Oxygen Isotope Effects in Superoxide Anion Oxidation by Tripodal Copper(II) Complexes

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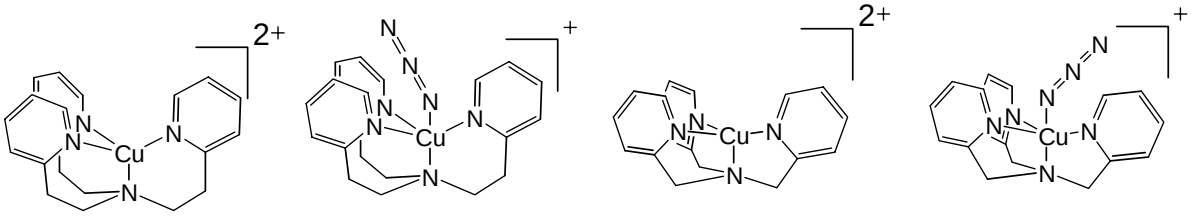
Dioxygen activation and superoxide scavenging by a variety of natural and synthetic copper containing complexes start with electron transfer (ET). Superoxo intermediate formation has been proposed in both cases. Mechanistic commonalities and fundamental aspects of bonding may be elucidated from oxygen isotope effect measurements. This presentation describes studies of oxygen kinetic isotope effects (^{18}O KIEs) upon oxidation of superoxide anion by tripodal Cu(II) complexes.

^{18}O KIEs were measured by the competitive fractionation method with non-enriched superoxide in anhydrous DMSO. Four Cu(II) complexes with tripodal ligands were investigated: $Cu^{II}(tepa)OTf_2$, $Cu^{II}(tepa)(N_3)OTf$, $Cu^{II}(tmpa)OTf_2$, and $Cu^{II}(tmpa)(N_3)OTf$ (tepa = tris(2-*o*-pyridylethyl)amine, tmpa = tris(2-*o*-pyridylmethyl)amine, N_3 = azide anion, OTf = triflate anion). Measured isotope effects fall within a very narrow range from 0.9824(11) to 0.9834(23).

The mechanism of superoxide oxidation will be discussed in the context of results from kinetics, electrochemical, and theoretical studies and analyzed using Marcus theory. The relative importance of inner-sphere and outer-sphere ET as well as the formation of Cu-O_2 adducts will be described.



$Cu^{II}(tepa)OTf_2$ $Cu^{II}(tepa)(N_3)OTf$ $Cu^{II}(tmpa)OTf_2$ $Cu^{II}(tmpa)(N_3)OTf$