Inorganic Chemistry
Communication
pubs.acs.org/IC

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

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Supporting Information

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 an apparent contrast to this trend, the recently synthesized $(HIPT_3tren)Cu^{II}O_2^{\bullet-}$ (**1**) was proposed to have an end-on geometry and a singlet ground state. However, reexamination of **1** with resonance Raman, magnetic circular dichroism, and ^2H NMR spectroscopies indicate that **1** is, in fact, an end-on superoxide species with a triplet ground state that results from the single $Cu^{II}O_2^{\bullet-}$ 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 species appears to be essential for the enzymatic function of the noncoupled binuclear copper monooxygenases (PHM, DβM, and TβM)[1] and has been recently proposed for the copper-dependent polysaccharide monooxygenases.[2] Because 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 copper(II) in a side-on (η^2) or end-on (η^1) 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 highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (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 $Cu-O_2$ plane (π^*_v) and an empty Cu $d_{x^2-y^2}$ LUMO that is antibonding with the filled π^* orbital, forming a very covalent σ bond with the copper ($\pi^*_\sigma + \alpha d$; Figure 1, left).

An end-on superoxide species, which has been structurally characterized in $(TMG_3tren)Cu^{II}O_2^{\bullet-}$ (TMG = tetramethylguanidino),[5] shares similar superoxide spectral features with the side-on complex (ν_{O-O} of 1120 cm^{-1}).[6] However, both NMR[7] and variable-temperature variable-field 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^*_v orbital and a Cu d_{z^2} orbital (that is, antibonding with the π^*_σ orbital; Figure 1, right).

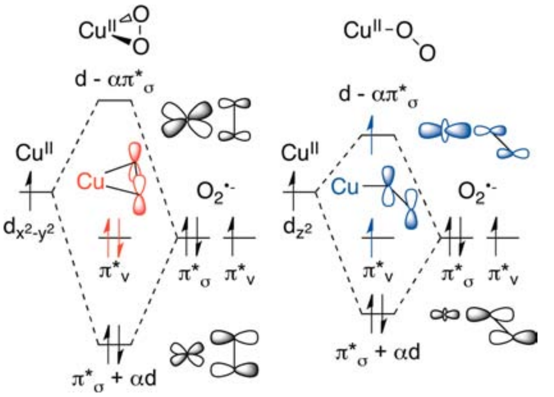
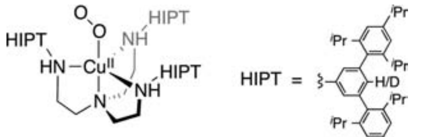


Figure 1. Molecular orbital diagrams of side-on (left) and end-on (right) copper(II) superoxide bonding.

Recently, Itoh and co-workers synthesized an end-on superoxide adduct **1**,[8] $(HIPT_3tren)Cu^{II}O_2^{\bullet-}$ (HIPT = hexaisopropylterphenyl; Scheme 1), which features the same tren ligand platform in $(TMG_3tren)Cu^{II}O_2^{\bullet-}$. Although **1** has vibrational features similar to those of $(TMG_3tren)Cu^{II}O_2^{\bullet-}$ [ν_{O-O} = 1095 cm^{-1} from rR excitation into the $O_2^{\bullet-} \rightarrow Cu^{II}$ charge transfer (CT) at 23000 cm^{-1}], they proposed that **1** has a *singlet* ground

Scheme 1. $(HIPT_3tren)Cu^{II}O_2^{\bullet-}$ Complex 1



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Received: September 17, 2013
Published: October 28, 2013

state due to the observation of chemical shifts between 8 and 0 ppm in its ^{1}H 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 $^{16}O_2$, $^{18}O_2$, and a $^{16}O-^{18}O$ mixed isotope dioxygen ($^{16,18}O_2$; Figure S1 in the Supporting Information, SI). Two ν_{Cu-O} were observed in the $^{16,18}O_2$ spectrum that have the same energy as ν_{Cu-O} in the $^{16}O_2$ and $^{18}O_2$ 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 because it formed an optical glass without affecting the absorption (Abs) or rR spectra of **1** (Figures S1 and S2 in the SI).

The Abs and low-temperature (5.0 K) MCD spectra of oxygenated samples of $(HIPT_3tren)Cu^I$ require five Gaussian bands to fit both experimental spectra up to and including the $O_2^{\bullet-} \rightarrow Cu^{II}$ CT transition (band 5; Figure 2 and Table S1 in the SI). 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 $(TMG_3tren)Cu^{II}O_2^{\bullet-}$:[6b] a derivative-shaped pseudo-*A* (bands 2 and 3), a negative transition to higher energy (band 4), and a positive transition resulting from the $O_2^{\bullet-} \rightarrow Cu^{II}$ CT transition (band 5). However, bands 2−4 are shifted up in energy by >3000 cm^{-1} in **1** relative to $(TMG_3tren)Cu^{II}O_2^{\bullet-}$, indicating that $HIPT_3tren$ possesses a weaker ligand field.[6b] An additional band (band 0) 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 in the SI) and is assigned as an $S = {}^1/_2$ contaminant because its VTVH-MCD isotherms overlay (Figure S4 in the SI). In contrast, VTVH-MCD isotherms collected on bands 1−4 (Figures 3 and S5 in the SI) show nonoverlapping (nesting) behavior, which results from zero-field splitting (ZFS). This ZFS requires that **1** has an $S > {}^1/_2$ 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 $0.22 \geq E/D \geq 0.12$ (see the SI for details).

