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A $N_3S_{(\text{thioether})}$ -Ligated Cu^{II} -Superoxo with Enhanced Reactivity

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Abstract

Previous efforts to synthesize a cupric superoxide complex possessing a thioether donor have resulted in the formation of an end-on *trans*-peroxodicopper(II) species, $[(\text{Ligand})Cu^{II}]_2(\mu-1,2-O_2^{2-})^{2+}$. Redesign/modification of previous N_3S tetradentate ligands has now allowed for the stabilization of the monomeric, superoxide product possessing a $S_{(\text{thioether})}$ -ligation, $[(\text{DMA}N_3S)Cu^{II}(O_2^{\bullet-})]^+$ (**2S**), as characterized by UV-vis and resonance Raman (rR) spectroscopies. This complex mimics the putative $Cu^{II}(O_2^{\bullet-})$ active species of the copper monooxygenase PHM and exhibits enhanced reactivity towards both O-H and C-H substrates in comparison to close analogues $[(L)Cu^{II}(O_2^{\bullet-})]^+$, where L contains only nitrogen donor atoms. $Cu-S_{(\text{thioether})}$ ligation with its weaker donor ability (relative to an N-donor) are demonstrated by comparisons to the chemistry of analogue compounds.

The copper monooxygenases peptidylglycine- α -hydroxylating monooxygenase (PHM) and dopamine- β -monooxygenase (D β M) possess a dicopper active site, but it is “noncoupled”; the two copper ions are about 11 Å apart.¹ Extensive biochemical and biophysical research has shown that one copper ion (designated Cu_H or Cu_A) receives and passes electron reducing equivalents to the $His_2Met N_2S_{(\text{thioether})}$ ligated Cu_M (or Cu_B) center, where O_2 and substrate binding occur. Recent computational analyses² lead to the hypothesis that an initial O_2 -adduct, a Cu_M centered cupric superoxide $\{Cu^{II}(O_2^{\bullet-})\}$ moiety, forms from oxygenation of the fully reduced ($Cu^I \dots Cu^I$) enzyme. This species performs the H-atom abstraction of the peptide prohormone substrate (in PHM) leading to C–H hydroxylation and formation of the product hormone. Other reaction mechanisms suggesting other possible reactive intermediates being responsible for substrate C–H attack have been proposed.³ In support of the importance of the $Cu^{II}(O_2^{\bullet-})$ reaction intermediate’s involvement, a crystal

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Notes

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Supporting Information.

Details concerning X-ray crystallography analyses including cif files, NMR, UV-vis, and rR spectroscopies, cyclic voltammetry, ESI mass spectrometry, and procedures for carrying out the reactivity studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

structure obtained by Amzel and co-workers in the presence of a substrate inhibitor, reveals dioxygen bound to Cu_M in an end-on fashion,^{1b} as depicted in Scheme 1a.

Undoubtedly, the thioether ligand plays a critical role in determining the electronic structure and functions of Cu_M site leading to C-H bond activation.² However, the precise role of Met coordination and the actual PHM reaction mechanism has yet to be fully elucidated.

Within the sub-field of copper-dioxygen synthetic bioinorganic chemistry, one long-standing goal has been to produce Cu^{II}(O₂^{•-}) species that can be studied in detail, and to this end several cupric-superoxo complexes have been reported with ligands containing either three or four N-atoms.⁴ In an attempt to mimic the active site donors of PHM and DβM, considerable effort has been devoted toward generating thioether containing tridentate or tetradentate ligands to study their Cu^I/O₂ reactivity.⁵ In our own efforts we have been able to generate binuclear peroxodicopper complexes with S_(thioether) ligation,⁶ but there has been no report of a mononuclear Cu^{II}(O₂^{•-}) species coordinated by a S_(thioether) donor. Herein, for the first time we present the spectroscopic evidence and reactivity of the new mononuclear cupric superoxo complex, (^{DMA}N₃S)Cu^{II}(O₂^{•-}) (**2^S**) (Scheme 1b) possessing thioether S-ligation that exhibits enhanced reactivity towards both O-H and C-H substrates.

