

S-15: Crystal Field Theory (Introduction) and Splitting of d-orbitals in Octahedral Complexes

Shortcomings of Valence Bond Theory (VBT)

- ❖ The geometry of the complexes (tetrahedral, octahedral or square planar) having the same number of unpaired electrons for d^1 , d^2 , d^3 and d^9 ions can not be distinguished from each other on basis of number of unpaired electrons
- ❖ Both the colour and the magnetic moments of transition metal complexes are due to their possessing d-orbital electrons. There should be a correlation between **spectra** and **magnetic moment**. VBT can't explain any correlation between these two properties.
- ❖ This theory can't explain why the complexes with d^8 central metal ion prefers only square planar geometry as compared to other possible geometries such as tetrahedral or trigonal bipyramidal with coordination number 5.
- ❖ Too much attention has been laid on the central metal ion while the importance of ligand is not properly stressed.

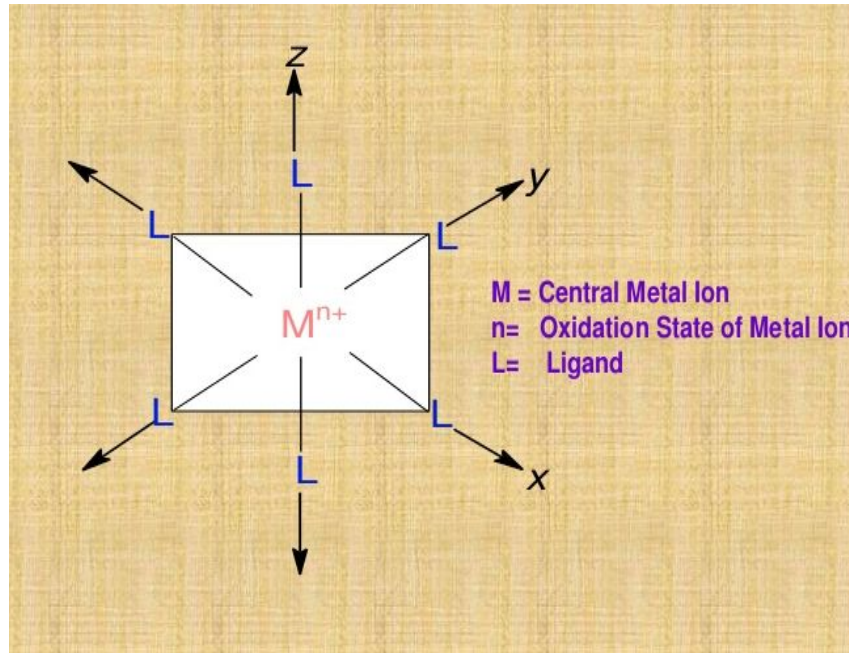
Crystal Field Theory (CFT)

- ❖ The crystal field theory was 1st given by Brethe in 1929 and then developed by Van Vleck in 1932
- ❖ A complex may be considered as consisting of a central metal atom or ion surrounded by a number of ligands.
- ❖ The interaction between the ligands with the central metal atom or ion is subject to crystal field theory (CFT)
- ❖ CFT describes the net change in crystal energy resulting from the orientation of d orbitals of a transition metal cation inside a coordinating group of anions, called as ligands
- ❖ CFT can explain many important properties of transition metal complexes

Crystal Field Theory

Central assumptions of CFT:

