Crystal Field Theory (CFT)

This theory was proposed by Bethe and Van Vleck. This theory was originally applied mainly to ionic crystals and is therefore called CFT.

Assumptions of CFT

In the crystal field theory following assumptions are made:

(1) The central metal cation is surrounded by ligands which contain atleast one lone pair of electrons.

(2) The ionic ligands (e.g., F^-, Cl^-, CN^- etc) are regarded as negative point charges or simply point charges and the neutral ligands (e.g., CO, NH_3, H_2O etc.) are regarded as point dipoles or simply dipoles. If the ligand is a neutral molecule such as NH_3, H_2O etc., the negative end of the dipole in the molecule is directed towards the central metal cation.

(3) There is no interaction between metal orbitals and ligand orbitals i.e., there is no orbitals overlap.

(4) According to this theory, the bonding between central metal cation and ligand is not covalent but it is regarded as purely electrostatic. Thus the bonding in complex may be ion-ion attraction between central metal cation and negative ligands such as Co^{3+} and Cl^-. If the ligand is neutral the bonding may be ion-dipole attraction such as Cr^{3+} and NH_3 or CO. NH_3 has dipole moment with the $\delta-$ charge on N and $\delta+$ charge on H atom. Thus in $[Cr(NH_3)_6]^{3+}$, the $\delta-$ charge on the N atom of each NH_3 molecule point towards the Cr^{3+} ion.

(5) The *d* orbitals on the metal all have the same energy (that is degenerate) in the free atom. However, when a complex is formed the ligands destroy the degeneracy of these orbitals, i.e., the orbitals now have different energies. In an isolated gaseous metal ion, the five *d* orbitals do all have the same energy, and are termed degenerate. If a spherically symmetrical field of negative charges surrounds the metal ion, the *d* orbitals remain degenerate. However, the energy of the orbitals is raised becuase of repulsion between the field and the electron on the metal. In most transition metal complexes, either six or four ligands surround the metal, giving octahedral or tetrahedral structures. In both of these cases the field produced by the ligands is not spherically symmetrical. Thus the *d* orbitals are not all affected equally by the ligand field.

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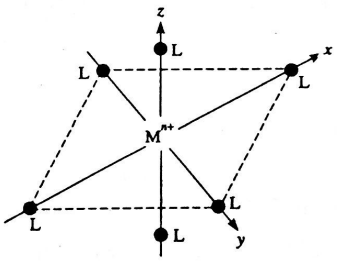
ystal Field Splitting of *d*-orbitals in Octahedral Complexes

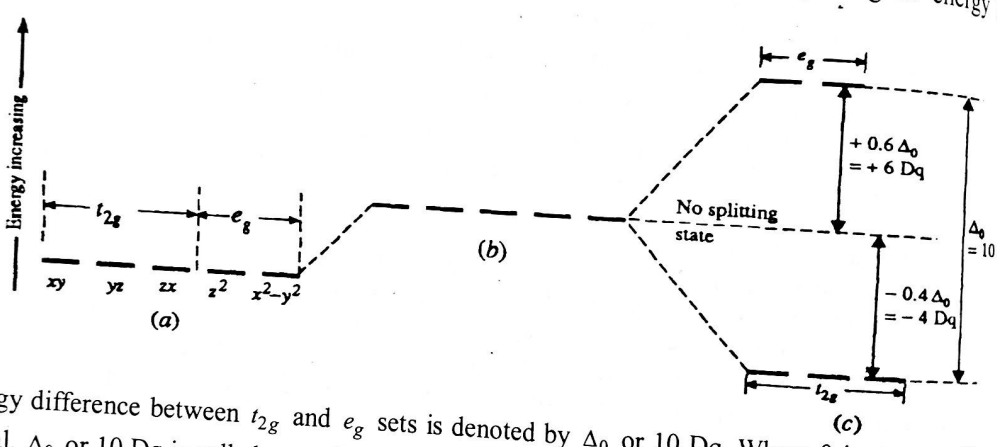
an octahedral complex, the central metal cation is at the centre (origin) of the octahedron and the ands are at the six corners of the octahedron as shown in the figure. The axes *x*, *y* and *z* point to three acent corners of the octahedron.



