MOLECULAR ORBITAL THEORY (MOT)

According to MOT the metal ligand bonding in octahedral complexes result from the overlap of suitable atomic orbitals on the central metal ion with ligand orbitals. Such bonding results

MO diagram of $[Co(NH_3)_6]^{3+}$, a low spin complex

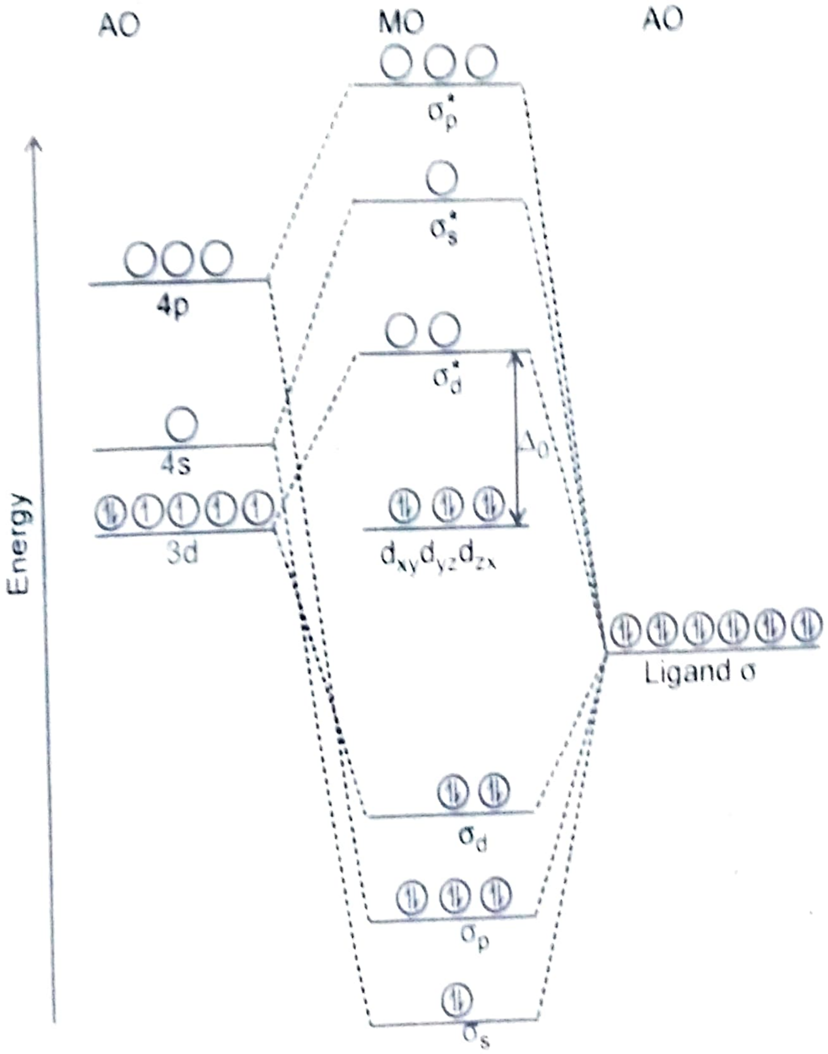

Figure - 20

Co(III) $[Co(NH_3)_6]^{3+}$ $6NH_3$

From the linear combination of atoms orbitals (LCAO) OF the metal and ligands. These MO's may be of bonding, antibonding or nonbonding in character. There are nine valence shell orbitals in the metal ion. Of these, the following six orbitals d_{z^2} $d_{x^2-y^2}$, s, p_x, p_y, and p_z lie along the metal ligand bond directions (i.e., suitable for s bonding)while the other three, namely d_{xy} d_{yz} and d_{zx} are so oriented as to be suitable for p bonding

Let us now apply the MOT to explain the metal-ligand bonding $[Co(NH_3)_6]^{3+}$ and $[CoF_6]^{3-}$ ions.

