CHAPTER I

Introduction and literature survey.

By the end of nineteenth century, the knowledge in the field of chemical bonding had developed just enough to explain the structure of simple inorganic compounds. It failed to formulate the structure of some compounds isolated and analysed as early as eighteenth century by Tassert and others. These were obtained by mixing cobalt(II) salts and ammonia in stoichiometric ratio. The notable feature of these compounds was that they did not give off ammonia when dissolved in water and were termed complex compounds. The importance of this class of compounds was later realized and a large variety of complex or coordination compounds have been prepared. They find application in analytical chemistry, in every day life and in industry. Recent work in the field of biochemistry has revealed the importance of metallic complexes in biochemical processes. The basic constituents of plant (Chlorophyll) and animal (Blood) life are metal chelates. The catalytic reactions of various enzymes proceed through complex formation. The study of the structure of the complex compounds, their stabilities and the mechanism of the reactions have thus been the fields of special interest.

It was in 1891 that Werner, for the first time, propounded something like a theory that proposed to bring under its protection all such compounds which now go by the name of complexes. According to him, besides primary valency the metal ions possess auxiliary valency and through this a fixed number of ligand molecules get bound in the coordination sphere around the metal ion. Sidgwick[1] first interpreted auxiliary valency in terms of electronic theory of valency and classified it as a coordinate linkage formed by the donation of a pair of electrons from the ligand to the metal ion. The central point of Sidgwick's discussion was that the metal ion attains an effective atomic number[2] same as the atomic number of the nearest inert gas and this accounts for the stability of the complex. The theory had certain limitations. The years to follow saw Sidgwick's idea of coordinate-bond being invested with quantum mechanical validity. Pauling[3] interpreted coordinate linkage as a special case of covalency and applied the concept of valency bond theory. According to his original treatment, the doubly filled orbital of the ligand transfers one electron to the vacant orbital of the metal ion. The metal and ligand orbitals with unpaired electrons then interact to form a covalent bond. In 1931 Pauling carried out studies to determine which states of the central ion are available to accept transferred electrons and concluded that the vacant s, p and d orbitals of the metal ion, which do not differ significantly in the energy undergo hybridization to provide equivalent orbitals to interact with ligand orbitals and to result in the specific geometry of the resulting complex.

One d state, two p states and an s state combine to result in four equivalent bonds (dsp^2) directed to the corners of a square plane. On the other hand, if an s state and three p states (sp^3) were available for hybridization, four equivalent bonds directed to the corners of a tetrahedron are produced. Combination of two d, one s and three p states gives rise to an octahedral configuration (d^2sp^3).

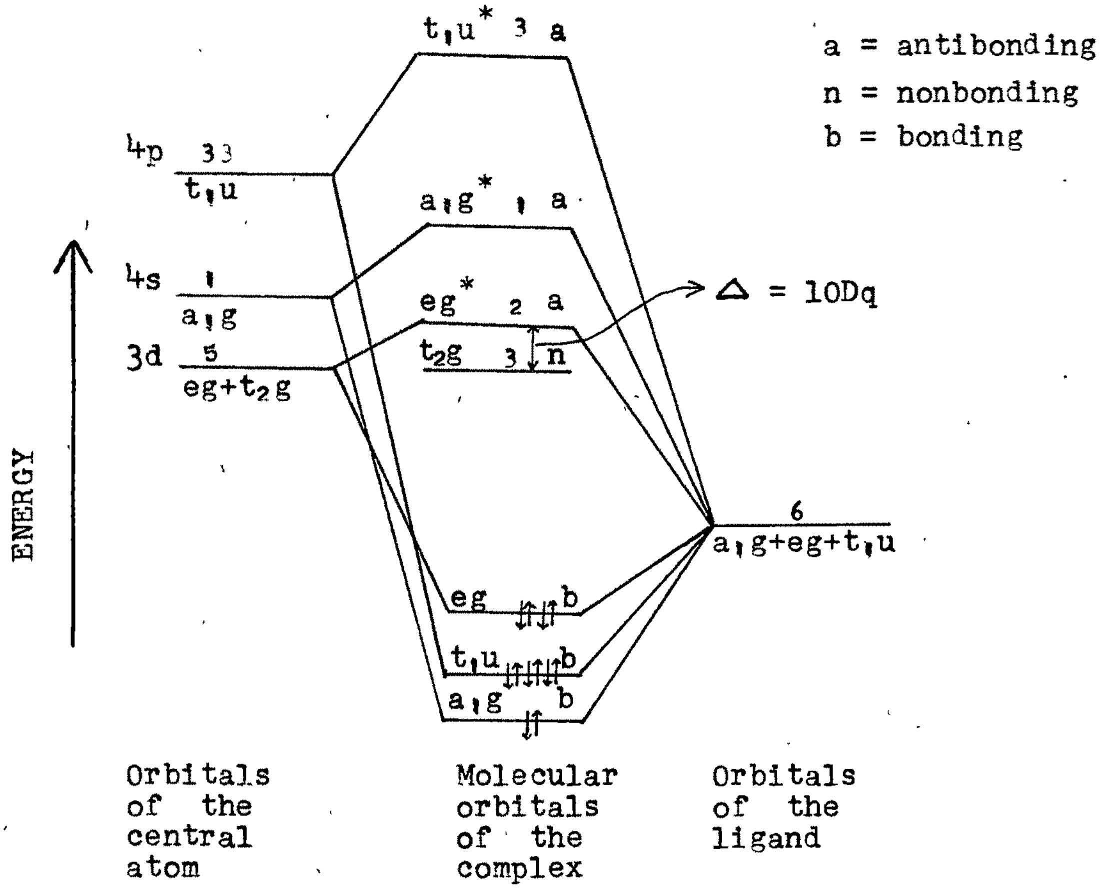
The spatial geometries and the types of hybridizations suggested by Pauling find support in magnetic studies. The known stereochemistry of the complexes is also consistent with the spacial arrangements predicted. In all these cases the metal ion attains an excited state due to pairing of electrons in the d orbitals. It has also been observed that the complexation can take place even with the metal ion in the ground state. sp^3d^2 hybridized orbitals of the metal ion involving outer d orbitals, are overlapped by weakly bonding ligands e.g.in $[FeF_6]^{3-}$ and $[Ni(NH_3)_6]^{2-}$ complexes. They are paramagnetic due to five and two unpaired electrons, respectively, and are also termed high spin outer orbital complexes.

