CHAPTER III

THEORIES OF CO-ORDINATE BOND

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3.1 INTRODUCTION

To explain the structures, stabilities and general properties of the co-ordinated compounds following theories are used.

- 1) Valence bond theory (VBT).
- The electrostatic theory with its modification of crystal field theory (CFT).
- 3) The molecular orbital theory (MOT).

A fourth theory known as Ligand Field Theory (LFT)(1, 2) is also in use. This theory is the combination of MOT and CFT.

For the understanding of the above theories, the concepts of atomic orbital, bond and bond formation are helpful.

Atomic Orbitals : Quantum mechanically, one electron wave functions are associated with usual quantum numbers, n, l, m. These wave functions obtained for a particular type of atom are termed as atomic orbitals. The number of orbitals for a particular l value is 21 + l and therefore the number of orbitals of s type will be always one, p type three and d type five and so on. The s orbitals are spherically symmetrical and each of the three p orbitals p_x , p_y , p_z consists in two lobes symmetric about the respective axes. There are two groups of d orbitals; d_{xy} , d_{yz} and d_{zx} form one group while $d_x^2-y^2$ and d_z^2 form another,



Fig.31: Boundary surfaces of the s, p and d atomic orbitals, showing the signs of ψ for the corresponding orbitals.

the former group being termed as t_{2g} or d and the latter as e_g or d (Fig. 3.1). The filling of the electrons in the orbitals takes place in accordance with Pauli's and Aufbau principles. The relative energies of different orbitals for elements of different atomic number are shown in Fig. 3.2.

In chemical compounds three types of bonding can take place, ionic, covalent and co-ordinate. The roots of the coordinate bond are found in Werner's postulation of auxiliary valency.

"Even when to judge by the valence number, the combining power of certain atoms is exhausted, they still possess in most cases the power of participating further in the construction of complex molecules with the formation of very definite atomic linkages. The possibility of this action is to be traced back to the fact that, besides the affinity bonds designated as principal valencies, still other bonds on the atoms, called auxiliary valences, may be called into action".

The molecular orbital theory starts by considering a system in which the nuclei are in the equilibrium position in the stable molecule and discusses the way in which the electrons associated in some way with all the nuclei, can be described by a wave-function, which is a molecular orbital. Like atomic orbitals, the mos are associated with appropriate quantum numers and they are filled following 'Aufbau'. The mo can be obtained by LCAO (Linear Combination of Atomic Orbitals) method. For a



Fig. 3.2: Variation of energy levels with atomic number.

diatomic molecule A-B, by using the technique called "variation method" two linear combinations of atomic orbitals each of which is a mo are obtained and are designated as \mathcal{V}_{+} or \mathcal{V}_{q} and \mathcal{V}_{-} or \mathcal{V}_{u} .

The linear combination of s atomic orbitals results in \mathcal{C}_s type of mo, the bonding orbital being written as \mathcal{C}_s and antibonding one as \mathcal{C}_s . When combining p orbitals two types of bonding is possible, \mathcal{C} type and π type. \mathcal{C} and π type of bonding is illustrated in Fig. 3.3.

3.2 HYBRID ORBITALS

The concept of hybrid orbitals is introduced in order to overcome the difficulty regarding the strength of the different bonds formed by an atom in a molecule with two or more identical atoms. In such a molecule the strength of the two identical bonds is the same whereas the orbitals which are used for bond formation are different. The different orbitals of the same atom



Fig. 3:3: σ and π bonding (a) The combination of s atomic orbitals to form σ and σ[#] molecular orbitals.
(b) the combination of p atomic orbitals to form σ and σ[#], and π and π[#] molecular orbitals.

combine linearly to form hybridized orbitals which effect bonding in molecules. The well known examples of such hybrid orbitals are sp in BeF₂, sp² in BF₃, sp³ in methane, d^2sp^3 in $[Co(NH_3)_6]^{3+}$. The type of hybridisation indicates the geometry of molecules. The directionality is definite for hybridized orbitals whereas the energies are definite with respect to parterners in the molecule and the physical state.

