# Crystal Field Theory

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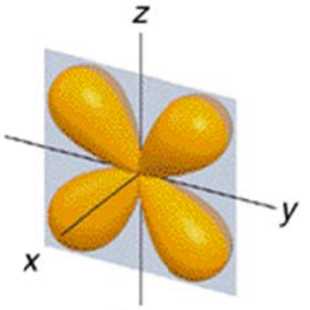
## Introduction

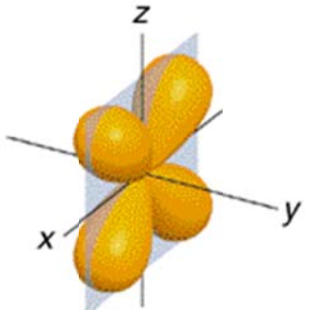
**What you must know?**

- Complexes are generally organometallic compounds. Organometallic compounds are associated with diverse biological and synthetic importance.
- For example Cis-platin (*cis*-diamminedichloroplatinum(II)) is complex of platinum and used as chemotherapeutic drug. Ferrocene is an important organic reagent in industrial processes, and one of most toxic compounds used in industry.
- The crystal field theory is all about such complexes and found very much useful in understanding their various properties.
- The theory was developed by **Bethe and Van Vleck in 1930**, individually. Bethe explained the structure and stability of complexes while Van Vleck explained the magnetic properties of complexes.
- The complex mainly contains transition metal at the centre and ligand joined to metal by non-bonded pair of electron.
- The metal ion links with the ligand due to interaction of metal electric field and ligand electric charge, which subsequently generate special type of electric field around the metal ion.
- This concept is known as **Crystal Field theory**. It is a model that describes the breaking of degeneracies of electronic orbital states, usually **d** or **f** orbitals, due to a static electric field produced by a surrounding charge distribution (anion neighbours).
- The effect produced due to the joining of ligand and central metal ion is known as ligand field effect.
- This theory has been used to describe various spectroscopies of transition metal coordination complexes, in particular optical spectra (colours).
- CFT (Crystal field theory) is useful to describe magnetic properties, colours, hydration enthalpies, and spinel structures of transition metal complexes, but it does not attempt to describe bonding.

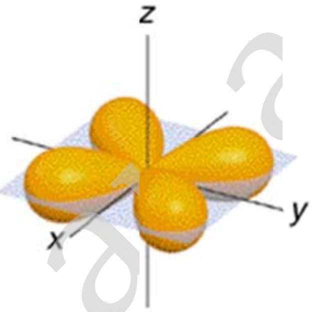
- s orbital is spherical and p orbitals are dumbbell shaped. So there is not much effect of ligands on s & p orbitals.
- **All five d orbitals are not equivalent.**
- d orbitals are distributed in different direction around nucleus.
- Therefore, ligand field affects more on d orbitals.



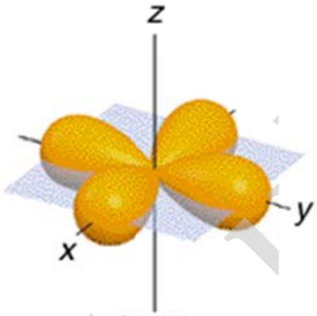
$d_{yz}$



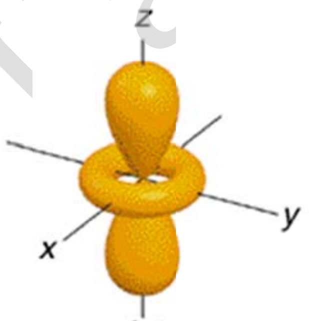
$d_{xz}$



$d_{xy}$



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

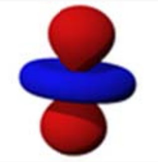
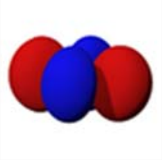
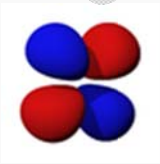
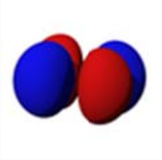


$d_{z^2}$

## Salient feature of Crystal Field Theory

- The central metal ion in the complex is positively charged.
- Central metal ion is attached to negative or neutral ligand by non-bonding electron.
- Ligand with negative charge attaches to central metal ion by negative charge.
- The neutral ligand attaches to metal ion by negative end as neutral ligands are polar.
- Central metal ion and ligands joins by electrostatic force.
- The interaction between metal and ligand produces special type of electrical field which causes changes in d orbitals of metal ion. This is called ligand field effect.
- All the five d orbitals are degenerated in ground state.
- But, the degeneracy of d orbitals is destroyed when ligand attacks the metal ion.

