ABSTRACT

Metalloenzymes are known to play pivotal role in catalyzing a plethora of biological and biochemical reactions. These transformations are directed by a variety of high valent reactive intermediates that undergo crucial redox reactions by atom transfer or electron transfer or radical reaction pathways. These high valent reactive intermediates of non-heme model systems are being studied for quite some time and are known to be influenced by factors like coordination motifs and topology, ligand architecture, pH, spin states of metal ions, solvation and temperature. However, designing efficient synthetic biomimetic catalysts remains a major challenge due to the unattainability of physiological conditions. The stability and reactivity of these metastable intermediates are hugely affected by simple modifications in the ligand backbone. The factors that govern the reactivity profiles are often associated with the mechanistic pathways followed. Hence in order to have a clear idea, it is important to dig deep into the mechanistic details of the reactions performed by these model systems.

Non-heme iron-oxo intermediates have been identified as potential reactive intermediates in a variety of electrophilic reactions. It can catalyze C-H activation reactions of active and inactive C-H bonds. Other than C-H activation reactions, it can also undergo heteroatom oxidation reactions. Herein, subtle modifications in a ligand skeleton can be seen to hugely accelerate reaction rates catalyzed by non-heme iron-oxo complexes. Also with the help of a series of structurally tweaked ligand frameworks, the governing factors that orchestrate the eccentric reactivity trends of iron-oxo moieties have been brought to the forefront. With the help of a couple of isomeric bispidine Mn(III)-peroxo complexes, a new mechanism for aldehyde deformylation reaction has been established. A very basic keto-enol tautomerism in the reaction mechanism can be seen to trigger an electrophilic pathway instead of the commonly portrayed nucleophilic mechanism in aldehyde deformylation reactions. Another intended engineering in the bispidine framework resulted in stabilizing a metastable non-heme iron(III)-alkylperoxo complex. These complexes are generally non-reactive. Surprisingly, however, versatile reactivity towards both electrophiles and nucleophiles have been observed for the same.