CHAPTER ONE

Introduction and literature survey.

A study of the existing literature reveals that from the inception of the twentieth century, the study of complex compounds has become a field of active interest. In tracing the stages of development of a specific field of science mostly two distinctly apparent, unconscious and conscious periods can be observed. In the field of complex compounds, however, such partition does not exist. Even after the scientists had found various useful applications of complex compounds, the knowledge about their chemistry was still in the infancy. Thus the complex compounds embody a field that is old in terms of its applications but is new so far as its chemistry is concerned. The complex compounds have now found enormous applications in the field of analytical chemistry, drugs and various industries. It has even been recognised that the very basis of human and plant lives are hinched on porphyrin complexes of iron (hemoglobin) and magnesium (chlorophyll), respectively. The natural consequence has been that the field has invited the attention of more and more research workers.

According to the definition of the commission on the nomenclature of inorganic compounds[1] " A complex or coordination species is a molecule or ion consisting of a central metal atom or cation with several anions or neutral molecules linked to it". The groups linked to the central metal atom are termed ligands. A close study of the development of the phenomenon of complex formation reveals that Hittorf[2] in 1859 was first to use the term complex in connection with chemistry. This was followed by the isolation and analysis of several "addition compounds" obtained by the combination of cobalt salt with ammonia. Claus, Blomstrand and Jorgensen made attempts to interpret the structure of the above so called complex compounds. No satisfactory explanation could, however, be put forth to explain the structure of the complex compounds till Werner propounded a theory in 1891.

Werner first proposed that even after the normal combining capacity (ionisable primary valency) of a metal ion is exhausted, neutral groups or negatively charged ions get linked in the first sphere of attraction of the metal ion by nonionisable auxiliary valency and lead to the formation of the complex compounds, with ions in the second sphere of attraction. A specific number of groups was found to be attached in the first sphere of attraction of the different metal ions in a definite geometrical pattern. The characteristic number of groups was termed coordination number.

With the introduction of electronic theory of valency, Sidgwick in 1921 rationalised Werner's concept of auxiliary valency in terms of coordinate linkage. He observed that the characteristics common to all molecules and ions capable of being linked with the metal ion is that they possess a lone pair of electrons. During complex formation these lone pair of electrons are donated by the ligands to the electron deficient central metal ions. By coordinating with a specific number of ligands, the metal ion attains an effective atomic number same as the atomic number of the nearest inert gas. This accounts for the stability of the complex compounds. Certain ligands possess more than one donor atom and result in the formation of ring structure by occupying more than one coordination position around the metal ion. Such ligands are termed polydentate and the resulting ring structures are known as chelates. Sidgwick's theory, however, failed in many cases. Further, with the advancement of the wave mechanical concept in the field of the interpretation of covalency, a new approach to the phenomenon of coordination was inavitable. Three different approximations were propounded to explain the formation of complex compounds during 1930's.

The valence bond theory was introduced in the case of complex formation by Pauling[3] with the presumption that the coordinate linkage is a special case of covalency and is formed by the interaction of a vacant orbital and a doubly filled orbital. The ligand molecules with one lone pair of electrons are supposed to provide the filled orbitals. In the metal ions vacant (n-1)d, ns and np orbitals, differing slightly in energy, undergo hybridization with redistribution of electrons in 3d orbitals, if necessary. Depending on the number of d orbitals available, different types of hybridizations d^2sp^3, dsp^2 or sp^3 take place resulting in hybridized orbitals directed towards the corners of an octahedron, square plane or tetrahedron, respectively. The overlap of such vacant hybridized orbitals with the filled orbitals of the ligand atoms results in complexes with the corresponding spacial geometry. In the cases, where redistribution of electrons takes place, the magnetic moment of the complexes differs from that of the free metal ion. Such complexes, involving in hybridization, d orbitals from (n-1) shell and s and p orbitals from n shell, are more stable and are termed penetration or inner orbital complexes[4]. This is possible in case of complexes of ligands with strong electron donating tendencies. In case of weaker ligands, energy of complex formation may not be sufficient to cause the pairing of electrons in lower d orbitals and hence the hybridization involves ns, np and nd orbitals. Such compounds are termed outer orbital complexes[4] and involve more of ionic wave function in terms of Pauling's ionic covalent resonance and are expected to be weaker complexes.

The M-L bond of the above type have a σ symmetry and hence d_{xy}, d_{xz} and d_{yz} orbitals of the metal with π symmetry undergo orthogonal overlap with the ligand atom orbitals. However, in case of ligands atoms with vacant π orbitals (e g. $d\pi$ in PH_3, SH_2, AsH_3 and $p\pi$ in CO, dipyridyl etc.) filled metal atom orbitals d_{xy}, d_{xz} and d_{yz} can interact with the above vacant π orbitals on the ligand atom and form M-L $d\pi$-$d\pi$ or $d\pi$-$p\pi$ type of bonds. The σ and the π bonds mutually stabilize each other and thus the complexes involving π bonds are more stable.

Because of its satisfactory pictorial representation of the phenomenon of complex formation, valence bond theory enjoyed sufficient popularity till 1950. However, the approach proved inadequate to allow quantitative predictions about the stability of the complexes and their absorption spectra.

The molecular orbital approximation of covalent bond formation was, therefore, ushered in the realm of complex formation by VanVleck[5] and Mulliken[6]. The theory starts with the presumption that the electrons of the metal and ligand are not localised but move in molecular orbitals extending over all the atoms involved in the complex formation. The molecular orbitals are considered to be formed by the combination of 3d(eg), 4s(a_1g) and 4p(t_1u) orbitals of the metal ions with the composite orbitals of same symmetry made up by the combination of ligand atom orbitals. This results in the formation of six bonding and six antibonding molecular orbitals with σ symmetry. The t_2g orbitals of the metal atom remain nonbonding in the absence of the composite orbitals with π symmetry. In cases where the ligand atoms have got vacant π atomic orbitals, they provide the composite orbitals of the required symmetry to combine with the t_2g orbitals of the metal atom and thus π bonding and π antibonding molecular orbitals are formed.

The electrons are fed in the molecular orbitals in the increasing order of energy and the total number of effective bonding electrons determines the stability of the complex. Greater the separation between the bonding and antibonding M.O's, the higher is the energy liberated by an electron going to a bonding M.O.. Consequently in case of complexes with greater overlap of metal and ligand atom orbitals and specially with π bonding, a higher order of stability can be expected.

Though the above theories considered metal-ligand bond to be purely covalent, the probability of electrostatic attraction between the metal ion and the anionic ligand or the negative end of the ligand dipole appeared equally convincing to another group of scientist. This led Bethe[7] and VanVleck[8] to propose the crystal field theory which is essentially an electrostatic approach. This made an advancement over the classical electrostatic theory in considering that herein the central metal ion is subjected to an electrical field of a specific symmetry and magnitude depending on the arrangement of the ligand anions or negative end of the polar ligand molecules. The electronic system of the metal ions is perturbed due to this electrical field and the degeneracy of the metal d orbitals is split up. In particular those electrons which lie in ligand direction will be repelled more strongly and therefore are raised in energy more than those lying away from the ligand. If six negative ligand ions are disposed closely around metal ion following an octahedral geometry along X, Y and Z axis, an electron in either the $d_{x^2-y^2}$ or d_{z^2} orbitals (eg) will be repelled more strongly by the negatively charged ligand as compared to the electrons in the d_{xy}, d_{xz} or d_{yz} orbitals (t_2g). The degeneracy of the d orbitals is thus resolved. The amount of energy by which the higher doubly degenerate eg orbitals are separated from the lower triply degenerate t_2g orbitals is termed crystal field splitting (Δ or 10Dq) and the value is dependent on the intensity of the electrical field created by the ligand.

Redistribution of the electrons with preferential filling of the low lying orbitals results in the liberation of crystal field stabilization energy and this accounts for the stabilization of the complex ion. The fact whether the pairing of the electrons will take place in the lower orbitals is dependent on whether the crystal field splitting is more than the pairing energy. In the weak field cases, therefore, pairing can not take place and high spin complexes are formed with liberation of lesser CFSE. Thus the crystal field theory explains the formation of Pauling's inner and outer orbital complexes.

