

SUMMARY

Porphyrins, the "pigments of life," are vivid and biologically significant. Their macrocycle behaviour can be tailored for specific applications. Over the past three decades, researchers have developed new derivatives of contracted porphyrins, leveraging their versatile chemistry for various applications. Corroles, the contracted porphyrins with a missing carbon atom have gained attention for their connection to the corrin nucleus of vitamin B₁₂. This thesis examines corroles and their metalated complexes in catalysis, aiming to create enhanced metal-catalyzed corrole complexes for diverse substrates. In this work, we present a comprehensive study on the synthesis and catalytic properties of oxo(corrinato)vanadium(IV) and nickel(II) corrole complexes. Chapter 1 outlines the biological significance, structural changes, and development of porphyrins, highlighting corrole synthesis, coordination chemistry, and spectroelectrochemical characterization. Chapter 2 reports the synthesis of two oxo(corrinato)vanadium(IV) complexes with *meso*-substitutions, serving as efficient catalysts for alkene epoxidation using H₂O₂ and KHCO₃. The catalytic reaction mixture was thoroughly analysed, a proposed mechanistic pathway was outlined, and it was confirmed that an oxo(peroxo)(corrinato)vanadium(V) complex serves as the true catalytic intermediate in the epoxidation reaction *via* electrophilic addition. Chapter 3 describes a vanadium(IV)-oxo corrole complex with NO₂ substitutions, existing in two tautomeric forms where the residual hydrogens present in either N²² or N²³ in solution. Corrole acts as a dianionic ligand in [V^{IV}O (HCorr)²⁻]. A novel oxidative cleavage of alkenes to aldehydes *via* an oxoperoxovanadyl(V) radical intermediate {O=V^V-O-O[•]} is demonstrated. Chapter 4 presents the synthesis and characterization of two anionic nickel(II) corrole complexes. We further explore Ni-corrole@CC (carbon cloth) as an electrocatalyst for oxygen evolution in alkaline conditions. Spectroscopic and electrochemical studies reveal the coexistence of the molecular complex and Ni(O)OH in the active catalyst structure.