I N T R O D U C T I O N

Coordination compounds have received great attention in the field of inorganic chemistry during recent years. The renaissance is due to the important roles they play in a large number of widely differing processes of technological and biological importance. A central metal ion bonded to other atoms, ions or molecules constitutes a coordination compound. The surrounding atoms, molecules or ions are called ligands. The metal ion is usually an electron pair acceptor and ligands are electron pair donors. The nature of bonding in coordination compounds can be predominantly electrostatic or predominantly covalent or intermediate between the two extremes depending on the mode of sharing of electron pairs between the metal ion and the ligands. The number of electron pairs involved in bonding is called the coordination number which is known to have the values from 1 to 12 but 4 and 6 mostly predominate. Ligands are called monodentate, bidentate or polydentate depending on numbers of coordination sites satisfied by them about the metal ion. Ligands, capable of forming a ring structure after coordinating with the metal ion, are called chelating agents and the resulting agglomeration is termed a metal chelate. The phenomenon is called chelation.

The tendency for coordination with ligands has been observed with all metal ions but transition metal ions have proved to be most versatile in this respect. On the other hand, the tendency to donate electron pairs is limited to the more electronegative elements such

as, carbon, nitrogen, phosphorus, arsenic, oxygen, sulphur,fluorine,
chlorine, bromine and iodine of groups IV, V, VI and VII of the
periodic system. The ability of a ligand to coordinate depends
mainly on the nature of atoms or groups present in it i.e. their
electronegativity and stereochemistry.

The historical development of the chemistry of coordination
compounds may be dated back to the end of the eighteenth century. In
1798, Tassaert was the first to isolate orange crystals of $CoCl_3.6NH_3$
by mixing aqueous solutions of $CoCl_2.6H_2O$ and ammonia and allowing
them to stand in air. Several compounds of this kind were reported
in the following century. However, theories prevailing in those days
were inadequate to explain the structure of the complexes and much
success was not achieved.

Towards the end of the nineteenth century, research in the
field of coordination chemistry was dominated by the Danish chemist
S.M. Jörgenssen and Swiss Alfred Werner as well as many others. These
two distinguished chemists prepared varieties of ammine complexes of
cobalt(III), platinum(II), platinum(IV), chromium(III) and
palladium(II) and studied their physical and chemical properties
such as transformation, occurence of isomers[1], ionisation etc. It
was Werner who had the genius to correlate the experimental facts
on many different systems and proposed his coordination theory in
1891 introducing the concept of primary and secondary valences and
suggested that the primary valences were those which satisfied the
charge of the metal ion and the secondary valences were those used in
attaching coordinating groups.According to the theory,the hexammine

cobaltic chloride is formulated as: $\underline{/}$Co(NH$_3$)$_6\underline{/}$Cl$_3$ where chloride ions satisfy the primary valences and ammonia molecules satisfy the secondary valences.

The nature of bonding in coordination compounds has been undeniably a challenging and exciting problem since the early days of coordination chemistry. Amongst the earlier workers, G.N.Lewis was the first who laid down the foundation of electronic theory of valence recognizing that stable shells of electrons could be created by the transfer of electrons from one atom to another forming ions or by the sharing of two electrons between two atoms forming a covalent bond. There has been phenomenological development on these concepts notably by I. Langmuir, N.V. Sidgwick and L. Pauling[2] which led to the emergence of valence bond theory. The theory has been successful in explaining the nature of bonding in most of the compounds and predicting their structures but was unable to expalin the bonding in electron deficient compounds like boron hydrides and certain other facts such as absorption spectra. In order to remove the inadequency of the valence bond theory, the crystal field theory was revived from the early works of Bethe[3] and Van Vleck[4].

The crystal field theory treats the interaction between the metal ion and the ligands as a purely electrostatic problem in which the ligand atoms are represented as point charges. At the opposite extreme, the molecular orbital theory describes the metal ligand interaction in terms of molecular orbitals formed by the overlap of ligand and metal orbitals.

The crystal field theory considers the effect of approach of ligands on the d-orbitals of a transition metal ion. The orientation of the five d-orbitals are depicted in Fig. 1 and the approach of the ligands in an octahedral complex by L's. The electrons of the d-orbitals are repelled when ligands approach along the cartesian axes, but the electrostatic repulsion is greater for $d_{x^2-y^2}$ and d_{z^2} as compared to d_{xy}, d_{yz} and d_{xz} since the lobes of the two former orbitals lie along the direction of approaching ligands. The result is that the energy of $d_{x^2-y^2}$ and d_{z^2} orbitals is raised relative to the energy of d_{xy}, d_{xz} and d_{yz} orbitals i.e. the degeneracy of the five d-orbitals is destroyed. In an octahedral field the d-levels are split into an upper group of two(e_g) and a lower group of three (t_{2g}) orbitals (Fig.2). The energy difference between the two levels is represented by the symbol ΔE or 10 Dq. It is apparent that the magnitude of splitting depends upon the strength of the crystal field. The splitting of d-levels in other symmetries can be considered in a similar way and the relative energy for Td and D_{4h} fields are also shown in Fig. 2. This theory has been successful in explaining the absorption spectra of the complexes[5-11]. However, it takes no account of the partly covalent nature of the metal-ligand bonds and therefore whatever effects and phenomenon stem directly from covalence, such as electron spin resonance spectra of $IrCl_6^-$, are entirely inexplicable in simple crystal field theory.