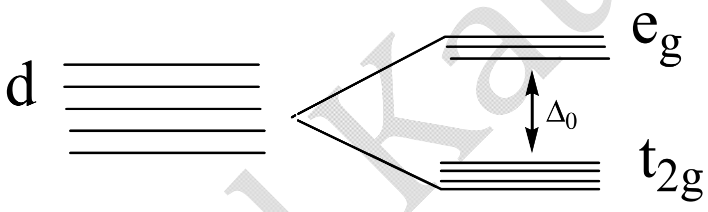
- When ligand moves nearer to metal ion, attraction force is generated due to interaction between positive charge of central metal ion and negative charge of ligand. As ligand moves more closely to metal ion, repulsion occurs due to electrical field of metal and ligand, and it causes increase in energy of d orbitals. As a result of it, the degeneracy of d orbitals is destroyed and they split. The phenomenon is known as **crystal field splitting.**
- The ligand field effect divides d orbitals in two types; $t_{2g}$ ($d_{xy}$, $d_{yz}$, and $d_{xz}$) and $e_g$ ($d_{x^2-y^2}$ and $d_{z^2}$).

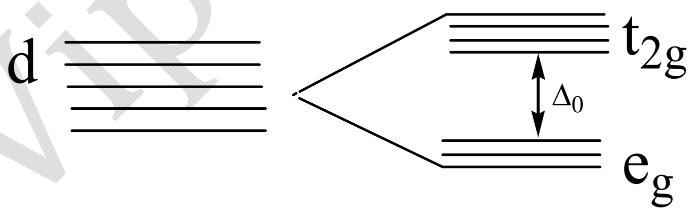
| $E_g$ | | $T_{2g}$ | | |
|---|---|---|---|---|
| $d_{z^2}$ | $d_{x^2-y^2}$ | $d_{xz}$ | $d_{yz}$ | $d_{xy}$ |
|  |  |  |  |  |

- The increase or decrease in energy of d orbitals under the ligand field effect is depending upon the type and direction of ligand. If the ligand is nearer to d orbitals repulsion will be higher and there will be increase in energy of the orbitals.
- If the ligand is away from the d orbitals repulsion will be lower and energy of the orbitals will be lower, and stable.
- For example: In case of octahedral complexes, ligand sets on x, y, and z axes so energy of $e_g$ ($d_{x^2-y^2}$ and $d_{z^2}$) orbitals will increase and energy of $t_{2g}$ ($d_{xy}$, $d_{yz}$, and $d_{xz}$) will decrease.
- Opposite to this, in tetrahedral complexes ligand not sets on axes, so energy of $t_{2g}$ ($d_{xy}$, $d_{yz}$, and $d_{xz}$) will increases and energy of $e_g$ ($d_{x^2-y^2}$ and $d_{z^2}$) orbitals will decreases.
- The difference in energy of $t_{2g}$ and $e_g$ occurs due to ligand field effect is designated by $\Delta$ or $10D_q$, and termed as **splitting energy of d orbitals**.

- Ligand field effect will affect the d orbitals, and its electronic arrangement. The electron will enter to the orbital having less energy. For example: In octahedral complexes, $t_{2g}$ orbitals will be filled first, and in case of tetrahedral complexes $e_g$ orbitals will be filled first.
- The energy d orbitals will be changed due to ligand field effect, and will split with change in electronic arrangement. As a result of this, energy of complex system will change, and the change in energy is known as **crystal field stabilization energy (C.F.S.E.)**.
- The change in energy is proportional to the strength of ligand. $H_2O$, $Cl^-$, $Br^-$, and $F^-$ are weak ligand while CO, CN-, $NO_2^-$ are strong ligand.

- **Splitting of d orbitals**





**What you should know? (Just for information)**

- The bright colours exhibited by many coordination compounds can be explained by Crystal Field Theory.
- If the *d*-orbitals of such a complex have been split into two sets as described above, when the molecule absorbs a photon of visible light one or more electrons may momentarily jump from the lower energy *d*-orbitals to the higher energy ones to transiently create an excited state atom.

