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

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Abstract

Reactions of Cu(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 Cu(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 biology¹ and catalysis, a great effort has been expended to uncover mechanistic information and, in particular, to identify possible copper-oxygen intermediates.³ Of notable interest are $[\text{CuO}]^+$ species ($\text{Cu(III)-O}^{2-} \leftrightarrow \text{Cu(II)-O}^{\bullet}$), which have been invoked in catalysis by enzymes⁴ and synthetic systems⁵⁻⁶ and characterized by theory^{4b-d,7} and in the gas phase.^{7b} For example, ligand-supported $[\text{CuO}]^+$ species have been postulated in order to rationalize ligand hydroxylations observed in the decay of Cu(II)-OOH complexes,⁵ the O₂-induced decarboxylation of Cu(I)- α -ketocarboxylates,⁶ and reactions of Cu(I) complexes with iodosylbenzene (PhIO).⁵ A $[\text{CuO}]^+$ intermediate has also been invoked as the active species responsible for regiospecific arene hydroxylations by Cu/Me₃NO systems,⁸ via a mechanism proposed on the basis of theory to involve O-N bond homolysis from an isolated Cu(II)-ONMe₃ complex.⁹ While a number of such Cu(II)-N-oxide complexes are known,¹⁰ to our knowledge Cu(I) variants have not been reported. Such Cu(I)-N-oxide adducts are of interest because they might provide a $[\text{CuO}]^+$ 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. Fe¹¹ and Ru¹²). We therefore sought to investigate the reactions of pyridine- and trialkylamine-N-oxides with Cu(I) complexes, using a range of supporting ligands with variable electronic and steric profiles that have been previously used in O₂ reactivity investigations.^{6,13} Herein we report initial results of this study, including the isolation and full characterization of the first examples of Cu(I)-N-oxide complexes, 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 iodosylbenzene (PhIO).

Reactions of $[(\text{L}^1)\text{Cu}(\text{O}_3\text{SCF}_3)]^6$ with substituted pyridine-N-oxides (1 equiv) or $[(\text{L})\text{Cu}(\text{CH}_3\text{CN})]$ ($\text{L} = \text{L}^3$ or L^4)^{13,14} with Me₃NO (1 equiv) in 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 ¹³C{¹H} NMR spectroscopy, CHN analysis, and X-ray crystallography (Figures 1 and S1–S3). All the structures feature 3-coordinate Cu(I) ions and ‘bent’ coordination of the N-oxide ligands (Cu–O–N angles 120–122°). Little ‘activation’ of the N-oxide is evident from the N–O distances, which for **1–3** (1.33–1.34 Å) are similar to those seen in Cu(II)-pyridine-N-oxide complexes,^{10e,f} and for

4 and **5** (1.40–1.41 Å) are similar to that of free Me₃NO (1.404(5) Å).¹⁵ The pyridine-N-oxide ring planes in **1–3** are parallel to the dimethylphenyl substituent in L¹, 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). Complexes **1–3** are quite stable in solution, showing no signs of decay by NMR spectroscopy in THF-*d*₈ solution after 1 d 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 L¹, we turned our attention to an analog of L¹ containing an electron donating *p*-Me₂N- group on the pyridyl ring (L²). Unfortunately, reaction of [(L²)Cu(CH₃CN)](O₃SCF₃) with Me₃NO resulted in extensive ligand redistribution and redox processes as indicated by the formation of a complex mixture of products, including the known complex [Cu(Me₃NO)₄]²⁺¹⁶ and [(L²)₂Cu](O₃SCF₃) (identified by X-ray crystallography; Figure S5). By using PhIO instead, oxo transfer was observed, yielding a dicationic tricopper cluster (with two CF₃SO₃[–] counterions) featuring hydroxylated forms of L² coordinated to 4-coordinate Cu(II) ions bridged by a central IO₃[–] ion (Figure 2; 57% isolated yield, also characterized by CHN analysis and ESIMS; Figure S6). 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)-ONMe₃ adducts when using L³ and L⁴, the Cu(I) complex of the more electron donating ligand L⁵ reacted rapidly with Me₃NO at room temperature to give a brown solution, from which a few crystals of the known¹⁷ complex [(L⁵)₂Cu₂(μ-OH)₂] were obtained; no Cu(I)-ONMe₃ 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 [(L⁵)₂Cu₂(μ-O)₂] (**6**) on the basis of comparison of its UV-vis (λ_{max} = 423 nm, ε ~ 16,000 cm^{–1}M^{–1}) and resonance Raman (ν(Cu₂O₂) = 608 cm^{–1}, λ_{ex} = 457.9 nm) spectroscopic properties to a sample prepared independently from O₂ and to data in the literature¹⁸ (Figure S7). 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 [Cu₂(μ-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)-ONMe₃ adducts prior to O-N bond cleavage.

In conclusion, explorations of the reactivity of Cu(I) complexes of ligands L¹ and L³–L⁵ with pyridine- and trimethylamine-N-oxides have led to (a) the isolation of novel, stable Cu(I)-N-oxide adducts for L¹, L³, and L⁴, and (b) observation of oxo transfer to the Cu(I) complex of L⁵ to yield a bis(μ-oxo)dicopper core. Reaction of the Cu(I) complex of L² with PhIO yields a unique tricopper cluster derived from aryl substituent hydroxylation. The processes of Cu(I)-N-oxide adduct formation, arene hydroxylation, and oxo transfer to yield a [Cu₂(μ-O)₂]²⁺ core that we have observed provide important precedence for possible steps in mechanisms of Cu/O mediated reactions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Scheme 1.

Reactions of Cu(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 nonhydrogen 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.

A drawing and a representation of the X-ray crystal structure of the dicopper cluster resulting from reaction of $[(L^2)Cu(CH_3CN)](O_3SCF_3)$ with PhIO. 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).