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Cu(I)/O₂ Chemistry Using a β -Diketiminato Supporting Ligand Derived from *N,N*-Dimethylhydrazine: A [Cu₃O₂]³⁺ Complex with Novel Reactivity

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Abstract

A Cu(I) complex, LCu(CH₃CN), was prepared and characterized, where L[−] is a sterically unencumbered β -diketiminato ligand, the deprotonated version of 4-(2,2-dimethylhydrazino)dimethylhydrazone-3-penten-2-one (LH). Analysis of FTIR spectra of the products of the reaction of LCu(CH₃CN) with CO indicate that L[−] is strongly electron donating, and support an equilibrium in solution between monomeric and dimeric forms with terminal and bridging CO ligands, respectively. Low temperature oxygenation of LCu(CH₃CN) generated a bis(μ -oxo)tricopper complex with a S = 1 [Cu₃O₂]³⁺ core that was identified on the basis of UV-vis (λ_{max} (ϵ , M^{−1}cm^{−1} per Cu) = 328 (10700), 420 (1500), 590 (835) nm) and X-band EPR spectroscopy (Δm_s = 2 transition at 1500 G), ESI mass spectrometry, and spectrophotometric titration (0.35(2) equivalents of O₂ per copper atom), magnetic susceptibility (μ_{eff} = 2.8(1) BM), and H₂O₂ detection experiments (no H₂O₂ evolved upon acidification). Unlike other reported variants supported by neutral N-donor ligands, L₃Cu₃O₂ is not reduced by ferrocene, does not abstract H-atoms from phenols or 1,2-dihydroanthracene, oxidizes PPh₃ to Ph₃P=O, and generates carbonate species upon exposure to CO₂. This unique reactivity for a [Cu₃O₂]³⁺ complex may be traced to the anionic charge and strong electron donating characteristics of L[−].

Introduction

Studies of the reactions of O₂ with Cu(I) complexes have led to important insights into the nature of possible intermediates in oxidation catalysis.¹ Thus, species with the core structures shown in Chart 1 have been characterized by spectroscopy and, in some cases, by X-ray crystallography, and several of these cores have been identified in biological or other catalytic oxidation systems.² Of the various factors that influence which core forms in oxygenations of Cu(I) complexes, the nature of the supporting ligand is paramount. For example, the monoanionic, strongly electron donating β -diketiminates (e.g., **1–7**, Chart 2) are a well-studied class of ligands³ which yield Cu(I) complexes that are highly reactive with O₂. For the most sterically hindered β -diketiminates (**1–3**) and related anilido-imines, reactions of their Cu(I) complexes with O₂ yield isolable monocopper-peroxo species (**C**, Chart I).^{1e,4,5} Copper(I) complexes of less hindered variants (**6** and **7**) form bis(μ -oxo)dicopper(III) complexes (**F**).⁶ No examples of related isomeric (μ - η^2 : η^2 -peroxo)dicopper(II) compounds (**E**) have been identified with β -diketiminato ligands, presumably because their strong electron donating capabilities stabilize the more oxidized metal centers of the bis(μ -oxo)dicopper(III) core.⁷ Effects of replacing backbone methyl

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Supporting Information Available. Experimental details and spectroscopic data (pdf) and X-ray crystallographic information (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

groups of the β -diketiminate frame with electron withdrawing CF_3 groups (**3–5**) have been evaluated through comparisons of electrochemical data, $\nu(\text{CO})$ values and ^{13}C NMR chemical shifts for CO adducts, and $\text{Cu(I)}/\text{O}_2$ reactivity.^{5,8} The expected effects of CF substitution on spectroscopic properties were observed (e.g., $\nu(\text{CO})$ increase of $\sim 13\text{ cm}^{-1}$ per CF_3 group),⁵ but for **3** and **5** the type of complex formed upon oxygenation of their Cu(I) complexes was the same as for the analogs **1** and **6**, respectively. Finally, it is notable that bis(μ -oxo)tricopper species **H**^{9,10} has not been accessed using β -diketiminate ligands, presumably because even the most unhindered aryl-substituted β -diketiminate are too bulky to allow formation of the compact tricopper cluster.