3.2(a) Localized and Delocalized Orbitals

The general molecular orbital theory describes the behaviour of electrons by means of orbitals which enclose all the nuclei in the molecule. However, the bond formation is such an important concept that it is customary to modify the general theory and discuss molecular orbitals enclosing two nuclei only. These are referred to as "localized molecular orbitals", as distinct from the delocalized ones which are associated with several nuclei.

3.3 BASIC CONCEPTS IN COORDINATE CHEMISTRY

Before discussing the theories on bonding, it is essential to know the basic terms in coordination chemistry.

1) <u>Complex ion</u> : A complex ion will be understood to be more or less stable charged aggregate formed when a metal atom or ion becomes directly attached to a group of neutral molecules and/or ions.

 Ligands : The latter are called ligands or donor groups and they are said to be coordinated or complexed to the central ion or acceptor in the first co-ordination sphere.

3) The first co-ordination sphere of the complex ion is indicated by enclosing the formula for the ion in square bracket for example $[Co(NH_3)_6]^{3+}$, $[Co(NO_2)_6]^{3-}$.

4) <u>Co-ordination Number (C.N.)</u>: The number of ligand groups arranged in a definite geometry and directly bonded to the central atom/ion is called the co-ordination number (C.N.).

5) <u>Chelate-multidentate ligand</u> : A group which can attach to the same metal ion through more than one of its atoms is termed as chelate or multidentate ligand. Multidentate may be bidentate, tridentate, tetradentate etc.

6) <u>Co-ordination compound</u> : A coordination compound may be one of the two types. Firstly, it may be a neutral complex where in the complex aggregate has no net charge. This may be due to either a central metal atom in the zero oxidation state surrounded by neutral ligands, such as $[Fe(CO)_5]$ or central metal ion surrounded by enough oppositely charged ligands to produce neutral aggregate like $[Co(NH_3)_3(NO_2)_3]$. Secondly, the compound may consist of ions, in which case at least one of these ions must be a complex ion. This is the most common type of complex compound encountered.







Fig. 3:4: Cis and trans isomers with (a) unidentate ligands. (b) bidentate ligands.

One of the characteristics of the complex compound is that the complex ion or neutral complex retains its identity in solution, although partial dissociation may occur. Complexes which exchange ligands rapidly, that is, within mixing times, are referred to as labile complexes, while those which exchange ligands at a slower rate are called nonlabile or inert complexes. Much of the chemistry of coordination compounds is determined by the electronic configuration of the central ion, by the donor and acceptor properties of the ligands, and by the nature of the linkage between the ligand and the central ion.

7) <u>Geometric isomerism</u> : Complexes that are 6-co-ordinated are usually octahedral in shape; very rarely planar and trigonal prismatic structures are also possible. Geometric isomerism and distortions of symmetry arise when all the ligands are not identical chemically. Complexes in octahedral symmetry are shown in Fig. 3.4(a). Two geometric isomers of complex cation $[Co(NH_3)_4Cl_2]^+$ are possible. A green coloured trans-isomer and the other violet coloured cis-isomer. Isomeric forms that can exist with chelates are shown in Fig. 3.4(b), taking example of dinitro-bis-ethylenediamine cobalt(III) ion.

3.4 VALENCE BOND THEORY

The application of the valence bond theory to complexes is originally and mainly due to Pauling (3). It deals with the electronic structure of the ground state of the central metal atom. The orbitals of the complex are designated only in terms

of the central atom orbitals and the hybridization of these to produce bonding orbitals. VBT rests on the following assumptions -

i) The central metal atom must make available a number of orbitals equal to its co-ordination number for the formation of covalent bonds with suitable ligand orbitals. The latter orbitals are not specified precisely by this theory but they are presumed to be filled 5-bonding orbitals.

ii) A covalent 5 bond arises from the overlap of a vacant metal orbital and a filled 6 orbital of the donor group. The metal orbital will be a hybrid orbital formed from the available s, p and d orbitals. The donor group must, therefore, be a chemical species which contains at least one lone pair of electrons. The resulting coordinate bond possesses considerable amount of polarity because of the mode of its formation.

iii) In addition to 6 bond, it is also possible that a π bond may be formed, provided that suitable d electrons of the metal ion are present in an orbital which can overlap with a vacant orbital on the donor atom. This bond will change the charge distribution on both the metal ion and the ligand in such a way as to strengthen the 5 bond.

