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β-Diketiminate Ligand Backbone Structural Effects on Cu(I)/O$_2$ Reactivity: Unique Copper−Superoxo and Bis(μ-oxo) Complexes

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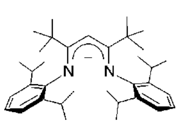
Reactive intermediates derived from the reaction of Cu(I) species and O$_2$ play a central role in many biological and catalytic processes.[1] Delineation of the structures and properties of these intermediates has been addressed through detailed studies of synthetic complexes, which have led to the isolation and characterization of a variety of superoxo, peroxo, and bis(μ-oxo) species.[2] Of particular importance to the involvement of these structures in biology and catalysis are their relative stabilities and interconversion pathways,[3] and understanding how these aspects are influenced by supporting ligand structural features is an important research objective. Herein, we report the results of an exploration of the O$_2$ reactivity of Cu(I) complexes of a set of β-diketiminate anions,[4] which by virtue of their charge and specific steric properties differ from the neutral N-donor ligands that have been more widely used in such studies.[5] Ligands **1**−**3** have identical 2,6-diisopropylphenyl flanking groups, but divergent backbone substituents which, although far removed from the coordinated metal ion, nonetheless significantly impact the course of Cu(I) complex oxygenations and yield novel superoxo or bis(μ-oxo) intermediates.



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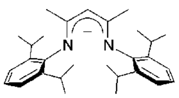

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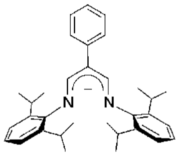

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Reaction of the lithium salts of **1**,[6] **2**,[7] and **3**[8] with [Cu(MeCN)$_4$]CF$_3$SO$_3$ in THF or toluene yielded complexes LCu(MeCN) (Figures 1 and S1). All the complexes display three-coordinate geometries, but subtle differences in the structures suggest disparities in the effective steric bulk imposed by their respective supporting ligands. In (**2**)Cu(MeCN), the ^{i}Pr group methine hydrogen atoms point inward toward the β-diketiminate, in a typical orientation that presumably arises from steric interactions between the backbone α-Me and the ^{i}Pr groups. In contrast, in (**3**)Cu(MeCN) that lacks the α-Me groups, one of the ^{i}Pr groups (bottom left ^{i}Pr in Figure 1b) is rotated by 180° in a unique orientation suggestive of an increased conformational flexibility and, thus, decreased steric encumbrance in **3** relative to **2**. In (**1**)Cu(MeCN) (Figure S1), C$_\alpha$−N−C$_{\text{aryl}}$ angles of 128−129° attest to a canting of the 2,6-diisopropylphenyl flanking groups toward the metal ion due to the α-*tert*-butyl substituents (cf. previously reported Fe complexes of **1**).[9] This drastic steric influence is absent in the complexes of **2** and **3**, which have similar C$_\alpha$−N−C$_{\text{aryl}}$ angles of 116−119°. In sum, the structural data imply an effective steric bulk order **1** > **2** > **3**.

Consistent with this order, treatment of Li(**1**) with CuCl$_2$ yielded three-coordinate (**1**)CuCl with similar spectroscopic properties to that of previously reported (**2**)CuCl,[10] but the same reaction using Li(**3**) formed [(**3**)CuCl]$_n$. This complex adopts a three-coordinate structure in CH$_2$Cl$_2$ (UV−vis, $n = 1$), but exhibits temperature-dependent UV−vis spectra in toluene (Figure S2). In addition, the EPR spectrum (X-band, 4 K, toluene) is quite different from that of (**1** or **2**)CuCl; it contains a broad signal at $g \approx 2$ with hyperfine features in both high- and low-field portions, as well as a signal at $g = 4.4$ attributable to a $\Delta M_S = \pm 2$ transition of a magnetically coupled dicopper system (Figure S3).[11] These combined data for [(**3**)CuCl]$_n$ in toluene indicate an equilibrium between a three-coordinate monomer ($n = 1$, predominant at high temperature) and a chloride-bridged dimer ($n = 2$, preferred at low temperature), and are consistent with **3** exerting less steric hindrance about a coordinated metal ion than **1** or **2**.

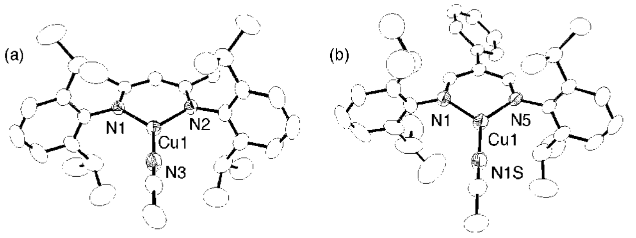

Figure 1. X-ray structures of (a) (**2**)Cu(MeCN) and (b) (**3**)Cu(MeCN), with all nonhydrogen atoms shown as 50% thermal ellipsoids.

