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

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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

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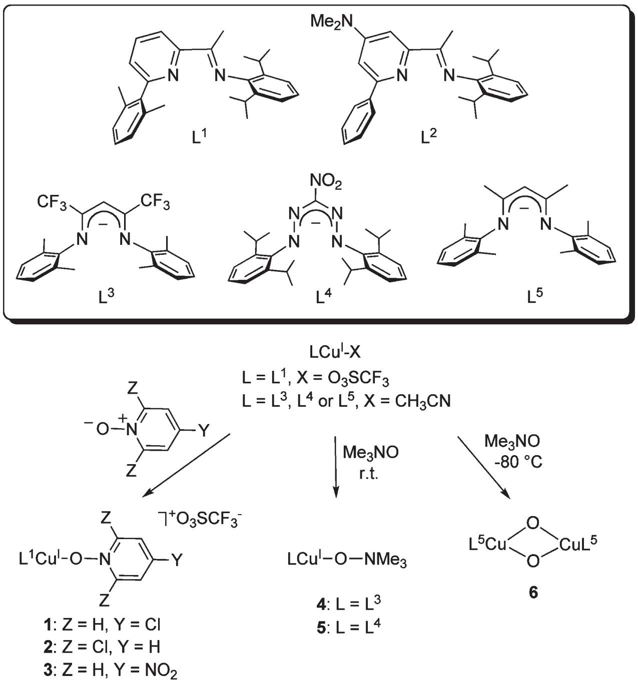
Scheme 1. Reactions of Copper(I) Complexes with Pyridine- and Trimethylamine-*N*-oxides



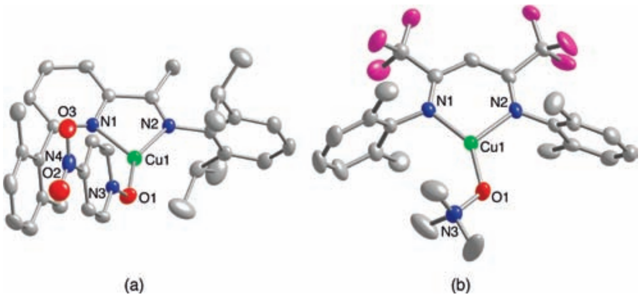


Figure 1. Representations of the X-ray structures of (a) the cationic portion of **3** and (b) **4**, showing all non-H atoms as 50% thermal ellipsoids. Selected interatomic distances (Å) and angles (deg) are as follows. **3**: Cu1−O1, 1.9048(19); Cu1−N1, 2.066(2); Cu1−N2, 1.993(2); O1−N3, 1.330(3); 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).

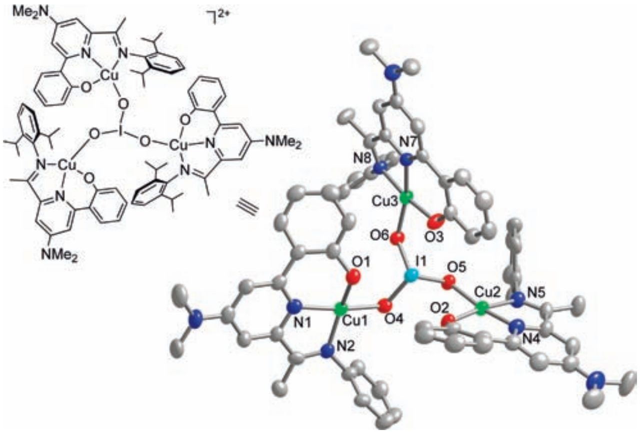


Figure 2. Drawing and representation of the X-ray crystal structure of the dicationic portion of the tricopper cluster resulting from the reaction of [(L^2)Cu(CH_3CN)](O_3SCF_3) with PhIO, with ligand iPr groups omitted for clarity. Selected interatomic distances (Å) and angles (deg) are as follows: 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).

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, 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)

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(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^IONMe_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^IONMe_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^IONMe_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.

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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.

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