CHAPTER I

INTRODUCTION
Every branch of science and technology has a never ending field of research. Whenever the Scientist in a particular field achieves some thing new, he finds, there is some more still to be achieved. It is just like conquering peaks after peaks and yet not reaching the goal.

The last two decades can be regarded as period of revolution in the field of coordination chemistry. Many new methods involving modern techniques have been advanced and are widely used in the study of complex compounds.

The present knowledge of coordination chemistry stands on the immortal contribution of Werner\textsuperscript{1}. The Werner's coordination theory has been a guiding principle in Inorganic Chemistry and the theory of valency.

**THE COORDINATION THEORY**

**Early developments :**

Probably the chemistry of complexes has originated in 1704 with the discovery of prussian blue by Diesbach, a colour maker. The first era of rapid activity in this field may be attributed to the investigations of Tassaert\textsuperscript{2} and the composition of cobalt (III) ammines\textsuperscript{3} may be regarded as the first reliable work in this field. The contributions of Graham\textsuperscript{4}, Claus\textsuperscript{5}, Blomstrand\textsuperscript{6} and Jorgensen\textsuperscript{7} have their own
place of importance in the development of the chemistry of complex compounds.

Werner's contribution:

The genius of Alfred Werner changed practically the whole field of coordination chemistry in 1891 when he published his paper 'Contribution to the theory of affinity and valency'\textsuperscript{8}. The theory was developed later in a more generalised form in 1893 and published the same year as "Werner's Coordination Theory"\textsuperscript{9}. In short, the fundamental principles of the theory may be summed up as follows:

A metallic ion has two kinds of valencies, principal (ionic) and auxiliary (coordinate). In the immediate neighbourhood of the central ion there will be a number of groups (usually but not invariably fixed) which are bonded directly to the central atom and retained with greater or lesser tenacity by it. In addition to these coordinated groups in the inner sphere there are present ions of charge opposite to that of the complex ion which are required to form an electrically neutral substance. When such a species is dissolved in water, the groups in the inner or coordination sphere will tend to remain bonded to the central atom while other remaining groups or ions required to build up a neutral molecule will behave as independent particles in solution.
The theory got ample support from the extensive work in this field of which conductivity studies on large number of metal ammines deserve mention\textsuperscript{10}. In 1911 resolution of $[\text{Co (en)}_2(\text{NH}_3)\text{Cl}]^{+2}$ via its $\pi$ bromocamphor sulphonate\textsuperscript{11} by Werner was the first successful attempt followed by X-ray crystal analysis\textsuperscript{12} measurement of dipole moments\textsuperscript{13} etc., which presented a powerful argument for the essential validity of Werner's theoretical postulates.

The development of electronic theory of valency by Lewis\textsuperscript{14} and Kossel\textsuperscript{15} lended a great support and final acceptance of Werner's theory. The principal and auxiliary valencies were recognised as electrovalency and covalency, respectively. Sidgwick\textsuperscript{16} made the first attempt to explain the formation of complex compounds on the basis of electronic theory of valency and introduced the concept of effective atomic number (E.A.N.).

Pauling provided quantum mechanical basis for qualitative ideas of Sidgwick, and this resulted in new knowledge of the basis of stereochemistry of complexes. The magnetic behaviour of these compounds was first accounted for by this approach. For about twenty years from this date tremendous amount of work was done in the field which resulted in the propagation of modern theories explaining the formation
of complex compound and affording other information about these type of compounds.

**ELECTROSTATIC THEORY**

This theory was first used by Kossel\textsuperscript{17} to explain the complex formation. According to this theory the complexes are held together by electrostatic attraction between oppositely charged ions or between ions and dipolar molecules. Van Arkel and De Boer\textsuperscript{18} and Garrick\textsuperscript{19} accounted for many of the properties of complex compounds by the help of this theory. It was developed further and refined and presented in a more general form as 'Crystal Field Theory'.