MO diagram of $[CoF_6]^{3-}$, a high spin complex

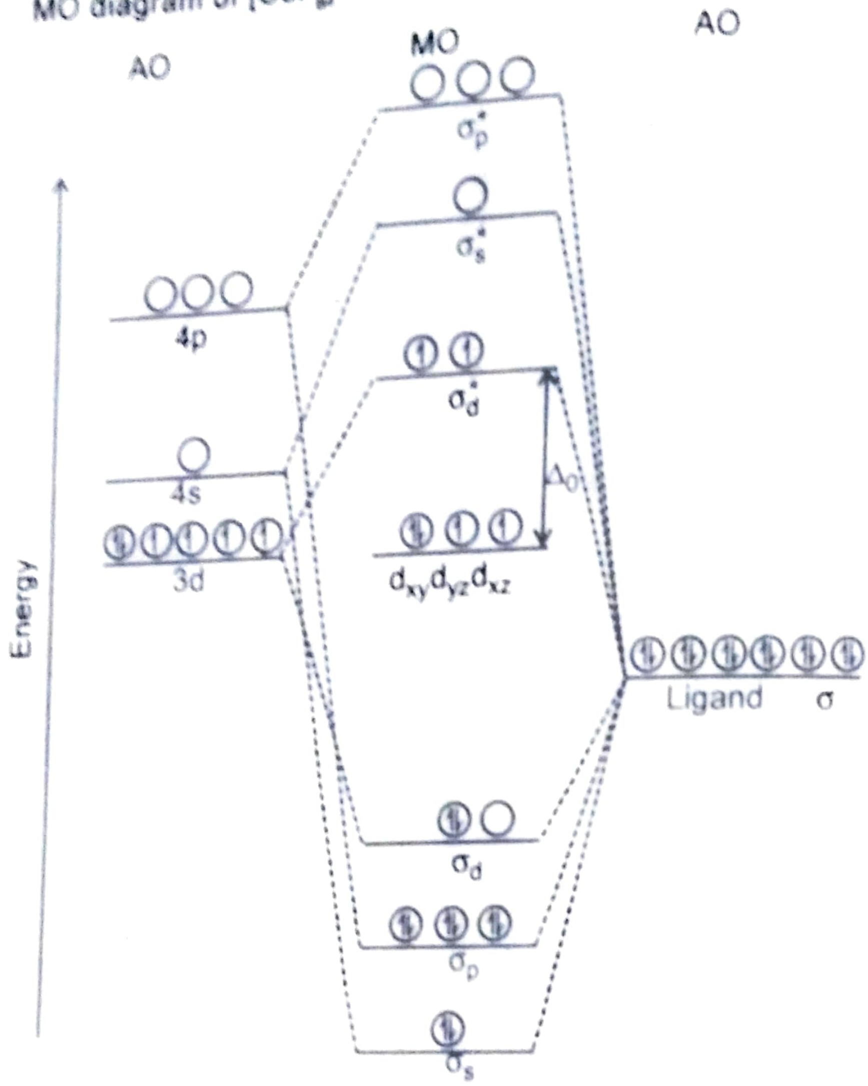

Figure - 21

Co(III) $[CoF_6]^{3-}$ 6F

Two *d* orbitals ($d_{x^2-y^2}$ and d_{z^2}), the 4*s* and the three 4*p* orbitals are oriented along the *x*, *y* and *z* axes where the ligands are located. Hence metal orbitals overlap with the ligand orbitals. As a result, six bonding molecular orbitals [σs(1), σ*p*(3) and σ*d*(2)] and six ant bonding molecular orbitals[σ*s(1)σ*p(3) and σ**d*(2)] are formed. The t_{2g} orbitals (d_{xy}, d_{yz}, d_{zx}) do not lie along the metal ligand bond directions. Hence they are not involved in σ bonding. Their energy remains unchanged and they are called **nonbonding orbitals**.

When the Co(III) and ligand electrons are placed in the complex MO's the six bonding MO's are filled. The remaining electrons are distributed among the nonbonding MO's (The t_{2g} orbitals) and the $\sigma^* d$ (antibonding) MO's. The $\sigma^* d$ MO's are obtained by the interaction of metal e_g *orbitals* ($d_{x^2-y^2}$ and d_{z^2}) with ligand orbitals. The energy of the $\sigma^* d$ MO's are nearer to the metal e_g orbitals. So, the placement of the excess electrons in the t_{2g} and $\sigma^* d$ MO's is identical to the arrangement predicted by the crystal field model, where the same number of electrons is distributed between the t_{2g} and e_g orbitals.

When the difference in energy (Λ) between the nonbonding t_{2g} orbitals and $\sigma^* d$ (antibonding) MO's is small, Hund's rule is obeyed. In $[CoF_6]^3$, the *d* electrons are distributed as $t_2{}^* g^4\ \sigma^* d^2$. The presence of two electrons in bonding s *d* orbitals. This leads to the weakening of Co-F bonds.

But Λ is large in $[Co(NH_3)_6]^{3+}$. So, all electrons go into the t_{2g} orbitals. According to CFT, the energy difference (Δ) between t_{2g} and $\sigma^* d$ or e_g orbitals depends on the electrostatic repulsion of *d* electrons by ligands. But according to MOT, the difference (Δ) depends on covalent bonding. The greater the overlap of e_g metal orbitals with the ligands orbitals, the higher in energy will be the $\sigma^* d$ orbitals.

