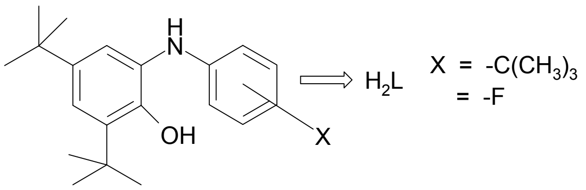
Transition Metal Complexes with Imine-phenolate and Imino-benzosemiquinone Ligands; Synthesis, Characterization and Their Catalytic Reactivity

Abstract:

Two apparently dissimilar subjects viz. molecular magnetism and metal sites in biology are at the center of this thesis. The principles of coordination chemistry e.g. ligand field theory constitute a common ground for molecular magnetism, biomimicking and bioinspired chemistry. Summarily, this thesis describes model complexes both of structural and functional types, for various metalloprotiens containing paramagnetic metal ions, with particular emphasis on the interactions of ligand radicals with transition metal ions using different spectroscopic techniques which help one to learn how nature has employed common transition metals in a number of intriguing catalytic transformations.

A series of 3d- di- and tetranuclear homometallic complexes have been synthesized with ligands which are imine-phenolate- and radical-containing imino-benzosemiquinone based. Some of the complexes act as structural models for enzymes like the Cu-Zn superoxide dismutase and the dinickel containing enzyme urease. A functional model of the dicopper containing enzyme catechol dioxygenase, which catalyzes the oxidation of catechols to quinones, is discussed. The concept of *ferromagnetism* and *spin polarization* were used in an attempt to bring the metal or radical centers in spin aligned arrangement i.e. coupling between the metal-metal or radical-radical centers are ferromagnetic.

In continuation with polyradical-based metal complexes, the effect of substitution on the aniline ring of the parent ligand 2-anilino-4,6 di-tert-butylphenol at different positions in tuning the spin ground state of a metal center have been studied.



The complexes synthesized are mono- or dinuclear with *three* or *four* imino-benzo-semiquinone radicals.