CHAPTER II

RESULTS AND DISCUSSION
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A brief account of the factors relating to the ability of metal ions in general, and that of the manganous ions which generally forms the outer orbital type of labile complexes, in particular, to undergo complexation with a large variety of electron donors, i.e., the ligands, has been recorded in the preceding pages which also contain a lucid discussion on the parameters to which the complexes owe their stability as well as the existence. The existing literature on the chemistry of coordination compounds shows that the manganous ion exhibits two coordination maxima, 4 and 6, depending upon the nature of the ligands with which it forms complex compounds. As discussed in the introductory part of this dissertation, the feeble electro-negativity, smaller second ionization potential value and the large ionic size of this metal ion, render it a weaker complex forming transition metal than other bivalent metal ions of the first transitional series; with the consequence that except in the cases of bi-, tri-, or multidentate strong complexing agents, the manganous complexes are expected to be quite unstable. Hence the experimental verification of the formation as well as the determination of the stability of the highly unstable complexes, called the imperfect complexes, formed in solution, have been carried out by
physico-chemical methods which make the study of such complex-esconvenient. The stoichiometry, the structure and the
dissociation constant of each of the complexes studied by
the Job's method of continuous variation\(^1\), taking the
electrical conductance and the spectrophotometric measurements
as the index properties, have been discussed in the following
paragraphs.

I  Complexes of Manganese (II) with formic, acetic,
propionic and butyric acids.

Aliphatic monocarboxylic acids form coordination
compounds with a large number of metal ions. Formate and
acetate ions form strong bonds, but monocarboxylic acids
with longer chains show a rapidly decreasing ability to
coordinate\(^2\). Formate and acetate ions often bind two metal
atoms as is represented by the following structure\(^3\):

\[
\begin{align*}
    \text{R} & \quad \text{M} = \text{O} - \text{C} = \text{O} - \text{M} \\
\end{align*}
\]

when the carboxyl group is attached to only one metal atom,
however, it fills all but one position in the coordination
sphere. Complexes of the types \([\text{Co (NH}_3\text{)}_5 \text{OOCH}]^+\) and
\([\text{Co (NH}_3\text{)}_5 \text{OOC.CH}_3]\) are well known\(^4,5\) indicating that the
aliphatic monocarboxylate ions also share the coordination
positions of the metal ions with the neutral ligands.
Cadmium and zinc have been found to form weak but definite complexes of the types [M(HCOO)]^+ and [M(HCOO)_2]^- with formate ion concentrations ranging from 0 to 1.98 M in solution held at a constant ionic strength. It is interesting to note that practically all the cases cited above 1:1 complex forms are formed. A physical-chemical study of the reaction of monoprotonic organic acids with a number of bivalent metal ions supports the formation of only [M(HCOO)]^+ type of complex in general, though certain strongly coordinating transitional metal ions, such as cobalt, nickel and zinc form [M(HCOO)_2]^- type of complex.

In view of the contradictory and rather conflicting opinions regarding the stoichiometry of the aliphatic monocarboxylate complexes of bivalent metal ions, a physical-chemical approach was made with an object to investigate into the nature of the reaction between the metal ion and the formate ion. The continuous variation method (figures 1A, 1B) shows that under the experimental conditions, in the present work, only one formate complex containing the metal ion and the formate ion in equimolar proportion results. The dissociation constant of the manganese formate complex as determined by the continuous variation method, taking non-equimolecular solutions of the metal chloride and the formic acid solutions in water is found to be K = 185 x 10^-3.
Like formic acid, acetic acid also forms strong bonds with metal ions that undergo complexation with it. Burns and Hume have reported that depending upon the concentrations of the acetate ions, three lead acetato complexes with the metal-ligand ratios of 1:1, 1:2 and 1:3 are formed. From the potentiometric investigation of electrolytic dissociation of copper and cadmium carboxylic salts, Ferrell and coworkers, have asserted that the metal-acetate bond is much stronger than the metal-formate bond, and that an appreciable amount of undissociated cadmium acetate is formed. Acetato complexes of many other bivalent cations with the general formula $[\text{M(OOC.CH}_3\text{)}]^+$ have been reported by many other workers.

Siddhanta has reported the complex $(\text{MnAc})^+$ from a study of the change in $H^+$ ion concentrations in the mixture of equimolecular manganese chloride and acetic acid solutions, by Job's method of continuous variation (loc.cit.). The present work is in tune with the observations made by Siddhanta, under similar conditions, applying conductance and optical density as the index properties. The results are represented in figures 21, 22.

The dissociation constant of the acetato complex comes out to be $K = 63 \times 10^{-3}$ which is in good agreement
with the value obtained by Siddhanta, figures 2B and 2D.

Though quite a large amount of work has been done regarding the acetato complexes of several metal ions, references of the propionate complexes are meagre. Cobalt, cadmium, lead, have been shown to form 1:1 and 1:2 propionate complexes. No propionate complexes of manganese (II) have been recorded in literature. The present investigation reveals that in the range of concentrations used only 1:1 complex propionate is detected (Figures 3A & 3C).

The dissociation constant of the manganous propionate complex appears to be quite large, i.e., $K = 42.3 \times 10^{-3}$, showing thereby considerable stability of the complex. (Figures 3C & 3D).

The only butyrate complexes studied so far are with the copper and cadmium metal ions. In the manganous butyrate complex, studied by the author, the metal ion and the ligand ion are present in equimolar proportions. (Figures 4A & 4C)

Contrary to the continuous decrease in the values of dissociation constants as we go towards the higher homologues of monocarboxylic (aliphatic) acids, in their
complexes, the butyrate complex shows nearly the same stability as that of the acetato, as is evident from the dissociation constant of the manganous butyrate complex, which attains the value $K = 31.7 \times 10^{-3}$. (Figures 4 B & 4 D).

**Structure:**

The following structures have been assigned to the formato (I), acetato (II), propionato and butyrate complexes:

$$
\begin{align*}
\text{I} & : \quad \left[ \begin{array}{c}
\text{H} \\
\text{O} = \overset{\ddagger}{\text{C}} - \overset{\ddagger}{\text{O}} - \text{Mn}
\end{array} \right]^+ \\
\text{II} & : \quad \left[ \begin{array}{c}
\text{CH}_3 \\
\text{O} = \overset{\ddagger}{\text{C}} - \overset{\ddagger}{\text{O}} - \text{Mn}
\end{array} \right]^+ \\
\text{III} & : \quad \left[ \begin{array}{c}
\text{C}_2\text{H}_5 \\
\text{O} = \overset{\ddagger}{\text{C}} - \overset{\ddagger}{\text{O}} - \text{Mn}
\end{array} \right]^+ \\
\text{IV} & : \quad \left[ \begin{array}{c}
\text{C}_3\text{H}_8 \\
\text{O} = \overset{\ddagger}{\text{C}} - \overset{\ddagger}{\text{O}} - \text{Mn}
\end{array} \right]^+
\end{align*}
$$

The above structures are justified in view of the fact that all the above mentioned aliphatic monocarboxylic acids form 1:1 complexes with manganese (II). Also, since manganese in its bivalent state is characterised by the formation of outer orbital type of complexes, which are labile and charged\(^{18}\), the above structures are therefore justified.
Nyholm and Sutton\textsuperscript{19} have categorically stated that because bivalent manganese has lowest ionization potential of the first transitional elements, its capacity to form covalent bonds is relatively small, with the result that most manganese (II) complexes which have been studied involve coordination with ligands of high electro-negativity, such as oxygen in water. Hence it is quite probable that the remaining coordination positions of manganese (II) will be held by water molecules.