In case of complexes with square planar or tetrahedral dispositions of the ligands, the metal d orbitals split up in accordance with the geometry. The t_2g and e_g orbitals undergo further splitting in a square planar field and the order of the energy of t_2g and e_g orbitals is reversed in a tetrahedral field. The magnitude of the Δ is always small for tetrahedral complexes and hence they are less abundant.

Absorption spectra of metal complexes :

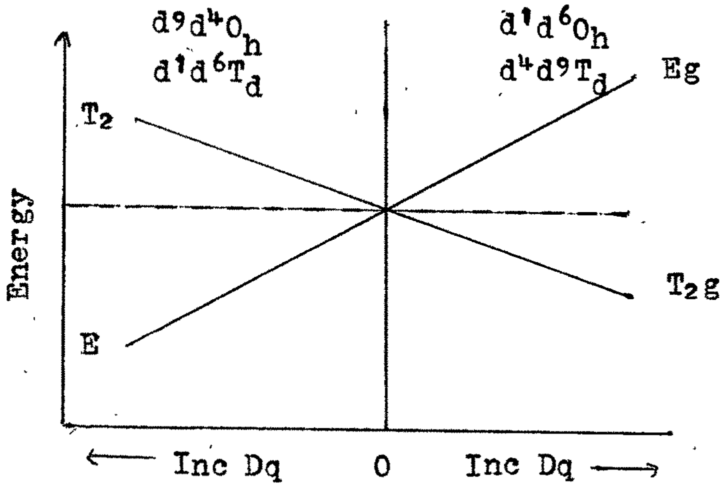
The crystal field theory can also explain the visible spectra of complexes very satisfactorily. The ground spectral state in the metal ion can be worked out by considering Russell Saunders coupling[9]. For the d^1 case the ground state is ^2D. With the splitting of the d orbitals due to the imposed ligand field, the ground spectral state also gets split up into lower T_2g and higher Eg states. The transition of electron from Eg → T_2g results in the absorption of energy in the visible range and a peak is observed in the absorption spectra as in case of $[Ti(H_2O)_6]^{3+}$[10]. In case of multielectronic systems, the individual orbital angular momentum of electrons add up vectorially to give the total azimuthal quantum number L. The individual spin moments undergo algebric summation to yield the total S. LS coupling takes place vectorially to yield the resultant momentum described by the quantum number J. In cases where the spin orbit coupling of the individual electron is high, the individual j's add up to yield the resultant J. This is known as j-j coupling. The rules for determining the term symbol of the ground state of an element can be summarised as follows :

(1) Maximize the spin multiplicity.
(2) Maximize orbital angular momentum
(3) Select the maximum J value for the ground state if the sub-shell is more than half field and the minimum value, if the sub-shell is less than half field.

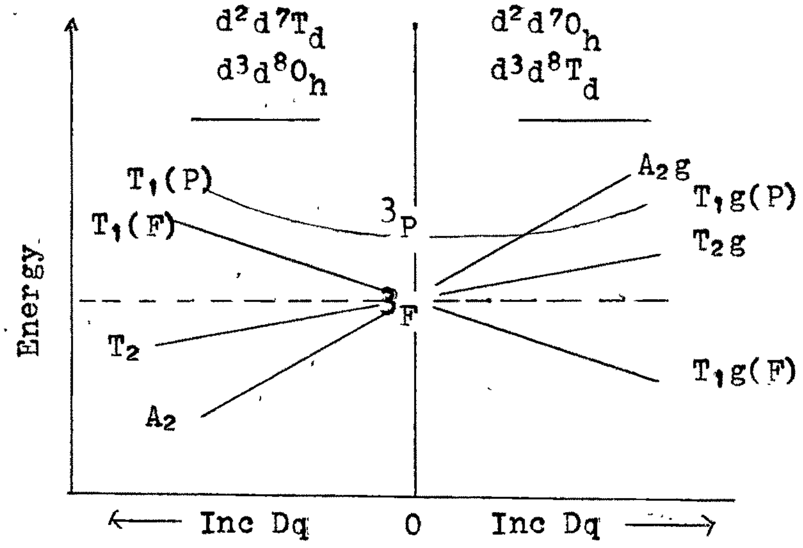
For the d^2 case V(III), the ground state works out to be $^3F_2$. This has L = 3 and hence should be heptadegenerate. The "Pigeon hall" diagram[11] gives better idea of the degenerate states. If the two electrons are arranged in the different pairs of d orbitals with parallel spin, ten possibilities will arise. Out of these seven have the same energy and represent the ground ^3F state. The rest three, where the electrons get nearer to one another are slightly higher in energy and represent ^3P state. Even at room temperature the transition of electron from ^3F to ^3P is possible. Ground state can be similarly worked out for the metal ions with d^3 to d^9. It is observed that the ground state for a metal ion with a specific number of electrons in the d orbitals is same as the ground state for the metal ion with equal number of holes. The metal ions with d^1 and d^9 configuration have got the ground state term ^2D. As discussed earlier for d^1 case, in d^9 case also, in an octahedral field, the ground spectral state

^2D gets split up into lower E_g and higher T_{2g} states. The order of the energy of the split up state is observed to be reverse of d^1 case, because a hole is stable where an electron is unstable. Only one transition should therefore be possible leading to a spectrum with a peak in the visible range.

d^2 and d^8 cases have the same ground state ^3F. The seven fold orbital degeneracy of the ^3F state gets split up into two triplet states $T_1g(F)$ and $T_2g(F)$ and a non-degenerate state $A_2g(F)$. The ^3P state degeneracy is not split up in the octahedral field and remains as $T_1g(P)$ state. To speak in general terms these split up states represent the position of two electrons in the t_2g and e_g orbitals. The ground state $T_1g(F)$ indicates the presence of both the electrons in t_2g orbitals, $T_2g(F)$ and $T_1g(P)$ indicate the presence of one electron each in the t_2g and another in e_g orbital. The non-degenerate A_2g indicates both the electrons being present in the higher e_g orbitals. The splitting of the spectral states in the d^1, d^9, d^2 and d^8 cases can be represented by the following Orgel diagram[12].



Orgel diagram for d^1, d^4, d^6 and d^9 complexes.



Orgel diagram for d^2, d^3, d^7 and d^8 complexes.

The d^8 case has similar splitting as d^2 but the order of energy is reverse of the d^2 because of same reason as extended in case of d^1 and d^9. Just as the splitting of orbitals in a tetrahedral field is reverse of octahedral field, the order of the spectral states in tetrahedral and octahedral field is also opposite. Thus d^9 tetrahedral and d^1 octahedral complexes have identical Orgel diagrams. Similarly Orgel diagram for d^8 tetrahedral and d^2 octahedral are alike.

Thus $Cu^{2+}(d^9)$ and $Ni^{2+}(d^8)$ have, respectively, ^2Eg and ^3A_2g ground states in octahedral field and ^2T_2g and ^3T_1g ground states in the tetrahedral field. On absorption of energy, the transition to higher energy state is possible. Since the absorption in the ultraviolet or visible range requires a change in the dipole moment, the following selection rules govern the absorption spectra of the complexes.

(1) Transitions between the states of different multiplicity are multiplicity forbidden.

(2) In a molecule which has a centre of symmetry $g \longrightarrow g$ and $u \longrightarrow u$ transitions are Laporte forbidden.

(3) Simultaneous excitation of more than one electron is not allowed.

Thus in accordance with the second condition no d — d transition should be allowed in octahedral complexes. However, due to vibronic coupling, the Laporte forbidden transitions are allowed in octahedral complexes. They result in absorptions of low intensity.

The multiplicity forbidden transitions are also allowed in same case e.g. Mn^{2+} (d^5). Excitation of two electrons may also take place. However, these will result in bands with lower intensity.

