CHAPTER 3

THEORIES OF COORDINATE BOND
In order to explain observed experimental facts and to predict new ones, a theory is essential. Lewis, in 1916, enunciated the electronic theory of valence, which was later extended by Langmuir and other scientists, by means of which it was possible for the chemists to explain Werner's valence concept in terms of electrons. Sidgwick and Lowry expressed and interpreted the Werner's primary valences as arising from electrovalence, which is due to complete electron transfer and secondary valences result from the sharing of an electron pair or the covalence. A primary valence may be ionic or not. An anion present in the first co-ordination sphere, satisfies both the primary and secondary valences. Simultaneously. The modern treatment of coordinate bond in electronic terms is based on quantum mechanics, proposed by Schroedinger and Heisenberg. The Lewis concept of the two-electron covalent bond between two atoms in a molecule was extended by Sidgwick by introducing a coordinate bond, in those cases where both shared pair of electrons originate from the


same atom. Each molecule or ion capable of donating at least
one pair of electrons to the metal ion, form a dative or
semipolar bond, which is represented by an arrow pointing
towards acceptor, M, from donor group, L, i.e. L \rightarrow M. Leaving
aside few exceptions, this donor metal atom will accept electron
pairs until sufficient number of electrons have been obtained
by the donor group in order to reach the effective atomic number
of the metal atom in the resulting complex.

Now-a-days, the following four theories — more or less
distinct approaches to the theoretical treatment of the bonding
and properties of complexes — have been put forward:

1. The Electrostatic Theory — The Crystal Field Theory
2. The Valence Bond Theory
3. The Molecular Orbital Theory
4. The Ligand Field Theory

It should be noted that out of these four theories, the
ligand field theory has specially been designed for co-ordination
compounds, but all these theories have achieved considerable
success in this respect. These theories are given in standard
works, and are, therefore, briefly summarised below:
1. THE ELECTROSTATIC THEORY — THE CRYSTAL FIELD THEORY:

The application of the simple electrostatic theory to the bonding in metallic complexes was first carried out by Van Arkel and DeBoer and by Grarrick. Both the electrostatic theory and the crystal field theories are the same. The crystal field theory, like electrostatic theory, treats the interaction between the metal ion and the ligand as a purely electrostatic problem. The crystal field theory was developed by Bethe, and was applied to transition metal complexes by Schlapp and Penney and by Vanleek to calculate the magnetic susceptibility.

The modifications caused by ligands to the metal ion, partially filled energy levels 'd' orbitals, are only responsible for the physical and chemical properties of the transition metal. In such complexes, where this pure electrostatic theory applies, the ligands may be either anions or neutral dipoles with their cathodic ends directed towards the metal ion. Only those complexes in which the central metal ion, and particularly in those of incomplete 'd' orbitals,

4 Van Arkel, A.; and DeBoer, J.; Rec. trav. chim., 47: 593, 1928.
where changes are brought about by the surrounding ligands, are considered in the crystal field theory.

If the arrangement is a regular octahedral one, e.g.

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\text{[\text{Co (NH}_3\text{)}_6\text{]}^{\text{2+}} \text{ and } \text{[Co (CN)}_6\text{]}^{-2}\text{, electrons in the 'eg' set, i.e., } dz^2\text{ and } dx^2 - y^2 \text{ orbitals will be less stable than those in 't}_{2g}\text{ set, i.e., } dxz, dyz, \text{ and } dx'y'z' \text{ orbitals, because they will be repelled more by the negatively charged ligands on the octahedral axes than will those in the latter orbitals which tend to put their electrons in the empty "corners" of the cube corresponding to the octahedron. In the tetrahedral arrangement of the ligands the geometry is reversed, and the negative ligands are directed towards the alternate corners of the cube, the octahedral axes remaining "empty". The energy level diagram is given below:}
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\text{Five fold degenerate 'd' orbitals.}
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\text{"OCTAHEDRAL COMPLEX"}
2. THE VALENCE BOND THEORY:

It was Pauling\(^9\), who primarily applied the valence bond theory to metal complexes, which deals with the electronic structure of the central metal atom in the ground state, nature of the bonding, stereochemistry and magnetic properties of the complexes. It is based upon the following assumptions.

