A new family of homodinuclear copper(II) complexes with different  $\mu$ -bis(tetradentate) Schiff base ligands in the presence of various exogenous bridging groups have been studied to establish the synthetic, structural, magnetic, spectral aspects and reactivity in relation to dicopper(II/II) coordination in bioinspired coordination chemistry. A novel group of tetranuclear copper[(II)4] complexes having double helical coordination are developed using a hexadentate ligand with in built 1,4-piperazine spacer to explore the new synthetic methodology, structural and magnetic aspects, the deprotonated ligand, shows conformational isomerism for *cis* coordination. Another group of  $\mu_2$  and  $\mu_4$  azide bridged dicopper and tetracopper complex has been synthesized to explore new structural flexibility of this bridging motif where sodium template assembly of the dinuclear unit leads to tetranuclear cluster formation. Dioximate bridged dicopper and tetracopper complexes have been synthesized showing different hexagonal metallacycles. Coordination driven hydrolytic cleavage of central imidazolidine rings and terminal imine linkages of the dinucleating ligands have been examined with Cobalt(III), and copper(II).

**Key words:** Hemocyanin; tyrosinase; nitrous oxide reductase; catechol oxidase; dinucleating; imidazolidine; μ-bis(tridentate); μ-bis(tetradentate); dicopper(II/II); phenoxo-bridging; exogenous; endogenous; azide bridging; single crystal; X-ray structure; molar susceptibility; cyclic voltammetry;; hexadentate; oxime coordination; amide coordination; tetracopper[(II)<sub>4</sub>]; alkali template; self-assembly; metallacycle; double helical; mononuclear cobalt(III); mononuclear copper(II); electron paramagnetic resonance.