CHAPTER 7

Metal-Ligand Bonding:

❖ Limitation of Crystal Field Theory

The main drawback of the crystal field theory is that it does not consider the covalent character in metal-ligand bonding at all. It treats the metal-ligand interaction in a purely electrostatic framework which is pretty far from reality. All the effects which originate from covalence cannot be explained by this theory. Therefore, the main limitations of crystal field theory can be concluded only after knowing the causes and magnitude of the covalence in the metal-ligand bonds.

➢ Evidences for the Covalent Character in Metal–Ligand Bond

The crystal field theory considers the metal center as well as surrounding ligands as point charges and assumes that the interaction between them is 100% ionic. However, quite strong experimental evidences have proved that there is some covalent character too which cannot be ignored. Some of those experimental evidences are as follows:

1. The nephelauxetic effect: The electrons present in the partially filled d-orbitals of the metal center repel each other to produce a number of energy levels. The placement of these levels on the energy scale depends upon the arrangement of filled electrons. The energy of these levels can be given in terms of "Racah parameters" B and C (a measure of interelectronic repulsion). The energy difference between same multiplicity states is expressed in B and Dq while between different multiplicity states is given in term of B, Dq and C. It has been observed that the complexation of metal center always results in a decrease in interelectronic repulsion parameters which in turn also advocates a decrease in the repulsion between d-electron density. Now, as the magnitude of this interelectronic repulsion is dependent upon the distance between the areas of maximum charge density, the decrease in its value is expected only when the d-orbital lobes extend in space. This is called as the nephelauxetic effect and measured as the nephelauxetic parameter (β).

This extension or nephelauxetic effect may be attributed to the larger orbital overlap between metal and ligand resulting in greater stabilization due to covalent bonding. Hence, the direct effect of covalent bonding between metal and ligand is to decrease the interelectronic repulsion parameters. In other words, greater the decrease in "Racah parameters", larger is the extent of covalent bonding between metal and ligand. Different ligands have different capacity to extend their d-orbital and are arranged in ascending order, known as the nephelauxetic series as:

$$F^- < H_2O < NH_3 < Ox^{2-} < en < NCS^- < Cl^- < CN^- < Br^- < I^-$$
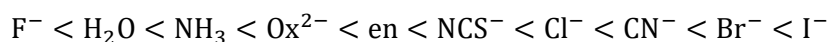
It has been observed that the nephelauxetic ratio always follows a certain trend with respect to the nature of the ligands present. However, there are many ligands that do not form complexes with a particular metal ion; the Racah parameter and for these complexes cannot be calculated empirical rather experimentally.
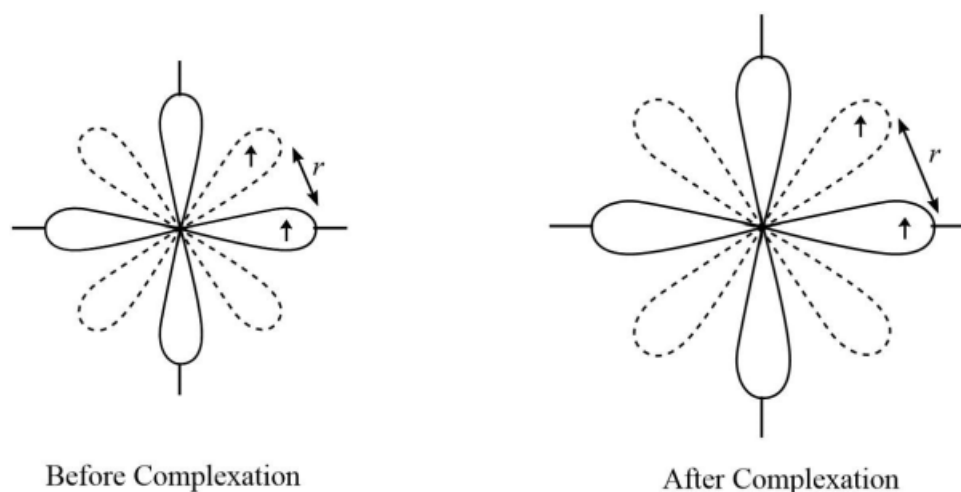
Before Complexation   After Complexation

Figure 1. The expansion of d-electron cloud in transition metal centre after complexation due to nephelauxetic effect.