**Stability:**

The dissociation constant values of the complexes of manganese (II) with the aforesaid aliphatic monocarboxylic acids show that the following sequence is obtained when the complexes are arranged in the order of their stability:

Formate \( \prec \) Acetate \( \approx \) Butyrate \( \prec \) Propionate .

The peculiarity in the above sequence is, that whereas the stability increases from formic acid to acetic acid, similar observation is not repeated when we proceed from acetic acid onwards. On the other hand, propionate complex appears to be a little more stable than the butyrate complex. This apparent discrepancy is explained when the dissociation constant of these acids (Formic: \( K = 24 \times 10^{-5} \); Acetic: \( K = 1.845 \times 10^{-5} \); Propionic: \( K = 1.32 \times 10^{-5} \); Butyric: \( K = 1.50 \times 10^{-5} \) ) are
taken into consideration as they play decisive role in the reaction of these acids with metal ions. The dissociation constants of these acids indicate that the weakest acid in the series is the propionic acid. And since it has been established that the conjugate bases of the weaker acids are more strongly bonded to the metal ions in whose contact they come, it is natural that the propionate complex would show maximum stability. That the difference between the stability of formato and acetato complexes is considerably large, while minute stability difference occurs in case of acetato, propionato and butyrate complexes, follows from the protophillic properties of these acids. Thus the above sequence is very well founded and hence justified.

II Complexes of manganese (II) with mono-, di-, and tri-chloro acetic acids.

Mono-chloroacetate complexes of uranyl and lead are the only ones the existing literature records. No complexes of di- and tri-chloro acetic acids have been reported. In order to see the effect of chloro substitution in the stability of the acetate complex ion the reaction of manganese chloride with each of them was studied by the conductance and optical density measurements.
Farrell and coworkers (loc. cit.) while studying the mono-chloroacetate complexes of copper and cadmium, observed that the introduction of a chlorine atom into the acetate ion brings about a pronounced decrease in the katiophillic property of the anion. This was explained as caused by the strong inductive effect of the chlorine atom.

The continuous variation method applied to the physico-chemical investigation of the reaction of manganese (II) ion with these chloroacetic acids lead us to the conclusion that all the three, monochloro acetato (figures 5A & 5C), di-chloroacetato (figures 6A & 6C) and trichloroacetato (figures 7A & 7C) complexes contain the metal ion and the ligand ions in equimolecular proportions. Thus it is seen that the introduction of chlorine atoms in the acetate ion does not alter the compositions of the complexes formed by the latter. This is expected because the introduced chlorine atoms do not get coordinated to the metal ion. Consequently the functional group, that is, the carboxyl group remains the same.

Structure:

As the coordinating atom in all the chloroacetate ions is the same as that in the acetate ion, the seats of
coordination in the acetate ion is not affected by the introduction of chlorine atoms. Therefore, the reasons put forward to justify the acetate complex of manganese, also are equally valid for the chloroacetate complexes; and hence the following structures have been assigned to the monochloro (I), dichloro (II), and trichloro acetate (III) complexes of manganese (II).

\[
\begin{align*}
& \text{Cl} \quad \text{Cl} \\
& H - C - H \quad \text{Cl} - C - H \quad \text{Cl} - C - \text{Cl} \\
& O = C - O - \text{Mn} \quad O = C - O - \text{Mn} \quad O = C - O - \text{Mn} \\
& \text{I} \quad \text{II} \quad \text{III}
\end{align*}
\]

The dissociation constants of the complexes as determined by the continuous variation method using non-equimolar solutions of manganese chloride and chloro acetic acids are as given below:

- Monochloroacetate: \( K = 11.7 \times 10^{-2} \), (Figures 5B & 5D)
- Dichloroacetate: \( K = 26.5 \times 10^{-2} \), (Figures 6B & 6D)
- Trichloroacetate: \( K = 86.5 \times 10^{-2} \), (Figures 7B & 7D)

Thus the following stability order is obtained:

Monochloroacetate > Dichloroacetate > Trichloroacetate.

The results, thus obtained, are in keeping with the results reported by Ferrell and coworkers (loc. cit.),
from the study of the copper and cadmium complexes of the chloro substituted acetic acids. It has been found that the katiophillic property of acetate ion records continuous decrease as the number of chlorine atoms introduced increases. Thus the acetate complex is much more stable than any of the chloro acetate complexes. The results seem to be natural in view of the considerable decrease in the stability of the acetate ion brought about by the introduction of chlorine atoms. The dissociation constant data of the three chloroacetic acids given below denote that the strengths of the acids increase with the increasing number of chlorine atoms. Trichloro acetic acid is the strongest as is evident from its greatest dissociation constant value.

\[
\begin{align*}
\text{Acetic acid} &: \quad K = 1.845 \times 10^{-5} \\
\text{Monochloro acetic acid} &: \quad K = 1.55 \times 10^{-3} \\
\text{Dichloro acetic acid} &: \quad K = 51.40 \times 10^{-3} \\
\text{Trichloro acetic acid} &: \quad K = 1210.0 \times 10^{-3}
\end{align*}
\]

Thus the protophillic property of the acetate ion goes on decreasing as the chlorine atoms are introduced into it, weakening thereby the ligand - metal bond contiguously. The results obtained are thus suitably explained.
III Complexes of manganese (II) with lactic and mandelic acids:

α-Hydroxy acids often coordinate readily, the hydroxyl and the carboxyl groups both coordinating, and the chelation effect enhancing thereby the stability of the compounds formed. The hydrogen of the hydroxyl group may be lost simultaneously, so that the organic group contributes a charge of minus two to the complex. Thus coordination with copper (II) ion gives:

\[
\left[ \text{Cu} \left( \begin{array}{c}
 0 - C = O \\
 0 - C - \text{CHR} \\
 2
\end{array} \right) \right]^{2-}
\]

The copper complexes containing glycollic and lactic acids are not so stable, but those containing the stronger mandelic acid are easily isolated. The work of Jantsch on the rare earth lactates indicates that some chelation takes place. Lactate complex of antimony was thoroughly studied by Mohanty and Pani who suggested the following structure for the antimony lactate complex on the basis of pH titration results of the system \( \text{SbCl}_3 - \text{CH}_3\text{CH(OH)COOH} \)

\[
\begin{array}{c}
 0 - C = O \\
 \text{Sb} < O - C = 0 \\
 \text{H} - C - O \\
 \text{CH}_3 < O - C - \text{H} \\
 \text{CH}_3
\end{array}
\]
These workers have suggested that the lactate ligand behaves as a bidentate group.

