

Q. What is Crystal Field Theory (CFT)? (Dr. Birendra Kumar Makaraj College J.)

Crystal field theory (CFT) explains the metal-ligand bonding in coordination compounds. In the CFT, the following assumptions are made:

1. Ligands are treated as point charges. As ligands are negatively charged or neutral polar molecules having a lone pair of electrons.

2. The transition metal which forms the central atom in the complex is regarded as a positive ion or cation.

3. Bonding between a central metal ion and its ligand arises from purely electrostatic attraction. If the ligand is an anion (-vely charged), the attraction towards the cation is as between any oppositely charged particles. If the ligand is a neutral molecule, the negative end of the dipole is attracted towards the cation.

4. The electrons on the central metal are under repulsive forces from the ligands, hence they will occupy the d -orbitals farthest away from the direction of approach of ligand.

5. There is no interaction between metal orbitals & ligand orbitals.

6. The d -orbitals on the central metal which were all the same energy that is degenerate in a free atom, have their degeneracy destroyed (d -orbitals splitted into eg & t_{2g} sets) by the ligands when a complex/coordination entity is formed.

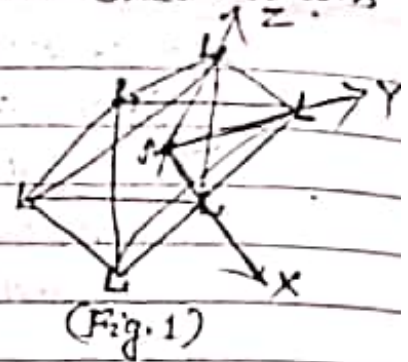
7. In the majority of complexes either 6 or 4 ligands surround the central metal giving octahedral or tetrahedral or square planar structures, and the field produced by the ligands is not spherically symmetrical so the d -orbitals are not all affected equally by the ligand field.

Q. Discuss Splitting of d -orbitals in octahedral & tetrahedral ligand field:

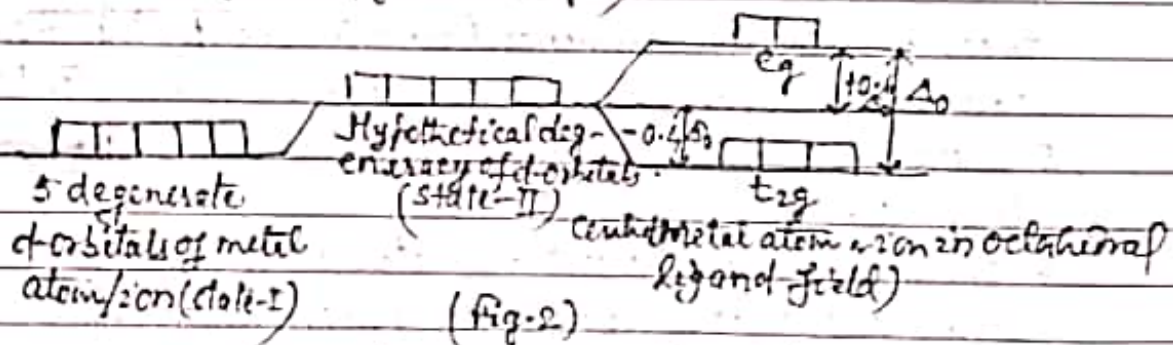
Crystal field splitting in tetrahedral complexes: In an octahedral complex, the metal is at the centre of the octahedron

(2)

and the ligands are at the six corners. The directions x, y & z point to the corners of the octahedron (Fig. 1). The e_g orbitals (d_{z^2} & $d_{x^2-y^2}$) are directed along the axes and the t_{2g} orbitals (d_{xy}, d_{yz} & d_{zx}) point in between the axes x, y & z .



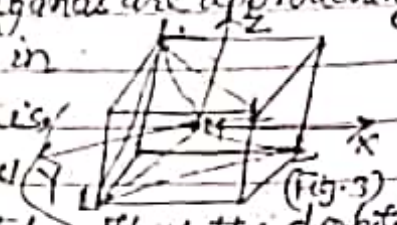
It follows that the approach of 6 ligands along the $x, y, z, -x, -y, -z$ ligands along the axes much more than the d_{xy}, d_{yz} & d_{zx} orbitals which point in between the axes. Thus under the influence of an octahedral ligand field, the d -orbitals split into two sets (e_g & t_{2g}) of different energy. The difference in energy between the two d -levels (e_g & t_{2g}) is given by symbol Δ_o or $10Dq$. It follows that the e_g orbitals are $+0.6\Delta_o$ above the average energy level and the t_{2g} orbitals are $-0.4\Delta_o$ below the average energy level (Fig. 2).