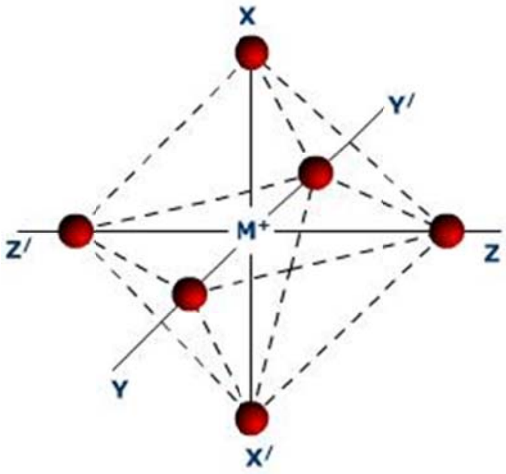
- The difference in energy between the atom in the ground state and in the excited state is equal to the energy of the absorbed photon, and related inversely to the wavelength of the light.
- Because only certain wavelengths (λ) of light are absorbed - those matching exactly the energy difference - the compounds appears the appropriate complementary colour.
- As explained above, because different ligands generate crystal fields of different strengths, different colours can be seen.
- For a given metal ion, weaker field ligands create a complex with a smaller Δ, which will absorb light of longer λ and thus lower frequency *v*.
- Conversely, stronger field ligands create a larger Δ, absorb light of shorter λ, and thus higher *v*.
- It is, though, rarely the case that the energy of the photon absorbed corresponds exactly to the size of the gap Δ; there are other things (such as electron-electron repulsion and Jahn-Teller effects) that also affect the energy difference between the ground and excited states.
- This colour wheel demonstrates which colour a compound will appear if it only has one absorption in the visible spectrum. For example, if the compound absorbs red light, it will appear green.

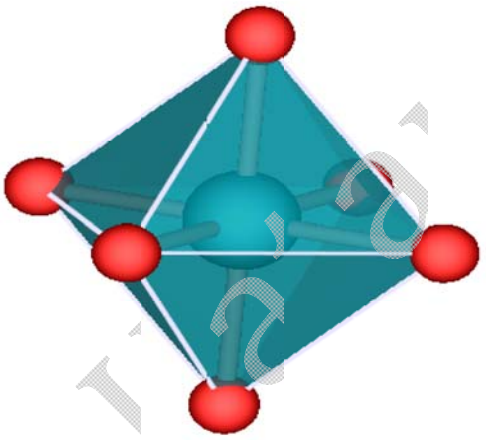
| **λ absorbed versus** | **colour observed** |
|---|---|
| 400 nm Violet absorbed | Green-yellow observed (λ 560 nm) |
| 450 nm Blue absorbed | Yellow observed (λ 600 nm) |
| 490 nm Blue-green absorbed | Red observed (λ 620 nm) |
| 570 nm Yellow-green absorbed | Violet observed (λ 410 nm) |
| 580 nm Yellow absorbed | Dark blue observed (λ 430 nm) |
| 600 nm Orange absorbed | Blue observed (λ 450 nm) |
| 650 nm Red absorbed | Green observed (λ 520 nm) |

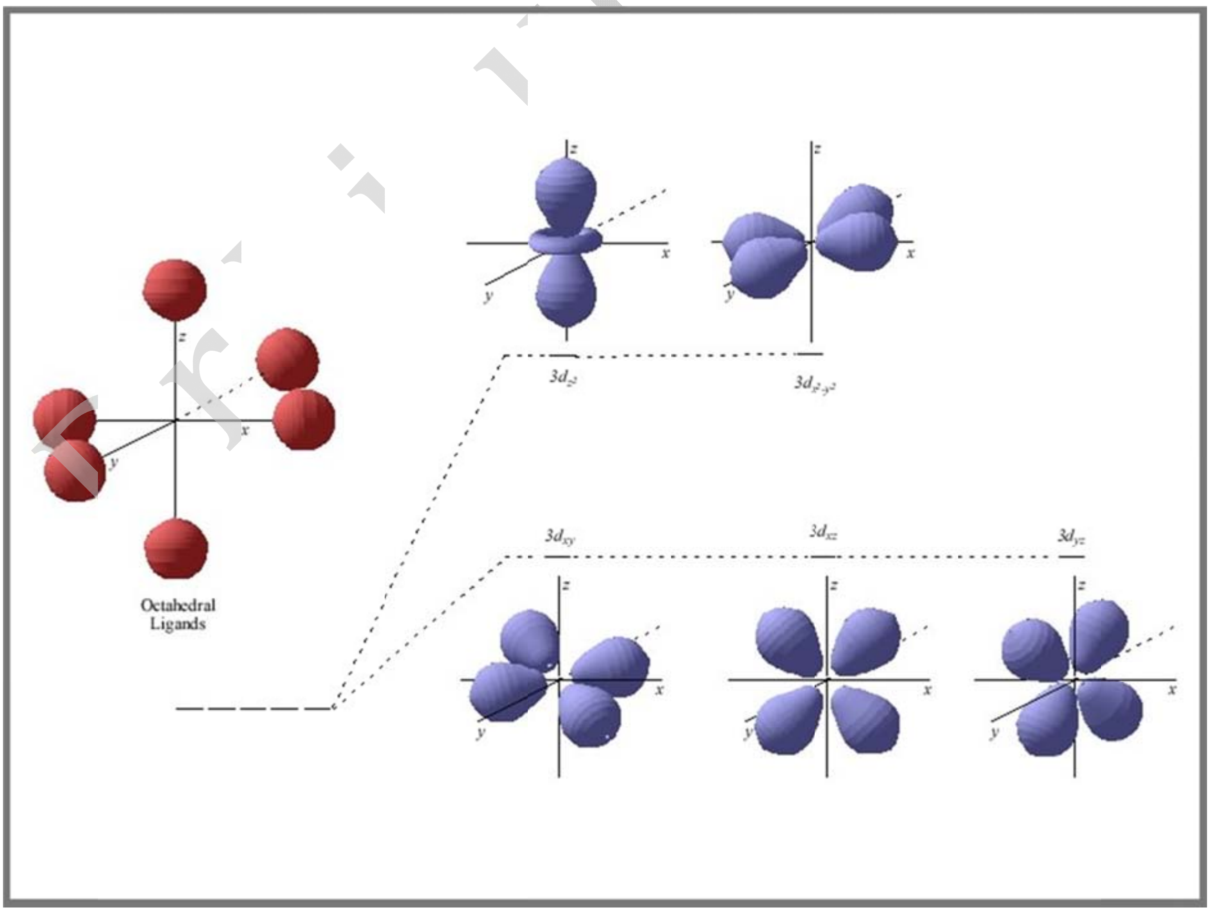
## Splitting of d orbitals in octahedral field

In respect of octahedral field, ligand with its negative charge attacks positively charged central metal ion which produces ligand field effect. As a result of this degeneracy of d orbitals of metal ion loses its degeneracy. It causes splitting of d orbital in two groups.

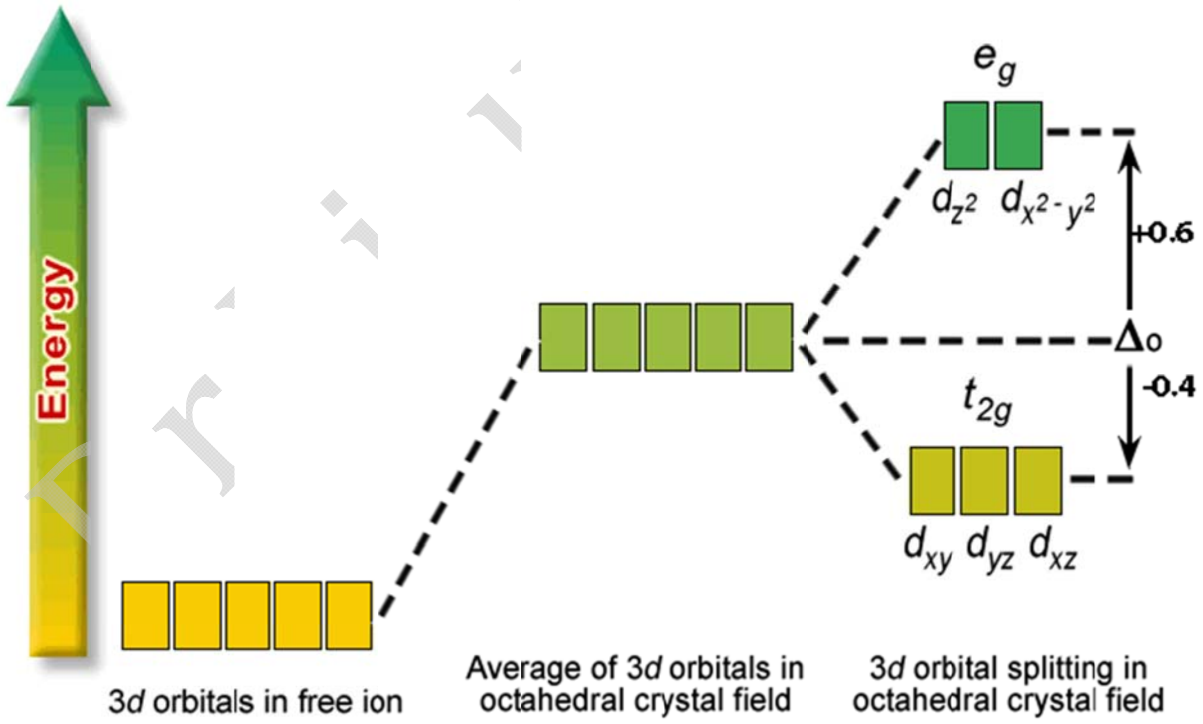
(i) $e_g$ group: ($d_{x^2-y^2}$ and $d_{z^2}$)   (ii) $t_{2g}$ group: ($d_{xy}$, $d_{yz}$, and $d_{xz}$)







- The ligand nearer to central metal ion causes increase in the energy of d orbitals.
- The ligand away from central metal ion causes decrease in the energy of d orbitals.
- In octahedral complexes, metal ion is at the centre of octahedron while six ligands set at the angles of octahedron. The octahedron arranged in the manner so that the axes remain at the angles of octahedron. So the repulsion force will be higher along the axes, and will cause increase in the energy of $e_g$ orbitals.
- So that, $e_g$ orbitals ($d_{x^2-y^2}$ and $d_{z^2}$) will be more repelled due to ligand field effect and causes increase in the energy as compare to $t_{2g}$ orbitals ($d_{xy}$, $d_{yz}$, and $d_{xz}$).
- In nutshell, with reference to octahedral field $e_g$ orbitals ($d_{x^2-y^2}$ and $d_{z^2}$) become excited and energy will be higher while $t_{2g}$ orbitals ($d_{xy}$, $d_{yz}$, and $d_{xz}$) will be stable with lower energy.
- The change in energy of d orbitals is referred as splitting energy $\Delta_o$.
- The increase in energy of $e_g$ orbitals is 0.6 $\Delta_o$, and decrease in energy of $t_{2g}$ is 0.4 $\Delta_o$.
- In this way gravitational force is balanced while change in energy of d orbitals.



- Ligand field effect causes change in electronic arrangement.
- Due to this, energy of complex system increase or decrease, the change in energy is known as **crystal field stabilization energy (C.F.S.E.)**.

- C.F.S.E. can be calculated by following equation.

$$\text{C.F.S.E.} = (-0.4n\, t_{2g} + 0.6n\, e_g)\, \Delta_o$$

Where, n = number of electron entering the $t_{2g}$ and $e_g$ orbitals

$\Delta_o$ = Splitting energy of d orbitals.

## High spin and low spin complexes:

CFSE depends on strength of ligand.

### (a) Octahedral splitting of d orbitals in strong ligand field.

- Strong ligand like $CN^-$ and CO has maximum attraction to positively charged central metal ion.
- As a result of this, the repulsion will be higher and ultimately there will be higher difference in the energy of $e_g$ and $t_{2g}$ orbitals. It will cause higher value for CFSE.

  According to Aufbau principle, electron enters into orbitals having low energy so in this case electron will first enter into $t_{2g}$ orbital, and afterwards it will enter into $e_g$ orbital.
- In such complexes pairing occurs in d orbitals, as a result of this spin of electron remains minimum.
- So, these complexes are known as low spin complexes.
- Magnetic momentum value (μ) can be calculated with respect to number of unpaired electrons in d orbital using following formula. (Magnetic moments are often used in conjunction with electronic spectra to gain information about the oxidation state and stereochemistry of the central metal ion in coordination complexes.)