The strongest covalent bond will be formed when the charge clouds overlap one another as much as possible. In order to satisfy this criterion, it has been shown that the original atomic orbitals should be hybridized to form a new set of equivalent bonding orbitals possessing definite directional

properties. With these hybridized orbitals, orbitals of ligand may be made to overlap (bonds) and electronic configuration can be assigned. From this assigned configuration, magnetic moment can be calculated and may be compared with the experimental value.

3.4(a) Defects in VB Model

When the number of central metal atom orbitals needed to accommodate all of the ligand \mathbf{C} -bonding electrons is too low, it is not possible to assign bonds on the basis of VB approach. As an example, consider the complex ion $[\text{FeF}_6]^{3-}$ which has a magnetic moment corresponding to five unpaired electrons. In this complex ion $d^2 \text{sp}^3$ hybridization can not occur.



Pauling overcame this difficulty by calling such complexes as ionic. The term ionic was criticized as such complexes behave like typical covalent compounds. An alternative suggestion was put forth by Huggin (4). He proposed that outer d orbitals might be used in bond formation. This has been upheld by Craig <u>et al</u>. (5) showing that for highly electronegative ligands inclusion of outer 4d orbitals leads to the stronger bonds than those formed by inner 'd' orbitals. Thus the complexes originally described by Pauling as ionic are supposed to be "upper level covalent" as opposed to "lower level covalent"

complexes. Other terms which are in use are outer and inner orbital complexes (Taube), spin free and spin paired complexes (Nylhom), high spin and low spin complexes (orgel), hypoligated and hyperligated complexes (Pauling).

Apart from the above difficulty the VB approach to complexes is limited due to the following reasons.

- i) VB approach provides only qualitative explanation.
- ii) VB approach fails to predict and to interpret the spectra.
- iii) The approach cannot account for detailed magnetic properties.
 - iv) VB approach does not take into account the splitting
 of the 'd' energy levels.

3.5(a) Electrostatic Theory and Crystal Field Theory

The application of a simple electrostatic theory to the bonding in metallic complexes was carried out primarily by Van-Arkel and De-Boer (6) and by Garrick, F. (7).

They applied the well known potential energy equations of classical electrostatics to their bonding model. This requires a knowledge of such variables as the charge and size of the central atom, and the charge, permanent dipole moment, polarizability and size of the ligand. When this purely electrostatic model is applied to metal complexes with identical ligands, regular configurations result for all coordination numbers. Thus for the common coordination numbers of 2, 4, 6 and 8 the configurations would be linear, tetrahedral, octahedral and square antiprismatic, respectively, since these will reduce the electrostatic repulsion between ligands to minimum. Using this simple model bond energies for some complexes have been calculated which agree with experimentally observed values (8). The model suffers from the following drawbacks.

i) On the basis of this model, the coordination number four corresponds to only tetrahedral configuration and hence the model can not predict square co-planar complexes.

ii) It can not justify the stability of the complexes with non-polar ligands such as CO, PF_3 etc.

iii) It can not justify the fact that ions of the second and third transition series elements form more stable complexes than those of the first series transition elements though the size of the ions of the second and third transition series elements is greater than that of the ions of the first series transition elements.

iv) Finally, along with the other shortcomings, this simple theory is of no help in predicting and explaining magnetic, spectral and kinetic properties of complexes.

3.5(b) Crystal Field Theory

Langmuir in 1919 suggested ionic bonding in complexes and a decade later crystal field theory was developed by Bethe (9). The first application of this theory to transition metal complexes was made in 1932 by Schlapp and Penny (10) and by Van Vleck (11). Significant contributions to this theory and particularly to its applications were made by Balhausen, Jorgensen, Griffith, Nyholm, Owen, Cotton and many others. Orgel (12) was the first to see the consequences of the theory on the stability of co-ordinated compounds of transition elements.