Hence, the observed decrease in inter-electronic repulsion parameters after complexation proves that there is always a somewhat more or less covalent character in the metal-ligand bond.

2. Lande's splitting factor: The value of Lande's splitting factor or simply "g-factor" for transition metal complexes was found to be different from what was expected from a pure ionic bonding perspective. The experimental value of g-factor showed that the electron from metal ion is always somewhat more or less delocalized to the ligand orbitals. This is possible only if metal orbitals are in overlap with the ligand orbitals via covalent interaction. Therefore, in view of the observed value of g-factor, we can claim that the partial covalence does exist in the metal-ligand bond.

3. Electron spin resonance spectra: It has been observed that the electron paramagnetic resonance or EPR spectra of some metal complexes is not that simple as expected. The fine lines were further split into hyperfine lines due to NMR active nuclei of ligands. This result can be explained only if the unpaired electrons of the metal center are delocalized to the nuclei centers of the ligands and as a consequence, electron-nucleus coupling occurs. Therefore, it quite obvious that we consider the metal-ligand as somewhat more or less covalent in nature. For example, the electron-spin resonance spectra of $[Ir(Cl_6)]^{2-}$ revealed that the unpaired $5d$-electron of Ir^{4+} spends 70% of its time on Ir^{4+} while 30% on chloride ligands.

4. Nuclear magnetic resonance spectra: The nuclear magnetic resonance of some ligands in metal complexes is markedly affected by the unpaired electrons of the metal center. This is possible only if metal orbitals are in overlap with the ligand orbitals. This proves a covalence in metal-ligand bond. For example, the chemical shift of tris-(acetylacetonato) vanadium(III) is shifted towards a position as if there is no paramagnetic contribution from the metal ion. This anomaly in the chemical shift may be attributed to the transfer of unpaired electron density from vanadium ion to the attached ligand.
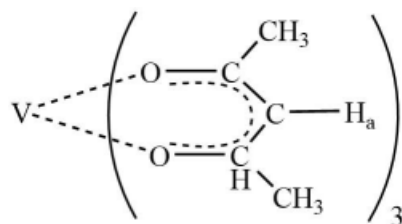
Furthermore, the F^{19} NMR of metal-fluoride complexes shows a significant effect arising from the unpaired electron from the metal centers, which obviously suggests that the electron on transition metal center does spend a non-zero time on the ligand too.

5. Nuclear quadrupole resonance: The nuclear quadrupole resonance spectra of some metal complexes having halide ions as ligands showed that the metal-halogen bond is not 100% ionic but has some covalent character too. In general, higher the NQR frequencies are, the larger will be the covalent character in metal-ligand bond. For example, one of the orders of the covalent character provided by nuclear quadrupole studies is Hg–X >> Cd–X > Zn–X, which is also supported by the Hard-Soft Acid-Base principal.

