



# WILSON COLLEGE, MUMBAI

DEPARTMENT OF CHEMISTRY

UNDERGRADUATE SEMESTER -VI

INORGANIC CHEMISTRY

MODULE IV

TOPIC: THEORIES OF THE METAL - LIGAND BOND

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<b>SUBJECT</b>	<b>CHEMISTRY</b>
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<b>Title</b>	Effect & drawback of crystal field splitting

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### **Learning outcomes:**

After studying this module, you shall be able to

- Know about Effect of crystal field splitting on :
  - (i) Ionic radii and (ii) lattice energy
- Know about experimental evidences for covalence in Coordination Compounds
- Drawbacks and limitations of CFT

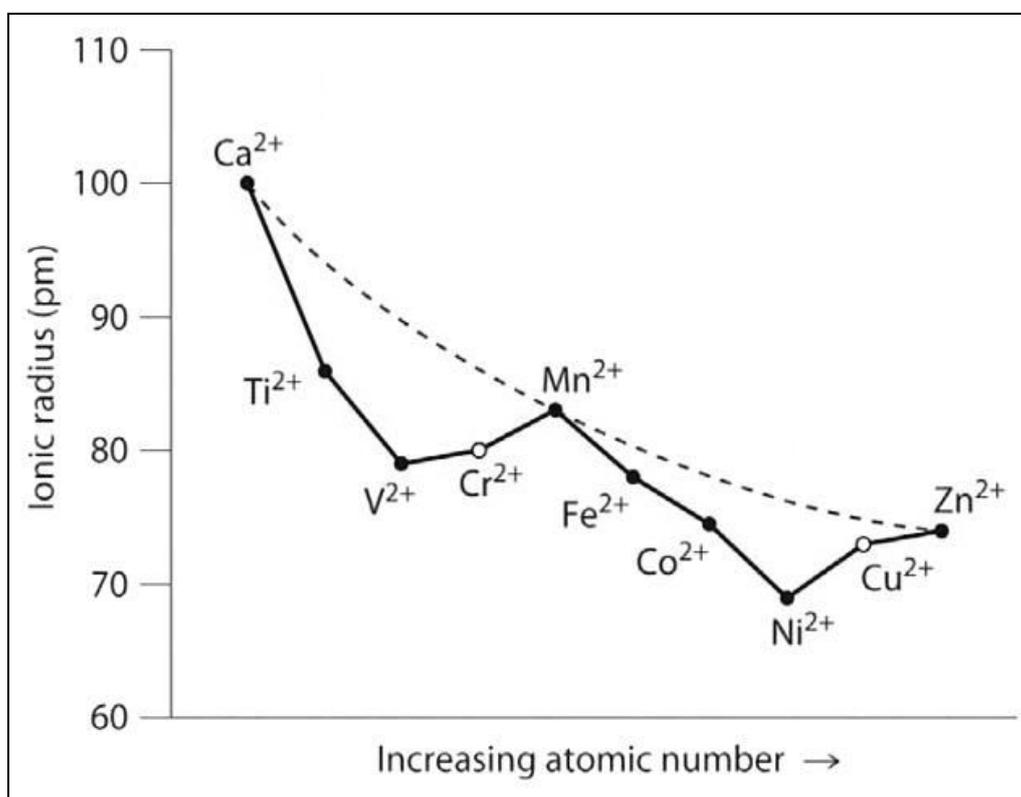
### Effect of crystal field splitting on (i) Ionic radii and (ii) lattice energy

