ABSTRACT

Enzymes that utilize nonheme iron centres to activate dioxygen and carry out oxyfunctionalization of hydrocarbons are of great fundamental and practical interest. To mimic these enzymes, several structural and functional models have been developed during the last few decades. In this chapter the advances in the title area is reviewed. Current challenges are discussed. The scope and the purpose of the present investigation is cast against this background.

In Chapter II, the catalytic reactivity of a group of diferric oxo-bridged complexes (**1**-**3**) based on terdentate bpmen ligand (bpmen= N,N'-dimethyl- N,N'-bis(2-pyridylmethyl)-1,2-diaminoethane) towards alkane hydroxylation has been evaluated. Among the three complexes, the μ-oxo diiron(III) complex [Fe(bpmen)(μ-O)$FeCl_3$] (**1**) has been synthesized for the very first time. The complex **1** has been characterized by spectroscopic analysis and X-ray crystallography. Moreover, the catalytic ability of the complexes in the oxidation of alcohols to ketones with mild hydrogen peroxide at room temperature has also been investigated.

Room temperature oxidation of olefins catalyzed by a symmetrical (μ-oxo)(μ-hydroxo)diiron(III) complex based on the amino pyridyl ligand bpmen (bpmen = N,N´-dimethyl-N,N´-bis(2-pyridyl methyl)ethane-1,2-diamine) with hydrogen peroxide under the conditions of limiting substrate is described in Chapter III. The symmetrical (μ-oxo)(μ-hydroxo) diiron(III) complex (**2**) is shown to be an excellent catalyst for oxidation of olefins at room temperature. The catalytic system has been shown to oxidize electron-deficient olefins to the corresponding *cis*-diols, while epoxidation is favoured in case of electron-rich olefins. The μ-oxo diiron(III) core of the catalyst **2** has been found be regenerated after the catalytic turnovers. Addition of second batch of substrate and oxidant at the end of the first cycle results in the formation of almost identical amounts of epoxides/diols. Interestingly, the regenerated catalyst exhibits a significantly higher preference towards the oxidation of electron-deficient olefins.

Chapter IV deals with the reactivity of a diferric complex of an aminopyridine ligand, $[(bpmen)_2Fe_2O(\mu\text{-}O)(\mu\text{-}OH)](ClO_4)_3$ (**2**), bpmen = N,N'-dimethyl-N,N'-bis(2-pyridylmethyl)-1,2-diaminoethane) towards aromatic hydroxylation with H_2O_2 and acetic acid. In biology, aromatic hydroxylation is carried out by a family of heme and nonheme oxygenases, such as cytochrome P450, toluene monooxygenases (TMOs), methane monooxygenase (MMO). In contrast, a vast majority of synthetic iron based catalysts employed so far in aromatic hydroxylation are monomeric in nature. In this chapter, we have successfully utilized the diiron(III) complex (**2**) in hydroxylation of benzene and alkylbenzenes at room temperature. The μ-oxo diiron(III) core has been shown to be regenerated at the end of catalytic turnover. Mechaniistic studies have indicated that the diiron(III) complex undergoes dissociation into its monomeric congener and the resulting iron(III) complex mitigates aromatic hydroxylation.

A novel non-heme complex containing the (μ-oxo)bis(μ-carboxylato) motif has been synthesized containing the tetradentate ligand, N,N-dimethyl-N,N-bis(2-pyridyl methyl)ethane-1,2-diamine (*iso*-bpmen). The diiron(III) complex has been characterized by ESI-MS and elemental Analysis. The molecular structure of the complex (**1**) has been determined by Single Crystal X-ray diffraction method. Each iron(III) atom in **1** is found to coordinate three nitrogen atoms of the ligand, one oxygen atom of the μ-oxo bridge and two oxygen atoms the μ-acetato bridges. The complex features a bent Fe_2O core (Fe—O—Fe bond angle of 115.4°) and exhibits a rather short Fe...Fe separation (3.056 Å). Synthesis, characterization and catalytic property of the diiron complex towards oxygenation of alkanes and alkenes at room temperature with mild and environmentally benign hydrogen peroxide have been described in Chapter V.

In Chapter VI, synthesis, characterization and catalytic reactivity of a high-spin mononuclear non-heme iron(III) cyclam complex, $[Fe^{III}(cyclam)(CH_3CN)_2](OTf)_3$ (**1**) have been delineated. The structure of the complex (**1**) has been elucidated by single crystal X-ray crystallography. Efficient and selective hydroxylation of alkanes and epoxidation of olefins has been achieved under mild condition using environmentally benign hydrogen peroxide.