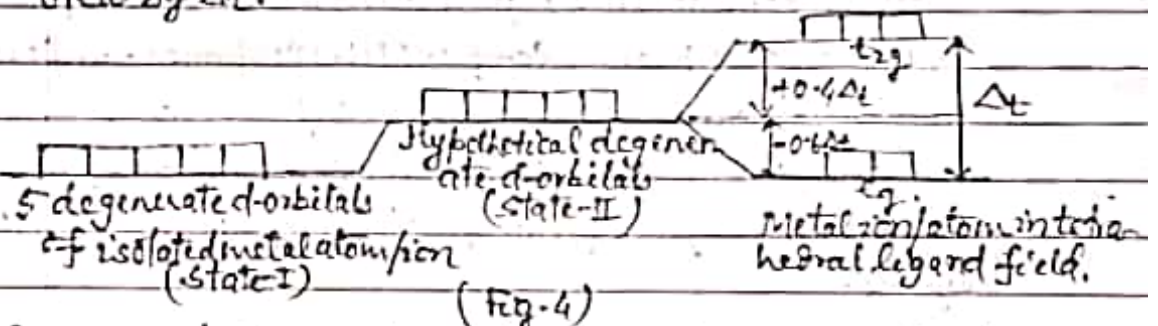
We know that an electron always prefers to move into an orbital of a lower energy for reason of stability. It is evident that if an octahedral complex contains one d -electron, it will reside in one of the t_{2g} orbital. This orbital has an energy $0.4\Delta_o$ less than that of hypothetical degenerate orbitals predicted by purely electrostatic theory. Hence, an electron going into t_{2g} orbitals is stabilised by $0.4\Delta_o$ while that going into e_g orbital is destabilised by $0.6\Delta_o$. The total crystal field stabilisation energy is given by $CFSE(\text{octahedral}) = -0.4\Delta_o n_{t_{2g}} + 0.6\Delta_o n_{e_g}$ (where $n_{t_{2g}}$ & n_{e_g} are the number of electrons occupying the t_{2g} & e_g orbitals respectively.)

* Crystal field splitting of d-orbitals in Tetrahedral Complexes

Tetrahedral complexes result from sp^3 hybridisation. The coordination No. in such case is 4. It can be shown that in a tetrahedral structure, the t_{2g} orbitals (d_{xy}, d_{yz}, d_{zx}) are pointing close to the direction in which ligands are approaching while e_g orbitals ($d_{x^2-y^2}, d_{z^2}$) are lying in between the ligands. (Fig. 3) As a result of this, the energy of the t_{2g} orbitals increases much more than that of the e_g orbitals. Thus, the d-orbitals are split into two groups/sets (t_{2g} & e_g) but in a reverse order to that of octahedral field. The three t_{2g} orbitals now have higher energy than the two e_g orbitals (Fig. 4).



The crystal field splitting, i.e., the energy gap or difference between e_g & t_{2g} sets of orbitals in this case is denoted by Δ_t .

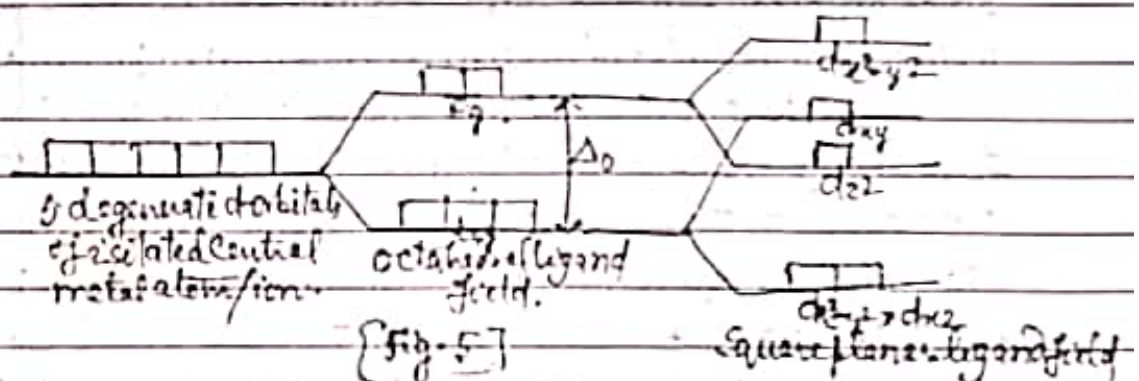


Since an electron going into e_g orbitals is stabilized by $0.6\Delta_t$ while that going into t_{2g} orbitals is destabilized by $0.4\Delta_t$. Here there are only four ligands instead of 6, the ligand field is only $2/3$ as great & the fact that the orbitals do not coincide with the direction of the ligands roughly reduce the splitting by a further $2/3$. Thus, tetrahedral crystal field splitting energy, Δ_t is roughly $4/9$ of the octahedral (Δ_o). A strong ligand field causes a bigger energy gap or difference between t_{2g} & e_g than a weaker field. However, the tetrahedral CFSE (Δ_t) is always much smaller than the octahedral CFSE (Δ_o), it is never energetically favourable to pair electrons, hence all tetrahedral complexes are high spin.

