CHAPTER ONE

INTRODUCTION

The properties of the metal complexes and chelates are mainly dependent on the nature of the metal ion and the nature of the ligand. In case of chelates the size of the chelating ring, the number of the rings formed with a given metal ion and the resonance interaction also govern the stability. However, in case of both simple complexes and the chelates, the nature of the coordinating atom has a significant role in deciding the stability of the compound. The most significant effect on complexation, as a result of change in the coordinating atom, is due to the change in the basicity of the ligand. The complex formation can be thought of as an acid-base reaction in which metal acts as an acid and ligand acts as a base. It can naturally be inferred, that the greater the basicity of the ligand, higher should be its tendency to form complex. Sidgwick[1] has given an exhaustive discussion of the coordinating tendencies of a large number of donor atoms. However, only chelates containing oxygen, nitrogen and sulphur[2-4] as coordinating atoms have been studied in detail and a comparative investigation of the chelating tendencies of these chelating atoms has been possible. Schwarzenbach and coworkers[5] determined the formation constants of the bivalent metal complexes containing ligands of the type N-Me, O-Me and S-Me and found the stability order O > N > S for the alkaline earth metal ions and N > S > O for transition metal ions with nearly filled d-orbitals. Cu(II) and Cd(II) complexes of secondary amines, alkyl ethers and alkyl thioethers[6-8]

exhibit the order N > S > O.

It is interesting to study first the relative tendencies of nitrogen and oxygen as coordinating atoms in complexes and then to compare oxygen and sulphur which are members of the same group. Oxygen and nitrogen containing ligands form very stable complexes or chelates with large number of metal ions and the coordinating atoms are found to be having similar affinity for metal ions. Further they behave alike in the fact that their coordinating tendencies go down[3] with increasing substitution, e.g.

$$H_2O > R.OH > R.OR$$

$$H_3N > R\text{-}NH_2 > R_2\text{-}NH > R_3\text{-}N$$

The amines represent the most important class of ligands coordinating through nitrogen. Since the nitrogen atoms have only one lone pair, $N \rightarrow M$ σ-bond is formed. However, dipyridyl and o-phenanthroline are known to form very stable M-N bond in metallic complexes. This is because in these complexes besides $M \leftarrow N$ σ-bonds, $M \rightarrow N$ $d\pi$-$p\pi$ interaction may take place and this accounts for the stability of these tertiary amine complexes.

Divalent oxygen, however, has two lone pairs of electrons and can share one or both of them in the formation of complexes. Bidentate behaviour of oxygen is observed in cases of basic acetates of metals like Be(II), Zn(II), Zr(II) and in polymeric alkoxides. However, such cases are not very common. In majority of complexes oxygen shares only one of the lone pairs with the metal ion e.g. the complexes of H_2O, alcohol, ethers, ketones and polyhydroxy phenols. From the

observation of the formation constant data of various metal complexes, it can be inferred that the majority of non transition metals have greater affinity for oxygen than for nitrogen. There are, however, some exceptions to this generalization. Sidgwick[9] has classified the metals into three classes depending on their tendencies to combine with oxygen or nitrogen.

$\overline{O} > N$ - Mg, Ca, Sr, Ba, Ga, In, Tl, Ti, Zr, Th, Si Ge, Sn, V^{+5}, V^{+4}, Ta^{+5}, MO^{+5}, U^{+6}, U^{+4}, Fe^{+3}, Co^{+2}.

$O = N$ - Be, Cr^{+3}, Fe^{+2} - Pt metals.

$N > \overline{O}$ - Cu^{+}, Ag^{+}, Au^{+}, Cu^{+2}, Cd, Hg, V^{+3}, Co^{+3}, Ni^{+2}.

It can be noticed that all the members of the first type are inert gas like ions. Those of the second group are very small ions like beryllium or larger transition metal ions. Third type includes metals of palladium type or with nearly filled d levels e.g. Ni(II). This general classification is applicable only when other factors, such as size of the ring, substitution in the N and O containing ligands are alike. Even for structurally related ligands, number of exceptions to this are observed.