In accordance with the above rules, the following transitions should be allowed in Ni^{2+} octahedral complexes.

$$^3A_{2}g(F) \longrightarrow {}^3T_{2}g(F)$$

$$^3A_{2}g(F) \longrightarrow {}^3T_{1}g(F)$$

$$^3A_{2}g(F) \longrightarrow {}^3T_{1}g(P)$$

These are all Laporte forbidden and hence extinction coefficient is low. The first one is a low energy transition and is observed in the near infra red region. The second one occurs in the visible range and the third is a high energy transition appearing in the ultraviolet region. This is true for a symmetrical octahedral field. In case of octahedral Ni^{2+} complexes with non-equivalent ligands, the cubic symmetry gets reduced to D_{4h} (distorted octahedral or square planar). This involves further splitting of the spectral state and hence the nature of the spectrum undergoes a change.

In the tetrahedral field the transitions possible are

$$^3T_1g(F) \longrightarrow {}^3T_2g(F)$$

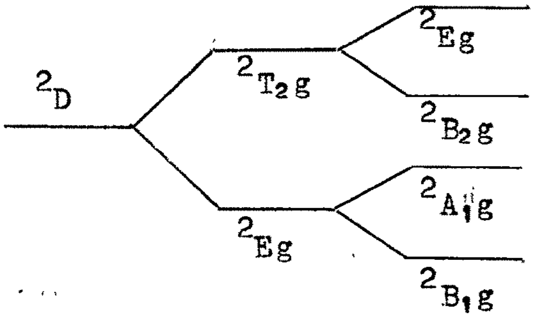
$$^3T_1g(F) \longrightarrow {}^3T_1g(P)$$

$$^3T_1g(F) \longrightarrow {}^3A_2g(F)$$

Since the tetrahedral complexes have no centre of symmetry, the d — d transitions are allowed and hence the extinction coefficient of the peaks in the spectra of tetrahedral Ni^{2+} complexes is expected to be high[13].

In Cu^{2+} complexes (d^9 case) there should be only one transition expected in both octahedral ($Eg \longrightarrow T_2g$) and tetrahedral ($T_2g \longrightarrow Eg$) complexes.

However, in accordance with Jahn-Teller theorem[14] the octahedral Cu^{2+} complexes undergo distortion. As a result of it there is further splitting of the t_2g and e_g orbitals and the redistribution of electrons results in the liberation of extra amount of energy and this stabilizes the complex. Consequently both the spectral states ^2Eg and ^2T_2g undergo further splitting into two components each as shown in the following figure :



Three transitions should, therefore, be possible corresponding to

$$^2B_1g \longrightarrow {}^2A_1g$$

$$^2B_1g \longrightarrow {}^2B_2g$$

$$^2B_1g \longrightarrow {}^2Eg$$

These bands are closely spaced and in some cases may overlap each other.

The d-d transition bands in the ultraviolet range may some time be overlaped by the charge transfer bands. The latter, however, have much higher extinction coefficient and can be differentiated from the d-d transition bands.

Magnetic susceptibilities of metal complexes :

The crystal field theory is also helpful in explaining the magnetic properties of complex compounds. The paramagnetism in a complex of a transition metal ion arises from the spin and orbital moments of the unpaired electrons. The presence of the two forms of the electronic motions turns an atom into small magnetic dipole with a magnetic moment - $\mu = (L + 2S)\beta$. (where L = total orbital angular moment and S = total spin moment).

As a result of the assembly of such a set of magnetic dipoles, a paramagnetic substance is attracted by an imposed magnetic field. It also leads to the Curie-Weiss law[15] for the variation of magnetic susceptibility of a substance with temperature.

In case of orbitals with paired electrons, the magnetic moment of the individual electrons cancel out and hence there is no resultant paramagnetism. They, however, contribute diamagnetic effect because on imposing a magnetic field, the planes of the doubly filled orbitals get tipped slightly so that a small orbital moment in the direction opposite to the applied field is induced. It is because of this opposition that diamagnetic substances are repelled from magnetic fields. Even in case of atoms with magnetic moment due to unpaired electrons, there is a diamagnetic effect working against paramagnetism due to the inner filled shells. The observed paramagnetism is therefore a difference of the true paramagnetism and the diamagnetic effect. This correction has to be considered in the determination of true paramagnetism of substances. The magnetic moment contributed by the electron by spinning on its axis in termed the spin moment and it is expressed by the equation :

$$\mu_s = g\sqrt{S(S + 1)}$$

where μ_s = spin moment, S = spin quantum number and g = Lande' splitting factor and has a value 2.00023 for a free electron. In case of many electrons systems the sum of the spin quantum number of all the spin unpaired electrons is put as the value of S in the above equation. (e.g. 3/2 in case of three unpaired electrons).

However, the electrons are associated with orbital moment contributing to paramagnetism and hence the equation for calculating the magnetic moments changes to

$$\mu_{s+L} = \sqrt{L(L + 1) + 4S(S + 1)}$$

where L = the total azimuthal quantum number. The spin and orbital moments, however, do not remain free and there is appreciable spin orbital coupling in a molecule or an ion. The magnetic moment expected in such cases is dependent on the value of the total angular momentum J of the ground state of the atom which is obtained by L - S coupling as discussed earlier (page 7). The net magnetic moment can be calculated in such cases by using the following equation :

$$\mu_{s.o.} = g\sqrt{J(J+1)} \qquad (1.0)$$

This is found to be true in case of gaseous ion and in case of the compounds of rare earth metal ions. The magnetic moments of the first row transition metal complexes, however, work out to be less than the value theoretically expected from the equation (1.0). The moments are often found to be close to those calculated considering the spin moments only. This difference arises because of the quenching of the orbital moment due to the resolution of the d orbital degeneracy by the imposed ligand field. For example when rotation occurs by occupation of d_{xy} and $d_{x^2-y^2}$ orbitals, this gives the electrons an orbital angular momentum around the Z axis. A ligand field splits the degeneracy of the $d_{x^2-y^2}$ and d_{xy} orbitals, thus restricting the rotation of electron around the Z axis and quenching the orbital momentum. In an octahedral or tetrahedral complex, e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) can not be used by the electron to rotate about the axis and these orbitals can not contribute to the orbital angular momentum.

Further in cases where t_2g orbitals are half filled or completely filled, rotation involving d_{xy}, d_{xz} and d_{yz}

orbitals is also not possible and hence there is no orbital moment contribution. Only in the cases where the ground state has incompletely filled t_{2g} orbitals, primary orbital moment contribution is present. The simplicity of the picture is, however, lost because even in some cases where complete quenching of the orbital momentum is expected from the above consideration, the magnetic moment values are higher than the spin only value. This may be possible where the higher energy state of the same multiplicity as the ground state but with the possibility of orbital moment contribution, is not very much separated from the ground state. There is some mixing of such higher levels with the ground states, thus bringing in some orbital moment contribution. The spin and orbital moment contribution in case of Ni^{2+} and Cu^{2+} complexes studied in the present investigation have been discussed later in the thesis.

Evidence of orbital overlap and ligand field theory :

Though the crystal field theory has been successful in interpreting various aspects of the magnetic and visible spectral characteristic of the complex compounds, the latter study gives evidence for the metal and ligand atom orbital overlap. The Orgel diagram (page 9,10) based on crystal field theory,have been drawn with the consideration that the difference in energy of the spectral states of a gaseous metal ion remains unchanged, even when the ligand field is imposed on the metal ion in the complexes. Thus the crystal field theory considers Δ as the only variable factor. However, with these consideration the experimental spectra obtained can not be fitted into the Orgel diagram. It is invariably observed that the fittings can be improved if it is considered that the separation between the ground spectral states is reduced in the complexes. A quantitative calculation of the energy of 3p state of the Ni^{2+} ion in complexes obtained from spectral data is found to be less than the free Ni^{2+} ion value as obtained from emission spectral studies[16]. This decrease is represented by the percentage decrease of Racah-parameter (β) which is a measure of inter electronic repulsion. Such decrease has been attributed to the increase in the distance between the electrons due to the expansion of d electron clouds of the metal ions on the ligand atom orbitals. This widening of the d electron cloud is termed Nephelauxetic effect[17] and the percentage decrease in the Racah-parameter is a measure of it. In other words this indicates the extent of the overlap between the metal and the ligand atom orbitals and shows the amount of covalency present in the metal ligand bond. The evidence of metal and ligand atom orbital overlaps has also been obtained from various other studies e.g. N.M.R., E.S.R. and Mossbauer spectral studies[18] etc..

