STUDIES ON PARAMAGNETIC AND REDOX PROPERTIES OF SOME METALLOPORPHYRINS

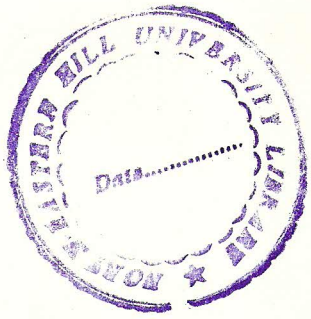
Thesis submitted in fulfillment of the

requirements for the degree of

Doctor of Philosophy

By

A. Murugan



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CERTIFICATE

This is to certify that the thesis entitled "Studies on paramagnetic and redox properties of some metalloporphyrins" is based on the original work done by A. Murugan, under my supervision in the Department of Chemistry, School of Physical Sciences, North Eastern Hill University, Shillong Meghalaya. This work has not previously formed the basis for the award of any degree, diploma, associateship, fellowship or any other similar title and that it represents entirely an independent work on the part of the candidate.

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Preface

Porphyrin chemistry is an old chemistry and is an area which is researched widely, in spite of the voluminous information available. New porphyrins are synthesized and more new results appear in the literature everyday. This is because porphyrins are not only biologically important but also find their way in the field of medicine and material sciences. Quite a good number of modified and new porphyrin ligands are available in the literature. But metal complexes of such porphyrins are not properly explored. This provides us an opportunity to venture into this field of research. This thesis embodies the physico-chemical studies of some vanadyl porphyrins and manganese porphyrins which are not reported so far in the literature.

This thesis consists of five chapters. Chapter 1 presents a brief review of the EPR and Cyclic voltammetric studies of some vanadyl porphyrins.

Chapter 2 describes different experimental techniques and measurements used in the course of the investigation.

Chapter 3 presents cyclic voltammetric studies of some vanadyl porphyrins.

Chapter 4 deals with cyclic voltammetric studies of some manganese, cadmium and copper porphyrins.

Chapter 5 describes EPR of some substituted vanadyl meso-tetraphenyl porphyrins oxidized with $SbCl_5$

INTRODUCTION

Metalloporphyrins are not only biologically important class of compounds but find their applications in the field of medicine and material sciences[1,2]. Some metalloporphyrins are also used as catalyses[3] in the oxidation of alkenes. Vanadyl porphyrins are also found in the oil shells[4], which are believed to be of biological origin and provide valuable molecular fossil record of the past environmental conditions of the geological era. Synthetic porphyrins such as supra molecular porphyrin arrays provide nano scale optical and magnetic materials[5-12]. Such self assembled materials provide the possibilities in the formation of molecular electronic devices. Metalloporphyrin macro cycles are known as molecular building blocks of one –dimensional molecular metals[7].

It is well known that metalloporphyrin π-cation radicals exhibit similar properties with that of *chlorophyll a* and B_{chl}[14-20]. Occurrence of Fe(II)porphyrins π-cation radicals in cytochromes and heme catabolism are well documented[21,22]. It is also known that the oxidation of Fe(III)P occur in catalase and peroxidase[23].

Obviously, study of redox properties of metalloporphyrins will give some interesting information. The redox behavior of metalloporphyrins also depends on substituents in the ring.

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