The fundamental theoretical basis was developed by Bethe\textsuperscript{20} and Van Vleck\textsuperscript{21}. The underlying principle of this theory is that the five d orbitals which are degenerate and equal in energy in the gaseous metal ion, become differentiated in the presence of electrostatic field generated due to ligands. In the electrical field the normally degenerate d levels are split as in familiar spectroscopic Stark effect. The extent to which the splitting would take place will depend upon the central ion, the symmetry and strength of applied field. Such a conception will give rise to (a) weak field, (b) moderate field, and (c) strong field - depending on the above factors.
In case of transition metal ion, during coordination the normally degenerate d levels are split into sublevels of lower and higher energy on account of strong electrostatic field set up by anions or dipoles. This is quite similar to Zeeman effect in magnetic field and Stark effect in an electrical field. The sub levels of lower energy are first filled and the unpaired electron may get paired thereby accounting for the magnetic properties of the complexes. The change in the electron cloud may be the cause for transition in light absorption.

This theory has been employed in explaining the magnetic behaviour and d-d spectra of complexes in the visible region by a number of workers.\textsuperscript{20}

The crystal field theory is of general validity due to its quantum mechanical approach, but fails to account for π bonding in complexes and their stereochemistry. This theory centres round the splitting of d orbitals and does not present the total energy picture of complexes.\textsuperscript{21,22}

\textbf{VALENCY-BOND THEORY}

Schrodinger's concept of wave nature of electron and its directional properties were first applied by Coulson\textsuperscript{23} to the general question of valency. The s, p, d sublevels may be regarded as being oriented in a particular direction in
space and the bond formation takes place by the overlap of bonding electrons. The extent of overlap will be responsible for covalent bond strength.

Pauling\textsuperscript{24} was the first to extend this theory in correlation and interpretation of the properties of coordination compounds. According to 'Valency bond theory', in the complex formation association results from overlap of an orbital of the ligand containing an unshared pair of electron with hybridized orbitals of metal ion. In other words it may be said that when the coordinate bond is formed, both electrons which were originally on one of the bonded atoms are now put in a linear combination of the atomic orbital of the bonded species.

Pauling\textsuperscript{24} has postulated that if a ligand has or can have by resonance vacant orbitals, and if the central atom has \(d\) electrons, \(\Pi\) bonding from metal to ligand will occur. This will strengthen the coordinate bond and help to reduce the negative charge formed on the central atom by addition of ligands. Chatt\textsuperscript{25} and Nyholm\textsuperscript{26} have shown the existence of \(\Pi\) bonding in metal complexes.

\textbf{MOLECULAR ORBITAL THEORY}

When an atomic orbital overlaps several atomic orbitals on different nuclei, then a more extended molecular orbital is obtained. In other terms, linear combination of
atomic orbitals results in molecular orbital. This is essence of molecular orbital theory.

Van Vleck\textsuperscript{27} applied this theory to complex compounds. According to him the bonding electrons are supplied by the ligand and the d electrons present in the central atom are accommodated in the non-bonding d orbitals and the antibonding molecular orbitals. The energy-separation of the non-bonding d orbitals as well as the energy required for the pairing of the originally unpaired electrons, determine the electron pair formation in complexes.

This theory has satisfactorily been used by a number of workers\textsuperscript{28} to explain various properties of the complex compounds. The metal olefines\textsuperscript{29} and metal cyclopenta-
dienes\textsuperscript{30} have successfully accounted for by this theory.

(Amongst all the theories discussed above the valency bond theory due to its limitation to qualitative explanation and failure to interpret the spectra and number of other inconsistencies has proved to be the poorest. In terms of quantitative approach the electrostatic theory along with crystal field theory is quite satisfactory, being very simple and affording a host of correct informations about the complexes. The combined approach of molecular orbital theory and crystal field theory is given the name "Ligand field theory" and this
has been widely used considering the proposed 'Jahn Teller Effect', in explaining the formation of most of the complex compounds.

**STABILITY**

The formation of a complex compound according to the electronic concept is 'Lewis acid-base' reaction, where metal ion is an acid and the ligand is the base. The formation and dissociation of complex compound is similar to that of poly basic acids and involves the following successive equilibria:

\[
M + A \rightleftharpoons MA \quad (1)
\]

\[
MA + A \rightleftharpoons MA_2 \quad (2)
\]

The stepwise formation finally gives:

\[
MA_n + A \rightleftharpoons MA_{n+1} \quad (3)
\]

where M is metal ion and A is ligand, n is number of ligand molecules. (The charges have been neglected for the sake of simplicity).

