

ABSTRACT

In recent years the attention of synthetic coordination chemists is increasingly directed to the creation of novel molecular spin clusters through subcomponent assembly. Complexes containing two or more metal ions in close proximity allow the interaction of different metal centers by offering new patterns in reactivity (as evidenced by many multimetallic centers in biology) and magnetic exchange interactions. Phenol-based dinucleating Schiff bases in association with several nucleating and ancillary donors facilitate the growth of the system into higher nuclearity species. Several solution based synthetic strategies have been adopted to explore the generation and isolation of increasingly complex architectures. The use of different bridges and the control over the stereochemical character of the chelating-cum-bridging ligands have afforded an impressive array of new structures. We have examined the binding pattern of the ligands towards Cu^{II} , Co^{II} and Mn^{II} and growth of higher nuclearity systems in association with external ligands like NO_3^- , ClO_4^- , Cl^- , Br^- , PhCO_2^- , MeO^- , N_3^- , NCO^- , SCN^- and in-situ generated CO_3^{2-} via fixation of atmospheric CO_2 . Water derived oxido and hydroxido ligand trapped copper benzoate quasi-tetrahedron and copper azide/thiocyanate stepped cubanes have been created and examined for structural diversity, core conversion reactions in solution and moist grinding condition and magnetic exchange interactions. Oxido and azido bridged Cu_4 tetrahedrons and rhomboids have been characterized by structure and variable temperature magnetic susceptibility determinations, and examined for peripheral ligand exchange induced core conversion reactions. We have also examined the novel uphill conversion reactions and direct synthesis of Cu_4 complexes correlated to capping and trapping of anionic ligands. With cobalt ions we have shown the distorted pentacoordinated Co^{II}_2 and cyclic pentagonal wheel Co^{II}_5 structures engaged in magnetic interactions. In case of manganese ions, the reaction medium pH control the nuclearity and hydroxido bridge driven formation of Mn_4 stepped cubane complex. Thus formation of different complexes and molecular clusters of Cu^{II} , Co^{II} and Mn^{II} can be controlled and tuned by the subtle changes in ancillary ligands which in turn dictate the effective direction of the subcomponent assembly processes.