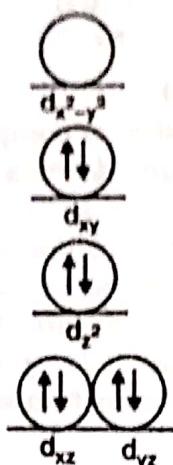
$$\begin{aligned} n - 6 &= -4 \\ n &= -4 + 6 = 2 \end{aligned}$$

Example

6

Draw the energy level diagram for $[\text{Pd}(\text{CN})_4]^{2-}$ square planar diamagnetic complex showing the d-electron distribution. (M.D.U. 2013)

Solution : Palladium in $[\text{Pd}(\text{CN})_4]^{2-}$ is in +2 oxidation state. It has d^8 electronic configuration as shown below :



Electronic configuration : $(d_{xz})^2 (d_{yz})^2 (d_{z^2})^2 (d_{xy})^2$

PRACTICE**Problems**

- Calculate the number of unpaired electrons in $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3-}$ complex ions. • Ans. one, five
- Calculate the CFSE for octahedral complex having
(i) low spin (ii) high spin d^6 configuration • Ans. (i) $-24Dq + 2P$ (ii) $-4Dq$
- Give the number of unpaired electrons in a strong and weak octahedral field for Co^{3+} ion. • Ans. 0, 4
- Which of the following complexes has larger crystal field splitting of d-orbitals ?
(i) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ or $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ (ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ or $[\text{Fe}(\text{CN})_6]^{3-}$
(iii) $[\text{CoF}_6]^{3-}$ or $[\text{Co}(\text{NH}_3)_6]^{3+}$ • Ans. (i) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (ii) $[\text{Fe}(\text{CN})_6]^{3-}$ (iii) $[\text{Co}(\text{NH}_3)_6]^{3+}$
- Which of the two $[\text{Rh}(\text{NH}_3)_6]^{3+}$ or $[\text{Ir}(\text{NH}_3)_6]^{3+}$ has greater Δ_0 value ? • Ans. $[\text{Ir}(\text{NH}_3)_6]^{3+}$.

COLOUR OF TRANSITION METAL COMPLEXES

Most of the transition metal compounds are coloured in their solid or solution form. The transition metals have the property to absorb certain radiations from the visible region of the spectrum and as a result, the transmitted or reflected light is coloured. The visible light, as we know, is a mixture of radiation of many wavelengths ranging from blue (about 400 nm) to red (about 700 nm). For example, if a substance absorbs blue light (short wavelength), then it appears to us to be red (long wavelength).

In the case of transition metal complexes, the energy difference between t_{2g} and e_g sets of d-orbitals is very small. When visible light falls on them, the electron gets raised from lower set of orbitals to higher set of orbitals (for example in case of octahedral complexes, the electron goes from t_{2g} to e_g orbitals). As a result of absorption of some selected wavelength of visible light corresponding to energy difference between t_{2g} to e_g energy levels, the transmitted light gives colour to complexes.

The amount of energy absorbed can be calculated from the relation,

$$E = h\nu = \frac{hc}{\lambda}$$

where c is the velocity of light and h is Planck's constant. For example, the complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is purple. This can be explained as follows :

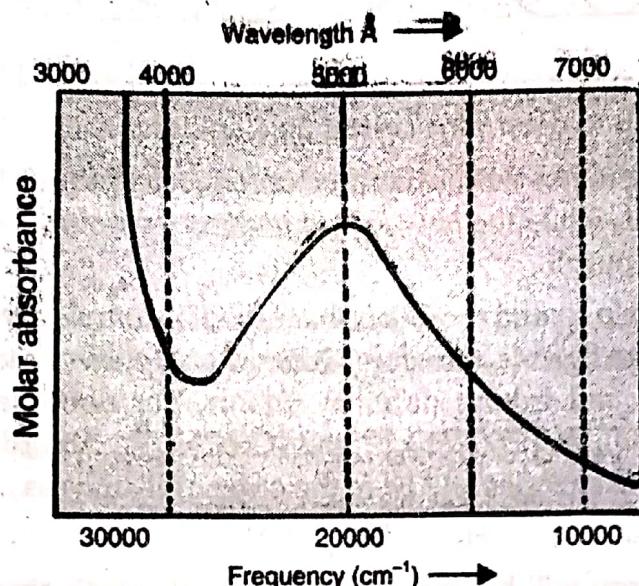


Fig. 22. Absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$.

