SUMMARY AND CONCLUSIONS
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Unlike the bivalent metals of the first transitional series, Manganese (II) has not received a thorough, adequate and conclusive investigations in so far as its chemistry of coordination compounds is concerned. Inspite of considerable data available no precise generalisations are forthcoming.

The present work is an attempt to study the complex forming tendency of manganese (II) with organic ligands. To this end, conductometric and spectrophotometric studies of the reactions of manganese (II) with the following four series of ligands have been made.

A. **Aliphatic monocarboxylic acids and their derivatives:**
   Acetic, formic, propionic, butyric, monochloro acetic, dichloro acetic, trichloro acetic, lactic and mandelic acids and glycine, dl-alanine, B-alanine, and dl-B-phenylalanine, bromopropionic and crotonic acids.

B. **Aliphatic dicarboxylic acids and their derivatives:**
   Oxalic, malonic, succinic, glutaric, adipic, malic, tartaric, maleic, fumaric, aspartic and glutamic acids.

C. **Tricarboxylic acids:**
   Citric and aconitic acids.
D. *Aromatic mono- and di-carboxylic acids and some of the derivatives of salicylic acid*:

Potassium salicylate, sulphasalicylic, p-amino salicylic, o-cresotic, m-cresotic and gallic acids; potassium hydrogen phthalate, salucylaldoxime and salicyloyl hydrazide.

Job's method of continuous variation has been employed to study the compositions as well as the dissociation constants of the complexes and from the data thus obtained the effect of substitution of various groups in the complexing agents have been examined. Suitable explanations have been advanced to justify the structures assigned to the complexes.

Experimental observations throughout the course of the present investigation lead to the following conclusions:

1. Except the glycinate and the alaninate complexes which have the composition 1:2, all other complexes contain the metal and the ligands in equimolar proportions.
2. Aliphatic mono carboxylate complexes of manganese (II) show the following sequence of stability:
   - Formate < Acetate ≈ Propionate < Butyrate.
3. Chlorine substitution brings about pronounced decrease in the complexing ability of the acetate ion as is evident from the following order of stability:
Acetate $>$ Monochloro acetate $>$ Dichloro acetate $>$ Trichloroacetate

(4) Bromine substitution also suppresses the complexing tendency of ligands as is apparent from the fact that the propionate and succinate complexes are more stable than the bromopropionate and dibromo succinate respectively. In both the cases, inductive effect of chlorine and bromine appears to be responsible for the decrease in stability.

(5) Hydroxy substitution in aliphatic mono- as well as dicarboxylic acids enhances the metal -ligand bond strength. This is clear from the order of stability in the series shown below:

- Acetate $<$ Mandelate $<$ Lactate.
- Succinate $<$ Malate $<$ Tartrate.

This is due to the increase in the basicity of the ligands and the increase in their dentate character brought about by the hydroxy substitution.

(6) Amino substitution in all the cases studied renders the ligands more strongly complex forming. Evidence is provided by the following stability order:

- Acetate $<$ Glycinate.
- Propionate $<$ dl-B-Phenylalaninate $<$ B-alaninate $<$ dl-alaninate.
- Succinate $<$ Aspartate
- Glutarate $<$ Glutamate
Increase in the basicity of the ligands caused by the amino substitution and coordination through nitrogen of the amino groups are responsible for the above observations.

(7) That the lactate and alaninate complexes are stronger than the mandelate and phenylalaninate complexes respectively can be attributed to the steric influences caused by the presence of bulky groups.

(8) As the distance between the two carboxyl groups in dicarboxylic acids increases, stability of the complexes formed by them decreases. Thus, oxalate complex is the most stable whereas adipate is the least.

Oxalate > Malonate > Succinate > Glutarate > Adipate.

As we go to the higher homologues increase in chain length appears to bring about this effect.

(9) Introduction of double bond in the ligand slightly increases the complex stability. This is clear from the fact that the maleate and the crotonate complexes are more stable than the succinate and the butyrate complexes respectively.

(10) Maleate complex is stronger than the fumarate possibly due to the fact that the cis isomer establishes stronger metal-ligand bond than the trans one.

(11) Citrate complex is the most stable due to the dentate
character of the citrate ion. Cut aconitate complex gets more readily dissociated as compared to the citrate.

(12) Salicylate acid and all its derivatives have been found to be strongly complexing. The following shows the order of their stability:

\[ p\text{-ami salicylate} > salicylate > sulphosalicylate > cresotate > salicylhydrazide > salicylaldoximate \]

It is evident from the above that as in the case of aliphatic mono and dicarboxylic acids the hydroxy and amino groups induce enhanced complexing ability to their parent acids. Sulphonyl group renders the salicylate ion more acidic with the consequence that the sulphosalicylate complex is less stable than the salicylate ion. Cresotate complexes are still weaker possibly due to the steric effect induced by the methyl group. Salicylaldazine and salicyloylhydrazide appear to possess the least affinity to unite with the metal in this series. This can be attributed to their larger ring sizes.

(13) Phthalate and gallate complexes have been found to be more stable than the salicylate. Gallic acid forms a green chelate at very high dilution possibly due to hydroxysis.