The metal ligand bonds of the above type have a σ symmetry. The dxy, dxz and dyz orbitals with π symmetry undergo an orthogonal overlap with the ligand σ orbitals. However, ligand atoms containing vacant $d\pi$ orbitals e.g. in PH_3, SH_2 and ASH_3 or $p\pi$ orbitals e.g. in CO, dipyridyl may undergo interaction with filled dxy, dxz and dyz metal atom orbitals to form M→L $d\pi$-$d\pi$ or $d\pi$-$p\pi$ type of bonds, respectively. The greater stability of such complexes is due to the mutual stabilization of σ and π bonds.

Valency bond theory has certain short comings. It is limited to qualitative explanation, does not permit the interpretation or prediction of spectra, does not account or predict the detailed magnetic properties and also is unable to account for or to predict even the relative energies of different structures. It does not explain how the degenerate d orbitals split into two groups as a result of complexation. The application of the molecular orbital theory to complex formation was the natural consequence. This was developed originally by Hund[4] and Mulliken[5] to explain the structures of simple, di or polyatomic molecules. The application of this theory to complexes is due to Van Vleck[6]. According to this, as a result of metal and ligand atom orbital overlap during complexation, the electrons do not remain localized in metal or ligand but there is maximum probability of finding them in path extending over the entire molecule around the central ion and the ligands. Such molecular orbitals (MO's) are formed by suitable linear combination of atomic orbitals with same symmetry. The nine metal orbitals involved in complex formation have been classified into four different types as follows :

1. Spherically symmetrical	a_1g	(s orbital)
2. Doubly degenerate	eg	($dx^2 - y^2$, dz^2 orbitals)
3. Triply degenerate	t_2g	(dxy, dyz, dxz orbitals)
4. Triply degenerate	t_1u	(px, py, pz orbitals).

Depending on the molecular geometry, out of six ligand atomic orbitals, those which undergo effective overlap with particular metal ion orbital, combine to form the composite orbitals having σ symmetry a_1g, t_1u or eg. The combination of composite orbitals with the corresponding metal ion orbitals results in the formation of six bonding and six antibonding molecular orbitals, bearing same symmetry as that of the interacting atomic orbitals. In absence of π orbitals on the ligand atom the metal t_{2g} orbitals remain non-bonding. In cases where the ligand atom has orbitals with π symmetry there is formation of π bonding and π antibonding molecular orbitals. Following is a schematic energy level diagram for the σ M-O's in an octahedral complex.



The bonding molecular orbitals have lower energy than the antibonding molecular orbitals, but the exact order of the energy of the molecular orbitals depends on the extent of overlap. dxy, dxz and dyz orbitals have been shown as non bonding. The eighteen electrons contributed by the metal ion and the ligands are filled in the molecular orbitals in the increasing order of energy. The distance between the non-bonding t_2g and the antibonding eg states corresponds to the value of Δ = 10 Dq. In case of complexes with greater overlap of metal and ligand atom orbitals and specially those with π bonding, a higher order of stability can be expected.

