A new family of symmetric homodinuclear complexes of copper(II) with different exogeneous bridging groups and μ-bis(tridentate) and μ-bis(tetradentate) Schiff base ligands have been studied to establish the synthetic, structural, magnetic and spectral aspects in relation to dicopper(II/II) coordination and biocoordination chemistry. Another novel group of tetranuclear copper[(II)<sub>4</sub>] complexes are developed using simple hexadentate ligands and double helical coordination. to explore the new synthetic methodology and structural and magnetic aspects in relation to a biological tetracopper site. Coordination driven hydrolytic cleavage of central imidazolidine rings and terminal imine linkages of the dinucleating ligands have been examined with manganese(III), iron(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; exogeneous; endogeneous; alkoxide; single crystal; X-ray structure; molar paramagnetic susceptibility; cyclic voltammetry; quasireversible; hexadentate; oxime coordination; tetracopper[(II)<sub>4</sub>]; self-assembly; metallacycle; double helical; mononuclear manganese(III); mononuclear iron(III); mononuclear copper(II); electron paramagnetic resonance.