In this complex, the metal ion has d^1 configuration. In ground state this electron occupies one of the t_{2g} orbitals. The visible spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is shown in Fig. 22. It is clear from the figure that absorption takes place at 5000 \AA or 20000 cm^{-1} . The energy corresponding to this wavelength can be easily calculated as :

$$E = N_0 h\nu = \frac{N_0 hc}{\lambda} \quad \nu = \frac{c}{\lambda}$$

where N_0 = Avogadro number

h = Planck's constant

c = Velocity of light

Substituting the values of $N_0 = (6.023 \times 10^{23})$, $h = (6.626 \times 10^{-34} \text{ Js})$, $c = (3.0 \times 10^8 \text{ ms}^{-1})$ and $\lambda = (5000 \text{ \AA} = 5000 \times 10^{-10} \text{ m})$, we get

$$E = \frac{6.023 \times 10^{23} \times 6.626 \times 10^{-34} \times 3.0 \times 10^8}{5000 \times 10^{-10}}$$

$$= 239 \text{ kJ mol}^{-1}$$

This corresponds to Δ_o for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex ion.

Alternatively, Δ_o can be calculated from wave number (20000 cm^{-1}). It can be easily calculated by remembering the conversion factor : $1 \text{ kJ mol}^{-1} = 83.7 \text{ cm}^{-1}$; so that

$$\Delta_o = \frac{20,000}{83.7} = 239 \text{ kJ mol}^{-1}$$

This corresponds to promotion of the single electron from a lower t_{2g} orbital to a higher e_g orbital as shown in Fig. 23.

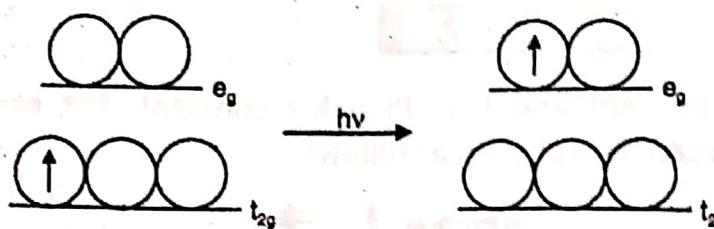


Fig. 23. Transition of one electron from t_{2g} orbital to e_g orbital in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex.

Therefore, the spectra help to determine crystal field splitting energy (Δ_o).

The energy corresponding to this wavelength corresponds to green and yellow lights which are absorbed from the white light, while the blue and red portions are emitted. The solution of complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, therefore, looks purple.

Since the difference between t_{2g} and e_g orbitals in octahedral complexes vary from one metal ion to another and the nature of the ligands, therefore, different complexes absorb different amounts of energies from visible region and exhibit different colours. For example, let us consider three complexes of Co^{3+} as $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{CN})_6]^{3-}$. According to spectro chemical series, the crystal field splitting energies will be in the order of ligands as :



Therefore, excitation energy will be smallest (largest wavelength absorbed) for $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ complex and largest (smallest wavelength absorbed) for $[\text{Co}(\text{CN})_6]^{3-}$ complex. That is why, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ absorbs orange colour and appears blue and $[\text{Co}(\text{CN})_6]^{3-}$ absorbs violet colour and appears as yellow.

	$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$	$[\text{Co}(\text{NH}_3)_6]^{3+}$	$[\text{Co}(\text{CN})_6]^{3-}$
Δ_o value	small	intermediate	large
Excitation energy (ΔE)	small	intermediate	large
Absorption wavelength (λ)	large	intermediate	small
Colour absorbed	orange	blue	violet
Colour transmitted	blue	orange	yellow

Colour of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

The Cu^{2+} ion is a d^9 system. The spectrum of d^9 shows the same behaviour in a crystal field as does d^1 ion. But in this case the system is viewed by means of the *hole formulism*. In this we may say that Cu(II) has spherically symmetrical d^{10} system with a hole or a missing electron. The hole behaves exactly in the same way as electron does. When radiations of visible light falls on it, the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution absorbs in the red region corresponding to 5750—5900 Å. Therefore, it transmits blue colour.

The cuprous compounds, Cu^+ (e.g. Cu_2SO_4) have the electronic configuration $3d^{10}$ and therefore no $d-d$ transitions are possible and these compounds are colourless.

Anhydrous copper sulphate (CuSO_4) is white. It is a $3d^9$ system but in anhydrous form, there is no crystal field of ligands. Therefore, all the five $3d$ orbitals are of equal energy and no transition is possible.

It may be noted that only those transition metal complexes are coloured which have incomplete d -subshells. The transition metal ions having completely filled or completely empty d -subshells are

colourless. For example, complexes of Cu^+ (d^{10}), Zn^{2+} (d^{10}), Ag^+ (d^{10}), Ti^{4+} (d^{10}) etc., are colourless. The detailed discussion of spectra of complexes is discussed later.

It may be noted that the spectra of transition metal complexes are not simple and require the study of various *spectroscopic terms* of a metal ion and *their splitting by different crystal fields*. These spectroscopic terms are related to electronic configurations of the metal ions.

