CHAPTER ONE

INTRODUCTION AND LITERATURE SURVEY

It is an uncontradicted fact that in recent years few branches of chemistry have received as much concentrated study with such fruitful results as coordination chemistry. The exponential growth of research publications in this subject indicates that the study of the chemistry of coordination complexes is fast attaining its full stature. It was in 1891 that Werner, for the first time, propounded some thing like a theory that proposed to bring under its protection all such compounds which now go by the name of complexes. The study, since then, has developed practically without any sign of decay. Though its importance appeared to wane in one small slumbering period, the interest never died down. It actually gained increasing momentum after the refreshing slumber and has rejuvenated itself with the application of the knowledge of the electronic structure of the atom and the theory of quantum mechanics. The study has been further fortified by the availibility of various refined and elegent physical methods of measurements in modern times. The formation of coordination compounds is now supposed to take place on a much wider scale than was usually suspected. Strictly speaking, even dissociation of metallic salts in water is regarded more or less as the chemistry of coordination of water molecules with metallic ions.

It is, therefore, necessary first to step in understanding the coordination compounds. As suggested by the commission on the nomenclature of inorganic chemistry[1] " Coordination entity may be defined as a molecule or ion

in which there is a metal atom or ion to which are closely attached other atoms or groups. The metal atom is called the central atom, or centre of coordination. The atoms directly attached to the central atom are called coordinating atoms or donor atoms and groups referred to as ligands !!

The phenomenon can, however, be better understood by tracing the stages in its development. The chemistry of complex compounds can be considered to have grown through four periods. The first of these has been styled as Pre-Werner period during which so called complex compounds were isolated and analysed. No satisfactory theory was,however, given to account for their structure.

Werner after whom the next period in the history has been named, was first to propound a theory to explain the formation of complex compounds. According to him " Even when, judged by the valance 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 by what are called auxiliary valencies !! He showed that the factor determining the structure of coordination compounds was not the primary valency of the central metal ion but the number of groups of any kind attached directly in the first sphere of attraction. This number was found to be specific for different metals and was termed coordination number. With his simple theory Werner could explain various aspects of

the formation of complex compounds.

Then followed the period of quiescence till Sidgwick[2] first interpreted complexes in terms of electronic theory of valency in 1923. He attributed the stability of complex compounds to the attainment by the central ion of an effective atomic number, same as the atomic number of the nearest inert gas. The theory, however, failed in many cases. Further, with the advancement of the wave concept of electrons, application of wave mechanics to coordination chemistry was inevitable. This interprets coordination as a special case of covalency where a bond is formed by the interaction between a vacant orbital and a doubly filled orbital. Application of valence bond and molecular orbital theories to complex formation was, therefore, a natural consequence.

The valence bond approximation, in principle, pictures the electron pair bond as ~~arising by~~ result of bringing together two atoms in a manner such that their ~~proximate~~ single electronic orbitals interact. In case of complex compounds, the association takes place as a result of overlaping of filled ligand atom orbitals with vacant hybridised orbitals of metal ions. Pauling[3] thought that due to a very slight energy difference among (n - 1) d, ns and np orbitals in the transition metal ions, a redistribution of electrons among these orbitals is possible. It is in this process that electrons in the d orbitals of the metal ions get paired in the lower d orbitals thus making some d orbitals available for hybridisation. Depending upon the availability

of d orbitals different types of hybridisation take place resulting in tetrahedral, square planar or octahedral geometry of the resulting complexes. When the inner d orbitals are used for hybridisation, the complexes are termed Inner Orbital Complexes. Some times the outer d orbitals are also involved in hybridisation resulting in what are called Outer Orbital Complexes. The valence bond theory has reasonably explained the bonding in coordination compounds but it has rather failed to putforth quantitative predictions.

The molecular orbital theory of Hund and Mullikan was applied to complex compounds by Van Vleck. According to this theory, in the formation of transition metal complexes the $3d(e_g)$, $4s(a_{1g})$ and $4p(t_{1u})$ orbitals of the cation combine with the composite orbitals formed by suitable combination of ligand σ-orbitals. This results in the formation of σ- bonding and σ-antibonding orbitals. The T_{2g} orbitals of the metal ions remain as non-bonding molecular orbitals. Electrons are fed in these molecular orbitals in the increasing order of energy. The higher the number of electrons in the bonding orbitals, greater is the stability of the complexes formed.