This has led to the introduction of ligand field theory to explain the formation of complexes. It is the outcome of the joint attempts of a number of scientists like Orgel, Nyholm, Owen, Liehr and others[19] who showed that the incorporation of some of the concepts of molecular orbital theory into the basic assumption of the crystal field theory leads to a better understanding of the magnetic and spectral characteristics of the complex compounds. Thus the ligand field theory has brought a happy compromise between the crystal field theory and the molecular orbital theory.

In this flexible hybrid approach the computational advantages of the crystal field theory are largely preserved and this helps in interpreting the stability and the lability of the complex compounds to a large extent. These two terms need being explained.

The stability of the complex compounds :

The term stability as applied to complexes indicates the extent to which metal and ligand have a tendency to combine. Bjerrum first introduced the concept that the formation and dissociation of complex molecules in solutions take place in the following successive steps :

$$M + L \rightleftharpoons ML \qquad (1.1)$$

$$ML + L \rightleftharpoons ML_2 \qquad (1.2)$$

$$ML_{i-1} + L \rightleftharpoons ML_i \qquad (1.2_i)$$

$$ML_{N-1} + L \rightleftharpoons ML_N \qquad (1.2_N)$$

each step being characterised by a step-wise formation constant K_1, K_2 ..... K_N. The overall stability constant is the product of all these constants. In these equations N is the metal ion and L the ligand shorn of all ionisable H atoms. The charges are omitted for clarity. Each step is governed by the corresponding equilibrium constant defined as :

$$\mathbb{K}_i = \frac{aML}{aML_{i-1} . aL} \quad ..... \qquad (1.3)$$

$\mathbb{K}_i$ is called the i^{th} metal ligand stability or formation constant governing an equilibrium of the type

$$ML_{i-1} + L \rightleftharpoons ML_i \quad ...... \qquad (1.4)$$

The term 'a' in (1.3) denotes the activities of the constituents.

As a first approximation the concentrations, denoted by [ ] can be used instead of activities provided the measurements are carried out with small concentrations of reacting ions in a solution of a highly dissociated neutral salt, e.g. a perchlorate. K_i is then defined as :

$$K_i = \frac{[ML_i]}{[ML_{i-1}].[L]} \quad \ldots\ldots \qquad (1.5)$$

K_i is termed the i^{th} stoichiometric metal ligand stability or formation constant.

Now β_i can be defined as :

$$\beta_i = \frac{[ML_i]}{[M]\,[L]^i} = \prod_{i=1}^{i} K_i \quad \ldots\ldots \qquad (1.6)$$

In addition, since the chelating agent is either an acid or base the ligand L, shorn of all ionisable protons, can take up j protons. Assuming this also to take place in steps, another set of equilibria is written as follows :

$$L + H \rightleftharpoons LH \qquad (1.7_1)$$

$$LH + H \rightleftharpoons LH_2 \qquad (1.7_2)$$

$$LH_{i-1} + H \rightleftharpoons LH_i \qquad (1.7_i)$$

$$LH_{j-1} + H \rightleftharpoons LH_j \qquad (1.7_j)$$

Each of the above equilibria is governed by its constant

$$K_i^H = \frac{aLH_i}{aLH_{i-1}.\ aH} \quad \ldots\ldots \qquad (1.8)$$

K_i^H is called the i^{th} proton ligand stability constant and is the reciprocal of the thermodynamic dissociation constant of the acid. LH_i dissociating as:

$$LH_i \rightleftharpoons LH_{i-1} + H \quad \ldots\ldots \qquad (1.9)$$

Using concentration instead of activities the stoichiometric proton ligand stability constant is given by :

$$K_i^H = \frac{[LH_i]}{[LH_{i-1}][H]} \quad \ldots\ldots \qquad (1.10)$$

now β_i^H can be defined as :

$$\beta_i^H = \frac{[LH_i]}{[H]^i\ [L]} = \prod_{i=1}^{i} K_i^H \qquad (1.11)$$

In order to determine the stability constants in the system described by the above equilibria, Bjerrum[20] introduced the concept of "Degree of formation or ligand number $\bar{n}$", which he obtained as the average number of ligands bound per metal ion present in whatever form i.e.

$$\bar{n} = \frac{[ML_1] + 2[ML_2] + \ldots\ldots\ldots N[ML_N]}{[M] + [ML_1] + [ML_2] + \ldots\ldots\ [ML_N]} \quad \ldots. \ (1.12)$$

It is now assumed that ionic or molecular species involving H, L and M other than those given in the above equilibria, do not exist in solution. This is equivalent to assuming the absence of polynuclear complexes, proton bearing complexes, unionised metal salt and hydroxyl bearing complexes. In subsequent treatment concentrations have been used for activities.

Substituting for the value of $[ML_i]$ from equation of the type (1.5), applied to equilibria (1.2_1) ... (1.2_i) ... (1.2_N) and eliminating $[M]$ the resulting expression would be

$$\bar{n} = \frac{K_1[L] + 2K_1K_2[L]^2 + \ldots\ldots NK_1K_2 \ldots\ldots K_N[L]^N}{1 + K_1[L] + K_1K_2[L]^2 + K_1K_2 \ldots\ldots K_N[L]^N} \qquad (1.13)$$

which may be arranged in the form

$$\bar{n} + (\bar{n} - 1) K_1 [L] + (\bar{n} - 2)K_2 [L]^2 + \ldots(\bar{n}-N)K_N[L]^N = 0 \qquad \ldots\ldots \quad (1.14)$$

or

$$\sum_{N=0}^{N=N} (\bar{n} - N) K_N [L]^N = 0$$

The equation (1.13) was termed 'formation function' by Bjerrum[20].

A similar function for the proton ligand complexes is given by :

$$\bar{n}_H = \frac{K_1^H [H] + 2K_1^H K_2^H [H]^2 + \ldots\ldots jK_1^H K_2^H \ldots\ldots K_j^H [H]^j}{i + K_1^H[H] + K_1^HK_2^H[H]^2 + \ldots\ldots K_1^H K_2^H \ldots\ldots K_j^H [H]^j} \qquad (1.15)$$

where $\bar{n}_H$ is the mean number of proton bound per non-complex bound ligand molecule. Using (1.11), $\bar{n}_H$ is written as :

$$\bar{n}_H + (\bar{n}_H-1) K_1[H] + (\bar{n}_H-2) K_2[H]^2 + \ldots (\bar{n}_H-j)K_j[H]^j = 0 \qquad \ldots\ldots (1.16)$$

Since the total amount of the metal salt and the chelating agent introduced into solution are known, the following relation can be stated :

$$T_M = \sum_{i=0}^{N} [ML_i] \quad \ldots\ldots \qquad (1.17)$$

and

$$T_L = \sum_{i=0}^{j} [LH_i] + \sum_{i=0}^{N} i\,[ML_i] \quad ..... \qquad (1.18)$$

Employing (1.6), the equation (1.17) becomes

$$T_M = [M] \sum_{i=0}^{N} \beta_i [L]^i \quad .... \qquad (1.19)$$

and using (1.6) and (1.11) the expression (1.18) becomes

$$T_L = [L] \sum_{i=0}^{j} \beta_i [H]^i + [M] \sum_{i=0}^{N} i\beta_i [L]^i ..(1.20)$$

In the above expression T_M and T_L are the total concentrations of M and L, respectively, present in solution in gram moles per litre.

The plots of $\bar{n}$ against log $1/[L]$ or $p[L]$ are called the formation curve of the systems. The solution of these formation functions lead to stepwise proton ligand and metal ligand formation constants.