According to Van-Uitert and Fernelius[10], smaller the difference in the electronegativities of the metal ion and the coordinating atom stronger is the M-L bond. The bond formed is more covalent in nature. With the increase in the difference in the electronegativities of the metal and the ligand atom there is development of dipole character in the M-L bond, resulting in the weakening of the M-L bond strength. The hybridization state of an atom is also known to affect the

electronegativity of an atom and hence the bond strength of the M-O or M-N bond will also be dependent on hybridization state of the atoms. The electronegativities of these atoms can be expected to increase in the order

$$-\mathrm{N}<\ ,\quad >\mathrm{N},-\ \mathrm{N}=\mathrm{N},\equiv\mathrm{N} \quad \text{and}$$

$$-\mathrm{O}^{-},\quad \overset{\curvearrowright}{\mathrm{O}}\ ,\ =\mathrm{O}\ .$$

The effective electronegativity of nitrogen and oxygen can be determined from their proton affinities. Single bonded nitrogen is strongly basic (amines), double bonded ring nitrogen is weakly basic (pyridine), diazo nitrogen is neutral (azo-benzene), and triple bonded nitrogen is acidic in character as observed in the dissociation of hydrogen in hydrocyanic acid. Similarly the cholate ion is basic, water is neutral and double bonded oxygen forms the acidic group $-\mathrm{COOH}$.

In general, however, the nitrogen containing ligands are more basic and are bound to the metal ion by coordinate linkage. The resulting complexes are, therefore, cationic in nature. On the other hand most of the oxygen rings are formed by the replacement of hydroxylic hydrogen and the resulting complexes are neutral or anionic e.g. the bis.β-diketonate and catecholate complexes, respectively. This difference in the charges of the resulting complexes result in different entropy changes. This in turn affects the stability of the complex. Thus comparison of the relative stabilities of such complexes, purely on the basis of the nature of coordinating atoms, will not be satisfactory.

In cases of the ligands where the coordinating atoms are in similar circumstances e.g. (NR_3, OR_2), interpretation in

terms of electronegativity succeeds [11]. In case of class III type of metals (page No. 3) the covalent donor bonding makes a significant contribution to the strength of the coordinate bond. These metals have available capture levels and can accept pair of electrons from the ligand atom. With the increase in the electronegativity of the ligand atom, the tendency to donate the electrons goes on decreasing resulting in the lowering in the strength of M-L bond. Since nitrogen is less electronegative than oxygen, the order M-N > M-O holds good in the complexes of the class III type of metal ions. Further, these metals have filled d-orbitals and hence there will be increasing lone pair repulsions between the d-orbitals of the metal ion and the non-bonding lone pairs in the orbitals of these small ligand atoms. As oxygen has two lone pairs and nitrogen has only one, the repulsion in case of M-O bond is more than the repulsion in M-N bond. This contributes to the greater stability of M-N bond compared to M-O bond.

The class I type metals (page No. 3) are, however, electropositive non transition metal ions or transition metal ions without any d-electrons or with few d-electrons. The M-L bond in the complexes of such metals is more or less electrostatic in nature. The more electronegative coordinating atom can be expected to form more stable complexes with such metal ions. This explains the order M-O > M-N.

Another point which needs attention is that donor atoms which give large ligand field splitting form their strongest complexes with the metal ions which are particularly sensitive to ligand field stabilization, whereas donor atoms which

produce small ligand fields tend to form relatively more stable complexes with cations which are insensitive to ligand field stabilization. Nitrogen containing ligands form stronger ligand fields directed towards metal ion than the oxygen containing ligands. The class III type metal ions, with d-electrons, are sensitive to ligand field stabilization and hence form more stable M-N bond. The type I metals, however, have little or no contribution from the ligand field stabilization and hence form less stable M-N bond.