By the application of Law of mass action and with usual notations, we have:

\[
K_1 = \frac{[MA]}{[M][A]} \quad (4)
\]

\[
K_2 = \frac{[MA_2]}{[MA][A]} \quad (5)
\]

and finally

\[
K_{n+1} = \frac{MA_{n+1}}{[MA_n][A]} \quad (6)
\]
The constants $K_1$, $K_2$, ..., $K_{n+1}$ etc., are designated as stepwise formation constants, and the product of these gives the total or overall formation constant $K_T$.

$$K_1 \cdot K_2 \cdot \ldots \cdot K_{n+1} = K_T$$

Overall stability has been widely studied by a number of workers.

**FACTORS DETERMINING THE STABILITY IN SOLUTIONS:**

There is now a great deal of quantitative information on the stability of coordination compounds. A number of factors are known to affect the stability of complexes in solutions. Here only a few and important ones are discussed.

1. **Nature of metal ion:**

   Most of the elements of periodic table are capable of forming complexes. The transition metals in particular are known to have strongest tendency for combining with electron donor groups. Schwarzenbach\(^{33}\) has classified the cations in three groups.

   **Group I - Cations with a Noble gas configuration:**

   This group includes alkali metals, alkaline earths and aluminium. In these cases purely electrostatic phenomenon predominates and the forces between small ions of high charge are specially strong and leads to stable complexes.

   **Group II - Cations with completely filled d subshells (18 electrons):**

   Cu(I), Ag(I) and Au(I) are typical metals of this
class. The ions are highly deformable and the bonds in their complexes are predominantly covalent. The complexing tendency of this group of metals is entirely different from group I metals. Charge and radius of the metal ions are not the dominating factors, but the difference in electronegativities of the metal ion and the donor atom is decisive.

*Group III - Transition metal ions with incomplete subshells:*

The tendency of this group of metal ions which predominates depends on three factors, the charge, the size, and the ionization potential of ion. Complexing ability of various metal ions can be easily explained by the help of these three factors.

The most extensively investigated series of divalent metals is Mn, Fe, Co, Ni, Cu and Zn, the so called Irving & William series. In this series ionic radius decreases and the ionization potential increases up to copper, accordingly the stability increases and is in the following order:

\[ \text{Mn} < \text{Fe} < \text{Co} < \text{Ni} < \text{Cu}. \]

In the formation of complexes of transition metals the formation of dative \(\dagger\) bonds plays an important role. \(\dagger\) bonding can be understood to result from interaction of filled \(d\) orbitals in the central atom and the vacant \(p\) or \(d\) orbitals in the
electron shell of the ligand. Such π bonds lead to an increase in stability of the complex formed. The inability to form π bonds is often responsible for the weak complexing tendencies of Tl⁺, Pb⁺⁺ and Bi⁴⁺⁺.

Here the mention may be made that elements to the right of the elements with 18 electron subshells do not follow the rule that higher valency states have a greater group I character than that of lower valency states. Thus Tl(III) has stronger group II character than Tl(I). Anhland, Chatt and Davis³⁵ suggest that the electrons which enter the metal ion during its reduction do not enter the d orbitals which are already filled, but the s orbitals, where they screen the d orbitals make them available for dative π bonding.

Regardless the nature of donor group the natural order³⁶ of stability of complexes of bivalent transition metals is:

\[
\text{Pd} > \text{Cu} > \text{Ni} > \text{Pb} > \text{Co} > \text{Zn} > \text{Cd} > \text{Fe} > \text{Mn} > \text{Mg}.
\]

only in very few cases the anomalies are observed.³⁷ The above series has been further extended as below, based on the enormous experimental evidence available:

\[
\text{Pt} > \text{Pd} > \text{Hg} > \text{Uo₂} > \text{Be} > \text{Cu} > \text{Ni} > \text{Co} > \text{Pb} > \text{Zn} > \text{Cd} > \text{Fe} > \text{Mn} > \text{Ca} > \text{Sr} > \text{Ba}. ³⁸
\]

