Inorganic Chemistry
Communication

Inorg. Chem. **2009**, *48*, 6323–6325 **6323**
DOI: 10.1021/ic900435p

Intermediates in Reactions of Copper(I) Complexes with *N*-Oxides: From the Formation of Stable Adducts to Oxo Transfer

Sungjun Hong, Aalo K. Gupta, and William B. Tolman*

Department of Chemistry and Center for Metals in Biocatalysis, University of Minnesota, 207 Pleasant Street SE, Minneapolis, Minnesota 55455

Received March 4, 2009

Reactions of copper(I) complexes of bidentate N-donor supporting ligands with pyridine- and trimethylamine-*N*-oxides or PhIO were explored. Key results include the identification of novel copper(I) *N*-oxide adducts, aryl substituent hydroxylation, and bis(μ-oxo)dicopper complex formation via a route involving oxo transfer.

Because copper-promoted oxidation reactions play important roles in biology[1] and catalysis,[2] great effort has been expended to uncover mechanistic information and, in particular, to identify possible copper−oxygen intermediates.[3] Of notable interest are $[CuO]^+$ species ($Cu^{III}O^{2-} \leftrightarrow Cu^{II}O^{\bullet-}$), which have been invoked in catalysis by enzymes[4] and synthetic systems[5,6] and characterized by theory[4b−4d,7] and in the gas phase.[7b] For example, ligand-supported $[CuO]^+$ species have been postulated in order to rationalize ligand hydroxylations observed in the decay of $Cu^{II}OOH$ complexes,[5] the O_2-induced decarboxylation of copper(I) α-ketocarboxylates,[6] and reactions of copper(I) complexes with iodosylbenzene (PhIO).[5] A $[CuO]^+$ intermediate has also been invoked as the active species responsible for regiospecific arene hydroxylations by Cu/Me_3NO systems,[8] via a mechanism proposed on the basis of theory to involve O−N bond homolysis from an isolated $Cu^{II}ONMe_3$ complex.[9] While a number of such copper(II) *N*-oxide complexes are known,[10] to our knowledge copper(I) variants have not been reported. Such copper(I) *N*-oxide adducts are of interest because they might provide a $[CuO]^+$ or related species through heterolytic N−O bond cleavage, as seen in a number of reactions of *N*-oxides with other metal centers (e.g., Fe[11] and Ru[12]). We therefore sought to investigate the reactions of pyridine- and trialkylamine-*N*-oxides with copper(I) complexes, using a range of supporting ligands with variable

*To whom correspondence should be addressed. E-mail: wtolman@umn.edu.

(1) (a) Solomon, E.; Sarangi, R.; Woertink, J.; Augustine, A.; Yoon, J.; Ghosh, S. *Acc. Chem. Res.* **2007**, *40*, 581–591. (b) Solomon, E. I.; Chen, P.; Metz, M.; Lee, S.-K.; Palmer, A. E. *Angew. Chem., Int. Ed.* **2001**, *40*, 4570–4590. (c) Klinman, J. P. *Chem. Rev.* **1996**, *96*, 2541–2561.

(2) (a) Punniyamurthy, T.; Rout, L. *Coord. Chem. Rev.* **2008**, *252*, 134–154. (b) Battaini, G.; Granata, A.; Monzani, E.; Gullotti, M.; Casella, L. *Adv. Inorg. Chem.* **2006**, *58*, 185–233.

(3) Recent reviews: (a) Hatcher, L. Q.; Karlin, K. D. *Adv. Inorg. Chem.* **2006**, *58*, 131–184. (b) Itoh, S. *Curr. Opin. Chem. Biol.* **2006**, *10*, 115–122. (c) Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P. *Chem. Rev.* **2004**, *104*, 1013–1045. (d) Lewis, E. A.; Tolman, W. B. *Chem. Rev.* **2004**, *104*, 1047–1076. (e) Suzuki, M. *Acc. Chem. Res.* **2007**, *40*, 609–617. (f) Cramer, C. J.; Tolman, W. B. *Acc. Chem. Res.* **2007**, *40*, 601–608.