Limitations of Crystal Field Theory

The crystal field theory considers the metal - ligand bond as purely electrostatic. It does not take into account partial covalent character of metal-ligand bonds. Therefore, all those effects which result from covalent character cannot be explained by this theory. The main limitations of crystal field theory are :

- (i) it does not take into account the partial covalent character of metal- ligand bonds.
- (ii) It does not consider the multiple bonding (π bonds) between metal ion and the ligands. Therefore, it does not explain the formation of π bonding in complexes.
- (iii) It does not explain the relative strengths of ligands. For example, it gives no explanation as to why neutral water appears as a stronger ligand in electrochemical series than negatively charged OH^- ion.
- (iv) It does not explain the charge transfer bands.
- (v) It considers only d -orbitals of metal ions and does not consider at all the other metal orbitals such as s , p_x , p_y , p_z orbitals and the ligand π orbitals.

Comparison of Valence Bond Theory and Crystal Field Theory

Crystal field theory is better than valence bond theory because it explains many properties of coordination compounds in a more satisfactory way. Crystal field theory easily accounts for stereochemistry, magnetic properties, absorption spectra and many other thermodynamic properties.

The main points of comparison between valence bond theory and crystal field theory are summarized below :

	Crystal field theory	Valence bond theory
1. Type of bonds	The bond between metal ion and the ligand is purely electrostatic.	The bond between metal ion and the ligand is purely covalent.
2. Splitting of d-orbitals	It takes into account the splitting of d -orbitals of the metal.	It does not take into account the splitting of d -orbitals of metal.
3. Hybridisation	It does not involve the concept of hybridisation.	It involves the concept of hybridisation of the orbitals of the metal ion before complex formation.
4. Magnetic properties	It gives theoretical basis to predict the magnetic properties of complexes and predict the variation in magnetic moments with temperature for complexes where Δ value is close to pairing energy.	It lays emphasis on number of unpaired electrons. It is unable to predict the effect of temperature on the magnetic properties.
5. Colour of complexes	It explains satisfactorily the colour of complexes.	It does not explain the colour of complexes.
6. Geometry	It explains the effect of distortion in regular geometry of molecules (e.g. tetragonal geometry).	It is unable to explain the distortion in regular geometry of molecules.
7. Energy	It helps to calculate the stabilization energies of complexes due to crystal field splitting.	It cannot explain the energy of complexes.

LIGAND FIELD THEORY

The problem about crystal field theory is that it considers the interactions between the metal ion and ligands as purely electrostatic. It does not take into account the partly covalent nature of metal-ligand bonds. But many studies of the complexes have shown that there is a significant overlap between the metal d -orbitals and ligand orbitals resulting some covalent character. Some of the studies showing the covalence character of metal-ligand bonds are :

- (i) Absorption spectra
- (ii) Electron spin resonance (ESR) spectra
- (iii) Nuclear magnetic resonance (NMR) spectra
- (iv) Magnetic susceptibility results

Therefore, a kind of modified CFT has been suggested in which some parameters are empirically adjusted to allow for the effects of orbitals overlap for covalence in complexes. The modified form of the CFT is called **ligand field theory**. It may be noted that the modified CFT or ligand field theory modifies the CFT by introducing some covalent character. The theory which takes into account the overlap of atomic orbitals of the central metal ion and ligands is called **molecular orbital theory**. The discussion of this theory is beyond the scope of the present syllabus.

Conceptual QUESTIONS

Q.1. Why does NH_3 readily form complexes but NH_4^+ does not ? Explain.

Ans. NH_3 contains a lone pair of electrons which coordinate with the metal ion to form the complex compound. However, in NH_4^+ ion, the lone pair is bound to H^+ and therefore, is not available for bonding to metal ion. Therefore, NH_4^+ does not form complexes readily.

Q.2. Which of the following complexes has larger crystal field splitting of d -orbitals in each pair ?

- (i) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
- (ii) $[\text{Co}(\text{NH}_3)_6]^{3+}$ or $[\text{Rh}(\text{NH}_3)_6]^{3+}$
- (iii) $[\text{Co}(\text{CN})_6]^{3-}$ or $[\text{Co}(\text{NH}_3)_6]^{3+}$

Ans. (i) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (higher oxidation state of Co)
(ii) $[\text{Rh}(\text{NH}_3)_6]^{3+}$ (element from 4d series)
(iii) $[\text{Co}(\text{CN})_6]^{3-}$ (strong ligand field of CN^-)

Q.3. Calculate CFSE for the following systems :

- (i) d^4 (high spin octahedral)
- (ii) d^5 (tetrahedral)
- (iii) d^6 (low spin octahedral)
- (iv) d^7 (high spin octahedral)
- (v) d^8 (tetrahedral)

Ans. (i) $t_{2g}^3 e_g^1$: CFSE = $-6Dq$
(ii) $e^2 t_2^3$: CFSE = 0
(iii) t_{2g}^6 : CFSE = $-24 Dq + 2P$
(iv) $t_{2g}^5 e_g^2$: CFSE = $-8 Dq$
(v) $e^3 t_2^3$: CFSE = $-6Dq$

(H.P.U. 2001)

(H.P.U. 2001)

(H.P.U. 2001)

Q.4. Cu (I) is diamagnetic whereas Cu (II) is paramagnetic. Why ?