The molecular orbital theory developed by Hund and Mulliken[12] for covalent molecules has been extended to construct molecular
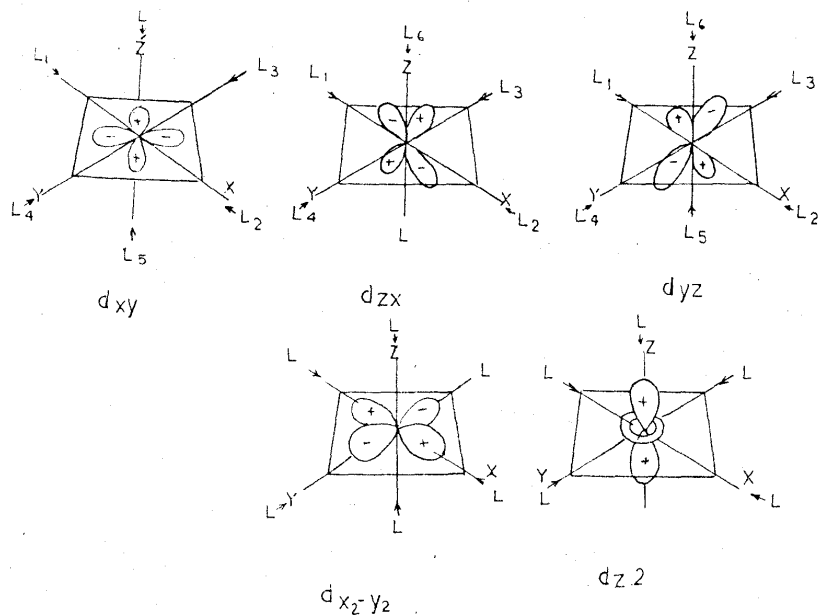
d_{xy}

d_{zx}

d_{yz}

$d_{x_2^-y_2}$

d_{z^2}

FIG.1. THE d-ORBITALS AND APPROACH OF LIGANDS IN
AN OCTAHEDRAL FIELD.

t_{2g}

e_g

e_g

$10D_q$

t_{2g}

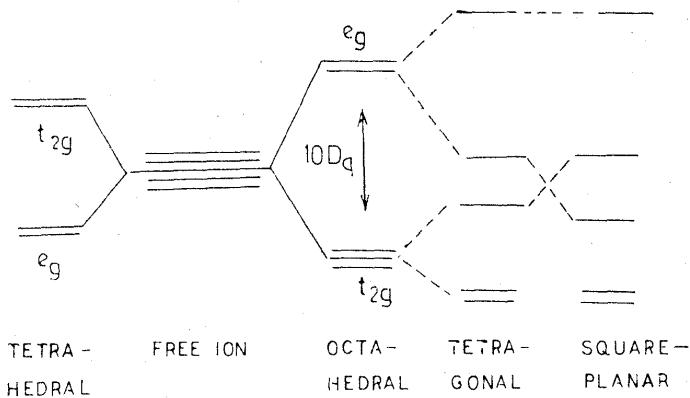| TETRA-HEDRAL | FREE ION | OCTA-HEDRAL | TETRA-GONAL | SQUARE-PLANAR |

FIG. 2. SPLITTING OF d-ORBITALS IN DIFFERENT CRYSTAL FIELDS.

orbitals of coordination complexes. These orbitals are of the form[13]

$$\Psi_{M.o} = \Psi(\Gamma) + \sum_i a_i \Psi_i$$

where $\Psi(\Gamma)$ represents the wave function of the central metal atom transforming in the molecular point group as the irreducible representation and $\sum_i a_i \Psi_i$ is a linear combination of the wave functions of the ligand transforming as the same irreducible representation. The theory has successfully accounted for several features of the complexes.

The most versatile and perhaps the most nearly correct is the ligand field theory which has been developed from an amalgamation of the crystal field theory and molecular orbital theory. Ligand field theory takes into account the extent of metal-ligand interaction by the parameter Dq, which can be experimentally determined. The parameter Dq can be theoretically evaluated by taking all metal-ligand interactions into consideration,

The splitting of the metal ion terms of all atomic configurations by the ligand field is dealt with in a more sophisticated way by ligand field theory. The most general and useful theoretical treatment for the interpretation of the visible spectra of chelates is proposed by Tanabe and Sugano[14]. The theory depends upon three parameters for interpretation, namely Dq, the ligand field parameter which has the same significance as in the crystal field theory and Racah electron repulsion parameters B and C. The Racah parameters for free metal ion are determined from atomic spectroscopy of the ion. From theoretical view point, these parameters are the numerical values of the coulombic repulsion and exchange integrals

between electrons of various states and measure the natural
separation of the terms of the metal ion.

Studies on metal cluster complexes have become of considerable
interest to inorganic chemists·in recent years. The reasons for this
interest are the fundamental importance in exchange interaction,with
theory of bonding, in new magnetic materials research and in
understanding their role in biological and technological processes.

Most of the metal chelates which have been extensively
studied involve the coordination of the various donor atoms of the
polydenate chelating agents towards a single metal ion. As a matter
of fact, there are only a limited number of chelating agents which
either form chelate rings with two metal ions or span towards two
metal ions during coordination yielding bi or polynuclear metal
complexes. In recent years, it has been realised that oxime
complexes can be further used to form metal cluster complexes and
clathro compounds. The present investigation deals with the studies
on some oximes and related ligand metal complexes which have been
further used to form polynuclear and encapsulated compounds.
Therefore, it would be appropriate to describe here a review of the
earlier work in this field inorder to provide a background to the
present work.