The nature of the M-L bond, in complexes containing coordinating atoms of the same group, is another interesting field of study. It has been observed earlier, that, the complex forming tendency of a ligand increases with the increase in its basicity. In case of the complexes of a metal ion with structurally related ligands, a linear relationship between the formation constant of the complex and the proton ligand stability constant of the corresponding ligand has been observed[12]. The non-transition metal complexes of tri alkyl ammonia are found to be more stable than that of tri alkyl derivatives of phosphine and arsine and this is in agreement with the basicity order $NR_3 > PR_3 > AsR_3$. Thus the non-transition metals are found to form more stable complexes with ligands containing the earlier members of a group as the coordinating atom[13]. It has been observed that coordinating tendency of $X(Me)_2$, where X = oxygen, sulphur, selenium and tellurium, with aluminium trimethyl is in the order $O > S > Se > Te$[14]. However, in case of transition metal complexes there is reversal in the order. The literature reveals number of

instances supporting the above observation. However, above pattern of the relative coordinating tendency of the ligand atoms with the metal ions is not universally valid and several cases of divergence are met with.

In spite of lack of uniformity, the metals have broadly been classified in to two classes by Ahrland, Chatt and Davies[11]. The class A consists of non-transition metals and earlier members of the transition series in their common valency state. They form more stable complexes with the first ligand atom in each group (N, O and F). The class B consists of the later members of transition series or the earlier members in lower oxidation states. They form more stable complexes with the ligand atoms which fall later in a periodic group. ($N < P < As < Sb$, $O > S < Se < Te$ amd $F < Cl < Br < I$).

In cases of many metals class A or class B character is very well defined and can be detected even by observing the stabilities of their complexes only qualitatively. There are, however, borderrline cases which exhibit different characters depending on the oxidation states or the specific group of ligand atom with which coordination takes place. Thus the border between class A and class B type of metals is not very sharp.

Pearson[15] on the basis of his independent observations, classified the metals into hard and soft acids depending, respectively, on their greater or lesser tendency to receive the electrons. He termed the ligands with higher tendency to donate their electrons as a hard bases and the ligands with lesser tendency to donate the electrons as soft bases. He

observed that the hard acids have greater tendency to combine with hard bases and vice-versa. Pearson's hard and soft acids are alternative nomenclatures for metals with A and B character and the terms hard and soft bases correspond to ligands containing earlier and later elements of the group as coordinating atoms, respectively.

Attempts have also been made to explain class A and class B character of metal ions in terms of wave mechanical concept of M-L bond in complexes. According to Pauling, besides σ-bonding, π-interaction can also stabilize the M-L bond. Such π-bonding is possible only between transition metal d-π orbitals (d_{xy}, d_{yz}, d_{zx}) and vacant p or d acceptor levels on the ligand atom. Except in special cases (pyridine, 2,2'-dipyridyl, cyanide or carbonyl complexes) where M-O or M-N $d\pi$-$d\pi$ interaction can take place, oxygen and nitrogen have no π- levels available to accept the electrons from suitably place d-orbitals on the metal atoms. On other hand, sulphur and phosphorous have vacant d-orbitals which can be used for $d\pi$-$p\pi$ bonding. The conditions for M-L $d\pi$-$d\pi$ interactions are more favourable in transition metals in their normal oxidation states. Thus for the complexes of these metal ions the stability increases in the order P > N or S > O. This accounts for the class B character of these metal ions. In case of non-transition metal ions and transition metals, without available $d\pi$-electrons, back donation M $\rightarrow$ L is not possible and only L $\rightarrow$ M σ-bonding accounts for the stability of their complexes. The ligands with N, O or F as coordinating atoms form more stable σ-bonds, and hence the above metals form more stable

M-O bond than M-S bond. This explains the class A character of these metal ions.

