SUMMARY

The present thesis deals with synthesis and characterization of metal chelates of some orthohydroxyazonaphthoquinones as well as oxime derivatives of 1,2-naphthoquinone. It constitutes a part of the programme carried out in our laboratories to understand chelation characteristics of naphthoquinone ligands.

The ligating system in 3-phenylazo-2-hydroxy-1,4-naphthoquinone (3-PHANQ) (I) is interesting for variety of reasons, e.g.:

1. Presence of five or six membered chelate cycle,
2. Possibility of altering the basicity of coordinating azo nitrogen,
3. Presence of azo-hydrazone equilibrium, and
4. Possible antivitamin K activity.

The first chapter of the composite provides a short
account of the chemistry of C-3 substituted 2-hydroxy-1,4-naphthoquinones along with their chelation reactions and biological activities.

The second chapter is concerned with the study of six derivatives of (I) bearing electron donating as well as withdrawing substituents in ortho-, meta- and para-positions in the side aryl ring by various physicochemical methods such as chromatography, IR and UV-VIS spectroscopy, ionization equilibria, and PMR spectroscopy. Such studies are thought to be necessary to gain information on the changes in structural parameters of the ligands brought about by their coordination with different metal ions. It is found that these derivatives are equilibrated in both azo as well as hydrazone tautomeric forms in a six membered chelate cycle and stabilization of a particular form is a function of substituents as well as the solvent. Generally electron withdrawing substituents and polar solvents seem to favour hydrazone form. Studies on ionization equilibria including the applicability of derived Hammett equation for predicting pK values of C-3 substituted 2-hydroxy-1,4-naphthoquinone derivatives indicate a facile charge transfer across the azo linkage.

The third chapter opens up with a brief review on metal
complexes of orthohydroxyazo dyes and includes structural characterization of some first row transition metal chelates of seven 3-PARNQ derivatives with help of adequate and available physical-chemical techniques. Four coordinate chelates structures which are characteristic of orthohydroxyazo ligands are obtained only with cobalt (II) and nickel (II) ions, while copper (II) chelates are found to be consisting of dimeric units. Spin-crossover behaviour is also seen in case of some of the ferrous chelates. It is observed that many times a particular steric requirement is imposed by the present ligand system in deciding final geometries of these compounds. Various correlations between ligand field strengths or d-orbital electron configurations and chelate stability/ thermal stability or metal-ligand IR frequencies are also attempted in this chapter.

In addition we have also synthesised and characterised lanthanide chelates of (I) in chapter IV which provides an opportunity to examine the chelation characteristics of nitrogen-oxygen donating atom system and compare it with more commonly occurring oxygen-oxygen coordinating system in naphthoquinones. The possibility of coordination number higher than six is also examined in this chapter for the synthesized chelates.

Fifth and final chapter deals with iron (II) and
manganese (II) complexes of 1,2-naphthoquinone oxime ligand systems which are found to yield square planar chelates similar to phthalocyanine compounds where possibility of metal-metal interactions is indicated. Square planar manganese complexes synthesized in the present work can serve as the starting compounds for preparation of various manganese complexes in different oxidation states similar to the ones described by Lever.