The crystal field theory, like the simple electrostatic approach, proposes to treat metal complexes as if the only interaction between the central atom and the surrounding ligands is a purely electrostatic one. Unlike the simple electrostatic theory, however, it deals with orbitals of the central metal ion. The orbitals of the central metal atom are considered separated from the ligand orbitals and the latter are ignored. Indeed the ligands are considered to be merely point charges or point dipoles. The theory accounts for the effect of the various possible electrostatic fields erising from the differing geometries and strengths of various ligands, on the five d orbitals of a transition metal ion. For the field-free ion or the atom in vacuo, the five d orbitals are degenerate, but the degeneracy is removed in the presence of electrostatic field of ligands. The orbitals $(d_x^2 - y^2)$ and d_2) which lie in the direction of ligands for octahedral symmetry are raised in energy in comparison with those which lie

between the ligands (d_{xy}, d_{yz}, d_{zx}) . The original degenerate levels are split into two parts for octahedral complexes, the $d_{x^2-y^2}$, d_{z^2}) orbitals assume a higher energy and d_{ϵ} (d_{xy} , d_{yz} , d_{zx}) orbitals assume a lower energy. This is illustrated in Fig. 3.5. The fact that all the d levels are repelled slightly by the ligands is indicated by the displacement of the entire set of d levels to some new but unknown value. The higher of these is doubly degenerate and is designated by d \checkmark or e_q and the lower is triply degenerate and is designated as $d_{m{\xi}}$ or t_{2q}. The crystal field splitting is the energy difference between the $\mathsf{d}_{\pmb{\varepsilon}}$ and $\mathsf{d}_{\pmb{\checkmark}}$ orbitals and is measured in terms of a parameter 10Dq. Stronger the field, larger is the 10Dq value. The magnitude of the splitting is erbitrarily set at 10Dq. A theorem of quantum mechanics requires the average energy of the perturbed 'd' levels to remain unchanged. This provides a convenient datum. Then according to this theorem if we add up the crystal field energy of the six $d_{\boldsymbol{\epsilon}}$ electrons with the energy of the four dy electrons, we should get zero. Therefore, the d_ level must be 4Dq below the unknown original energy and d, level must be 6Dq above this original level. The gain in energy achieved by the preferential filling of the low lying 'd' levels is called the crystal field stabilization energy (CFSE).

3.5(c) Distribution of Electrons in the 'd' orbitals

Let us how see carefully at the factors that determine the distribution of the d electrons among the e_g and t_{2g} orbitals.



Fig. 3.5 : Crystal field splitting .

Considering the ground state we find that there are at least two important and opposing, factors which determine the population distribution of d electrons under the influence of a purely electrostatic crystal field. One is the tendency for electrons to occupy, as far as possible, the lower energy orbitals. The other is the tendency for electrons to enter different orbitals with their spins parallel in accordance with Hund's rule. The latter occurrence lowers the Coulombic repulsive energy among the electrons. If there are 1, 2, 3, 8, 9 or 10 d electrons, there are no uncertainties as to where the electrons will go, regardless of magnitude of Δ . This may be seen from Table 3.1 in which d^{10} case is not shown.

On the other hand, for d^{4-7} systems we have two extreme possibilities for each system depending upon the relative magnitudes of the crystal field splitting energy, Δ . This leads to the necessary consideration of two limiting situations known as the strong field or low spin case and the weak field or high spin case, as shown in Table 3.1. The number of unpaired electrons do not always serve to distinguish between strong field and weak field complexes. In d^4 , d^5 , d^6 and d^7 systems, as the magnetic criteria are different for the two types of complexes, the necessary distinction can be brought about. In the d^1 , d^2 , d^3 , d^8 and d^9 systems, however, the magnetic moments of both strong and weak field complexes remain unchanged, hence they must be differentiated by some other technique such as spectroscopic examination.