The concept of π-bonding has also been incorporated in the molecular orbital and ligand field theories of complex formation. According to molecular orbital concept, in the complexes with Oh point symmetry, the ligand atom orbitals combine to form composite orbitals of a_{1g}, t_{1u} and e_g symmetry. Metal atom orbitals $d_{x^2-y^2}$, $d_{z^2}(e_g)$, $4S(a_{1g})$ and $4P(t_{1u})$ combine with the ligand composite orbitals of same symmetry resulting in the formation of six bonding and six antibonding molecular orbitals. The molecular orbitals formed are all σ- in character. However, d_{xy}, d_{yz} and d_{xz} orbitals of the metal atom, which are having π symmetry remain as non-bonding molecular orbitals. In cases, where π-orbitals are available on the ligand atom, they may combine to form the composite orbitals having the required symmetry to combine with the metal d_{xy}, d_{yz} and d_{xz} (t_{2g}) orbitals and this results in the formation of the bonding and anti-bonding π molecular orbitals. If the ligand π-orbitals is vacant and is of higher energy, M-L π-interaction results in an increase in the value of Δ i.e. separation between t_{2g} bonding and e_g antibonding molecular orbitals. The redistribution of the electrons in the molecular orbital liberates energy and stabilizes the complex. Thus π-bonding can explain the greater stability of M-S bond in case of class B type of metals.

Though the concept of π-bonding seems to explain class A and class B character of the metal ions satisfactorily but

the extent to which π-interaction occurs in the M-L bond is still shrouded in controversy. Nyholm and coworkers[16] indicated that π-bonding does occur in the M-L bond in transition metal complexes with phosphine and arsine. Number of studies[17-21] on the sulphur containing ligands have been reported and it has been shown that M-S bond is more stable than M-O bond in transition metal complexes. In some of the publications from our laboratory,[22-28] the relative stabilities of M-O and M-S bonds have been studied and class A and class B characters have been assigned to the metals. Metal to ligand π-bonding has been firmly established in number of transition metal complexes. Recently Gerlach and Holm[29] carried out NMR studies on β-amino thione and the corresponding oxygen containing ligand complexes of Ni(II) and indicated π-interaction in M-L bond. Contact shifts in ligand proton indicated metal π-electron delocalization in the highest energy molecular orbital of the ligand. In these complexes, however, there is π-interaction in both M-O and M-S bonds and is of dπ-pπ type.

Nanjo and coworkers[30] obtained the NMR spectra of $Ni(EX)_2$, and $Ni(EAF)_2$ (HEX = $EtOCS_2H$, HEAF = $(EtO)_2PSSH$) complexes in pyridine $CdCl_3$ solutions and observed the shift in the sulphur ligand protons in $Ni(EX)_2$ indicating that the unpaired electrons of the Ni were partially delocalised to the π-system of the ligand. No significant shift of S-ligand protons was observed in $Ni(EAF)_2$ complex due to the lack of π-character of the P-O bonds. Ricḳrds and Johnson[31] have also shown the possibility of M-S π-interaction on the basis of Mossbauer studies on (di-cyano 1,2-dithioethylene complex

of iron(III). The magnitude of the isomer shift on varying the temperature was comparable with that observed in the iron(III) N-N dialkyl-di-thio carbamates and the high value has been interpreted presumably as a consequence of the electron donation from the ligand orbitals into metal d-orbitals with little contribution from back donation from metal orbital into empty ligand π-orbitals. Bonamica and Dessy[32] carried out X-rays studies of complexes involving M-S and M-Se bonds and observed the greater stability of M-Se bonds. This can be explained by considering the back donation of electrons from metal orbitals to vacant π-orbitals of S and Se atoms. ESR studies of Cu(II) diethyl-dithio carbamate complex also indicated the presence of Cu-S π-bond. Kenneth and coworkers[33] have also indicated M-S π-interaction in some thiolate complexes of transition metals. They have observed that though normally there is an increase in the σ-bonding tendency of the ligand with increase in the basicity, but in cases where the ligand is a π-acceptor, an increase in basicity is associated with reduced $M \rightarrow L$ π-interaction, resulting in the lowering of the stability of the complex. Chatt and coworkers[34] have also proposed that the trans directed substitution in the complexes of some sulphur and phosphorous containing ligands are also due to $M \rightarrow L$ π-bonding.

