

• CHAPTER-II •

CHAPTER IINATURE OF THE PRESENT PROBLEM

Lot of work has been reported on the electrophilic substitution reactions of metal complexes, mainly complexes of the type  $M(\text{ptdn})_n$ . A similar study of the metal complexes containing aromatic ligands have drawn comparatively less attention. When an aromatic ring is one of the groups attached to the metalloheterocyclic ring, the general impression is that polarisation of aromatic ring by the metal ion has no spectacular effect on the chemical reactivity of an aromatic ring, except that there is some influence on the rate of the reaction. These conditions are however based on limited experimental data. Careful study of the literature shows controversial reports on the halogenation reaction, which should have been an extensively studied problem.

The metalloheterocyclic ring in  $M(\text{ptdn})_n$  is supposed to be pseudoaromatic. These complexes are acid labile. The reactions of the metal complexes in which metalloheterocyclic ring retains its integrity are of three types; (a) addition on central metal ion; (b) reaction of reactive sites and functional groups depending on the chelate ring; (c) substitution of hydrogen or other group attached to

coordinated ligand. In the present problem we shall be considering mainly (c) type of reactions.

For such studies, metal complexes (i) Should be stable (ii) Ligand coordinating with main group and transition metal ions will be preferred. (iii) It should be possible to vary electron densities on different carbon atoms by varying the substituents in order to study the effect of such group on chemical reactions.

Our present problem consists of the study of the complexes of the type (M-Salicylaldehyde); M(N-Rsalim); (M-chalkone) and (M-ortho-hydroxyacetophenone). In such type of complexes, both the effect of R-group keeping same metal ion and effect of metal ion keeping same R-group, on the chemical reactivity of the complex can be investigated. Stereochemical factors involved in the chemical reactivity are to be considered. The products obtained by electrophilic substitution reactions can be characterised by spectroscopic techniques. Preliminary experiments show that these reactions are moderately fast. Thus kinetic studies under normal conditions can be carried out.

Literature survey shows that reports on nitration and acetoxylation reactions are scanty. On the basis of the current information, efforts will be directed towards the

systematic study of nitration reactions using different nitrating and acetoxyating reagents in definite mole ratios. Preferably the reagents selected will hydrolyse the complexes. The products will be characterised by usual spectroscopic techniques. The results will be supplemented by isolating ligands and their characterisation.

Other reactions like thiocyanation, halogenation, acetoxylation with silver acetate will be characterised by usual methods. In case of imines care will be taken not to hydrolyse them. This report will also include the study of bromination reactions of imine complexes.

Effect of R-group and effect of metal ion on the kinetics of bromination reaction will be studied, which will further help to study the mechanism of bromination reactions. For this study  $M(N-Rsalim)_2$  will be chosen, NBS will be used as brominating agent, because of acid labile nature of imine group. Pure and anhydrous 1,4-dioxane and a mixture of 1,4-dioxane and acetonitrile will be used as the solvent. Reactions will be carried out under normal atmospheric conditions. It will be possible to study the effect of M-L covalency on the kinetics of the bromination reactions by varying metal ions in  $M(N-Rsalim)_2$  and keeping same R group. Analysis of kinetic data will be done in the light of the mechanism proposed for the bromination reaction of  $Ni(N-Rsalim)_2$ .