In an extension of our previous work using ligands **1–7** and congeners,^{1e,4–6,8} we sought to examine a derivative that would be more electron donating and less sterically encumbered. We hypothesized that a Cu(I) complex of a strongly electron donating ligand would be highly reactive with O_2 and other oxidants, and that the small steric profile would allow for the formation of potentially unique multinuclear copper-oxygen species. Herein, we describe the synthesis and characterization of a Cu(I) complex of the deprotonated version of 4-(2,2-dimethylhydrazino)dimethylhydrazone-3-penten-2-one (LH, Figure 1), a ligand precursor used previously to generate volatile group IIA metal complexes for chemical vapor or atom layer deposition experiments.¹¹ The Cu(I) complex $\text{LCu}(\text{CH}_3\text{CN})$ reacts with O_2 at low temperatures to yield a thermally unstable intermediate, which we propose on the basis of spectroscopic and other results containsprecedented core **H**. However, this intermediate is unusual because it has an overall neutral charge, unlike previously reported trications supported by neutral N-donor ligands.^{9,10} This difference underlies new reactivity for the intermediate distinct from that reported previously for complexes with core **H**, thus demonstrating an important effect of the supporting ligand L^- on Cu/O_2 chemistry.

Experimental Section

General Considerations

All solvents and reagents were obtained from commercial sources unless otherwise noted. Solvents were thoroughly degassed via three cycles of freezing, evacuating, and thawing. The solvents THF and d_8 -THF were dried over Na/benzophenone and distilled under vacuum, and CH_2Cl_2 and CH_3CN were dried over CaH_2 and distilled under vacuum; CH_3CN was stored over molecular sieves (4 Å). Acetone was dried over 4 Å molecular sieves, distilled, and stored over sieves (4 Å) in the glove box. Toluene, Et_2O , and pentanes were passed through solvent purification columns (Glass Contour, Laguna, CA) and stored over CaH_2 in the glove box. All metal complexes were prepared and stored in a Vacuum Atmospheres inert atmosphere glove box under dry nitrogen or were manipulated under argon or dry nitrogen using standard Schlenk techniques. The proligand LH was prepared according to literature procedures,¹¹ dried over 4 Å molecular sieves, and distilled under vacuum prior to use.

Physical Methods

NMR spectra were recorded on either Varian VI-300, VXR-300, or VI-500 spectrometers at room temperature unless indicated otherwise. Chemical shifts (δ) for ^1H and ^{13}C NMR spectra were referenced to residual protium in the deuterated solvent (^1H) or the characteristic solvent resonances of the solvent nuclei (^{13}C). Variable temperature ^1H NMR spectra were obtained on a Varian VI-300 spectrometer fitted with a liquid nitrogen cryostat. Stem coaxial inserts used for Evans method experiments were purchased from Wilmad Lab Glass. UV-vis spectra were collected on a HP8453 (190–1000 nm) diode array spectrophotometer. Low temperature UV-vis experiments were performed using an Unisoku low temperature UV-vis cell holder. UV-vis spectra that had drifting baselines due to minor

frosting caused by the low-temperature device were corrected when necessary by subtracting the average of a region with no absorbance from the entire spectrum. X-band electron paramagnetic resonance (EPR) spectra were recorded on a Bruker E-500 spectrometer with an Oxford Instruments EPR-10 liquid-helium cryostat (4–x20 K, 9.61 GHz). Elemental analysis was performed by Robertson Microlit Lab (Madison, NJ). Electrospray ionization mass spectrometry (ESI-MS) was performed on a Bruker BioTOF II instrument with high-resolution data acquired by internally referencing samples to a polyethylene glycol standard. All GC-MS experiments were conducted on an Agilent Technologies 7890A GC system and 5975C VL MSD. The GC column was a HP-5ms with dimensions 30 m × 0.250 mm. The standard method used for all runs involved an initial oven temperature of 60 °C (held for 4 min) followed by a 20 °C/min ramp to 230 °C that was held for 15 min. Infrared spectra were collected on a Nicolet Avatar 370 FT-IR equipped with an attenuated total reflectance attachment, using a CaF₂ solution cell (International Crystal Laboratories) or a Smart OMNI-Sampler for solid samples.

