



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI  
SHORT ABSTRACT OF THESIS

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Thesis Title: Reactivity of Nitrosyl Complexes of  $\text{Co}^{\text{II}}$  - and  $\text{Mn}^{\text{II}}$  - Porphyrinates with Reactive Oxygen Species: Putative Formation of Peroxynitrite Intermediates.

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SHORT ABSTRACT

The thesis primarily focuses on nitric oxide dioxygenase enzymes activity, which converts nitric oxide (toxic when overly produced) to nitrate. The reaction of a cobalt porphyrin complex in dichloromethane with nitric oxide (NO) led to the bent nitrosyl complex of  $\{\text{CoNO}\}^8$  description. It was stable in presence of oxygen gas. However, it reacts with  $\text{H}_2\text{O}_2$  in acetonitrile (or THF) solution at  $-40\text{ }^\circ\text{C}$  (or  $-80\text{ }^\circ\text{C}$ ) to result in the corresponding  $\text{Co}^{\text{III}}$ -nitrate complex. The reaction presumably proceeds via the formation of a  $\text{Co}^{\text{III}}$ -peroxynitrite intermediate. X-Band electron paramagnetic resonance and electrospray ionization–mass spectroscopic studies suggest the intermediate formation of the  $[(\text{porphyrin})\text{Co}^{\text{III}}-\text{O}^\bullet]$  radical, which in turn supports the generation of the corresponding  $\text{Co}^{\text{IV}}$ -oxo species during the reaction. This is in accord with the homolytic cleavage of the O–O bond in heme-peroxynitrite proposed in the nitric oxide dioxygenase activity. Then it was found out that three linear manganese nitrosyl complexes of  $\{\text{MnNO}\}^6$  description are capable of showing the NOD activity in the presence of superoxide and forms the corresponding  $\text{Mn}^{\text{III}}$ -nitrate or nitrite complexes in THF medium. The  $\text{Mn}^{\text{III}}$ -peroxynitrite intermediates were involved in these reactions. Out of these three complexes in the case of one manganese nitrosyl complex, when superoxide ion was subjected the formation of manganese(IV) oxo species was confirmed by UV-visible, X-Band electron paramagnetic resonance and electrospray ionization–mass spectroscopic techniques. The formation of the transient metal peroxynitrites was established by the widely accepted chemical evidence, phenol ring nitration.