SRI YERRAMILLI NARAYANA MURTHY COLLEGE (AUTONOMOUS)

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DEPARTMENT OF CHEMISTRY

A Project Work on

"Crystal Field Theroy"

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Submitted to

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Crystal Field Theory was developed to describe important properties of complexes (magnetism, absorption spectra, oxidation states, coordination,). The basis of the model is the interaction of d-orbitals of a central atom with ligands, which are considered as point charges. According to CFT, *the attraction between the central metal and ligands in a complex is purely electrostatic.*

The theory is developed by considering energy changes of the five degenerate d- orbitals being surrounded by an array of point charges consisting of the ligands. As a ligand approaches the metal ion, the electrons from the ligand will be closer to some of the d-orbitals and farther away from others, causing a loss of degeneracy. The electrons in the d-orbitals and those in the ligand repel each other due to repulsion between like charges. Thus, the d-electrons closer to the ligands will have a higher energy than those further away, which results in the d-orbitals splitting in energy.

Crystal Field Theory (CFT)

As originally developed, crystal field theory was used to describe the electronic structure of metal ions in crystals, where they are surrounded by oxide ions or other anions that create an electrostatic field with symmetry dependent on the crystal structure. The energies of the d orbitals of the metal ions are split by the electrostatic field, and approximate values for these energies can be calculated.

CFT was developed in 1930,. Shortly afterward, it was recognized that the same arrangement of charged or neutral electron pair donor species around a metal ion existed in crystals and coordination complexes.

In order to understand clearly the interactions that are responsible for crystal or ligand field effects in transition metal complexes, it is necessary to know the geometrical relationships of the d orbitals. There are five wave functions that can be written for orbitals having the typical four-lobed form.
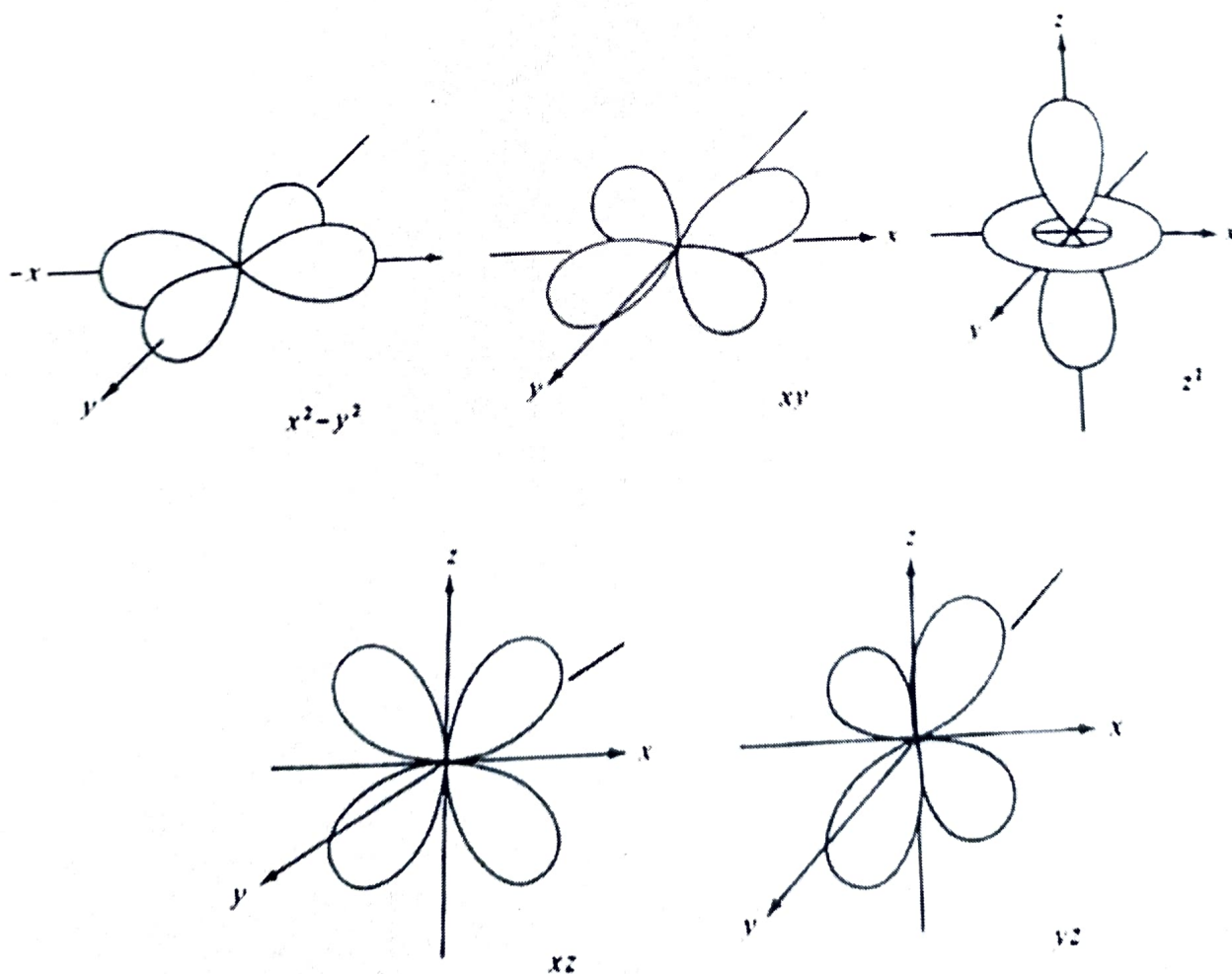
Crystal Field Effects in Octahedral Complexes