(4) (a) Crespo, A.; Marti, M. A.; Roitberg, A. E.; Amzel, L. M.; Estrin, D. A. *J. Am. Chem. Soc.* **2006**, *128*, 12817–12828. (b) Kamachi, T.; Kihara, N.; Shiota, Y.; Yoshizawa, K. *Inorg. Chem.* **2005**, *44*, 4226–4236. (c) Yoshizawa, K.; Kihara, N.; Kamachi, T.; Shiota, Y. *Inorg. Chem.* **2006**, *45*, 3034–3041. (d) Chen, P.; Solomon, E. I. *J. Am. Chem . Soc.* **2004**, *126*, 4991–5000. (e) Evans, J. P.; Ahn, K.; Klinman, J. P. *J. Biol. Chem.* **2003**, *278*, 49691–49698.

(5) (a) Maiti, D.; Lee, D.-H.; Gaoutchenova, K.; Wurtele, C.; Holthausen, M. C.; Narducci Sarjeant, A. A.; Sundermeyer, J.; Schindler, S.; Karlin, K. D. *Angew. Chem., Int. Ed.* **2008**, *47*, 82–85. (b) Maiti, D.; Narducci Sarjeant, A. A.; Karlin, K. D. *Inorg. Chem.* **2008**, *47*, 8736–8747. (c) Cvetkovic, M.; Batten, S. R.; Moubaraki, B.; Murray, K. S.; Spiccia, L. *Inorg. Chim. Acta* **2001**, *324*, 131–140. (d) Reglier, M.; Amadei, E.; Tadayoni, R.; Waegell, B. *J. Chem. Soc., Chem. Commun.* **1989**, 447–450.

(6) Hong, S.; Huber, S. M.; Gagliardi, L.; Cramer, C. C.; Tolman, W. B. *J. Am. Chem. Soc.* **2007**, *129*, 14190–14192.

(7) (a) Yoshihide, N.; Kimihiko, H.; Tetsuya, T. *J. Chem. Phys.* **2001**, *114*, 7935–7940. (b) Schroder, D.; Holthausen, M. C.; Schwarz, H. *J. Phys. Chem. B* **2004**, *108*, 14407–14416. (c) Gherman, B. F.; Tolman, W. B.; Cramer, C. J. *J. Comput. Chem.* **2006**, *27*, 1950–1961. (d) Decker, A.; Solomon, E. I. *Curr. Opin. Chem. Biol.* **2005**, *9*, 152–163. (e) Huber, S. M.; Ertem, M. Z.; Aquilante, F.; Gagliardi, L.; Tolman, W. B.; Cramer, C. J. *Chem. Eur. J.* **2009**, *15*, 4886–4895.

(8) (a) Kametani, T.; Ihara, M. *J. Chem. Soc., Perkin Trans. I* **1980**, 629–632. (b) Capdevielle, P.; Sparfel, D.; Baranne-Lafont, J.; Cuong, N. K.; Maumy, M. *J. Chem. Soc., Chem. Commun.* **1990**, 565–566. (c) Reinaud, O.; Capdevielle, P.; Maumy, M. *J. Chem. Soc., Chem. Commun.* **1990**, 566–568. (d) Reinaud, O.; Capdevielle, P.; Maumy, M. *J. Mol. Catal.* **1991**, *68*, L13–L15. (e) Rousselet, G.; Capdevielle, P.; Maumy, M. *Tetrahedron Lett.* **1995**, *36*, 4999–5002.

(9) (a) Buijs, W.; Comba, P.; Corneli, D.; Pritzkow, H. *J. Organomet. Chem.* **2002**, *641*, 71–80. (b) Comba, P.; Knoppe, S.; Martin, B.; Rajaraman, G.; Rolli, C.; Shapiro, B.; Stork, T. *Chem. Eur. J.* **2008**, *14*, 344–357.

