

E-Content Study Material

B. Sc. Chemistry (H)

3rd Year

Paper III B

Inorganic Chemistry

Chapter II: Metal-Ligand Bonding in Transition Metal
Complexes

Topic: Crystal Field Theory (CFT)

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Crystal Field Theory (CFT)

The crystal field theory developed by H. Bethe and V. Bleck (1935) proved to be far more successful in explaining the bonding in and the properties of coordination complexes than the valence bond theory. According to the crystal field theory, bonding between a central metal ion and its ligand arises from purely electrostatic interactions. If the ligand is an anion, the attraction towards the cation is as that between any oppositely charged particles. If the ligand is a neutral molecule such as NH_3 or H_2O , the negative end of the dipole is attracted towards the central positive ion. Knowing the arrangement of ligands around the central metal ion, assuming the bonds between metal ion and the ligands to be purely electrostatic and considering the metal ion and the ligands as point charges q_1 and q_2 , separated by a distance r , the metal-ligand bond energies for various complexes can be calculated using the Coulomb's law, $B.E = -q_1q_2/r$. The values obtained were found to be in close agreement with those obtained experimentally in the case of non-transition metal complexes. The values were, however, too low compared to the experimentally observed values, in the case of transition metal complexes. The cause of discrepancy, according to the crystal field theory, lies in the manner of the orientation of the d orbitals in space, as explained below.

Orientation of d Orbitals and Crystal Field Splitting of Energy Levels

The d orbitals can be divided into two groups depending upon the nature of their orientation in space. One of the groups consists of three orbitals (d_{xy} , d_{xz} , d_{yz}) which are oriented in the regions in between the coordinate axes while the other comprises of two orbitals ($d_{x^2-y^2}$, d_z^2) which are oriented along the axes. In the case of a free metal ion, all the five d orbitals have the same energy, i.e., they are degenerate, meaning energetically alike. Consider a hypothetical case in which the set of five d orbitals of the metal ion is spherically surrounded by a uniformly spread negative charge. The electrostatic repulsion between d electrons and the said charge would result in uniform increase in the energies of d orbitals. In other words, although the orbitals acquire higher energy, they would still remain degenerate. Now consider that the negative charge surrounding d orbitals of the metal ion gets concentrated in a number of point charges in certain specific positions. The energy of the orbitals lying in the directions of the point charges ($d_{x^2-y^2}$, d_z^2) would be raised to a larger extent than that of the orbitals (d_{xy} , d_{xz} , d_{yz}) lying in between the point charges because the electrons in the former type of orbitals would experience greater repulsion from point charges than the electrons in the latter type of d orbitals. This means that some of the d orbitals would get associated with a higher energy than the other d orbitals.

The splitting of five degenerate d orbitals of the metal ion into sets of orbitals having different energies is called crystal field splitting. The concept forms the basis of crystal field theory. In the crystal field theory we consider ligands as point charges. The number of ligands and their arrangements around the central metal ion will naturally affect the relative energies of the five d orbitals. In other words, the magnitude and the type of the crystal field splitting will be different in complexes of different geometries in which metal ions have different coordination numbers. We would illustrate this concept by considering complexes with coordination numbers 6 and 4 which are the most common. The discussion would be restricted to the most common structures which are octahedral, tetrahedral and square planar complexes.

Crystal Field Splitting in Octahedral Complexes

In an octahedral complex, the co-ordination number is 6. The metal atom/ion is at the centre and the ligands occupy the six corners of the octahedron, as shown in Fig.