This new ligand, ^{DMA}N₃S,⁷ differs from our previously reported N₃S ligands in two important ways. First, it possesses highly electron-rich dimethylamino (DMA)⁸ groups at the *para* position of the two pyridyl donors, a strategy from previously stabilized a mononuclear Cu^{II}(O₂^{•-}) complex containing N₄ tripodal tetradentate ligand.^{4c,4h,9} Second, the thioether moiety is capped with a bulkier *o*-methyl benzyl substituent to slow dimerization relative to previous designs.^{6d} Treatment of ^{DMA}N₃S with [Cu^I(CH₃CN)₄]B(C₆F₅)₄ in THF, followed by pentane addition leads to the isolation of bright yellow powders with formula [(^{DMA}N₃S)Cu^I]B(C₆F₅)₄ (**1**).⁷ Single crystals could be grown from 2-methyltetrahydrofuran (MeTHF)/pentane at RT under Ar. As shown in Figure 1a, the cuprous complex is a four-coordinate monomer ligated by two pyridyl, one tertiary amine, and one thioether atom in a distorted pyramidal geometry providing a very open site for potential dioxygen binding. The Cu-S bond length in **1** (2.2327(5) Å) falls in the usual range (2.2 – 2.44 Å) for Cu^I-S_(thioether) complexes.⁶ Many previously studied N₃S_(thioether)-Cu^I complexes form dimers in the solid state,^{6d} and the incorporation of the larger *o*-methylbenzyl group may disfavor their formation.

Furthermore, the copper(II) complex [(^{DMA}N₃S)Cu^{II}(H₂O)(ClO₄)](ClO₄) (**3**) (Figure 1b) was generated and structurally characterized.⁷ A slightly distorted octahedral coordination is observed. The thioether donor group is found in an axial position with Cu-S bond distance of 2.6974(6) Å. Electron paramagnetic resonance (EPR) measurement on **3** reveals a standard axial spectrum of copper(II) complex.⁷

Bubbling O₂ into a MeTHF solution of **1** at -135 °C led to the immediate formation of a new species (λ_{max} = 425 nm) that rapidly (~50 s) converted to the thermodynamically more stable end-on *trans*-peroxodicopper(II) species [{(^{DMA}N₃S)Cu^{II}}]₂(μ-1,2-O₂²⁻)²⁺ (**2^P**) (Figure 2, top) exhibiting strong UV-vis absorptions at λ_{max} = 534 (6500 M⁻¹cm⁻¹) and 604 (6600 M⁻¹cm⁻¹) nm (Figure 2, bottom) consistent with the feature of previously synthesized

$S_{(\text{thioether})}$ -ligated $(\mu\text{-}1,2\text{-peroxo})\text{Cu}^{\text{II}}_2$.⁶ The formulation of **2^P** is confirmed by rR spectroscopy ($\nu_{\text{O-O}} = 821 \text{ cm}^{-1}$, $\nu_{\text{Cu-O}} = 547 \text{ cm}^{-1}$).⁷ Although the initially formed species has a short lifetime, the characteristic λ_{max} value of 425 nm and the transformation to a more stable $(\mu\text{-}1,2\text{-peroxo})\text{Cu}^{\text{II}}_2$, strongly suggest it is the S-ligated cupric superoxo species $[(^{\text{DMA}}\text{N}_3\text{S})\text{Cu}^{\text{II}}(\text{O}_2^{\bullet-})]^+$ (**2^S**).

Interestingly, when polar or potentially hydrogen-bonding solvents such as acetone, ethanol, methanol, or trifluoroethanol (TFE) are mixed with MeTHF, $[(^{\text{DMA}}\text{N}_3\text{S})\text{Cu}^{\text{II}}\text{-OO}^{\bullet-}]^+$ (**2^S**) is much more persistent than is found in MeTHF only (Figure 3a; $\lambda_{\text{max}} = 418, 605, 743 \text{ nm}$). There appears to be a shift of the equilibrium constant to the mononuclear superoxide over the binuclear *trans*-peroxo complex. This result could be due to the formation of a hydrogen bond between an O-atom of the superoxide ligand and the TFE solvent, as observed in a 'classical' cobalt(III)-superoxo complex with TFE.¹⁰

The rR spectra of **2^S** ($\lambda_{\text{ex}} = 413 \text{ nm}$) reveal two dioxygen isotope sensitive vibrations (Figure 3b). An O–O stretch is observed at 1117 cm^{-1} which shifts to 1056 cm^{-1} upon $^{18}\text{O}_2$ substitution ($^{18}\text{O}_2 = -61 \text{ cm}^{-1}$) and a Cu–O stretch at 460 cm^{-1} ($^{18}\text{O}_2 = -20 \text{ cm}^{-1}$). The energy and isotope shifts of these vibrations confirm the assignment of **2^S** as an end-on superoxide species. In fact, these parameters closely match those for previously described cupric-superoxo complexes with tripodal tetradentate N_4 ligands ($^{\text{DMA}}\text{tmpa}$ and $^{\text{DMM}}\text{tmpa}$), (Table 1) both having $\nu_{\text{O-O}} = 1121 \text{ cm}^{-1}$.^{4c,4h} The species **2^S** is assigned as having an $S = 1$ (triplet) ground state by EPR spectroscopy.^{7,11}

