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Snapshots of Dioxygen Activation by Copper: The Structure of a 1:1 Cu/O$_2$ Adduct and Its Use in Syntheses of Asymmetric Bis(μ-oxo) Complexes

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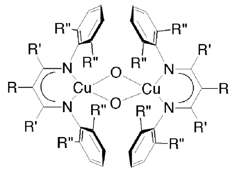
To understand how dioxygen is activated at copper sites in biological and industrial catalytic systems,[1,2] the reactions of discrete Cu(I) complexes with O$_2$ have been studied extensively.[3] By using low-temperature isolation and/or stopped-flow kinetic techniques, novel intermediates have been identified. Typically, an initial 1:1 Cu/O$_2$ adduct either is presumed or is established by transient spectroscopy,[4] and it reacts rapidly with a second Cu(I) complex to yield peroxo- and/or bis(μ-oxo)dicopper species that are sufficiently stable to be characterized in detail. Efforts aimed at the isolation and characterization of the 1:1 Cu/O$_2$ adducts have been hindered in large part by the generally low barriers and large K_{eq} values for their reaction with a second Cu(I) ion.[5] Only one such adduct has been structurally defined by X-ray crystallography, Tp^{tBu,iPr}Cu(η^2-O$_2$),[6] and there are few reports of definitive identification of 1:1 species using data such as ν(O−O) from vibrational spectroscopy.[7,8]

We recently discovered that variation of the steric properties of coordinated β-diketiminate ligands (L) enables control over the nature of the intermediate observed in low-temperature reactions of LCu(I)(MeCN) (**1**) with O$_2$.[9,10] Thus, when L is relatively unhindered, bis(μ-oxo) species (**2**) are observed, but when L is sufficiently bulky, a 1:1 adduct (**3**) forms that features side-on (η^2) O$_2$ coordination according to resonance Raman spectroscopic data.[11] Herein we report confirmation of this topology via an X-ray crystal structure determination of **3b**·3THF and density functional calculations that suggest an unusual bonding description. In a first demonstration of the notion that **3** might be used as a synthetic reagent for the stepwise construction of novel multicopper species, we report that addition of various Cu(I) reagents to **3a** yields bis(μ-oxo) complexes (**4**) that feature unique asymmetry due to the presence of divergent N-donor ligands.



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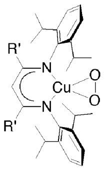
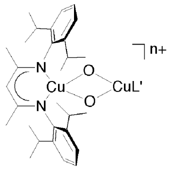
(R = H, R' = Me, R" = Me or Et;
R = aryl, R' = H, R" = Me, Et, or iPr)



3a (R' = Me)
3b (R' = tBu)



4a (L' = H(Me$_2$L^{Me2})$^-$, n = 0)
4b (L' = Me$_3$TACN, n = 1)
4c (L' = TMPDA, n = 1)

The X-ray structure of **3b**·3THF (Figure 1) shows η^2 coordination of O$_2$, but because of severe disorder problems, the O−O distance of 1.44(2) Å is not reliable.[12] Density functional (DFT) calculations[13] predict a C_{2v} minimum energy structure for **3b** that corroborates the X-ray diffraction results (see caption to Figure 1). Predicted Raman vibrational data are also in reasonable agreement with experiment.[11,14] The calculated O−O distance (1.376 Å) is significantly longer than is characteristic for metal-superoxo complexes (~1.2−1.3 Å)[15] and is more akin to the value associated with metal-peroxo compounds (~1.4−1.5 Å).[16] In conjunction with the low ν(O−O) values measured by Raman spectroscopy,[11] this finding suggests significant contribution of a Cu(III)−(O$_2^{2-}$) resonance form in the 1:1 adducts **3** (previously denoted[9] as superoxo species). Analysis of the Kohn−Sham (KS) molecular orbitals (MOs) indicates that the highest occupied MO (HOMO) is essentially a pure π^*_{OO} with the participating p orbitals being perpendicular to the plane of the diketiminate (Figure 2, left). The lowest unoccupied MO (LUMO, right) lies at very low energy (suggesting that **3b** should have a high reduction potential) and is dominated by the other (i.e., in-plane) π^*_{OO} orbital. This same π^*_{OO} hybrid contributes significantly to the HOMO-2 orbital in a fashion that is net bonding with copper. To the extent that the in-plane π^*_{OO} hybrid contributes significantly to both occupied and unoccupied orbitals and may be viewed as having a formal occupation number between 1 and 2, this rationalizes a structure intermediate between superoxide and peroxide. As final theoretical support for significant Cu(III)−(O$_2^{2-}$) character, we note that Cu(III) is formally d^8, and natural bond orbital analysis[17] of the KS density for **3b**