Now suppose the ligands on each of the three axes are allowed to approach towards the central al cation (M^{n+}) from both the ends of the axes. In this process the electrons in *d*-orbitals of the central al cation are repelled by negative point of point charge or by negative end of the dipole at the ligands. s repulsion will raise the energy of all the five *d*-orbitals. If all the ligands are symmetrically itioned (ligands are at equal distance from each of the orbitals), the energy of each of five *d*-orbitals l raise by the same amount (i.e. all the *d*-orbitals will still degenerate), but now they will have higher

energy than before (free metal cation). This is only a hypothetical situation and this energy state is ... barycentre or centre of gravity. It is obvious that not all of the *d*-orbitals will be affected to the ... extent. The lobes of the e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) point along the axes *x*, *y* and *z*. The lobes of the ... orbitals (d_{xy}, d_{yz} and d_{zx}) point in between the axes. The *d*-orbitals lying along the axes ($d_{x^2-y^2}$ and ... will be more strongly repelled than the orbitals with lobes directed between the axes (d_{xy}, d_{yz} and ... Thus the energy of e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) will increase much more than the t_{2g} orbi... (d_{xy}, d_{yz} and d_{zx}). Under the influence of an octahedral ligand field the *d*-orbitals are, thus split into ... sets with e_g orbitals at higher energy than t_{2g} orbitals.

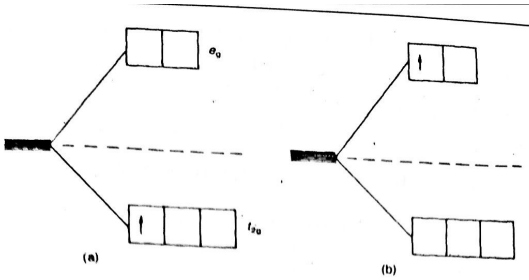
Greater is the repulsion, greater will be the increase in energy. Thus under the influence of octahe... ligand field the *d*-orbitals split into two sets of different energies. In other words the degeneracy of five ... orbitals is removed under the influence of the ligands. The separation of five *d*-orbitals of the cen... metal cation into two sets having different energies is called crystal field splitting or energy le... splitting.



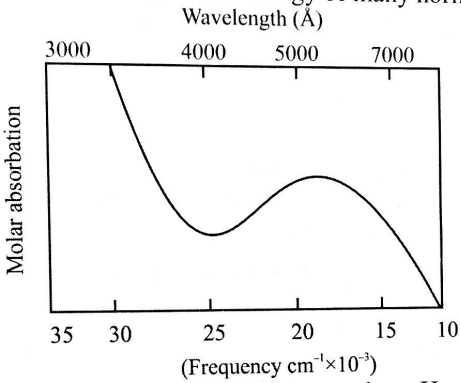
The energy difference between t_{2g} and e_g sets is denoted by Δ_0 or 10 Dq. Where 0 in Δ_0 standing f... octahedral. Δ_0 or 10 Dq is called crystal field splitting energy. The energy of the e_g orbitals is 0.6 Δ_0 (... 6 Dq) higher than the hypothetical energy state (bary centre) and energy of the t_{2g} orbitals is 0.4 Δ_0 (=... Dq) lower than the hypothetical energy state. In other words we can say that the t_{2g} orbitals are stabilize... by amount – 0.4 Δ_0, while the e_g orbitals are destabilized by 0.6 Δ_0 with respect to the average energ... state.

Measurement of value of Δ_0

The size of the energy gap Δ_0 between the t_{2g} and e_g, levels can be measured easily by recording th... UV-visible spectrum of the complex. Consider a complex like $[Ti(H_2O)_6]^{3+}$. The Ti^{3+} ion has one ... electron. In the complex this will occupy the orbital with the lowest energy, that is one of the t_{2g} orbita... (figure (a)). The complex absorbs light of the correct wavelength (energy) to promote the electron fro... the t_{2g} level to the e_g level (figure (b)).



The electronic spectrum for $[Ti(H_2O)]^{3+}$ is given in following figure. The steep part of the curve from 27000 to 30000 cm^{-1} (in the UV region) is due to charge transfer. The *d-d* transition is the single broad peak with a maximum at 20300 cm^{-1}. Since 1 kJ mol^{-1} = 83.7 cm^{-1}, the value of Δ_0 for $[Ti(H_2O)]^{3+}$ is 20300/83.7 = 243 kJ mol^{-1}. This is much the same as the energy of many normal single bonds.



The above method is the most convenient way of measuring Δ_0 values. However, Δ_0 values can also be obtained from values of observed lattice energies and those calculated using the Born-Lande equation.

Solution containing the hydrated Ti^{3+} ion are purple coloured. This is because yellow and green light are absorbed to excite the electron. Thus the transmitted light is the complementary colour red-violet.

Because of the crystal field splitting of *d* orbitals, the single *d* electron in $[Ti(H_2O)_6]^{3+}$ occupies an energy level $2/5\,\Delta_0$ below the average energy of the *d* orbitals. As a result the complex is more stable. The crystal field stabilization energy (CFSE) is in this case $2/5 \times 243 = 97$ kJ mol^{-1}.