$$\mu = \sqrt{n(n+2)}\ \text{B.M.}$$

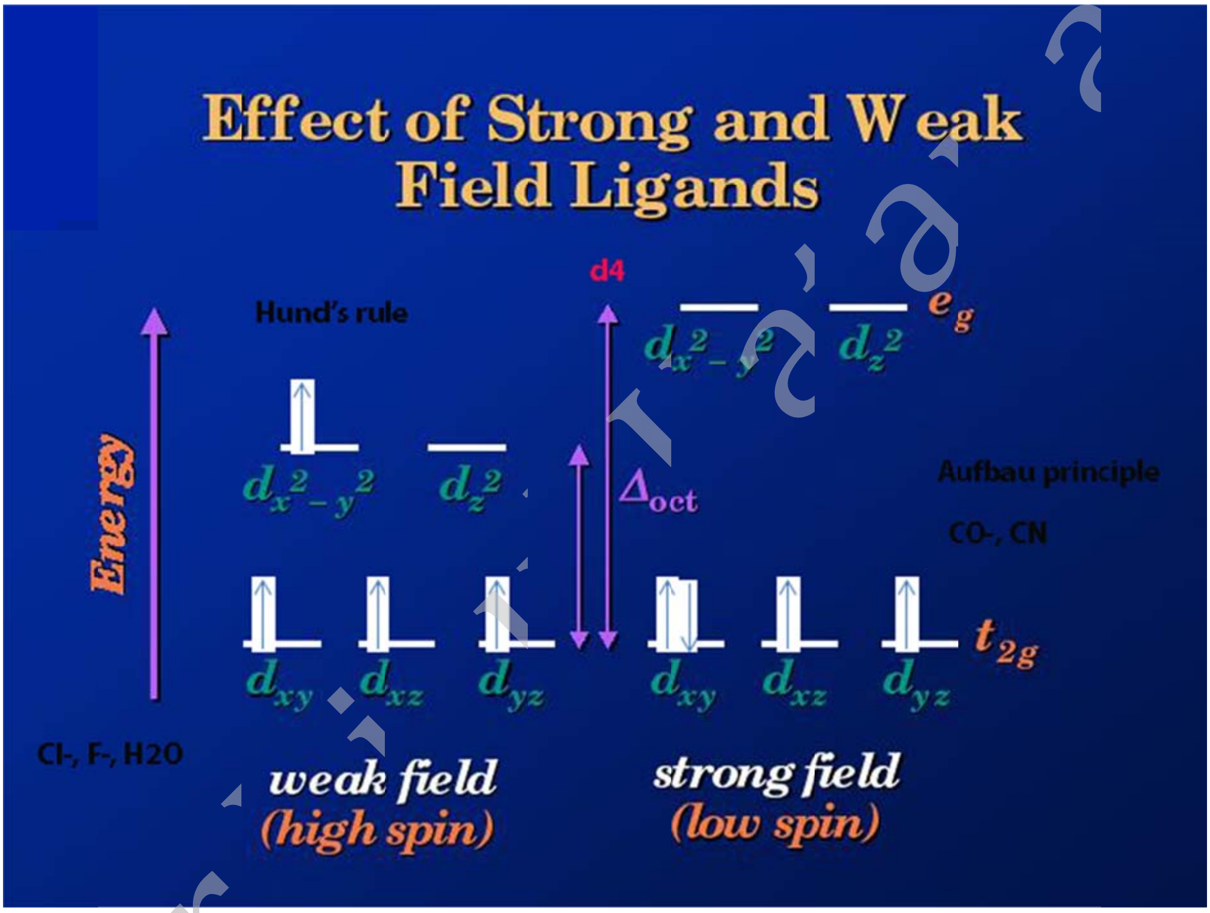
Where, n = No. of unpaired electron in d orbital

### (b) Octahedral splitting of d orbitals in weak ligand field.

- Weak ligand like $Cl^-$, $F^-$and $H_2O$ has minimum attraction to positively charged central metal ion.
- As a result of this, the repulsion will be lower and ultimately there will be lower difference in the energy of $e_g$ and $t_{2g}$ orbitals. It will cause lower value for CFSE.

According to Hund's principle if two or more orbitals of equal energy are available, electrons will occupy them singly before filling them in pairs. In this case electron will enter one by one to each orbital and afterwards pairing will be occurred.

- In such complexes pairing will not occur in d orbitals easily, as a result of this spin of electron remains maximum.
- So, these complexes are known as high spin complexes.



Effect of Strong and Weak Field Ligands

- CFSE values are higher in low spin complexes (strong field).
- So, low spin complexes (Strong field) are more stable.
- In octahedral complexes $d^1$, $d^2$, $d^3$, $d^8$, $d^9$, and $d^{10}$ electronic system configuration is same in both the field however it is different in the case of $d^4$, $d^5$, $d^6$, And $d^7$.

