

Abstract

In coordination chemistry development of newer molecular architectures demands the use of newer ligand system, continually developing synthetic routes, chemical and physical characterizations, and applied studies aiming toward identification of functional properties. Fulfillment of coordination demand of the ligand-bound metal ions trigger the self-assembly of initially generated fragments and has provided the growth across many sub-disciplines of chemistry. In this regard a negotiation between the preferred coordination geometry of the metal ion and the coordination mode via backbone and side arms of the ligand is crucial. Availability of many such arms enormously increases the coordinative flexibility of the used ligand in a particular synthetic attempt. This flexibility in turn allows stabilization of literature unknown structures with potential of having interesting properties. Depending upon the reaction conditions in most cases further ancillary bridging ligands such as hydroxido, alkoxido, oxido etc. groups were almost invariably incorporated. Ligands having phenol backbone with side arms can provide charged $\{M_2L\}$ type fragments if two metal ions are getting trapped side by side. These fragments are liable to self-assemble for coordination demand and charge neutralization in presence of *in situ* generated or externally added ancillary bridging anions (e.g., O^{2-} , HO^- , MeO^- , NO_2^- , NO_3^- , N_3^- , RCO_2^-). Considerable planning in the conditions for any reaction scheme involves choice of ligand, metal ion salt, pH, ligand to metal ion ratio, solvent, concentration of solution, temperature, crystallization methods and reaction time. Herein three new N,O donor ligands have been chosen with a range of ancillary ligands to provide several class of coordination aggregates of selected *3d* metal ions (Mn, Co, Ni and Cu) showing interesting structural, magnetic and enzyme mimic properties. Aggregation of charged $\{Cu_2L\}$ fragments in presence of three different carboxylates have been scrutinized for the trapping of paddle-wheel Cu(II) carboxylate resulting in dumbbell shaped $[Cu_6]$ aggregates registering characteristic magnetic property. They were efficient to catalyze oxidation of substituted catechol. Cubic $[Ni_4]$ and polymeric $[Ni_2]_n$ complexes have been synthesized and examined through X-ray structure determinations and magnetic susceptibility measurements. The involvement of imine-amine-alcohol arms along with the HO^- , MeO^- and $RCOO^-$ bridges were described in building of two mixed-valent $[Co^{III}_4Co^{II}]$ complexes. The SIM type magnetic behaviors were examined for a single Co^{II} center within a diamagnetic quadrangle of four Co^{III} centers in two compounds. Usefulness of *in-situ* generated HO^- and available RCO_2^- groups has been identified in a linear $[Mn^{III}_2Mn^{II}]$ and di-adamentane shaped $[Mn^{III}_6]$ complexes. The complexes were further examined for their magnetic properties supported by DFT based calculations and solvent dependent catechol binding-*cum*-oxidations.

Keywords: Multimetallic aggregate; Ancillary bridge; Schiff base; Self-aggregation; X-ray crystal structure; Magnetic susceptibility; DFT based calculations; Catechol oxidation.