Reactivity of a 1:1 copper–oxygen complex: isolation of a Cu(II)-*o*-iminosemiquinonato species†

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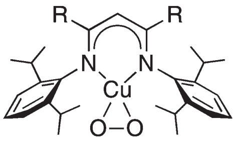
While a 1:1 Cu–O_2 adduct is generally unreactive with organic substrates, phosphines displace O_2 *via* an associative process and added Cu(I) leads to a novel internal ligand oxidation to yield a Cu(II)-*o*-iminosemiquinone complex.

Dioxygen activation by copper(I) centers is a critical first step in many fundamentally important biological and catalytic processes.[1] Significant mechanistic understanding of these reactions has been obtained through studies of synthetic Cu/O_2 intermediates.[2] The manner by which O_2 may bind to a single copper center has recently been modeled by complexes **1**. In addition to having been characterized by spectroscopy, theory, and X-ray crystallography, the mechanism of formation of these adducts has been defined[3] and their utility as synthons for the construction of asymmetric bis(μ-oxo)dimetal complexes has been demonstrated.[3b,4] Herein, we report results of further investigations of the reactivity of this class of 1:1 Cu/O_2 adducts. We have found that while **1a** is generally unreactive toward exogenous organic substrates, in the presence of $[Cu(MeCN)_4]O_3SCF_3$ **1a** undergoes a novel internal ligand oxidation process to yield a Cu(II)-*o*-iminosemiquinone complex.



1a: R = Me
1b: R = tBu

Solutions of **1a** decompose upon warming to give as-yet unidentified Cu(II)-containing species, which upon removal of copper yield a complex mixture of organic products (>25 different species by GC/MS).† The few that could be identified by comparison to independently synthesized material include ligand (*m*/*z* 418), 2,6-diisopropylaniline (*m*/*z* 177), and $(C_6H_3i\text{-}Pr_2)NCMe_2$ (*m*/*z* 217). Some of the other ligand fragments contain an oxygen atom derived from **1a** on the basis of ^{18}O labeling experiments. Due to the complexity of the product mixture, however, characterization of the decomposition reaction has not been feasible.

No acceleration of the decay of **1a** was observed when reagents were added that typically undergo hydrogen- or oxygen-atom transfer reactions with dinuclear copper–oxygen adducts at low temperatures.[2] For example, treatment of degassed solutions of **1a** with phenols, phenolates, thioanisole, cyclohexene, ferrocene or acids such as HBF_4 at temperatures as high as −60 °C did not result in changes in the UV-vis spectrum, even after prolonged reaction times. Addition of $PMePh_2$ to **1a** at −80 °C did not result in appreciable phosphine oxidation; instead, displacement of the bound O_2 to yield $LCu(PMePh_2)$ occurred.[5] A similar displacement was observed with PPh_3, but only upon warming. In both cases, the identities of the Cu(I)-phosphine adducts were confirmed by comparison of spectral features to independently prepared samples that were fully characterized, including by X-ray crystallography.†,‡ No reaction was observed with the bulkier trimesitylphosphine. Monitoring of the displacement reaction with excess $PMePh_2$ (15–35-fold) by UV-vis spectroscopy showed pseudo-first-order kinetics. A plot of k_{obs} *vs.* $[PMePh_2]$ was linear with an intercept of zero, indicating an overall second-order rate law, $-d[\mathbf{1a}]/dt = k[\mathbf{1a}][PMePh_2]$, $k = (8.4 \pm 0.4) \times 10^{-3}\ M^{-1}\ s^{-1}$ (−80 °C). These data are consistent with an associative mechanism, implicating accessibility of the copper center in **1a** to added substrates. The lack of reactivity with other molecules thus appears not to be solely due to the steric bulk imposed by the β-diketiminate ligand, and points to notably enhanced stabilization of the bound O_2 in the complex.