When the d orbitals of a metal ion are placed in an octahedral field of ligand electron pairs, directed at the surrounding ligands, are raised in energy. The d_{xy}, d_{xz}, and d_{yz} orbitals, which are directed between the surrounding ions, are relatively unaffected by the field. The resulting energy difference is identified as Δ_o (o for octahedral; some older references use the term 10Dq instead of Δ_o).
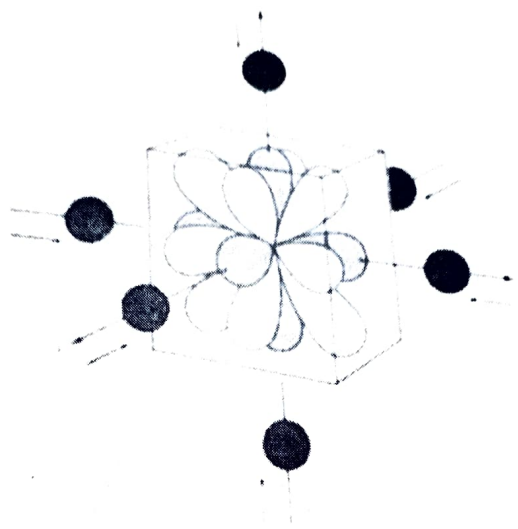
In case of free metal ion all the five d-orbitals are degenerate (these have the same energy. Now consider an octahedral complex, $[ML_6]^{n+}$ in which the central metal cation, M^{n+} is placed at the center of the octahedral and is surrounded by six ligands which reside at the six corners of the octahedral.

Now suppose both the ligands on each of the three axes are allowed to approach toward the metal cation, M^{n+} from both the ends of the axes. In this process the electrons in d-orbitals of the metal cation are repelled by the negative point charge or by the negative end of the dipole of the ligands. (Remember CFT the ionic ligands as negative point charges and neutral ligands as dipoles). This repulsion will raise the energy of all the five d-orbitals. Since the lobes of the $d_{x^2-y^2}$ orbitals (eg orbitals) lie directly in the path of the approaching ligands, the electrons in these orbitals experience greater force of repulsion than those in d_{xy}, d_{yz}, and d_{zx} orbitals

(t_{2g} orbitals) whose lobes are directed in space between the path of the approaching ligands (the energy of e_g orbitals is increased while that of t_{2g} is decreased (greater the repulsion. greater the increase in energy).

