INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Programme of Study : Ph.D.

Thesis Title: Nitrosyl complexes of Co(II) and Mn(II) porphyrins - Reactivity towards reactive oxygen species and utility as HNO donor

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Thesis Submitted to the Department/ Center : Chemistry

Date of completion of Thesis Viva-Voce Exam : 07/09/2022

Key words for description of Thesis Work : Porphyrin, nitrosyl, peroxynitrite, HNO

SHORT ABSTRACT

This thesis broadly covers our endeavor to comprehend some interesting reactivity of nitrosyl complexes of Co(II) and Mn(II) porphyrinates. A series of these complexes were synthesized by varying the substitutions at the *meso* positions of the porphyrin ring (e.g. phenyl, pentafluorophenyl and 4-methoxyphenyl) and central metal ion (e.g. Co^{2+} and Mn^{2+}). The reactivity of these complexes towards reduced oxygen species (O_2^- and O_2^{2-}) was explored following an attempt to mimic the mechanism of the nitric oxide dioxygenase (NOD) enzyme, which has been discussed in the chapters 2 to 4. In every instance formation of a putative PN intermediate was observed. Tedious efforts to identify and characterize the associated intermediates that form during its formation and decomposition led to some significant findings. For instance, in chapter 2, the formation of a $[Co^{II}(NO)(O_2^-)]$ species was evidenced spectroscopically prior to the formation of a [Co(II)-PN] intermediate. In chapter 3, a Co(III) porphyrin cation radical species has been detected in the decomposition of a [Co(III)-PN], which in turn confirms the involvement of a [Co(IV)=O] intermediate in the reaction. In chapter 4, we could prove the involvement of [Mn(IV)=O] in the decomposition of an [Mn(III)-PN] intermediate both spectroscopically and chemically. A $[Mn^{III}(NO)(O_2^-)]$ species was also observed prior to the formation of the [Mn(III)-PN]. We believe that these findings will contribute crucially to our existing knowledge of NOD chemistry and extensively to the field of metalloenzyme chemistry. However, despite our best efforts, the characterization of the PN complex itself was not very successful because of its highly unstable nature.

In chapter 5, the HNO donation ability of a nitrosyl of Mn(II)-porphyrin complex was investigated in presence of HBF_4. Previously, $\{Mn(NO)\}^6$ complexes were not considered as HNO/NO^- donors due to their $[Mn(I)\text{-}NO^+]$ nature. However, we have shown that presence of electron donating ligand environment along with an electron rich sixth ligand may induce $[Mn(III)\text{-}NO^-]$ character and result in release of HNO. This is a new type of reactivity for such complexes and definitely needs more investigation in future. The mechanism of the process needs further experimental support which may be achieved by tuning the ligand framework with appropriate electron donating groups.