In MeTHF:TFE (4:1 v:v), an approximately 4:1 (mol/mol) equilibrium mixture of (**2^S**)/(**2^P**)¹² forms within ~150 s following oxygenation of $[(^{\text{DMA}}\text{N}_3\text{S})\text{Cu}^{\text{I}}]^+$ (**1**) at $-135 \text{ }^\circ\text{C}$. This mixture shows minimal decomposition over an hour and thus, we could carry out reactivity studies of **2^S** with the O–H and C–H substrates; 2,6-di-*tert*-butyl-4-methoxyphenol (*p*-OMe-DTBP) and N-methyl-9,10-dihydroacridine (AcrH₂). Pseudo first-order kinetic behavior was observed upon addition of *p*-OMe-DTBP (with $t_{1/2} = 3 \text{ min}$) or AcrH₂ ($t_{1/2} = 2 \text{ min}$) as monitored by the disappearance of the 418 nm UV-vis band of **2^S**. Following workup at RT the products were analyzed as 2,6-di-*tert*-butyl-1,4-benzoquinone and 10-methyl-9-acridone, respectively.⁷ Independent observations demonstrate that the complex **2^P** is unreactive toward these substrates. Warming up the **2^S** solution does not lead to sulfur oxygenation which occurs by bis($\mu\text{-oxo}$) Cu^{III}_2 species.^{6d}

To assess the effect of the thioether donor in **2^S**, we compared the reactivity of $(\text{L})\text{Cu}^{\text{II}}(\text{O}_2^{\bullet-})$ complexes ($\text{L} = ^{\text{DMA}}\text{tmpa}$ or $^{\text{DMM}}\text{tmpa}$) toward the same substrates.^{4c,4h} Notably, both cupric superoxide complexes showed no reactivity under identical conditions (Table 1), although they do react above $-100 \text{ }^\circ\text{C}$. Thus, **2^S** with $S_{(\text{thioether})}$ -ligation is more reactive than the closely related N_4 superoxide compounds. The difference in reactivity is rationalized by the different donor strengths of the corresponding ligands. The substitution of a $S_{(\text{thioether})}$ for a $\text{N}_{(\text{pyridine})}$ donor decreases the ligand field strength, consistent with the $\text{Cu}^{\text{II/I}}$ redox potentials for the separately isolated Cu^{II} complexes in which thioether coordination raises the reduction potential by 230 mV (Table 1).⁷ As a result, we hypothesize that **2^S** is more electrophilic and hence better able to accept an H-atom from either an O–H or C–H substrate, as compared to the N_4 complexes.

The influence of the Cu–S interaction on the oxygenated products was further probed by comparing Cu/O₂ species with different donor atoms binding Cu. Three structurally analogous ligands were synthesized replacing the sulfur site with carbon, oxygen, and nitrogen (Scheme 2).⁷ The isolated Cu^I complex with tridentate ^{DMA}N₃ ligand exhibits a distinctive 382 nm absorption band⁷ upon O₂ addition at –135 °C in MeTHF. This absorption spectrum is consistent with a bis(μ-oxo)Cu^{III}₂ complex, which is known for many other products from low-temperature oxygenation of Cu^I-N₃ precursors.^{6d,14} Under identical reaction conditions, oxygenation of the Cu^I(^{DMA}N₃O), possessing three N-donors and an ether O-atom, leads to the initial formation of a (μ-1,2-peroxo)Cu^{II}₂ which rapidly (~1 min) converts to a bis(μ-oxo)Cu^{III}₂ species with very similar UV-vis spectrum as for the case with ^{DMA}N₃.^{6d,15} Thus, as seen before,^{6d,16} the oxygen atom of the ether arm in ^{DMA}N₃O has an extremely weak to non-existent interaction with the copper ion in the oxygenated product. We find that for Cu^I(^{DMA}N₄) in MeTHF (Scheme 2c), both Cu^{II}–superoxo and (μ-1,2-peroxo)Cu^{II}₂ complexes are generated⁷ as in the case of ^{DMA}N₃S. This strongly suggests that the S_(thioether)-atom donor of ^{DMA}N₃S ligand is coordinated in both Cu^{II}–superoxo/μ-1,2-peroxo complexes, **2^S** and **2^P**. If it were not, a bis(μ-oxo)Cu^{III}₂ complex would prominently form.¹⁷