Though the wave concept explained various aspects of complex formation, another group of scientists felt convinced about the electrostatic nature of the phenomenon. In 1930 Van Arkel and DeBoer[4] applied the simple electrostatic theory to the bonding in metallic complexes. They applied simply the well known potential energy equation

of classical electrostastics to their bonding model and suggested structures having minimum electrostatic repulsion. Though the concept is simple, one does not have to go too far to search for many phenomena which are inexplicable in terms of the simple electrostatic model. The most significant defect is that the electrostatic theory does not consider the effect on the central atom orbitals of the electrical field created by the charges on the ligands, or the negative ends of the dipole. The remedy can be sought in the crystal field theory which starts with the basic assumption of the electrostatic theory but also considers as to how far a given steric arrangement of the ligands, the electronic system of the central atom is perturbed and how far that perturbation stabilizes the postulated arrangement of the ligands. In the ground state all five d-orbitals are of equal energy and the electrons will occupy each of the orbitals with equal possibility. If six ligands are brought close to the metal ions in a octahedral configuration along the x, y and z axes, the d orbitals are no longer equivalent. An electron in either the $d_{x^2} - y^2$ or d_{z^2} (e_g) orbital will interact strongly with the negatively charged ligand, compared to a small interaction if the electron is in the d_{xy}, d_{xz} or d_{yz} orbitals. The electron will prefer to occupy the orbitals in which the repulsion interaction is small. The difference in the energies of the e_g and t_{2g} orbitals is known as crystal field splitting and its value depends on the strength of the field created by the ligand.

This theory is useful in predicting the stereochemistry, magnetic properties, absorption spectra and thermodynamic properties of the complexes. But due to its emphasis on d orbitals and electrons of the central atom, the crystal field theory must necessarily become less accurate in case of complexes where E.S.R., N.M.R. and visible spectral studies hold significant evidence of delocalization of metal electron on ligand orbitals indicating increasing covalent character in the M-L bond.

Ligand Field Theory :

In an attempt to explain such cases, ligand field theory was advanced by the joint attempts of a number of scientists like Orgel, Nyholm, Owen, Liehr and others. This theory retains the basic concepts of the crystal field theory but incorporates certain modifications to take account of the deviation from the electrostatic idealisation. It considers that after the splitting of the metal atom d orbitals by the crystal field, there is a linear combination between the metal and the ligand atom orbitals of required symmetry to an extent depending upon the nature of the ligand. This leads to more complete understanding of electronic spectra and magnetic properties of the complex compounds. According to this theory, the stability of a complex depends upon the electrostatic perturbation, metal-electron, ligand-electron repulsion and the extent of covalent bond formation. The ligand field theory has brought a happy compromise between the Crystal field theory and the Molecular orbital theory. At its one extreme are the cases of complexes which

can be explained purely from electrostatic considerations and at the other end are cases explicable by pure molecular orbital theory. In between these two extremes lies the realm of ligand field theory.

Simultaneously, as theoritical chemists were trying to unfold the structural mystery of the complexes and the nature of M-L bond, the solution chemists like Bjerrum[5] and Leden attempted to give a sense of direction to the equilibrium studies of complex systems in solutions. They introduced the concept that formation and dissociation of complex molecules in solution take place in the following successive steps :

$$M + L \rightleftharpoons ML \quad \ldots\ldots\ldots \quad (1.0)$$

$$ML + L \rightleftharpoons ML_2 \quad \ldots\ldots\ldots \quad (1.1)$$

$$ML_{i-1} + L \rightleftharpoons ML_i \quad \ldots\ldots\ldots \quad (1.1_i)$$

$$ML_{N-1} + L \rightleftharpoons ML_N \quad \ldots\ldots\ldots \quad (1.1_N)$$

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 M 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 :

$$K_i = \frac{a_{ML}}{a_{ML_{i-1}} \cdot a_L} \quad \ldots\ldots\ldots \quad (1.2)$$

K_i is called the i^{th} metal ligand stability or formation constant governing an equilibrium of the type

$$ML_{i-1} + L \rightleftharpoons ML_i \quad \ldots\ldots\ldots \quad (1.3)$$

The term 'a' in (1.2) 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 :

$$K_i = \frac{[ML_i]}{[ML_{i-1}] \cdot [L]} \quad \ldots\ldots \qquad (1.4)$$

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

Now β_i can be defined as :

$$\beta_i = \frac{[ML_i]}{[M] \cdot [L]^i} = \prod_{i=1}^{i} K_i \quad \ldots. \qquad (1.5)$$