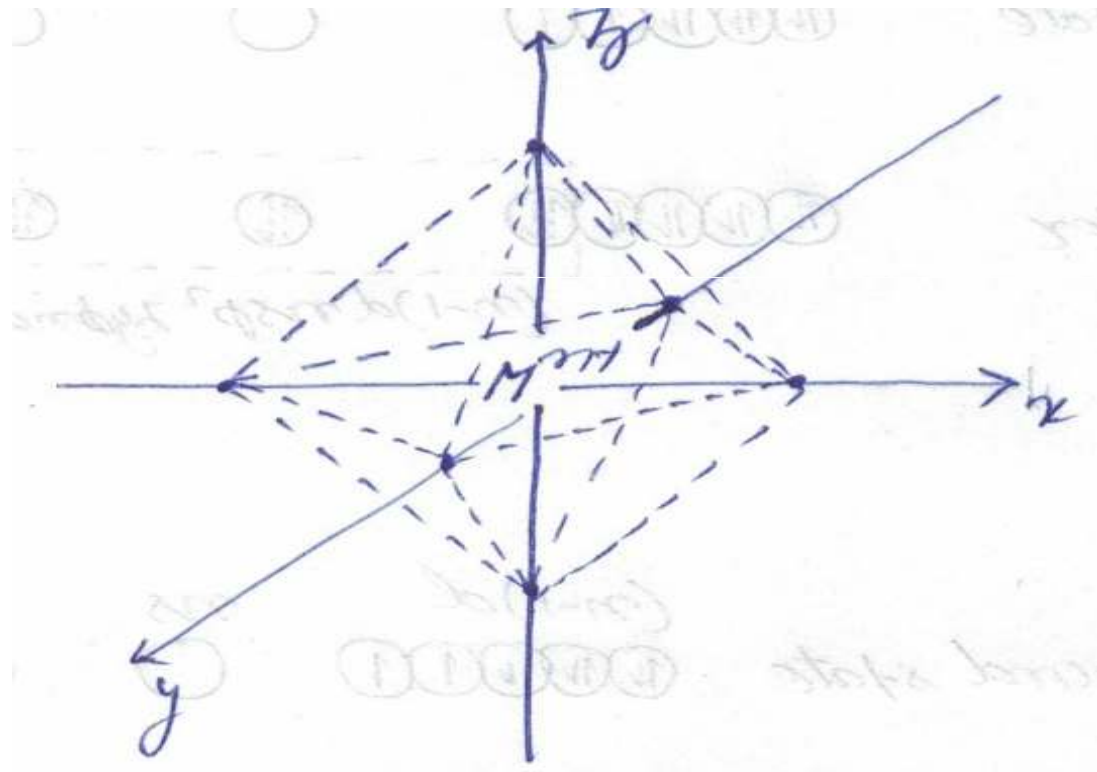


Fig. Six ligands at the corners of an octahedron surrounding the metal ion, M^{n+} .

The three axes x, y and z pointing along the corners of the octahedron are also shown. Let us suppose that the metal ion M^{n+} has a single d electron (d^1 configuration). In the free ion, when there are no ligands, the electron can occupy any one of the d orbitals because all are of the same energy. Such orbitals having the same energy are called degenerate orbitals, as already mentioned.

However, in the octahedral complex MX_6 , all the five d orbitals will not remain of equal energy. This can be easily understood from the following discussion.

As already explained, the two orbitals, $d_{x^2-y^2}$ and d_z^2 are oriented along the axes while the remaining three orbitals, d_{xy} , d_{xz} and d_{yz} are oriented in between the axes.

In the case of octahedral complexes, the former two orbitals are designated as e_g orbitals while the latter three orbitals are designated as t_{2g} orbitals. As the six ligands approach the central ion along the axes, the electron, if present in the e_g orbitals, is repelled more by the ligand electrons than if it is present in the t_{2g} orbitals. In other words, the energy of the d_z^2 and $d_{x^2-y^2}$ orbitals increases much more than the energy of the d_{xy} , d_{xz} and d_{yz} orbitals. It should be remembered that when a charge is repelled by a similar charge, its potential energy increases. The greater the repulsion, the greater is the increase of energy. Thus, in octahedral complexes, the five d orbitals split up into two sets: one set consisting of two orbitals of higher energy (e_g orbitals) and the other set consisting of three orbitals of lower energy (t_{2g} orbitals). The crystal field splitting in an octahedral complex is shown in Fig.

