

## An Anionic, Tetragonal Copper(II) Superoxide Complex

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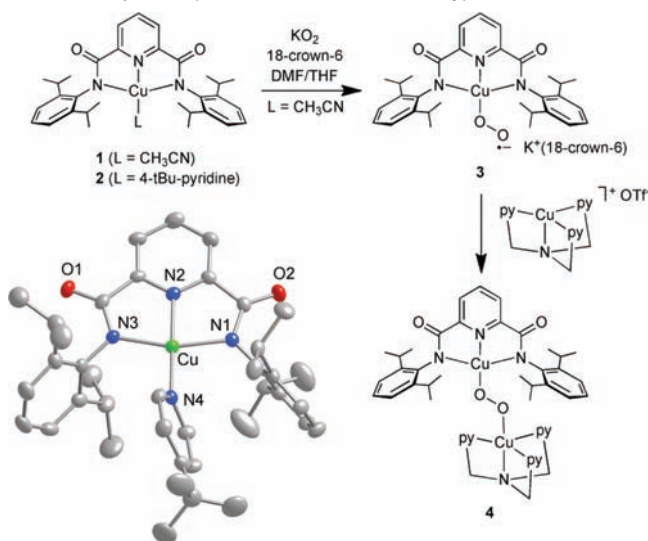
**Abstract:** Insight into copper–oxygen species proposed as intermediates in oxidation catalysis is provided by the identification of a Cu(II)-superoxide complex supported by a sterically hindered, pyridinedicarboxamide ligand. A tetragonal, end-on superoxide structure is proposed based on DFT calculations and UV–vis, NMR, EPR, and resonance Raman spectroscopy. The complex yields a *trans*-1,2-peroxodicopper(II) species upon reaction with [(*tmpa*)Cu(CH<sub>3</sub>CN)]OTf and, unlike other known Cu(II)-superoxide complexes, acts as a base rather than an electrophilic (H-atom abstracting) reagent in reactions with phenols.

An important first step in copper-promoted aerobic oxidations in biology<sup>1</sup> and catalysis<sup>2</sup> is the formation of a 1:1 Cu/O<sub>2</sub> adduct, in which the O<sub>2</sub> molecule is activated for subsequent reactions, either with substrate or to form different copper–oxygen species. In one approach aimed at understanding such adducts, synthetic 1:1 Cu/O<sub>2</sub> complexes have been targeted for detailed structural, spectroscopic, and reactivity studies.<sup>3</sup> To date, three types have been identified: (a) end-on, triplet Cu(II)-superoxos supported by tetradentate tripodal<sup>4</sup> or, in one case, tridentate<sup>5</sup> N-donor ligands; (b) side-on, singlet Cu(II)-superoxos supported by facially coordinating tris(pyrazolyl)hydroborates;<sup>6</sup> and (c) side-on, singlet Cu(III)-peroxos supported by strongly electron-donating, bidentate β-diketiminates or anilido-imines.<sup>3,7</sup> A key finding from reactivity studies of type (a) compounds is that they are electrophilic, with the ability to perform biologically relevant H-atom abstractions from phenols and weak C–H bonds.<sup>4b,5</sup> Investigations of the reactivity of type (b) compounds have not been reported and type (c) compounds are relatively unreactive with external organic substrates. Herein we report that in seeking to expand the repertoire of available 1:1 Cu/O<sub>2</sub> structures for comparative evaluations, we have discovered an end-on Cu(II)-superoxide complex that displays unique characteristics, including a tetragonal geometry and non-electrophilic reactivity.

Inspired by a recent report,<sup>8</sup> we prepared complex **1** (Scheme 1) by treating *N,N'*-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamide<sup>9</sup> with NaOMe followed by CuCl<sub>2</sub> in the presence of CH<sub>3</sub>CN.<sup>10</sup> In methanol or THF solution, **1** is green, whereas it is red-brown in the presence of CH<sub>3</sub>CN or pyridine. Consistent with this solvatochromism (Figure S2), attempts to obtain crystals of **1** suitable for X-ray crystallographic analysis were complicated by apparent CH<sub>3</sub>CN lability. The addition of 4-*t*Bu-pyridine, however, yielded X-ray quality dark red crystals of **2** (Scheme 1). The complex is square planar with a geometry similar to that of other known 2,6-pyridinedicarboxamide Cu(II) complexes.<sup>11</sup>

