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This thesis entitled "ESR AND ELECTROCHEMICAL STUDIES ON THE OXIDATION PRODUCTS OF SOME METALLO-PORPHYRINS" discusses the results of investigations on the electron spin resonance and electrochemical studies on the oxidation products of some transition metal porphyrins. It consists of six chapters.

A brief review is presented in Chapter I on the structural studies (with emphasis on esr data) on the oxidation products of Ti, V, Cr, Mn, Fe, Ni and Cu porphyrins. This review provides a background material to give a proper perspective for the results of the investigations presented in subsequent chapters on the oxidation products of vanadyl porphyrins.

The details of the experimental procedures adopted in this thesis are presented in Chapter II.

The esr spectrum of the radical cation of vanadyl-octaethylporphyrin at liquid nitrogen temperature is presented in Chapter III. The esr spectrum indicates the presence of hyperfine coupling from two $^{51}$V nuclei. Hence a dimer formation is indicated by the esr spectrum. The dimer has a triplet ground state in which the two unpaired electrons pair up while the electrons on the vanadium atoms are ferromagnetically coupled. This dimer
is similar to that obtained from the radical cation of 
Cu(II) octaethylporphyrin. Assuming that the zero field 
interaction arises mainly from the dipolar coupling 
between the electrons on the vanadium atom, as has been 
done in the case of CuOEP, the esr spectrum has been 
simulated to obtain the spin Hamiltonian parameters. 
The distance between the two unpaired electrons and 
hence between the two vanadium atoms has been obtained 
as 4.7Å.

The results of the cyclic voltammetric studies on 
Zn and VO complexes of proto and mesoporphyrins are 
presented in Chapter IV. The highlights of the experi-
mental results are Zn and vanadyl protoporphyrin exist 
predominantly as dimers in solution in the concentration 
range 10⁻³M. Vanadyl mesoporphyrin is monomeric in the 
same concentration range and both monomer and dimer 
exist in equilibrium at a concentration range 10⁻²M. 
Oxidation potentials have been obtained for both the 
monomer and dimer in the case of VO mesoporphyrin. 
The difference between the oxidation potentials of the 
monomer and dimer is about 150 millivolts.

The results of cyclic voltammetric studies presented 
in Chapter VI are substantiated by the detailed esr studies 
on the oxidation products of VO proto- and mesoporphyrins,
which form the contents of Chapter V. An one-electron oxidation product of the dimer of VO (protoporphyrin) was identified in solution at room temperature from a study of the esr spectrum. This system has three unpaired electrons (one each on the vanadium atom and one unpaired \( \hbar \) electrons per two molecules). The esr spectrum obtained at room temperature from this system has been shown to arise from \( M_S = \pm \frac{1}{2} \) states of \( S = \frac{3}{2} \) manifold. VO mesoporphyrin yields monomeric radical cation on one-electron oxidation at room temperature in the concentration range \( 10^{-3} \text{M} \). At higher concentrations, a dimer similar to that obtained for VO protoporphyrin is formed. ESR spectrum of the dimer with \( S = \frac{3}{2} \) state has been obtained at 77°K and is analyzed for the spin Hamiltonian parameters.

A monomeric radical cation of VO-mesoporphyrin has been identified around 10K. The parent compound has been oxidised with at least tenfold excess of antimony pentachloride. This system yields a typical triplet state-esr spectrum with a single \( ^{51}\text{V} \) hyperfine coupling. The distance between the unpaired \( \hbar \) electron and the electron on the vanadium atoms has been obtained as \( 3.7\text{Å} \), from the esr spectrum.
Cyclic voltammetric data on some of the metal complexes of tetrabromotetraphenyl porphyrin are presented in Chapter VI. It has been noticed that the oxidation potentials are only marginally affected by the substituents in the \( \beta \) positions, in contrast to the reduction potentials which are considerably shifted under similar conditions. Wherever possible esr and optical data had been used to assign the oxidation products.