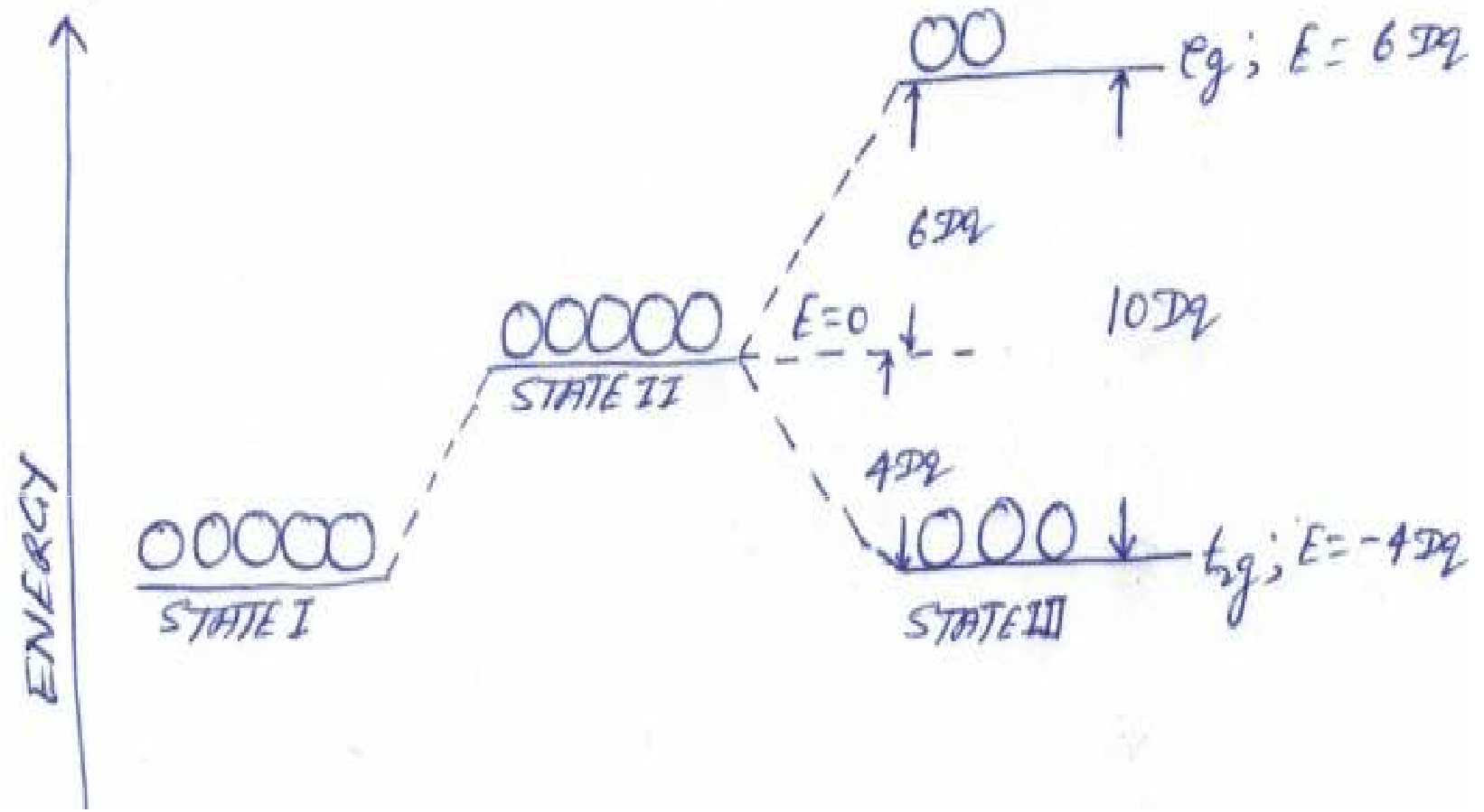


Fig. Crystal field splitting in an octahedral complex.

The crystal field splitting is measured in terms of the energy difference between t_{2g} and e_g orbitals Δ_o (The subscript $_o$ indicating octahedral complex). The crystal field splitting is generally measured in terms of a parameter, Dq . By convention, Δ_o is taken to be equal to $10 Dq$.

It can be shown that for an octahedral system, the energy of the t_{2g} orbitals is $4 Dq$ or $0.4 \Delta_o$ less than the energy of the hypothetical degenerate d orbitals which would result if crystal field splitting is ignored (Fig, state II). It follows, therefore, that the energy of the e_g orbitals is $6 Dq$ or $0.6\Delta_o$ above that of the hypothetical degenerate d orbitals. (The total energy of the unsplit d orbitals must be equal to the energy of the split d orbitals).