The pH titration results of the above mentioned system carried out by Patra and Pani reveals, however, that depending upon the pH of the system two complex lactates, namely, 1:1 and 1:2 exist. At lower pH the former predominates while at higher pH the latter does so. While Mohanty and Pani (loc. cit.) could provide no direct evidence for the hydroxyl group to unite with the liberation of hydrogen ion, Patra and Pani (loc. cit.) could adequately explain that the complex formation takes place as a result of the liberation of hydroxyl proton. They have assigned the following structure to the 1:1 complex.

\[
\begin{align*}
\text{Cl} & \quad \text{Sb} \quad \begin{array}{c}
\text{O} - \text{C} = \text{O} \\
\text{Cl} & \quad \text{O} - \text{C} - \text{H} \\
\end{array} \\
\end{align*}
\]

\text{CH}_3

The physico-chemical study of the system manganous chloride - lactic acid, carried out by the author provides an evidence for the existence of only a 1:1 lactate complex of manganese (II) under the experimental conditions (Figures 8 A & 8 C) in striking agreement with the observation of Patra and Pani (loc. cit.) that at lower pH the complex species containing one lactate ion per atom of the metal exists.
On the assumption that both, the carboxyl and the hydroxyl protons are liberated as observed by Patra and Pani (loc. cit.) the following structure has been assigned to the lactate complex of manganese:

\[
\text{Mn} - \begin{array}{c}
\text{CH}_3 \\
\text{O} - \text{C} = \text{O} \\
\text{O} - \text{C} - \text{H}
\end{array}
\]

The dissociation constant of the lactate complex has been calculated to be \( K = 29 \times 10^{-4} \) (figures 8B & 8D).

Mandelic acid, like lactic acid, behaves as a complexing agent and a few complex mandelates have been reported in literature \(28 - 30\). These complexes possess more stability than the complex lactates in certain cases \(24\). Since the present literature records no work regarding the reaction of this acid with the bivalent manganese, the author thought it worth while to undertake this work. The physico-chemical approach to the problem in the present work provides a definite proof for the existence of a 1:1 manganese lactate complex when the electrical conductance (figure 9 A) and optical density (figure 9 C) values of the mixtures containing the metal ion and the ligand in the various molecular proportions are measured after allowing sufficient time to the systems for attaining equilibrium.
On the assumption that in analogy to the lactate complex, both, the hydroxyl as well as the carboxyl protons are liberated as a consequence of complex formation, the following structure has been assigned to the manganese mandelate complex:

$$\text{Mn} \quad \text{O - C = O}$$

$$\quad \text{O - C - H}$$

$$\text{C}_6\text{H}_5$$

The above structure is in agreement with the observation of Kapoor and Mehrotra\textsuperscript{31} who noted that the reaction of zirconyl chloride with mandelic acid in aqueous solution yields mainly the monomandelate complex which dissolves in one equivalent of alkali.

The dissociation constant of the complex assumes the value $K = 33.6 \times 10^{-4}$ (figures 9 B & 9 D).

**Stability**:

Unlike the results obtained in the case of the copper lactate and copper mandelate complexes\textsuperscript{24}, the lactate complex of manganese (II) has been found to be more stable than its mandelate complex as is observed from the dissociation constant values of the two complexes found in the present work. The proper explanation of this
observation lies in: (i) that the introduction of a bulky group into the ligand causes steric hindrance and (ii) that the phenyl group brings about greater polarisability with the natural consequence that the liberation of the carboxyl hydrogen ion of mandelic acid is facilitated to a greater extent compared to that of the lactic acid, rendering thus, the mandelic acid less protophillic. The net result, therefore, is a weaker metal ligand bond formation between mandelic acid and the metal ion. The mandelate complex, however, appears to be more stable than the propionate complex. This can, very reasonably, be attributed to the bidentate character of the mandelate ion.

IV Complex compound of manganese (II) with bromo-propionic acid:

Bromoacetate complexes of copper and cadmium have been studied potentiometrically by Ferrell and coworkers. Except this no significant effort has been made to study the effect of bromo substitution on the stability of complexes. The present work affirms that the bromo-propionate ion behaves similar to the propionate ion in so far as the stoichiometric composition of the complex is concerned (figures 10 A & 10 C); but an altogether different behaviour is seen regarding the stability, in as
much as, the bromopropionate complex is much more unstable (figures 10 B & 10 D), than the propionate one.

The following structures, based on the reasoning advanced in the case of propionate complex has been suggested:

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{CH}_3 \\
\text{Br}
\end{array}
\quad
\begin{array}{c}
\text{C} \\
\text{C} \\
\text{O} \\
\text{Mn}
\end{array}
\] ^+

The decrease in the value of the stability on the introduction of a bromine atom into the propionate ion seeks proper justification in the pronounced decrease in the protophillic property brought about by the bromine atom as will be evident from the dissociation constant data of propionic acid and the bromopropionic acid given below:

Propionic acid \[ K = 1.32 \times 10^{-5} \]

Bromopropionic acid \[ K = 1.08 \times 10^{-3} \]

Ferrell and coworkers (loc. cit.) have, however, observed that the replacement of chlorine atom by bromine causes a pronounced increase in the katiophilic property, a result in agreement with the weaker inductive effect of bromine. If chelation occurs, then a factor contributing to the above result will be the more highly deformable nature of the bromine atom compared to that of the chlorine atom. They
have similarly noted that the replacement of bromine by iodine causes a still more decrease in the katiophilic property. This, rather anomalous result, has been suitably explained by them.

V Complexes of manganese (II) with glycine, β-alanine, dl-alanine and dl-β-phenylalanine:

Practically all the amino acids are characterised by their ability to form inner complexes with an appreciable number of metals. It has also been observed that α-amino acids get coordinated to metal ions more firmly than β-amino acids, which also form inner complexes as the former. Many metals, such as, ferrous, ferric, calcium, barium and a good number of other metals have been known to form 1:2 complexes with glycine. There appear to be very few cases in which 1:1 complex formation results.