Though several scientists were convinced about the covalent nature of the M-L bond, a purely electrostatic approach was being developed by Van Arkel and DeBoer to explain the structure and the stability of the complexes. Though this theory was partly successful, but one has not to go a long way in finding its pitfalls. It fails to explain the magnetic and the spectral characteristics of the complexes. Bethe[7] and Van Vleck[8] adopted the electrostatic approach with the necessary extension, and this theory is termed as the crystal field theory. According to it there exists an interplay of attraction between the electropositive central cation and the electronegative ligand anions or negative ends of dipolar ligand molecules, and this brings them closer. There is also repulsion between the clouds of electrons in the ligands which operates to push the ligands away from one another as widely as possible. Thus the ligands get arranged around the metal ion adopting definite geometry to counteract two opposing forces. The theory further considers that in the free uncomplexed metal ion, an electron can occupy any one of the five d orbitals with equal preference i.e. d orbitals are degenerate. However, in octahedral complex, an electron in dz^2 or $dx^2 - y^2$ orbital, which are directed along the axis, is subjected to much greater repulsion as contrasted with one in any of the dxy, dxz or dyz orbitals, as they lie away from the ligand. Hence, under the influence of an approaching ligand, the five d orbitals split into two separate sublevels of differing energy. In the higher energy level (eg) are found the dz^2 and dx^2-y^2 orbitals, in the lower energy level (t_2g) are found dxy, dxz and dyz orbitals. Thus there is separation of the free uncomplexed set of five orbitals, hitherto energitically equivalent, into orbital subgroups of differing energies. The separation between two sets of orbitals is known as crystal field splitting (Δ or 10 Dq).

The gain in energy achieved by the preferential filling of the lower lying t_2g levels is called the crystal field stabilization energy (CFSE), which accounts for the stabilization of the complex ion. Depending on the extent of crystal field splitting complexes are classified as "strong field" and "weak field" (ex. CN^- and F^-, Cl^-, Br^- or I^-, respectively).

The nature of the splitting of the metal d orbitals undergoes change in accordance with the symmetry of the surrounding field. The t_2g and eg orbitals undergo further splitting in a square planar field with D_4h symmetry and the order of energies of t_2g and eg is reversed in tetrahedral field. The magnitude of Δ or 10Dq is always small for tetrahedral complexes and hence they are less abundant.

This crystal field theory is useful in predicting the stereochemistry, magnetic properties, absorption spectra as well as thermodynamic properties of complexes. However, because of the emphasis on the orbitals and electrons of the central atom, the crystal field theory must necessarily become less accurate as delocalisation of ligand electrons and orbitals becomes important, that is as covalent bonding increases. Thus this theory cannot properly explain the relative strengths of ligands and the possibility of double bonding between metal ion and ligand.

The assumption made in the electrostatic theory that the metal ion orbitals do not in any way mix with ligand atom orbitals, can never be literally true in real chemical compounds. There are sufficient experimental evidences from ESR, NMR and absorption spectral studies which give a fair picture of how far many real complexes do deviate from this idealization. The ligand field theory uses the basic electrostatic view point and the method of calculation of the crystal field theory with certain modifications to account for the deviation from the electrostatic idealization. The credit for the advancement of this theory jointly goes to a number of scientists like Orgel, Nyholm, Owen, Liehr and many others[9].

The ligand field theory takes into account the basic assumption of crystal field theory, but also considers the overlap between the orbitals of the central atom and the ligand to form the molecular orbitals, depending on the extent of mixing. It leads to better understanding of electronic as well as magnetic properties of the complex compounds. On one extreme there are complex compounds with purely covalent M-L bond and on the other hand there are compounds, the formation of which can be explained by crystal field theory. The ligand field theory provides a good explanation for the intermediate cases.

Complex equilibria in solutions :

Jannik Bjerrum[10] first introduced the concept of stepwise formation or dissociation of a complex species. For the formation of complex (ML_n) the steps can be shown as follows :

$$M + L \rightleftharpoons ML \qquad (1.1_1)$$

$$ML + L \rightleftharpoons ML_2 \qquad (1.1_2)$$

$$ML_{n-1} + L \rightleftharpoons ML_n \qquad (1.1_n)$$

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

In these equations M is metal ion and L is the ligand ion formed by the liberation of hydrogen ions. The charges on the ligand ions have not been shown. The equilibrium constant governing each step K_1, K_2 ...... is termed the stepwise formation constant. Thus the nth metal ligand stability or formation constant corresponding to the equilibrium of the type

$$ML_{n-1} + L \rightleftharpoons ML_n \qquad (1.2)$$

is represented as

$$K_n = \frac{aML_n}{aML_{n-1} \cdot aL} \qquad (1.3)$$

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

In the dilute solutions of highly dissociated metal salt, concentration denoted by [ ] can be used instead of activity. The equation can be written as

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \quad (1.4)$$

Now B_n can be defined as

$$B_n = \frac{[ML_n]}{[M][L]^n} = K_1.K_2.K_3 \;....\; K_n \quad (1.5)$$

In addition the chelating agent is either an acid of a 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 can be written as follows :

