DIOXYGEN ACTIVATION AT MONOCOPPER ENZYME SITE MODELS

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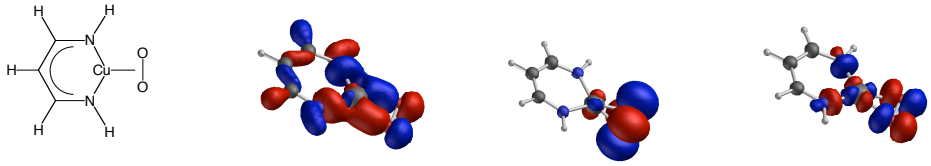

The activation of molecular oxygen at monocopper centers plays an important role in biology, and in particular with regard to the biosynthesis of neurohormones by the Cu-containing enzymes dopamine β-monooxygenase (DβM) and the peptidylglycine α-hydroxylating monooxygenase (PHM) component of the bifunctional peptidylglycine α-amidating monooxygenase (PAM). In order to gain an understanding of the first stage of the catalysis (i.e. dioxygen activation at the monocopper active sites), 1:1 Cu/O_2 adducts coordinated to various biomimetic ligands of Tolman and co-workers have been studied using a combination of DFT and CASPT2 methods. The O_2 fragment can vary in character from superoxide-like to peroxide-like as a function of the ligand and this is expected to strongly influence reactivity. In addition to their interesting chemistry, these 1:1 complexes pose unique challenges to Kohn-Sham DFT when they are singlets.

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