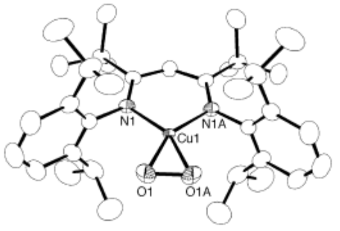


Figure 1. X-ray crystal structure of **3b**·3THF, showing all non-hydrogen atoms as 50% thermal ellipsoids. Selected distances (Å) and angles (deg): Cu1−N1, 1.858(8); Cu1−O1, 1.852(8); O1−O1A, 1.44(2); N1−Cu1−N1A, 102.1(5); O1−Cu1−O1A, 45.8(5). The corresponding DFT predicted values are 1.898, 1.908, 1.376, 102.6, and 42.3.

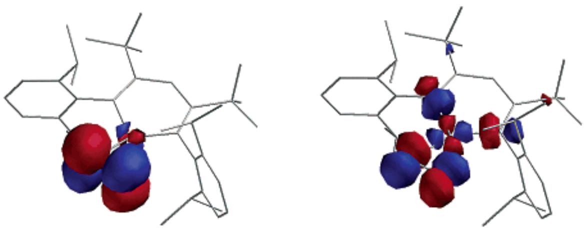


Figure 2. HOMO (left) and LUMO (right) of **3b** (0.026 and 0.035 bohr^{-3} contour levels, respectively, for clarity in depiction).

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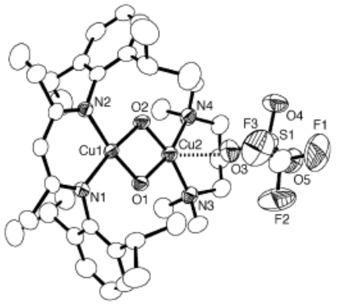

Figure 3. X-ray crystal structure of (**4c**)(O_3SCF_3), showing all non-hydrogen atoms as 50% thermal ellipsoids.

indicates that there are indeed precisely four pairs of unshared d electrons on copper.

Removal of free O_2 from solutions of **3** at −80 °C did not result in degradation of its UV−vis spectral features, thus setting the stage for its potential use as a building block in reactions with Cu(I) complexes that would otherwise bind O_2 if it were present. We injected solutions of the Cu(I) reagents $[L'Cu(MeCN)]^{n+}$ ($L' = H(Me_2L^{Me2})^-$, $n = 0$; L' = TMPDA, $n = 1$; $L' = Me_3TACN$, $n = 1$)[18] into degassed green solutions of **3a** at −80 °C.[19] The solutions remained EPR silent, but rapidly became yellow-brown, with growth of an intense UV−vis absorption at $\lambda_{max} \approx 400-430$ nm (Table S1). Titration data for the reaction with [(TMPDA)Cu(MeCN)]-O_3SCF_3 showed that maximum absorbance was reached when the ratio of reactants was 1:1. Raman data were acquired on solutions derived from **3a** that had been prepared with $^{16}O_2$ or $^{18}O_2$ (λ_{ex} = 413.1 or 457.9 nm, −196 °C). Resonance enhanced ^{18}O-isotope sensitive features were observed in the 600−650 cm^{-1} region ($\Delta^{18}O = 23-28$ cm^{-1}; Table S1). The spectral data are consistent with formulation of the products as bis(μ-oxo) complexes,[20] although the Raman shifts for the monocationic species are anomalously high (~650 cm^{-1}).[21] Importantly, formation of the "asymmetric" species **4** is indicated by spectral features that are distinct from those associated with the "symmetric" bis(μ-oxo) species that would result from reaction of the added Cu(I) reagent with free O_2.[10,22,23]

To prove this assignment, we obtained the X-ray crystal structure of (**4c**)(O_3SCF_3) (Figure 3). The $[Cu_2(\mu\text{-}O)_2]^{2+}$ core parameters are similar to others reported previously (cf., Cu−Cu = 2.8492(5) Å).[3e] Despite differences in Cu−N distances (avg. 1.89 Å for the β-diketiminate versus 1.99 for TMPDA), the Cu−O bond distances are essentially equivalent (1.817−1.819 Å). A significant interaction between the triflate counterion and Cu2 is indicated by the Cu2−O3 distance of 2.614(2) Å. Similar triflate interactions to yield five-coordinate centers in $[(TMPDA)_2Cu_2(\mu\text{-}O)_2](O_3SCF_3)_2$ were identified previously by EXAFS (Cu−O = 2.32 Å).[22]

