T.Y.B.Sc. Chemistry

Inorganic Chemistry -I(CH-504)

Sem-V

Topic: 1. Molecular Orbital Theory of Coordination compounds

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8. MOLECULAR ORBITAL THEORY

Postulates of MOT for an octahedral complex:

1. The central metal ion contributes nine atomic orbitals s, p_x, p_y, p_z, $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{yz} and d_{xz} for bonding.
2. Out of the nine orbitals, the metal ion contributes six orbitals viz. s, p_x, p_y, p_z, $d_{x^2-y^2}$ and d_{z^2} which have their lobes directed along the axis to overlap with ligand orbitals to form σ bonds.
3. Each of the six ligands contributess orbital or some combination of s – and p – orbitals, pointing towards the central metal ion to form σ bonding.
4. The six ligand orbitals combine and forms a new set of orbitals called Ligand Group Orbitals (LGOs) or Composite Ligand Orbitals. (CLOs). This set can be broken into six smaller sets of orbitals with symmetries matching to the symmetries of metal orbitals forming σ bonds.
5. Each of the metal ion orbitals combines with its matching symmetry orbital of the ligand to form σ bonding and antibonding MOs.
6. If the ligands also possesses π orbitals, they also combine to form a new set of symmetry orbitals. These ligand orbitals will then combine with metal ion orbitals of proper symmetry to form bonding and antibonding MOs.
7. The total number of electrons of the metal ion and the ligands are then filled in molecular orbitals following Aufbau principle, Hund's rule and Pauli's exclusion principle.

MO Treatment of Bonding: (Octahedral complex without πBonding):

$d_{x^2-y^2}$ and d_{z^2} orbitals together with 4s, $4p_x$, $4p_y$ and $4p_z$ combines with ligand orbitals and forms σ bonds. Molecular Orbital diagram can be prepared for different complexes between metal and ligands. The d_{xy}, d_{yz} and d_{xz} orbitals will not participate in the σ bond formation, because of unsymmetry of orbitals.

For σ bonding, the ligand orbitals must lie in the direction of the lines joining the ligand and central ion. The atomic orbitals are classified according to their symmetry. The 4s orbital has a_1g symmetry, the 4p orbitals have t_1u symmetry. The ligand group orbitals break into similar sets of symmetry viz. one with a_1g symmetry, three with t_1u symmetry and two with e_g symmetry. Above figures shows that metal orbitals and ligand group orbitals matching in symmetry which can combine to form an octahedral complex.

If the six ligands are denoted as L_1, L_2, L_3, L_4, L_5 and L_6 various possible arrangements of ligand orbitals in relation to orbitals on the central ion are shown in below fig.

