Limitation of Crystal field theory.

As we know that the Crystal Field theory satisfactorily deals with many properties of metal complexes and it is more generalised approach to the study of metal complexes than the valence bond theory, but C.F.T has also some limitations. So the most important limitations of C.F.T is as follows.

(i) The crystal field theory emphasised on the orbitals and electron of the central atom. This CFT theory must necessarily become less accurate as delocalisation of Ligand electrons and orbitals becomes more important.

This CFT theory is unable to explain accurately regarding increase in covalent bonding.

(ii) The point-charge model assumed by this theory does not exactly represent the acutal situation of a metal ion in the field of the surrounding ligands.

(iii) This theory fails to account for the relative Strength of ligands.

(iv) —— It gives no explanation as to why negatively Charged hydroxyl ion appears in the spectrochemical series as a weaker ligand than the neutral water.

(v) In several complexes, the bonding strength and chemical properties cannot be explained on the basis of electrostatic attractive forces as it is emphasised by this theory.

Now existing metal-ligand covalent bonding in complexes has been supported by some evidences.

The presence of Metal-Ligand covalent bonding in metal complexes is evidenced by several spectroscopic studies.

(i) **ESR Spectra:-** Electron Spin Resonance Spectra.

The most direct evidence for Metal-Ligand π bonding is obtained from the ESR Sepectra of Complexes.

For example $[IrCl_6]^{2-}$ gives hyperfine structure which can be explained by assuming that some of the Iridium orbitals and Chloride ions orbitals overlap to such an extent that the single unpaired d-electrons is not localised on the metal ion but it about 5% localised on each chloride ion. This result is similar in many cases of complexes

Pro

(2) NMR studies:- Nuclear Magnetic Resonance Spectra

NMR Studies of the complexes like $K[MnF_3]$ & $K[NiF_3]$, spectral studies clearly indicate that the spin of an unpaired electron of a metal ion interacts with the nuclear spin of "F" in the fluoro complex of a para magnetic metal ion.

This electron spin nuclear spin interaction is possible only if the unpaired electron spends more than negligible time on the F⁻ nucleus. This is possible through the overlapping of orbitals of the ligand and the metal ion in the covalent bond formation.

(3) Inter electronic Repulsion:-

Due to inter electronic repulsion the lobes of d-orbital is extended, this extention in lobes of d orbital indicates the expansion of d electron charge cloud. which is known as Nephelauxeti effect. (i.e. Cloud expansion)

The extension of d orbitals of the complex metal ion in space occurs obviously to Maximise the overlap of these orbitals with the orbitals of the ligand. it is essential condition for covalent bonding. it means a covalent bonding in M–L bond which decreases the inter electronic repulsion Parameters when a free metal ion gets complexed.

The capacity of d orbitals of different metal ions to extend themself in space and forms the basis of the nephelauxetic series.

(4) NQR Spectra:- Nuclear Quadrupole Resonance spectra.

The NQR data on the complexes containing halide ions as the ligands clearly show that the metal halogen bond is partly ionic and partly covalent in character.

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