Spectroscopic Investigation of Tris-Hydroxo and μ_3-oxo Bridged Trimeric Cu(II) Complexes: Geometric and Electronic Structures of the Native Intermediate of the Multicopper Oxidases

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Multicopper oxidases, which include laccase, Fet3p and ceruloplasmin, catalyze the $4e^-$ reduction of O_2 to H_2O. Reaction of the fully reduced enzyme with O_2 produces the native intermediate (NI) that consists of four oxidized copper centers, three of which form a trinuclear cluster site, all bridged by the product of full O_2 reduction. The most characteristic features of NI include an EPR signal with $g < 2.00$ and an intense MCD pseudo-A term (temperature dependent MCD features of opposite signs) which are derived from the unique bridged structure of the trinuclear cluster site. The physical origin of these spectral features had been elusive.

Two structures for the trinuclear Cu(II) site in NI would be consistent with its reactivity and spectral features. One has three μ_2-OH ligands each bridging a Cu(II) pair where two OH^-'s derive from O_2 reduction and the third from an ambient H_2O, whereas the other has a single μ_3-oxo ligand bridging all three Cu's at the center of the cluster with the second oxygen atom from O_2 reduction either remaining bound or dissociated from the trinuclear site. In this study, a combination of powder/single-crystal EPR, absorption, VT/VTVH MCD spectroscopies and DFT calculations has been applied to relevant model complexes, TrisOH[1-2] and μ_3O.[3] In particular, we have performed a comprehensive analysis of the spin-orbit coupling mechanisms that are involved in both the ground and the excited state interactions which result in the zero-field splitting of the spin-frustrated doublet ground states[1] and the prominent MCD pseudo-A terms in the charge-transfer region, respectively. This study allows a specific assignment of the geometric and electronic structures of the trinuclear Cu(II) site of NI and thus a better understanding of the O-O bond cleavage and the catalytic cycle of the multicopper oxidases.

References:
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