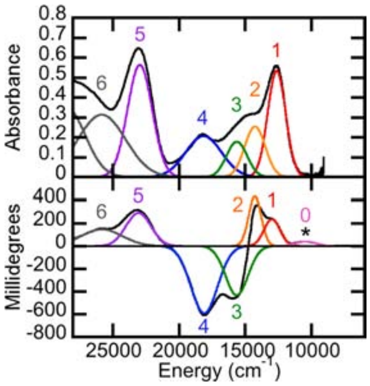

Figure 2. Absorption (183 K, top) and MCD (5.0 K, bottom) spectra of **1** and Gaussian fits. Band 0 (*) indicates an $S = {}^1/_2$ contaminant.

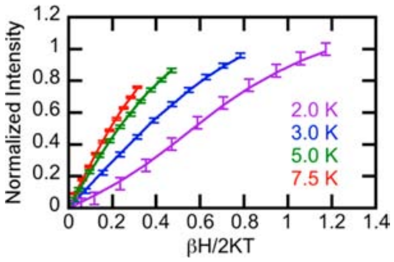

Figure 3. VTVH-MCD isotherms and fit (D = +3.0 and E/D = 0.17) for band 2 collected at 14040 cm^{-1}.

While the nesting observed in the VTVH-MCD isotherms requires **1** to have a paramagnetic ground state (S = 1), ref 8 reported the ground state to be diamagnetic (S = 0) from NMR spectroscopy. Therefore, the NMR spectroscopy of **1** was reexamined. The ^{1}H NMR spectra of oxygen-saturated samples of $(HIPT_3tren)Cu^I$ in acetone were indistinguishable from the original $(HIPT_3tren)Cu^I$ at 183 K (−90 °C; Figure S7 in the SI). However, the previously determined equilibrium constant for O_2 binding (K_{eq} = 0.11 mM^{-1})[8] indicates that **1** is only approximately half-oxygenated under these conditions ($[Cu]_0$ = 3.0 mM, $[O_2]_0 \approx 14$ mM[11]). Because no new chemical shifts were initially observed in the ^{1}H NMR spectra, deuterium was incorporated into a single position on each HIPT substituent (see Scheme 1). ^{2}H NMR spectra of oxygen-saturated samples of $(d_3\text{-}HIPT_3tren)Cu^I$ show two resonances with approximately equal intensity: one corresponding to $(d_3\text{-}HIPT_3tren)Cu^I$ and a new paramagnetically shifted resonance at −24 ppm (Figure 4), which is assigned to **1**. The addition of CO to **1** resulted in a single chemical shift corresponding to $(d_3\text{-}HIPT_3tren)Cu^ICO$, indicating that the resonance at −24 ppm did not arise from an $S = {}^1/_2$ contaminant. Reanalysis of the ^{1}H NMR spectra indicated the presence of a broad, weak resonance at −24 ppm (Figures S7 and S8 in the SI). 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 (Figures S9 and S10 and Tables S3 and S4 in the SI), in agreement with the experimental data presented above.

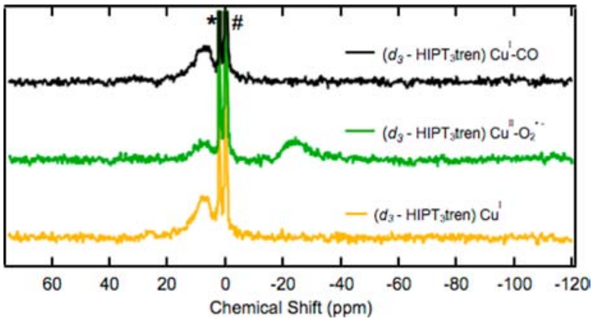

Figure 4. ^{2}H NMR spectra of 3 mM d_3-$HIPT_3$tren derivatives in acetone at 183 K (−90 °C): Cu^I (gold, 7.3 ppm), $Cu^{II}O_2^{\bullet-}$ (**1**) (green, 7.3 and −24 ppm), and Cu^ICO (black, 7.4 ppm). # indicates d_{12}-$SiMe_4$ (0 ppm) and * natural abundance deuterium in acetone (2.05 ppm).

In summary, rR spectroscopy with mixed isotope dioxygen confirms the end-on superoxide geometry of **1**, while VTVH-MCD and NMR spectroscopies determine that **1** has a triplet ground state. While the Cu−O bond in **1** is stronger than that in $(TMG_3tren)Cu^{II}O_2^{\bullet-}$, 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.

ASSOCIATED CONTENT

Supporting Information

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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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by NIH Grants DK31450 (to E.I.S.), GM28962 (to K.D.K.), and a Ruth L. Kirschstein National Research Service Award F32-GM105288 (to R.E.C.).

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