Generally the transition metals undergo chelation with α- and β-amino acids though, as stated earlier, the complexes formed by them with α-amino acids are more stable than those formed with β-amino acids. Thus, copper and beryllium have been reported to form weak 1:2 β-alaninate complexes.
Dl-alanine and dl-β-phenylalanine too show considerable tendency to cause strong metal-ligand bonding. Conductometric study has provided evidence for the existence of glycinate and alaninate complexes of manganese (II) which contain the two entities in the 1:2 ratio in both the cases. There is, however, no reference relating to the reaction of B-alanine and dl-β-phenylalanine with this metal ion. Glycinate (figures 11 A & 11 C), β-alaninate (figures 12 A & 12 C), dl-alaninate (figures 13 A & 13 C) and dl-β-phenylalaninate (figures 14 A & 14 C) complexes of manganese (II) have been found to possess two ligand ions for one atom of the metal ion in the present investigation.

Since all the above mentioned amino acids possess a bidentate character, both the carboxyl oxygen and the amino nitrogen unite with the metal ion, the former covalently and the latter coordinately; the following structures have been assigned to the glycinate (I), β-alaninate (II), dl-alaninate (III) and dl-β-phenylalaninate (IV) complexes:

\[
\begin{align*}
\text{I} & : \begin{array}{c}
\text{CH}_2 \text{NH}_2 \\
0 = \text{C} - \text{O} \quad \text{Mn} \quad \text{NH}_2 \text{CH}_2
\end{array} \quad 0 - \text{C} = 0\\
\text{II} & : \begin{array}{c}
\text{CH}_2 \text{CH}_2 \text{NH}_2 \\
0 = \text{C} - \text{O} \quad \text{Mn} \quad \text{NH}_2 \text{CH}_2
\end{array} \quad 0 - \text{C} = 0
\end{align*}
\]
It is interesting to note that all the above amino acids form neutral complexes. This seeks justification in that the N-O bonding in the case of the manganous ion is very strong.

**Stability:**

The dissociation constants of the complexes of manganese (II) with glycine (figures 11 B & 11 D), B-alanine (figures 12 B & 12 D), dl-alanine (figures 13 B & 13 D) and dl-β-phenylalanine (figures 14 B & 14 D) have been found to be $13.5 \times 10^{-4}$, $15.23 \times 10^{-4}$, $16.6 \times 10^{-4}$ and $18.2 \times 10^{-4}$ respectively in the present investigation. The highest stability of the glycinate complex is consequent upon its acid and base dissociation constants, which are the lowest in the series. Dl-β-phenylalanine appears to form the least stable complex due to the steric hindrance caused by the bulky phenyl group which induces strain in
the ring structure of the complex and hence facilitates its
dissociation rendering it unstable thereby. β-alaninate
complex shows less stability than the dl-alaninate complex.
This can be understood in the light of the structural difference
between them in that whereas the former contains a six membered
ring, the latter is characterised by the formation of a five
membered ring.

VI Complex of manganese(II) with crotonic acid:

No attempt has so far been made to study the complex
forming tendency of crotonic acid. The system manganous
chloride - crotonic acid has been studied by conductometric
( figure 15A ) and spectrophotometric ( figure 15 C ) measurement;
and it has been found that manganese (II) forms a 1 : 1 complex
with this acid.

The dissociation constant value, \( K = 28.7 \times 10^{-3} \)
of the crotonate complex of manganese as obtained by the
aforesaid method, ( figures 15 B & 15 D ) suggest that this
complex is more stable than the butyrate. This sounds as an
apparent discrepancy in view of the fact that the protophillic
property of the crotonic acid is less than that of butyric as
is evident from the dissociation constant value ( \( K = 2.04 \times 10^{-5} \) )
of the former. Promotion of this stability may be due to the introduction of a double bond in the butyrate ion. This explanation is well found in that the maleate complexes have been observed to be more stable than the succinate \(^{48-50}\). The following structure of the crotonate complex is a suitable one.

\[
\begin{array}{c}
\text{O} \\
(\text{CH}_3 - \text{CH} = \text{CH} - \text{C} - \text{O} - \text{Mn})^+ \\
\end{array}
\]

The above structure follows from that of the butyrate complex.
Complexes of manganese (II) with aliphatic dicarboxylic acids.

All the aliphatic dicarboxylic acids exhibit complex forming tendency with metal ions though this tendency gradually decreases in the higher homologues of the series because of the increase in the distance between the two carboxyl groups caused by the greater number of \(-\text{CH}_2\) groups\(^{51}\). All the aliphatic dicarboxylate complex compounds and chelates are characterised by ring formation, the size of the ring increasing as one proceeds from oxalate to the higher homologues.

I Complex of manganese (II) with oxalic acid:

The oxalate ion, as stated earlier, forms the most stable complexes, usually acting as a bidentate group. Alkaline earth metals, calcium\(^{52}\), strontium\(^{53}\) and barium\(^{54}\) form stable oxalate complexes of the types 1:1 and 1:2 depending upon the relative concentrations of the metal ion and the ligand ion present in the mixture of the metal salt and the ligand solutions. Bivalent,\(^{55-60}\) as well as, trivalent\(^{61-63}\) transition metals as also the rare earth metals\(^{64-66}\) form chelates with oxalic acid and in most of the cases the coordination number of the metal is satisfied by the oxalate ion. Solubility of normal oxalates in excess
of the oxalate ion concentration, due to complex formation has been observed in a good majority of metal-oxalate systems\textsuperscript{67,68}.

The system MnSO$_4$-oxalic acid was studied by the e.m.f. measurements\textsuperscript{69} which provided evidence for the formation of 1 : 1 and 1 : 2 manganese oxalate complexes, the latter getting isolated at a considerably high concentration of the oxalate ion. In the present investigation the continuous variation studies (figures 16 A & 16 C) of the system MnCl$_2$-oxalic acid in aqueous solution, however, detects only a 1 : 1 complex oxalate.

The following structure has been assigned to the oxalate complex of manganese (II):

\[
\begin{array}{c}
\text{Mn} \\
\text{O} \quad \text{C} \quad \text{O}
\end{array}
\]

The above structure is supported by the following statement:

Vibrational analysis of oxalato complexes can be taken by considering only the local symmetry of one chelate ring as a first approximation. X-ray studies\textsuperscript{70,71} reveal planar rings with different C - O distances but it appears that the differences are due to incomplete refinement of the structures, and it may be presumed that the ring is symmetrical as shown below:

\[
\begin{array}{c}
\text{M} \\
\text{O} \quad \text{C} \quad \text{O}
\end{array}
\]

The dissociation constant of the complex oxalate has been found to be $K = 6.34 \times 10^{-4}$ (figures 16 B & 16 D).
II Complex of manganese(II) with malonic acid:

Like the oxalate ion, the malonate ion is also a significant complexing ligand in that several malonate complexes of a good number of metal ions such as magnesium\(^ {72} \), calcium\(^ {73} \) and also practically all the metals of the transition series\(^ {74-79} \) have been reported.