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

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

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

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

Each of the above equilibria is governed by its constant. The ith proton ligand stability constant can be shown as below :

$$K_i^H = \frac{[LH_i]}{[LH_{i-1}][H]} \quad (1.7)$$

Now B_i^H can be defined as

$$B_i^H = \frac{[LH_i]}{[H]^i[L]} = K_1^H \,.\, K_2^H \,.\, K_3^H \,..\, K_i^H \quad (1.8)$$

In order to determine the stability constants in the systems described by the above equilibria, Bjerrum[10] introduced the concept of " Degree of formation or ligand number $\bar{n}$ ". This can be defined as the average number of ligands bound per metal ion present in whatever form i.e.

$$\bar{n} = \frac{[ML_1] + 2[ML_2] + \ldots\ldots\ldots\ldots N[ML_N]}{[M] + [ML_1] + [ML_2] \ldots\ldots\ldots\ldots [ML_N]} \qquad (1.9)$$

It is thus assumed that above are the only species present in the solution and the possibility of the existence of polynuclear complex ions, protonated complex, hydroxy complex and undissociated metal salt is ruled out.

Substituting the value of $[ML_i]$ from equation of the type (1.4) in equilibria (1.9) and eliminating $[M]$, the resulting expression would be

$$\bar{n} = \frac{K_1[L] + 2K_1K_2[L]^2 + \ldots\ldots NK_1K_2 \ldots\ldots K_N[L]^N}{1 + K_1[L] + K_1K_2[L]^2 + K_1K_2 \ldots\ldots\ldots K_N[L]^N} \qquad (1.10)$$

which may be arranged in the form

$$\bar{n} + (\bar{n}-1)K_1[L] + (\bar{n}-2)K_2K_1[L]^2 + \ldots\ldots(\bar{n}-N)K_NK_2K_1[L]^N = 0 \qquad (1.11)$$

This equation is called the " formation function ".

A similar formation function for the proton ligand complexes can be shown as

$$\bar{n}_H = \frac{K_1^H[H] + 2K_1^HK_2^H[H]^2 + \ldots\ldots jK_1^HK_2^H \ldots\ldots\ldots K_j^H [H]^j}{1 + K_1^H[H] + K_1^HK_2^H[H]^2 + \ldots K_1^HK_2^H \ldots\ldots\ldots K_j^H [H]^j} \qquad (1.12)$$

where $\bar{n}_H$ may be defined as the mean number of protons bound per not complex bound ligand molecule.

The plots of $\bar{n}$ against log $1/[L]$ or pL are called the formation curves of the systems. The solution of these formation functions leads to stepwise metal ligand formation constants.

The statistical effect prevents the successive 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. From statistical consideration it may be assumed that the tendency of the compound MA_n 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. A spreading factor has to be included to account for the nonstatistical factors like ligand ion repulsion or steric effects. It has been shown[11] that in a system where ML_2 is the highest complex and the spreading factor K_1/K_2 is high, the values of pL at $\bar{n}$ equal to 0.5 and 1.5 correspond to $\log K_1$ and $\log K_2$, respectively.

This method is, however, not applicable in cases where spreading factor is low. Even in the cases, where spreading factor is high it is not desirable to depend on the value of pL at specific points only because this may involve experimental error.

Different workers have, therefore, adopted different methods suitable to their experimental conditions. These have been reviewed by Irving and Rossotti[12] and Hearon and Gilbert[13]. These methods based on the use of equation (1.11) are useful when the formation of the different stages of complexation are simultaneous. In cases where first and second stage of formation are separated, only method available to improve the values of formation constants obtained from the formation curve, is the method of linear plot[14]. The use of this method in present investigation has been discussed in the proceeding chapter.

Factors effecting stability constants :

The major factors affecting the stability of complex ion are the nature of the metal ion and the nature of the ligand.

Nature of the metal ion :

The factors which govern the relative tendencies of the various metal ions to combine with a given donor may be divided into two parts .

(i) The ionic forces which are related to both charges and radius of the metal ion.

The stability of the complex increases with the ionic charges and decreases with the ionic radius of the metal ion. The metal with large ionic potential i.e. charge size ratio, should form more stable complexes. It is observed that the transition metal ions form more stable complexes as compared to alkali and alkaline earth metals.

(ii) The relative tendencies of various metals to form homopolar bonds with electron donor.

Since the metal ligand bond is not only electrostatic but there is also interaction of doubly filled ligand atom orbitals and vacant orbitals of the metal ion, the strength of the coordinate covalent bond also depends on the available vacant orbitals on the metal ion. Thus ionic and covalent wave functions have to be considered to determine the stability of the M-L bond.