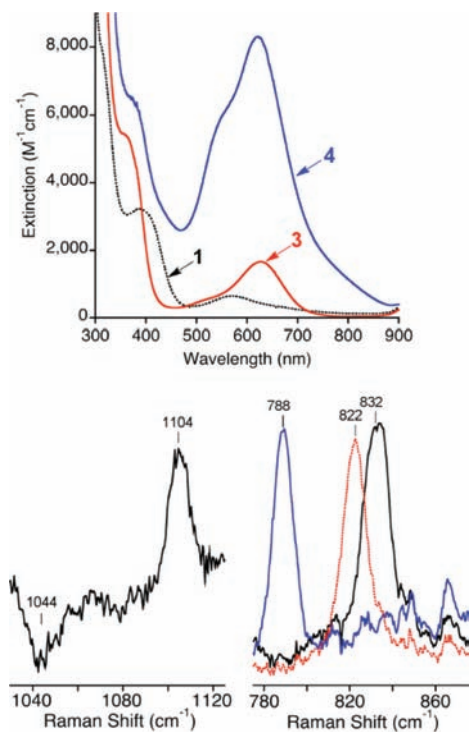
Addition of **1** to a slurry of KO<sub>2</sub> and 18-crown-6 in DMF/THF (1:1 v/v) at –80 °C immediately yielded an azure solution comprising compound **3**. This species is stable at –80 °C for hours but decomposes upon warming above –60 °C as indicated by

**Scheme 1.** Compounds Prepared in This Work and a Representation of the X-ray Crystal Structure of **2** Shown as 50% Thermal Ellipsoids (H Atoms Omitted for Clarity)<sup>a</sup>



<sup>a</sup> Selected bond distances (Å) and angles (deg): Cu–N1, 2.004(2); Cu–N2, 1.920(2); Cu–N3, 1.994(2); Cu–N4, 1.973(2); N1–Cu–N2, 80.56(10); N1–Cu–N3, 161.19(9); N1–Cu–N4, 99.57(9); N2–Cu–N3, 80.84(10); N2–Cu–N4, 173.28(10); N3–Cu–N4, 99.23(10).

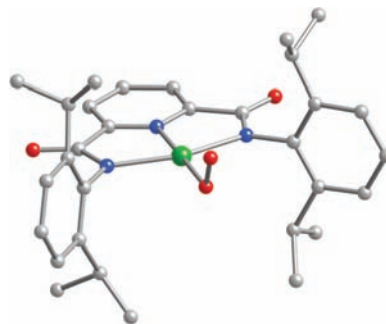
bleaching of its UV–vis spectral features. These features are compared to those of the starting material **1** in Figure 1. Particularly notable is an absorption at 627 nm ( $\epsilon \approx 1700 \text{ M}^{-1} \text{ cm}^{-1}$ ) with sufficient intensity to suggest that it is a charge transfer transition. Laser excitation at 647.1 nm yields a resonance Raman (rR) spectrum with an O-isotope sensitive peak at 1104 cm<sup>–1</sup> ( $\Delta^{18}\text{O} = 60 \text{ cm}^{-1}$ ; Figure 1). These data support formulation of **3** as a Cu(II)-superoxo complex with  $\nu(\text{O}=\text{O}) = 1104 \text{ cm}^{-1}$ , a value slightly lower than that reported for other end-on Cu(II)-superoxos ( $\sim 1120 \text{ cm}^{-1}$ ).<sup>4,5</sup> Attempts at characterizing **3** by negative-ion electrospray ionization mass spectrometry have not been successful due to its thermal instability. Monitoring by EPR spectroscopy (X-band, parallel and perpendicular modes, 2 K) of a titration of **3** by KO<sub>2</sub>/18-crown-6 showed only the disappearance of the axial signal for **1** (Figure S1) and appearance of the  $g \approx 2$  signal for superoxide; complex **3** is apparently EPR silent, which is consistent with a singlet or a triplet ground state.<sup>12</sup> <sup>1</sup>H NMR spectra of **1** and **3** in 1:1 d<sub>8</sub>-THF/d<sub>7</sub>-DMF at –80 °C only showed residual solvent peaks, with the spectrum of **3** also showing peaks in the diamagnetic region for 18-crown-6 overlapping that of CH<sub>3</sub>CN. These data rule out an  $S = 0$  ground state formulation and are consistent with both **1** and **3** being paramagnetic species, with the absence of paramagnetically shifted peaks for both suggesting very fast relaxation leading to extensive peak broadening.