Crystal Field Splitting in Tetrahedral Complexes

The coordination number for tetrahedral complexes is 4. The tetrahedral arrangement of four ligands surrounding a metal ion may be visualized by placing ligands at the alternate corners of a cube, as shown in Fig.

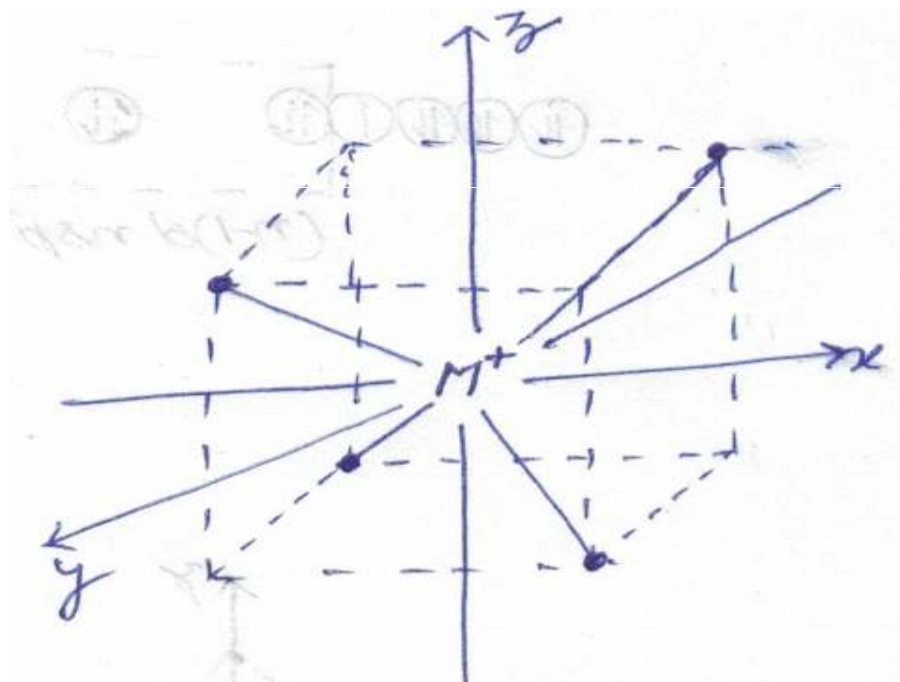


Fig. Tetrahedral arrangement of four ligands around the metal ion.

It can be shown that in a tetrahedral structure, none of the d orbitals points exactly towards the ligands.

The three d orbitals d_{xy} , d_{xz} and d_{yz} are pointing close to the direction in which ligands are approaching while the two orbitals $d_{x^2-y^2}$ and d_z^2 are lying in between the ligands. as a result of this, the energy of the former three orbitals increases compared to the energy of the latter two orbitals because the electrons in the former orbitals would be repelled by ligands electrons more strongly than electrons in the latter orbitals. Thus, the d orbitals are again split into two groups but in a reverse order. The three orbitals, d_{xy} , d_{xz} and d_{yz} designated as t_2 orbitals, now have higher energy than the two orbitals $d_{x^2-y^2}$ and d_z^2 designated as e orbitals. This is diagrammatically shown in Fig.

