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

Anne M. Reynolds, Elizabeth A. Lewis, Nermeen W. Aboelella and William B. Tolman*

Received (in Cambridge, UK) 17th December 2004, Accepted 11th February 2005 First published as an Advance Article on the web 24th February 2005 DOI: 10.1039/b418939f

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/O2 intermediates.² The manner by which O₂ 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 defined³ 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/O2 adducts. We have found that while 1a is generally unreactive toward exogenous organic substrates, in the presence of [Cu(MeCN)₄]O₃SCF₃ 1a undergoes a novel internal ligand oxidation process to yield a Cu(II)-o-iminosemiquinone complex.



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 (C₆H₃*i*-Pr₂)NCMe₂ (*m*/*z* 217). Some of the other ligand fragments contain an oxygen atom derived from **1a** on the basis of ¹⁸O 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 HBF₄ at temperatures as high as -60 °C did not

result in changes in the UV-vis spectrum, even after prolonged reaction times. Addition of PMePh2 to 1a at -80 °C did not result in appreciable phosphine oxidation; instead, displacement of the bound O₂ to yield LCu(PMePh₂) occurred.⁵ A similar displacement was observed with PPh₃, 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 PMePh₂ (15-35-fold) by UV-vis spectroscopy showed pseudofirst-order kinetics. A plot of k_{obs} vs. [PMePh₂] was linear with an intercept of zero, indicating an overall second-order rate law, $-d[1a]/dt = k[1a][PMePh_2], k = (8.4 \pm 0.4) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ $(-80 \ ^{\circ}\text{C})$. 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 $bis(\mu-oxo)dimetal complexes,^{3b,4}$ 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 $bis(\mu-oxo)$ 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).

[†] Electronic supplementary information (ESI) available: experimental details, and kinetic and X-ray crystallographic data. See http:// www.rsc.org/suppdata/cc/b4/b418939f/ *tolman@chem.umn.edu



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

isolated in the presence of an added coordinating ligand, 3,5diphenylpyrazole, showed that **2** arises from oxo-transfer to one of the aryl moieties of the β -diketiminate in conjunction with a 2,3isopropyl-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 ($\varepsilon = 17\ 000\ M^{-1}\ cm^{-1}$); this feature bleached upon warming above $-80\ ^{\circ}$ 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.* BF₃·Et₂O or AgO₃SCF₃) or redox agents (*e.g.* ferrocene, Cu(O₃SCF₃)₂) or Fe(MeCN)₂(O₃SCF₃)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



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

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-O₂ 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.

We thank the NIH (GM47365), the NSF (pre-doctoral fellowships to A.M.R. and N.W.A.), and the University of Minnesota (Louise T. Dosdall Fellowships to A.M.R. and N.W.A.) for financial support, and Dr Neil Brooks for assistance with the X-ray crystallography.

Anne M. Reynolds, Elizabeth A. Lewis, Nermeen W. Aboelella and William B. Tolman*

Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, 207 Pleasant Street, SE, Minneapolis, MN 55455, USA. E-mail: tolman@chem.umn.edu; Fax: 612-624-7029; Tel: 612-625-4061

Notes and references

‡ X-Ray data for LCu(PMePh₂): C₄₂H₅₄CuN₂P, M = 681.38, monoclinic, a = 11.6105(10), b = 21.0202(12), c = 15.9832(9) Å, $\beta = 97.837(2)$, V = 3864(1) Å³, T = 173 K, space group $P2_1/n$, Z = 4, μ (Mo K α) = 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(PPh₃): C₄₇H₅₆CuN₂P, M = 743.45, monoclinic, a = 23.439(2), b = 15.9011(15), c = 24.217(2) Å, $\beta = 111.850(2)$, V = 8377.2(14), T = 173 K, space group $P2_1/n$, Z = 8, μ (Mo K α) = 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**: C₄₉H₆₀CuF₃N₄O₅S, M = 937.61, monoclinic, a = 29.967(3), b = 13.6607(12), c = 23.462(2) Å, $\beta = 92.711(2)$, V = 9593.9(15) Å³, T = 173 K, space group C2/c, Z = 8, μ (Mo K α) = 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.