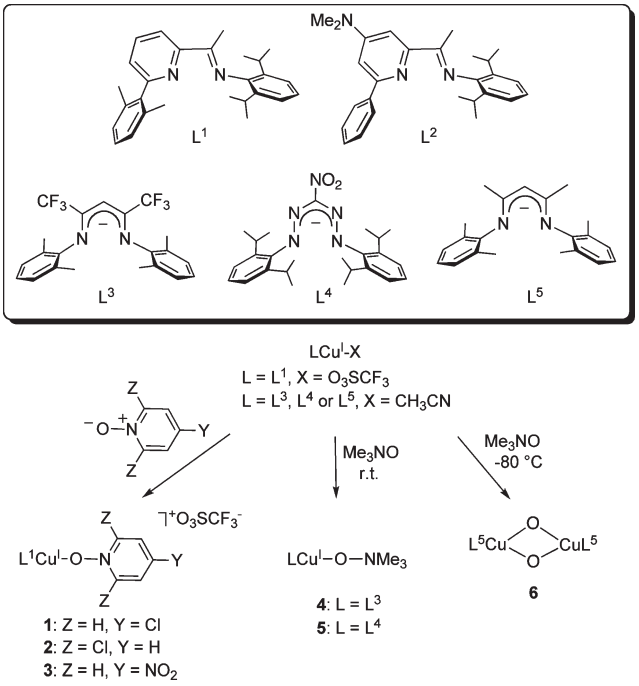
(10) Selected examples: (a) Hatfield, W. E.; Muto, Y.; Jonassen, H. B.; Paschal, J. S. *Inorg. Chem.* **1965**, *4*, 97–99. (b) Richardson, H.; Wasson, J.; Hatfield, W.; Brown, E.; Plasz, A. *Inorg. Chem.* **1976**, *15*, 2916–2920. (c) West, D. X.; Hartley, R. J. *J. Inorg. Nucl. Chem.* **1981**, *43*, 957–961. (d) Carlin, R. L.; De Jongh, L. J. *Chem. Rev.* **1986**, *86*, 659–680. (e) Shi, J.-M.; Chen, J.-N.; Wu, C.-J.; Liu, L.-D. *Acta Crystallogr. E* **2005**, *61*, m2621–m2622. (f) van Albada, G. A.; Mutikainen, I.; Turpeinen, U.; Reedijk, J. *Inorg. Chem. Commun.* **2006**, *9*, 441–443.

(11) Selected examples: (a) Shin, K.; Goff, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 3140–3142. (b) Nee, M. W.; Bruice, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 6123–6125. (c) Ostovic, D.; Knobler, C. B.; Bruice, T. C. *J. Am. Chem. Soc.* **1987**, *109*, 3444–3451. (d) Rowe, G. T.; Rybak-Akimova, E. V.; Caradonna, J. P. *Inorg. Chem.* **2007**, *46*, 10594–10606.

(12) Gross, Z.; Ini, S. *Inorg. Chem.* **1999**, *38*, 1446–1449.

Published on Web 05/08/2009

Scheme 1. Reactions of Copper(I) Complexes with Pyridine- and Trimethylamine-*N*-oxides



electronic and steric profiles that have been previously used in O_2 reactivity investigations.[6,13] Herein we report the initial results of this study, including the isolation and full characterization of the first examples of copper(I) *N*-oxide complexes, a demonstration of oxo transfer from an *N*-oxide resulting in the formation of a bis(μ-oxo)dicopper core, and ligand oxidation from a related reaction with PhIO.

