Interconversion of μ-η^2:η^2-Peroxodicopper(II) and Bis(μ-oxo)dicopper(III) Complexes: A Theoretical Study

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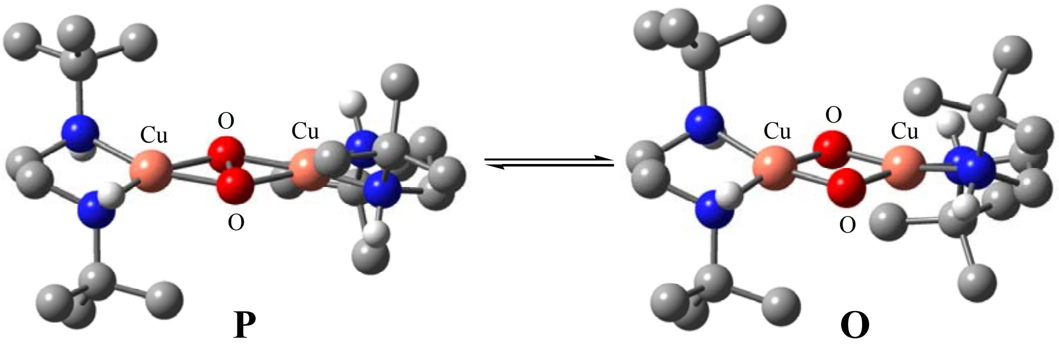
The role of copper in biological oxidative processes that involve O_2 activation is critical to aerobic life.[1] Synthetic model complexes have been extensively employed to understand the structure-reactivity relationships of such systems, and density functional theory (DFT) calculations can often aid in these analyses. Herein we report the theoretical investigation of the interconversion of the μ-η^2:η^2-peroxodicopper(II) (**P**) and the bis(μ-oxo)dicopper(III) (**O**) species, which is observed experimentally with a limited number of simple diamine and triamine ligands.[1] Calibration of the theoretical methods to experimental structural and spectroscopic parameters for these species provides confidence in their calculated structures and relative energies. A comparison among several closely related ligand systems provides a clearer understanding of the factors that lead to these intriguing, measurable equilibria.[2] Extension of this methodology to imidazole ligation in such species and possible mechanistic implications will also be presented.



(1) Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P. *Chem. Rev.* **2004**, *104*, 1013-1045.

(2) Mirica, L. M.; Vance, M.; Rudd, D. J.; Hedman, B.; Hodgson, K. O.; Solomon, E. I.; Stack, T. D. P. *J. Am. Chem. Soc.* **2002**, *124*, 9332-9333.