**Figure 1.** (Top) UV-vis spectra of compounds **1**, **3**, and **4** ( $-80\text{ }^{\circ}\text{C}$ , DMF/THF). (Bottom Left) Resonance Raman difference spectrum ( $^{16}\text{O}$ – $^{18}\text{O}$ ) for compound **3** prepared from  $\text{K}^{16}\text{O}_2$  or  $\text{K}^{18}\text{O}_2$  ( $-196\text{ }^{\circ}\text{C}$ ,  $\lambda_{\text{ex}} = 647\text{ nm}$ ). (Bottom Right) Resonance Raman spectra for compound **4** prepared from **3**( $^{16}\text{O}$ ) (black line) or **3**( $^{18}\text{O}$ ) (blue line), overlaid with spectrum of [(tmpa)<sub>2</sub>Cu<sub>2</sub>( $^{16}\text{O}_2$ )](OTf)<sub>2</sub> (red dotted line) ( $-196\text{ }^{\circ}\text{C}$ ,  $\lambda_{\text{ex}} = 647.1\text{ nm}$ ).

In order to better characterize the electronic structure of **3**, unrestricted DFT calculations were performed using the mPW functional and a broken-symmetry (BS) formalism for the singlet state.<sup>10</sup> Various initial Cu(II)-superoxo complex geometries for either spin state all smoothly minimized to a structure showing end-on coordination of the superoxide to the copper center (Figure 2). The triplet state is computed to be lower in energy than the spin-purified singlet state by 6.2 kcal/mol. Previous analysis of various computational methods has suggested that the mPW functional may underestimate the energy of an end-on bound singlet state meaning that the triplet state may be even more strongly favored.<sup>13</sup> The Cu–O distances were calculated to be 1.966 and 2.778 Å, with a Cu–O–O angle of 115.1° and an O–O bond length of 1.292 Å, all consistent with superoxide character. The superoxide orients perpendicular to the plane of the N-donor ligand. A saddle point on the potential energy surface for superoxide rotation was identified with the O<sub>2</sub> moiety in the plane of the ligand. After inclusion of zero-point energy, the minimum and saddle point structure are essentially degenerate in energy, suggesting that rotation about the Cu–O bond is effectively barrierless. A singlet structure with symmetrical  $\eta^2$  coordination of the superoxide was also located and identified as a transition-state structure corresponding to interconversion of one  $\eta^1$  superoxide species with another; the barrier on the singlet surface is 19.8 kcal/mol. Computed  $\nu(\text{O}–\text{O})$  frequencies for the end-on minima are 1182 cm<sup>-1</sup> ( $\Delta^{18}\text{O} = 66\text{ cm}^{-1}$ ) for the triplet state and 1160 cm<sup>-1</sup> ( $\Delta^{18}\text{O} = 64\text{ cm}^{-1}$ ) for the singlet state (for the side-on singlet TS structure,  $\nu(\text{O}–\text{O})$  is 1042 cm<sup>-1</sup> ( $\Delta^{18}\text{O} = 58\text{ cm}^{-1}$ )). The computed frequencies are somewhat high compared to the rR values, likely because the calculations do not include a counterion or solvation, thereby reducing the tendency for negative charge to concentrate on the O<sub>2</sub> fragment and raising the stretching frequencies. Time dependent DFT calculations using

the B98 functional<sup>10</sup> identified a UV-vis transition at 625 nm. The orbitals involved correspond to the transition from the superoxide  $\pi^*$  orbital to an antibonding combination of the Cu  $d_{x^2-y^2}$  and the four ligand sigma donors (Figure S8). The calculated data are collectively consistent with assigning **3** as an end-on, Cu(II)-superoxo species.



**Figure 2.** Calculated structure of end-on triplet Cu(II)-superoxo complex **3**. Carbon (gray), nitrogen (blue), oxygen (red), and copper (green) are shown. Hydrogens omitted for clarity.