Martell and Plumb³⁹ reported the order of stability of rare earth chelate of EDTA in the order

\[
\text{Y} > \text{Sm} > \text{Nd} > \text{Pr} > \text{La}.
\]
The order of stability of acetyl acetone complexes with tervalent ions has been shown to be as:

Fe > Ga > Al > Se > In > Y > Pr > Ce > La

2. Nature of ligand:

The nature of ligand influences the stability of a complex compound as does the nature of the central atom. The most important characteristics of ligand which determine the stability are:

(a) Electrostatic characteristics: The charge and radius for ions or the dipole moment for molecules and ions. The greater this characteristic, the more stable will be the complex formed.

(b) The tendency of the ligand to form covalent $\pi$-bonds: The nature of the atom by means of which the ligand (donor atom) is linked to the central metal ion is responsible for this type of tendency in the ligands. For alkaline earth metals the sequence of stability\(^{41}\) is $0 > N > S$, but for transition metals with nearly filled $d$ orbitals it is $N > S > 0$.

(c) The possibility of dative $\pi$ bond formation by the ligand: This arises when valency cloud of the ligand atom contain vacant $p$ orbitals, (ligands with multiple bonds) or vacant $d$ orbitals (Cl, Br, I, S, Se, P, As, etc.).
(d) **The number of coordination positions which may be occupied by one ligand particle**: The greater the number of coordination positions occupied by a given ligand, greater will be the stability of the complex formed (chelate effect). Thus the ethylenediamine complex of nickel is stable even in such high dilution, as would result in complete dissociation of the analogous methylamine complex to precipitate nickel hydroxide.\(^ {42} \)

(e) **Basicity of the ligand**: The relation between basic strength of ligand and stability was first pointed out by Calvin.\(^ {43} \) Since then a lot of experimental data has accumulated correlating the stability with the basicity of the ligands.\(^ {44} \) A linear relationship between basic strength of closely related ligands and stabilities of complexes formed thereof has been shown by Calvin and Wilson.\(^ {43} \)

3. **Size of the chelate ring**:

Early work of Ley\(^ {45} \) on amino acid complexes and Boeseken\(^ {46} \)'s on boric acid - glycol complexes have revealed that practically all chelates formed have five or six membered rings, the five membered ring being the most stable one. Pfeiffer\(^ {47} \) in 1940 said in a more generalised manner that five membered ring is more stable when the ring is saturated but the six membered rings are favoured when one or more double bonds are
present. Nickel-dimethylglyoxime complex is an exception to this rule, according to Pfeiffer\textsuperscript{48} the five membered ring is stabilised by hydrogen bonding and hence multiple ring formation. This has further been confirmed by X-ray data.\textsuperscript{49}

4. \textbf{Influence of steric effects:}

The presence of non-chelating substituents in the chelating ligand may introduce either or both of two effects i.e., an inductive effect which alters the basicity of electron donor atom, or a steric interference which prevents the most favourable metal-ligand orientation in complex formation. Brown\textsuperscript{50} describes the second effect as F-strain. The investigations of Basolo and Murmann\textsuperscript{51} on Cu(II) and Ni(II) chelates of a series of alkylsubstituted ethylenediamine derivatives have shown such steric effects. The stability of complexes decreases with substitution of alkyl groups for hydrogen atom on the nitrogen. Most important and common cases of steric inhibition are where a bulky group is attached either to the donor atom or near enough to it to cause mutual repulsion, resulting in the weakening of metal-ligand bonds. Quite a lot of experimental data is available correlating the influence of stability of complexes with steric effect of the groups present in the ligand molecule.\textsuperscript{52}

5. \textbf{Resonance effect:}

Calvin and Wilson\textsuperscript{53} probably were the first to show
the significance of resonance effect on the stability of coordination compounds. They studied Cu(II) chelates of acetylacetone, 2-hydroxy-1-naphthaldehyde, salicylaldehyde and 2-hydroxy-3-naphthaldehyde, and observed that the decrease in order of stability is in the order of decrease in double bond character of chelate rings (decrease in resonance character of chelate rings).

