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Correlation of Electronic and Geometric Structure in Mononuclear Copper(II) Superoxide Complexes

Jake W. Ginsbach[†], Ryan L. Peterson[‡], Ryan E. Cowley[†], Kenneth D. Karlin^{‡,*}, and Edward I. Solomon^{†,*}

[†]Department of Chemistry, Stanford University, Stanford, California 94305

[‡]Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218

Abstract

The geometry of mononuclear copper(II) superoxide complexes has been shown to determine their ground state where side-on bonding leads to a singlet ground state and end-on complexes have triplet ground states. In apparent contrast to this trend, the recently synthesized (HIPT₃tren)Cu^{II}-O₂^{•-} (**1**) was proposed to have an end-on geometry and a singlet ground state. However, re-examination of **1** with resonance Raman (rR), magnetic circular dichroism (MCD), and ²H NMR spectroscopy indicates that **1** is in fact an end-on superoxide species with a triplet ground state that results from the single Cu^{II}-O₂^{•-} bonding interaction being weaker than the spin pairing energy.

The activation of dioxygen at a single copper(I) site to produce a copper(II) superoxide appears to be essential for the enzymatic function of the non-coupled binuclear copper monooxygenases (PHM, DβM, and TβM)¹ and has been recently proposed for the copper-dependent polysaccharide monooxygenases.² Since isolation of a discrete copper(II) superoxide species in enzymatic systems has been limited to a crystal structure of PHM,^{1c} insight into the electronic structure and bonding in copper(II) superoxide species has been derived from model complexes.

In these synthetic complexes, two structures have been observed: superoxide coordinated to Cu(II) in a side-on (η²) or end-on (η¹) binding mode. The side-on superoxide species, structurally characterized in a tris(pyrazolyl)borate model complex,³ has an O–O stretching frequency of 1043 cm⁻¹ and a copper(II) X-ray absorption pre-edge feature at ~8979 eV.⁴ Magnetic susceptibility measurements indicated that the side-on superoxide has a singlet ground state.^{4a} This ground state is a direct result of the two strong Cu–O bonds of the side-on geometry (1.84 Å) causing the HOMO/LUMO splitting to be larger than the spin pairing energy.^{4a} This results in a doubly occupied HOMO that is a superoxide-based π* orbital that is vertical to the Cu–O₂ plane (π*_v) and an empty Cu d_{x²-y²} LUMO that is antibonding with the filled π* orbital that forms a very covalent σ bond with the copper (π*_σ + ad, Figure 1, left).

An end-on superoxide species, which has been structurally characterized in (TMG₃tren)Cu^{II}-O₂^{•-},⁵ shares similar superoxide spectral features with the side-on complex (ν_{O–O} of 1120 cm⁻¹).⁶ However, both NMR⁷ and variable-temperature variable-field

*Corresponding Author: edward.solomon@stanford.edu (E.I.S.), karlin@jhu.edu (K.D.K.).

ASSOCIATED CONTENT

Additional synthetic details, rR, Abs, VTVH-MCD, NMR, and DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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magnetic circular dichroism (VTVH-MCD)^{6b} spectroscopies indicate that the end-on superoxide possesses a triplet ground state, in contrast to the singlet ground state of the side-on isomer.^{4a} For the end-on superoxide, the single Cu–O bond (1.93 Å)⁵ is significantly weaker than the two bonds in the side-on complex and hence the bonding/antibonding interaction between the superoxide π^*_σ and the Cu d orbital is unable to overcome the spin pairing energy.^{6b} This results in a triplet ground state with two singly occupied, orthogonal orbitals: a superoxide, π^*_σ orbital and a copper, d_{z^2} orbital (that is antibonding with the π^*_σ orbital, Figure 1 right).

Recently, Itoh and co-workers synthesized an end-on superoxide adduct **1**,⁸ (HIPT₃tren)Cu^{II}–O₂^{•−} (HIPT = hexaisopropylterphenyl, Scheme 1) which features a tren ligand platform like (TMG₃tren)Cu^{II}–O₂^{•−} (TMG = tetramethylguanidino). Although **1** has similar vibrational features to (TMG₃tren)Cu^{II}–O₂^{•−} ($\nu_{\text{O–O}}$ = 1095 cm^{−1} from rR excitation into the O₂^{•−} → Cu^{II} charge transfer (CT) at 23,000 cm^{−1}), they proposed that **1** has a *singlet* ground state due to the observation of chemical shifts between 8–0 ppm in its ¹H-NMR spectrum.⁸ This intriguing result prompted us to probe the electronic structure of **1** in the context of the end-on triplet/side-on singlet correlation described in Figure 1.

To probe the geometric structure of **1**, resonance Raman (rR) spectra were collected on samples prepared with ¹⁶O₂, ¹⁸O₂, and ¹⁶O–¹⁸O mixed isotope dioxygen (^{16,18}O₂, Figure S1). Two $\nu_{\text{Cu–O}}$ were observed in the ^{16,18}O₂ spectrum, which have the same energy as the $\nu_{\text{Cu–O}}$ in the ¹⁶O₂ and ¹⁸O₂ spectra, indicating an asymmetric (i.e., end-on) coordination mode of superoxide.⁹ The ground state and electronic structure of **1** were then probed with VTVH MCD spectroscopy. A 9:1 mixture of *n*-propanol and acetone was selected as an appropriate solvent since it formed an optical glass without affecting the absorption (Abs) or rR spectra of **1** (Figures S1–S2).