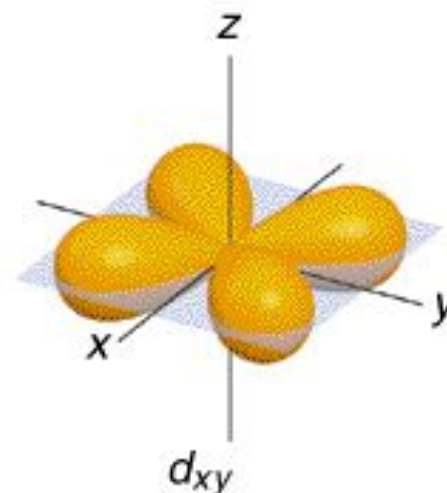
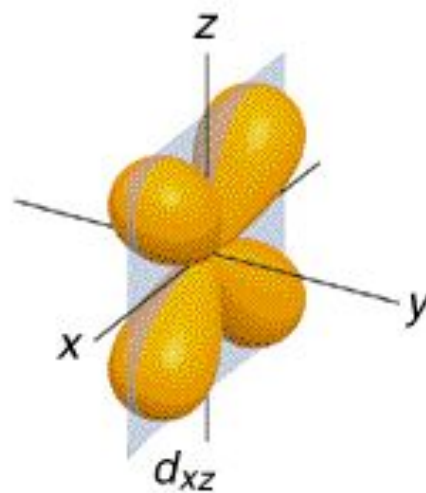
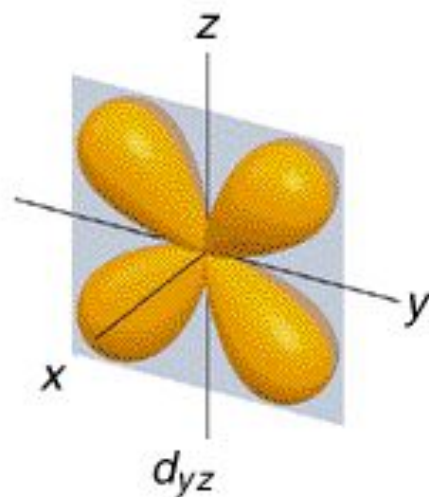
- ❖ The ligands are considered as **point charges** which are either ions or neutral molecules with negative poles oriented towards metal cation
- ❖ The transition metal cation is surrounded by the ligands with lone pairs of electrons
- ❖ The attraction between metal cation and ligands is purely **electrostatic**



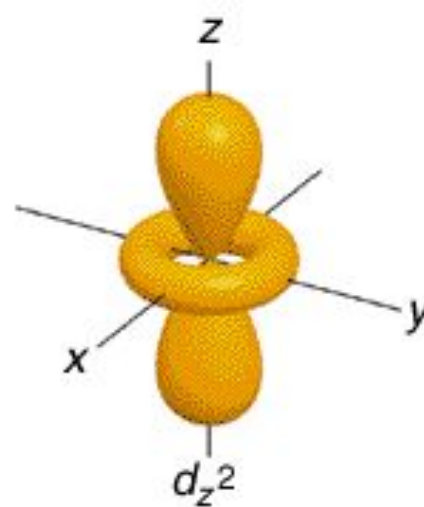
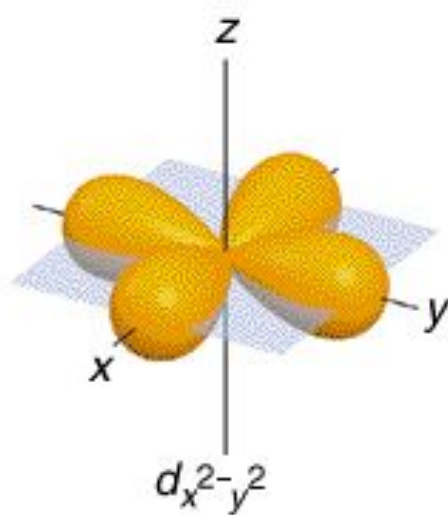
- ❖ The valence electrons of metal will be repelled by negative field of ligands so these electrons occupy those d-orbitals which have their lobe away from the direction of the ligands
- ❖ The electrons of ligand do not enter metal orbital. Hence there is no orbital overlap taking place
- ❖ The effect of ligands is particularly marked on the d-electrons of metal and it depends upon:
 - (i) the number of ligands,
 - (ii) arrangement around the cation and
 - (iii) nature of the ligands