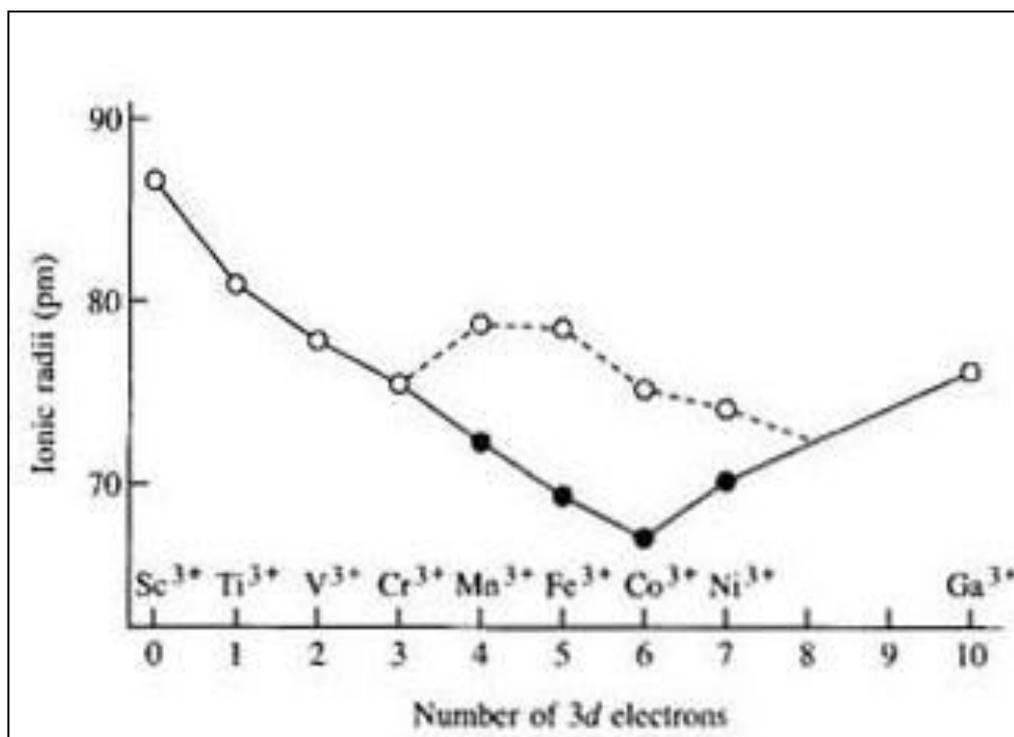
#### I. Ionic Radii

- Along a transition metal series, with the increase in nuclear charge, ionic radii are expected to steadily decrease. But the variation in their size is not regular and an unusual curve is observed when ionic radii are plotted against number of d electrons. This unexpected nature of curve can be attributed to crystal field effects.
- The ionic radii of elements of first transition series ( $M^{+2}$ ) are plotted against the number of *d* electrons. From  $Ca^{+2}$  to  $Zn^{+2}$  with the increase in nuclear charge their ionic radii are expected to decrease and form a smooth declining curve, but only for  $Ca^{+2}$ ,  $Mn^{+2}$  and  $Zn^{+2}$ , the radii are as expected but not for the remaining ions. This is because complexes of  $Ca^{2+}(d^0)$ ,  $Mn^{2+}(d^5)$  and  $Zn^{2+}(d^{10})$  show no CFSE and crystal field splitting does not affect their ionic radii whereas other metal ion complexes show CFSE and get affected by crystal field splitting.
- In high spin complexes, from  $Ca^{+2}$  to  $V^{+2}$  ( $d^0$  to  $d^3$ ), as electrons enter only  $t_{2g}$  level, ligands move closer to the metal and their ionic radii gradually decrease. As the  $e_g$  orbitals point directly towards the ligands, the repulsion between the metal electrons and ligand electrons will be higher than normal, leading to the eventual increase in the ionic radius From  $Cr^{+2}$  ( $d^4$ ) to  $Mn^{+2}$

( $d^5$ ) electrons enter  $e_g$  level and their size increases. The same trend is observed in the second half of the series.

- In low spin complexes, from  $Ca^{+2}$  to  $Fe^{+2}$  ( $d^0$  to  $d^6$ ) as electrons enter only  $t_{2g}$  level, their ionic radii decrease. But from  $Co^{+2}$  ( $d^7$ ) to  $Zn^{+2}$  ( $d^{10}$ ) as electrons enter  $e_g$  level, their ionic radii increase.
- Even with tripositive metal ions, almost the same trend is obtained in high and low spin complexes. Therefore, the variation in ionic radii of transition metal ions is because of the effects of crystal field splitting.