Thus we find that under the influence of approaching ligands, the five d-orbitals which were originally degenerate in free metallic cation are now split (or resolved) into two levels. t_{2g} level which is triply degenerate and is of lower energy. and e_g level which is doubly degenerate and is of higher energy.
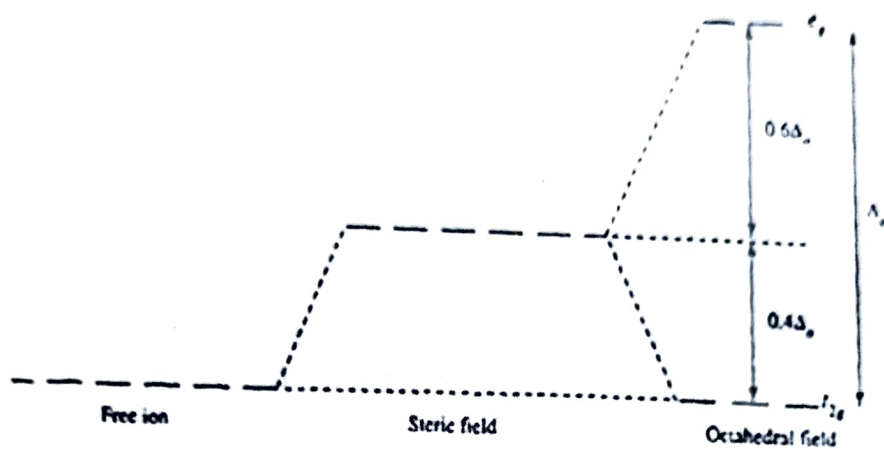

The resulting energy difference is identified as Δ_o (o for octahedral) or 10Dq. This approach provides a simple means of identifying the d- orbital splitting found in coordination complexes and can be extended to include more quantitative calculations.
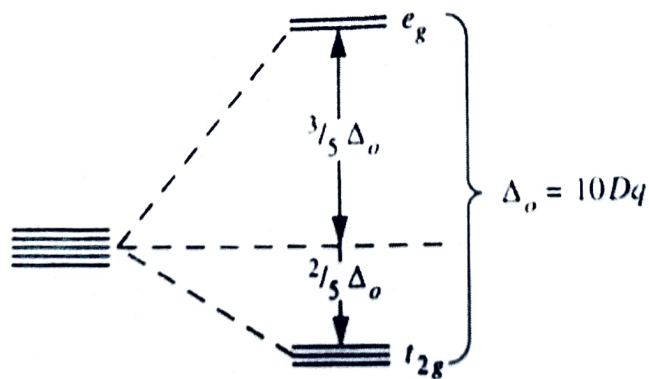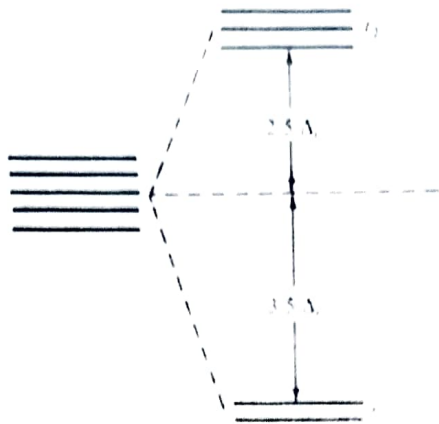
CFT for Tetrahedral Complexes