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 :

$$L + H \rightleftharpoons LH \quad \ldots\ldots \qquad (1.6_1)$$

$$LH + H \rightleftharpoons LH_2 \quad \ldots\ldots \qquad (1.6_2)$$

$$LH_{i-1} + H \rightleftharpoons LH_i \quad \ldots\ldots \qquad (1.6_i)$$

$$LH_{j-1} + H \rightleftharpoons LH_j \quad \ldots\ldots \qquad (1.6_j)$$

Each of the above equilibria is governed by its constant

$$K_i^H = \frac{a_{LH_i}}{a_{LH_{i-1}} \cdot a_H} \quad \ldots\ldots \qquad (1.7)$$

K_i^H is called the i^{th} proton ligand stability constant and is the reciprocal of the thermodynamic dissociation constant

of the acids LH_i dissociating as :

$$LH_i \rightleftharpoons LH_{i-1} + H \quad \ldots\ldots \quad (1.8)$$

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

$$K_i^H = \frac{[LH_i]}{[LH_{i-1}] \cdot [H]} \quad \ldots\ldots \quad (1.9)$$

Now β_i^H can be defined as :

$$\beta_i^H = \frac{[LH_i]}{[H]^i \cdot [L]} = \prod_{i=1}^{i} K_i^H \quad \ldots\ldots \quad (1.10)$$

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 and metal ions. Now in subsequent treatment concentrations are used for activities.

In order to determine the stability constants in the system described by the above equilibria, Bjerrum[5] introduced the concept of "Degree of formation or ligand number $\bar{n}$ ", which he defined as the average number of ligands bound per metal ions present in whatever form, i.e.

$$\bar{n} = \frac{\sum_{i=0}^{N} i\ [ML_i]}{\sum_{i=0}^{N} [ML_i]} \quad \ldots\ldots\ldots \quad (1.11)$$

substituting for the value of $[ML_i]$ from equation of the type (1.4), applied to equilibria (1.1_1), (1.1_2)....(1.1_N) and eliminating $[M]$ the resulting expression would be

$$\bar{n} = \frac{K_1[L] + 2K_1K_2[L]^2 + \ldots\ldots NK_1K_2 \ldots K_N[L]^N}{1 + K_1[L] + K_1K_2[L]^2 + \ldots\ldots K_1K_2 \ldots K_N[L]^N} \quad \ldots(1.12)$$

which may be arranged in the form

$$\bar{n} + (\bar{n}-1)K_1[L] + (\bar{n}-2)K_2[L]^2 + \ldots\ldots(\bar{n}-n)K_n[L]^n = 0 \quad \ldots (1.13)$$

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

The equation (1.12) was termed 'formation function' by Bjerrum[5].

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

$$\bar{n}_H = \frac{K_1^H[H] + 2K_1^H K_2^H[H]^2 + \ldots\ldots jK_1^H K_2^H \ldots\ldots K_j^H[H]^j}{1 + K_1^H[H] + K_1^H K_2^H[H]^2 + \ldots\ldots K_1^H K_2^H \ldots\ldots K_j^H[H]^j} \quad \ldots(1.14)$$

where $\bar{n}_H$ is the mean number of proton bound per non-complex-bound ligand molecule. Using (1.10), $\bar{n}_H$ is written as :

$$\bar{n}_H + (\bar{n}_H - 1)K_1[H] + (\bar{n}_H - 2)K_2[H]^2 + \ldots\ldots (\bar{n}_H - n)K_n[H]^n = 0 \quad \ldots\ldots (1.15)$$

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

$$T_M = \sum_{i=0}^{N} [ML_i] \quad \ldots\ldots\ldots \quad (1.16)$$

and

$$T_L = \sum_{i=0}^{j} [LH_i] + \sum_{i=0}^{N} i\,[ML_i] \quad \ldots\ldots \quad (1.17)$$

Employing (1.5), the equation (1.16) becomes

$$T_M = [M] \sum_{i=0}^{N} \beta_i [L]^i \quad \ldots\ldots \quad (1.18)$$

and using (1.5) and (1.10) the expression (1.17) becomes

$$T_L = [L] \sum_{i=0}^{j} \beta_i [H]^i + [M] \sum_{i=0}^{N} i\beta_i [L]^i \ldots\ldots \quad (1.19)$$