Calvin[15] showed that the chelating tendencies may be measured as a product of equivalence of ionization potential and electronegativity. It has been observed that the electronegativities of the metal ions show a regular linear relationship when plotted against the stability constants.[16-18]

Mellor and Maley[19,20] pointed out that as a first approximation stability decreases with increasing basicities of the metal. Therefore, the weakly basic Cu and Pd form the strongest and the most strongly basic metal Mg forms the weakest chelates. This suggests that the strength of the bonding in chelates depends on the ability of the metal to form homopolar bonds. The metal which forms the strongest homopolar bonds, forms the most stable chelates. Mellor and Maley[20] gave an order by considering the stability constants of a particular chelating agent with a series of bidentate metals.

$$Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg$$

Irving and Williams[21] observed the same order of the stability constants of the chelates which increases steadily from atomic number 25 (i.e. Mn) to reach maximum with copper (at.No. 29), in the plot of the graph of stability constants against the atomic number of the metal i.e.

$$Zn < Cu > Ni > Co > Fe > Mn$$

The suggestion made by Irving and Williams[22] was that the factors governing the stabilities of the complexes are second overall ionization potential which is measure of covalent contribution and reciprocal ionic radius of the metal ion which is measure of electrostatic contribution. The enthalpy and entropy are contributed from the former and latter changes, respectively. The above order holds good for more than eighty ligands containing the donor atoms nitrogen and oxygen. After Irving[23] many scientists carried on the work on non transition metals and included them in the order established by Irving-Williams. Of course, there are some dearrangements observed in the series and these can be accounted for by considering special effects such as stereochemical consideration, d orbitals stabilization etc.

The sequence $Ni^{2+} \angle Zn^{2+} \angle Cu^{2+}$ should hold good in all cases if all the above conditions are valid. But there are some anamolies. In some cases Zn^{2+} forms less stable complexes than Ni^{2+} [24], Cr^{2+} complexes are more stable than those of Mn^{2+} or Ni^{2+} complexes are more stable than those of Cu^{2+}. [21,25,26] The above anamolies arise because the Irving-Williams's order does not consider the stabilization energy due to the effect of the ligand field. In the weak ligand field complexes involving metal ions with d^1, d^2, d^3, d^6 and d^8 configurations, more electrons occupy t_{2g} levels and contribute crystal field stabilization energy. For the metal ions with d^4, d^5, d^9 and d^{10} configurations, electrons are forced to occupy the eg levels and extra stabilization is cancelled out. In the case of metal ions with d^0, d^5 and d^{10} configurations no CFSE is liberated. In the first case no electron is present and in the latter two cases the electrons occupy both t_{2g} and eg levels and hence there is no liberation of CFSE. Thus it is seen that the order of CFSE due to the ligand field in ions with d^0, d^1, d^2, d^3, d^4 and d^5 electron configurations is 0.0Δ, 0.4Δ,

0.8Δ, 1.2Δ, 0.6Δ, 0.0Δ, respectively. Similar sequence is followed in metal ions with $d^6 - d^{10}$ configurations.

The lesser stability of Zn^{2+} and Mn^{2+} can be explained by the consideration of ligand field stabilization. The Jahn-Tellor effect brings the additional stabilization energy in the metal complexes with d^4 and d^9 configurations.

From the above considerations, for the ligation enthalpy changes, the following order has been suggested.

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

In cases where Jahn-Tellor stabilization is low or where there are five or six coordinated donor atoms, $d^3 > d^4$ and $d^8 > d^9$. In such cases Cu(II) forms less stable complexes than Ni(II).

If a series of complexes of different metal ions with the same ligand is considered, the enthalpy changes ΔS can be expected to be almost same and hence the above is the order of the stability of the complexes because $-RT \log K = \Delta F = \Delta H - T\Delta S$ where R = gas constant, ΔH and ΔS are the changes of enthalpy and entropy, respectively.

Nature of the ligand :

Complex formation can be interpreted as an acid-base reaction in which metal acts as an acid and ligand as a base, in the Lewis sense. Calvin and Wilson[27] showed that for a series of closely related ligands, the greater the basic strength i.e. pKa, higher is the stability of copper complex.

Some positive deviations which have been observed from these plots, can be explained to be due to the following other factors in the ligand.

(i) Ring size :

The work of Ley[28] on chelates of amino acids demonstrated that chelates with five and six membered rings are most stable. By the consideration of the examples of the complexes of oxalate, malonate ions, 8-hydroxyquinoline and 1,10-o-hydroxyphenyl isoquinoline, it is revealed that for a chelate ring without any double bond the five membered rings are more stable whereas six membered ones are favoured if the chelate ring involves unsaturation. It is seen that chelation is most favoured when the groups are in the 1, 4 or 1, 5 positions.

(ii) Number of rings :

It is observed from the work of Schwarzenbach[29] and polarographic work carried out by Calvin and Bailes[30] that an increase in the number of the rings in a chelate structure results in greater stability of the chelate. The maximum numbers of rings are reported for EDTA complexes of metals and these are found to be most stable.

(iii) Substitution in the ligand :

Substitution affects the basicity of a ligand due to the inductive effect of the entering group. Due to positive inductive effect of-CH_3 group, CH_3CH_2COOH forms more stable complexes than CH_3COOH. Substitution may favour complexation by providing additional coordinating atoms resulting in the formation of chelates. This is the reason why glycollic acid

($CH_2(OH)COOH$) is more complexing than acetic acid (CH_3COOH).

