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Dioxygen Reactivity of a Copper(I) Complex with a N_3S Thioether Chelate; Peroxo–Dicopper(II) Formation Including Sulfur-Ligation

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Employing a tetradentate $N_3S_{(thioether)}$ ligand, L^{N3S}, dioxygen reactivity of a copper(I) complex, $[(L^{N3S})Cu^I]^+$ (**1**) was examined. In CH_2Cl_2, acetone (at –80 °C), or 2-methyltetrahydrofuran (at –128 °C), **1** reacts with O_2 producing the end-on bound peroxodicopper(II) complex $[\{(L^{N3S})Cu^{II}\}_2(\mu\text{-}1,2\text{-}O_2{}^{2-})]^{2+}$ (**2**), the first reported copper–dioxygen adduct with sulfur (thioether) ligation. Its absorption spectrum contains an additional low-energy feature (but not a Cu–S CT band) compared to the previously well-characterized N_4 ligand complex, $[\{(TMPA)Cu^{II}\}_2(\mu\text{-}1,2\text{-}O_2{}^{2-})]^{2+}$ (**3**) (TMPA = tris(2-pyridylmethyl)amine). Resonance Raman spectroscopy confirms the peroxo formulation $\{\nu_{(O-O)} = 817\ cm^{-1}$ ($^{16\text{-}18}O_2\ \Delta = 46\ cm^{-1}$) and $\nu_{(Cu-O)} = 545\ cm^{-1}$ ($^{16\text{-}18}O_2\ \Delta = 26\ cm^{-1}$), in close analogy to that known for **3** $\{\nu_{(O-O)} = 827\ cm^{-1}$ and $\nu_{(Cu-O)} = 561\ cm^{-1}\}$. Direct evidence for thioether ligation comes from EXAFS spectroscopy {Cu K-edge; Cu–S = 2.4 Å}

One aspect of contemporary interest in Cu^I/O_2 chemistry is the influence of thioether sulfur ligation, in comparison to the large recent literature on such reactivity studies with all nitrogen ligands.[1–3] Inspiration comes from the unique active-site chemistry of the monooxygenases dopamine β-hydroxylase (DβH) and peptidyl glycine α-hydroxylating monooxygenase (PHM), two structurally related copper enzymes involved in neurotransmitter biosynthesis–hormone regulation.[4–6] X-ray structures[5,6] reveal the key active-site Cu ion in PHM, Cu_M, to be ligated by two His and one Met ligands;[7] this O_2-binding site generates a substrate H-atom abstracting agent, possibly a superoxo–Cu(II) moiety.[4,5,8,9] An important issue is how the thioether ligation influences the structure(s), spectroscopy, and reactivity of $Cu^I{}_n-(O_2)$-derived species while precluding irreversible thioether oxidation.

Recent literature includes (i) extensive studies of Rorabacher and Ochrymowycz on Cu–thioether ligand complex redox properties,[10] (ii) a dicopper(I) complex with Met-based ligands shown by Casella to react with O_2 and exhibit C–H hydroxylation chemistry,[11] (iii) a study by Reglier showed a $N_3S_{thioether}$ ligand–Cu(I) complex transforms to a Cu(II) species with O_2,[12] (iv) via $Cu^{II}-H_2O_2$ reactivity, Kodera characterized a novel Cu^{II}–OOH species with a related ligand,[13] and (v) Tolman reported Cu^I/O_2 chemistry with $N_2S_{thioether}$ ligands (however, the S donor does not coordinate to copper ion in O_2 adducts characterized).[14] Thus, until now, there has not been any discrete well-characterized copper–O_2 complex which includes thioether ligation.

In this report, we describe copper(I)/O_2 reactivity employing a tetradentate ligand L^{N3S} (Scheme 1). Physical data, including X-ray absorption spectroscopy (XAS) and resonance Raman (rR) provide definitive evidence for S(thiother) coordination in the observed peroxo–dicopper(II) complex (Scheme 1). This is the first achievement of (reversible) copper(I)–O_2 binding and adduct formation/characterization in a sulfur ligand environment. The chemistry follows in close analogy to that for the tripodal tetradentate ligand

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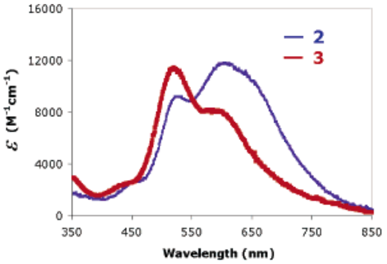
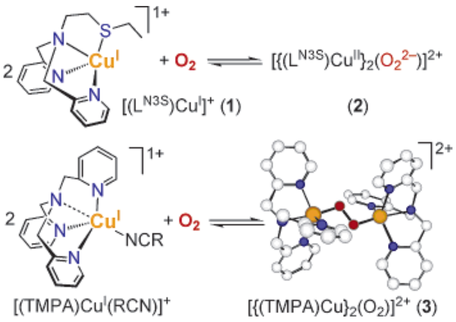


Figure 1. Absorbance spectra of μ-1,2-peroxodicopper(II) complexes **3** (red) with N_4 TMPA ligand (EtCN or acetone solvents, −93 °C) and **2** (blue) with thioether N_3S ligand L^{N3S} (MeTHF solvent, −125 °C).