LCu(CH₃CN)

LH (145 mg, 0.79 mmol) was dissolved in CH₃CN (5 mL) and added to a slurry of Cu₄Mes₄ (142 mg, 0.19 mmol) in THF (5 mL). The cloudy solution became clear over 20 min yielding a golden solution. After stirring for 2 h the solution became dark brown with a brown precipitate. The solution was filtered and solvent removed *in vacuo* yielding a brown residue. The residue was dissolved in approximately 2 mL of fresh THF and cooled to –20 °C. Addition of pentanes to this solution resulted in the rapid formation of yellow needle crystals of product that were isolated by vacuum filtration (128 mg, 66%). ¹H NMR (*d*₈-THF, 300 MHz, –80 °C): δ 2.89 (s, 1H), 2.46 (s, 3H), 2.28 (s, 12 H), 1.91 (s, 6H). ¹³C{¹H} NMR (75.0 MHz, *d*₈-THF): δ 165.1, 121.95, 86.37, 49.53, 21.84, 2.36. Anal. Calc. for C₉H₁₉CuN₄ (LCu; the CH₃CN ligand was lost upon drying of the crystals under vacuum prior to analysis): C, 43.80; H, 7.76; N, 22.70. Found: C, 42.73; H, 7.37; N, 22.43.

Reaction of LCu(CH₃CN) with CO

A 5 mL Schlenk flask was charged with a 40 mM solution of LCu(NCCH₃) in THF and sealed by a septum. Carbon monoxide was bubbled through the solution at room temperature until all solvent had evaporated, leaving a solid residue. Samples of this residue were transferred by spatula to the FTIR spectrometer and infrared spectra collected on an attenuated total reflectance attachment. For characterization in solution, THF was added to the residue under an inert atmosphere to obtain a concentration of approximately 40 mM, and the solution was loaded and sealed in a CaF₂ solution cell (International Crystal Laboratories) for analysis by FTIR spectroscopy.

Low Temperature Oxygenations of LCu(CH₃CN)

Anaerobically prepared solutions of LCu(CH₃CN) in THF or acetone (1 mM or 0.1 mM) were cooled to –80 °C in a septum sealed quartz cuvette under a constant argon purge. Dry O₂ was bubbled through the cooled solutions and the reaction was monitored by UV-vis spectroscopy. **(a) Spectrophotometric Titrations.** In titration experiments, a 3.5 mL solution of LCu(CH₃CN) in THF (1 mM) was placed in a 1 cm path length cuvette and cooled to –80 °C under an argon atmosphere. An O₂ saturated THF solution was prepared by bubbling dry O₂ through argon saturated THF for 20 min.¹² Aliquots (70 μL) of the THF solution were transferred by gastight syringe to the cuvette and the sample allowed to equilibrate under stirring. The absorption band at 590 nm was monitored by UV-vis spectroscopy. **(b) EPR Spectroscopy.** Solutions for examination by parallel X-band EPR spectroscopy were prepared by first charging a 5 mL Schlenk flask with LCu(CH₃CN) in THF (60 mM) to obtain a 20 mM final concentration of the putative product L₃Cu₃O₂. The flask was sealed with a septum and cooled to –78 °C in a dry ice/acetone bath under argon.

Dry O₂ was bubbled through the solution for 10 min followed by 45 min of an argon purge to remove excess O₂. Samples were transferred to precooled EPR tubes taking care to avoid any bubbles and rapidly frozen in liquid N₂ and stored for analysis. Samples were examined with the spectrometer set in the parallel mode (9.3970 GHz) at a temperature of 13 K. (c) **ESI-MS Analysis.** A 5 mL Schlenk flask was charged with a 1 mM solution of LCu(CH₃CN) and cooled to -78 °C under argon in a dry ice/acetone bath. Dry O₂ was bubbled through the solution for 10 min followed by 20 min of an argon purge. An aliquot (40 µL) of the dark green solution was rapidly loaded into 100 µL gastight syringe followed by 40 µL of fresh methanol and the sample directly injected into the spectrometer while continuously collecting spectra in the positive ion detection mode. As the deep green portion entered the instrument the peaks of interest were observed and became more intense. Samples prepared from PhIO were prepared by placing 1 equiv. PhIO in a 5 mL Schlenk flask with THF (3.2 mL) and a stir bar. After sealing with a septum, the heterogeneous mixture was cooled to -78 °C in a dry ice/acetone bath under argon. A solution of LCu(CH₃CN) in THF was added this mixture by gastight syringe to yield a final copper concentration of 1 mM in the flask. The solution was stirred for 5 h at -78 °C. The insoluble solids were removed by rapidly passing the solution through a 0.45 µm PTFE filter into a precooled 5 mL Schlenk flask. This process caused an instantaneous color change in the solution from deep green to a pale gold/green, and no peaks in the ESI-MS spectrum were assignable to L₃Cu₃O₂. (d) **Evans Method Determination of Magnetic Susceptibility.** A stock solution of LCu(CH₃CN) (38.4 mg, 0.133 mmol) and 1,3,5-trimethoxybenzene (22.4 mg, 0.133 mmol) in *d*₈-THF (2.5 mL) was prepared in the glove box. An aliquot of the stock solution (0.6 mL) was sealed in an NMR tube by a septum and cooled to -78 °C in a dry ice/acetone bath under a positive argon atmosphere. The solution was oxygenated by bubbling dry O₂ through the solution for 5 min followed by an argon purge (15 min) to remove excess O₂. A separate stock solution of 1,3,5-trimethoxybenzene (22.5 mg, 0.134 mmol) in *d*₈-THF (2.5 mL) was prepared and loaded into a coaxial NMR insert and sealed in the glove box. The insert was placed into the NMR tube containing the oxygenated solution and the ¹H NMR spectrum obtained of the combined apparatus at -80 °C.