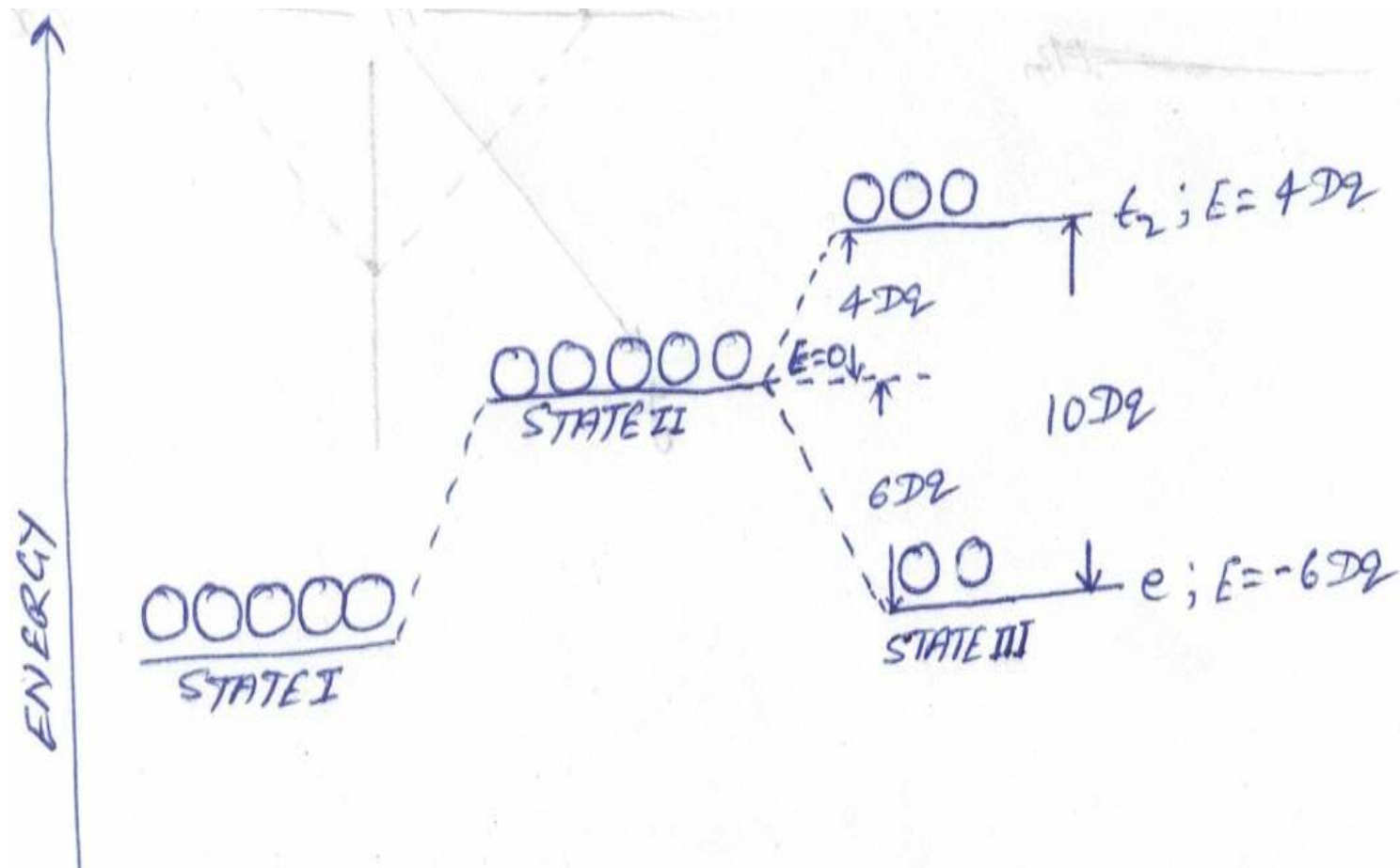


Fig. Crystal field splitting in tetrahedral complexes. State II represents a hypothetical state if it is assumed that negative charge of ligands uniformly affects the charge of d electrons.

The crystal field splitting (i.e. the energy difference between the two sets of orbitals), in this case, is denoted by Δ_t , the subscript t indicating tetrahedral complexes. It is less than Δ_o observed in the case of octahedral complexes, discussed earlier. It has been estimated that $\Delta_t \approx -4/9\Delta_o$; the minus sign denotes that the order of splitting in tetrahedral complexes is the reverse of that in octahedral complexes. The smaller value of Δ_t as compared to Δ_o is partly due to lesser number of ligands in the tetrahedral field.

Since an electron prefers to move into a region of lower energy for reasons of stability, it follows that if a tetrahedral complex contains a d electron, that electron will reside in one of the $d_{x^2-y^2}$ and d_z^2 orbitals.

An electron going into either of the $d_{x^2-y^2}$ and d_z^2 orbitals is stabilized by 6 Dq (or $0.6 \Delta_t$) while that going into any of the other three orbitals is destabilized by 4 Dq (or $0.4 \Delta_t$).