MO Theory also explains the formation of π bonds between the metals and ligands.

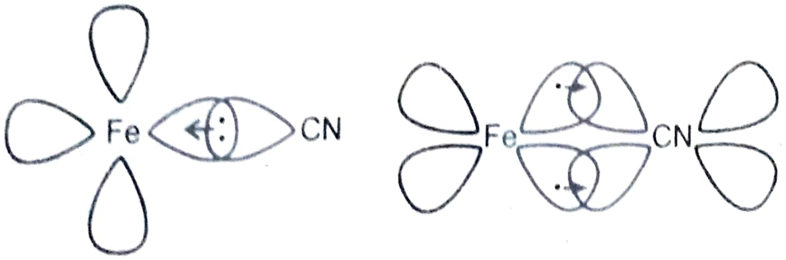

Figure - 22

Fe - CN σ bond

Fe - CN π bond

Both σ and π bonds occur in $[Fe(CN_6)]^4$. In the formation of a σ bond, the ligand acts as a Lewis base and shares a pair of electrons with an empty e_g orbital. In the π bond, CN^- ion acts as a Lewis acid and accepts electrons from the filled t_{2g} orbital of the metal. The presence of π bonding as well as σ bonding strengthens the metal-ligand bond and contributes unusual stability to $[Fe(CN)_6]^3$ ion.

The t_{2g} orbitals of a metal in an octahedral complex are oriented corre for π bonding. Since the t_{2g} orbitals point between the ligands they can form σ bonding. In a π bond with a ligand such as CN^-, t_{2g} electrons a partially transferred to the ligand. This process of bonding interaction lowe the energy of t_{2g} orbitals. So, Δ_0 increases.

Comparison between crystal field theory and molecular orbi theory:

Similarities:

Both CFT and MOT describe complexes in terms of interactions betwe the metal orbitals and ligands. The greater this interaction the greater w be the value of 10 Dq. The 12 electrons donated by six ligands will occupy t and e_g levels depending on the influence of the size of 10Dq. Thus the distributio of electrons according to MOT is identical to that predicted by CFT.

Differences: 1 CFT assumes ligands as point changes. This is drastic over simplification. In CFT it is assumed that the splitting of *d* orbita is a result solely of electrostatic effects. According to CFT the bonding i complexes is ionic with no covalent character.

According to the MOT there must be some orbital overlap and so some covalent bonding is involved in complexes. According to this theory the orbitals on the metal and ligand combine to form larger molecular orbitals.

MOT thus contains best aspects of both VB and CF theories.

LIGAND FIELD THEORY (LFT)

The CFT regards the bonding in complexes as purely electrostatic (ionic). It takes no account of possible covalent bonding in complexes. But the physical measurements such as electron spin resonance (ESR), NMR and nuclear quadruple resonance suggest that there is some measure of covalent bonding also in complexes. It is because of this reason that a kind of modified form of CFT has been suggested in which some parameters are empirically adjusted to allow for covalence in complexes without explicitly introducing covalence into CFT. This modified form of CFT is often called **Ligand Field Theory**. However, LFT is sometimes also used as a general name for the whole gradation of theories from CFT to the molecular orbital theory MOT. Cotton and Wilkinson have called LFT, Adjusted Crystal Field theory ACFT.

LFT is therefore a combination of crystal field and MO theories. While accepting the electrostatic attraction between the ligands and metal ions, it allows for some covalent bonding between the orbitals of the metallic ion and the orbitals of the ligand. Depending upon the nature of the metal ion and the ligand the bonding orbitals may be of covalent type, where in the electrons are shared approximately equally between the ligands and the metal or may represent ionic bonding by concentrating more electron density on the ligands.

Thus LFT is a theory of (i) Origin of splitting of inner orbitals of ions be their chemical environment and (ii) the consequences of such a splitting.

Note: If there is a question of LFT, the students should write CFT and LFT.

Jahn-Teller effect *(Distortion in d^9 configuration)*: Any non-linear molecule in a degenerate electrons state will be unstable and will undergo some kind of distortion which will lower its symmetry and split the degenerate state. This is called **Jahn-Teller effect**.

Let us consider Cu^{2+} ion, which has 9 electrons in its 3*d* orbital. This ion when present at the center of an octahedral complex, it will have one vacant orbital in e_g level. According to Jahn-Teller effect, such a system cannot be a perfect octahedron. It will be distorted in some way.

Significance : This effect helps us in understanding the structure of some co-ordination complexes.