

Abstract

Synthesis of 3d metal coordination aggregates containing two or more of them in close proximity and bound to one or more anionic Schiff bases are of particular interest in recent years because of their importance in synthesis, structural chemistry, magnetic materials, and catalysis. Phenol-based Schiff bases in association with other nucleating and ancillary donors facilitate the growth of multinuclear metal complexes. Several solution based synthetic strategies have been adopted to explore the generation and isolation of increasingly complex architectures. Desired coordination mode of flexible chelating-*cum*-bridging ligand in presence of different other bridges can afford an impressive array of new structures. Isolation of discrete multinuclear species at the initial stage led to modify the reaction conditions for further growth, ligand exchange and core conversion. In this methodology the transition metal ions in the first step bind to the organic ligand to provide cationic building units inclined for self-assembly. In the next step these units react with small bridging ligands (e.g., O^{2-} , HO^- , MeO^- , NO_2^- , NO_3^- , N_3^- , RCO_2^-) to produce stable multinuclear end products. In the present thesis, we have explored the coordination behavior and aggregating potential of several Cu, Ni, and Mn ion bound phenol bearing tridentate and pentadentate Schiff bases in presence of one or more *in situ* generated and/or externally added ancillary bridges. Unique nitrito-bridge tetranuclear Cu^{II} complexes have been synthesized for the first time and characterized by X-ray structure determination and variable temperature magnetic susceptibility measurement. Theoretical support based on DFT calculations are in agreement with the experiments. A new family of trinuclear linear $Mn^{III}_2Mn^{II}$ and tetranuclear adamantane shaped Mn^{III}_4 complexes have been described and studied through X-ray structure determination and binding-*cum*-oxidation of substrate catechol. Usefulness of *in-situ* generated and trapped HO^- , MeO^- and CO_3^{2-} ions, from water, methanol and atmospheric carbon dioxide, has been discovered for the sustenance of two tetranuclear Ni_4 and one hexanuclear Ni_6 coordination cages. We have also explored the unique anion coordination directed assembly of three topologically different Cu^{II} complexes having 1D chain, cubane and quasi-tetrahedral structures by ClO_4^- , NO_3^- and $HCOO^-$.

Keywords: Metal complex; Multinuclear aggregate; Ancillary bridge; Phenol-based Schiff base; Self-assembly; X-ray structure; Magnetic susceptibility; DFT study; Catechol oxidation.