



INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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SHORT ABSTRACT

This thesis originates from our interest to study the redox reaction of NO assisted with transition metal complexes. Initial aim of the thesis was to synthesize stable metal–nitrosyl complexes and to study the redox reactivity of the coordinated nitrosyl. Since most of the roles played by NO in biological systems are attributed to the formation of nitrosyl complexes of the metallo-proteins, this work would have been helpful to understand the basic chemistry involved in biological reactions. To achieve those, the reactivity of Cu(II) complexes of N-donor ligands have been studied and described in second and third chapters of the thesis. In both the cases, initial attack of NO resulted in the reduction of Cu(II) centre to Cu(I) and the Cu(I) intermediate complex thus formed further reacts with excess NO to afford N₂O. In chapter 2, the N₂O moiety is found to bind with metal centre to give a stable nitrous oxide complex. DFT calculation suggests that N₂O binds to copper centre through nitrogen atom. It loses N₂O easily in solution indicating a weak binding of N₂O to the metal ion.

In chapter 3, NO reactivity of a copper complex of imidazole based ligand is studied. The reaction describes c-nitrosation of a ligand by NO with concomitant reduction of Cu(II) to Cu(I). The corresponding Cu(I) complex with C-nitrosylated ligand further reacts with NO to give Cu(I)-NO intermediate. This Cu(I)-NO intermediate reacts with another equivalent of NO to form N-nitrosohydroxylaminato complex or decomposes to Cu(II) complex of c-nitrosylated ligand and N₂O.

Since cobalt-nitrosyls having {CoNO}⁸ configuration are known to be stable, the fourth chapter has been originated from our interest to develop stable {CoNO}⁸ complex. It has been reported in literature that Co(II) centres react with different ways with NO. For instance, in some cases, they undergo reductive nitrosylation; on the other hand, simple adduct formation is also known. In this connection, fourth chapter of this thesis describes a comparative account of the roles of ligand frameworks to control the NO reactivity of cobalt complexes. The fifth and final chapter describes the oxidation of NO in presence of a Co(II)- superoxo complex.