INFLUENCE OF AXIAL METHOXO AND HYDRIDE LIGANDS ON THE STRUCTURAL AND ELECTRONIC PROPERTIES OF COBALT PORPHYRIN COMPLEXES: A DFT AND NBO STUDY

Anan Haj Ichia Arisha [a],[b]*

[a]*Department of Organic Chemistry, School of Chemistry, Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 6997801, Israel*
[b]*Department of Education, Beit Berl College, Beit Berl, Israel*
**e-mail: ananarisha@gmail.com*

Abstract. Density functional theory and natural bond orbital analysis were used to examine the effects of axial methoxo and hydride ligands on cobalt porphyrin complexes. Neutral and anionic methoxo- and hydride-bound species were compared with the parent cobalt(II) porphyrin. Methoxo coordination produced a charge-sensitive Co–O interaction: reduction lengthened the Co–O bond, weakened ligand-to-metal donor–acceptor interactions, and localized added electron density near the methoxo oxygen atom. In contrast, the Co–H bond underwent only minor structural changes and retained predominantly Co $3dz^2$–H 1s axial σ-bonding character. Reduction of the hydride species mainly caused electronic reorganization and increased spin delocalization over the porphyrin framework. The anionic hydride species displayed the smallest calculated HOMO/SOMO–LUMO gap. These findings clarify how axial ligands and charge control cobalt porphyrin electronic structure relevant to methanol activation.

Keywords: methanol activation, cobalt complexes, spin density, frontier molecular orbitals, donor–acceptor interactions.