Let us consider a tetrahedral complex ion, $[ML_4]^{n}$ in which the central metal ion (M^n) is surrounded by four ligands.
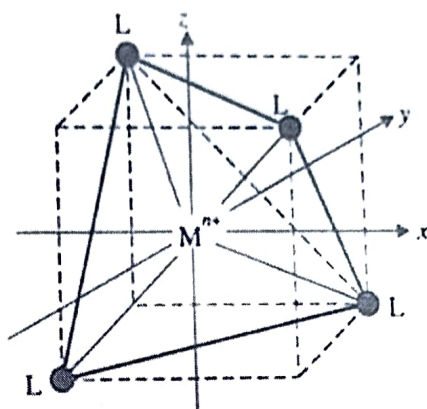
A tetrahedron may be supposed to have been formed from a cube. The center of the cube is the center of the tetrahedron at which is placed the central metal ion (M^{n}). Four alternate corners of the cube are the four corners of the tetrahedron at which the four ligands, L are placed. The four ligands are lying between the three axes x,y and z which pass through the centers of the six faces of the cube and thus go through the center of the cube. Now since the lobes of t_2 orbitals (d_{xy}, d_{yz} and d_{zx}) are lying between the axes (are lying directly in the path of the ligands), the orbitals will experience greater force of repulsion from the ligands than those of e orbitals (d_{z^2} and $d_{x^2-y^2}$) whose lobes are lying along axes (are lying in space between the ligands).

Thus the energy of t_2 orbitals will be increased while that of e orbitals will be decreased. Consequently the d orbitals are again split into two sets.

The energy difference between t_2 and e sets for tetrahedral complex is represented as Δ_t

The crystal field splitting in a tetrahedral field is smaller than that in an octahedral field because in an octahedral complex there is a ligand along each axis and in a tetrahedral complex no ligand lies directly along any axis. For this reason and also because there are only four ligands in the tetrahedral complex, while in an octahedral complex there are six ligands, the tetrahedral orbital splitting, Δ_t is less than Δ_o for the same metal ion, ligands and metal-ligand distances.

$$\Delta_t = 4/9\ \Delta_o$$

As a result, orbital splitting energies in tetrahedral complexes generally are not large enough to force electrons to pair, and low spin configurations are rarely observed.

Crystal Field Splitting in an Octahedral Field
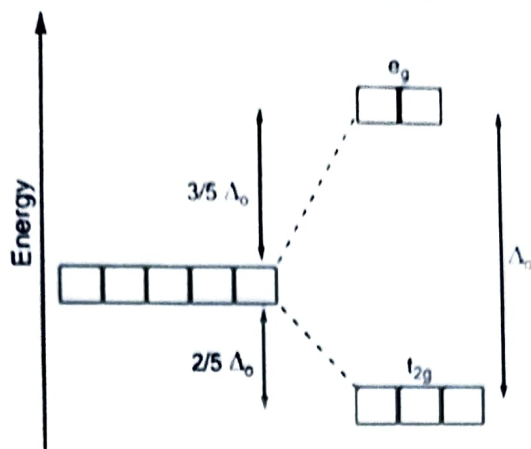
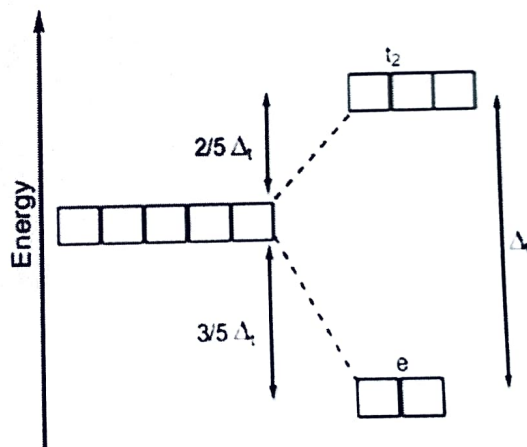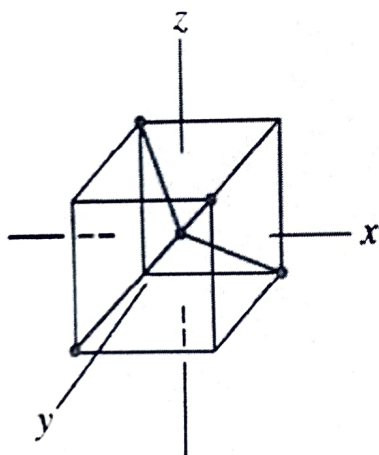e_g - The higher energy set of orbitals (d_{z^2} and $d_{x^2-y^2}$)
t_{2g} - The lower energy set of orbitals (d_{xy}, d_{yz} and d_{xz})

Δ_o or 10 Dq - The energy separation between the two levels

The e_g orbitals are repelled by an amount of $0.6\,\Delta_o$
The t_{2g} orbitals to be stabilized to the extent of $0.4\,\Delta_o$.