## II. Lattice Energy;

- It is observed that experimentally measured lattice energies of some complexes are higher than the values calculated on the basis of Born Lande equations.

$$\Delta U = -\frac{N_A M |Z^+||Z^-| e^2}{4\pi\epsilon_0 r}$$

$N_A$  is Avogadro's constant ( $6.022 \times 10^{23}$ )

$M$  is the Madelung Constant (a constant that varies for different structures)

$e$  is the charge of an electron ( $1.6022 \times 10^{-19} \text{C}$ )

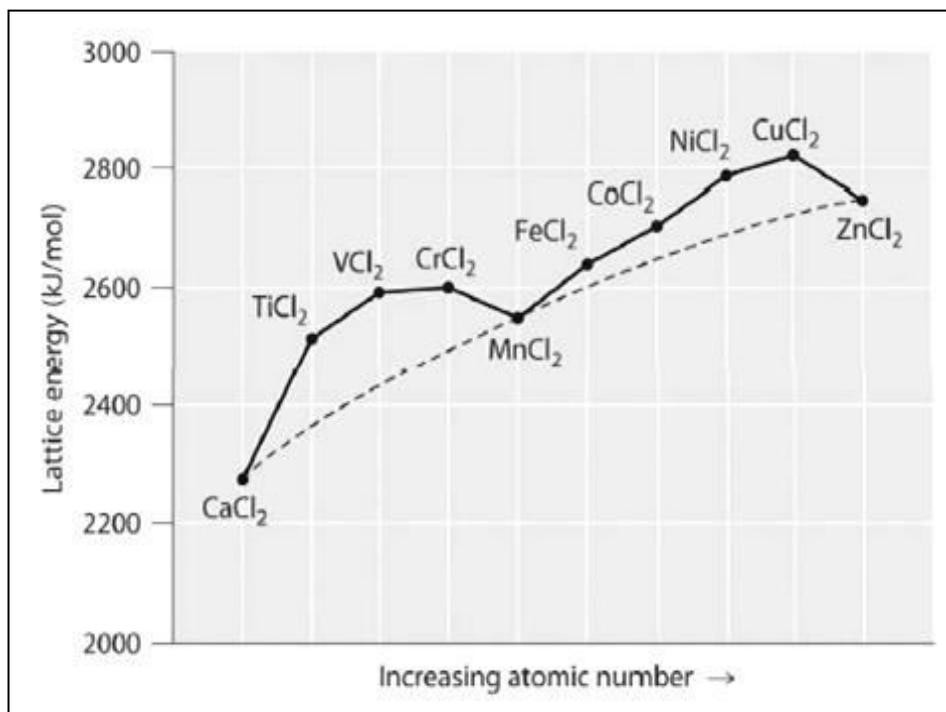
$Z^+$  is the cation charge

$Z^-$  is the anion charge

$\epsilon_0$  is the permittivity of free space

- Lattice energy is generally inversely proportional to ionic radii of metal and is expected to increase with the decrease in ionic radii. From  $\text{Ca}^{+2}$  to  $\text{Zn}^{+2}$ , ionic radii are expected to gradually decrease and accordingly their

lattice energies are expected to steadily increase and show a gradual and smooth rise. But the expected smooth rise is not observed instead a double humped curve with two peaks is observed. These variations in lattice energies are due to crystal field effects.



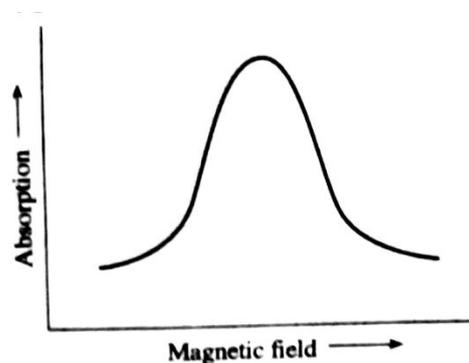
- As clear from the graphs, for Ca<sup>+2</sup> ( $d^0$ ), Mn<sup>+2</sup> ( $d^5$ ) (high spin) and Zn<sup>+2</sup> ( $d^{10}$ ) lattice energy values are as expected on the steadily rising line (dotted line) This is because they show zero CFSE. But for other metal ions they are higher than expected as they show CFSE
- Two maxima on each curve are observed at V<sup>+2</sup> and Ni<sup>+2</sup>. This is because high spin complexes with  $d^3$  and  $d^8$  configurations show maximum CFSE
- The others with  $d^2$ ,  $d^4$ ,  $d^7$  and  $d^8$  configurations show less variation as they show comparatively less CFSE. Thus, the double humped curve and the variation in lattice energies are explained by crystal field splitting.

