The influence of overlap interactions between the bridging ligands and the metal d orbitals on the super-exchange coupling constant are studied by means of *ab-initio* restricted Hartree-Fock molecular orbital calculations. The interaction between the magnetic d orbitals and the HOMOs of the carboxylate oxygen atoms are investigated in homologous asymmetrically dibridged dicopper(II) complexes which have significantly different $-2J$ values (the energy separation between the spin-triplet and spin-singlet states). In order to determine the nature of the fronter orbitals, extended Hückel molecular orbital (EHMO) calculations are also reported. The differences in the magnitude of the coupling constants and magnetic behaviour are rationalized in terms of the bridging ligand orbital complementary/countercomplementary concept.

**Key words:** Dinuclear Copper(II) Complex; Antiferromagnetic Coupling; *Ab-initio* Calculations; Molecular Orbitals; Orbital Complementary.