To further corroborate the formulation of **3**, we sought to trap it with a Cu(I) complex to generate a (peroxo)dicopper species, a transformation known to occur in reactions of Cu(I) complexes with O<sub>2</sub>.<sup>14</sup> Treatment of a solution of **3** with [(tmpa)Cu(CH<sub>3</sub>CN)]OTf<sup>15</sup> at  $-80\text{ }^{\circ}\text{C}$  yielded a purple solution with an intense UV-vis absorption at 624 nm ( $\epsilon \approx 8300\text{ M}^{-1}\text{ cm}^{-1}$ ) and a shoulder around 550 nm (**4**, Figure 1). The rR spectrum of this solution using 647 nm excitation showed an isotope sensitive peak at 832 cm<sup>-1</sup> ( $\Delta^{18}\text{O} = 44\text{ cm}^{-1}$ ; Figure 1) that we assign as the  $\nu(\text{O}–\text{O})$  for a (peroxo)dicopper complex. Taken together, the available evidence supports formulation of **4** as a (1,2-peroxo)dicopper species (Scheme 1). The similarities of the data to those reported for trans-1,2-peroxo complexes<sup>4d,16</sup> suggest a similar geometry for **4**, although the intensity pattern for the UV-vis absorptions is reversed from the typical pattern (higher energy peroxo  $\pi_{\sigma^*} \rightarrow \text{Cu(II)}$  more intense than lower energy peroxo  $\pi_{\sigma^*} \rightarrow \text{Cu(II)}$  transition), perhaps due to distortions of the CuOOCu atoms from planarity. To confirm that the UV-vis and rR features attributed to **4** are not due to [(tmpa)<sub>2</sub>Cu<sub>2</sub>(O<sub>2</sub>)]<sup>2+</sup>, which might be envisioned to form from reaction of [(tmpa)Cu(CH<sub>3</sub>CN)]OTf with adventitious O<sub>2</sub> or KO<sub>2</sub>, we collected UV-vis and rR data for [(tmpa)<sub>2</sub>Cu<sub>2</sub>(O<sub>2</sub>)](OTf)<sub>2</sub> generated by purposeful addition of O<sub>2</sub> to [(tmpa)Cu(CH<sub>3</sub>CN)]OTf in 1:1 DMF/THF at  $-80\text{ }^{\circ}\text{C}$ . The pattern of UV-vis absorptions (Figure S2) and the  $\nu(\text{O}–\text{O})$  value (822 cm<sup>-1</sup>, Figure 1) are similar to literature data<sup>16</sup> but are different from the data obtained for **4**.

Preliminary examination of the reactivity of **3** with phenols and acids revealed behavior distinct from that reported for other Cu(II)-superoxo complexes. For example, no reaction was observed upon addition of excess 4-*tert*-butyl-, 2,4-di-*tert*-butyl-, or 2,4,6-tri-*tert*-butyl-phenols to solutions of **3** at  $-80\text{ }^{\circ}\text{C}$ , whereas other Cu(II)-superoxo complexes generate phenoxyl radicals or derived coupled products via H-atom abstraction from these substrates.<sup>4b,5</sup> Even upon warming of the solution, no hydroxylated, coupled, or other phenolic products could be identified from the reaction mixtures (GC/MS). Addition of PPh<sub>3</sub> to a solution of **3** at  $-80\text{ }^{\circ}\text{C}$  similarly yielded no change of the UV-vis spectral features, and upon warming to room temperature and acidic workup, GC/MS analysis showed recovery of 78% of the PPh<sub>3</sub> and no OPPh<sub>3</sub>. On the other hand, addition of HOAc or 4-nitrophenol to **3** resulted in immediate quenching of the features due to **3** and, for the latter case, the growth of an intense absorption at 407 nm attributable to the 4-nitrophen-

noxiide anion, likely complexed to Cu(II). This was confirmed by observation of the same UV–vis spectrum upon addition of sodium 4-nitrophenoxide to a solution of **1** (Figure S3). Upon acidic workup of the product solution from the reaction of *p*-nitrophenol with **3**, only 4-nitrophenol was identified in the reaction mixture (80% yield by GC/MS) suggesting that the Cu(II)-superoxo species was being protonated and not undergoing any radical processes. We surmise that the unique reactivity exhibited by **3** is due to the fact that it is anionic and thus more prone to act as a base or nucleophile, whereas other end-on Cu(II)-superoxo complexes are supported by neutral N-donor ligands and are therefore cationic and electrophilic.

In summary, a new type of tetragonal, anionic, end-on Cu(II)-superoxo species has been characterized by spectroscopy and theory. The reactivity of this species is significantly different from that of previously reported Cu(II)-superoxo complexes. Taken together, these results provide new insights into the chemistry of copper–oxygen species proposed to be key intermediates in oxidation catalysis.

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**Supporting Information Available:** Experimental procedures, spectra, computational details (PDF), and CIF. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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