The statistical effect prevents the successive metal ligand formation constants from being equal, and the ratio between the two consecutive constants can be determined statistically, provided asymmetry and chemical and electrical forces are ignored. For statistical consideration it may be assumed that the compound $ML_{\bar{n}}$'s tendency to split off a group is proportional to n, the number of groups already attached, and that the tendency to add an additional group is proportional to $N-\bar{n}$, the number of unfilled positions. For the ratio of two successive constants, therefore, we have :

$$\frac{K_n}{K_{n+1}} = \frac{(n+1)}{n} \cdot \frac{(N-n+1)}{(N-n)} \quad \ldots\ldots \qquad (1.21)$$

To account for the non-statistical forces, Bjerrum introduced a spreading factor X, such that :

$$\frac{K_n}{K_{n+1}} = \frac{(n+1)(N-n+1)}{n(N-n)} X^2 \quad \ldots\ldots\ldots \qquad (1.22)$$

for the special case when N=2

$$\frac{K_1}{K_2} = 4X^2 \quad \ldots\ldots \qquad (1.23)$$

and the equation (1.13) is reduced to

$$\bar{n} = \frac{K_1[L] + 2K_1K_2[L]^2}{1 + K_1[L] + K_1K_2[L]^2} \quad \ldots\ldots \qquad (1.24)$$

The spreading factor X is a constant quantity for the whole system and may assume any value between zero and infinity. The coefficient to X^2 (for N = 2) is chosen in such a way that for X = 1, the ratio between successive formation constants is exactly that predicted by purely statistical considerations. Thus larger the value of X, greater will be the difference between two successive formation constants.

To obtain the greatest possible symmetry, Bjerrum has introduced an average constants K_{av} so that for the simple case of N = 2

$$K_{av} = \sqrt{K_1K_2} = \sqrt{K} \quad \ldots\ldots \qquad (1.25)$$

When K is overall stability constant defined by :

$$K = \frac{[ML_2]}{[M] + [L]^2} \quad \ldots\ldots \qquad (1.26)$$

hence it follows that

$$K_1 = 2X \cdot K_{av} \ldots\ldots \qquad (1.27)$$

$$K_2 = K_{av} / 2X \ldots\ldots \qquad (1.28)$$

Inserting these expressions in the equation (1.20) for the formation function $N = 2$ we find

$$\bar{n} = \frac{2X\, K_{av} [L] + 2K_{av}^2 [L]^2}{1 + 2X\, K_{av}[L] + K_{av}^2 [L]^2} \ldots\ldots\ldots \qquad (1.29)$$

for $\bar{n} = \underline{1}$ (mid point of the formation curve) this equation leads to $K_{av}[L] = 1$ or $\log K_{av} = p[L]$ and

$\log K = 2 \log K_{av} = 2\, p[L]$.

Thus the average constant K_{av} is equal to the reciprocal of the free ligand concentration and the degree of formation i.e. n / N is 0.5 regardless of the value of spreading factor.

When $\bar{n} = 0.5$ equation (1.24) may be combined with equation (1.22) (for $N = 2$ and $n = 1$) to give the following relationship between K_1 and $[L]$:

$$\frac{K_1 [L] + K_1^2 [L]}{4X^2} = 1 \ldots\ldots \qquad (1.30)$$

when X is very large as compared to $K_1[L]$, the second term becomes negligible and under these conditions,

$$K_1 = 1 / [L] \ldots\ldots\ldots \qquad (1.31)$$

Similarly at $\bar{n} = 1.5$ equation (1.28) and (1.29) may be combined to give the following relationship between K_2 and $[L]$:

$$K_2[L] - \frac{3}{4X^2 . K_2[L]} = 1 \quad .... \qquad (1.32)$$

Again for large values of X, it may be seen from equation (L.32) that

$$K_2 = 1/[L] \quad .... \qquad (1.33)$$

Therefore the relationship between K_1, K_2 and $[L]$ depends upon the value of X, and the solution is simple only when X is very large. Under this condition K_1 and K_2 may be determined graphically as in the case of K_{av} from a plot of $\bar{n}$ versus log $1/[L]$ or $\bar{n}$ versus $p[L]$.

It is clear from the equation (1.14) that this simplification is not called for if N equation of this types are available for the system with ML_N as the highest complex. In actual practice experimental data exceeds this minimum requirment and the real problem is to choose those values in the experimental data which are more representative.

Different workers have adopted different methods suitable to their experimental condition. These have been reviewed by Irving and Rossotti[21] and Hearon and Gilbert.[22] These methods based on the use of equation (1.14) are useful when the formation of the different stages of complexation are simultaneous. In cases where the first and second stage of formation are separated, only method available to improve the values of formation constant obtained from the formation curve, is the method of linear plots[23]. The use of this method in the present investigation has been discussed in the succeeding chapter.

Factors affecting stability constants :

Interpretation of formation constants of complexes in solution implies consideration of the M-L bond energy, the heats of solvation of various species and the entropy changes involved. These factors are dependent upon

1. Temperature
2. Nature of the solvent
3. Other ions present in the solution
4. Nature of the metal ion
5. Nature of the ligand

Since in the Irving-Rossotti titration technique of determining the formation constant, the first three factors are maintained constant, the nature of the metal ion and the nature of the ligand are most effective in determining the relative stabilities of the complexes. They have been discussed briefly below :

Nature of the metal ion :

The complex formation is favoured in case of less basic cation with a higher ionic potential. Such ions will have a greater tendency to accept electrons from the ligand molecules. The available electron capture level in the ion also goes a long way in determining the complex forming tendency of the metal ion. The transition and inner transition metals with vacant d and f orbitals, respectively, are more efficient in forming complexes. Recently Calvin[24] has demonstrated the ionisation potential and the hybrid bond strength as measure of the chelating tendency of metal ion.

However, both these corelations neglect entropy effects and neither of them can be considered theoretically significant without more detailed consideration of the enthalpy and entropy changes involved in chelation.

The influence of central metal atom on the stability has been studied comparing the relative stabilities of complexes formed by a particular ligand with a series of metal ion in the same oxidation states. Irving and Williams[25] have shown that for a number of ligands the stability sequence for the first row bivalent transition metal ions is

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

This sequence, called the natural order or Irving Williams order of stability, has been shown to hold for a variety of ligands containing donor nitrogen and/or oxygen[26] and sulphur[27] atoms. Similar order had been previously observed by various authors[28]. Recently Meller and Maley[29] have suggested a longer series including other metal ions. This expanded form of the Irving-Williams[30] order is as follows :

$$VO^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Se^{2+} > Mn^{2+}$$

Irving and Williams regarded the second overall ionisation potential and reciprocal ionic radius of the metal ion as a measure of covalent and electrostatic contribution to the enthalpy changes, respectively, and reciprocal ionic radius as a measure of entropy changes and suggested that the variation of these two factors gives a good account for the observed sequence. If the above conditions are valid the sequence $Ni^{2+} < Zn^{2+} < Cu^{2+}$ should have hold good in all the cases. However, in some cases Zn^{2+} may form less stable complexes than Ni^{2+} [31]. The higher stability of Cr^{2+} complexes than Mn^{2+} complexes cannot also be explained in terms of the above consideration alone. Similarly some times a reversal to Ni$^{2+} >$ Cu^{2+} is found in the absence of a strong tetragonal field or when there are more than four coordinated atoms[32]. This normaly arises because the Irving-Williams order does not consider the stabilization energy due to the effect of ligand field. In weak ligand field complexes, the d^1, d^2, d^3, d^6 and d^8 the electrons occupy t_{2g} levels and contribute CFSE. In case of metal ion with d^4, d^5, d^9 and d^{10} configurations of electrons are forced to occupy the e_g levels and extra stabilization is cancelled out. In case of metal ions with d^0, d^5 and d^{10} configuration no CFSE is liberated. Thus the CFSEs due to the ligand field in ions with d^0 to d^5 electron configuration are in the order $0.0\Delta, 0.4\Delta$, 0.8Δ, 1.2Δ, 0.6Δ, and 0.0Δ. Similar sequence is followed from d^6 to d^{10}. The ligand field stabilization consideration can explain the lesser stability of the Mn^{2+} and Zn^{2+} complexes. In cases of d^4 and d^9 configuration additional stabilization energy is available due to Jahn-Teller effect. This is the reason why in cases where Jahn-Teller stabilization is low or there are five or six coordinated donor atoms $d^3 > d^4$ and $d^8 > d^9$. In such cases Cu^{2+} forms less stable complexes than Ni^{2+}.

