INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title: Influence of the Ligand Architecture on Reactivity of High-Valent Non-Heme Metal Intermediates

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Reactivities of the high-valent non-heme metal intermediates have also been investigated exhaustively in past few decades in various oxidation reactions. It has also seen that the reactivities of the high-valent intermediates are highly influenced by primary and secondary coordination spheres along with spin states, solvents, pH etc. In a quest for an efficient biomimetic catalyst with high selectivity and reactivity, one have to understand the factors that control reactivities of non-heme metal complexes in various oxidation reactions. The ligand structure around the central metal ion is one of the important factors that influence these reactivities.

In the present work, the reactivity studies towards S-oxidation, C-H activation, aldehyde deformylation, ClO_2 formation with high-valent Mn(IV)-oxo, Mn(III)-peroxo, Fe(IV)-oxo and Fe(IV)-imido species supported by pentadentate ligands have been evaluated. These reactivity studies provide remarkable insights into the mechanistic pathway of these intermediates with changing ligand architecture.

The reactivities of two isomeric bispidine Mn(IV)-oxo complexes were compared in oxidation reaction and observed that one of the isomer was more reactive and also showing an opposite reactivity pattern with corresponding $Fe^{IV}=O$ complexes. Deformylation reaction by Mn(III)-peroxo has been evaluated and was found that it reacts through hydrogen atom abstraction reactions instead of the commonly proposed nucleophilic addition reaction. Reaction bifurcation was observed with changing ligand structure during the formation of chlorine dioxide. Steric factor at terminal oxidants plays a crucial role in Fe(IV)-oxo and Fe(IV)-imido complexes towards alcohol oxidation reaction.