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

The plot of $\bar{n}$ against log $1/[A]$ or $p^{[A]}$ are called the formation curve of the systems. The solution of these formation functions lead to step wise 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_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 - n, the number of unfilled positions. For the ratio of two successive constants, therefore, we have :

$$\frac{K_n}{K_{n+1}} = \frac{(n+1)}{n} \cdot \frac{(N-n+1)}{(N-n)} \quad \ldots\ldots \quad (1.20)$$

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

$$\frac{K_n}{K_{n+1}} = \frac{(n+1)\ (N-n+1)}{n(N-n)}\ x^2 \quad \ldots\ldots \quad (1.21)$$

fpr the special case when N = 2

$$\frac{K_1}{K_2} = 4x^2 \quad \ldots\ldots \quad (1.22)$$

and the equation (1.12) is reduced to

$$\bar{n} = \frac{K_1[A] + 2K_1K_2[A]^2}{1 + K_1[A] + K_1K_2[A]^2} \quad \ldots\ldots \quad (1.23)$$

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 constant K_{av} so that for the simple case of N = 2

$$K_{av} = \sqrt{K_1K_2} = \sqrt{K} \quad \ldots\ldots\ldots \quad (1.24)$$

When K is overall stability constant defined by :

$$K = \frac{[MA_2]}{[M] + [A]^2} \quad \ldots\ldots\ldots \quad (1.25)$$

hence it follows that

$$k_1 = 2x \cdot K_{av} \quad \ldots\ldots \quad (1.26)$$

$$k_2 = K_{av} / 2x \quad \ldots\ldots \quad (1.27)$$

Inserting these expressions in the equation (1.19) for the formation function N=2 we find

$$\bar{n} = \frac{2xK_{av}[A] + 2K_{av}^2[A]^2}{1 + 2x K_{av}[A] + K_{av}^2[A]^2} \quad \ldots\ldots \quad (1.28)$$

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

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

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 (1.23) may be combined with equation (1.21) (for N=2 and n=1) to give the following relationship between k_1 and [A] :

$$\frac{k_1[A] + k_1^2[A]}{4x^2} = 1 \quad \ldots\ldots \quad (1.29)$$

When x is very large as compared to $k_1[A]$, the second term becomes negligible and under these conditions

$$k_1 = 1 / [A] \quad \ldots\ldots \quad (1.30)$$

Similarly at $\bar{n} = 1.5$ equation (1.27) and (1.28) may be combined to give the following relationship between k_2 and [A] :

$$k_2 [A] - \frac{3}{4x^2 k_2 [A]} = 1 \quad \ldots\ldots\ldots \qquad (1.31)$$

Again for large values of x, it may be seen from equation (1.31) that

$$k_2 = 1 / [A] \quad \ldots\ldots\ldots \qquad (1.32)$$

Therefore the relationship between $k_1 k_2$ and [A] 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 / [A] or $\bar{n}$ versus $\mathfrak{p}[A]$.

Determination of the formation curve :

The formation curve is generally obtained by the Bjerrum Calvin pH titration technique. Here [H] is measured by pH measurements and titration technique allows large amount of data to be obtained in a short period of time. This method as used by Irving and Rossotti[6] has several advantages. Here it is neither necessary to convert the pH meter readings to stoichiometeric [H] ion concentration nor to know the stoichiometric concentration of neutral salt added to maintain the ionic strength constant. Moreover, the acid dissociation constants of the reagents which are required in calculations are determined under the same experimental conditions as the formation constants. The method can be readily applied even when water - organic solvent mixtures are employed to provide a homogeneous medium without knowing the exact relation between the glass electrode pH measurements in these media and stoichiometric hydrogen ion concentration. This method, consequently, has

been used in the present work and has been discussed in later chapters.

