Abstract

The thesis presents structural and functional biomimetic model studies of metalloenzymes *phenoxazinone synthase* (PHS) and *quercetin 2,4-dioxygenases* (2,4-QDs). For this purpose, several transition metal complexes with tailor-made ligands have been synthesised as pseudo-active-site models of the metalloenzymes. The enzyme-like reactivity of the model compounds has been explored, and the results are presented in the thesis. Out of seven chapters, the introductory **Chapter 1** briefly discusses the importance of biomimetic studies and provides a general overview of the enzymes PHS and 2,4-QDs, including their structural and functional properties. It also includes a brief literature overview of the metal complexes reported for the model studies of PHS and 2,4-QDs. **Chapter 2** describes the synthetic procedure of various ligand-precursors, general methods, and physical measurements. **Chapter 3** reports the catalytic activities of three mononuclear copper(II) complexes towards the aerial oxidation of 2-aminophenol to the phenoxazinone chromophore as a functional mimic of phenoxazinone synthase-like reactivity. A correlation between structure and reactivity has been established in present studies. Detailed mechanistic investigations using spectroscopic and kinetic studies have been performed. Valence tautomerism within the complex-substrate adduct, generating reactive "Cu(I)-substrate radical" intermediate, is found to be an essential phenomenon. This "Cu(I)-substrate-radical" species is believed to promote dioxygen activation in PHS reactivity. **Chapters 4-6** describe the chemistry of flavonol dioxygenation as a functional mimic of 2,4-QDs. In **Chapter 4**, the oxygenolysis of a series of Cu(II)-flavonolato complexes, $[Cu(L^{R})(fla)]$, has been demonstrated. The supporting ligands' R substituents have been varied from electron-donating to electron-withdrawing to see the electronic impacts on dioxygenation reactivity. The electron-donating properties of R substituents highly govern the reactivity rate, displaying the order –OMe > –H > –Cl > $–NO_2$. The reaction proceeds *via* forming a flavonoxyl radical ($fla^{\bullet}$) intermediate. Experimental and theoretical studies support a single-electron transfer (SET) from the coordinated flavonolate to O_2, rather than valence tautomerism $\{[Cu^{II}(fla^{-})] \leftrightarrow [Cu^{I}(fla^{\bullet})]\}$, generating a reactive Cu(II)-flavonoxyl radical species that reacts further with superoxide ion to bring about the radical-based oxygenolysis of the bound-flavonolate. **Chapter 5** illustrates the metal ion effects on flavonol dioxygenation. This chapter describes the synthesis and characterisation of five acetate-bound metal(II) complexes, $[M^{II}(L)(OAc)]$ (M = Mn, Co, Ni, Cu, Zn), and their flavonolato adducts. Catalytic activities of the M(II)-acetato complexes towards the oxygenative degradation of flavonol have been investigated in detail. A metal-ion-dependent reactivity order of Co > Ni > Zn > Mn >> Cu has been observed. The studies establish that the reactivities of the $[M^{II}(L)(OAc)]$ complexes are regulated primarily by three factors: the catalyst-substrate adduct formation constant (K_f), the redox potential (E_{pa}) of the bound $fla^{-}/fla^{\bullet}$ couple, and the degree of delocalisation of the $fla^{\bullet}$ radical with the metal electrons. **Chapter 6** presents a comparative reactivity study between two model Co(II)-acetato complexes, one containing a carboxylate donor moiety in the supporting ligand and the other not [3N(COO) *vs* 4N], to elucidate the precise role of glutamate in native 2,4-QDs. The Co(II) complex supported with the 3N(COO) donor ligand shows higher reactivity than the 4N-ligand-supported cobalt complex. The carboxylate coordination determines the reaction rate *via* its influence on the $fla^{-}/fla^{\bullet}$ oxidation potential. In final **Chapter 7**, the overall summary and conclusions have been presented.