The Abs and low temperature (5.0 K) MCD spectra of oxygenated samples of (HIPT₃tren)Cu^I require five Gaussian bands to fit both experimental spectra up to and including the O₂^{•−} → Cu(II) CT transition (band 5) (Figure 2, Table S1). Agreement between the transition energies in both spectra indicates that the MCD intensity in these bands can be assigned to **1**. The MCD spectrum of **1** is also similar to that previously obtained for (TMG₃tren)Cu^{II}–O₂^{•−}:^{6b} a derivative-shaped pseudo-A (band 2 and 3), a negative transition to higher energy (band 4), and a positive transition resulting from the O₂^{•−} → Cu^{II} CT transition (band 5). However, bands 2–4 are shifted up in energy by > 3,000 cm^{−1} in **1** relative to (TMG₃tren)Cu^{II}–O₂^{•−} indicating HIPT₃tren possesses a weaker ligand field.^{6b} An additional band (band 0 in pink) is required to fit the lowest energy feature in the MCD spectrum. While the relative intensity of bands 1–5 were constant between multiple samples, the intensity of band 0 was variable (Figure S3) and is assigned as an $S = \frac{1}{2}$ contaminant since its VTVH-MCD isotherms overlay (Figure S4). In contrast, VTVH-MCD isotherms collected on bands 1–4 (Figures 3 and S5) show non-overlapping (nesting) behavior, which results from zero-field splitting (ZFS). This ZFS requires that **1** has an $S > \frac{1}{2}$ ground state. The saturation magnetization curves for bands 1–5 fit to the spin Hamiltonian for an $S = 1$ system with axial (D) and rhombic (E) zero field parameters of $D = +3.0$ and 0.22 $E/D = 0.12$ (see Supporting Information for details).

While the nesting observed in the VTVH-MCD isotherms require **1** to have a paramagnetic ground state ($S = 1$), reference 8 reported the ground state to be diamagnetic ($S = 0$) from NMR spectroscopy. Therefore the NMR spectroscopy of **1** was re-examined. The ¹H NMR spectra of oxygen-saturated samples of (HIPT₃tren)Cu^I in acetone were indistinguishable from the original (HIPT₃tren)Cu^I at 183 K (−90 °C) (Figure S7). However, the previously determined equilibrium constant for O₂ binding indicates that **1** is only approximately half oxygenated under these conditions.⁸ Since no new chemical shifts were initially observed in

the ^1H NMR spectra, deuterium was incorporated into a single position on each HIPT substituent (see Scheme 1). ^2H NMR spectra of oxygen-saturated samples of $(\text{d}_3\text{-HIPT}_3\text{tren})\text{Cu}^{\text{I}}$ show two resonances with approximately equal intensity: one corresponding to $(\text{d}_3\text{-HIPT}_3\text{tren})\text{Cu}^{\text{I}}$ and a new paramagnetically-shifted resonance at -24 ppm (Figure 4), which is assigned to **1**. Addition of CO to **1** resulted in a single chemical shift corresponding to $(\text{d}_3\text{-HIPT}_3\text{tren})\text{Cu}^{\text{I}}\text{CO}$, indicating that the resonance at -24 ppm did not arise from an $S = 1/2$ contaminant. Reanalysis of the ^1H NMR spectra indicated the presence of a broad, weak resonance at -24 ppm (Figure S7–S8). Similarly, density functional theory (DFT) calculations on a truncated model of **1** predict a triplet ground state, with both closed-shell singlet ($+23.2$ kcal/mol) and broken-symmetry singlet ($+13.0$ kcal/mol) states at significantly higher energy (Figure S9–S10, Table S3–S4), in agreement with the experimental data presented above.

In summary, rR spectroscopy with mixed isotope dioxygen confirms the end-on superoxide geometry of **1** while VTVH-MCD and NMR spectroscopy determine that **1** has a triplet ground state. While the Cu–O bond in **1** is stronger than $(\text{TMG}_3\text{tren})\text{Cu}^{\text{II}}\text{-O}_2^{\bullet-}$, this single Cu–O bond is unable to overcome the pairing energy required to form a singlet ground state (Figure 1). To date, only a side-on superoxide complex with two Cu–O bonds has the required bond strength to overcome the spin pairing energy resulting in a singlet ground state.^{4a} These results suggest that the end-on superoxide intermediate proposed in the enzymatic systems^{1c} should also have a triplet ground state. This prediction awaits experimental evaluation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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- A single $\nu_{\text{Cu-O}}$ at intermediate energy would be expected from a symmetric (i.e. side-on) coordination mode.¹⁰

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Figure 1.
Molecular orbital diagram of side-on and end-on copper(II)-superoxide bonding.

Figure 2. Absorption (183 K, top) and MCD (5.0 K, bottom) spectra of **1**. Band 0 (*) indicates an $S = \frac{1}{2}$ contaminant.

Figure 3.
VTVH-MCD isotherms and fit ($D = +3.0$ and $E/D = 0.17$) for band 2 collected at 14,040 cm^{-1} .

Figure 4. ^2H -NMR spectra of 3 mM $d_3\text{-HIPT}_3\text{tren}$ derivatives in acetone at 183 K (-90°C). Cu^{I} (gold, 7.3 ppm), $\text{Cu}^{\text{II}}\text{-O}_2^{\bullet-}$ (1) (green, 7.3 and -24 ppm), $\text{Cu}^{\text{I}}\text{-CO}$ (black, 7.4 ppm). # indicates $d_{12}\text{-SiMe}_4$ (0 ppm) and * natural abundance deuterium in acetone (2.05 ppm).

Scheme 1.
HIPT₃tren copper(II) superoxo complex **1**.