From the above consideration, for the ligation enthalpy changes, following order has been suggested :

$$d^0 < d^1 < d^2 < d^3 \lesseqgtr d^4 > d^5 < d^6 < d^7 < d^8 \lesseqgtr d^9 > d^{10}$$

If a series of complexes of different metal ions with the same ligand is considered the entropy change ΔS can be expected to be almost same and hence the above is also the order of the stability of the complexes because

$$-RT \log K = \Delta F = \Delta H - T\Delta S$$

where the terms have the usual meanings.

The occasional derangement of the above order is attributed to specific effects such as orbital stabilization, stereochemical consideration etc. The order does not hold good also in cases where M-L π bonds are formed or there is a change in the oxidation state of the metal ion.

Nature of the ligand :

The complex formation can be interpreted as an acid base reaction in which metal acts as an acid and the ligand as a base in the Lewis[33] sense. It can be inferred, that the ligand with a higher basicity should have a greater tendency to form complexes. A linear relationship between the stability of the complex and the base dissociation constant of the ligands has been shown by a number of scientists[34]. This relationship, however, holds good in the case of structurally related ligands. Schwarzenbach[35] and his coworkers have shown positive deviation from plots of this type. Irving and Rossotti[36] have derived, thermodynamically, a general relation between lnK and $P_K{}^H$

$$\ln K = P_K{}^H + A + B$$

where A and B are constants.

The deviation can be explained to be due to other factors in the ligand, besides its proton affinity which affect the stability of the complex. They can be listed as follows :

A. The number of metal chelate rings :

The number of rings present in a particular chelate directly affect the stability. Generally an increase in the number of rings increases the stability.

B. The size of the chelates :

As observed from the work of Ley[37], Pfeiffer[38] and others, the chelates of five and six membered rings are most stable. Generally, five membered rings are most stable, if entirely saturated. If, however, the ring contains one or more double bonds i.e. is unsaturated, a six membered ring is more stable.

C. The steric effect :

Substitution in the ligand has pronounced effect on stability. It may :

(i) change the acidity of the ligand,
(ii) change or interfere with the resonance of the chelate ring and
(iii) make the ligand bulky.

In the case of bulky ligands, when different groups of neighbouring ligands clash, a distortion of bond angles takes place. This, in turn decreases the stability. If the metal ligand bonds directed in space overlap with the ligand orbitals, without any serious distortion of either set of orbitals, a more stable structure results. In other words the stability increases in such cases. In absence of such a basic geometry the stability is observed to be less.

D. The possibility of the metal ligand bond participating in resonating structures :

The presence of resonance in the ligand or the chelate structure usually increases the stability. If the metal-ligand bond, which is formed, participates into or favours the resonating structures, the stability is found to increase markedly.

E. Nature of the ligand atom :

In most of the complexes metal-ligand bond is formed by the donation of pair of electrons from the ligand to metal ion and is σ in nature. However as discussed earlier (page 4), if a vacant π orbital is available on the ligand atom, the electrons from the non-bonding π orbitals of the metal ion can be donated back to it and thus M-L π bond is formed. This π interaction stabilizes the complex compound. When atoms of second period e.g. nitrogen and oxygen are in such ligands as ammonia and water, they have no vacant orbitals which can accept π electrons from the metal ion. However, in other systems e.g. cyanide ion, carbon monoxide or pyridine, vacant antibonding $p\pi$ molecular orbitals are available and can act as accepters in $d\pi$-$p\pi$ bonding. The heavy donor atoms such as sulphur, phosphorous and arsenic etc., however, have vacant d orbitals which can take part in M-L $d\pi$-$d\pi$ interaction.

Consequently, although majority of the metal ions (non transition and earlier members of the transition series) form their most stable complexes with lighter donor atoms, the transition metal ions with full or nearly full $t_{2}g$ orbitals form more stable complexes with heavier donor atoms.

These two types of metal ions have been classified as class A and class B type of metals[39]. For example for the alkaline earth cation, the relative order of the stabilities is $O > S$ but is reverse $O < S < Se$ for transition metal ions with nearly filled or filled t_2g orbitals.

The ligand with conjugated double bonds also serve as a strong complexing agents because of the interaction of the metal d orbitals with the delocalised π electron cloud on the ligand molecule. This is examplified by the Sandwich type of complexes e.g. Ferrocene.

It was with the point of view of studying these effects that the present investigation has been undertaken.

Metal and ligand replacement reactions :

It can be expected that when a more complexing ligand L' is added to a metal complex ML, there may be formation of ML' by the replacement of L. The reaction can be shown as follows :

$$ML + L' \rightleftharpoons ML' + L$$

In cases of multidentate ligands the equilibrium constants of the ligand replacement reaction will not only depend on the relative tendencies of L and L' to combine with M but will also be governed by the mutual compatibility between the steriochemical requirments of the metal ion and the nature of the ligand. This explains the lower values of equilibrium constants for the replacement reaction in a square planar complexes containing ligands preferring planar geometry by another relatively more complexing ligand preferring tetrahedral geometry.

The rate, at which the replacement reaction proceeds, determines the lability or the inertness of the complexes. The term labile is applied to very reactive complexes whereas less reactive complexes are called inert. The inertness and the higher stability of the complexes do not always go together. The former depends on the kinetic stability whereas the latter has a thermodynamic meaning. It is true that normally thermodynamically stable substances are slow to react whereas unstable compounds react rapidly, but it is not necessary that this should be always true. The lability of the system depends on the nature of the metal ion and the mechanism of substitution reactions. Following the terminology of Hughes and Ingold[40] developed for organic reactions, the mechanisms in case of ligand and metal substitution reaction in coordination compounds can be called S_N (nucleophilic substitution) and S_E (electrophilic substitution) reactions respectively.

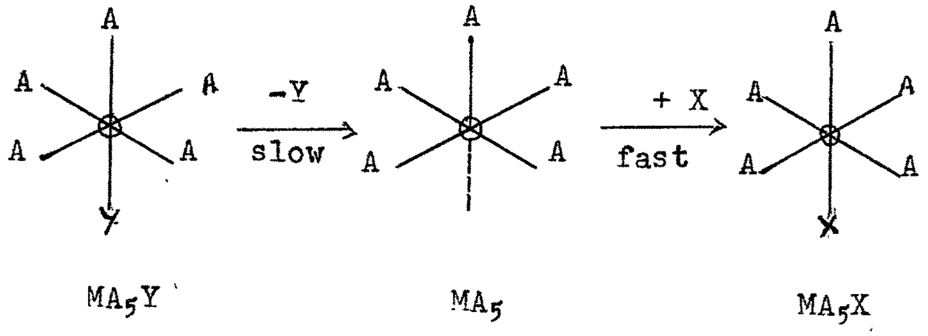
$$Y + MX \rightleftharpoons MY + X \quad \ldots\ldots \qquad (S_N)$$

$$M' + MX \rightleftharpoons M'X + M \quad \ldots\ldots \qquad (S_E)$$

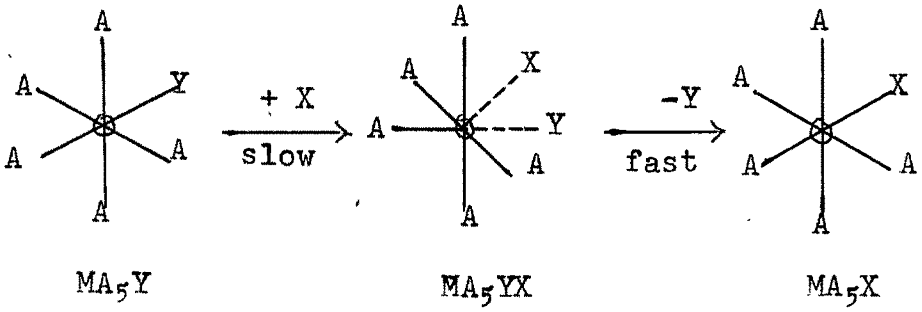
The electrophilic substitution reaction involving metal exchange are not many. Some studies have been made and reported in the literature[41]. In the present investigation also in few cases substitution of Ni^{2+} by Cu^{2+} has been studied.