(1) The covalent bonds equal to the coordination number of the central metal atom are formed with suitable ligand orbitals. The latter electron pairs enter the metal ion orbitals maintaining its original electronic configuration present in the ligand. The ligands orbital are taken for granted to be filled 6'-bonding orbitals.

(2) The overlapping of a vacant hybrid metal orbital formed from the available 'S', 'p' and 'd' orbitals and a filled orbital of the donor group gives rise to a sigma bond. Hence, it must be noted that the donor group must contain at least one lone pair of electrons. The bond so formed is called coordinate bond which is simply a covalent bond making necessary as a consequence the characteristic overlap of two directed orbitals.

(3) If suitable 'd' orbitals and electrons available on the central metal atom overlap with the ligand orbitals, there

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is also a possibility for a $\pi\pi$ bond to be formed, in addition to the sigma bond. Such a bond, i.e. $(M\rightarrow L)\pi\pi$, changes the charge distribution both on the metal atom and the ligand, consequently sigma bond is strengthened. The bond is weakened if it is $(M\leftarrow L)\pi\pi$ bonding.

A covalent bond will be strongest, if the charge cloud overlapping between the metal atom and ligand orbitals is maximum. In order to fulfill the above criterion, the original atomic orbitals are hybridised forming inequivalent bonding orbitals possessing definite directional properties. In an octahedral complex the $d_{x^2-y^2}$ and $d_z^2$ are pointed towards the ligand with $d^2sp^3$ hybridisation, while in a square planar hybrid orbitals, $d_{sp^3}$, $d_{x^2-y^2}$ are utilised.

Since electronegativity$^{10-13}$ is a qualitative concept and defined as the ability of an atom to attract the bonding electrons, Craig et al.$^{14}$ also extended the above concept and showed that with highly electronegative ligands the use of '4d' orbitals probably leads to stronger bonds than those formed with hybrids of '4 sp$^{3}$' orbitals alone.

12 Hinze, J.; and Jaffe, H.H.; ibid, 84: 540, 1962.
The major defects of the valence bond theory applied to metal complexes\textsuperscript{15} are listed below:

1. It is limited to qualitative explanations.
2. The interpretation and prediction of spectral results is not possible.
3. With its aid the detailed study of the magnetic properties is not possible.
4. It is not possible to predict or calculate even the relative energies of the different structures.
5. It does not take into account the splitting 'd' orbitals.

The complexes, which were described by Pauling to be ionic originally, were later on termed "covalent". The other terms, introduced to distinguish apparent two types of complexes are: outer and inner orbital (Taube), spin-free and spin-paired (Nyholm) and high-spin and low-spin (Orgel). Later on Pauling\textsuperscript{16} introduced the new terms hypoligated and hyperligated.


3. THE MOLECULAR ORBITAL THEORY:

In the valence bond method the bonds are the consequences of the overlapping of the electrons in atomic orbitals (often hybridised). The molecular orbitals\(^\text{17}\) start by considering a system of molecular orbitals characterised by a set of quantum numbers, and the molecular orbital will be polynuclear, i.e., it is associated with all the nuclei of the whole molecule. The physical significance of the wave function of these orbitals is the same as the atomic orbitals in atom. The bonding electron pairs are said to be localised between particular atomic nuclei. The electrons are added when the molecules are formed. The Pauli exclusion principle\(^\text{18}\) is obeyed. The lowest energy molecular orbitals are filled first by the electron, following Hund’s rule.\(^\text{19}\)