(iv) Steric effect :

Substitution in the ligand can have two other effects on stability:

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 observed is less. Substitution in the ligand may make it bulky and may thus bring in steric effect.

(v) Resonance effect :

The significance of resonance effect contributing to the stability of chelate rings was first demonstrated by Calvin and his group.[30, 31-34] The presence of resonance in the ligand of 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. The Fe(II) chelates of α-α'-dipyridyl or o-phenanthroline and naturally occuring pigments such as chlorophyll, haemoglobin, phthalocyanines are good examples of resonance stabilization.

(vi) Nature of the coordinating group :

This problem is somewhat complicated since the donor atoms must also be considered in relation to the acceptor atom. Ahrland and his associates[35] classified the elements into two types, Type A and Type B, on the basis of their tendency to combine with the ligand molecule.

Type A embodies those metal ions which forms more stable complexes with ligand molecules having earlier members of a group as the coordinating atom. Type B includes those metal ions which form more stable complexes when the ligand atom is a later member of a group. For example, in the boron complexes of the following ligands, the bond strengths and stabilities fall in the sequence

$$L = (CH_3)_3N \gg (CH_3)_3P > (CH_3)_3As.$$

This can be explained by considering that $L \rightarrow B$ bond is purely σ- in character and is weakened with the decrease in the tendency of the ligand atom to donate the pair of electrons. However, while $(CH_3)_3N$ does not form stable complexes with transition metals, yet the trialkyl phosphine and arsine form extremely stable complexes. The best example of it is $PtCl_2.2As(CH_3)_3$ which can be melted and even distilled without decomposition.[36] It can be explained by the consideration of the possibility of $M \rightarrow L$ π interaction. π bond can arise from the combination of filled $d\pi$ orbitals of the metal ion with $p\pi$ or $d\pi$ orbitals of the ligand atom, acting as acceptor. The capacity of a metal to form π bond depends upon the number of filled d orbitals in the central atom. Hence the π bonded complexes are favoured by the metals at the end of the transition series. The π bonding may be of $d\pi$-$p\pi$ type as in the case of carbonyl, cyano or nitro complexes or of $d\pi$-$d\pi$ type as in the complexes of ligands with P, S and As as coordinating atoms. The presence of π interaction in M-L bond has been amply supported by various spectroscopic studies. However, the extent of contribution of π bonding in stabilizing the bond between class B metal ions and the ligand atoms with vacant $p\pi$ or $d\pi$ orbitals is questionable. According to Jorgenson[37] and Klopman[38] the stability of M-S bond is due to the strengthening of M-S σ bond and the contribution of M-S π interaction is not significant.

It is also interesting to observe the formation of complexes in systems containing one metal and two ligands.

Martell[39] has classified the types of the reactions possible in a mixture of a metal ion and the two ligands as follows :

(i) A simple complex is formed between one ligand and the metal ion while the other ligand remains unbound in solution.

$$A + L + M \rightleftharpoons ML + A$$

(ii) Combination of the metal ion with both ligands simultaneously to form a mixed ligand chelate in a single step.

$$A + L + M \rightleftharpoons MLA$$

(iii) Formation of a mixed ligand chelate in two overlapping steps reflecting slight difference in the affinities of the ligands for the metal ion.

$$A + L + M \rightleftharpoons ML + A \rightleftharpoons MLA$$

(iv) Formation of a mixed ligand chelate in two distinctly separated steps, reflecting a large difference in the affinity of the ligands for the metal ion.

$$A + L + M \rightleftharpoons ML + A \rightleftharpoons MLA$$

(v) Formation of a mixture of two simple chelates rather than a mixed ligand chelate.

$$xL + yA + 2M \rightleftharpoons ML_x + MA_y$$

Among the five types of reactions classified by Mattell, reactions (ii), (iii) and (iv) give rise to mixed ligand complexes. The reaction of type (iv) has invited the attention of many chemists.

Mixed ligand complexes are rare among the labile complexes but are very common among the inert complexes. One has to account all the possibilities of mixed ligand formation depending upon the number and nature of ligands present, especially when more than two ligands are present. Three types of mixed ligand complexes can be thought of depending on whether the ligands involved are (i) unidentate-unidentate, (ii) unidentate-multidentate, or (iii) multidentate-multidentate. In the present investigation, reactions of the type (iv) have been studied. The primary ligands : A = dipyridyl, nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), iminodiacetic acid (IMDA) and histidine, and secondary ligand= L = catechol, pyrogallol, 2,3-dihydroxynaphthalene, protocatechuic acid, salicylic acid and thiosalicylic acid were selected for the formation of mixed ligand complexes of the type MAL, where M = Zn(II) or Cd(II). The formation of ternary complexes have been studied in solution and the compounds have been isolated, wherever possible. The study of the binary systems ML where M = UO_2^{2+}, Zn^{2+}, Cd^{2+}, Mg^{2+} or Tl^{+}, L = catechol, pyrogallol, 2,3-dihydroxynaphthalene or protocatechuic acid has also been carried out for comparison.