6. Kramers-Anderson superexchange: The phenomenon of superexchange was first suggested by H. Kramers in 1934 when he observed that in some crystals such as MnO, the Mn atoms interact with each another despite having diamagnetic intermediates like the oxide ions between them. Later on, Phillip Anderson modified the Kramers' model in the years of 1950. The superexchange phenomenon is the strong antiferromagnetic interaction between two nearest neighboring cations via a non-magnetic intermediate. Therefore, it is different from the direct-exchange in which the interaction is between nearest-neighbor cations without involving an intermediate anion.
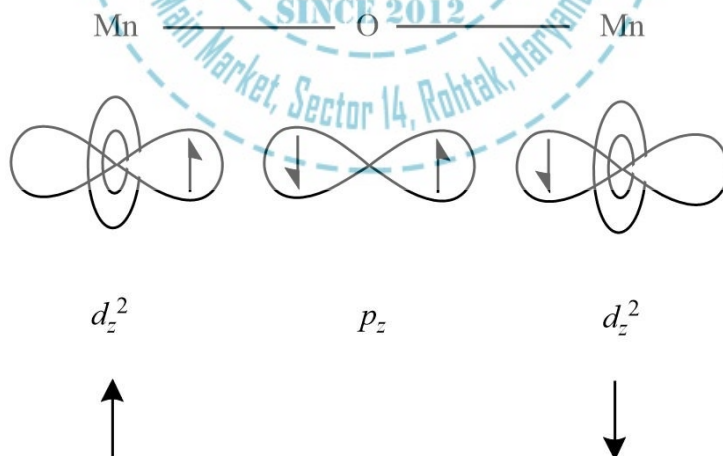
Figure 2. The superexchange phenomenon in MnO.

However, it may also be worthy to mention that if two neighboring cations are joined at 90 degrees to the diamagnetic bridge, then the coupling can be ferromagnetic in nature.

The phenomenon of superexchange can be rationalized with the help of Pauli exclusion principle which governs that the superexchange would lead to anti-ferromagnetic behavior if the coupling occurs between two ions each of which has half-filled orbital; and would yield ferromagnetic behavior one metal ion is having half-filled orbital while the other ion has fully-filled orbitals; provided that in both cases, they interact via a diamagnetic intermediate like O^{2-}. Moreover, the interaction between an ion with either filled or a half-filled orbital and one with an empty orbital can be either ferromagnetic or antiferromagnetic, however, it usually favors ferromagnetism. However, if multiple kinds of interactions are simultaneously present, the antiferromagnetic ordering is the one that usually dominates because of its independence of the intra-atomic exchange term. The whole of the above explanation is based on the fact that the bonding between the metal center and ligand is not 100% ionic but does have a significant extant of orbital-overlap which confirms the presence of covalent character.

> ➢ *Limitations of CFT*

Now as we have discussed the covalence in metal-ligand bond, the main limitations of the crystal field theory can be summarized as follows:

1. The predictions of crystal field theory deviate from experimental results more and more as the extent of covalence between the metal center and ligands increases.

2. This theory does not give any satisfactory explanation for the relative strength of different ligands and hence is unable to explain the trends in the spectrochemical series. For example, ionic ligands are expected to show greater splitting effect due to the assumption of ligands as point charges but the neutral ligands like NH_3 or H_2O are actually stronger ligands than that of halide ions.

3. The crystal field theory gives no insight of back-bonding between the metal and ligand and fails to explain the π-bonding or multiple bonds.

4. It does not explain the charge-transfer bands observed in the UV-visible spectra of transition complexes.

5. The crystal field theory considers only the *d*-orbitals of central metal ion but takes no account of the *s* and *p*-orbitals for its calculations.

6. The crystal field theory does not consider the orbitals of ligands at all and hence does not explain any properties associated with ligand orbitals and their interaction with orbitals of the metal center.

7. The assumption of the interaction between metal and ligand as purely electrostatic in nature is an idealistic one and is pretty far from reality.

8. This theory does not explain the effect of π-bonding on crystal field splitting Δ and therefore cannot compare the π-acid characters.

9. It could not explain the color the metal complexes having full or empty *d*-orbitals.

10. The CFT overlooks the attractive forces acting between the *d*-electrons of the metal center and nuclear charge on the ligands attached, which results in an unclear image of the properties dependent upon the same.

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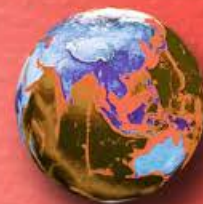
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Volume I

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