Photometric H₂O₂ Detection with Ti(IV)Oxysulfate

A stock solution of aqueous H₂O₂ (1.96 mM) was prepared from a H₂O₂ solution (30% in H₂O) and serially diluted to known concentrations (0.899, 0.448, and 0.268 mM). Aliquots from the H₂O₂ solution (3 mL) were loaded into a UV-vis cuvette and 0.1 mL of Ti(IV)oxysulfate added (15% in dilute sulfuric acid). The UV-vis spectra of the solutions were recorded and the absorbance at λ_{max} = 408 nm recorded and plotted against the concentration of H₂O₂ to obtain a standard curve. This standard curve was used to detect and/or quantitate peroxide species derived from Cu/O₂ reactions as described in the literature.¹³ To validate the method, a solution of [(TMPA)Cu(NCCH₃)]OTf in THF (22 mM) at -78 °C was oxygenated for 20 min, which resulted in the formation of a characteristic purple solution for [(TMPA)₂Cu₂O₂]²⁺.¹⁴ Formic acid (2.4 equivalents per dicopper species) was added and the solution warmed to room temperature. Addition of Ti(IV)oxysulfate and quantification of the chromophore observed at λ_{max} = 408 nm to a standard curve showed the recovery of 79% of the expected amount of H₂O₂ (Figure S1). An identical procedure was used to evaluate the blue/green species resulting from oxygenation of LCu(CH₃CN), and in this case no absorbance at 408 nm was observed, indicating no formation of H₂O₂ (Figure S2).

Reactions of Oxygenated Product with Exogenous Substrates

Solutions of L₃Cu₃O₂ in 3.5 mL of THF (1 mM) were generated as described above. After complete formation of L₃Cu₃O₂ as determined by UV-vis spectroscopy, samples were purged for 20 min with argon. Substrates were introduced as THF solutions by syringe

(9,10-dihydroanthracene, 2,6-di-*tert*-butylphenol, 2,4,6-tri-*tert*-butylphenol, 2,4-di-*tert*-butylphenol, ferrocene, triphenylphosphine), added as a 30% by weight in water solution (H_2O_2), or bubbled through the reaction as a gas (CO_2). Reactions were monitored by UV-vis spectroscopy for 2 h and then warmed to room temperature and analyzed by GC-MS. Samples for GC-MS analysis were demetallated by the following steps. Solvent was removed under vacuum and the remaining residue dissolved in CH_2Cl_2 (~5 mL). The solution was washed with dilute aqueous HCl (3×5 mL of 0.1 M HCl). The organic layer was dried over K_2CO_3 , filtered, and injected into the GC-MS instrument.

Results and Discussion

Synthesis and Characterization of $\text{LCu}(\text{CH}_3\text{CN})$

Reaction of LH with Cu_4Mes_4 in $\text{CH}_3\text{CN}/\text{THF}$ (1:1 v/v) generated $\text{LCu}(\text{CH}_3\text{CN})$, which was isolated as a crystalline solid in 66% yield and characterized by NMR spectroscopy, CHN analysis, and X-ray crystallography (Figure 1). The anticipated peaks were observed in the room temperature ^1H NMR spectrum of the complex in d_8 -THF (Figure S3), although the signal for the hydrogen atoms on the CH_3CN ligand overlap with those for the $-\text{NMe}_2$ groups of L^- (2.32 ppm). These peaks were resolved in a spectrum recorded at -80°C , suggesting lability of the CH_3CN group or an ill-defined fluxional process in solution. In support of the former possibility, extended drying of the crystals of the complex under vacuum resulted in loss of the CH_3CN ligand (CHN analysis). Air-sensitive crystals of the complex suitable for X-ray diffraction analysis were obtained from THF/pentanes solutions kept at -80°C (Figure 1). Similar to other reported Cu(I) complexes of β -diketiminates,^{1e,4–6,8} $\text{LCu}(\text{CH}_3\text{CN})$ contains a 3-coordinate Cu ion in a trigonal planar geometry (sum of donor angles = 360°) ligated by two nitrogen atoms from L^- and one nitrogen from bound CH_3CN . The structural parameters of L^- are similar to those reported for η^2 -bound complexes of group IIA metals (cf. N–N distances of 1.45–1.46 Å, N-methyl groups splayed away from the diketiminate backbone substituents).