In summary, [(^{DMA}N₃S)Cu^{II}(O₂^{•–})]⁺ (**2^S**) is the first reported example of a cupric superoxo species supported by a S_(thioether) donor. This advance allowed us to determine that a superoxide species from an N₃S donor was more reactive towards O–H and C–H bonds than the corresponding N₄ complex. These results indicate that one role of the Met ligand in PHM and DβM is to activate the superoxide species for reaction by increasing their electrophilicity. The synthesis of this species will also allow us to further consider the role of thioether ligation on critical downstream O₂-reduced (and protonated) derivatives, such as Cu^{II}-hydroperoxo and to perform detailed kinetic analysis of the preliminary reactivity study presented here.

Supplementary Material

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Acknowledgments

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9. We believe the increased stability comes about as a result of great rate (constant) for formation of a $\text{Cu}^{\text{II}}(\text{O}_2^{\bullet-})$ complex, because of the ligand donor group, where the rate of reaction of $\text{Cu}^{\text{II}}(\text{O}_2^{\bullet-})$ with a second ligand- Cu^{I} species is not as enhanced a reaction.
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12. The ratio or relative amount of superoxo complex 2^{S} to 2^{P} was determined by first finding and calculating the molar absorptivity (ϵ) for a solution of pure 2^{P} in MeTHF at -135°C . Note: as described, initial oxygenation of a solution of a known concentration of **1** gives the $2^{\text{S}}/2^{\text{P}}$ mixture but waiting 5 min leads to complete conversion to 2^{P} .
13. See the SI for CV's and redox potential values for the $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ complex couples for the DMA_{N_3} , $\text{DMA}_{\text{N}_3}\text{O}$, DMA_{N_4} ligands.
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17. More direct confirmation of a Cu-S(thioether) bond such as by X-ray Absorption Spectroscopy, is not possible here, due to the short lifetime of 2^{S} and the related fact that higher concentrations need only lead to transformation of 2^{S} to 2^{P} .

Figure 1. Displacement ellipsoid plots of the cations; (a) $[(\text{DMA})_3\text{S}]\text{Cu}^{\text{I}}+$ (**1**) and (b) $[(\text{DMA})_3\text{S}]\text{Cu}^{\text{II}}(\text{H}_2\text{O})(\text{ClO}_4)^+$ (**3**). Hydrogen atoms were removed for clarity.

Figure 2.

Low-temperature UV-vis absorption spectra of the reaction of **1** with O₂ at –135 °C in MeTHF (0.2 mM). The super-oxo product **2^S** is observed immediately upon O₂ addition (red) and converted to the peroxo **2^P** (t = 50 s, blue).

Figure 3.

(a) Low-temperature ($-135\text{ }^{\circ}\text{C}$) UV-vis absorption spectrum of 2^{S} (containing $\sim 11\%$ 2^{P} , $\lambda_{\text{max}} = 526\text{ nm}$, $\epsilon = 6500$)¹² as recorded $\sim 40\text{ s}$ after bubbling O₂ into a MeTHF:TFE (4:1) solution of **1** (0.098 mM), and (b) rR spectra of frozen 2^{S} (0.62 mM, $\lambda_{\text{ex}} = 413\text{ nm}$, 77 K) in MeTHF:TFE (4:1).⁷

Scheme 1.

Scheme 2.

Oxygenated products of ligand- Cu^{I} complexes.¹³

Table 1Comparison of $\text{LCu}^{\text{II}}/\text{LCu}^{\text{I}}$ Redox Potentials and Reactivity of Derived $[(\text{L})\text{Cu}^{\text{II}}(\text{O}_2^{\bullet-})]^+$ Complexes.

	$\text{DMA}_{\text{tmpa}}^{4c}$	$\text{DMM}_{\text{tmpa}}^{4h}$	$\text{DMA}_{\text{N}_3\text{S}}$

$p\text{-OMe-DTBP}^a$	No ^b	No ^b	Yes
AcrH_2^a	No ^b	No ^b	Yes
$E_{1/2}, \text{mV}^c$	-700	-570	-470

^a Reaction comparisons of $[(\text{L})\text{Cu}^{\text{II}}(\text{O}_2^{\bullet-})]^+$ complexes (MeTHF:TFE (4:1) at -135°C) toward substrates.^b Reactions do occur, but only above -100°C .^c $E_{1/2}$ (vs Fc^+/Fc) $[(\text{L})\text{Cu}^{\text{II}}(\text{solvent})](\text{ClO}_4)_2$ complexes as determined by cyclic voltammetry.⁷