## Experimental evidences for Covalence in Coordination Compounds

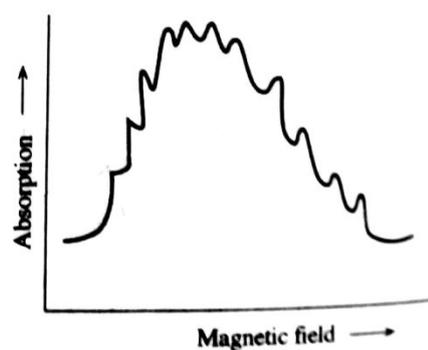
The following are some of the important experimental evidences to prove covalent bonding in complexes:

### 1) Electron spin resonance(ESR) Spectra

- An ESR spectrum is observed when molecules or ions containing one or more unpaired electrons are placed in magnetic field.
- In complexes, if the unpaired electrons are localised on the metal, then ESR spectrum is expected to show a smooth curve as shown in fig.



**(a) ESR spectrum indicating smooth peak**



**(b) ESR spectrum of  $[\text{IrCl}_6]^{2-}$  indicated serrated curve (hyperfine structure)**

- But in most of the complexes, it was observed that though they have unpaired electrons, their ESR spectra shows complicated structure with a number of sub-bands called hyperfine structure.
- This hyperfine splitting is mainly due to the interaction of the unpaired electron with spin with the nuclear spin of the ligand and the magnitude of splitting is proportional to the fraction of electronic charge on the ligand.
- This indicates that the odd electrons is no more localised on the metal orbital alone but part of the time it is occupying the orbital of the ligand. In other words, there is some overlapping between the metal and ligand orbitals, which proves the covalent character of the bond.
- $[\text{IrCl}_6]^{2-}$  is a low spin octahedral complex and have one unpaired electron.

ESR spectrum of  $[\text{IrCl}_6]^{2-}$  ion is expected to show a smooth curve as it has an unpaired d electron. But it shows a hyperfine structure. This hyperfine structure is due to the interaction of unpaired electron spin of  $\text{Ir}^{+4}$  with nuclear spin of  $\text{Cl}^-$  ligands which is possible when there is some overlapping of d orbitals of  $\text{Ir}^{+4}$  ion with orbitals of  $\text{Cl}^-$  ion.

- The nature of hyperfine splitting in  $[\text{IrCl}_6]^{2-}$  would be accounted only by assuming that the single unpaired electron is not completely localised on the metal ion but is also found to the extent of 5% on each  $\text{Cl}^-$  ion. Thus the unpaired electron is localised to the extent of about 30% on the ligands and only 70% on  $\text{Ir}^{+4}$  ion and not 100% as assumed by CFT.

## 2) Nephelauxetic effect

- It has been observed that the d-d electron repulsion is less in a complex metal ion than in a free metal ion.
- The decrease in the inter-electronic repulsion is due to the increase in the distance between the *d* electrons. This increase in the distance is attributed to the increase in the size of d orbitals (expansion of d electron cloud).
- The expansion of d electron cloud is due to the overlap of metal d orbitals with ligand orbitals. Such overlapping reduces the effective nuclear charge on the metal and for partial removal of electron density from the central metal atom.
- This effect of ligand in expanding the d electron cloud of the metal is called nephelauxetic effect. The ability to expand the electron cloud of the metal varies from ligand to ligand. Depending on the ability of the ligands to expand the d electron cloud of metal they are arranged in the form of series called nephelauxetic series.



- Although parts of this series may seem quite similar to the spectrochemical series of ligands - for example, cyanide, ethylenediamine, and fluoride seem to occupy similar positions in the two - others such as chloride, iodide and bromide (amongst others), occupy very different positions. The ordering roughly reflects the ability of the ligands to form good covalent bonds with metals - those that have a small effect and are at the start of the series, whereas those that have a large effect are at the end of the series.
- From the series it is clear that  $F^-$  and  $I^-$  are at the two end of the series. Therefore iodo complexes are more covalent than fluoro complexes.