Earlier workers\(^ {80} \) prepared and isolated the manganese malonate complex containing the metal and the ligand in the proportion of 1 : 2. Nothing has, however, been said regarding the stability of the complex malonate ions formed in solution.

Malonate complex in which manganese and oxalate ion are present in equimolecular proportions has been indicated by the conductance and optical density measurements as applied to the continuous variation method (figures 17 A & 17 C).

Based on the same arguments as advanced to justify the structure suggested for the oxalate complex, the following structure has been assigned to the malonate complex of manganese (II):

\[
\begin{array}{c}
\text{Mn} \\
\text{C} \\
\text{CH}_2
\end{array}
\]
The value of the dissociation constant of the above complex has been found to be equal to $8.7 \times 10^{-4}$.

**III Complex of manganese (II) with succinic acid**

Due to a further separation of the two carboxyl groups in this acid its tendency to unite with metal ions suffers a further setback with the result that its domain of complexation appears to be restricted to the alkaline earth metals\textsuperscript{81, 82} which, unlike, other metals, unite with the ligands containing oxygen donors more readily than with those in which nitrogen atom forms the coordinate bond with the central metal ion\textsuperscript{83}.

An effort to explore into the complexing nature of this acid with manganese (II) particularly in a quantitative sense is lacking as the existing literature has not recorded any succinate complex of Mn (II) with the sole exception of the work of Norman and coworkers\textsuperscript{84} who have detected a 1 : 1 manganese succinate complex by using ion exchange technique. The result obtained by these workers (loc. cit.) with Mn-54 cation is in conformity with the result, the present work yields as is evident from the conductance (figure 18A) and spectrophotometric measurements (figure 18C).
The following structure has been assigned to the succinate complex:

\[ \text{Mn} \quad 0 \quad - \quad \overset{\text{O}}{\text{C}} \quad - \quad \overset{\text{CH}_2}{\text{O}} \]

In keeping with the theoretical expectation, the succinate ion shows further weakness to establish a strong metal ligand bond than does the malonate ion as is evident from the dissociation constant of the complex succinate which has the value, \(11.5 \times 10^{-4}\) (figures 18 B & 18 D).

**IV Complex of manganese (II) with glutaric acid:**

Since this acid is still weaker a complexing agent for the same reasons as mentioned earlier, very few glutarate complexes, e.g., the beryllium glutarate\(^{85}\), magnesium, calcium and barium glutarate\(^{86}\) have been reported. Norman and co-workers (loc. cit.) obtained a 1 : 1 glutarate complex with manganese-54 by using ion exchange technique.

The physico-chemical studies applied to the system manganous chloride - glutaric acid indicate the same stoichiometry of the glutarate complex of manganese (II) as has been observed in the case of Mn-54. The results of conductance and spectrophotometric measurements are represented in figures 19A and 19C respectively.
The following structure has been assigned to the glutarate complex:

\[
\begin{align*}
\text{Mn} & \left\langle \begin{array}{c}
0 \\
\text{CH}_2
\end{array} \right. \\
0 & - \text{C} - \text{CH}_2
\end{align*}
\]

In striking agreement with the theoretical expectation, the glutaric complex is found to be less stable than the succinate complex as is evident from the dissociation constant of the glutarate complex of manganese (II) \( K = 14.37 \times 10^{-4} \) (figures 19 B & 19 D).

V Complex of manganese (II) with adipic acid:

Only copper, cadmium\(^{87}\) and beryllium\(^{45}\) complex adipates have been reported. Adipic acid has mainly been used as an alkalimetric standard by the earlier workers\(^{88-91}\).

The present investigation provides an evidence for the formation of only a 1:1 adipate complex on the basis of the conductance (figure 20 A) and spectrophotometric (figure 20 C) measurements.

On the grounds discussed in the case of oxalate complex, the following structure has been assigned to the adipate complex:
The dissociation constant of the adipate complex attains the value $17.6 \times 10^{-4}$ (figures 20 B & 20 D).

VI Complexes of Manganese (II) with aspartic and dibromo succinic acids.

Aspartic acid, being an amino acid, possesses much stronger coordinating ability than its parent acid with the result that many metal ions such as magnesium, calcium, strontium and barium, ferrous, ferric, zinc, cobalt, nickel, and manganese commonly form strong complexes with it. Except beryllium dibromo succinate complex, no other dibromo succinate complexes have so far been reported. The complex dibromo succinate (figures 21 A & 21 C) and aspartate (figures 22 A & 22 C) have been found to possess the composition of $1:1$.

The structures I and II have been assigned to the dibromo succinate and the aspartate complexes respectively.
whereas the structure of the dibromo succinate complex follows from the structures of other dicarboxylate complexes, the structure assigned to the aspartate complex does so from that of the ferric aspartate complex studied by Perrin\textsuperscript{92} who holds that aspartic and glutamic acids should show tridentate character by virtue of their atomic models.

The dissociation constants of dibromo succinate (figures 21 B & 21 D) and aspartate (22 B & 22 D) complexes have been found to be $11.9 \times 10^{-4}$ and $9.98 \times 10^{-4}$ respectively showing that the aspartate complex is more stable than the dibromo succinate complex. It is further observed that whereas the aspartate complex possesses more stability than the succinate complex, the latter is more stable than the dibromo succinate complex.

VII Complexes of manganese (II) with malic and tartaric acids:

Both these ligands have been reported to behave as tridentate ones in a number of their complex compounds\textsuperscript{93-95}. Barium\textsuperscript{96}, copper\textsuperscript{97} and antimony\textsuperscript{98} have been found to form malate and tartrate complexes containing the ligand and the metal in equimolecular proportions in both the cases.

Tartaric acid has much more developed complexing properties compared to malic acid and hence forms chelates with
a still larger number of metals$^{99-102}$.

The malate (figures 23 A & 23 C) and the tartrate (figures 24 A & 24 C) complexes have been found to possess the composition of 1:1 in the present case.

It has been established by Bobtelski and coworkers$^{98}$ that in the case of the malate complex the metal ion gets bonded to one hydroxyl and the other two carboxyl oxygen atoms, while in the case of the tartrate complex the two hydroxyl and one carboxyl oxygen atoms form bonds with metal ion. Hence the following structures I and II have been assigned to the malate and the tartrate complexes respectively.

$$\begin{align*}
\text{I} & : \begin{bmatrix}
0 \\
O - C \\
Mn - O - C \\
\text{CH}_2 \\
0 \\
\end{bmatrix} \\
\text{II} & : \begin{bmatrix}
0 \\
O - C \\
Mn - O - C - H \\
\text{CH}_2 \\
0 \\
\end{bmatrix}
\end{align*}$$

The dissociation constants of the malate (figures 23 B & 23 D) and the tartrate (figures 24 B & 24 D) complexes assume the values $10.37 \times 10^{-4}$ and $9.6 \times 10^{-4}$ respectively indicating that the introduction of hydroxyl groups imparts greater stability to the complex. The tartrate complex thus
appears to have attained maximum stability.