Reactions of $[(L^1)Cu(O_3SCF_3)]$[6] with substituted pyridine-*N*-oxides (1 equiv) or $[(L)Cu(CH_3CN)]$ (L = L^3 or L^4)[13,14] with Me_3NO (1 equiv) in tetrahydrofuran (THF) yielded the adducts **1**−**5**, respectively (Scheme 1). The products were isolated as red-brown crystalline solids in good yields (67−95%) and were characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, CHN analysis, and X-ray crystallography (Figures 1 and S1−S3 in the Supporting Information). All of the structures feature three-coordinate Cu^I ions and "bent" coordination of the *N*-oxide ligands (Cu−O−N angles 120−122°). Little "activation" of *N*-oxide is evident from the N−O distances, which for **1**−**3** (1.33−1.34 Å) are similar to those seen in copper(II) pyridine-*N*-oxide complexes[10e,10f] and for **4** and **5** (1.40−1.41 Å) are similar to that of free Me_3NO [1.404(5) Å].[15] The pyridine-*N*-oxide ring planes in **1**−**3** are parallel to the dimethylphenyl substituent in L^1, consistent with π-stacking interactions. In solution, however, the pyridine-*N*-oxides undergo rapid fluxional processes, as indicated by the presence of broad peaks in the room temperature ^1H NMR spectra that were found in the case of **3** to split and sharpen upon cooling to −78 °C (Figure S4 in the Supporting Information). Complexes **1**−**3** are quite stable in solution,

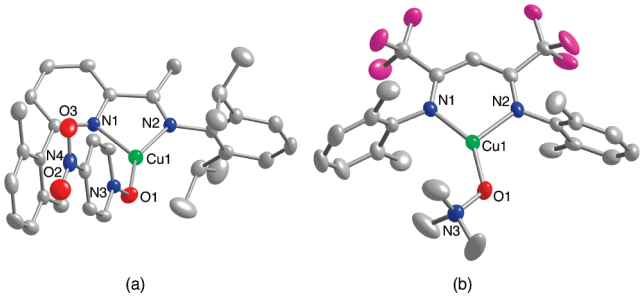


Figure 1. Representations of the X-ray structures of (a) the cationic portion of **3** and (b) **4**, showing all non-H atoms as 50% thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows. **3**: Cu1−O1, 1.9048(19); Cu1−N1, 2.066(2); Cu1−N2, 1.993(2); O1−N3, 1.330(3); O1−Cu1−N2, 150.42(9); O1−Cu1−N1, 128.78(9); N2−Cu1−N1, 80.66 (9); N3−O1−Cu1, 121.96(16). **4**: Cu1−O1, 1.9076(18); Cu1−N1, 1.941 (2); Cu1−N2, 2.001(2); N3−O1, 1.407(3); O1−Cu1−N1, 143.82(8); O1−Cu1−N2, 117.59(8); N1−Cu1−N2, 98.58(8); N3−O1−Cu1, 121.94(14).