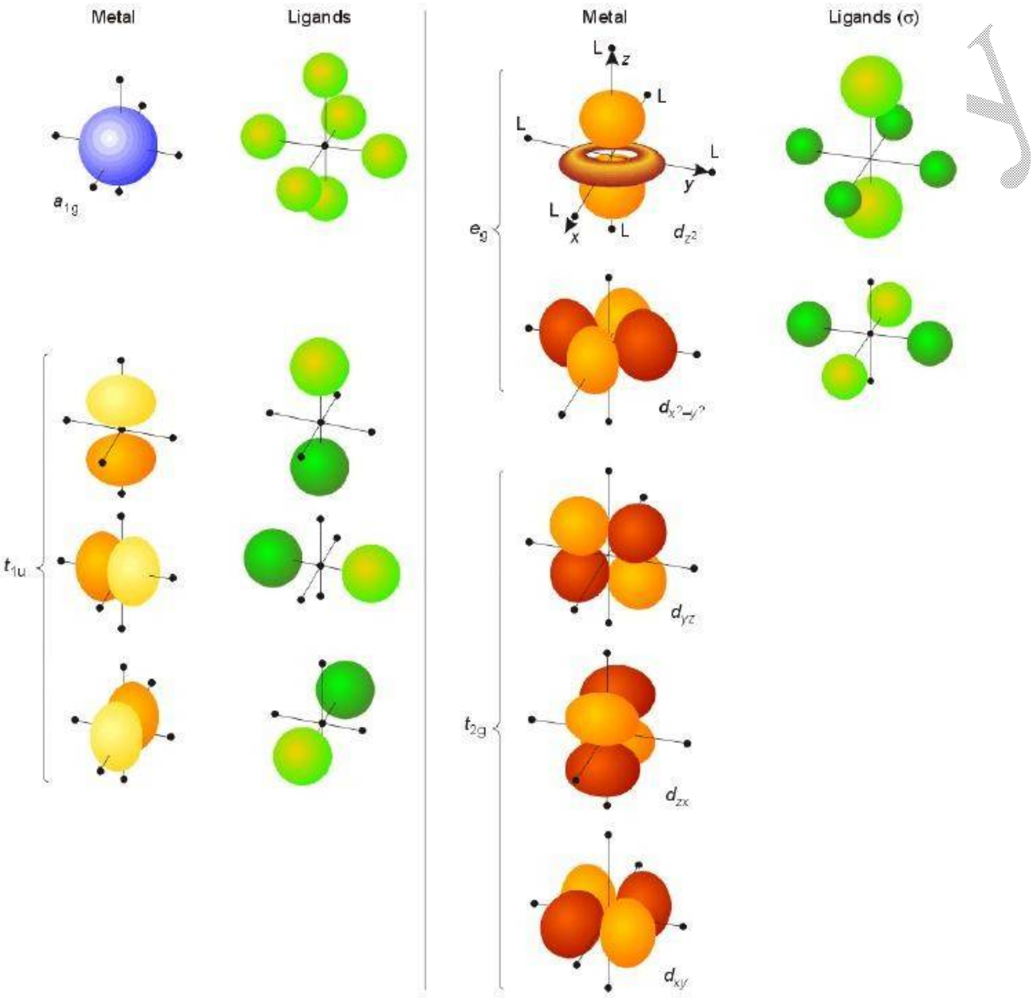


Fig:1 Metal matching ligand group orbitals for an octahedral complex.

The ligand group orbitals could be designated as (L_1, L_2, L_3, L_4, L_5 and L_6). The ligand group orbitals, which could be symmetrical with the p_x orbital of the central ion would be (L_1-L_2). Similarly, (L_3-L_4) & (L_5-L_6) would be symmetrical with the p_y- and p_z- orbitals and (L_1,+ L_2 - L_3- L_4) would be symmetrical with the $d_{x^2-y^2}$ orbitals as shown in figure.

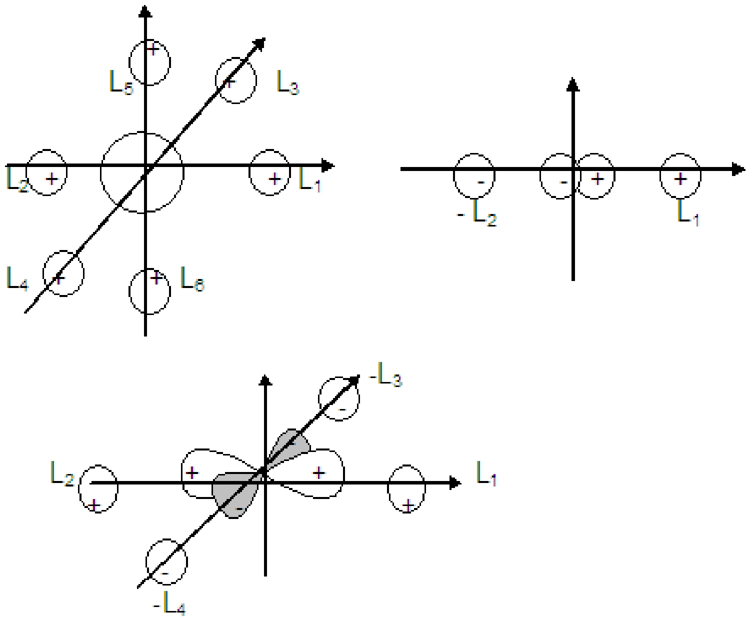


Fig: 2 possible combinationsof orbitals of the central ion & of the ligands s_x – orbital, p_x – orbital & $d_{x^2-y^2}$ orbitals.

Metal orbitals	Ligand Group Orbitals
S	$L_1 + L_2 + L_3 + L_4 + L_5 + L_6$
P_x	$(L_1 - L_2)$
p_y	$(L_3 - L_4)$
p_z	$(L_5 - L_6)$
$d_{x^2-y^2}$	$(L_1, + L_2 - L_3 - L_4)$
d_{z^2}	$(2L_5 + 2L_6 - L_1 - L_2 - L_3 - L_4)$

MO Energy Level Diagram:

When two atomic orbitals combine, they give two molecular orbitals. One of lower energy, is called bonding orbital and the other of higher energy, is called as an antibonding orbital. Combination of six metal orbitals and six ligand orbitals give twelve molecular orbitals. The relative energy levels are shown in the below figure.

The metal orbitals are shown on the left hand side. There are in all nine metal orbitals but the three t_{2g} (d_{xy}, d_{yz} and d_{xz}) orbitals are unaffected by combination with ligand σ orbitals. The six σ orbitals of the ligands are shown on the right hand side and the twelve molecular orbitals with the three t_{2g} orbitals are shown in the center.

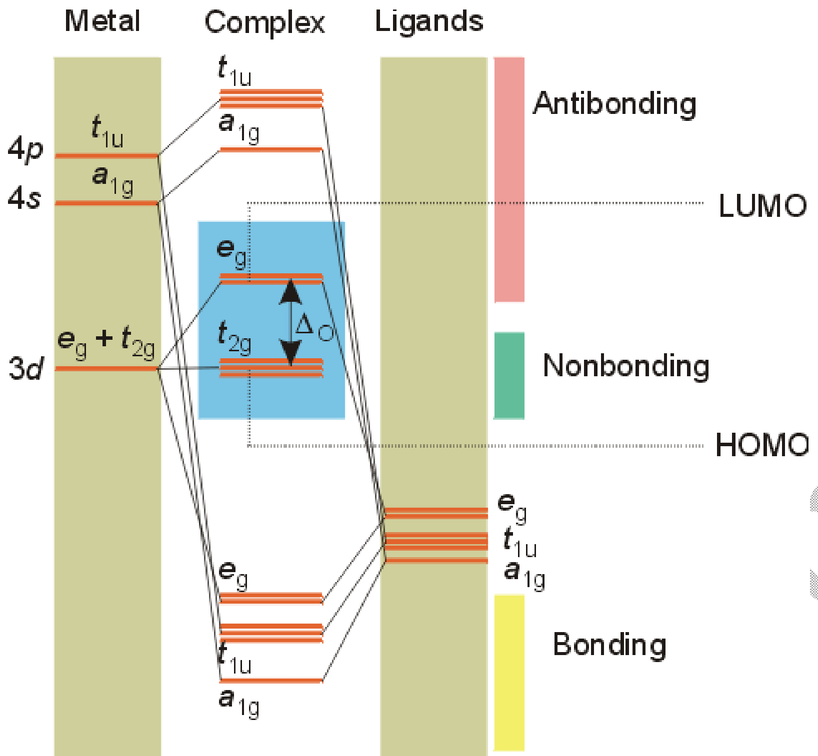


Fig: 3 combination of metal orbitals and ligand orbitals to form MOs in an octahedral complex.

The orbitals having a_{1g} symmetry give two MOs labeled as a_{1g} and a^*_{1g}. The first is bonding and other is antibonding orbital. The orbitals having t_{1u} symmetry, give six MOs. Out of them, three are called BOs which are degenerate and are labeled as t_{1u}. The remaining three are called ABOs which are degenerate and are labeled as t^*_{1u}. The orbitals having e_g symmetry give four MOs. Out of them, two are called BOs which are degenerate and are labeled as e_g. The remaining two are called ABOs which are degenerate and are labeled as e^*_g. three t_{2g} metal orbitals are unaffected so far as σ bonding is concerned, they are nonbonding orbitals.

The overlap of the metal s and p orbitals with ligand group orbitals is extensive, so there are large difference in energy between the resulting a_{1g} and a^*_{1g} and t_{1u} & t^*_{1u} bonding and antibonding orbitals. Thus the a_{1g} and t_{1u} BMOs are lower and a^*_{1g} and t^*_{1u} BMOs are highest in energy. The e_g and e^*_g orbitals are less widely separated because of poor overlap between $d_{x^2-y^2}$ and d_{z^2} orbitals and ligand group orbitals. In a system without π bonding the t_{2g} orbitals are nonbonding and therefore have the same energy as in the metal ion. The energy difference between the t_{2g} and e^*_g MOs is called Δ_o as in CFT.

From the figure it is clear that six σ BMOs which are nearer to the ligand orbitals have more character of ligand orbitals than the metal orbitals. Hence, it can be said that the electrons occupy the BMO mainly the ligand electrons. Similarly in AMOs mainly electrons of metals are filled.

The filling of Molecular Orbitals:

Electrons are filled in MOs from lower energy to higher energy as per the common electron filling rules. e.g. d^1 complex $[Ti(H_2O)_6]^{3+}$ there will be 13 electrons to be accommodated. One from titanium and twelve from the ligands. Twelve of these electrons will occupy the bonding orbitals viz. $(a_{1g})^2$, $(t_{1u})^6$ and $(e_g)^4$. There will be one electron in the t_{2g} orbital.

In d^n complexes t_{2g} & e_g orbitals will be filled as per CFT rules. Whether high or low spin complexes will be formed on the basis of value of Δ_o. The Δ_o value will be essentially the same as in CFT. The difference on this point between CFT and MOT is simply same. On the basis of CFT t_{2g} and e^*_g orbitals have different energy levels simply because of the different effect on them of an electrostatic field. On the basis of MOT, the t_{2g} and e^*_g orbitals have different energies because one set is antibonding and the other is non-bonding.

Now compare the two complex ions $[CoF_6]^{3-}$ and $[Co(CN)_6]^{3-}$ following fig. 4 show MO energy level diagram for $[CoF_6]^{3-}$. In this complex ion 18 electrons are present i.e. six from Co^{3+}ion and 12 from the ligands. Out of the 18 electrons, 12 electrons are filled in $(a_{1g})^2$, $(t_{1u})^6$ and $(e_g)^4$ orbitals from the remaining six four are filled in t_{2g} orbitals and two are placed in e^*_g orbitals. Since the energy gap between t_{2g} & e^*_g orbitals is small and pairing energy is large. Three electrons first go to t_{2g} orbitals with parallel spin, two electrons go to the e^*_g orbitals with parallel spin and then the sixth electron pairs up with one of the electrons in t_{2g} orbital. The smaller energy gap Δ_o between t_{2g} and e^*_g is attributed to the lesser extent of overlap between e_g orbitals of the metal and the ligands. Hence the $[CoF_6]^{3-}$ ion contains four unpaired electrons. It shows paramagnetism and it is high spin complex.

Fig. 5 show MO energy level diagram for $[Co(CN)_6]^{3-}$. In this complex ion 18 electrons are present i.e. six from Co^{3+}ion and 12 from the ligands. Out of the 18 electrons , 12 electrons are filled in $(a_{1g})^2$, $(t_{1u})^6$ and $(e_g)^4$ orbitals from the remaining six , all six electrons are filled in t_{2g} orbitals and no any electron placed in e^*_g orbitals. Since the energy gap between t_{2g} & e^*_g orbitals is high and pairing energy is less. Hence $[Co(CN)_6]^{3-}$ ion have not any unpaired electrons. It shows diamagnetism and it is low spin complex.

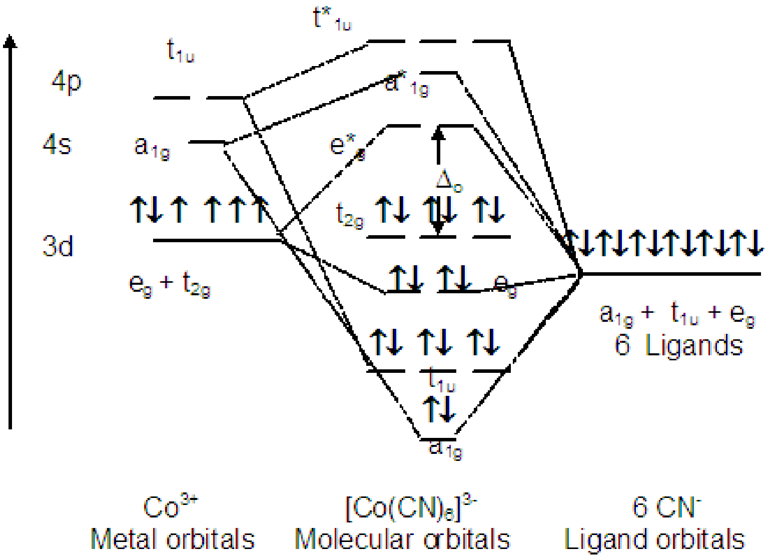


Fig: 5 Energy level diagram of $[Co(CN)_6]^{3-}$ ion without π bonding

Fig. 6 show MO energy level diagram for $[Co(NH_3)_6]^{2+}$. In this complex ion 20 electrons are present i.e. eight from Co^{3+}ion and 12 from the ligands. Out of the 20 electrons, 12 electrons are filled in $(a_{1g})^2$, $(t_{1u})^6$ and $(e_g)^4$ orbitals from the remaining eight , six electrons are filled in t_{2g} orbitals and two electron placed in e^*_g orbitals.

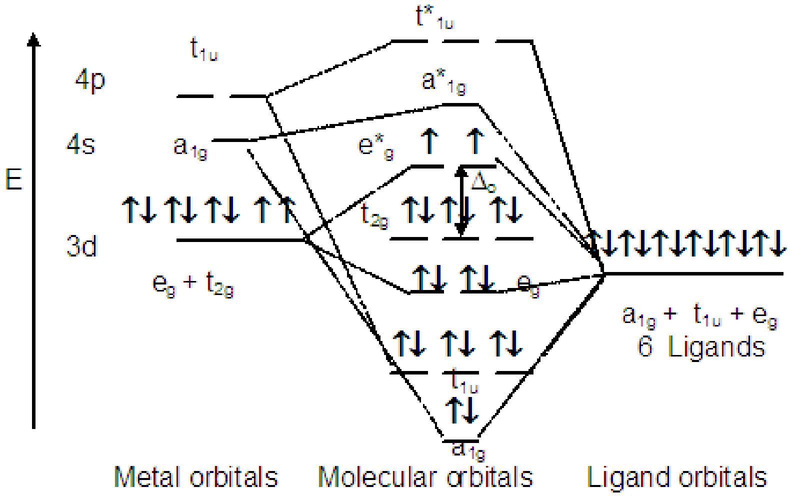


Fig: 6 Energy level diagram of $[Co(NH_3)_6]^{2+}$ ion without π bonding

Hence $[Co(NH_3)_6]^{2+}$ ion have two unpaired electrons. It shows paramagnetism.

Complexes with π bonding:

If the ligands have π orbitals, filled or unfilled, it is necessary to consider their interaction with the metal orbitals. Let us consider this simplest case where each ligand offers a pair of π orbitals, which are perpendicular to each other, for π bonding. (Usually out of the three orbitals one is used for σ bonding and the remaining two are used for π bonding). Thus six ligands offer 6 x 2 = 12 orbitals for π bonding. Following fig. show ligand π orbitals.

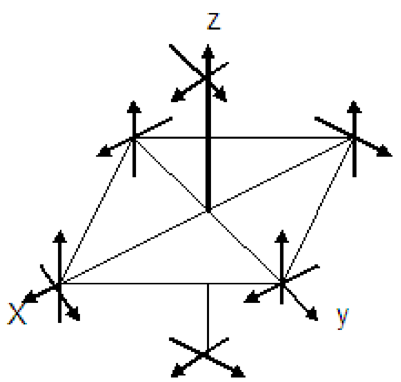
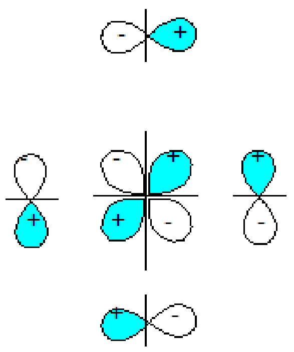
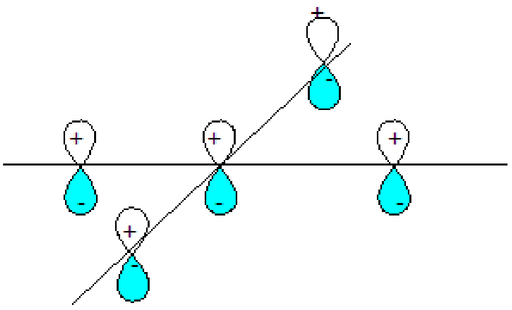


Fig: 7 Ligand π orbitals in an octahedral complex. The arrowheads represents the lobe of each orbit with positive phase.

From the group theory, it is found that these may be combined into four triply degenerate sets belonging to symmetry classes t_{1g}, t_{1u}, t_{2g} and t_{2u}. There are no metal orbitals of the t_{1g} and t_{2u} symmetries. These π ligand group orbitals are, therefore, carried over, unmodified, into the full molecular orbital description. Thus t_{1g} and t_{2u} ligand orbital remain non-bonding, with respect to π bonding.



8 a) Combination of metal d_{xz} orbital with p_x and p_z orbital of the ligands



8 b) Combination of metal p_z orbital with p_z orbital of the ligands.

The t_{1u} set of ligand group orbitals can interact with metal ion p orbital (with t_{1u} symmetry)). But the metal ion p orbitals with t_{1u} symmetry have been already used in σ bonding with ligand orbitals. So if at all π bonding takes place between metal orbitals of t_{1u} symmetry and ligand group orbitals of t_{1u} symmetry. It will be weak. Then only t_{2g} orbitals of metal and t_{2g} orbital of ligand of same symmetry can form π bondings. Fig.8 (a) shows combination of metal d_{xz} orbital (t_{2g} symmetry) with p_x and p_z orbital of the ligand (t_{2g} symmetry).and fig 8(b) shows combination of metal p_z orbitals (t_{1u} symmetry).

Following fig.9 shows splitting of t_{2g} orbitals into t_{2g} (bonding) and t^*_{2g} (antibonding) MOs due to interaction of t_{2g} metal and t_{2g} ligand orbitals. Orbitals of t_{2g} symmetry on metal and ligand.

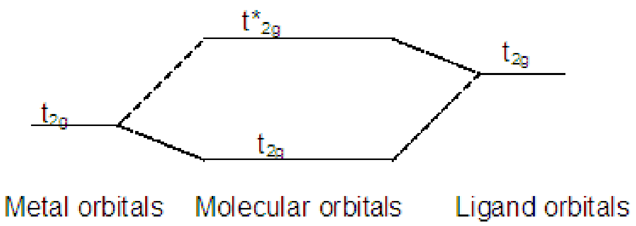


Fig. 9 Energy level diagram for formation of MOs from π bonding

Effect of π bonding on complexes:

Consider the formation of π bonding, the ligand can use its-

1) P orbitals perpendicular to the σ bond axis as in the halide ion.
2) d orbitals lying in the plane which includes the metal atom as in phosphates or arsines.
3) An antibonding π^* orbital in a plane that includes the metal atom as in Co, CN^-, pyridine.

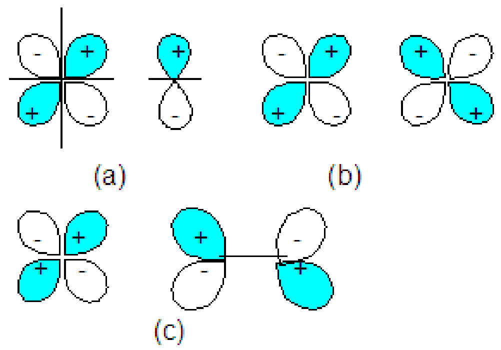
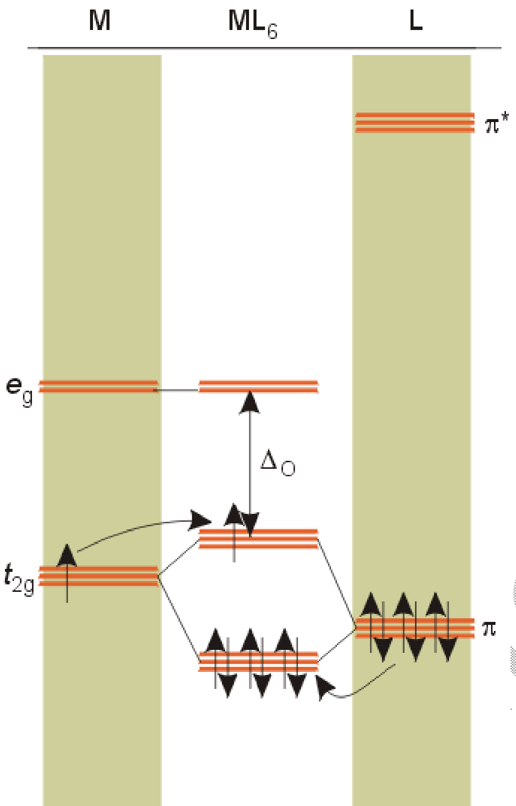


Fig. 10 π bond formation between a metal t_{2g} orbital and a ligan (a) p orbital, (b) d orbital (c) π^* orbital.

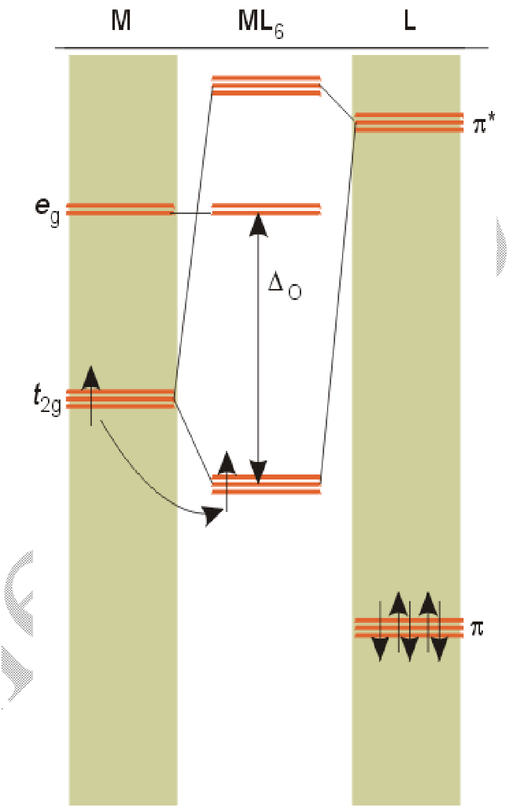
4) π bonding modifies the energy level diagram of a σ bonded complex, particularly the central part of the fig. 3 where Δ_o is the difference between the t_{2g} and e^*_g orbitals.

Effect of π bonding on the magnitude of Δ_o

1) Filled (donor) ligand orbitals of low energy:



Ligands that are π donors decrease Δo.



Ligands that are π acceptors increase Δo.

If the filled ligand orbitals lie at a lower energy than the metal t_{2g} orbital (e.g. if the ligand is a halide ion and uses its filled p orbital for π bonding), π bonding affects the energy level diagram as shown in fig.

In this case, the π bonding MOs resemble the ligand orbitals more than the metal orbitals. The e^*_g orbitals are not affected by π bonding. But the $\pi^*(t^*_{2g})$ molecular orbitals (originally coming from metal t_{2g} orbitals) are raised in energy subsequently. Δ_o which was originally the difference between the t_{2g} and e^*_g orbitals in a σ bonded complex, becomes the difference the between t^*_{2g} and e^*_g molecular orbitals. Since the t^*_{2g} orbitals are raised in energy with respect to t_{2g} metal orbitals, the magnitude of Δ_o is reduced. As a result a complex is destabilized. This type of π bonding is called ligand to metal (L→ M) π bonding.