The other factors which affect the stability are, nature of ions outside the coordination sphere, entropy effect, environmental and concentration factors, and orbital hybridization etc.

**AZO DYES AS COMPLEX FORMERS**

Any organic compound containing an intramolecular hydrogen bonding will be capable of reacting with a metal ion to form coordinate bonds. A dye molecule having two or more donor groups properly arranged in positions capable of forming metal chelates and for direct resonance linking of these groups, will be acting as chelating agents. The most common electron donors in chelating azo dyes are the, amino, carboxyl and phenolic groups. The following illustrates the general and common skeleton of an azo dye molecule:

![Chemical Structure](attachment:structure.png)

where \( X, X', Y \) and \( Y' \) may be OH, -COOH or NH₂. Either of the rings A or B may be a phenyl, naphthyl or pyrazolone residue.
Generally all classes of dyes are capable of forming metal complexes, but the knowledge of the constitution and structure of metal complexes of azo dyes is very extensive. As early as 1900 Bamberger\textsuperscript{54} reported an alcohol soluble copper compound of ortho hydroxy azo benzene having $1:2$ metal-dye composition.

The credit for the development of systematic investigation of composition and stability, etc., of metal dye chelates goes to Pfeiffer, Morgan, Smith and Drew.\textsuperscript{55} They investigated cobaltic complexes of Eriochrome Red B and some other related dyes. Drew and co-workers\textsuperscript{56} studied copper chelates of some hydroxy azo benzenes and o-carboxy o-o' dihydroxy, o-hydroxy o-carboxy, and o-o'-dicarboxy azo benzenes and reported $1:2$ (metal-dye) complexes in all cases.

The stability of the chelates of o-carboxy compound was found to be less than that of o-hydroxy compound. In case of o-o' dihydroxy compound Drew has observed that the metallic ion is covalently attached to both hydroxyl groups and these compounds form coordination compounds more readily than o-hydroxy azo compounds. The stability of metal chelates in the former case is more because of the metal being held between both the hydroxyl groups and the azo group.

Drew and Fairbairn\textsuperscript{57} have reported that a single
ortho hydroxy group is insufficient to hold chromium, iron, manganese and zinc atoms in stable coordination with azoic nitrogen. This is in contrast with the behaviour of copper, nickel and cobalt. Elkins and Hunter\textsuperscript{58} have shown the existence of trans arrangement of groups attached to azo group in the metal complex of o-hydroxy azo benzene.

Studies of the metal complexes of o-hydroxy azo dyes\textsuperscript{59} have shown that a six membered ring possesses somewhat greater stability than a five membered ring and considerably more than that of a seven membered ring. The introduction of one or more hydroxy group (ortho to azo group), and sulphonic group in dye molecule, renders the configuration of metal-azo dye complex more complicated and the azo dye exhibits remarkable adaptability in the positional adjustments of the azo group and aromatic nucleus attached to each nitrogen, as a result of which metal complexes are formed. Discussing the copper complex of o-hydroxy azo compounds Drew and Landquist\textsuperscript{56} have not excluded in principle the probability of five membered ring in certain cases.

The azo salicylic acids constitute the largest class of dyes, the characteristic of which is the presence of \(-\text{COOH},\)
and \(-\text{OH}\) groups on adjacent carbon atoms. Morgan and Main Smith have studied some complexes of this class of dyes. Chromium complex of Alizarin yellow 2G, a dye of this type, has been
investigated by Brass and Wirtnitzer who prepared compounds having different Cr-dye ratios.

Aquopentammine cobalt (III) and tetrammine copper(II) complexes of Mordant yellow G have been prepared. The cobalt dye composition is \([\text{Co(dye)}_3]^6\) indicating that all the ammonia and water molecules in cobalt ammine were replaced by dye molecules.

REVIEW OF THE WORK DONE ON Mn(II), Ni(II) AND Co(II) COMPLEXES:

The work done on the complexes of these metals with simple ligands is very extensive. The survey here, has therefore been limited to azo dyes and some closely related ligands. Metal - dyes containing manganese, nickel and cobalt are known since very early times and are greatly used in dye industry.

