SYNOPSIS
This thesis entitled "EFFECTS OF AXIAL LIGANDS ON THE REDOX PROPERTIES OF SOME METALLOPORPHYRINS" discussed the information and results of investigations on the physico-chemical studies of some Metalloporphyrins. It consists of six chapters. We restrict our investigations mainly to UV-Visible absorption spectroscopy and Cyclic Voltammetric studies of some transition metal porphyrins like Manganese, Zinc and Copper porphyrins.

In the Introduction, natural occurrence of some metalloporphyrins and their biological functions are briefly mentioned. Also, the importance of UV-Visible spectroscopy and cyclic voltammetry in understanding the redox behaviour of metalloporphyrins is highlighted in the Introduction.

A Brief Review on the theory behind UV-Visible and Cyclic Voltammetric studies on the Effects of Axial Ligands in some Metalloporphyrins (emphasis is given to Manganese porphyrins) is presented in Chapter 1. This
review provides us the background information to pursue our research investigation in the right direction and to give a proper perspective for the results of the investigations presented in subsequent chapters.

**Chapter 2** describes the details of the experimental procedures adopted for purification of solvents and chemicals, synthesis, purification and characterization of samples used during the course of our investigation. Besides this, brief description of physical measurements is also presented.

The Effects of Axial ligands on the UV – Visible spectra of some manganese porphyins are discussed in **Chapter 3**. In general, all three Manganese porphyins chosen to study, viz., Mn(III)[T(2-OMeP)P]OAc, Mn(III)[T(Naphthyl)P]OAc and Mn(III)[T(4-OMeP)P]OAc, exhibit similar spectral pattern. A UV – Visible absorption spectrum of a manganese porphyrin consists of one B – band or Soret band (Band V) in the range 440 – 480 nm and two Q – bands (Band III and Band IV) in the range 500 – 650 nm. Additional bands (Band Va and Band VI)
are also observed in the range 350 – 420 nm. Nitrogenous bases like Diethylamine, Triethylamine and Imidazole are used as axial ligands. It is found out that on initial addition of amine to the three Manganese porphyrins the Soret band suffers a Blue shift. This is attributed to the replacement of the axial ligand OAc\(^{-}\) by amine molecule which comes as a fifth ligand. On continuous addition of amine to the reaction mixture the intensity of the original Soret band diminishes and a new Soret band appears at a shorter wavelength. This could be due to two possibilities: (i) the coordination of another amine molecule as the sixth ligand, with the oxidation state of Mn remaining +3, and (ii) the second possibility is the reduction of Mn(III) to Mn(II) with amine molecules coordinating as the fifth and sixth ligands. In our studies, the first possibility is more probable. The details of this are presented in Scheme 3.1 and 3.2 in Chapter 3.

In our discussion, we also incorporate the conformations of metalloporphyrin which are affected by axial ligand – metalloporphyrin interactions. This effect brings about a change in the energy levels of the
porphyrin when the axial ligand binds with the central metal atom which appears as shift in the position of absorption bands in the UV–Visible spectrum.

Chapter 4 describes the Cyclic Voltammetric studies of the three Manganese porphyrins i.e., Mn(III)[T(2-OMeP)P]OAc, Mn(III)[T(4-OMeP)P]OAc and Mn(III)[T(naphthyl)P]OAc. All these three exhibit voltammograms of similar pattern. The positive scan voltammogram consists of three redox couples. This is attributed to the oxidation of Mn(III) to Mn(IV) and the first and second porphyrin ligand oxidations. Similarly, the negative scan gives a voltammogram which consists of three redox couples. This may be due to the reduction of Mn(III) to Mn(II) and the first and second porphyrin ligand reductions. It has been observed that out of the three Manganese porphyrins, redox potential of the first ligand oxidation is lowest in the case of Mn(III)[T(naphthyl)P]OAc. This is because non-planar porphyrins are easier to oxidize due to the interaction of d-orbitals of the metal atom with the porphyrin ligand orbitals (a_{1u}/a_{2u}) and Mn(III)[T(naphthyl)P]OAc, being
more distorted due to steric hindrance, gets oxidized at a lower potential. Thus structural effect on the redox potentials is reflected in the voltammograms which also supplements the results observed in Chapter 3.

**Chapter 5** discusses the Axial Ligand Effects On The UV-Visible Spectra and the Cyclic Voltammetric studies of Zinc(II)porphyrins viz., Zn(II)[T(4-OMeP)P] and Zn(II)[T(naphthyl)P]. Zn(II) porphyrins belong to regular porphyrins which contain closed shell metal toms (d^0 or d^{10}). On axial ligation with amine the absorption bands in the UV – Visible spectrum of these Zinc porphyrins experience a Bathochromic shift (Red shift). This is due to the flow of charge from the axial ligand to the porphyin ring through the Zinc ion.

The results of the Cyclic Voltammetric studies of these Zn(II)porphyrins are also presented in this chapter. Two reversible redox couples are observed although their ΔE values are quite large. We also observed that the oxidation potentials of these Zinc porphyrins studied are lower than that of Zn(II)TPP. We attribute this to the
presence of electron donating substituents which makes oxidation easier.

Chapter 6 deals with the Axial Ligand Effects On The UV-Visible Spectra and the Redox Tuning of Copper (II) porphyrins viz., Cu(II)[T(4-OMeP)P] and Cu(II)[T(naphthyl)P]. Copper porphyrins belong to $d^9$ complexes. Addition of amine does not affect the UV – Visible spectra of Copper porphyrins which indicate that they do not accept axial ligands readily. In the Cyclic Voltammetric studies, the Voltammogram consists of two redox couples whose potentials are lower than that of CuTPP. This is attributed to the presence of electron donating substituents.