The polyhydroxy derivatives of phenols, phenolic acids and naphthelene with -OH groups at ortho positions are known to be efficient complexing agents. Their complexes with different metal ions have been reported in literature.

Starting from the year 1956, an extensive work on catechol complexes of various metal ions has been reported.

The formation constants of titanium complex with catechol and gallic acid in acid medium was demonstrated spectrophotometrically by Okac and Sommer[40]. Timberlake[41] studied the Cu(II) complex of catechol using potentiometric method. The molybdenum complexes with catechol, gallic acid and protocatechuic acid were studied by Buchwald and Richardson[42]. Titanium-catechol complex in presence of quinoline was studied by Babko and Gordeeva[43]. Colour reactions of catechol, pyrogallol and gallic acid with molybdenum were reported by Buchwald and Richardson.[44] The formation of zirconium complex of catechol having composition $Zr(cat)_2Cl$ has also been reported by Sandhu and coworkers.[45] V(IV) complexes of catechol have also been reported by Magee.[46] Titanium complex with catechol was studied by Shnaiderman and coworkers.[47] Using polorographic method, Cu(II) complexes of catechol were studied by Spacu and coworkers[48]. Antimony[49] is also known to form complexes with catechol. Milkos and coworkers[50] showed the formation of the compound $H_2[Ge(cat)_3]$. Ge(IV) complexes with catechol have been reported by Milkos Nadasy and coworkers.[51] Complexes have been prepared by treating niobium and tantalum hydroxide with alkaline solution of catechol.[52] Bhattacharya and coworkers[53] reported the V(IV) complex of catechol. Catechol, pyrogallol and protocatechuic acid complexes of titanium have been studied in aqueous solution.[54,55] Spectrophotometric study of molybdenum and tungsten complexes of catechol was carried out by Brown and McCallam.[56] Arsenic is also known to form complexes with catechol.[57] Andrianov and Nagarenko[58] studied the Ge(IV)-catechol complexes. Tantalum complexes with catechol have also been reported by Lukachina.[59] Thorium complexes of catechol were studied by Mehrotra and coworkers.[60] Formation constants of bivalent Sr, Ca, Mg, Cu, Zn, Co and Ni chelates of catechol have also been determined by Murakami and coworkers.[61]

Rare earth complexes of catechol and pyrogallol were studied potentiometrically.[62-64] Al(III) complexes of catechol have also been studied by thermometric, conductometric and potentiometric technique by Dubey and Mehrotra.[65] Bartels[66] studied the silicon complexes of catechol. Be(II) complexes of catechol 1:1 and 1:2 have also been reported.[67] Nazaronko and coworkers[68] carried out the study of Ge(IV) complexes with catechol. Formation of 1:2 complex of V(IV) with catechol has also been investigated by proton magnetic resonance studies.[69] Knyazeva and Shnaiderman[70] studied the ternary systems containing titanium-catechol and a secondary ligand. Catechol, pyrogallol and protocatechuic acid complexes of titanium have been reported in non aqueous solution.[71] Dow Corning[72] studied the silicon-catechol complexes. Uranyl complexes were studied potentiometrically by Baratusek.[73] Gut and coworkers[74] reported the catechol complexes of tantalum. 1:1 and 1:2 complexes of V(IV) with catechol have also been studied potentiometrically.[75] Jameson and coworkers[76] carried on the potentiometric study of Cu(II) complexes of catechol.

Shnaiderman and coworkers[77] reported titanium complexes with catechol. Complex formation of Cr(III) with catechol, pyrogallol and gallic acid was detected polarographically.[78] Using potentiometric methods, uranyl complexes were studied by Bartusek and coworkers.[79] Cu(II) complexes of catechol have also been studied by potentiometric method.[80] Athavale and coworkers[81] studied Cu(II), Zn(II), Ni(II), Cd(II) and Mg(II) complexes of catechol and protocatechuic acid using Calvin-Bjerrum titration technique.

Shnaiderman, Chernaya and coworkers[82] reported the titanium complex with catechol. Rare earth complexes of catechol and pyrogallol were studied potentiometrically by Poluektov and Tserkasevich.[83] Kapoor and Prakash[84] studied the reaction 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.[85] Goina and coworkers[86] reported the thermometric, conductometric and potentiometric studies of Al(III) complexes of catechol. The stability constants of Cu(II) and Ni(II) systems have also been determined by absorptiometric method.[87]

Separation of metals as catechol complex using solvent extraction technique has been suggested by Vrchlabsky and Sommer.[88] Catechol and 2,3-dihydroxynaphthalene were shown to react with silicon halides resulting in the formation of $[H_2SiL_3]$[89](where L = catechol or 2,3-dihydroxynaphthalene). The stability of Ga(III) complex with catechol was studied by polarographic and potentiometric methods.[90] Verma and Agarwal[91] have shown the polymerisation of uranyl catechol chelates. Be(II) and Sn(IV) complexes of catechol have been studied by potentiometric method.[92]