The molecular orbitals are represented by a combination of atomic orbitals and referred to as linear combination of atomic orbitals (abbreviated as LCAO). For a molecular orbital to be formed it is essential for the atomic orbitals to interact and must (i) possess the similar energy, (ii) they must overlap each other appreciably, and (iii) have the same symmetry with respect to the bonding molecular axis. In an octahedral complex nine valence shell\(^\text{20}\) five ‘d’, three ‘p’ and one ‘S’ of the


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metal ions are available. Six out of these nine (i.e., $d_{z^2}$, $d_{x^2-y^2}$, $s$, $p_x$, $p_y$ and $p_z$) have their lobes lying along the direction of metal-ligand bond (i.e., suitable for sigma bonding), while the remaining three valence shell $d_{xy}$, $d_{yz}$ and $d_{zx}$ are oriented in such a way to form $\pi$ bond. The six ligand sigma orbitals must first be combined so as to form a set of six composite "symmetry" orbitals, each constructed to effectively overlap with a particular one of the six sigma bonding metal atom orbitals. Then each metal atom orbital is combined with its matching symmetry ligand orbital by the LCAO method to give a bonding and an antibonding molecular orbital pair of orbitals. Most ligand atoms possess $\pi$ orbitals. In such cases these must combine with the metal ion $\pi$ orbitals (i.e., $d_{xy}$, $d_{xz}$ and $d_{yz}$ set), and the bonding and antibonding molecular orbitals are formed by effective overlap. To a first approximation, the energies of a bonding and antibonding orbitals are at the same distance below and above respectively, the mean of the energies of the combining orbitals.

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When molecular orbital theory is applied to octahedral complexes it gives satisfactory results. It may also be applied to planar, tetrahedral, linear complexes. But these complexes are less symmetric, hence, simplicity of the energy level diagrams is rapidly lost. Even in tetrahedral complexes there is no centre of symmetry, therefore, it is not possible to keep various kinds of orbital symmetrically distinct from one another.
4. **THE LIGAND FIELD THEORY:**

The term "Ligand-Field Theory" has been suggested and quite widely accepted to cover a more general hybrid approach to transition metal chemistry. A simple model for the description of the bonding in transition metal complexes and the effect of the ligands on the degeneracy of the five 'd' orbitals of the metal ion can be provided with the aid of the ligand field theory.\(^{21,22}\) The latter phenomena helps one to predict the structure \(^{23}\) and magnetic properties \(^{24}\) of the complexes. The 'd' orbitals may be divided into two groups: (i) \(d_{x^2-y^2}\) and \(d_{z^2}\), which are concentrated along the \(z\), \(x\) and \(y\), and are called 'eg' orbitals, (ii) \(d_{xz}\), \(d_{yz}\) and \(d_{xy}\) which bisect the twelve edges of the cube and lie in the \(xz\), \(yz\) and \(xy\) plane respectively and are called 't\(_{2g}\)' orbitals. The basis of the crystal field theory is that in any case metal ion do not mix with the ligands. It never considers the covalency in the metal ligand bond and differs from ligand field theory in this respect. The energy difference between the two sets of orbital is represented by the term 10 Dq or \(\Delta\).


whose magnitude varies for different complexes. But this is not always true. There is some mixing and, therefore, some sort of bonding is present.

The above conclusion may be proved using electron spin resonance spectroscopy, nuclear magnetic resonance spectroscopy, and orbital absorption bands. The essential treatment of the ligand field theory and the crystal field theory is the same except the above difference.

The three interaction parameters, spin orbit coupling constant, \( \lambda \), and the interelectronic repulsion parameters, also known as Racah parameters, \( B \) and \( C \) are of great importance. The spin orbit coupling constant is widely applied in determining the detailed magnetic properties of the transition metal complexes. It accounts for the deviation of real magnetic moments to the calculated spin only value and temperature dependence of the magnetic properties of the complexes. The value of the spin orbit coupling constant, \( \lambda \), is usually found to be 70% to 85% of the free ion value.

This brief survey of the modern theories of the co-ordinate bonding would enable one to appreciate the current researches in co-ordination chemistry.