Orientation of different d-orbitals

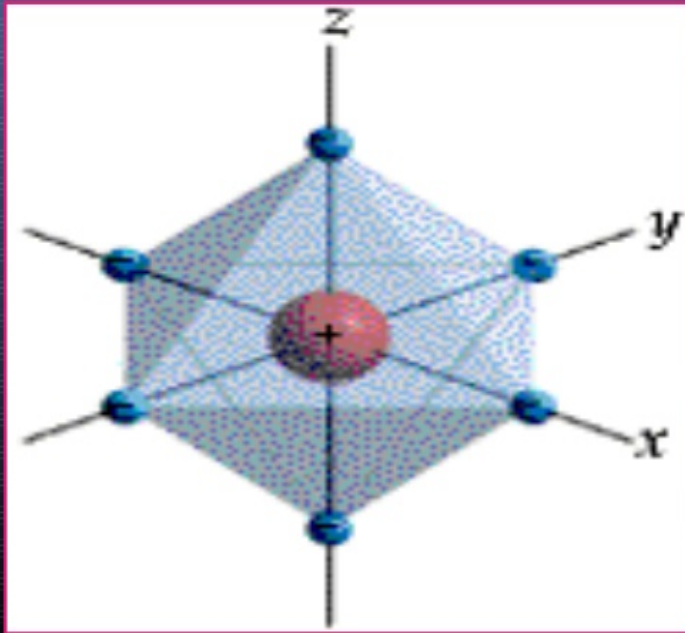
Lobes in
between axes



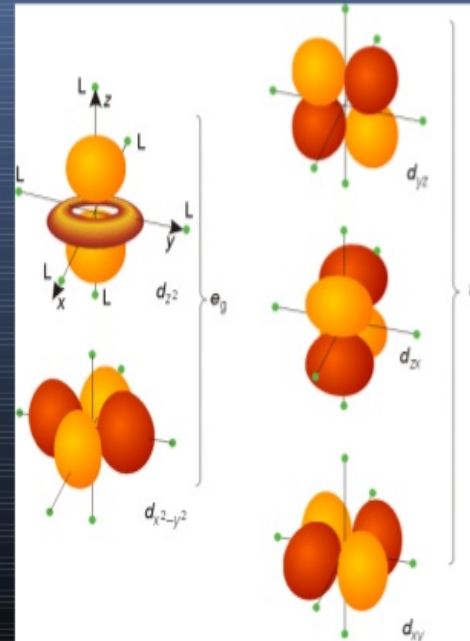
Lobes along the axes



Approach of ligands - O_h field



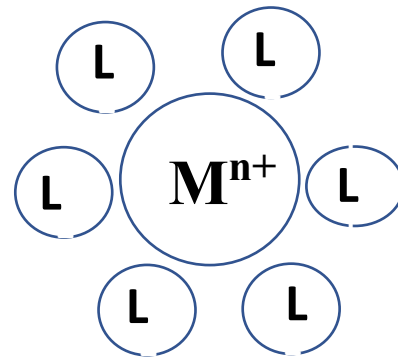
Crystal Field Theory



The repulsion between ligand lone pairs and the d orbitals on the metal results in a splitting of the energy of the d orbitals.

