

Biomimetic models for dinuclear copper proteins: structure and oxidation chemistry from a quantum chemical point of view

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In the past two decades major research activities have been devoted to the understanding of structure/activity relationships associated with binding and activation of dioxygen by copper-based metalloproteins like hemocyanin, tyrosinase, dopamine b-hydroxylase, or particulate methane monooxygenase. Remarkable progress in bioinorganic research has led to a number of studies in which small synthetic Cu(I) complexes bind O₂, cleave the O-O bond, and/or incorporate O₂-derived oxygen atoms into C-H bonds of organic substrates at low temperatures. By design these complexes contain a [Cu₂O₂] core as a key structural motif to mimic the biocatalytically active paragons. A considerable body of structural, spectroscopic, and kinetic data for several biomimetic models has promoted the general understanding of these systems. Despite all efforts, however, only limited insights into the mechanistic details of the chemical transformations observed could be gained by experimental means alone.

In the first part of the talk quantum chemical studies on several models for the structure of enzymatic active sites are reported. The results are compared to experimental data in order to calibrate the accuracy that can be expected from the density functional approach chosen. In the second part a detailed view on mechanistic scenarios is presented for the aliphatic and aromatic hydroxylation activity observed in experimentally characterized model systems containing a [Cu₂O₂] core. Evidence is provided that also the mononuclear [CuO] species can selectively hydroxylate C-H bonds rendering it an interesting candidate as an alternative active site to be considered in investigations on the chemistry of Cu(I)/O₂ systems.