VIII Complex of manganese(II) with glutamic acid:

Though glutaric acid has a feeble complexing property, glutamic acid shows a considerable tendency to form chelates. Magnesium, calcium and strontium\(^{99}\) as also many other transitional metals\(^{100-106}\) form stable glutamate complexes.

The physico-chemical methods as applied to the system manganous chloride - glutamic acid by the author provide an evidence for the presence of a 1 : 1 glutamate complex in aqueous solution (figures 25 A & 25 C).

Though the possibility that the two carboxyl groups and the amino group take part in the complex formation has not been supported by the experimental results in the case of other amino acids, Perrin (loc. cit.) is of the view that aspartic and glutamic acids should behave as terdentate ligands from the point of view of their atomic models. Hence the following structure of the glutamate complex is the most adequate one:

\[
\begin{align*}
\text{CH} & \quad \text{CH} \quad \text{CH} \quad \text{CO} \\
\text{CO} & \quad \text{NH}_2 \\
0 & \quad \text{Mn} \quad 0
\end{align*}
\]

The dissociation constant of the glutamate complex (\(K = 18.1 \times 10^{-4}\)) as found in the present case (figures 25 B
and 25 D) suggest an appreciable stability of the complex.

IX Complexes of Manganese (II) with maleic and fumaric acids:

Maleic acid forms chelates with calcium and strontium\textsuperscript{107} and also with other bivalent metals of the first transitional series while fumarate complexes of thorium\textsuperscript{108}, copper\textsuperscript{97} and cobalt\textsuperscript{98} have been studied by conductometric and spectrophotometric measurements. There is, however, no mention of fumarate and maleate complexes of manganese (II) in literature.

An indication of manganese (II) undergoing complexation with these acids has been provided by the conductometric and spectrophotometric measurements in the present case. Maleate (figures 26 A & 26 C) as well as fumarate (figures 27 A & 27 C) complexes have been found to possess the composition of 1 : 1.

The following structure represents the complexes suitably.

\[ \text{Mn} \quad \begin{array}{c}
\text{0} \\
\text{0}
\end{array} \quad \text{C} \\
\text{0} \quad \text{CH} \]

Malate (figures 26 B & 26 D) and fumarate (figures 27 B & 27 D) have the dissociation constants $8.85 \times 10^{-4}$ and $21 \times 10^{-4}$ respectively. In the present case.
It is interesting to note that with the exception of malate and tartrate complexes all the other aliphatic dicarboxylate complexes of manganese (II) are neutral. Anionic malate and tartrate complexes owe their negative charges to the tridentate character of malic and tartaric acids. The unoccupied coordination positions of the metal ions are presumably occupied by water molecules in order to satisfy the coordination maxima of manganese (II). This assumption appears to be logical and well founded when it is observed that the oxalate ion generally shares the coordination sphere with neutral molecules such as ammonia, ethylenediamine and water \textsuperscript{109-112}. Werner has pointed out that a large number of compounds containing complex oxalate anions crystallise with water, even if the cation is one, which is usually anhydrous\textsuperscript{113}. That the manganous ion, with the exception of malate and tartrate complexes, does not form anionic complexes under the experimental conditions, may be due to (i) its basic character and (ii) its large ionic size. The tridentate behaviour of the malate and tartrate ions has been adequately explained by Nanda and Pani (loc.cit.)

\textbf{X Complexes of manganese (II) with citric and aconitic acids:}

Citric acid, being an \(\alpha\)-hydroxy acid with tridentate character possesses very strong chelating tendency
with the consequence that a large number of citrate complexes have been reported. Calcium, strontium, barium\textsuperscript{114} and magnesium\textsuperscript{115} have been reported to form 1 : 1 citrate complexes. Bobtelski and coworkers\textsuperscript{95-99} on the basis of conductometric and spectrophotometric studies arrived at the conclusion that copper, nickel, cobalt and thorium, all of them form 1 : 1 citrate complexes. No citrate complex of manganese has, however, been studied so far.

Except for the aconitate complex of manganese-\textsuperscript{54} reported by Norman and coworkers (loc. cit.) there is no reference relating to the complex forming behaviour of aconitic acid whose hydration results in the formation of citric acid.

Manganese (II) has been found to undergo complexation with each of these acids, forming 1 : 1 anionic complexes in both the cases. The results of citrate and aconitate complexes have been represented in figures 28 A and 28 C & 29 A and 29 C respectively.

The following structures I and II have been assigned to the citrate and aconitate complexes respectively:

\[
\begin{align*}
\text{I} & : \quad \begin{array}{c}
\text{OOC-CH}_2\text{CH}_2\text{COO} \\
\text{CHO} \\
\text{Mn}
\end{array} \\
\text{II} & : \quad \begin{array}{c}
\text{CH}_3\text{COO} \\
\text{C}_2\text{OOC} \\
\text{CH}_2\text{COO} \\
\text{Mn}
\end{array}
\end{align*}
\]
In the case of the citrate complex the hydrogen of one hydroxyl group is liberated and oxygen is linked to the metal. This behaviour of citrate ion has been explained by Bobtelski and co-workers (loc. cit.) in the case of several bivalent cations of the first transitional series. Manganese (II) belonging to the above series, is expected to behave similarly and hence the above structure of the citrate complex is suitable.

The aconitate ion behaves differently in that all the three carboxyl oxygen atoms occupy the three coordination positions of the metal ion.

The dissociation constants of the citrate (figures 28 B & 28 D) and the aconitate (figures 29 B & 29 D) have been found to be $4.9 \times 10^{-4}$ and $8.8 \times 10^{-4}$ respectively.

**Stability:**

The following sequence is obtained when the complexes of manganese II with di- and tri-carboxylic acids and their derivatives are arranged in the order of their stability.

Citrate > Tartrate > Oxalate > Malonate > Aconitate > Aspartate > Malate > Maleate > Succinate > Dibromo succinate > Glutamate > Glutarate > Adipate > Fumarate.
The dissociation constant of the complex oxalate shows that compared to the other dicarboxylate complexes, it is the most stable. This finds its justification in two factors, viz., (i) the distance between the two carboxyl groups in this acid is minimum and (ii) it forms a five membered ring which imparts maximum stability to the complex.

In the higher homologues the distance between the two carboxyl groups as well as the size of the ring continuously increase, with the consequence that the following order of stability of the complexes results:

Oxalate > Malonate > Succinate > Glutarate > Adipate.

Bromo substitution:

The dibromo succinate complex shows less stability than the succinate complex. It is due to (i) the inductive effect of the bromine atom (ii) the deformability of the bromine atom and (iii) the steric hindrance brought about in the succinate ion due to the introduction of bulky atoms which cause strain in the complex ring rendering it more deformable.