Ans. In Cu (II), the outermost electronic configuration is $3d^9$ and therefore, it has one unpaired electron. Hence, it is paramagnetic. However, in Cu (I), the outermost electronic configuration is $3d^{10}$. There is no unpaired electron and therefore, Cu (I) is diamagnetic.

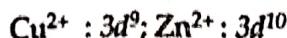
Q.5. Predict which of the following statements are true or false :

- Crystal field splitting for tetrahedral field is always less than that for octahedral field.
- $[\text{CoCl}_4]^{2-}$ is tetrahedral and diamagnetic.
- NO_2^- is weak field ligand as compared to NH_3 .
- Fe^{3+} octahedral weak field has 5 unpaired electrons.

Ans. (a) True (b) False
(c) False (d) True

Q.6. Cu^{2+} ions are coloured and paramagnetic while Zn^{2+} ions are colourless and diamagnetic. Explain.

Ans. The electronic configuration of Cu^{2+} and Zn^{2+} are :



Cu^{2+} has one unpaired electron and therefore is paramagnetic. On the other hand, Zn^{2+} has all electrons paired and therefore, is diamagnetic.

In Cu^{2+} , there is one vacancy in $3d$ orbitals to which an electron can be excited resulting in $d-d$ transition. Therefore, Cu^{2+} ions are coloured. In Zn^{2+} , there is no such possibility because $3d$ orbitals are completely filled and hence are colourless.

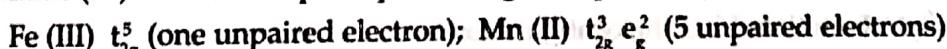
Q.7. Zn forms only Zn^{2+} and not Zn^{3+} . Why ?

(Pb. U: 2012)

Ans. During the formation of Zn^{2+} , it acquires completely filled ($3d^{10}$) configuration which is stable. Therefore, it is difficult to remove an electron from this filled $3d^{10}$ stable configuration and hence Zn^{3+} is not formed.

Q.8. Though both Mn(II) and Fe (III) ions have $3d^5$ configurations, yet most of the complexes of manganese (II) are high spin while those of iron (III) are low spin. Why?

Ans. The magnitude of crystal field splitting, Δ_o depends on the oxidation state of the metal atom, apart from other factors. Higher the oxidation state, larger the crystal field splitting. Therefore, iron (III) has a higher oxidation state than manganese (II), despite both have $3d^5$ configuration. As a result, iron (III) will have greater Δ_o value as compared to Mn (II) of the same geometry. Thus, the valence electrons in Fe (III) will tend to pair up resulting low spin complexes.



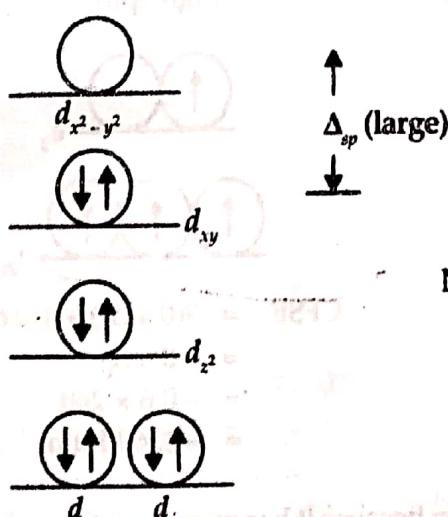
Q.9. Draw crystal field splitting and calculate the number of unpaired electrons in

(i) $[\text{Ni}(\text{CN})_4]^{2-}$: square planar

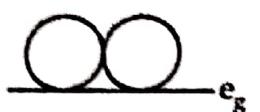
(ii) $[\text{NiCl}_4]^{2-}$: tetrahedral

(iii) $[\text{Mn}(\text{CN})_6]^{3-}$: octahedral

Ans. (i) Ni (II) : $3d^8$



No. of unpaired electrons = 0

(ii) Ni (II) : $3d^8$  t_2 , No. of unpaired electrons = 2(iii) $[\text{Mn}(\text{CN})_6]^{4-}$ Mn(III) : $3d^4$  Δ_o (large) No. of unpaired electrons = 2Q.10. Calculate CFSE for d^6 configuration in weak field and strong field (oct). (Pb.U. 2008)Ans. d^6 weak field

strong field

 $t_{2g}^4 e_g^2$

$$\begin{aligned} \text{CFSE} &= 4(-4Dq) + 2(6Dq) \\ &= -4Dq \end{aligned}$$

 t_{2g}^6

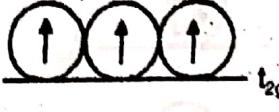
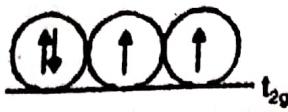
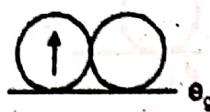
$$\begin{aligned} \text{CFSE} &= 6(-4Dq) + 2P \\ &= -24 Dq + 2P \end{aligned}$$