Scheme 1



TMPA (Scheme 1); $[\{(TMPA)Cu^{II}\}_2(\mu\text{-}1,2\text{-}O_2^{2-})]^{2+}$ (**3**) has been extensively characterized, in terms of kinetics of formation, electronic structure, and other physical−spectroscopic properties, $\lambda_{max} = 525$ ($\epsilon = 11\,500$), 600 nm, (Figure 1, red spectrum).[15−17] Our hypothesis, which has been borne out, was that an L^{N3S} analogue, where one pyridyl arm of TMPA is replaced by a thioether donor, would exhibit related chemistry.

Complex $[(L^{N3S})Cu^I]^+$ (**1**) was synthesized as an off-white air-sensitive solid, either as a ClO_4^- or $B(C_6F_5)_4^-$ salt.[18] Oxygenation of **1** at −80 °C in CH_2Cl_2, acetone, or 2-methyltetrahydrofuran (MeTHF) gives dark blue solutions which persist for only 10−20 min and which possess apparent ϵ values (i.e., at 530 nm) which are low in comparison to established copper−dioxygen complexes,[1] including **3**. However, oxygenation of **1** under colder conditions, −125 °C in MeTHF, leads to a quite stable situation, (Figure 1, blue spectrum); the new dioxygen adduct, formulated as a μ-1,2-peroxodicopper(II) complex $[\{(L^{N3S})Cu^{II}\}_2(\mu\text{-}1,2\text{-}O_2^{2-})]^{2+}$ (**2**), is EPR silent and exhibits peaks with intensities rather similar to those of **3**, with $\lambda_{max} = 530$ ($\epsilon \approx 9200$ M^{-1} cm^{-1}) and 605 nm ($\epsilon \approx 11\,800$ M^{-1} cm^{-1}) (Figure 1). In fact, the binding of O_2 to **1** is fully reversible; as monitored by UV−vis spectroscopy, warming −125 °C solutions of **2** (MeTHF solvent) to −80 °C, followed by application of a vacuum, releases O_2 and regenerates copper(I) complex **1**.[19]

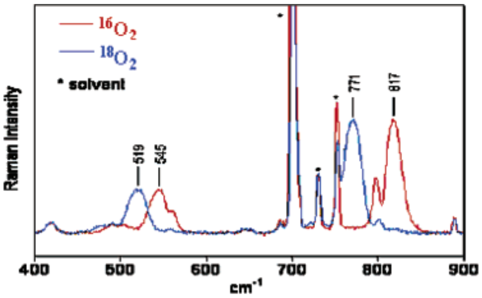


Figure 2. rR spectra of CH_2Cl_2 solutions of **2**, with $^{16}O_2$ (red) and $^{18}O_2$ (blue) isotopic substitution {77 K, $\lambda_{exit} = 620$ nm}. See text.

The absorbance spectrum of **2** has a more intense lower-energy band, opposite to that observed for **3** (Figure 1) and other μ-1,2- end-on peroxo dicopper(II) complexes.[1] The absorbance spectrum of **3** exhibits three peaks: a dominant absorption at 525 nm ($\epsilon = 11\,500$ M^{-1} cm^{-1}) and peaks at 615 ($\epsilon = 5800$ M^{-1} cm^{-1}) and at 435 nm ($\epsilon = 1700$ M^{-1} cm^{-1}), assigned as electric dipole-allowed singlet transitions from the peroxide π^*_σ and π^*_v orbitals and the spin-forbidden triplet transition from the peroxide π^*_v orbital, respectively.[15] However, the absorption features of **2** cannot be resolved with only these three bands. The asymmetry in the dominant low-energy band indicates that another transition is present, which rR shows has only Cu−O character.[20] Four bands at ~15 400, 16 800, 19 000, and 22 500 cm^{-1} are required to fit the absorbance spectrum (see Figure S2).[18] The fact that the additional transition is present indicates that the coordination geometry for the N_3S ligand around the Cu is distorted from the idealized trigonal bipyramidal coordination present in **3**.[16] Such a distortion is known for a Cu(II) complex of a tripodal tetradentate ligand with one thioether arm and is also seen for other modified N_4 tripodal ligand copper complexes.[13,21,22] The geometric distortion would decrease overlap of the peroxide π^*_σ orbital with the half-occupied Cu orbital and weaken the Cu−O bond (see rR spectroscopic discussions, below). This distorted coordination geometry around the Cu and the distorted Cu_2O_2 core would invert the π^*_σ/π^*_v intensity pattern in the absorbance spectrum relative to the TMPA complex, as well as reduce the symmetry of the complex leading to absorption intensity in both of the π^*_v components.