Species	strong field complex	uncomplexed metal km	wakfield consider
ď1	(ag) ^a	•	(eg)#
aspelerd *	(1 ₂₆) ¹ <u>+</u>	(n.g., Tµlli, VIV)	±(i_{2q}) ¹
e,	(1y) ⁶	• •	(eg) ^d
unpaired -	('m) ⁶ <u>t</u> <u>t</u>	(6.g., Tj#, VW) 2	<u>† † _ (1₂₀)²</u> 2
C.	(4)*	• '• ••	
unpaired *	(14) ⁶ <u>1</u> <u>1</u> <u>1</u> 3	(4.8., ∀8, Cr48, Moss) 3	$\frac{1}{3} \frac{1}{3} \frac{1}{(1_{20})^2}$
d*	(•e)•	* * * *	<u>†</u> (e _g) ¹
unpeirod -	(124) ⁴ <u>14</u> <u>1</u> <u>1</u> 2	(e g., Cr ⁰ , Mn ¹⁰)	<u>† † †</u> (1 ₃₀) ³ 4
ď	(ag) ⁴		$\frac{1}{2}$ $\frac{1}{2}$ $(e_g)^2$
u: iređ #	(124) ² <u>†ř †ř †ř</u> 1	(e.g., Fe ^m , Mn ^u)	$\frac{1}{5} \frac{1}{5} \frac{1}{(1_{2g})^3}$
6	(eg)*		<u>+</u> <u>+</u> () ²
1 1 1997 - 7	(t ₂₄) ⁴ <u>14</u> <u>14</u> <u>14</u> 0	(e.g., Fell, Coll, Rhm, Irm, Ptrv)	$\frac{\underline{1}}{4} \underline{1} \underline{1} (1_{28})^4$
e	(eg) ¹ <u>+</u>	*1 *1 * * *	<u>1</u> <u>1</u> (• ₀) ²
unpaired =	(1 ₂₀) ⁴ <u>14</u> <u>14</u> <u>14</u> 1	(e.g., Co ^{II} , Ni ^{III})	<u>†4 †4 †</u> (1 ₂₀) ⁸ 3
<i>C</i> *	(eg) ² <u>1</u> <u>1</u>	93 93 93 9 9	上土 (•*)2
uspatred -	(t ₂₀) ⁴ <u>tři tři tři</u> 2	(s.g., Ni ²³) 2	<u>11 11 11 (120)⁴</u>
٤.	(ay) ² 11 1	93 93 93 94 9	11 1 (4)*
unpaired -	(134) ⁴ <u>14</u> <u>14</u> <u>14</u> 1	(a.g., CuH)	14 14 14 (140 ⁹

Table 3-1 : Distribution of Electrons in Octahedral Disposition

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4

3.5(d) Factors affecting the magnitude of 10Dg

The magnitude of 10Dq or Δ largely depends upon the magnitude of the electrostatic field presented by the ligands. The factors which are responsible for the field are the size, charge, dipole moment (permanent and induced) and polarizability of the ligands. The ionic charge on the metal ion has a direct effect upon the magnitude of Δ . This is to be expected in terms of the electrostatic crystal field model. The increased charge on the metal ion will draw the ligands in more closely, hence they will have a greater effect in perturbing the metal d orbitals. A few generalizations concerning the magnitude of Δ are given below.

1) \triangle increases about 30 % to 50 % from 3dⁿ to 4dⁿ and by about the same amount again from 4dⁿ to 5dⁿ complexes.

2) \triangle is about 40 % to 80 % larger for complexes of trivalent than for divalent cations.

3) In general, it is possible to list ligands in order of increasing field strength in a spectro-chemical series arrived at experimentally by Tsuchida in 1938 (14) following the work of Fajans (15). The series is as follows -

 $I^{-} < Br^{-} < s^{-2} < scn^{-} < c1^{-} < NO_{3}^{-} < F^{-} < OH^{-} < OH^{-2} < H_{2}O < NCS^{-} < CH_{3}CN < NH_{3} < en < dipy < phen < NO_{2}^{-} < pho sph < CN^{-} < CO.$

3.6 MOLECULAR ORBITAL THEORY AND LIGAND FIELD THEORY

It explains bonding between atoms through the concept of molecular orbitals which are formed by the combination of suitable atomic orbitals of bonded atoms. Formation of molecular orbitals is based on Linear Combination of Atomic Orbitals (LCAO) principle. The method is rather complicated and it is best to consider it in a number of steps.

1) Taking an octahedral complex as an example (Fig. 3.6), the first step in this procedure is to consider how the unhybridised orbitals of the central atom can interact with the ligand orbitals. The orbitals of the central atom involved in \bigtriangledown bonding are, just as in the valance bond approach, the s, p_x , p_y , p_z , $d_x^2-y^2$, d_z^2 . From the spatial arrangements of these orbitals (Fig. 3.1) it would be anticipated that the interaction would be with combinations of ligand orbitals; for example, it would be expected that the p_x orbital would interact with ligand orbitals ς_1 and ς_4 , both to an equal extent.

