ABSTRACT

The design and synthesis of new family of di-, tetra- and multi-nuclear metal complexes of N, O donor dinucleating ligands has received special attention in recent years due to their potential application in multi-metal active sites, in metalloenzymes and metalloproteins, in molecular magnetism, in DNA binding and cleavage, and in fluorescence sensing, gas storage 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. 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 explored the multinucleating complexation behaviour of several metal ions such as iron, cobalt, nickel, copper, zinc and cadmium ions towards the Schiff base ligands. The growth of such cluster complexes are coupled with co-ligands like NO₃⁻, ClO₄⁻, Cl⁻, Br⁻, PhCO₂⁻, MeO⁻, N₃⁻, NCO⁻, NCS⁻ and in-situ generated CO_3^{2-} via fixation of atmospheric CO₂. We have also utilized the substituted imidazolidinly tris-phenolate based ligand for cation and anion mediated assembly of two neutral [Cu₂] units and examined the role of steric crowding on the ligand periphery and core conversion reactions in solution and magnetic exchange interactions as well as DNA binding studies. Pseudohalide bridged dinuclear nickel and copper complexes have been characterized by X-ray structure and variable temperature magnetic susceptibility determinations and examined by DFT calculations for the agreement with experiments. Trapping of spherical, linear and angular shaped bridges has been seen to change the structure and topology of the synthesized metal complexes. Novel uphill conversion reactions and direct synthesis of Cu₄ complexes has been correlated for unique capping and trapping of anionic linkers and ligands. The coordination driven change in fluorescence properties of some ligands have been examined during binding of zinc(II) and cadmium(II) and role of anion binding for structural diversity and modulation of fluorescence behavior.

Keywords: coordination; metal ions; multinuclear; exogenous; endogenous; co-ligands; selfassembly; phenolate; imidazolidinyl; oxido; hydroxido; X-ray structure; molar susceptibility; DNA binding; fluorescence.