SHORT ABSTRACT

In this thesis, redox reactions of NOx (x=1, 2) assisted by transition metal complexes are presented. The thesis originates from the interest to mimic the various reactivity of NOx in biological system.

The first chapter of the thesis presents some recent literature reports for the properties and reactivity of nitrosyl complexes of first row transition metal complexes. In addition to that the oxo transfer reactivity of metal coordinated nitrite ligand, which is attracting an enormous interest in recent years are briefly discussed.

Chapter 2 proposes the first example of oxo transfer reactivity with a Cu(II)-nitrito complex towards NO_2. Oxo transfer from free NO_2 to the nitrito complex leads to the formation of the corresponding Cu(II)-nitrate complex with concomitant release of NO.

Oxo transfer reactivity of cobalt(III)-nitro complexes with tetradentate and pentadentate ligands are discussed in chapter 3. Differences in reactivity for the complexes, where nitro complexes with tertradentate schif's base ligands are found to be active towards oxo transfer reactivity unlike the pentadentate ligand counterparts. These results are in good agreement with the previously reported cases for the nitro porphyrin cobalt complexes.

Since cobalt-nitrosyls having $\{CoNO\}^8$ configuration are known to be stable, chapter 4 has been originated from our interest to develop $\{CoNO\}^8$ complex and thereby to study its dioxygenation reactivity. Dioxygenation of the cobalt(II)-nitrosyl complex resulted in the generation of a superoxocobalt(III)nitrosyl intermediate *via* an associative pathway. This intermediate then decomposes to the corresponding nitrite complex. Chemical evidence suggests the involvement of putative peroxynitrite formation in the decomposition pathway.

The final chapter discusses the disproportionation of a $\{FeNO\}^7$ species into equivalents amounts of $\{Fe(NO)_2\}^9$ DNIC and a ferric complex. The spectroscopic characterization and the single crystal x-ray determination of the nitrosyl complexes then offer some new possibilities in biological system with this type of unusual decomposition pathway.