Most significantly, these steric differences are manifested in the formation of divergent intermediates upon low-temperature oxygenation of the Cu(I) complexes.[12,13] Treatment of a yellow solution of (**3**)Cu(MeCN) in THF with O$_2$ at −80 °C resulted in a color change to yellow-brown, with new UV−vis spectral features at $\lambda_{\max} \approx 380$ nm ($\epsilon \approx 20\,000$ M^{-1} cm^{-1} per Cu) and ≈ 420 nm (sh, $\epsilon \approx 5000$ M^{-1} cm^{-1}) (Figure S4). The former band is most likely a ligand-based $\pi \rightarrow \pi^*$ transition,[14] while the latter resembles a CT transition exhibited by bis(μ-oxo)dicopper complexes.[3a,15] Consistent with this assignment, the oxygenated THF solution is EPR silent (9.61 GHz, 20 K) and spectrophotometric titration data showed a Cu:O$_2$ stoichiometry of 2.0(2):1. Finally, in resonance Raman spectra ($\lambda_{\text{ex}} = 457.9$ nm, THF, 77 K) the only O-isotope sensitive feature seen was a single peak at 580 cm^{-1} that shifted to 559 cm^{-1} when ^{18}O$_2$ was used (Figure 2a).[15,16] In an alternate synthetic route, addition of 1−5 equiv of a 1:1 solution of H$_2$O$_2$(aq) (31.3%) and Et$_3$N to a solution of [(**3**)CuCl]$_n$ in THF or toluene at −40 °C yielded spectral features similar to those seen upon oxygenation of (**3**)Cu(MeCN). The combined data allow unequivocal identification of the intermediate as [(**3**)$_2$Cu$_2$(μ-O)$_2$], a rare example of a neutral bis(μ-oxo)dicopper complex.[5]

In contrast, oxygenation of (**2**)Cu(MeCN) in THF or acetone at −80 °C resulted in a color change to green, with development of UV−vis features at 385 nm (sh, $\epsilon \approx 2400$ M^{-1} cm^{-1}) and 600 nm

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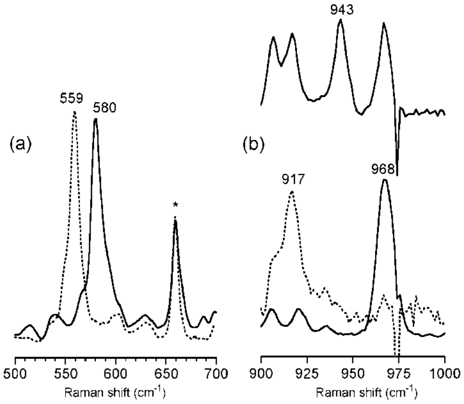

Figure 2. Resonance Raman spectra of oxygenated solutions of (a) (**3**)Cu(MeCN) (($\lambda_{ex} = 457.9$ nm, THF, 77K) and (b) (**2**)Cu(MeCN) ($\lambda_{ex} = 413$ nm, acetone, 77 K). In (a) and (b, bottom) data obtained using $^{16}O_2$ or $^{18}O_2$ are denoted by a solid or a dashed line, respectively. The spectrum in (b, top) was obtained using a mixture of $^{18}O_2$, $^{16}O^{18}O$, and $^{16}O_2$. The * indicates a solvent band.

(br, 200) (Figure S5). This new species is EPR silent and spectrophotometric titration data showed a Cu:O_2 uptake ratio of 1.0(2):1. The resonance Raman spectrum ($\lambda_{ex} = 413$ nm, acetone, 77 K) contained no O-isotope sensitive peaks in the region typical for peroxo or bis(μ-oxo)dicopper complexes (550−850 cm^{-1}). Instead, a peak was observed at 968 cm^{-1} that shifted by 51 cm^{-1} when $^{18}O_2$ was used (Figure 2b, bottom), consistent with an O−O stretch [$\Delta^{18}O_2$(calcd) = 55 cm^{-1}]. When a mixture of $^{18}O_2$, $^{16}O^{18}O$, and $^{16}O_2$ (40% ^{18}O, statistical) was used, a single peak was observed at 943 cm^{-1} with a line width identical to those of the peaks arising from $^{18}O_2$ and $^{16}O_2$ (Figure 2b, top). Similar UV−vis and Raman data were obtained for the product of oxygenation of (**1**)CuMeCN.[17] The combined data are consistent with formulation of the intermediates as unprecedented low-coordinate (superoxo)copper(II) complexes ($LCuO_2$) with symmetric “side-on” (η^2) superoxo ligation.[2,18] The vibrational spectral data are similar to those reported for a structurally characterized Co(η^2-O_2) compound,[19] but differ from the only available data for a Cu complex[20] postulated to contain an end-on superoxo ligand on the basis of the presence of two peaks for $^{16}O^{18}O$.

In sum, despite having identical diisopropylphenyl flanking units, the different backbone substitution patterns in the ligands **1**−**3** result in structural variation among their Cu(I) and Cu(II) complexes and the formation of divergent intermediates in reactions of their Cu(I) complexes with O_2. These intermediates were identified as (superoxo)copper or bis(μ-oxo)dicopper species, the formation of which depends on the steric encumbrance of the supporting β-diketiminate. This tuning of the effective steric bulk at the metal center by the distant backbone substituent arrangement represents a notable ligand structural influence on biologically relevant Cu(I)/O_2 reactivity.[21]

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Supporting Information Available: Text giving synthetic procedures and characterization data, Figures S1−S4 (PDF) and X-ray crystallographic data files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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