2) The next step is to combine the orbitals within these sets by taking a linear combination of them. For the above example the combination would be $(\zeta_1 - \zeta_7)$, the negative sign being required because of the change of sign of γ for the p_x orbital on crossing the origin. This new wave function is then normalised. Such orbitals are referred to as "ligand group orbitals". The L.G.O.s are shown in Table 3.2.



Fig.36:Arrangement of the six 6 orbitals about the central atom (at the origin) in an octahedral complex ion.

Central atom Ligand group orbital orbital		Symmetry label	
f	$\frac{1}{\sqrt{6}} \{\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6\}$	¢1,	
Þ.	$\frac{1}{\sqrt{2}} \{\sigma_1 - \sigma_4\}$		
P ₇	$\frac{1}{\sqrt{2}} \{\sigma_2 - \sigma_5\}$	l ₁₀	
P.	$\frac{1}{\sqrt{2}} \{\sigma_3 - \sigma_6\}$		
دو _ د ر ه	$\frac{1}{2}\left\{\sigma_1+\sigma_4-\sigma_2-\sigma_5\right\}$		
4 ₅₂	$\frac{1}{\sqrt{12}}\left\{2\sigma_3+2\sigma_6-\sigma_1-\sigma_2-\sigma_4-\sigma_5\right\}$		

Table 32: L.G.O. for 6 bonding in an octahedral complex.

3) MOs are constructed by taking a linear combination of orbitals. The orbitals which are combined are (i) a central metal orbital, with (ii) the ligand group orbital with the same symmetry. Such a process gives rise to a bonding MO and an antibonding MO, the former lower in energy than the original central atom and ligand orbitals, the latter higner. MOs are labelled using the appropriate symmetry labels given in Table 3.2. Antibonding MOs bear an asterisk. Thus we have six bonding orbitals, the a_{1g} (one), t_{1u} (three) and e_g (two) and six antibonding orbitals the a_{1g}^* (one), t_{1u}^* (three) and e_g^* (two). Their energies, relative to those of original atomic orbitals of the central atom and of the donor orbitals of the ligands, are shown schematically in Fig. 3.7. It should be noted that the t_{2g} d orbitals are non-bonding.

4) The final stage is the filling of the mos with electrons in accordance with the Pauli exclusion principle and Hund's rule.

From the energy level diagram Fig. 3.7, it is seen that the twelve ligand electrons can be accommodated by the bonding orbitals and the n metal d electrons must be placed in the nonbonding t_{29} orbitals and in the antibonding e_g^* orbitals. The electrons may be excited from t_{29} orbital by absorption of energy into the antibonding e_g^* orbital. The greater the overlap of the 3d orbitals of the metal ion and the ligand orbitals, the higher will be the energy of the antibonding e_g^* orbitals. The overlap will be greater, the smaller the effective nuclear charge on the



Fig. 37: Molecular orbital scheme for **S** bonding in an octahedral complex ion.

bonding ligand atom and/or the greater the electronegativity of the central ion. These two properties will help to explain respectively the spectrochemical series of ligands and the so called natural order of stability of complexes. In both the theories, MOT and CFT splitting of 3d orbitals is predicted. In former, splitting is caused by co-ordinate bond formation. π bonding is of greater importance in the square planar and tetrahedral complexes, whereas it is of less importance in octahedral complexes,

The simple and straight forward CFT accounts for 'd' orbital splitting by considering interaction between the central metal ion and crystal field produced by ligands. It gives qualitative and simple explanation for the most of the properties of the co-ordinate complexes. The major fault with CFT is that it does not take into account the partial covalence nature of metal ligand bond. On the other hand the more general Mulliken's molecular orbital theory offers quntitative explanation for the properties of the co-ordinate complexes but is quite lengthy and laborious. Therefore without completely neglecting CFT, people modified it, taking into consideration the main aspect of MOT namely the metal-ligand orbital overlap. Thus the ligand field approach is basically MOT, simplified in the direction of CFT. The main problem continues to be the construction of the mos from the orbitals of the metal ion and those of the ligands.

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