Resonance raman data for **2** with $^{16}O_2$ and $^{18}O_2$ isotopic substitution (Figure 2) show primary features at 817 ($^{16\text{-}18}O_2$ $\Delta = 46$ cm^{-1}) and 545 cm^{-1} ($^{16\text{-}18}O_2$ $\Delta = 26$ cm^{-1}).[23] These values are similar to those observed for **3** {$\nu_{(O-O)} = 827$ cm^{-1} and $\nu_{(Cu-O)} = 561$ cm^{-1}}.[15] Thus, the rR features of **2** can be assigned as $\nu_{(O-O)}$ and $\nu_{(Cu-O)}$, respectively, belonging to a μ-1,2-peroxodicopper(II) species. No Cu−S vibration is observed, consistent with the absence of a S→Cu charge-

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(23) Note that the $^{16}O_2$-derived features are slightly split with additional peaks at ~800 and ~560 cm^{-1}, which gain some intensity through Fermi mixing, as they are not present in the $^{18}O_2$-prepared sample.

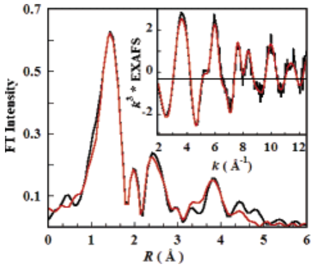

Figure 3. Fourier transforms (non-phase-shift-corrected) and EXAFS data (Inset) of **2** in frozen MeTHF solution. Data (black), fit (red).

transfer band in the absorption spectrum.[24] However, the observed vibrational data indicate the Cu_2-O_2 bonding is weaker overall in **2** than **3**; the lower $\nu_{(Cu-O)}$ frequency observed in **2**, indicating a weaker Cu−O bond, means less electron density is donated from the peroxide π^* orbitals, which in turn weakens the O−O bond and lowers $\nu_{(O-O)}$. These effects can be ascribed to increased thioether donation in **2** when compared to pyridyl nitrogen donation in **3**.

Direct evidence for thioether ligation in **2** comes from EXAFS carried out on frozen (MeTHF) solutions. The k^3-weighted Cu K-edge EXAFS ($k = 2-12.7$ Å^{-1}) data and the corresponding Fourier transform fit are shown in Figure 3. The first shell was fit with 1 Cu−O/N at 1.89 Å, 3 Cu−O/N at 2.04 Å, and 1 Cu−S at 2.4 Å (Table S1). The Cu−S contribution is essential to obtain good fits to the data. The Cu−O/N is longer than that observed in **3** (1.85 Å) consistent with the rR data. The Cu−S distance is in the range (2.33−2.46 Å) found for equatorial Cu(II)−$S_{thioether}$ bonds in pentacoordinate (square pyramidal or trigonal bipyramidal (TBP)) complexes.[12,26−28] Axially ligated Cu−$S_{thioether}$ bond lengths in 5- or 6-coordinated complexes are significantly longer (2.54−2.94 Å).[13,20,29,30] Thus, the structural data on **2** (EXAFS) and comparisons to Cu(II)−thioether complexes further support its formulation as a μ-1,2-peroxo-dicopper(II) complex, where each Cu(II) ion is in a distorted 5-coordinate environment.

With thioether coordination demonstrated, the results presented here are in accord with expectations from known copper−dioxygen chemistry. If the thioether donor in L^{N3S} were to dangle (as in Tolman's recently described chemistry (see above)[14] and not coordinate, the remaining "tridentate amine" ligand (N_3 portion of L^{N3S}) would likely form a metastable side-on-bound η^2:η^2-peroxo dicopper(II) species ($\lambda_{max} \approx 350$ nm) or its bis-μ-oxo dicopper(III) isomer ($\lambda_{max} \approx 385$ nm).[31,32] Tripodal tetradentate ligand-containing systems, however, typically give μ-1,2-peroxodicopper(II) complexes, as demonstrated here, even with a thioether instead of nitrogen donor. Future studies will address the effects of thioether coordination and the electronic structure of **3**. We will also attempt (using flash-and-trap approaches)[33] to detect and characterize a mononuclear adduct, $[(L^{N3S})-Cu-O_2]^+$, which would likely be a kinetic precursor intermediate to peroxo complex **3** and relevant to Cu−enzyme (PHM and DβH) chemistry.

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Supporting Information Available: Synthetic procedures, absorption spectrum (vs cm^{-1}), and rR experimental and EXAFS fit results. This material is available free of charge via the Internet at http://pubs.acs.org.

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