



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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SHORT ABSTRACT

This dissertation addresses our attempt to understand the potential of Co(II) and Mn(II) nitrosyl complexes as nitroxyl (HNO/NO⁻) donors. A series of nitrosyl complexes were synthesized by varying the ligand framework (from electron deficient to electron rich) with a central metal ion (e.g. Co²⁺ and Mn²⁺). The ability of these metal-nitrosyl complexes to act as HNO/NO⁻ donors under different reaction conditions was discussed in chapters 2 to 5. The potential of cobalt-nitrosyl complexes as nitroxyl donors was extensively discussed in chapters 2 to 4, whereas chapter 5 addresses the manganese-nitrosyl complex, which led to some significant observations. For instance, in chapter 2, the nitroxyl releasing ability of a {Co(NO)}⁸ complex in presence of anionic sixth ligands like BF₄⁻ and DTC⁻ was observed, which is the first example of such kind of reaction. Chapter 3 describes our in detailed findings of the reaction between a {Co(NO)}⁸ complex and DTC⁻ anion, which also leads to the NO⁻ donation. In chapter 4, a neutral imidazole ligand mediated NO⁻ release from a highly electron rich {Co(NO)}⁸ complex was studied. All of these sixth ligand mediated nitroxyl release from cobalt-nitrosyl complexes are found to be concomitant in nature. The kinetic inertness of low-spin d⁶ cobalt-centre of {Co(NO)}⁸ complexes makes the release of HNO very difficult. Our recent findings on the methodology for HNO/NO⁻ release from {Co(NO)}⁸ complexes will contribute significantly to the existing knowledge of nitroxyl donation from cobalt-nitrosyl complexes.

Lastly, in chapter 5, photo-induced HNO donation from the nitrosyl complex of Mn(II)-porphyrinate was investigated. The formal [Mn^I-NO⁺] electronic character of the {Mn(NO)}⁶ complex makes them unsuited for HNO donation. However, by modulating the ligand framework appropriately, the {Mn(NO)}⁶ complex can also act as an HNO donor. Upon exposure to the visible light, the {Mn(NO)}⁶ complex was found to donate NO⁻. Although many photo-induced NO release from {Mn(NO)}⁶ complexes were reported earlier, this is the only example of HNO/NO⁻ release. The incorporation of more electron donating groups in the ligand framework makes it electron rich, which in turn affects the reactivity of the [Mn-NO] centre, leading to the HNO donation.