

Spectroscopy of Copper-Superoxo Complexes: a Revival Based on Correlated Methods

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Copper-dioxygen complexes play a crucial role in numerous (bio)-chemical processes, including oxygen activation in several enzymes, such as copper-containing monooxygenases. Many efforts have been devoted to studying bioinspired cupric-superoxide end-on complexes for their capacity to perform oxidation reactions: [1,2] understanding the electronic structure of these species is essential for elucidating their reactivity and catalytic mechanisms.

Copper-dioxygen complexes represent challenging systems for DFT based methods due to the presence of the d^9 copper center and, possibly, π -conjugated ligands. As UV-vis spectroscopy is routinely employed to characterise these often short-lived, unstable species, a comprehensive investigation of the low-lying excited states of some $[\text{LCu}(\text{O}_2)]^+$ complexes is highly desirable from a theoretical point of view. We performed state-of-the-art multireference calculations using MS-RASPT2, DMRG and ICE-CI to probe the electronic structure of some challenging systems. The energies of the different states are extremely sensitive to charge-transfer mechanisms between the ligand and metal center, which are notably difficult to model, even with wavefunction based methods.[3,4,5] This work offers the opportunity to discuss the methodological implications of combining these approaches to provide new insights on the electronic structure of this class of strongly correlated systems. Our aim is to provide a solid reference for future theory-experience studies and assess the tools at our disposal to diagnose the possible shortcomings of the more widely applicable DFT.

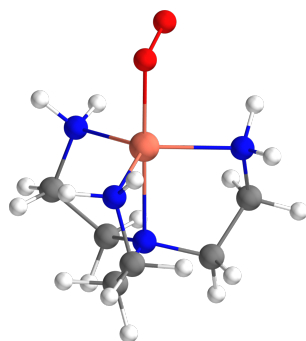


Figure 1: $[\text{LCu}(\text{O}_2)]^+$ studied in this work

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