Amino substitution:

It is seen that the aspartate complex is more stable than the succinate, while the glutamate complex is more stable
than the glutarate. This is due to the basic nature of the 
$\text{-NH}_2$ group, which brings about considerable decrease in the
dissociation constant values of the succinic and glutaric
acids, enhancing thereby, the katiophilic nature of both,
the succinate and the glutarate ions.

**Hydroxy substitution:**

The ions, malate and tartrate, behave in a way
different from that of their parent acid. It has been observed
that the introduction of one or more such groups causes a
diminution in the separation of the two functional carboxyl
groups. It would, therefore, appear that the substitution
leads to a bending of the zig zag chain so as to bring the
carboxyl groups closer together. Succinic acid, in which the
two carboxyl groups are far from one another is unable to
produce the effect that the other dicarboxylic acids, viz.,
oxalic and malonic do. On the other hand, the hydroxy
derivatives of succinic acid, viz., malic and tartaric acids
behave like oxalic and malonic acids. This shortening of the
distance between the two carboxyl groups as a result of the
introduction of -OH groups in the succinic acid is mainly
responsible for the more stable character of the malate and
tartrate complexes as compared to that of the succinate
complex.
Apart from the shortening of distance between the two carboxyl groups, the acid dissociation constant value also suffers a slight decrease due to the hydroxy substitution and therefore, the metal-ligand bond strength is also enhanced and hence the malate and tartrate complexes exhibit more stability than does the succinate complex.

**Effect of unsaturation**:  

The introduction of a double bond into the succinate ion causes a decided increase in the metal-ligand bond strength as is evident from the dissociation constant value of the maleate complex, which is less than that of the succinate complex. Since, in this case, no appreciable shortening of distance between the carboxyl groups occurs, the stability increase is attributed to a pronounced polar effect caused by the double bond.

**Effect of structural isomerism**:  

The fumarate complex indicates considerable decrease in stability. This can only be owing to the structural dissimilarity between the maleic and fumaric acids. Since the carboxyl groups in fumaric acid are farther than in maleic acid, the latter being a cis-isomer while the former a trans-isomer, the metal-ligand bond is much weakened in case of the fumarate complex.
Complexes of manganes (II) with salicylic acid and its certain derivatives:

As is common with the $\alpha$-hydroxy acids, salicylic acid and its various derivatives form strong chelates with an appreciable number of metal ions$^{118}$. Argen$^{119}$ has reported his investigation on the ferric complexes of sulphosalicylic acid, salicylic acid, para-amino salicylic acid and other derivatives of the salicylic acid by potentiometric and photometric techniques. From the theoretical consideration he has advanced an argument that since all these compounds contain a common chelating ring the complexes formed by them might be expected to possess the same degree of stability relative to the strength of the acids. This view has been contradicted by other workers$^{120}$ who have put forward an adequate explanation of their disagreement with the view of Argen.$^{(loc.cit)}$

On the basis of their experimental verification they hold that all these substances are stabilised by resonance in the benzene ring and the strongest complexes are formed where $X_3 = 0$ as is seen in case of sulphosalicylic, salicylic and para-amino salicylic acids.

The various substituted groups have their specific influence on the liberation of carboxyl as well as phenolic protons and hence though the chelating ring in all the cases is
the same, nevertheless, the stability of the complexes formed by them with any metal ion depends largely on the pK values of these compounds. Thus salicylic acid and its various derivatives provide an interesting class of compounds offering a good problem to the chemist to examine critically the role played by different substituents (in the benzene ring) in determining the stability of the complexes formed by the above mentioned compounds with ammetal ion.

I _Salicylate complex_:  
Quite an appreciable amount of work has been done regarding the complexing behaviour of salicylic acid. Thus copper$^{121}$ and iron (III)$^{122}$ have been found to form salicylate complexes by spectrophotometric measurements. Copper has been reported to form 1 : 1 and 1 : 2 salicylate complexes while the ferric ion forms 1 : 1, 1 : 2 and 1 : 3 complex salicylates. Recently Mehrotra and Kapoor$^{123}$ studied the reaction between beryllium sulphate and potassium salicylate by pH and conductance measurements. All these workers have reported the liberation of phenolic and carboxylic protons in contradiction to the earlier views that the phenolic hydrogen may not ionise. They have categorically stated that the protons must be liberated from the reagent even after the carboxyl group is completely ionised.
The present investigation affirms that only a 1:1 salicylate complex of manganese (II) is formed, when manganous chloride and potassium salicylate solutions are mixed in different molecular proportions and their electrical conductance (figure 30 A) and optical density (figure 30 C) are measured. On the basis of the assumption that both the carboxylic and phenolic protons are liberated during complex formation as confirmed by the workers mentioned above the following structure of the manganese salicylate complex is to be the most probable one:

![Salicylate Complex Diagram]

The dissociation constant of the salicylate complex has been found to be $2.3 \times 10^{-4}$ (figures 30 B & 30 D).

II **Sulphosalicylate complex:**

Sulphosalicylic acid is obtained by the introduction of a sulphonic group in the meta position to the carboxyl group of the salicylic acid. This substitution brings about a decrease in the proton affinity of the acid with the result that this ligand forms complexes with slightly less stability compared to the salicylate complexes.
A large number of sulphosalicylate complexes of various metals such as copper, iron, aluminium, radium and beryllium have been studied by different workers who have found that the sulphonic, phenolic and carboxylic protons are liberated as a result of complex formation. Reaction of manganese (II) with this reagent has not been studied so far. The author has been able to detect only a 1 : 1 sulphosalicylate complex of manganese (II) with the help of conductance (figure 31A) and spectrophotometric (figure 31C) observations. Assuming the liberation of all the three protons as reported by earlier workers from the acid the following structure has been assigned to the complex

![Complex Structure]

The dissociation constant of the complex has been calculated to be $5.7 \times 10^{-5}$ (figures 31D & 31B). The low stability of the sulphosalicylate complex as compared to that of the salicylate complex is in keeping with the theoretical expectations.

III Para-amino salicylate complex:

Para-amino salicylic acid is obtained as a result of the substitution of an amino group in the meta position to the carboxyl group of the salicylic acid. Introduction of
this group has a definite bearing on the complexing behaviour of the salicylate ion in two ways, viz., the effect of the amino group on the proton affinity of the reagent and the basicity of the amino group which too plays an important role in determining the strength of the metal-ligand bond established due to complexation. The net result of these two effects is that this ligand behaves as a very strong chelating agent. Strontium\textsuperscript{128}, thorium\textsuperscript{129}, and many other metals\textsuperscript{130-131} have been reported to get chelated; with this ligand; but any investigation of the reaction between manganese\textsuperscript{(II)} and para-amino salicylic acid is strikingly missing. The conductance and the spectrophotometric investigations carried out by the author offer an indication of complexation of manganese\textsuperscript{(II)} with sulphosalicylic acid, the complex containing the two reagents in equimolecular proportions (figures 32 A & 32 C).