The study of the solutions stabilities and the structures of the solid complexes have furnished significant information to theoritical chemists. It was felt that the consideration of the covalency in terms of σ-bonding alone is not sufficient to explain all the experimental facts. Ammonia is found to form more stable complexes with non-transition elements than phosphine and arsine. However, reverse is the case in transition metal complexes. Pauling drew attention to the abnormally short M - C bond distances in the metal carbonyls and complex cyanides. He interpreted the bond lengths and the stability of these complexes as indicating some double bond character in the metal ligand bonds. According to him besides the σ-bond, π-bond formation can also take place in complexes as a result of the combination of d orbitals on the metal atoms which act as donors, with vacant p or d orbitals on the ligands acting as acceptors. It is now generally recognised that multiple or π-bonding in metallic complexes may arise in the following two ways :

(1) Donation of T_{2g} electrons which can not form σ-bonds to empty $p\pi$ orbitals located on the ligand atom.

(2) Donation of T_{2g} electrons to empty $d\pi$ orbitals located on the ligands.

An interpretation of π-bonding has been attempted in terms of molecular orbital theory. In the normal mode of overlap the T_{2g} orbitals do not find orbitals of the required symmetry on the ligand atom and hence remain as non-bonding molecular orbitals. In cases where the ligands have vacant

$p\pi$ or $d\pi$ atomic orbitals on the ligand atom or the ligand molecules have vacant anti-bonding π molecular orbitals, they combine to form the composite orbitals of the required symmetry to combine with the π metal orbitals. π-bonding and π-antibonding molecular orbitals are formed in this way.

Ligand field theory provides the best explanation for the π-bond formation. It considers that the formation of π-bonding and π-antibonding molecular orbitals increase the ligand field splitting and thus contributes towards the stability of the complexes. In case of the cyanide and carbonyl complexes the stability is attributed to $d\pi - p\pi$ interaction. In case of the ligands involving the latter group atoms vacant $d\pi$ orbitals are available which enable $d\pi - p\pi$ interactions to take place in the transition metal complexes.

The possibility of $d\pi - p\pi$ interaction has been substantiated by the various investigations on the M - L bond in the transition metal complexes involving ligand atoms of the third (P,S) and fourth (As, Se) periods of a group.[7] Nitrogen and oxygen containing complexes in special circumstances exhibit partial double bond character in the M - L bond due to $d\pi - p\pi$ type of interaction.

In case of ammonia and primary amine complexes, there is no possibility of π-bonding but the possibility of π-bonding exists in case of pyridine complexes.

Pyridine and substituted pyridines are heterocyclic tertiary bases. They contain a lone pair of electrons which can be donated to the central metal ion forming a σ-complex.

If metal also possesses a pair of π-electrons, they are back donated to the ligands. It is therefore, interesting to study the complex forming tendencies of pyridine and substituted pyridines. Bjerrum[8] determined the stability in solution of pyridine and substituted pyridines with Cu^{++} and Ag^{+} metal ions. P.C.Sinha and R.C.Ray[9] carried out the stability titration of copper perchlorate with pyridine. The compound was synthesized too and the nature of the bond established. Cu(II) complexes with pyridine and substituted pyridines have also been studied by S.F.A.Kettle and J.P. Pilloi[10] and R.N.Patel and D.V.Raman Rao[11]. The stabilities of Ag(I) complexes with some 3- and 4- substituted pyridines were also determined by Kent Murman[12] and coworkers. Bhattacharya and Sinha[13] as well as G.Beech[14] et al have shown that greater the basicity of the ligand, more stable is the complex formed. P.S.Relan and P.K.Bhattacharya[15] studied the stability of Be(II), Cr(III) and Mn(II) complexes with pyridines and substituted pyridines in aqueous solutions whereas Tl(III) complexes with hydroxy pyridine were studied by B.I.Lobov[16] and his coworkers.

Polarographic studies on stoichiometry and stabilities have also been attempted. Dissociation constants for cadmium complexes with dipyridyl were determined by Bailor[17] et al as early as in 1950 and they reported the existance of 1:4 complex in Cd-pyridine system. Later on Morinaga[18] in 1956, Liu and Fu[19] in 1957, Desai and Kabadi[20] in 1961 and Liang-Nien Chi[21] et al in 1965 studied the stepwise formation constants of cadmium-pyridine complexes polarographically.

The dissociation constants of Cu^{++} complexes[22] were also determined. The determination of overall constants of Zn(II) complexes[23] with pyridine show 1:1 to 1:4 composition. Nickel pyridine instability constants were calculated by Defered and Hyne method[24]. The basic strength of 3-amino-pyridine[25] was determined by polarography and pH metry.