Tetrahedral Field

The higher energy set of orbitals (d_{xy}, d_{yz}, d_{xz}) is labeled as t_2 and the lower energy set (d_{z^2} and $d_{x^2-y^2}$) is labeled as e.

The crystal field splitting in the tetrahedral field is intrinsically smaller than in the octahedral field. For most purposes the relationship may be represented as $\Delta_t = 4/9\,\Delta_o$

Square Planar Complexes

The other common geometry is square planar. It is possible to consider a square planar geometry as an octahedral structure with a pair of *trans* ligands removed. The removed ligands are assumed to be on the z-axis. This changes the distribution of the d orbitals, as orbitals on or near the z-axis become more stable, and those on or near the x- or y-axes become less stable. This results in the octahedral t_{2g} and the e_g sets splitting and gives a more complicated splitting pattern (Figure 2).
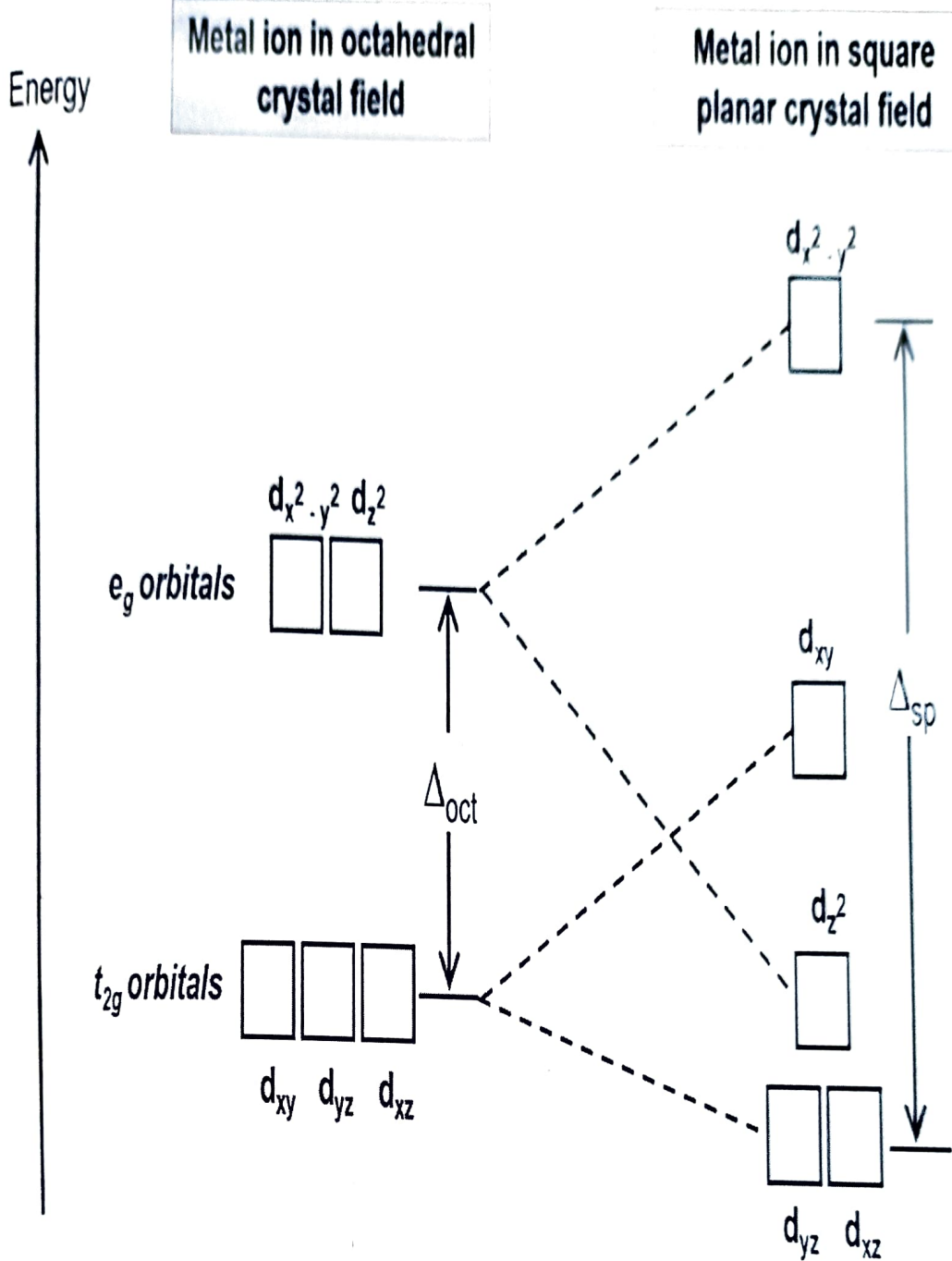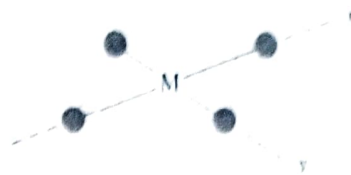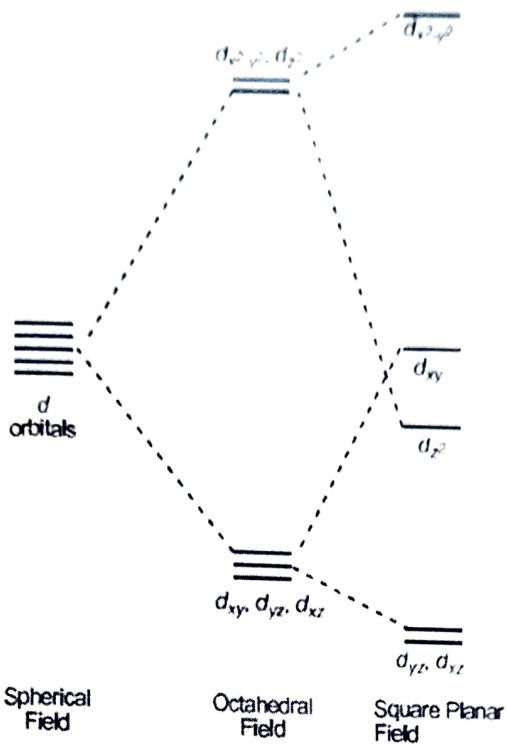
Figure 2. Splitting of the t_{2g} set and the e_g set of orbitals in a square planar crystal field. The crystal field splitting energy of square planar complexes, or Δ_{sp}, is larger than Δ_{oct}.