Earlier workers have suggested that both, the carboxylic as well as the phenolic protons are liberated due to complex formation. On the basis of this suggestion the following structure can be allotted to this complex:

\[
\text{NH}_2
\text{C} - \text{O} \quad \text{Mn}
\]
The dissociation constant of the complexes as calculated from the conductance (figure 32 B) and spectrophotometric (figure 32 D) data attains the value $3.2 \times 10^{-4}$.

IV Ortho- and meta-cresolate complexes:

Ortho- and meta-cresotic acids are formed when the hydrogen atoms in the ortho- and meta- positions corresponding to the phenolic group in salicylic acid, respectively, are substituted by the methyl group. Substitution of this group causes steric hindrance facilitating thereby the liberation of protons from the carboxyl and phenolic groups, with the result that the cresotate complex is expected to be less stable than the salicylate complex. Recently o-cresotate complexes of aluminium\textsuperscript{132}, copper\textsuperscript{133} and uranium\textsuperscript{134} and m-cresotate complex of beryllium\textsuperscript{45} have been reported by physico-chemical methods. No complexes of manganese (II) with either ortho- or meta- cresotic acids have been investigated. In an attempt to bridge this gap the author has been able to detect a 1 : 1 complex of manganese (II) with both, ortho- and meta- cresotic acids by studying the electric conductance and optical density of the mixtures, containing manganous chloride and sodium ortho- and meta-cresotes in different molecular proportions. The results are represented in figures 33A & 33 C and 34 A & 34 C respectively.
On the same reasoning as put forward in the case of other substituted salicylates the following structure of the complex cresotates appear to be the suitable ones:

\[ \begin{array}{c}
\text{Mn-o-cresotate} \\
\text{Mn-m-cresotate}
\end{array} \]

The dissociation constants of the ortho cresotate and meta cresotate complexes are \( 7.8 \times 10^{-4} \) and \( 7.5 \times 10^{-4} \) respectively (figures 33B & 33 D, 34 B & 34 D).

V Phthalate complex:

Reaction of phthalic acid with a few metals such as copper, cadmium has been investigated and in all the cases the phthalate complex was formed.

In the present work the system manganous chloride - potassium hydrogen phthalate was studied by conductivity and spectrophotometry and it has been observed that the complex contains the metal and the ligand in equimolecular proportions (figures 35 A & 35 C).
As in the case of aliphatic dicarboxylic acids the following structure has been assigned to the phthalate complex:

![Structure](image)

The dissociation constant of the above complex assumes the value $1.74 \times 10^{-4}$ (figures 35 B & 35 D).

VI Gallate complex:

Gallic acid is a very strong chelating agent. Many gallate complexes namely, titanium$^{136}$, uranium$^{137}$, cerium$^{138}$, copper$^{139}$, bismuth$^{140}$ and lead$^{141}$ have been reported by various workers. No gallate complex of manganese (II) has, however, been recorded in literature. During the course of the physico-chemical study of the system manganese chloride - gallic acid, an interesting observation has been made by the author that the dilution factor plays an important role in the reaction between these two reactants, in that, whereas no colour reaction is observed at higher concentrations, an intense green colour develops at very high dilution (0.0005 M) for the two reagents, twenty hours after the solutions are mixed. It is probable that the colour reaction
is as a result of hydrolysis. When to a constant volume of manganous chloride kept in different vessels, different quantities of gallic acid are added and the optical densities of the mixtures are measured after twenty hours, the mixture containing the reactants in equimolecular proportions attains the highest optical density value. The colour intensity increases with the increase in the quantity of the added gallic acid till it reaches a maxima where the composition of the complex is 1 : 1. Further addition of the acid causes diminution in the colour intensity. The colour is ultimately discharged when the mixture contains the acid in a very large excess.

It is quite probable that the colour development at higher dilutions seeks the cause of its origin in the hydrolysis which causes a drop in pH and facilitates the liberation of protons from the acid, helping thus, the chelation of metal ion with the ligand. The following structure has been assigned to the complex:

![Structure Diagram]

\[ \text{Mn} \]
Figures 36 A & 36 C represent the composition of the complex.

The dissociation constant of the complex has been found to be $1.24 \times 10^{-5}$ (figures 36 B & 36 D).

VII salicylaldoxime complex

A very few complexes of salicylaldoxime have been reported. Manganese (II) has been found to undergo complexation with this ligand. The complex has the composition of 1:1 as confirmed by conductance (figure 37 A) and spectrophotometric (figure 37 C) measurements.

Feigl and Bondi have shown in the case of salicylaldoxime that if the solutions employed are not highly alkaline, complex formation takes place through the displacement of phenolic hydrogen and results in the binding of the metal ions by the phenolic oxygen and oxime nitrogen. Following their view, the mechanism of complexation can be assumed to take place in a similar manner on the basis of the analogy in structures of all the compounds containing the oxime group. The same reasoning can be applied to complex formation of other compounds containing oxygen as donor.

On the basis of the above arguments the following structure has been assigned to the salicylaldoximate complex.

\[
\left[ \begin{array}{c}
\text{CH} = \text{NOH} \\
\text{O}
\end{array} \right]^{+} \stackrel{\text{Mn}}{\rightarrow}
\]
The dissociation constant of the complex as calculated from the conductance (figure 37 B) and spectrophotometric (figure 37 D) studies finds the value $1.17 \times 10^{-4}$.

VIII *Salicyloyl hydrazide complex*:

In this case the metal ion may be expected to coordinate with the basic group just as in the case of copper ammoniates. It has been found by earlier workers\(^{144}\) that protons attached to the basic nitrogen are displaced at the same time as the phenolic proton. The structure of salicyloyl hydrazide is as given below:

\[
\begin{array}{c}
\text{H} \\
\text{N - N} \\
\text{C} \quad \text{H} \\
\text{O} \\
\end{array}
\]

The examination of this structure reveals the possibility of the presence of an additional hydrogen bond besides the one embracing the ketonic oxygen and the phenolic hydrogen. Because of this additional hydrogen bond the phenolic hydrogen will be less strongly held by the ketonic oxygen, which again is responsible for the formation of second hydrogen
bond. If such be the case the phenolic hydrogen will be much easily ionised with the result that complex formation will take place between the phenolic oxygen and the ketonic oxygen. The following structure has, therefore, been assigned to the 1:1 complex as indicated by the conductance (figure 38 A) and spectrophotometric (figure 38 C) measurements.

![Diagram](image)

The dissociation constant of the complex has been found to be $9.7 \times 10^{-4}$ (figures 38 B & 38 D).
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