- E. I. Solomon, P. Chen, M. Metz, S.-K. Lee and A. E. Palmer, *Angew. Chem., Int. Ed*, 2001, 40, 4570.
- 2 Recent reviews: (a) L. Que, Jr. and W. B. Tolman, Angew. Chem., Int. Ed., 2002, 41, 1114; (b) S. Itoh and S. Fukuzumi, Bull. Chem. Soc. Jpn., 2002, 75, 2081; (c) L. M. Mirica, X. Ottenwaelder and T. D. P. Stack, Chem. Rev., 2004, 104, 1013; (d) E. A. Lewis and W. B. Tolman, Chem. Rev., 2004, 104, 1047.
- 3 (a) D. J. E. Spencer, N. W. Aboelella, A. M. Reynolds, P. L. Holland and W. B. Tolman, J. Am. Chem. Soc., 2002, **124**, 2108; (b) N. W. Aboelella, E. A. Lewis, A. M. Reynolds, W. W. Brennessel, C. J. Cramer and W. B. Tolman, J. Am. Chem. Soc., 2002, **124**, 10660; (c) N. W. Aboelella, S. V. Kryatov, B. F. Gherman, W. W. Brennessel, V. G. Young, Jr., R. Sarangi, E. V. Rybak-Akimova, K. O. Hodgson, B. Hedman, E. I. Solomon, C. J. Cramer and W. B. Tolman, J. Am. Chem. Soc., 2004, **126**, 16896.
- 4 N. W. Aboelella, J. T. York, A. M. Reynolds, K. Fujita, C. R. Kinsinger, C. J. Cramer, C. G. Riordan and W. B. Tolman, *Chem. Commun.*, 2004, 1716.
- 5 Similar displacements have been observed in dinuclear Cu–O₂ systems: (a) K. D. Karlin, R. W. Cruse, Y. Gultney, A. Farooq, J. C. Hayes and J. Zubieta, J. Am. Chem. Soc., 1987, 109, 2668; (b) N. Kitajima, T. Koda, Y. Iwata and Y. Moro-oka, J. Am. Chem. Soc., 1990, 112, 8833; (c) P. P. Paul, Z. Tyeklár, R. R. Jacobson and K. D. Karlin, J. Am. Chem. Soc., 1991, 113, 5322; (d) N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi and A. Nakamura, J. Am. Chem. Soc., 1992, 114, 1277.
- 6 (a) P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller and K. Wieghardt, J. Am. Chem. Soc., 2001, **123**, 2213; (b) H. Chun, C. N. Verani, P. Chaudhuri, E. Bothe, E. Bill, T. Weyhermüller and

K. Wieghardt, *Inorg. Chem.*, 2001, **40**, 4157; (c) V. Bachler, G. Olbrich, F. Neese and K. Wieghardt, *Inorg. Chem.*, 2002, **41**, 4179; (d) H. Chun, E. Bill, E. Bothe, T. Weyhermüller and K. Wieghardt, *Inorg. Chem.*, 2002, **41**, 5091; (e) H. Chun, P. Chaudhuri, T. Weyhermüller and K. Wieghardt, *Inorg. Chem.*, 2002, **41**, 790.

- 7 (a) C. G. Pierpont and C. W. Lange, *Prog. Inorg. Chem.*, 1994, 41, 331;
 (b) G. Speier, A. M. Whalen, J. Csihony and C. G. Pierpont, *Inorg. Chem.*, 1995, 34, 1355;
 (c) C. G. Pierpont, *Coord. Chem. Rev.*, 2001, 216–217, 99.
- 8 J. Rall, A. F. Stange, K. Hübler and W. Kaim, Angew. Chem., Int. Ed., 1998, 37, 2681.
- 9 (a) K. D. Karlin, J. C. Hayes, Y. Gultneh, R. W. Cruse, J. W. McKown, J. P. Hutchinson and J. Zubieta, J. Am. Chem. Soc., 1984, 106, 2121; (b) K. D. Karlin, M. S. Nasir, B. I. Cohen, R. W. Cruse, S. Kaderli and A. D. Zuberbühler, J. Am. Chem. Soc., 1994, 116, 1324.
- 10 P. L. Holland, K. R. Rodgers and W. B. Tolman, *Angew. Chem., Int. Ed.*, 1999, 38, 1139.
- 11 (a) K. D. Karlin, B. I. Cohen, R. R. Jacobson and J. Zubieta, J. Am. Chem. Soc., 1987, 109, 6194; (b) M. S. Nasir, B. I. Cohen and K. D. Karlin, J. Am. Chem. Soc., 1992, 114, 2482.
- 12 D. S. Laitar, C. J. N. Mathison, W. M. Davis and J. P. Sadighi, *Inorg. Chem.*, 2003, 42, 7354.