Consistent with the demonstrated reactivity of **1a** with added redox-active metal reagents that provides bis(μ-oxo)dimetal complexes,[3b,4] addition of 1 equiv. $[Cu(MeCN)_4]O_3SCF_3$ to a degassed solution of **1a** at −80 °C in THF or acetone resulted in a rapid color change from pale green to yellow/brown. Interestingly, however, the product was found not to be a bis(μ-oxo) complex, but instead a new species (**2**, Fig. 1). An X-ray structure of crystals

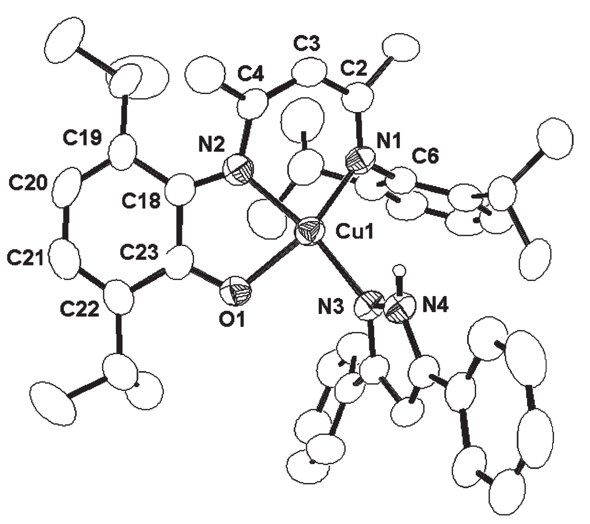


Fig. 1 Cationic portion of the crystal structure of **2** (the triflate anion has been omitted for clarity).

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† Electronic supplementary information (ESI) available: experimental details, and kinetic and X-ray crystallographic data. See http://www.rsc.org/suppdata/cc/b4/b418939f/
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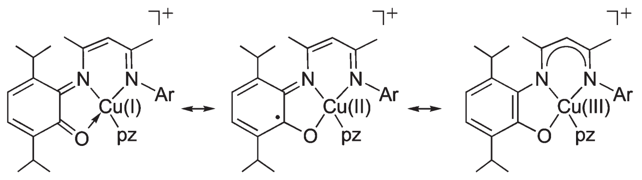

2a **2b** **2c**

Fig. 2 Resonance formulations for the cationic portion of **2**. Pz = 3,5-diphenylpyrazolyl; Ar = 2,6-diisopropylphenyl.

isolated in the presence of an added coordinating ligand, 3,5-diphenylpyrazole, showed that **2** arises from oxo-transfer to one of the aryl moieties of the β-diketiminate in conjunction with a 2,3-isopropyl-group shift.‡ A triflate counterion is associated with the complex hydrogen-bonded to the 3,5-diphenylpyrazolyl unit (N4–O3 = 2.732 Å), indicating an overall charge of +1. The low temperature UV-vis spectrum of **2** features an intense shoulder at ≈385 nm (ε = 17 000 M^{-1} cm^{-1}); this feature bleached upon warming above −80 °C, indicating complex decomposition. Solutions of **2** are EPR silent (X-band, 20 K).

In view of its diamagnetic character and overall charge of +1, the bonding in **2** may be envisioned in terms of the resonance formulations shown in Fig. 2. Careful analysis of the ligand bond lengths in the X-ray crystal structure (Fig. 3) allows the Cu(III)-*o*-amidophenolate form **2c** to be ruled out.[6] The six C–C bonds in the oxygenated ring are distinctly different, with two alternating shorter C=C bonds and four longer C–C bonds, indicating a quinone-type distortion. The two ligand "aryl" C–N bonds are also significantly different, and the C–O bond length of 1.284(4) Å is in the range of those reported for transition metal *o*-iminosemiquinonato(−1) species, supporting structure **2b**.[7] In further support of this assignment, all metal–ligand bond lengths are typical of Cu(II), where the three Cu–N distances average 1.94 Å. The results of a bond valence sum analysis are also consistent with a +2 oxidation state for the copper center, and argue against structures **2a**[8] and **2c**.† Taken together, the available data are thus most consistent with the Cu(II)-*o*-iminosemiquinonato assignment **2b**.