Pfeiffer and co-workers in 1937 prepared Ni(II) and Co(II) complexes of benzene azo, \(-p\)-cresol, resorcinol, \(\beta\)-naphthol, \(\beta\)-naphthylamine and its 4 sulphonic acid. Hendler and Smith prepared Mn(II), Ni(II) and Co(II) complexes of some \(o\)-hydroxy azo dyes and measured their absorption maxima and extinction coefficients.

1:1 complexes of these metals have been prepared from dyes obtained from arylamines devoid of \(-OH\) group in the ortho position to \(-\text{NH}_2\), \(-\text{COOH}\), and \(\text{SO}_3\text{H}\) group and
2-hydroxy 3 naphthoic acid.

4-nitro-2-amino phenol was diazotised and coupled with N-(3-amino phenyl)anthranilic acid, nickel and cobalt complexes of the dye so obtained have been prepared by Bestehorn and Morgan. The same authors have also prepared cobalt complex of a dye obtained by diazotising 2-hydroxy-3-amino benzoic acid and coupling it with diethyl amino phenol. In all these cases a 1:1 complex has been suggested.

Callis, Nielson and Bailar Jr have prepared nickel and cobalt lakes of a number of dyes having different metal - dye composition.

Klotz and Ming have investigated these metal chelates of pyridine 2-azo p-dimethylaniline and have reported the formation of a 1:1 complex at pH 6. The stability constant has been determined at constant ionic strength at 25°C.

The complex formation between Eriochrome black T and nickel and cobalt has been investigated and the molar ratio of metal - ligand was found to be 1:2 and 1:4 respectively.

Polarographic investigation of manganese, nickel and cobalt complexes of Pontachrome Violet SW has been carried out by Dean and Bryan.
Complexes of some azo pyrazolone dyes have been studied by Shively and Fernelius\textsuperscript{72}. Nickel and cobalt form 2 : 1 (metal - dye) complex in 75\% dioxane - water mixture.

I.R. absorption studies of o-hydroxy azo dye chelates of nickel and cobalt\textsuperscript{73} have shown that the metallisation takes place between azo nitrogen and the phenolic group. In case of dyes derived from 8-hydroxy quinoline -5-sulphonic acid the chelation is found to be between phenolic oxygen and pyridine nitrogen and not the azolic nitrogen.\textsuperscript{74}

Nickel and cobalt ions have been reported to form complexes with Eriochrome Cyanine R in neutral media, while manganese forms complex in alkaline medium only.\textsuperscript{75} The dissociation constants have been determined spectrophotometrically.

Acid Chrome Blue forms 1 : 3 (metal-dye) complex with nickel and cobalt.\textsuperscript{76} Chromatographic studies on the 1:2 cobalt complex of some o-hydroxy o'-carboxy azo dyes have been made by Shetty and Kuster.\textsuperscript{77}

Frieser and co-workers\textsuperscript{78,79} have investigated metal complexing behaviour of pyridyl azo-naphthols and resorcinols in 50\% dioxane-water mixture. Nickel and cobalt form 1 : 2 (metal-dye) complexes at all pH and manganese complex of same composition is formed only in neutral or alkaline medium.
Nickel complexes of Solochrome Violet R and RV having molar ratio 1:1 and 1:2 (metal - dye) have been studied by Coates and workers.\textsuperscript{80,81} Solochrome Violet RV forms only a 1:1 complex.

Murakami and Takagi\textsuperscript{82} have prepared \(5-(p\text{-sulphophenylazo})\)-salicylates of these metals having 1:1 and 2:1 (ligand - metal) composition. The \(p\text{-sulphophenylazo}\) group demonstrated an electron withdrawing effect, the magnitude of which was slightly greater than that of a sulphonate group.