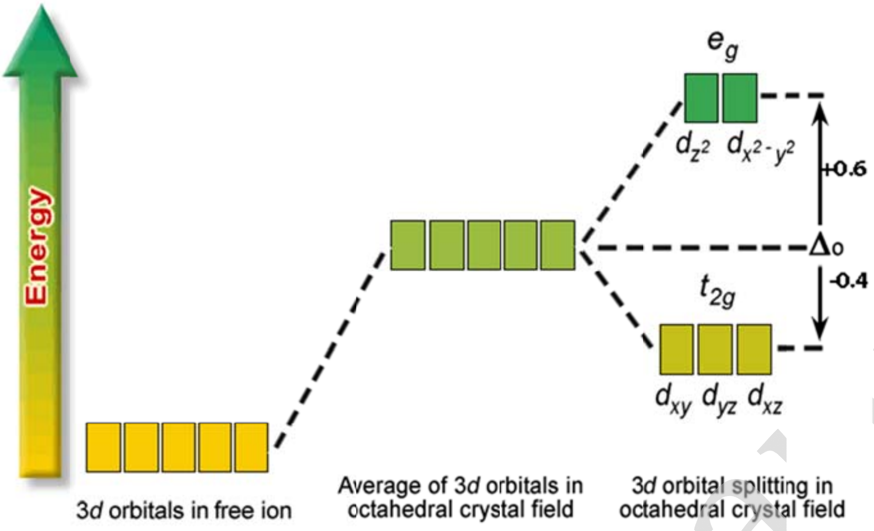
| **Total d-electrons** | **Strong ligand field** | | | **Weak ligand field** | | |
|---|---|---|---|---|---|---|
| | Configuration | **CFSE** | $\mu$ B. M. | configuration | **CFSE** | $\mu$ B. M. |
| $d^1$ | $t_{2g}^{1}$ | -0.4 Δo | 1.73 | $t_{2g}^{1}$ | -0.4 Δo | 1.73 |
| $d^2$ | $t_{2g}^{2}$ | -0.8 Δo | 2.83 | $t_{2g}^{2}$ | -0.8 Δo | 2.83 |
| $d^3$ | $t_{2g}^{3}$ | -1.2 Δo | 3.87 | $t_{2g}^{3}$ | -1.2 Δo | 3.87 |
| $d^4$ | $t_{2g}^{4}e_g$ | -1.6 Δo | 2.83 | $t_{2g}^{3}e_g^{1}$ | -1.6 Δo | 4.90 |
| $d^5$ | $t_{2g}^{5}e_g$ | -2.0 Δo | 1.73 | $t_{2g}^{3}e_g^{2}$ | -2.0 Δo | 5.90 |
| $d^6$ | $t_{2g}^{6}e_g$ | -2.4 Δo | 0.00 | $t_{2g}^{4}e_g^{2}$ | -2.4 Δo | 4.90 |
| $d^7$ | $t_{2g}^{6}e_g^{1}$ | -1.8 Δo | 1.73 | $t_{2g}^{5}e_g^{2}$ | -1.8 Δo | 8.87 |
| $d^8$ | $t_{2g}^{6}e_g^{2}$ | -1.0 Δo | 2.83 | $t_{2g}^{6}e_g^{2}$ | -1.0 Δo | 2.83 |
| $d^9$ | $t_{2g}^{6}e_g^{3}$ | -0.6 Δo | 1.73 | $t_{2g}^{6}e_g^{3}$ | -0.6 Δo | 1.73 |
| $d^{10}$ | $t_{2g}^{6}e_g^{4}$ | -0.0 Δo | 0.00 | $t_{2g}^{6}e_g^{4}$ | -0.0 Δo | 0.00 |

**What you should know?**

**Crystal field stabilization energy**

The crystal field stabilization energy (CFSE) is the stability that results from placing a transition metal ion in the crystal field generated by a set of ligands. It arises due to the fact that when the *d*-orbitals are split in a ligand field (as described above), some of them become lower in energy than before with respect to a spherical field known as the barycenter in which all five *d*-orbitals are degenerate. For example, in an octahedral case, the $t_{2g}$ set becomes lower in energy than the orbitals in the barycenter. As a result of this, if there are any electrons occupying these orbitals, the metal ion is more stable in the ligand field relative to the barycenter by an amount known as the CFSE. Conversely, the $e_g$ orbitals (in the octahedral case) are higher in energy than in the barycenter, so putting electrons in these reduces the amount of CFSE.