* Crystal field splitting of d-orbitals in square planar complexes:

The splitting of d-orbitals in square planar complexes can be understood by withdrawing two trans ligands lying ^{along} the z-axis from an octahedral complex. As the ligands lying on the z-axis are removed away, the ligands in the xy plane tend to approach the central metal ion/atom more closely. As a result of this, the d-orbitals in the xy plane experience a greater repulsion from the ligands than is the case in an octahedral structure. This causes an increase in the energy of d-orbitals in xy plane i.e., $dx^2 - y^2$ & xy orbitals. Further, since the ligands lying on the z-axis have been moved away, the d-orbitals along the z-axis as well as in the xz & yz planes experience relatively smaller repulsions from the ligands. This results in a noticeable fall in the energy of d_{z^2} orbitals as well as dxz & dyz orbitals.

As the trans ligands, lying along the z-axis drop out completely, a square planar complex (M_4) is formed. This is accompanied by a further rise in the energies of $dx^2 - y^2$ & xy orbitals, and a further fall in the energies of d_{z^2} , dxz & dyz orbitals. (Fig. 5). The crystal field splitting in this case is indicated by Δ_{sp} .



Q. What is crystal field stabilisation energy?

Ans. We know that an electron always prefers to move into an orbital of a lower energy. It is evident that if an octahedral complex contains one d-electron, that electron will reside in one of the t_{2g} orbitals. This orbital has an energy 0.42 less than that of hypothetical degenerate orbitals. Thus, complex

(5)

Compound/ion will be $0.4\Delta_0$ more stable than predicted by the purely electrostatic theory. Hence, $0.4\Delta_0$ is called crystal field stabilisation energy (CFSE) of the octahedral complex under consideration.

The total crystal field stabilisation energy (CFSE) for octahedral complex is given by: $CFSE = -0.4\Delta_0 \times n_{eg} + 0.6\Delta_0 \times n_{tg}$

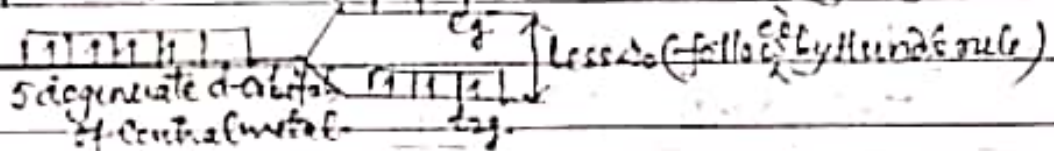
Similarly, in tetrahedral complexes an electron going into e_g orbitals is stabilised by $0.6\Delta_t$. Hence, $0.6\Delta_t$ is called crystal field stabilisation energy (CFSE) of the tetrahedral complex.

The total CFSE for tetrahedral complexes is given as:

$$CFSE = -0.6\Delta_t \times n_{eg} + 0.4\Delta_t \times n_{tg}$$

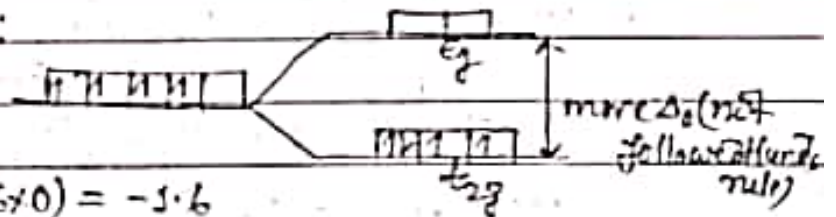
(Where n_{eg} & n_{tg} are no. of electron(s) in e_g & t_{2g} sets of d-orbitals respectively)

For example, Calculate CFSE of d^3 system in octahedral/tetrahedral complexes. Octahedral complexes (a) In weaker ligand field:



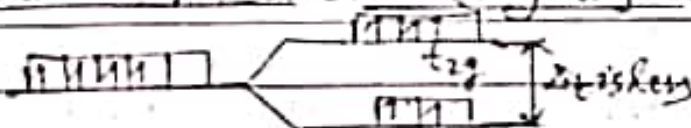
$$CFSE = (-0.4 \times 3 + 0.6 \times 0) = -1.2 + 0.6 = -0.6 \Delta_0$$

(b) Stronger ligand field:



$$CFSE = (-0.4 \times 3 + 0.6 \times 0) = -1.2 + 0 = -1.2 \Delta_0$$

(2) Tetrahedral complexes: (a) weaker ligand field:



$$CFSE = (-0.6 \times 2 + 0.4 \times 2) = -1.2 + 0.8 = -0.4 \Delta_t$$

(b) Stronger ligand field:

