

## Quadrant II – Transcript and Related Materials

<b>Programme</b>	<b>: Bachelor of Science (Third Year)</b>
<b>Subject</b>	<b>: Chemistry</b>
<b>Paper Code</b>	<b>: CHC 106</b>
<b>Paper Title</b>	<b>: Bonding in Co-ordination Compounds</b>
<b>Unit</b>	<b>:2</b>
<b>Module Name</b>	<b>: Effect of <math>\pi</math> - bonding on splitting parameters</b>
<b>Module No</b>	<b>: 24</b>
<b>Name of the Presenter</b>	<b>: Dr. Shridhar M. Gurav</b>

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### Notes

**Effect of  $\pi$  bonding on splitting parameter,  $\Delta_o$**  : Metal  $t_{2g}$  orbitals take part in  $\pi$  bonding and in molecular orbital diagram, they are lowered or raised in energy. According to the energy gap between  $t_{2g}$  and orbitals i.e.,  $e_g^*$  orbitals i.e.,  $\Delta_o$ ,  $\Delta_o$  changes. This effect of  $\pi$  bonding on  $\Delta_o$ , value depends mainly upon two factors. (1) The energy level of ligand orbitals with respect to that of metal  $t_{2g}$  orbitals and (2) whether ligand  $\pi$  orbitals are empty or filled: Accordingly there are two types of  $\pi$  interactions, i.e.,  $L \rightarrow M$  and  $M \rightarrow L$   $\pi$  interactions.

#### **(A) filled (donor) Ligand Orbitals of Low Energy ( $L \rightarrow M\pi$ interaction)**

In an octahedral complex ion like  $[\text{FeF}_6]^{3-}$  the ligands F have filled  $\pi$  orbitals. Hence the complex involves both  $\sigma$  and  $\pi$  bonding. The  $\sigma$  system of the complex ion will be almost similar to the one mentioned earlier. Regarding  $\pi$  bonding, the interactions between  $t_{2g}$  ligand orbitals and  $t_{2g}$  metal orbitals are to be studied. Since fluorine is more electronegative than  $\text{Fe}^{3+}$ , fluorine orbitals lie at a lower energy than the corresponding  $t_{2g}$  metal orbitals. Under these circumstances, the bonding  $\pi$  orbitals will resemble ligand

orbitals more than the metal orbitals and  $\pi^*$  orbitals will more closely resemble the metal orbitals.

The energy level diagram for the  $\pi$  system of the octahedral complex is shown in Fig. 5.31A. Since  $p$  orbitals of  $F^-$  are filled, these electrons fill the resultant molecular  $t_{2g}$   $\pi$  orbitals. The electrons from the  $t_{2g}$  orbitals of metal occupy  $t_{2g}^*$  orbitals, i.e., energy level higher than what they would be if  $\pi$  bonding had not taken place. Since the energy level of  $e_g^*$  orbitals remains unaffected, (as they do not take part in  $\pi$  bonding)  $\Delta_o$  is reduced as a result of  $\pi$  bonding. Thus the net result of interaction is destabilisation or raising of  $t_{2g}$  orbitals relative to  $e_g^*$  orbitals and thus the value of  $\Delta_o$  decreases. This type of interactions are called ligand to metal  $\pi$  or  $L \rightarrow M\pi$  interaction and the ligands are called  $\pi$  donor ligands. These  $L \rightarrow M\pi$  interactions probably explain why  $F^-$  and other halides cause less splitting of  $d$  orbitals, i.e., low  $\Delta_o$ .

#### (B) Empty(acceptor)ligand orbitals of high energy( $M \rightarrow L\pi$ interactions)

Another important type of  $\pi$  bonding takes place with ligands like phosphine and arsine which have empty  $\pi$  orbitals, that can receive electron density from the metal [Fig. 5.31B]. Such ligands are called  $\pi$  acceptor ligands. The empty ligand  $\pi$  orbitals are at higher energy than metal  $t_{2g}$  orbitals. The net result of  $\pi$  interaction is that the metal 'd' electrons fill the resulting molecular  $t_{2g}$  orbitals which are lowered or stabilised as compared to the original  $t_{2g}$  orbitals. This leads to increase in the value of splitting energy, i.e.,  $\Delta_o$ . Such interactions are called metal to ligand or  $M \rightarrow L \pi$  interactions. These interactions are similar to back bonding explained by VBT.

There are some ligands like CO and  $CN^-$  which have both filled as well as empty  $\pi$  orbitals. In such cases there is a competition between the two types of  $\pi$  interactions with metal  $t_{2g}$  orbitals. In complexes like  $[Fe(CN)_6]^{3-}$  the main  $\pi$  interaction is between empty antibonding  $\pi^*$  orbitals of  $CN^-$  and  $t_{2g}$  orbitals of  $Fe^{3+}$ . This leads to stabilisation of  $t_{2g}$  molecular orbitals, increasing the splitting energy,  $\Delta_o$  i.e.,  $M \rightarrow L \pi$  interaction. In general, ligands which can form  $\pi$  bonds in addition to  $\sigma$  bonds cause more splitting of  $d$  orbitals, i.e.,  $\Delta_o$  more, than those which form only  $\sigma$  bonds. This explains why ligands like CO and  $CN^-$  cause more splitting of  $d$  orbitals and are strong field ligands. They are at the extreme end in the spectrochemical series.

