- The magnitude of  $\Delta_o$  or  $\Delta_t$  depends upon the field strength of ligand around the metal.
- Ligands which cause large splitting (large △) are called strong field ligands while those which cause small splitting (small △) are called weak field ligands.

## **Spectrochemical Series**

• Arrangement of ligand in order of their ability to cause splitting ( $\Delta$ ) is called spectrochemical series.  $I^- < Br^- < S^{2-} < SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O < NCS^- < NH_3 < en < NO_2^- < CN^- < CO$ 

# **Crystal Field Splitting in Octahedral Complexes**

• The octahedral arrangement of six ligands surrounding the central metal ion can be shown as follows:



Octahedral arrangement of six ligands surrounding the central metal ion

It is obvious from the figure, that ligands approach the x, y and z axis. The two d-orbital lying along the axis namely  $d_{x^2-y^2}$  and  $d_{z^2}$  will suffer more electrostatic repulsion and hence their energy will be greater than the other three d-orbitals  $d_{xy}$ ,  $d_{yz}$  and  $d_{yy}$  which have their lobes lying between the axis.

Thus degenerate set of *d*-orbitals split into two set :  $e_s$  orbitals of higher energy including  $d_{x^2-y^2}$  and  $d_{z^2}$  and  $t_{2s}$  orbitals of lower energy including  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz'}$ .

The crystal field splitting is measured in terms of energy difference between  $t_{2g}$  and  $e_g$  orbital and is denoted by symbol  $\Delta_o$ . It is generally measured in terms of a parameter, Dq. It is called as **crystal field splitting energy or crystal field stabilization energy (CFSE)**.  $e_g$  orbitals are  $0.6\Delta_o$  or 6 Dq above the average energy level and  $t_{2g}$  orbitals are  $0.4 \Delta_o$  or 4 Dq below the average energy level.



Formation of Low-spin and High-spin Complex

- When strong field ligands approach metal atom/ion, the value of  $\Delta_o$  is large, so that electrons are forced to get paired up in lower energy  $t_{2g}$  orbitals. Hence a low-spin complex is resulted from strong field ligand.
- When weak field ligands approach metal atom/ion, the value of  $\Delta_o$  is small, so that electrons enter high energy  $e_\sigma$

orbitals rather than pairing in low energy  $t_{2g}$  orbitals. Hence a high-spin complex is resulted from weak field ligands.

Strong field ligands have tendency to form inner orbital complexes by forcing the electrons to pair up. Whereas weak field ligands have tendency to form outer orbital complex because inner electrons generally do not pair up.

#### **Magnetic Behaviour of Complexes**

 Low spin complexes are generally diamagnetic because of pairing of electrons, whereas high spin complexes are usually paramagnetic because of presence of unpaired electrons.

Larger the number of unpaired electrons, stronger will be the paramagnetism.

However magnetic behaviour of a complex can be confirmed from magnetic moment measurement.

Magnetic moment =  $\sqrt{n(n+2)}$  B.M.

where n = number of unpaired electrons.

Greater the number of unpaired electrons, more will be the magnetic moment.

#### **Colour of Coordination Complexes**

- Colour of a complex is not because of the light absorbed but it is due to the light reflected (complementary colour).
- *e.g.* If radiation corresponding to red light are absorbed from visible region, the compound appears to have blue colour (complementary colour).
- In coordination complexes energy difference (Δ) between two sets of *d*-orbitals is small. Radiations of appropriate frequency absorbed from visible region can cause excitation of *d*-electrons from lower energy orbital to higher energy orbitals. Remaining light is transmitted and compound appears coloured.
- If there are no *d*-electrons present or completely filled *d*-orbitals are present then there is no *d*-*d* transition possible and complex appears colourless.

### **Crystal Field Splitting in Tetrahedral Complexes**

• The tetrahedral arrangement of four ligands surrounding the metal ions can be shown as follows :



Tetrahedral arrangement of four ligands surrounding the metal ions. It is obvious from the figure that none of the *d*-orbitals points exactly towards the ligands. However, three *d*-orbitals  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  are pointing close towards ligands. As a result of this, the energy of these three orbital increases