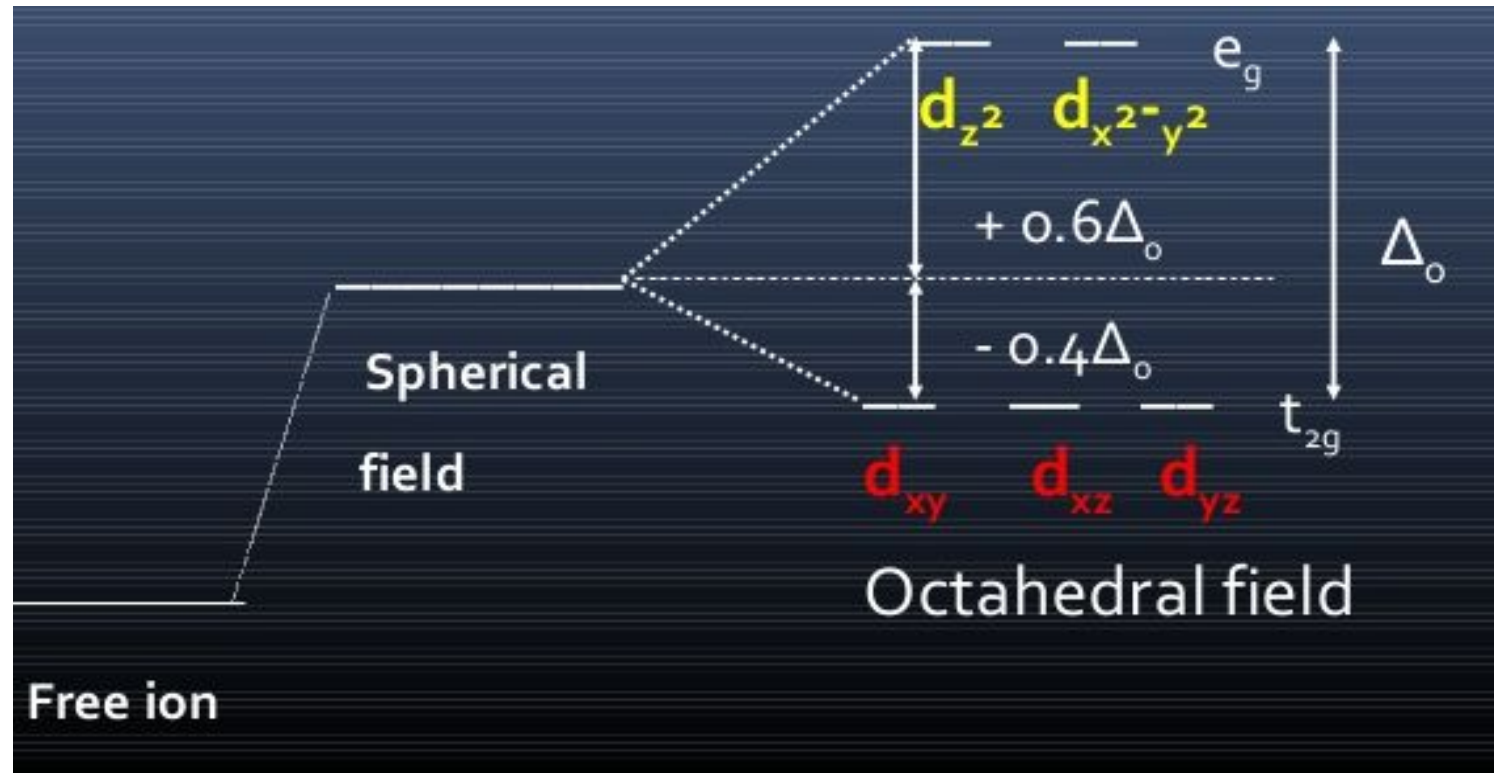
***d*-Orbital Splittings**

- ❖ The $d_{x^2-y^2}$ and d_{z^2} orbitals (***e_g* orbitals**) point directly at the six (-ve) charges, increase their energy as compared with a spherical distribution of negative charges
- ❖ The d_{xy} , d_{xz} and d_{yz} (***t_{2g}* orbitals**) are oriented at 45° to the coordinate axes and point between the six (-ve) charges, which decrease their energy as compared with spherical distribution of charge



Spherical field

Splitting of d-orbitals in octahedral field



- ❖ Five d orbitals of central metal are initially degenerate (same energy).
- ❖ When the 6 (-) charges are distributed uniformly over surface of a sphere, d orbitals remain degenerate. However, the energy of electrons in these orbitals rises because of the repulsive interaction with the ligand lone pairs

Factors affecting the magnitude of Δ

1. Charge on metal ion

Higher the charge on metal ion, stronger the repulsion and higher the CF splitting energy.

2. Effective nuclear charge on metal ion

Down the group, the effective nuclear charge increases. Higher the effective nuclear charge, higher the repulsion between the e^- s in the metal and ligands results in higher CF splitting energy.

3. Nature of ligand

Strong field ligand \longrightarrow More repulsion \longrightarrow Higher Δ

Weak field ligand \longrightarrow Less repulsion \longrightarrow Lower Δ

4. Geometry of complex

$$\Delta_{sp} > \Delta_o > \Delta_t$$

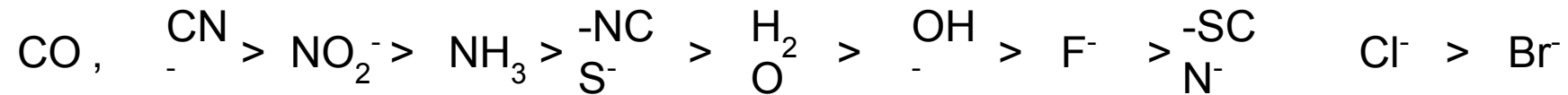
5. Chelating ligands

Spectrochemical series

Low spin and high spin complexes

The experimentally observed order of the crystal field splitting energies produced by different ligands is called the *spectrochemical series*

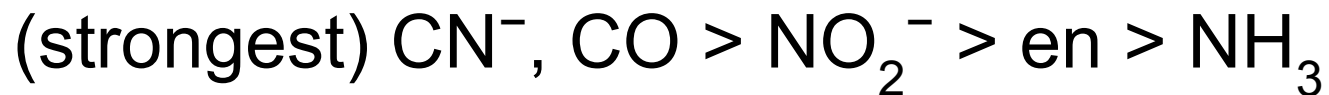
When geometry & **the metal** are held constant, splitting of d orbitals decreases in the following order:



strong-field
ligands

weak-field ligands

Strong Field Ligands:



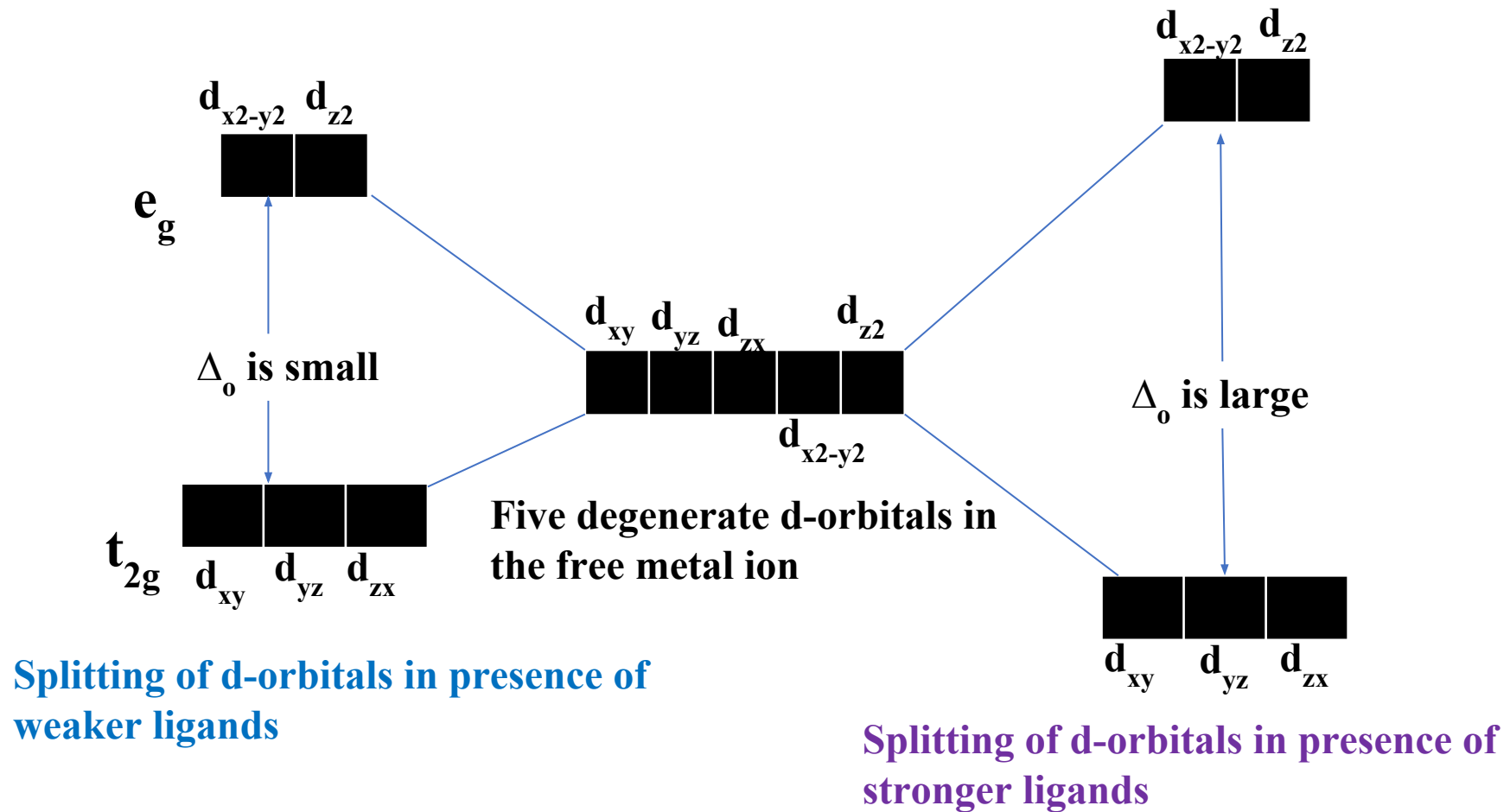
Weak Field Ligands:



Nature of the ligands

1. ***Strong-field*** ligands interact strongly with d orbitals of metal ions and give a **large Δ_o**
2. ***Weak-field*** ligands interact more weakly and give a **smaller Δ_o**

Low Spin and High Spin Complexes



- ❖ If CFSE (Δ_o) is less than pairing energy (p) of electrons, then the electrons after occupying three t_{2g} level will go to higher e_g level and there will be higher number of unpaired electrons. This leads to high spin complex.
- ❖ If $\Delta_o > p$, then the electrons will be paired up in t_{2g} level resulting in low spin complex.