To evaluate the electron donating characteristics of L^- , we examined the reaction of $\text{LCu}(\text{CH}_3\text{CN})$ with CO with the aim of preparing a simple CO adduct and comparing its $\nu(\text{CO})$ value to those reported for Cu(I)–CO complexes (Table 1).^{5,8, 15–26} Thus, solutions of $\text{LCu}(\text{CH}_3\text{CN})$ in THF were treated with CO (1 atm) and examined by FTIR spectroscopy, both in solution and, after removal of THF, in the solid state (Figure 2). The solid-state sample (solid line) displays a single sharp peak at 2047 cm^{-1} consistent with formation of $\text{LCu}(\text{CO})$. This feature is lower in energy than reported $\nu(\text{CO})$ values for CO bound in terminal fashion to Cu(I) centers in a variety of ligand environments, including complexes supported by other β -diketiminates (Table 1, entries 9–18). The data thus demonstrate the exceptionally strong electron donating properties of L^- .

The solution state spectrum (dotted line, Figure 2) displays two peaks at 2056 and 1968 cm^{-1} , indicating either (a) binding of two CO molecules to the $\text{LCu}(\text{I})$ moiety to yield $\text{LCu}(\text{CO})_2$, or (b) the presence of two types of CO adducts, possibly in equilibrium. Rationale (a) seems unlikely because while several $[\text{Cu}(\text{CO})_2]^+$ species have been reported (cf. entry 2, Table 1),^{16,27–31} they display $\nu(\text{CO})$ values higher in energy than free CO (2143 cm^{-1}) due to competition between the multiple CO ligands for dp electron density at the metal center.²⁷ In support of rationale (b), equilibria between Cu(I) species with bridging or terminal CO ligands (Figure 3) have been described for complexes supported by bidentate peralkylated diamines, which exhibit a pattern of $\nu(\text{CO})$ values similar to that which we observe (entries 4–6, Table 1).¹⁸ We deem it likely that a similar equilibrium occurs for our system, with the caveat that we have not performed more extensive characterization to support this hypothesis unambiguously. An alternative hypothesis reported recently¹⁷ for tris(methylpyridyl)amine (TMPA) complexes involving adducts with a ligand arm either

bound or dissociated (entry 3, Table 1) would seem less likely for L^- , as dissociation of one donor in a β -diketiminato complex of copper has yet to be observed.³²

O₂ Reactivity

Oxygenation of $LCu(NCCH_3)$ in THF or acetone at $-80\text{ }^\circ\text{C}$ resulted in a rapid color change of the solution from pale yellow to deep blue/green. This color remained unchanged at low temperature for many hours, but bleached upon warming, with an approximate half-life of 1 h at $-10\text{ }^\circ\text{C}$ (Figure S4). Attempts to isolate the blue/green species as a pure solid were unsuccessful, so characterization in solution was pursued. UV-vis spectra measured for the oxygenation (1 mM Cu(I), THF, $-80\text{ }^\circ\text{C}$, using 1 cm or 0.2 cm path length cells) are presented in Figure 4 with the starting complex (*dashed*), a transient species (*dotted*), and the final oxygenation product shown (*solid*). The transient species (Figure 4, *dotted*) forms instantaneously and gives way to the final blue/green product (Figure 4, *solid*) in seconds; because of its instability, further characterization of the transient species was not possible. The λ_{max} values and extinction coefficients for the blue/green final product are compared to those of $[Cu_3O_2]^{3+}$ species reported previously in Table 2. Despite differences in detail that likely arise from divergent supporting ligand donor characteristics, the overall patterns of the features are roughly similar, consistent with analogous core structures. To test this notion, we sought to determine the nuclearity (Cu:O ratio) of the blue/green product species through a spectrophotometric titration. Aliquots of THF saturated with O₂ (10 mM)³³ were added to a solution of $LCu(NCCH_3)$ in THF (10 mM) at $-80\text{ }^\circ\text{C}$ and the spectral feature at 590 nm was monitored (Figure 5). The absorption feature reached a maximum intensity (intersection of shown best fit lines) at 0.35(2) equivalents of O₂ per copper atom ($\sim 3:2$ Cu:O ratio), consistent with a $[Cu_3O_2]^{3+}$ core.