Little mechanistic information concerning the formation of **2** is currently available. We do know that [Cu(MeCN)$_4$]$^+$ is critical for the reaction, as the UV-vis spectral features of **1a** are not perturbed by addition of other Lewis acids (*e.g.* BF$_3$·Et$_2$O or AgO$_3$SCF$_3$) or redox agents (*e.g.* ferrocene, Cu(O$_3$SCF$_3$)$_2$ or Fe(MeCN)$_2$(O$_3$SCF$_3$)$_2$). We speculate that [Cu(MeCN)$_4$]$^+$ may lead to formation of a species in which a bound dioxygen ligand is activated for attack at the aryl ring of the β-diketiminate, perhaps as a μ-η^2:η^2-peroxide- or bis(μ-oxo)dicopper unit. After electrophilic attack at the aryl ring, an NIH shift of an isopropyl group and an oxidation step would rationalize generation of **2**. Precedence for this pathway is provided by previous reports of aromatic hydroxylation of internal ligand substrates by discrete dicopper-O$_2$ adducts[9,10] and of hydroxylation coupled to an NIH shift in selected cases.[11] Also relevant is a report of hydroxylation of the open position of a fluorinated β-diketiminate ligand, albeit in the absence of an observable intermediate.[12] The reaction we have discovered is unique in that hydroxylation of the substrate is followed by oxidation to a semiquinone-type ligand.

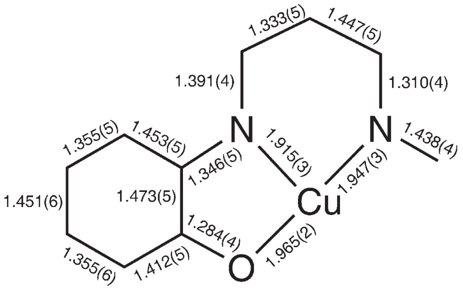

Fig. 3 Selected bond distances (Å) in **2**.

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Notes and references

‡ X-Ray data for LCu(PMePh$_2$): C$_{42}$H$_{54}$CuN$_2$P, M = 681.38, monoclinic, a = 11.6105(10), b = 21.0202(12), c = 15.9832(9) Å, β = 97.837(2), V = 3864(1) Å^3, T = 173 K, space group $P2_1/n$, Z = 4, μ(Mo Kα) = 0.636 mm^{-1}, 37565 reflections measured, 6828 unique (R_{int} = 0.0543), R_1 = 0.0452, wR_2 = 0.0907 (F^2, all data). X-Ray data for LCu(PPh$_3$): C$_{47}$H$_{56}$CuN$_2$P, M = 743.45, monoclinic, a = 23.439(2), b = 15.9011(15), c = 24.217(2) Å, β = 111.850(2), V = 8377.2(14), T = 173 K, space group $P2_1/n$, Z = 8, μ(Mo Kα) = 0.593 mm^{-1}, 79358 reflections measured, 14812 unique (R_{int} = 0.0497), R_1 = 0.0416, wR_2 = 0.0978 (F^2, all data). X-Ray data for **2**: C$_{49}$H$_{60}$CuF$_3$N$_4$O$_5$S, M = 937.61, monoclinic, a = 29.967(3), b = 13.6607(12), c = 23.462(2) Å, β = 92.711(2), V = 9593.9(15) Å^3, T = 173 K, space group $C2/c$, Z = 8, μ(Mo Kα) = 0.559 mm^{-1}, 23905 reflections collected, 8490 unique (R_{int} = 0.0712), final R_1 = 0.0551, wR_2 = 0.1188 (F^2, all data). CCDC 258882–258884. See http://www.rsc.org/suppdata/cc/b4/b418939f/ for crystallographic data in .cif or other electronic format.

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