The order of the stabilities of complexes has been determined in our laboratory[26-28] by carrying out metal displacement studies in the complexes of sulphur containing ligands. Cd(II), Hg(II), Ag(I) and Pb(II) are found to displace Ni(II) and Zn(II) from the complexes. The greater

stability of M-S bond in case of first three metal ions can be explained in terms of their greater tendency to form M-S π-bond. However, Pb(II), with S^2 electron screen can not affect significant $d\pi$-$d\pi$ interaction, and hence greater stability of Pb-S bond has to be attributed to some factor other than π-bonding. Further Petit and coworkers[35] observed low values of K_1 and K_2 in the metallic complexes of a number of sulphur containing ligands. It is expected to be high in complexes involving M-L π-bonding. The metal having donated π-electron to the first ligand should have less tendency to lose π-electron to the secondary ligand. Petit and coworkers also observed lowering in the values of formation constants of these complexes with increase in Hammet σ -function, (electron withdrawing power) of the substituents in the ligands. This means that there is a decrease in the formation constant with the increase in the acidity of the ligand as in case of normal σ -bonding ligands. This is in contradiction with the reversal in the order as observed by Kenneth and coworkers[33] in case of thiolate complexes.

The above observations have alluded to the fact that the contribution of π-interaction in stabilizing M-S bond may not be very significant. Alternative explanation have, therefore, been extended to understand the nature of M-S bond. Williams and Hale[36] tried to explain the class A and class B character of the metals in terms of the factors affecting the strength of covalent bond between metal and ligand without any consideration of back donation of electrons from metal to ligand. Ahrland[11], on the basis of Pearson's classification

of soft and hard characters of acid and bases observed that the soft-soft interactions are more covalent in nature, whereas hard-hard interactions are more ionic in nature. The former is stabilized due to the favourable enthalpy changes, whereas latter is stabilized due to favourable entropy changes. Soft-hard or hard-soft interactions lead to the formation of weak bonds. An increased strength of the M-S bond in transition metal complexes can be attributed to the fact that the transition metals are soft acids and ligands containing sulphur atom are soft bases.

Jorgenson[37] and Klopman[38] extended alternative explanation to explain the greater stability of M-S bond. Jorgenson put forth the concept of charge transfer into the continuum orbitals of the ligands. In case of the soft ligands e.g. PR_3 or SR_2 the continuum orbitals have much lower energies. However, in case of hard ligand atoms NR_3 or OR_2 the continuum orbitals start at much higher energies. Thus the charge transfer into continuum orbitals of phosphorous or sulphur is more probable than the charge transfer to the orbitals of nitrogen or oxygen. This accounts for the greater stability of M-P and M-S bonds. The concept of charge transfer into continuum orbitals can be considered similar to the polarization. However, Jorgenson's concept is difficult to understand.

According to Klopman[38], in case of heteronuclear compounds with larger difference in the energies of outermost orbitals of the reactants, the extent of overlap is less resulting in very small covalent interaction. The interaction

is mostly ionic in nature. However, if the difference in the energies of the interacting orbitals is less, there can be better overlap. The interaction of class B metals and soft base ligands like sulphur containing ones, can, therefore, be expected to be more covalent in nature. Thus the greater stability of the M-S bond in the transition metal complexes can be explained only in terms of the stabilization of δ -bond.

In order to make a comparative study of the M-N, M-O and M-S bonds, systematic investigation of the amino, hydroxy and mercapto acid complexes has been undertaken in the present investigation. The formation constants of the complexes have been determined in solution. Whereever the work has been already done, the values reported in the literature have been used for comparison. The study has been extended to ternary complexes in solutions and this throws some light on the nature of M-S bond. Attempt to isolate the ternary complexes has been made and the compounds have been characterised by various studies.

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