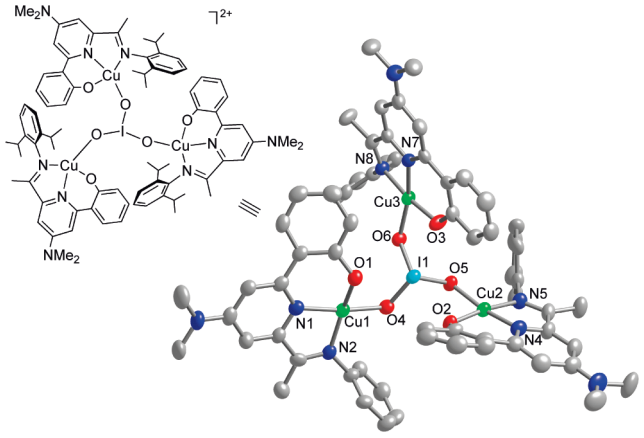


Figure 2. Drawing and representation of the X-ray crystal structure of the dicationic portion of the tricopper cluster resulting from the reaction of $[(L^2)Cu(CH_3CN)](O_3SCF_3)$ with PhIO, with ligand iPr groups omitted for clarity. Selected interatomic distances (Å) and angles (deg) are as follows: I1−O4, 1.814(5); I1−O5, 1.825(4); I1−O6, 1.829(5); Cu1−O1, 1.897(5); Cu1−N1, 1.921(6); Cu1−O4, 1.934(5); Cu1−N2, 1.971(6); Cu2−O2, 1.870(5); Cu2−N4, 1.918(6); Cu2−O5, 1.940(5); Cu2−N5, 1.961(6); Cu3−O3, 1.868(5); Cu3−N7, 1.928(6); Cu3−O6, 1.947(5); Cu3−N8, 1.968(5); O4−I1−O5, 97.7(2); O4−I1−O6, 98.9(2); O5−I1−O6, 96.1(2); O1−Cu1−N1, 93.5(2); O1−Cu1−O4, 89.0(2); N1−Cu1−O4, 168.4(2); O1−Cu1−N2, 163.3(2); N1−Cu1−N2, 83.3(3); O4−Cu1−N2, 97.4(2); O2−Cu2−N4, 93.8(2); O2−Cu2−O5, 87.7(2); N4−Cu2−O5, 170.1(2); O2−Cu2−N5, 172.4(2); N4−Cu2−N5, 83.6(3); O5−Cu2−N5, 96.0(2); O3−Cu3−N7, 93.6(2); O3−Cu3−O6, 87.2(2); N7−Cu3−O6, 166.5(2); O3−Cu3−N8, 172.6(2); N7−Cu3−N8, 83.8(2); O6−Cu3−N8, 96.9(2).

showing no signs of decay by NMR spectroscopy in a THF-d_8 solution after 1 day at 80 °C (sealed tubes). Under the same conditions, complexes **4** and **5** decompose to paramagnetic species that have yet to be identified.

Working under the hypothesis that the stability of **1**−**3** is due to a relatively low degree of electron donation from the ligand L^1, we turned our attention to an analogue of L^1 containing an electron-donating *p*-Me_2N group on the pyridyl ring (L^2). Unfortunately, the reaction of $[(L^2)Cu(CH_3CN)](O_3SCF_3)$ with Me_3NO resulted in extensive ligand redistribution and redox processes, as indicated by the formation of a complex mixture of products, including the known complex $[Cu(Me_3NO)_4]^{2+}$[16] and $[(L^2)_2Cu](O_3SCF_3)$

(13) Hong, S.; Hill, L. M. R.; Gupta, A. K.; Naab, B. D.; Gilroy, J. B.; Hicks, R. G.; Cramer, C. J.; Tolman, W. B., *Inorg. Chem.* **2009**, in press (DOI: 10.1021/ic9002466).

(14) (a) Gilroy, J. B.; Otieno, P. O.; Ferguson, M. J.; McDonald, R.; Hicks, R. G. *Inorg. Chem.* **2008**, *47*, 1279–1286. (b) Gilroy, J. B.; Patrick, B. O.; McDonald, R.; Hicks, R. G. *Inorg. Chem.* **2008**, *47*, 1287–1294.

(15) Caron, A.; Palenik, G. J.; Goldish, E.; Donohue, J. *Acta Crystallogr.* **1964**, *17*, 102–108.

(16) Drago, R. S.; Donoghue, J. T.; Herlocker, D. W. *Inorg. Chem.* **1965**, *4*, 836–839.

(identified by X-ray crystallography; Figure S5 in the Supporting Information). By using PhIO instead, oxo transfer was observed, yielding a dicationic tricopper cluster (with two $CF_3SO_3^-$ counterions) featuring hydroxylated forms of L^2 coordinated to four-coordinate Cu^{II} ions bridged by a central IO_3^- ion (Figure 2; 57% isolated yield, also characterized by CHN analysis and electrospray ionization mass spectrometry; Figure S6 in the Supporting Information). While the overall structure of this cluster is unique, the observation of ligand aryl group hydroxylation by PhIO has parallels in the literature[5] and similarly may be attributed to a $[CuO]^+$ intermediate or some type of CuOIPh species.

