

Geometric and Electronic Influences on the Reactivity of Mn^{III}-hydroxo and Mn^{III}-alkylperoxo Complexes

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A variety of manganese-dependent enzymes utilize mid-valent manganese(III) centers to promote redox reactions with substrates. The enzymes manganese superoxide dismutase and manganese lipoxygenase respectively defend organisms from the problematic superoxide radical and promote peroxidation of polyunsaturated fatty acids. In these enzymes, Mn^{III}-hydroxo intermediates commonly perform proton-coupled electron-transfer reactions (PCET) with substrates. Proposed catalytic cycles of these enzymes also invoke the formation of Mn(III)-peroxo intermediates. In order to understand the fundamental properties and chemical reactivity of such mid-valent manganese adducts, our lab has generated models of Mn^{III}-hydroxo and Mn(III)-alkylperoxo intermediates that are amenable to detailed structure-function studies. Using an amide-containing pentadentate ligand, we have generated Mn(III)-hydroxo and Mn(III)-alkylperoxo complexes with systematically perturbed geometric and electronic structures. Perturbations to the primary coordination spheres of these complexes reveal that electron-deficient ligands support Mn^{III}-hydroxo adducts that perform more rapid PCET reactions with substrates, while electron-deficient ligands lead to more stable Mn(III)-alkylperoxo complexes. Using a newly developed amide-containing pentadentate ligand, we generated a novel Mn(III)-hydroxo adduct with a hydrogen-bond acceptor in the second coordination sphere. Combined experimental and computational studies of these Mn(III)-hydroxo and Mn(III)-alkylperoxo complexes provide a basis for linking the reactivities of these complexes with their geometric and electronic structures.