### 3) **Intensity of d-d transition;**

- Transition metal complexes are generally coloured which is due to d-d transition ,however this transition are very weak and are not expected to give intense band which are actually observed.
- Other interactions which may contribute to the enhanced intensities of d-d transitions which are:
  - a) Interaction of d orbital with other orbital such as s and p orbitals of the same metal ion.
  - b) Interaction between d orbital wave function and vibrational wave function of the molecule.
- But there are number of complexes in which the observed spectral intensity cannot be explained just on the basis of these interactions.
- In such cases, the observed intensities can be explained satisfactorily by assuming some mixing of metal d orbitals with ligand orbitals occurs to a sufficient extent which prove that there is a covalent bonding between M and L

## DRAWBACKS OF THE CRYSTAL FIELD THEORY.

- Though spectrochemical series allows us to rationalise differences in spectra, it creates many serious problems which could not be accounted for, on the basis of crystal field theory.
- If the ligands are considered as point charges or dipoles (as assumed by CFT) then anionic ligands should bring out more crystal field splitting than the neutral molecules.
- According to CFT, among negative ions  $F^-$  is expected to be a stronger ligand than  $CN^-$  and among neutral molecules  $H_2O$  is expected to be stronger than  $NH_3$ .  $H_2O$  has high dipole moment than  $NH_3$ . But in the spectrochemical series, their positions are just the reverse.
- The position of these ligands can be explained only when covalent ( $\pi$ ) bonding is assumed between the central metal and the ligand.
- Since CFT completely neglects covalent bonding, it cannot account for the position of all the ligands in the spectrochemical series.
- This failure to interpret the ligand field strength remains as one of the major drawbacks of the crystal field theory.

### LIMITATIONS OF CFT :

- 1) Crystal field theory keeps the total emphasis on the metal orbitals without giving any consideration to the ligand orbitals. Therefore, all properties depending upon the ligand orbitals and their interaction with metal orbitals are not explained at all.
- 2) The simple ionic model which is the basis of CFT does not accurately represent the bonding in all transition metal complexes. There is ample

experimental evidence to show that both ionic and covalent bonding play an important role.

- 3) CFT cannot explain satisfactorily the relative strength of the ligands. If ligands are treated as point charges, anionic ligands like  $\text{OH}^-$  should exert more effect and bring out more crystal field splitting than the neutral molecules. But most of the anionic ligands lie at the lower end of the spectrochemical series. Thus  $\text{OH}^-$  lies below the neutral  $\text{H}_2\text{O}$ . Similarly  $\text{NH}_3$  produces greater field than  $\text{H}_2\text{O}$  although the dipole moment are just the reverse. Such results lead to doubt the original assumption of purely electrostatic interactions occurring between the metal and the ligands.
- 4) In spite of the above drawbacks, the crystal field theory has an enormous influence in inorganic chemistry during the last thirty years, because of its essential simplicity. Since the electrostatic model is most nearly valid as in complex halides it is still the treatment most widely used.

### Questions

1. Explain theoretical failure of CFT model.
2. Write short notes on:
  - a) ESR spectrum of metal complexes.
  - b) The nephelauxetic effect.
  - c)  $\text{M} \rightarrow \text{L}\pi$  and  $\text{L} \rightarrow \text{M}\pi$  interactions in complexes.
  - d) High spin and low spin complexes.
3. Write a note on “experimental evidences for covalency in coordination compounds”.
4. Write a note on limitation on CFT.

## Summary

1. Along a transition metal series, with the increase in nuclear charge, ionic radii are expected to steadily decrease. But the variation in their size is not regular and an unusual curve is observed
2. The double humped curve and the variation in lattice energies are explained by crystal field splitting.
3. This hyperfine splitting in ESR is mainly due to the interaction of the unpaired electron of metal with spin with the nuclear spin of the ligand and the magnitude of splitting is proportional to the fraction of electronic charge on the ligand.
4. The expansion of *d* electron cloud is due to the overlap of metal *d* orbitals with ligand orbitals. Such overlapping reduces the effective nuclear charge on the metal and for partial removal of electron density from the central metal atom.
5. Limitation of Crystal field splitting.