In contrast to the formation of stable $Cu^{I}ONMe_3$ adducts when using L^3 and L^4, the copper(I) complex of the more electron-donating ligand L^5 reacted rapidly with Me_3NO at room temperature to give a brown solution, from which a few crystals of the known[17] complex $[(L^5)_2Cu_2(\mu\text{-}OH)_2]$ were obtained; no $Cu^{I}ONMe_3$ adduct was observed. When the reaction was performed at −78 °C, smooth conversion to an intermediate occurred over ∼1 h that was identified as the bis(μ-oxo)dicopper complex $[(L^5)_2Cu_2(\mu\text{-}O)_2]$ (**6**) on the basis of a comparison of its UV−vis (λ_{max} = 423 nm, $\varepsilon \sim 16\,000$ cm^{-1} M^{-1}) and resonance Raman [$\nu(Cu_2O_2)$ = 608 cm^{-1}, λ_{ex} = 457.9 nm] spectroscopic properties to a sample prepared independently from O_2 and to data in the literature[18] (Figure S7 in the Supporting Information). To our knowledge, this is the first report of a bis(μ-oxo) dicopper complex derived from an oxo transfer reagent.[5,19] An adduct akin to **4** and **5** is a likely intermediate in the reaction. It is tempting to speculate that the $[Cu_2(\mu\text{-}O)_2]^{2+}$ core is formed via dimerization of a $[CuO]^+$ species, but we recognize that other routes are equally viable, such as ones involving dimerization of $Cu^{I}ONMe_3$ adducts prior to O−N bond cleavage.

In conclusion, explorations of the reactivity of copper(I) complexes of ligands L^1 and L^3-L^5 with pyridine- and trimethylamine-*N*-oxides have led to (a) the isolation of novel, stable copper(I) *N*-oxide adducts for L^1, L^3, and L^4 and (b) the observation of oxo transfer to the copper(I) complex of L^5 to yield a bis(μ-oxo)dicopper core. Reaction of the copper(I) complex of L^2 with PhIO yields a unique tricopper cluster derived from aryl substituent hydroxylation. The processes of copper(I) *N*-oxide adduct formation, arene hydroxylation, and oxo transfer to yield a $[Cu_2(\mu\text{-}O)_2]^{2+}$ core that we have observed provide important precedence for possible steps in the mechanisms of Cu/O-mediated reactions.

Acknowledgment. We thank Joe B. Gilroy and Robin G. Hicks for providing a sample of ligand L^4, L. Que, Jr., for access to the resonance Raman facility, and the NIH (Grant GM47365 to W.B.T.) for financial support of this research.

Supporting Information Available: Experimental details, Figures S1−S7, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

(17) Dai, X.; Warren, T. H. *Chem. Commun.* **2001**, 1998–1999.

(18) Spencer, D. J. E.; Reynolds, A. M.; Holland, P. L.; Jazdzewski, B. A.; Duboc-Toia, C.; Pape, L. L.; Yokota, S.; Tachi, Y.; Itoh, S.; Tolman, W. B. *Inorg. Chem.* **2002**, *41*, 6307–6321.

(19) Reactions of PhIO with copper(I) complexes that yield other types of products have been reported. See, for example: (a) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitagawa, T.; Morooka, Y. *J. Am. Chem. Soc.* **1991**, *113*, 5664–5671. (b) Obias, H.; Lin, Y.; Murthy, N.; Pidcock, E.; Solomon, E.; Ralle, M.; Blackburn, N.; Neuhold, Y.; Zuberbühler, A.; Karlin, K. *J. Am. Chem. Soc.* **1998**, *120*, 12960–12961. (c) Franklin, C.; Vanatta, R.; Tai, A.; Valentine, J. *J. Am. Chem. Soc.* **1984**, *106*, 814–816.