Azo lakes of various metal ions have been prepared from a number of commercial azo dyes also.\textsuperscript{83}

The dissociation constants of \(o\text{-o}^{'\prime}\) hydroxy azo dyes of general formula:

\[
\begin{align*}
&\text{OH} &\text{HO} \\
&\text{SO}_3\text{H} &
\end{align*}
\]

where \(X = \text{Me, H, Cl or NO}_2\) groups,

and the stability of nickel and cobalt chelates of these dyes have been determined.\textsuperscript{84} It was found that the phenolic hydrogen dissociated first and then dissociated naphthyl hydrogen. The stability constants increased with decreasing electron withdrawing power of substituent \(X\). Linear plot of Hammett's \(\sigma^p\) value vs \(pK_2\) and \(\sigma^m\) vs \(pK_3\) values were obtained.
Polarographic study on Co(II) - Rhodamine B complex of 1 : 1 composition has been reported. Palmer and Reynolds have also made polarographic investigation of Mn(II) and Ni(II) complexes of Solochrome Violet RS.

Chromotrope 2B complexes of nickel and cobalt have been studied spectrophotometrically and the formation of 1 : 1 and 1 : 2 (metal - dye) complex respectively, have been reported.

Some extraction studies on metal chelates of Thiazolyazo naphthol dyes have been reported. The metal chelates of substituted 4- (2-pyridyl azo) resorcinol have been studied in the light of the analytical application of these dyes.

Recently Baumann and Hensel have given an account of structure and dyeing properties of some metal-dye complexes specially of the complexes of azo dyes.

Apart from the dye chelates described above manganese, nickel and cobalt form stable complexes with compounds closely related with azo dyes so far as the complexing groups are concerned, such as salicylic acid, sulphosalicylic acid etc. Spectrophotometric studies on 5-sulphosalicylates of Mn(II) and Ni(II) reveal the formation of stable complexes. Manganese forms 1 : 2 complex, while nickel forms 1 : 1, 1 : 2 and 1 : 3 complexes at different pH.

The salicylic acid and 5-sulphosalicylic acid
complexes of manganese, nickel and cobalt have been investigated by Perrin. Banks and Singh have also studied 5-sulphosalicylic acid complexes of these metals using potentiometric methods. Ni(II)-5-sulphosalicylate complex has been studied by Lasater and Anderson. In all these cases 1:1 complex formation has been reported and possibility of formation of any other species has been ruled out. Perrin has made use of Calvin and Melchior's extension of Bjerrum's method for determining the stability constant at constant ionic strength of 0.15 M.

The amino phenol chelates of these metals have been studied by Charles and Fieser and those of 5-sulphoanthramilic acid and its derivatives have been studied by Harris and Sweet.

Very recently nickel and cobalt complexes of thiosalicylic acid have been studied by Kumar and Nigam. In both cases two complexes are formed having metal-ligand ratio of 1:2 and 1:3 in case of Ni(II) and 1:1 and 1:3 in case of Co(II).

THE PRESENT WORK, ITS AIM AND SCOPE:

A birds eyeview of the above paragraphs shows that interest of the chemist has always been concentrated on the metal-bound complexes from dying point of view mainly. Some
experimental data is available regarding the composition, behaviour etc., of metal chelates of o-hydroxy azo dyes, but very little is available about the azo dyes derived from salicylic acid and particularly 5-sulphosalicylic acid. In most of the papers referred to as above pertaining to metal - dye complexes the chelation has been observed between a -OH, -COOH or -NH₂ group in ortho position to azo linkage and the azo group. The relevant information about the systematic investigations is lacking for salicylic and 5-sulphosalicylic acid dyes.

Ordinarily azoic nitrogen acts as a weak electron donor, but by the introduction of other electron donor groups like -OH, -COOH or -NH₂ in its ortho position, its donor activity is enhanced and it becomes in a position of forming stable metal complexes. The literature does not seem to have an example of such a metal dye complex in which the dye molecule has three electron donor groups viz., -N=N-, -OH and -COOH, in ortho positions to each other in such a way that -OH and -COOH groups lie on one side of the azo group.

The author has, therefore, thought it worthwhile to undertake the detailed and thorough investigation of the metal chelates of azo dyes bearing three electron donor groups in ortho position with respect to each other viz., azoic nitrogen, phenolic and carboxyl groups. The sulphonylic group
has been introduced in the molecule to render it soluble in water. This particular type of azo dye has been obtained making use of 5-sulphosalicylic acid in the preparation of azo dyes chosen for the present investigation.