Nucleophilic substitution reactions are more important and have been classified into S_N1 (dissociation) and S_N2 (displacement) mechanism. The reactions are represented as follows :

S_N1 mechanism :



S_N2 mechanism :



Thus S_N1 reaction proceeds through a pentacoordinated (trigonal bipyramidal) intermediate whereas S_N2 reaction proceeds through a seven coordinated intermediate.

The lability or the inertness of the complex can be explained by considering the mechanism by which the reaction proceeds and the ease with which the intermediate is formed. Attempts have been made to interpret the observed facts in terms of valence bond theory and later by applying crystal field theory. The latter seems to be more convincing. Orgel[42] and K.Jorgensen[43] calculated the crystal field stabilization energy for the intermediate pentacoordinated and heptacoordinated ligand fields in case of metal ions with d^0 to d^{10} configuration. The difference between the CFSE of the original octahedral structure and that of the intermediate is considered as a contribution $-\Delta Ea$ to the total activation energy for each reaction. A large value of $-\Delta Ea$ implies a slow reaction by that particular path. On observing the tables showing the ΔEa values[44] it can be predicted that in a strong field the reaction will be fast for d^0, d^1 and d^2 cases and will be slow for the ions with d^3, d^4, d^5 and d^6 configuration. In weak field, however, the ions with d^4 to d^{10} configuration are all labile except d^8. Thus it is observed that the reaction will be slow for d^3, strong field d^6 and d^8 cases whether it proceeds by S_N1 or by S_N2 mechanism. On the other hand the reactions in case of d^0, d^1, d^2 and d^{10} system are always expected to be fast. Thus there is agreement between the predictions of both the valence bond theory and crystal field theory except in case of d^8 system. Valence bond theory predicts the lability in the d^8 system to be almost of the same order as other d^4 to d^9 systems. However, the experimental results in case of $Ni^{2+}(d^8)$ are in agreement with the inertness as predicted by the crystal field theory. Thus the Ni^{2+} complexes are expected to be more inert than the Cu^{2+} complexes. What is predicted, however, is not the absolute rate of reaction but the relative rates in case of d^8 and d^9 systems. Several Ni^{2+} complexes are quite rapid and justify the assignments of lability to such systems[45]. Similar reactions in Cu^{2+} complexes are observed to be still faster.

Ligand displacement reactions have been carried out in the present investigation in Ni^{2+} and Cu^{2+} complexes. Reactions are quite fast in both the cases and the results have been detailed in the later chapters.

A survey of the products obtained by the reaction of secondary ligands with a metal ligand system indicates that these reactions can be classified into following types :

(1) If a complex of the type $[ML_6]$ is treated with a bulky secondary ligand A, the latter may not be able to occupy more than four positions around the metal ion by the replacement of L's and hence two of the L's may be retained in the coordination sphere resulting in the formation of mixed ligand complex $[M(A)_4(L)_2]$. If the secondary ligand is bidentate, product having composition $[M(A\text{-}A)_2(L)_2]$ may result. Similar compound may or may not be formed by the treatment of $[M(A\text{-}A)_2]^{2+}$ with excess L. These are sometimes known as adducts.

Dutta and coworkers have prepared the pyridine adducts of the cobalt complexes of biguanide[46] and ethylacetoacetic acid[47], acetoacetanilide[48] complex of Ni(II) and picolinic acid[49] complex of V(IV). The same workers prepared the compounds of the type $[Cu(A\text{-}A)_2 X_2]$ [50] (where (A-A = α-α' dipyridyl or o-phenanthroline and X = CNS, NO_2 or N_3). Dimethylformamide and dimethylsulphoxide adducts of Cu(II) aryl carboxylate were prepared by Bose and Patel[51]. Adducts of bis salicylato diaquo Cu(II) were prepared[52] by the replacement of water by pyridine and aniline. Paramagnetic adducts of Ni(II) chelates of monothio β-diketones have been obtained with pyridine and Y-picoline[53]. Adducts of Ni(II) phthalamide with tertiary bases have also been reported[54]. Gruddon and Walton[55,56] have also reported the adducts of Cu(II) β-diketone chelates with heterocyclic bases.

(2) In various reactions addition of a ligand L to the chelate $[M(A\text{-}A)_2]$ results in the formation of mixed ligand complex $[M(A\text{-}A)_2\,(L)_2]$ but this is an unstable species and disproportionates into $[M(A\text{-}A)_3]$ and $[M(L)_4]$.

It has been reported that 1:1 complex of Cu(II) and ethylenediamine forms $[Cu(en)(OH)_2]$ [57] on being treated with alkali. Any attempt to isolate the compound results in the disproportionation of mixed ligand complex $[Cu(en)(OH)_2]$ into $Cu(OH)_2$ and $[Cu(en)_2]^{2+}$. Bis ethylenediamine complex of Ni(II) on treatment with alkali also results in the formation of $[Ni(en)_3]^{2+}$ through the disproportionation of the intermediate mixed ligand complex $[Ni(en)_2(OH)_2]$. Treatment of the metallic carbonyls with thio acids also results in the formation of an unstable mixed ligand complex which undergoes disproportionation[58]. Bellucci's salts $K_4[Ni(CN)_6]$ has also been shown to undergo disproportionation on treatment with CO or CNR[59] (where R = cyclohexyl Me, iso-pr, tert-Bu, $phCH_2$, ph or 1-naphthyl).

(3) The addition of a secondary ligand,monodentate L or bidentate L-L to a complex $[M(A\text{-}A)_2]$ may result in complete displacement of (A-A) and the complex $[ML_4]$ or $[M(L\text{-}L)_2]$ may be formed. If (A-A) happens to be neutral base and L or (L-L) are charged ions, resulting complex anion $[ML_4]^{2-}$ or $[M(L\text{-}L)_2]^{2-}$ is formed and the liberated base gets protonated. The charge

on the complex anion is neutralized by the protonated base, acting as the cation and the compound precipitates out.

The cases of the displacement of the basic ligand from the coordination sphere by the another ligand[60] and also isolation in solid state of complexes with protonated primary or tertiary bases as a cation have been reported[61a,b,c]. However, the reactions of the type, wherein the bases replaced from the coordination sphere go out to the outer sphere as protonated cation, were not met with in the literature. Reactions of this type have been reported in the present investigation.

(4) In the cases where the two ligands (L-L) and (A-A) have almost the same complexing tendency, the addition of (L-L) to $[M(A-A)_2]$ or the addition of (A-A-) to $[M(L-L-)_2]$ in any ratio may result in the formation of the heterochelates $[M(L-L)(A-A)]$.

Mixed ligand complexes of cobalt containing biguanide and oxine[62], ethylenediamine[63] or 1-amidino-o-ethylurea[64] are known. Complexes of Cu(II) phthalamide and ethylenediamine or propylenediamine have been reported by Gopal Narayan[65]. 1:1:1 complexes of Cu(II) o-o' dihydroxy azobenzene and ethylenediamine or ethanolamine have also been prepared[66]. Various reactions of this type have also been studied in solution[67-72].

(5) The last type of reactions are those where the two ligands combine with a metal ion at different pH ranges and the complex species $[M(L-L)]$ formed at lower pH is stable even at higher pH. In some cases addition of one equivalent

of another ligand (A-A) to equimolar mixture of metal ion and (L-L) raised to higher pH may result in the formation of [M(L-L)(A-A)].

α-α' dipyridyl and o-phenanthroline are known to combine with the metal at low pH. Various secondary ligands combining with the metal at higher pH have been added to the mixture of metal and dipyridyl or o-phenanthroline in 1:1 ratio. The mixed ligands complex (1:1:1) using dipyridyl, o-phenanthroline or histamine as primary ligand and glycine[68,72] or catechol[69-72] as secondary ligands have been reported in the literature.

The above classification is, however, based on our observations and may not be exhausive. Amongst the five types of reactions listed above, the first four types have been met with in the present investigation and have been discussed in the later chapters.

