

Abstract

During $3d$ metal ion complex synthesis the chemical reactions between metal ions and ligands are purposefully executed in presence of several other ancillary groups to obtain a multinuclear product. These are known as coordination aggregates when two or more metal ions are present in close proximity under the control of several bridges in three dimensions. Reproducible nature of these syntheses leads to several standardized reaction recipes. The work in this area have gain renewed interest due to their importance in synthesis, chemical and physical characterization, structural diversity and studies aiming toward identification of functional properties. Phenol-based Schiff base ligands with the potential for bridging two or three metal ions are the primary choice for ligand in this context. A balance between preferred coordination geometry of the metal ion, vacant coordination sites and coordination from the primary ligand is important. The coordination mode of ligand backbone and side arms of the ligand system are also important as inclusion of many such ligand arms increases the ligand flexibility for coordination. Available donor groups close to the phenoxido oxygen can generate $\{M_2L\}$ or $\{ML\}$ type fragments bearing cationic charges according to the added $3d$ metal ion in solution. In the following step, aggregation of such fragments involving externally added or *in situ* generated anionic ancillary ligands (NO_3^- , ClO_4^- , $RCOO^-$, CO_3^{2-} , SCN^- , HO^- , O^{2-} or RO^-) are important for the growth of multinuclear complexes of $3d$ metal ions. Tuning of reaction procedure is thus important to explore the generation and isolation of an impressive array of newer structural features. In this thesis, four new phenoxido based di nucleating Schiff base ligands have been examined with a range of ancillary ligands to provide new family of coordination aggregates of selected $3d$ metal ions (Cu, Ni and Co) showing different geometrical arrangements and interesting magnetic, catalytic and biophysical properties. Alteration of reaction conditions and ancillary bridges resulted anion coordination directed formation of three topologically different $[Cu_2]$, $[Cu_4]$ and $[Cu_5]$ complexes. Usefulness of *in-situ* generated and trapped HO^- ions from water and anionic diol amine group from ligand hydrolysis reaction has been discovered for the formation of cubane and partial dicubane $[Ni_4]$ cages upon changing the ancillary groups from acetate to thiocyanate. In the absence and presence of three different carboxylate anions, one diphenoxido bridged $[Cu_2]$, two μ_4 -oxido-bridged quasi-tetrahedral $[Cu_4]$ and one Cu^{II} trapped $[Cu_5]$ complexes has been synthesized and examined through X-ray structure determinations. They were efficient in catalyzing the oxidation of model substrate 3,5-DTBCH₂ for catalytic catechol oxidation study. In another study, two mixed-valent-mixed-geometry $[Co^{III}_4Co^{II}]$ complexes were prepared through the involvement of imine-thioether-alcohol arms with the help from HO^- and $RCOO^-$ bridges. Usefulness of *in-situ* generated HO^- and MeO^- bridges has been identified in three dinuclear $[Cu_2]$ complexes bearing phenoxido-bridging thioether-capping ligands. The complexes were also studied for solvent and *pH* dependent catalytic catechol oxidation activity along with interaction and cleavage of DNA.

Keywords: Phenol-based Schiff base; Multinuclear complexes; Ancillary ligands; Self-aggregation; X-ray crystal structure; Magnetic susceptibility; DFT calculations; Catechol oxidation; DNA binding and cleavage activity.