In sum, a novel electronic structure for a structurally defined 1:1 Cu/O_2 adduct that features significant Cu(III)−(O_2^{2-}) character is indicated by DFT calculations. Reaction of this adduct with Cu(I) reagents leads to unique asymmetric bis(μ-oxo) complexes identified by spectroscopy and X-ray diffraction. This demonstration of the use of an isolable 1:1 Cu/O_2 adduct as a synthon for building multicopper species in stepwise fashion provides important precedent for future applications of the methodology to other systems, including those containing alternative metal ions.

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Supporting Information Available: Experimental details (PDF) and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Raman data (ref 9, cm^{-1}): **3a**, $\nu(^{16}O^{16}O) = 968$, $\Delta\nu(^{16}O^{18}O,^{18}O^{18}O) = 25, 51$. **3b**, $\nu(^{16}O^{16}O) = 961$, $\Delta\nu(^{16}O^{18}O,^{18}O^{18}O) = 24, 49$.

(12) X-ray data for **3b**·3THF: orthorhombic, space group *Imm*2, $a = 15.464(4)$ Å, $b = 17.324(4)$ Å, $c = 8.763(2)$ Å, $V = 2348(1)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.151$ g/cm^3.

(13) Calculations employed the *m*PWPW91 functional (Adamo, C.; Barone, V. *J. Chem. Phys.* **1998**, *108*, 664) with the mixed basis set: H (STO-3G), C (6-31G), N and O (6-311G(d)), and Cu (CEP-31g). This level was validated against structural and Raman spectroscopic data for experimentally well-characterized binuclear copper species and found to be highly accurate. For instance, the computed Cu−O and Cu−Cu distances for $[(TMPDA)_2Cu_2(\mu\text{-}O)_2]^{2+}$ are 1.837 and 2.869 Å, and the $[Cu_2(\mu\text{-}O)_2]^{2+}$ A_g breathing vibration is predicted to be 608 cm^{-1} ($\Delta^{18}O = 28$ cm^{-1}). These data closely agree with previously reported (ref 22b) experimental values of 1.81 Å, 2.85 Å, and 608 cm^{-1} ($\Delta^{18}O = 26$ cm^{-1}). All closed-shell KS wave functions were checked for stability.

(14) DFT predicted Raman data for **3b** (cm^{-1}): $\nu(^{16}O^{16}O) = 1013$, $\Delta\nu(^{16}O^{18}O,^{18}O^{18}O) = 28, 57$.

(15) The O−O bond distances in the few reported (η^2-superoxo)metal complexes are: (a) $Tp^{tBu,iPr}CuO_2$, 1.22(3) Å, ref 6. (b) $Tp^{tBu,Me}CoO_2$, 1.262(8) Å: Egan, J. W., Jr.; Haggerty, B. S.; Rheingold, A. L.; Sendlinger, S. C.; Theopold, K. H. *J. Am. Chem. Soc.* **1990**, *112*, 2445. (c) $(Tp^{Me2})_2SmO_2$, 1.319(5) Å: Zhang, X.; Loppnow, G. R.; McDonald, R.; Takats, J. *J. Am. Chem. Soc.* **1995**, *117*, 7828. (d) $Tp^{tBu,Me}Cr(pzH)O_2$, 1.327(5) Å: Qin, K.; Incarvito, C. D.; Rheingold, A. L.; Theopold, K. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 2333.

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(18) For the cases where $n = 1$, the counterion is $O_3SCF_3^-$. Abbreviations used: $H(Me_2L^{Me2})^-$ = L with R = H, R′ = R″ = Me; TMPDA = *N,N,N′,N′*-tetramethyl-1,3-propanediamine; Me_3TACN = 1,4,7-trimethyl-1,4,7-triazacyclononane.

(19) Because of sluggish reactivity in initial experiments, similar reactions of **3b** have not yet been studied.

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(23) A small amount of $[(TMPDA)_2Cu_2(\mu\text{-}O)_2](O_3SCF_3)_2$ is evident in the Raman spectra for the TMPDA case (Figure S4), which we suspect is due to adventitious O_2. Experiments to test this notion are in progress.

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