Spectroscopic methods are also now available for finding out the stability and thermodynamic data of complexes. R.W.Green[26] titrated Ni^{++} with picolinic acid. The higher values of stability constants obtained by this method are ascribed to undetected coordination at the carboxylic ion which introduces a great error in the pH titration method. The study of the complexes of pyridine and substituted pyridines, carboxylic acids and quinoline were carried out by Bireswar Banerjee[27]. They also confirmed the composition of ferrous picolinate[28] to be $\left[Fe\left(\begin{matrix}\leftarrow N \\ OCO\end{matrix}\rightarrow C_5H_4\right)_3\right]^-$ spectroscopically and determined its instability constants. A.V.Ablov and V.V.Nazarora[29,30] studied the tertiary base complexes of nickel, cobalt and copper in different solvents spectrophotometrically. Spectral evidence for the competitive metal bonding in metal complexes was found by Naseem and E.L.Anma[31].

The chelate effect was studied by calorimetry, pH metry and E.S.R. by G.Atkinson and J.E.Bauman[32]. The enthalpy and entropy contribution to the chelate have also been analysed. Possibility of using E.S.R. as a tool for studying complex stability have been illustrated by them. The E.S.R. spectra of Cu^{++} complexes of pyridine and substituted pyridines were studied in frozen aqueous solutions[33]. Stepwise formation

constants[34] of α-, β- and γ-picoline complexes of Cu^{++} and Cu^{+} have also been determined spectrophotometrically.

A.M.Rubinshtein investigated the nature of chemical bond in aminopyridine[35] and steric hinderences[36] and the formation of complex compounds with complicated amines. 2-aminopyridine[37] enters the inner coordination sphere which is a cis type.

An extensive review of isolation, spectrophotometry and I.R. study has also been made. Thiocyanate complexes of pyridine and substituted pyridines with palladium were studied by Spacu and Camboli[38] and by Bertini and Sabatini[39] in 1966. The visible and I.R. spectra of vanadium(III) complexes with pyridine have been studied by Clark, Nyholm[40] et al, whereas that of thallium was studied by William and Whinnie[41]. Spectral studies (I.R., U.V. and visible) of ruthenium nitroso compounds containing pyridine and nitro-pyridine were made by Zvyagintsev[42] et al. Far I.R.spectra of charge transfer complexes between iodine and substituted pyridines in cyclohexane solution was studied by Lake and Thomson[43]. R.C.Paul[44] and his coworkers studied the interaction of sulphuryl chloride with pyridine and substituted pyridines. The I.R.spectra of the adducts has revealed the coordination of tertiary amine through the nitrogen atom to the sulphur atom of sulphuryl chloride. I.R.spectra of Zn(II)[45], manganese[46] and other transition metal[47] complexes with pyridine and substituted pyridines were also studied. Compounds of pyridine with cobalt salts,[48,49] three spatial isomers of pt-chloroiodopyrineamine[50], some

compounds of uranium[51], copper dithionate pyridine complex,[52] compounds of TeF_4 with pyridine,[53] effect of pH of the solution on the composition of the complexes[54] $(Py)SeF_4$ Et_2O, complexes of decaborane with pyridine and 2-bromopyridine[55] and complexes of Pd^{++} and Pt^{++} with 2-aminomethylpyridine[56] have all been studied. Most of them are mixed ligand complexes.

Some instances of magnetic,[57,58,59] N.M.R.[60-62] and P.M.R.[63,64] studies of pyridine and substituted pyridine complexes have also been noticed recently.

The literature, however, reveals that no systematic study of pyridine and substituted pyridine complexes with Ni(II), Cd(II) and Mg(II) in aqueous medium has so far been made. For solution studies Irving-Rossotti method[6] has been used in the present investigation which has not been used before. The complexes have been isolated from their aqueous solutions with nitrate, glycolate and lactate ions in the outer sphere. The idea of selecting these metals is to explore the effect of M - L π-bonding on the stabilities of the complexes. The Mg^{++} ion having no d orbitals can not form π-bonds but Cd^{++} with d^{10} configuration and Ni^{++} with d^8 configuration are capable of M $\rightarrow$ L π-interaction.

An attempt has been made to establish the nature of the bond and the structures of the complexes on the basis of magnetic susceptibility determination, absorption studies in visible range (in case of Ni-complexes) and I.R.studies. The subsequent chapters will present an account of the investigation carried out.

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