The metals chosen for the study are manganese, nickel and cobalt which belong to the first transition series of the periodic table. The metals of this series with incomplete subshells, possess a dominating tendency of complex formation, which is mainly due to the charge, the size and the ionisation potential of the ion. Some of these properties of the metal ions chosen for the present study are tabulated below:

<table>
<thead>
<tr>
<th>Ions</th>
<th>Radius</th>
<th>Second ionisation potential (Volts)</th>
<th>Mode of forming hybrid orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn²⁺</td>
<td>0.91</td>
<td>15.7</td>
<td>dsp² and d²sp³ (for CN=4&amp;6 respectively)</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>0.78</td>
<td>18.2</td>
<td>dsp² and d²sp³</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>0.82</td>
<td>17.3</td>
<td>dsp² and d²sp³</td>
</tr>
</tbody>
</table>

Studies carried out in recent years have shown that the formation of dative \( \Pi \) bonds leads to increased stability of the complex compounds. The formation of dative \( \Pi \) bonds depends upon (i) the presence of considerable free d electrons in the central atom, (ii) the presence of vacant p or d orbitals in the outer cloud of same atom, and (iii) the
formation of a sufficiently stable σ-bond between the central atom and one of the ligand atoms. The formation of a stable σ-bond depends upon high electron affinity of central ion which in its turn is numerically equal to n th ionisation potential of the atom (for ion M^{+n}), here in the specific case of bivalent metal ion, to the 2 nd ionisation potential. The ionisation potential of metal ion guides the mobility of d electrons on which depends the strength of π bonds. In short it can be said that the strength of π bond should be great, the greater the electron affinity of cation and the lower its ionisation potential and charge.

The values for these metals (Mn, Ni and Co) tabulated above lead to conclude that they possess all the required conditions to form a dative bond and hence quite stable complexes.

5-sulphosalicylic acid and salicylic acid are known to form stable 1 : 1 complexes with Mn(II), Ni(II) and Co(II). It was expected that they would also be forming stable complexes with the azo dyes derived from 5-sulphosalicylic acid.

Almost a new aspect of the present investigation is that the ligands chosen for the study are all azo dyes having three coordinating centres viz., azo group, -OH group and -COOH group in ortho position with respect to each other. As all these three are capable of coordinating with the metal ion, the
studies would reveal the nature and dominating effect of the groups involved in the formation of the complex. In light of the above it was hoped that the data obtained would be of interest in the field.

Out of the ligands proposed to be used in this study, the unsubstituted dye (phenyl azo 5-sulphosalicylic acid) has the following structure:

(1) \[
\begin{array}{c}
\text{N=N} \\
\text{OH} \\
\text{SO}_3\text{H}
\end{array}
\text{CH}_3
\begin{array}{c}
\text{N=N} \\
\text{OH} \\
\text{COOH} \\
\text{SO}_3\text{H}
\end{array}
\]

Phenyl azo 5-sulphosalicylic acid
(abbreviated as unsubstituted dye)

The other three compounds are:

(2) \[
\begin{array}{c}
\text{CH}_3 \\
\text{N=N} \\
\text{OH} \\
\text{COOH} \\
\text{SO}_3\text{H}
\end{array}
\]

\textit{p-methyl phenyl azo 5-sulphosalicylic acid.}
(Methyl dye)

(3) \[
\begin{array}{c}
\text{CH}_3\text{O} \\
\text{N=N} \\
\text{OH} \\
\text{COOH} \\
\text{SO}_3\text{H}
\end{array}
\]

\textit{p-methoxy phenyl azo 5-sulphosalicylic acid.}
(Methoxy dye)
p-chloro phenyl azo 5-sulphosalicylic acid.
(Chloro dye)

By introducing different substituents in the same position (para) in the amino residue, it was possible to study the effect of these substituents on the stability of metal complexes obtained from them.

As these azo dyes were not commercially available, their synthesis had to be taken up as described in the third chapter.
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