Q.11. Calculate CFSE for CoCl_4^{2-} . (G.N.D.U. 2008)Ans. CoCl_4^{2-} i.e., Co(II) is tetrahedral and has the configuration : $e^4 t_2^3$ CFSE : $-12Dq$ Q.12. For $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ ion, the crystal field splitting energy is 260 kJ mol^{-1} and electron pairing energy is 342 kJ mol^{-1} . Predict whether the complex will have low spin or high spin configuration.Ans. In $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ complex, Mn(III) ion is a $3d^4$ system. CFSE energy for low spin and high spin configuration will be

low spin



high spin



$$\text{CFSE} = 4(-0.4 \Delta_o) + P$$

$$= -1.6 \Delta_o + P$$

$$= -1.6 \times 260 + 342$$

$$= -416 + 342$$

$$= -74 \text{ kJ mol}^{-1}$$

$$\text{CFSE} = 3(0.4 \Delta_o) + 1(0.6 \Delta_o)$$

$$= -0.6 \Delta_o$$

$$= -0.6 \times 260$$

$$= -156 \text{ kJ mol}^{-1}$$

The complex will have high spin configuration because it has more negative value of CFSE and hence more stable than low spin configuration.

Q. 13. Why is the magnitude of crystal field splitting in tetrahedral complexes Δ_t smaller than in octahedral complexes, Δ_o ? (K.U. 2010, Pbi. U. 2012, Jammu U. 2012)

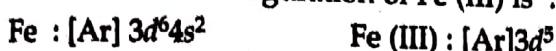
Ans. The magnitude of crystal field splitting in tetrahedral complexes, Δ_t , is smaller because of the following two reasons :

- In tetrahedral complexes, there are only four ligands while there are six ligands in octahedral complexes. Therefore, lesser ligands produce less crystal field splitting. Since there are only two third ligands in tetrahedral complexes as compared to octahedral complexes, the crystal field splitting in tetrahedral field is about two third of the octahedral field.
- In tetrahedral field, none of the orbitals is pointing directly towards the ligands. Therefore, splitting is less. This also reduces the crystal field splitting by roughly two third.

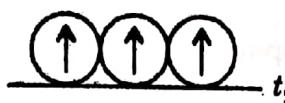
Therefore, the tetrahedral crystal field splitting is roughly $\frac{2}{3} \times \frac{2}{3} = \frac{4}{9}$ of the octahedral field splitting, Δ_o .

Q. 14. Draw crystal field energy level diagram for $[\text{FeCl}_4]^-$ tetrahedral complex. Also predict the number of unpaired electrons in it.

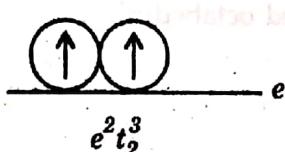
Ans. The electronic configuration of Fe (III) is :



Since all tetrahedral complexes are high spin complexes, therefore, the crystal field energy level diagram is



$$\text{No. of unpaired electrons} = 5$$



Q. 15. All tetrahedral complexes are high spin complexes. Explain. (Pb. U. 2008)

Ans. The crystal field splitting energy (CFSE) for tetrahedral complexes, in general, is small as compared to pairing energy (P). Therefore, the pairing of electrons will never be energetically favourable. Thus, all the tetrahedral complexes are high spin complexes. In fact, no tetrahedral complex with low spin has been found experimentally.

Q. 16. Why is anhydrous copper sulphate colourless?

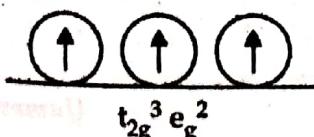
Ans. In case of pure anhydrous copper sulphate (CuSO_4), the Cu^{2+} ion is not surrounded by ligands. As a result, all the five $3d$ orbitals have same energy in the absence of crystal field splitting of ligands. Therefore, there is no possibility of transition within d -orbitals (*i.e.* $d-d$ transition) and hence the compound CuSO_4 is colourless.

Q. 17. Calculate the value of CFSE for d^5 weak field system for octahedral complexes. (H.P.U. 2013)

Ans. For weak field system for octahedral complexes, the configuration is :