The stability constants of Cu(II) and Ni(II) systems have been reported by Yoshinaga Oka and coworkers[93] using absorption method. Various mixed ligand studies involving catechol have also been carried out.[94] The ternary system containing titanium-catechol and a secondary ligand has been studied by Vrchlabsky and coworkers.[95] Havelkova and coworkers[96] studied spectrophotometrically molybdenum and tungsten complexes of catechol. Be(II) and Sn(IV) complexes of catechol have been studied potentiometrically by Mehrotra and coworkers.[97] Kondratenko and coworkers[98] reported the Ge(IV) complexes with catechol. Formation constant studies of vanadyl complexes of catechol, pyrogallol, protocatechuic acid and gallic acid have been carried out potentiometrically.[99]

Extractive potentiometric determination in tungsten-catechol complexes were reported by Tananaiko and coworkers.[100] Talipor and coworkers[101] used titanium-catechol complex in solvent extraction. Formation constants of aluminium ion chelate with pyrocatechol were determined potentiometrically by Goina and coworkers.[102] Ferrous compounds of pyrocatechol were studied by Beltran Martinez and coworkers.[103]

The interaction of chromic sulphate with pyrogallol and gallic acid has been studied by using ion exchange technique.[104] The complexes of pyrogallol with iron[105], tungsten[106] and titanium[107] have also been studied by spectrophotometric method. Gore and Newman[108] studied the complexes of pyrogallol with iron. Osmium[109] and thorium[110] complexes of pyrogallol have been reported. Complexes of pyrogallol, protocatechuic acid and gallic acid with Ge(IV) have been investigated by using polarographic technique.[111] Zirconium and hafnium complexes with pyrogallol have been studied by spectrophotometric method.[112] The complex formation of pyrogallol with Al(III)[113] and Be(II)[114] has been investigated by potentiometric, conductometric and polarographic methods. Pyrogallol has also been used for photometric determination of Ta(V) by Sarry and coworkers.[115] V(IV) complexes with pyrogallol have been studied by spectrophotometric method.[116,117] V(V) complexes of pyrogallol and gallic acid were reported by Shnaiderman and coworkers.[118] Combination of boric acid with pyrogallol and α- or β-picoline was also reported.[119] Shagisultanova and coworkers[120] studied the tetravalent germanium complexes of pyrogallol and gallic acid.

Cu(II) complexes with protocatechuic acid have been studied by spectrophotometric method.[121] Niobium pentaoxide has been shown to react with protocatechuic acid to produce a yellow coloured complex which has been studied by spectrophotometric method.[122] Protocatechuic and gallic acids have been used in the spectrophotometric determination of Fe(III) and Ti(IV).[123] Sommer and coworkers[124] studied complex of Nb_2O_5 with protocatechuic acid using spectrophotometric method. Tl(I) complexes of protocatechuic acid and gallic acid have also been reported.[125] Spectrophotometric study of Ti(IV)-protocatechuic acid has also been carried out.[126,127] V(IV) is known to react with protocatechuic acid to form a stable yellow coloured complex which has been studied by spectrophotometric method.[128] Jayadevappa and coworkers[129] determined the stability constants of Cu(II), Zn(II), Cr(II) and Ni(II) complexes with protocatechuic acid by potentiometric method. Dhaneshwar[130] has shown that in Ti(IV)-protocatechuic acid system, studied by spectrophotometric method, Ti(IV) undergoes reduction. Protocatechuic and gallic acid complexes of Ti(IV) have also been studied using potentiometric method by Athavale and coworkers.[131,132]

Cherepakhin[133] studied the analytical properties of 2,3-dihydroxynaphthalene complexes. Complex systems involving uranyl and 2,3-dihydroxynaphthalene were studied by potentiometric method in dilute aqueous solution by Bartusek.[134] Shimer George Monroe[135] reported the Iron-complexes of 2,3-dihydroxynaphthalene. Potentiometric study of boric acid complexes with pyrogallol, 2,3-dihydroxynaphthalene, pyrocatechol and its mono-sulphonic acid were reported by Havelkova and coworkers.[136] Andrae Kalus[137] observed that the reaction of $NbCl_5$ and $TaCl_5$ in benzene with 2,3-dihydroxynaphthalene gives hexa coordinated complexes of the type $H[M(2,3\text{-dihydroxynaphthalene})_3]$. The stability constant of the anionic chelate of 2,3-dihydroxynaphthalene diol with boric acid was studied potentiometrically.[138] Bhattacharya and coworkers[139] studied the Cu(II) and Ni(II) complexes of 2,3-dihydroxynaphthalene.

However, not much work has been done in the ternary systems containing the polyphenolic ligands. An attempt to study such complexes has been made in the present investigation. Some binary systems have also been studied for the sake of comparison.

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