INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Programme of Study : Ph.D.

Thesis Title: “***Synthesis, Characterization and Spectroscopic Studies of Transition Metal Complexes with Chalcogen (O, S, Se and Te) Bridged Non–innocent Ligands***”

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SHORT ABSTRACT

Amidophenolate based non–innocent ligands and their corresponding transition metal (M) complexes are very effective for enzymic mimicking, catalytic C–C cross coupling reaction, $–CF_3$ group transferring agent, C–O/N/S bond activation, valence tautomeric species formation, synthesis of M–quinone species, etc. Thus, a few non–innocent ligands with two orthogonally placed aminophenol units were designed and synthesized by placing a common chalcogen (O, S, Se and Te) bridge between two $\mathbf{H_2L^{AP}}$ [N(2–hydroxy–3,5–di–*tert*–butyl phenyl) aniline] ligand units. The sulfur bridged ligand $\mathbf{H_4L^{S(AP/AP)}}$ provided an unprecedented octahedral complex, **2E**, where one of the two coordinated amidophenolate units was present in its two electron oxidized iminoquinone {$[IBQ]^0$} form and other was in its one–electron oxidized iminosemiquinone {$[ISQ]^{\bullet 1-}$} form. The oxygen bridged ligand $\mathbf{H_4L^{O(AP/AP)}}$ provided a mononuclear octahedral cobalt complex **3A** by two set of successive homolytic $C_{aryl}–O_{bridge}$ bond breaking and homolytic $Co–O_{bridge}$ bond formation. Complex **3A** showed solvent and solid phase thermal tautomerization and the solid phase tautomeric conversion depends upon the availability of the lattice solvent within the crystalline matrix. An unprecedented one–step synthesis of Cu(II)–bis(iminoquinone) complex using amidophenolate based ligand has been established by using non–innocent ligand $\mathbf{H_2L^{AP(o–NO_2–OPh)}}$ and the Cu(II)–complex mimicked the function of coenzyme ubiquinone. A hemilabile $–NH_2$ group appended aminophenol based ligand $\mathbf{H_2L^{AP(o–NH_2–OPh)}}$ was also designed and synthesized by reduction of ligand $\mathbf{H_2L^{AP(o–NO_2–OPh)}}$. This ligand provided a square pyramidal Cu(II)–bis(iminosemiquinone) complex (**5D**), which possessed two closely located dublet spin states. Thus, the extent of coupling between Cu(II) and radical has been explored.