$$\begin{aligned} \text{CFSE} &= 3(-4Dq) + 2(6Dq) \\ &= 0 \end{aligned}$$



Objective**QUESTIONS**

Select the correct answer from various alternatives given

- Which of the following complex ion would have the smallest crystal field splitting?
 (a) $[\text{Co}(\text{NH}_3)_6]^{2+}$ (b) $[\text{Rh}(\text{NH}_3)_6]^{3+}$
 (c) $[\text{Ir}(\text{NH}_3)_6]^{3+}$ (d) $[\text{Co}(\text{NH}_3)_6]^{3+}$
- The largest crystal field splitting will be for the ligand (same metal ion)
 (a) Ox^{2-} (b) NO_2^-
 (c) NH_3 (d) CN^-
- The number of unpaired electrons in NiCl_4^{2-} (tetrahedral) are
 (a) two (b) zero
 (c) one (d) four
- The CFSE for a high spin d^4 octahedral complex ion is
 (a) -14 Dq (b) -6 Dq
 (c) $-12 \text{ Dq} + \text{P}$ (d) zero
- Which of the following systems has maximum number of unpaired electrons?
 (a) d^6 (tetrahedral) (b) d^9 (octahedral)
 (c) d^7 (octahedral, high spin) (d) d^4 (octahedral, low spin)
- The order of splitting in cubic geometry is same as that in
 (a) tetrahedral (b) square planar
 (c) octahedral (d) tetragonally distorted octahedral
- Which of the following has no CFSE in octahedral field?
 (a) Fe^{3+} (high spin) (b) Co^{2+} (low spin)
 (c) Fe^{3+} (low spin) (d) Cr^{3+} (high spin)
- Which of the following is a ligand which causes maximum crystal field splitting?
 (a) NH_3 (b) F^-
 (c) CO (d) Ox^{2-}
- The number of unpaired electron in a d^7 tetrahedral configuration is
 (a) 3 (b) 2
 (c) 1 (d) 7
- Which of the following has highest CFSE?
 (a) $[\text{TiF}_6]^{3-}$ (b) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
 (c) $[\text{FeCl}_4]^{2-}$ (d) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- CFSE for d^4 tetrahedral is
 (a) -4 Dq (b) -20 Dq
 (c) -8 Dq (d) -12 Dq
- The type of hybridisation in $[\text{Pt}(\text{CN})_4]^{2-}$ complex ion is
 (a) sp^3 (b) sp^3d^2
 (c) dsp^2 (d) sp^3d
- CFSE for d^4 tetrahedral ion is :
 (a) -4 Dq (b) -20 Dq
 (c) -8 Dq (d) -12 Dq .

14. The number of unpaired electrons in $[\text{NiCl}_4]^{2-}$ (tetrahedral) are :

 - (a) two
 - (b) zero
 - (c) one
 - (d) four.

(Jammu U. 2012)

Answers to Objective Questions

1. (a) 2. (d) 3. (a) 4. (b) 5. (a) 6. (a) 7. (c) 8. (c) 9. (a) 10. (d) 11. (a) 12. (c)
13. (a) 14. (a).

QUESTIONS

A. Very Short Answer Questions

1. Define crystal field stabilization energy.
 2. Give one example of an outer orbital complex.
 3. Calculate CFSE for d^4 high spin octahedral complex.
 4. Draw energy level diagram showing splitting of five d -orbitals in octahedral field.
 5. Calculate CFSE for d^9 tetrahedral complex.
 6. Which complex has larger Δ_0 value $[\text{Co}(\text{CN})_6]^{3-}$ or $[\text{Co}(\text{NH}_3)_6]^{3+}$? (G.N.D.U. 2012)
 7. Which of the two $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ has smaller Δ_0 value ? (G.N.D.U. 2012)
 8. Explain limitations of valence bond theory.
 9. What is the basic assumption of crystal field theory ?
 10. Why are cuprous compounds, Cu_2SO_4 colourless ?
 11. Cu^{2+} ions are coloured and paramagnetic whereas Zn^{2+} ions are colourless and diamagnetic. Why ? (Pb. U. 2012)
 12. What is the effect of nature of ligands on the magnitude of Δ value ? (G.N.D.U. 2012)
 13. Which of the following complexes have larger crystal field splitting of d orbitals
 $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Co}(\text{NH}_3)_6]^{3+}$? (Pb. U. 2013)
 14. Calculate CFSE for d^4 (high spin) octahedral and $d^6(\text{Td})$ complexes. (Pb. U. 2013)
 15. Calculate CFSE for d^9 tetrahedral complex. (G.N.D.U. 2013)

B. General Questions

- How does Valence Bond Theory explain the following complexes :
 - [Ni(CN)₄]²⁻ is diamagnetic and square planar.
 - [NiCl₄]²⁻ is paramagnetic and tetrahedral.
 - [Ni(CO)₄] is diamagnetic and tetrahedral ?
(Z for Ni = 28)
 - (a) How do the *d*-orbitals split when a transition metal ion is placed in octahedral crystal field of ligands ?
(b) Give the number of unpaired electrons in a strong and weak octahedral field for
(i) Cr²⁺ (ii) Co³⁺ (iii) Fe³⁺
(c) Explain the effect of nature of ligands on the magnitude of Δ .
 - (a) Bring out clearly how the crystal field theory explains satisfactorily the magnetic properties of complexes of transition metals.
(b) Discuss the structures of following complexes on the basis of crystal field theory :
(i) [Co(NH₃)₆]³⁺ (ii) [CoF₆]³⁻ (iii) [Fe(H₂O)₆]²⁺ (iv) [Fe(CN)₆]⁴⁻
 - (a) What is Crystal Field Theory ? How does it differ from the valence bond theory ? How does this theory account for the fact that [CoF₆]³⁻ is paramagnetic but [Co(NH₃)₆]³⁺ is diamagnetic, though both are octahedral ? (Z for Co is 28).
(b) How does the crystal field theory explain the colour of co-ordination compounds ?