If the splitting of the *d*-orbitals in an octahedral field is $\Delta_{oct}$, the three $t_{2g}$ orbitals are stabilized relative to the barycenter by $^{2}/_{5}\ \Delta_{oct}$, and the $e_g$ orbitals are destabilized by $^{3}/_{5}\ \Delta_{oct}$. As examples, consider the two $d^5$ configurations shown further up the page. The low-spin (top) example has five electrons in the $t_{2g}$ orbitals, so the total CFSE is $5 \times {^{2}/_{5}}\ \Delta_{oct} = 2\Delta_{oct}$. In the high-spin (lower) example, the CFSE is $(3 \times {^{2}/_{5}}\ \Delta_{oct}) - (2 \times {^{3}/_{5}}\ \Delta_{oct}) = 0$ - in this case, the stabilization generated by the electrons in the lower orbitals is canceled out by the destabilizing effect of the electrons in the upper orbitals.



Crystal Field stabilization is applicable to transition-metal complexes of all geometries. Indeed, the reason that many $d^8$ complexes are square-planar is the very large amount of crystal field stabilization that this geometry produces with this number of electrons.

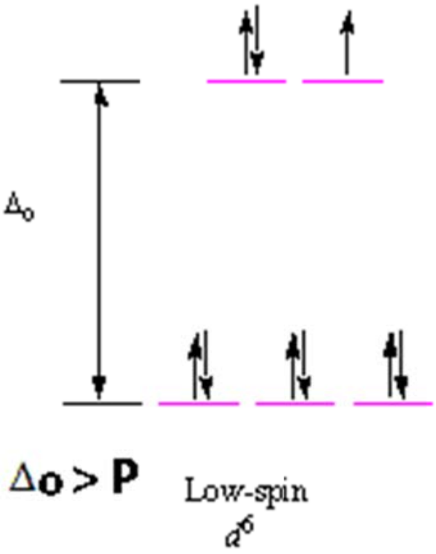
## Explanation of high spin and low spin complexes by pairing energy

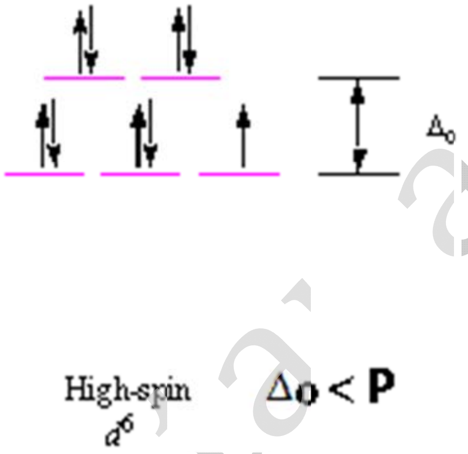
Spin pairing energy refers to the energy associated with paired electrons sharing one orbital and its effect on the molecules surrounding it. In simple words, it is energy required to pair the two unpaired electrons in one orbital is known as pairing energy P.

## Low spin complexes

- In octahedral field, in presence for strong ligand, energy of $t_{2g}$ orbital decreases, and energy of $e_g$ orbital increases, and the difference of energy between both the orbital will be higher.
- In presence of strong ligand field, the energy gap will be higher between $t_{2g}$ and $e_g$ orbitals. So first electron will be entered into $t_{2g}$ orbital and then electron will enter $e_g$ orbital (according to Aufbau principle pairing will occur).
- In this case, the splitting energy of d orbital will be higher than pairing energy hence number of unpaired electrons will be less (Δo > P).

- Such complexes are known as low spin complexes.





## High spin complexes

- In octahedral field, in presence for weak ligand, energy of $t_{2g}$ orbital decreases, and energy of $e_g$ orbital increases, and difference of energy between both orbitals will be less.
- In presence of strong ligand field, the energy gap will be lower between $t_{2g}$ and $e_g$ orbitals. So first electron will be entered into $t_{2g}$ orbital and then electron will enter $e_g$ orbital (according to Hund's principle pairing will not occur).
- In this case, the splitting energy of d orbital will be lower than pairing energy hence number of unpaired electrons will be more ($\Delta o < P$).
- Such complexes are known as high spin complexes.

*I have work hard preparing this material……*

*You also work hard preparing from this material!!!!*

*Best Luck….*