2) Empty (acceptor) ligand orbitals of high energy:

If the empty ligand orbitals lie at a higher energy than the metal t_{2g} orbital (e.g. if the ligand is a phosphine and uses its empty d orbital or the ligand is carbon monoxide and uses its empty π^* molecular orbital for π bonding), π bonding affects the energy level diagram as shown in fig.12

In this case, the π bonding MOs resemble the ligand orbitals more than the metal orbitals. Due to pi bonding overlap, the π (t_{2g}) level of the MOs (originally coming from metal t_{2g} orbitals) gets lowered in energy in the complex, The e^*_g orbitals are not affected by π bonding. While π^*(t^*_{2g}) level (originally coming from metal t_{2g} orbitals) is raised above the ligand orbitals.

Subsequently, Δ_o which was originally the difference between the t_{2g} and e^*_g orbitals is increased. As a result, a complex is stabilized. This type of π bonding is called metal to ligand ($M \rightarrow L$) π bonding. In this case electronic charge is removed from central metal to the ligands. This is called back donation or back bonding.

Ligand Field Theory:

Van Vleck developed this theory between 1939 and 1940. The CFT treats the interaction between the metal ion and ligands as a purely electrostatic problem in which the ligand atoms are represented as point charge. At the opposite extreme, so to speak, the metal ligand interaction can be described in terms of MOs formed by the overlap of ligand and metal orbitals. These two approaches use different physical interpretation of the problem but both use symmetry properties of the complex. The basic difficulty with the CFT treatment is that it takes no account of the partly covalent nature of the metal- ligand bonds and therefore, whatever effects and phenomena arise directly from covalence are entirely unexplainable in simple CFT. On the other hand CFT can provide a very simple and easy way to treat numerically many aspects of the electronic structure of complexes. MOT, in contrast, does not provide numerical results in such an easy way. Therefore, a kind of modified CFT has been developed in which certain parameters are empirically adjusted to allow for the effects of covalence without introducing covalence into the CFT formalism. This modified CFT is called Ligand Field theory.

Charge Transfer Spectra:

Absorption of light takes place to cause electronic transition within as atom or molecule, it is essential that the absorption results in a displacement of charge density. The displacement of charge density may take place within an atom (d-d transition) or the displacement of the charge density may takes place from one atom to another, we call it as charge transfer transition.

The CFT can't explain the charge transfer transition because it does not take covalent bonding into account. MO treatment is necessary to explain charge transfer transition. Thus when the absorption of radiation causes an electronic transition between two MOs such that one MO is more concentrated at one atom while the other MO is more concentrated on a different atom we call it a charge transfer transition. And the graph of absorption versus wavelength of light as a charge transfer band or spectrum. For transition metal complexes the charge transfer bands occur in the UV region. They are generally far more intense than the d → d bands. Charge transfer bands can be classified into two groups.

i) Ligand → Metal (Reduction) Transition:

These are a common type of transition in which a ligand electron is transferred to a metal orbital and the charge separation within the complex is thereby reduced. In these transitions the electrons from BMOs are excited to the empty t_{2g} or e^*_g MOs. Such charge transfer bands are shown by the oxides, chlorides, bromides etc. the dark colour of $[CuCl_4]^{2-}$, the yellow colour of $[FeCl_6]^{3-}$ is due to charge transfer transition.

ii) Metal → Ligand (Oxidation) Transition:

In these transition, an electron is transferred to a metal orbital to ligand orbital. In such transitions, the electrons from σ BMOs are excited to the empty π MOs localized predominantly on ligands. Such charge transfer bands are shown by the CO, CN^-, NO ligands. The Metal → Ligand charge transfer also occur in the red complexes of iron (+II) with dipyridyl or o-phenanthroline. These transition is favoured if the metal is in a low oxidation state and the ligand has a low-lying antibonding orbital.