5. (a) Describe the bonding in $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ in terms of Valence Bond Theory and Crystal Field Theory.
 (b) How will you account for the non-existence of tetrahedral complexes with low spin configurations?
 (c) Write a short note on spectrochemical series.
6. (a) Draw the energy level diagram to show the way in which the degeneracy of $3d$ -orbitals is removed by the
 (i) octahedral ligand field
 (ii) octahedral with tetragonal distortion ligand field in which trans ligands are more distant than others.
 (b) Give the crystal field stabilization energy for the following systems :
 (i) d^5 low spin octahedral (ii) d^6 tetrahedral (iii) d^7 high spin octahedral
7. (a) Give the d -electron configuration of the following complexes :
 (i) Square planar $[\text{Pd}(\text{CN})_4]^{2-}$ (ii) $[\text{Co}(\text{NCS})_4]^{2-}$ tetrahedral (iii) $[\text{Pt}(\text{NH}_3)_6]^{4+}$ low spin
 (b) Which of the following complexes has larger crystal field splitting of d -orbitals and why ?
 (i) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
 (ii) $[\text{Co}(\text{NH}_3)_6]^{3+}$ or $[\text{Rh}(\text{NH}_3)_6]^{3+}$
 (iii) $[\text{Co}(\text{CN})_6]^{3-}$ or $[\text{Co}(\text{NH}_3)_6]^{3+}$
8. (a) Define crystal field stabilization energy. Calculate its value for the following systems :
 (i) d^5 low spin octahedral (ii) d^3 low spin octahedral
 (iii) d^4 tetrahedral (iv) d^6 tetrahedral
 (b) Which of the two Zn^{2+} or Ti^{3+} is coloured in aqueous solution and why ?
 (c) Would the complex ion $[\text{Cu}(\text{CN})_4]^{3-}$ be expected to be (i) square planar or tetrahedral (ii) colourless or coloured ? Explain.
9. (a) How does Crystal Field Theory explain the magnetic character of coordination complexes? Give the number of unpaired electrons in the following octahedral complexes :
 (i) Ni (III) low spin (ii) Cr (III) low spin
 (iii) Rh (III) high spin (iv) Ti (III) low spin
 (b) Discuss the factors affecting the magnitude of Δ_o .
10. (a) Draw the energy level diagrams to indicate the occupancy of orbitals in the following systems :
 (i) d^4 —octahedral, low spin (ii) d^6 —tetrahedral
 (iii) d^9 —square planar (iv) d^5 —octahedral, high spin
 (b) Using Valence Bond theory, predict the geometry of the following :
 (i) FeCl_4^- (five unpaired electrons) (ii) $[\text{MnCl}_4]^{2-}$ (five unpaired electrons)
 (iii) $[\text{FeF}_6]^{3-}$ (five unpaired electrons) (iv) $[\text{Ni}(\text{CO})_4]$ (diamagnetic)
11. (a) Explain crystal field splitting of d -orbitals in octahedral complexes.
 (b) Calculate CFSE for the following :
 (i) d^4 high spin (octahedral) (ii) d^5 strong field (octahedral)
 (iii) d^6 tetrahedral (iv) d^9 tetrahedral
 (c) Explain why the complex ion of transition metals are mostly coloured.
12. (a) How does valence bond theory explain :
 (i) $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic and square planar.
 (ii) $[\text{Ni}(\text{CO})_4]$ is diamagnetic and tetrahedral.
 (b) Give the no. of unpaired electrons in octahedral strong field for :
 (i) Cr^{3+} (ii) Co^{3+} (iii) Fe^{3+}
 (c) Why are salts of zinc, cadmium and mercury white ?
13. (a) Define crystal field splitting energy and discuss the crystal field splitting of d -orbitals in case of octahedral complexes. Also calculate CFSE for d^5 (low spin O_h complex).
 (b) Give reasons for the smaller value of crystal field splitting in tetrahedral than in octahedral complexes.
 (c) Discuss the bonding in $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ in terms of crystal field theory. (Pbi.U. 2006)