Square Planar Field

$d_{x^2-y^2}, d_{z^2}$

$d_{x^2-y^2}$

d orbitals

d_{xy}

d_{z^2}

Ligands along the Z axis are removed from an octahedral complex to get a square planar complex

d_{xy}, d_{yz}, d_{xz}

d_{yz}, d_{xz}

Energy

Spherical Field

Octahedral Field

Square Planar Field

What are High Spin Complexes?

High spin complexes are coordination complexes containing unpaired electrons at high energy levels. Since they contain unpaired electrons, these high spin complexes are paramagnetic complexes. This means these complexes can be attracted to an external magnetic field.
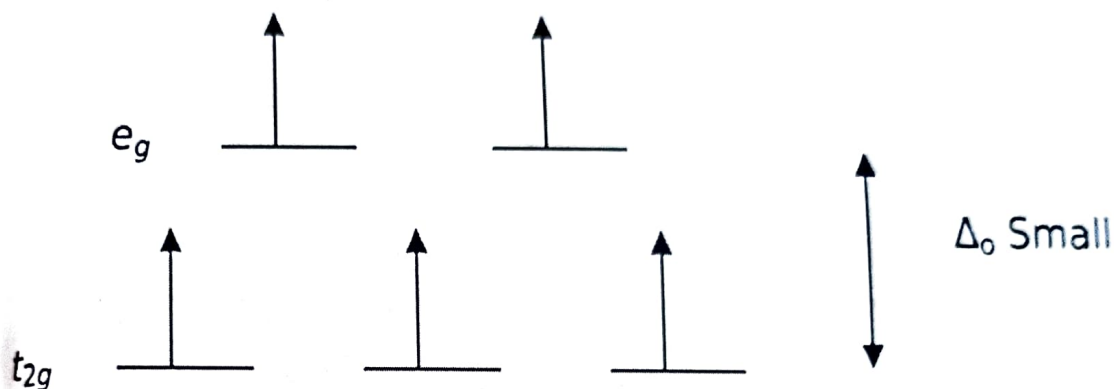

Figure 01: Energy Splitting Diagram for High Spin Complexes

A high spin energy splitting of a compound occurs when the energy required to pair two electrons is greater than the energy required to place an electron in a high energy state. Usually, octahedral and tetrahedral coordination complexes are high spin complexes.

What are Low Spin Complexes?

Low spin complexes are coordination complexes containing paired electrons at low energy levels. Since there are no unpaired electrons in the low spin complexes (all the electrons are paired), they are diamagnetic. This means these compounds cannot be attracted to an external magnetic field. The low energy splitting of a compound occurs when the energy required to pair two electrons is lower than the energy required to place an electron in a low energy state. Usually, square planar coordination complexes are low spin complexes.
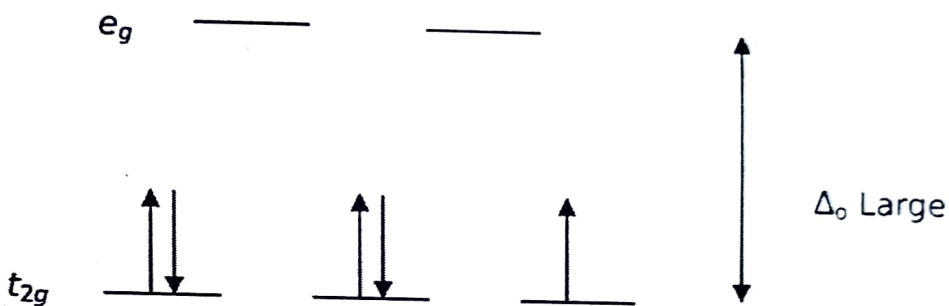

Figure 02: Energy Splitting Diagram for Low Spin Complexes

In order to determine whether a given coordination complex is a high spin complex or a low spin complex, we can use the following tips.

1. Determination of the shape of the complex
2. Determination of the oxidation state of the metal centre
3. Determination of the d electron configuration of the metal

What is the Difference Between High Spin and Low Spin Complexes?

The key difference between high spin and low spin complexes is that high spin complexes contain unpaired electrons, whereas low spin complexes tend to contain paired electrons. In high spin complexes, the energy required to pair up two electrons is greater than the energy required to place an electron of that complex in a high energy level. In contrast, in low spin complexes, the energy required to pair two electrons is lower than the energy required to place an electron in a high energy level.

Furthermore, another significant difference between high spin and low spin complexes is that the high spin complexes are paramagnetic because they have unpaired electrons, but low spin complexes are diamagnetic because they have all electrons paired. Generally, tetrahedral and octahedral compounds are high spin while square planar compounds are low spin.

This splitting is affected by the following factors:

- the nature of the metal ion.

- the metal's oxidation state. ...

- the arrangement of the ligands around the metal ion.

- the coordination number of the metal (i.e. tetrahedral, octahedral...)

- the nature of the ligands surrounding the metal ion.