The systems studied are the Cu(II) and Ni(II) complexes of catechol, 2,3-dihydroxynaphthalene, pyrogallol, protocatechuic and gallic acid. The formation constants of reactions taking place due to the direct addition of the ligand to the metal ion have been determined. The study of the reactions of the above ligands with Cu(II) and Ni(II) complexes of ethylenediamine, propylenediamine and the tertiary bases has also been carried out. A chapter has been devoted to the study of the reactions of tertiary bases (pyridine, α-, β-, γ-picoline) with Ni(II) complexes of 8-hydroxyquinoline, ethylenediamine and propylenediamine.

The polyhydroxy derivatives of phenols, phenolic acids and naphthalene with two -OH groups at ortho position are known to be efficient complexing agents. Various studies of their metallic complexes have been reported in the literature.

Catechol complexes have been studied extensively with different metal ions. The formation constants of titanium complex with catechol and gallic acid in acid medium was demonstrated spectrophotometrically by Okac and Sommer[73]. Titanium-catechol complex in presence of quinoline was studied by Babko and Gordeeva[74]. Titanium complex with catechol has also been studied by Shnaiderman and coworkers[75-77]. Talipor and coworkers[78] used titanium-catechol complex in solvent extraction. Babko and other coworkers[79-81] studied the ternary systems containing titanium-catechol and a secondary ligand. Catechol, pyrogallol and protocatechuic acid complexes of titanium have also been studied in aqueous[82,83] and nonaqueous solvents[84]. Buchwald and Richardson[85] studied molybdenum complexes with catechol, gallic acid and protocatechuic acid. Colour reactions of catechol, pyrogallol and gallic acid with molybdate were reported by Buchwald and Richardson[86]. Molybdenum and tungsten complexes of catechol were studied spectrophotometrically[87,88].

Rareearth complexes of catechol and pyrogallol were studied potentiometrically[89-91]. Complex formation of Cr(III) with catechol, pyrogallol and gallic acid was detected polarographically[92]. Kapoor and Prakash[93] studied the reactions of pentaethoxides of metals with catechol. Complex formation of zirconium and hafnium with catechol in strongly acidic solution has also been reported using ion exchange method[94]. The formation of zirconium complex of catechol having composition $Zr(cat)_2Cl$ has also been reported by Sarjit Singh Sandhu and coworkers[95]. Al(III) complexes of catechol have been studied by thermometric, conductometric and potentiometric technique by Goina and coworkers[96] and others[97]. Separation of metals as catechol complex using solvent extraction technique has also been suggested[98]. Catechol and 2,3-dihydroxynaphthalene were shown to react with silicon halides resulting in the formation of $H_2[SiL_3]$ [99] (where L = catechol or 2,3-dihydroxynaphthalene). Silicon complexes of catechol have also been studied by other workers[100, 101].

The stability of Ga(III) complexes with catechol were studied by polarographic and potentiometric methods[102]. Verma and Agarwal[103] have shown the polymerisation of uranyl catechol chelates. Uranyl complexes have also been studied by spectrophotometric[104], potentiometric methods[105,106]. Antimony[107] and arsenic[108] are also known to form complexes with catechol. Be(II) complexes of catechol 1:1 and 1:2 have also been reported[109]. Be(II) and Sn(IV) complexes of catechol have been studied by potentiometric method[110,111].

Ge(IV) complexes with catechol have been reported[112-115]. Milkos and coworkers[116] showed the formation of the compound $H_2[Ge(cat)_3]$. Complexes have been prepared by treating niobium and tantalum hydroxides with alkaline solution of catechol[117]. Tantalum complexes with catechol have also been reported by Gut and coworkers[118], and Lukachina[119].

Thorium complexes of catechol were studied by Mehrotra and coworkers[120]. V(IV) complexes of catechol, pyrogallol and gallic acid[121] were shown to form highly coloured solution at pH 4-10. V(IV) complex of catechol has also been reported[122,123], 1:1 and 1:2 complexes of V(IV) with catechol have also been studied potentiometrically[124] and 1:2 complex has been further investigated by proton magnetic resonance studies[125]. Formation constants of vanadyl complexes of catechol, pyrogallol, protocatechuic and gallic acid have been carried out potentiometrically[126]. Shnaiderman and coworkers studied various ternary systems containing V(IV)-catechol and a third ligand[127-134].

Cu(II) complexes of catechol have been studied by polarographic [135,136] and potentiometric[137-139] method. Athavale and coworkers[140] studied Cu(II), Zn(II), Ni(II), Cd(II) and Mg(II) complexes of catechol and protocatechuic acid using Calvin-Bjerrum titration technique. Formation constants of bivalent Sr, Ca, Mg, Cu, Zn, Co and Ni chelates of catechol have also been determined by Murakami and coworkers.[141] The stability constants of Cu(II) and Ni(II) system have also been determined by absorptiometric method[142,143].

Various mixed ligands studies involving catechol have also been carried out[69,144]. It has been observed in the ternary systems containing Cu(II)-dipyridyl or histamine that the tendency of catechol to combine with copper is more[71,72].

The interaction of chromic sulphate with pyrogallol and gallic acid has been studied by using ion exchange technique.[145] The complexes of pyrogallol with Fe(III)[146,147] molybdenum and tungsten[148,[illegible]] and titanium[149] have also been studied by spectrophotometric method. Babko and coworkers[150, 151] studied the complexes of Ta(V) and Nb(V) with pyrogallol and EDTA in the ternary system. Pyrogallol has also been used for the photometric determination of Ta(V)[152]. Complexes of pyrogallol, protocatechuic and gallic acid with Ge(IV) have been investigated by using polarographic technique[153]. The complex formation of pyrogallol with Al(III)[154] and Be(II)[155] has been investigated by potentiometric, conductometric and polorographic methods.

Osmium[156] and Thorium[157] complexes of pyrogallol have been reported. Zirconium and hafnium complexes with pyrogallol have been studied by spectrophotometric method[158]. V(IV) complexes with pyrogallol have been determined by spectrophotometric method[159, 160]. The ternary systems containing V(V), pyrogallol, protocatechuic acid and antipyrine have also been studied[161].

Cu(II) complexes with protocatechuic acid have been studied by spectrophotometric method[162]. Nb_2O_5 has been shown to react with protocatechuic acid to produce a yellow coloured complex which has been studied by spectrophotometric method[163, 164]. Spectrophotometric study of Ti(IV)-protocatechuic acid has also been carried out[165, 166] and in this system Ti(IV) has been shown to undergo reduction[167]. Protocatechuic and gallic acid complexes of Ti(IV) have also been studied using potentiometric method by Athavale and coworkers[168, 169]. Protocatechuic and gallic acid have been used in the spectrophotometric determination of Fe(III) and Ti(IV)[170]. Mixed ligand system containing Ti(IV) and protocatechuic acid and oxalic, tartaric or citric acid have also been studied[171]. Tl(I) complexes of protocatechuic and gallic acid have also been reported[172]. V(IV) is known to react with protocatechuic acid to form a stable yellow complex which has been studied by spectrophotometric method[173]. The stability constants of Cu(II), Zn(II), Cr(II) and Ni(II) with protocatechuic acid have also been determined by potentiometric method[174].

Gallic acid has been used as a spectrophotometric reagent for the investigation of niobium, tantalum, vanadium, titanium and iron[175,176]. Gallic acid has also been used in quantitative determination of Ge(IV)[177]. Germanium complexes of gallic acid was studied potentiometrically and spectrophotometrically by Shagisultanova and coworkers[178]. Gallic acid is also known to form polynuclear complexes with uranyl[179]. Boric acid has also been reported to combine with gallic acid resulting in the formation of anionic complexes.[180] Cobalt-gallate was prepared by the interaction between sodium gallate and cobalt chloride[181]. Gallic acid has been found to form 1:2 and 1:3 complexes with rare earth metals[182]. Mo(VI) complex of gallic acid was studied by spectrophotometric, polarographic and I.R. methods[183]. The ternary systems containing Ti(IV), gallic acid and antipyrine have also been reported[184]

Though some work on Cu(II) and Ni(II) complexes have been carried out, the type of the study undertaken in the present investigation was not met with in the existing literature. An account of the work is being presented in the succeeding chapters.

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