24. (a) Discuss the crystal field splitting of d -orbitals in d^2 (Tc) and d^6 (Td).
 (b) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is coloured compound while CuSO_4 (anhydrous) is white. Explain on the basis of CFT. (P.U. 2018)
25. (a) What are the factors affecting the crystal field splitting?
 (b) Write electronic configuration and calculate CFSE for d^6 (high spin octahedral).
 (c) How will crystal field theory account for the fact that $[\text{CoF}_6]^{3-}$ is paramagnetic but $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic though both are octahedral? (P.U. 2019)
26. (a) Discuss the crystal field splitting of d -orbitals in tetrahedral complexes.
 (b) What is CFSE? Calculate CFSE for the following ions in octahedral complexes:
 (i) d^4 strong field. (ii) d^6 weak field. (iii) d^4 strong field.
 (c) What are inner and outer orbital complexes? Discuss giving one example for each type. (H.P.U. 2019)
27. (a) Define CFSE and calculate its value for d^6 system in octahedral and tetrahedral fields.
 (b) Explain crystal field splitting of d orbitals in octahedral complexes.
 (c) Give an account of limitations of valence bond theory in transition metal complexes. (P.U. 2019)
28. (a) What do you understand by crystal field theory? Explain its limitations too.
 (b) What are the factors affecting the crystal field parameters? Explain in detail. (G.N.D.U. 2019)
29. (a) Draw diagram showing crystal field splitting of d -orbitals in octahedral complexes.
 (b) Explain why FeF_6^{3-} is colourless whereas CoF_6^{3-} is coloured. (M.D.U. 2019)
30. (a) What are the salient features of crystal field theory and discuss its limitations.
 (b) Calculate the CFSE for the following systems:
 (i) d^5 (low spin octahedral)
 (ii) d^3 (Tetrahedral) (M.D.U. 2019)
31. (a) Explain crystal field splitting in octahedral complexes.
 (b) How does oxidation state of metal ion affect crystal field splitting? Explain giving example.
 (c) Draw the shapes of d_{2-x}^x , d_{2-y}^y and d_z^z orbitals. (H.P.U. 2011)
32. (a) Both Mn(II) and Fe(III) have d^5 configuration but Mn(II) forms high spin complexes while Fe(III) forms low spin complexes. Why?
 (b) Draw crystal field splitting diagram and calculate number of unpaired electrons in $[\text{Mn}(\text{CN})_6]^{3-}$.
 (c) Draw CFSE diagram for d^6 configuration in weak and strong field for octahedral complexes.
 (d) Discuss the factors on which crystal field splitting depends. (H.P.U. 2011)
33. (a) Discuss the splitting of d -orbitals in tetrahedral complexes.
 (b) What is spectrochemical series? Give its importance.
 (c) What is crystal field theory? How does this theory account for the fact that $[\text{CoF}_6]^{3-}$ is paramagnetic but $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic though both are octahedral? (P.U. 2011)
34. (a) How do the d -orbitals split when a transition metal ion is placed in octahedral field of ligands?
 (b) Define CFSE and calculate its value for d^6 system in octahedral and tetrahedral field.
 (c) Discuss the factors affecting the magnitude of Δ_o . (P.U. 2011)
35. (a) Discuss crystal field splitting of d -orbitals in case of tetrahedral complexes.
 (b) Calculate CFSE for the following systems:
 (i) d^5 low spin octahedral
 (ii) d^5 high spin octahedral
 (iii) d^4 system in tetrahedral field.
 (c) What is spectrochemical series? Give its importance. (P.U. 2011)
36. (a) What do you understand by $d-d$ transitions?
 (b) $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar and diamagnetic while $[\text{NiCl}_4]^{2-}$ is tetrahedral and paramagnetic. Explain.
 (c) Why are compounds of Ti(IV) and Zn(II) typically white? (Jammu U. 2012)

HINTS & ANSWERS TO SELECTED QUESTIONS

A : Very Short Answer Type Questions

- $[\text{CoF}_6]^{3-}$
 - t^4 (high spin octahedral) : $t_{2g}^3 e_g^1$
CFSE = $-6Dq$
 - $t^4 t_2^5$
CFSE = $-4 Dq$
 - $[\text{Co}(\text{CN})_6]^{3-}$

7. $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$
9. Crystal field theory considers the metal ion and the ligands in a complex as point charges. The interaction between them is purely electrostatic.
10. Cu^{+} ion in Cu_2SO_4 has $3d^9$ electronic configuration. As a result, there is no $d-d$ transition possible and hence the cuprous compounds such as Cu_2SO_4 are colourless.
13. $[\text{Co}(\text{NH}_3)_6]^{3+}$

B. General Questions

7. (b) (i) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ (ii) $[\text{Rh}(\text{NH}_3)_6]^{3+}$ (iii) $[\text{Co}(\text{CN})_6]^{3-}$
8. (b) Ti^{3+} is coloured in aqueous solution
9. (a) (i) 1 (ii) 3 (iii) 4 (iv) 1

- ① Splitting oct & tetrahedral numerical 
- ② Magnetic \rightarrow quinonoid-like complex d_1, d_2 quin.
- ③ Fow method
- ④ n.
- ⑤ Brønsted effect.
- ⑥ Thermodynamic stability
- ⑦ Orgel diagram

LEARNING OUTCOMES OF THIS CHAPTER