Further evidence in the favor of the formulation of the blue/green oxygenation product as $L_3Cu_3O_2$ was obtained using electrospray ionization mass spectrometry (ESI-MS). The starting sample solution was kept at $-78\text{ }^\circ\text{C}$ and the sample transfer tube that is typically used to introduce an ESI-MS sample was removed to minimize sample warming/decomposition and maximize the peak intensities of the species of interest. Initial spectra of THF or acetone solutions did not display any signal in either the positive or negative ion detection modes, indicating that no easily ionizable species were present under these conditions. Samples doped with methanol lost their characteristic blue/green color when warmed and displayed a strong peak envelope at $m/z = 429.2640$ in the mass spectrum that we assign on the basis of simulation as an apparent decomposition product $[L_2Cu]^+$ (Figure S5). However, by first loading a 100 μL sample syringe with 40 μL of an acetone solution of the blue/green species (at $-80\text{ }^\circ\text{C}$), followed by 60 μL MeOH, and rapidly injecting the solution into the spectrometer a mass spectrum was obtained with multiple peak envelopes indicative of multicopper species (high m/z region in Figure 6; full spectrum in Figure S6). The highest m/z peak envelopes feature isotope patterns diagnostic for three copper atoms and were identified on the basis of simulations as $L_3Cu_3O_2$ plus variable solvent molecules: $C_{32}H_{68}Cu_3N_{14}O_3 [L_3Cu_3O_2 + MeOH + 2CH_3CN + H^+]^+$ (mass 887.1967; Figure 6) and $C_{34}H_{72}Cu_3N_{13}O_4 [L_3Cu_3O_2 + MeOH + CH_3CN + THF + H^+]^+$ (mass 917.2197; Figure S7). These results support the presence of $L_3Cu_3O_2$ in the blue/green oxygenation product solutions.

Previous work demonstrated that the $[Cu_3O_2]^{3+}$ core contains one Cu(III) and two Cu(II) ions in a valence localized $S = 1$ ground state.^{9,34,35} For comparison, we examined the electronic structure of the blue/green oxygenation product through solution state magnetic susceptibility (Evans method)^{36–39} and EPR spectroscopy measurements. In the Evans method experiment, a 54 mM solution of $LCu(NCCH_3)$ was oxygenated in d_8 -THF at $-78\text{ }^\circ\text{C}$ in the presence of an internal standard 1,3,5-trimethoxybenzene. Comparison of the peak assignable to the aryl proton originating from 1,3,5-trimethoxybenzene appearing between

5–7 ppm for this sample and one for an inserted coaxial tube with only the internal standard provided a peak separation that upon analysis (Figure S8 and associated text in the supporting information) yielded $\mu_{\text{eff}} = 2.8(1)$ BM. This value is indicative of an $S = 1$ ground state ($\mu_{\text{eff}} = 2.83$ BM)⁴⁰ and is in agreement with the value determined via similar methodology for $[(\text{TMCD})_3\text{Cu}_3\text{O}_2]^{3+}$.^{9a}

The parallel mode X-band EPR spectrum of the blue/green product solution is shown in Figure 7 with the $g \sim 4$ region enlarged and shown in the inset. The feature observed at ~ 1500 G is attributed to a $\Delta m_s = 2$ transition and the high field signal at ~ 3300 G is a $\Delta m_s = 1$ transition, consistent with what would be expected for a triplet ground state species.^{35,41} These features are qualitatively similar to those reported previously for $[(\text{TMCD})_3\text{Cu}_3\text{O}_2]^{3+}$, which exhibits a strong derivative feature at 3525 G and a $\Delta m_s = 2$ transition at 1400 G.³⁵

In order to evaluate the possibility that the blue/green species is a peroxide complex, we attempted to detect H_2O_2 after treatment with protic acid using a precedented Ti(IV)oxysulfate titration procedure (see experimental section for details).¹³ We first validated the procedure by testing the known 1,2-peroxide complex $[(\text{TPA})_2\text{Cu}_2\text{O}_2](\text{OTf})_2$,¹⁴ and from the absorbance at 408 nm obtained a 79% yield of the expected amount of H_2O_2 . The same method applied to the blue/green solution derived from oxygenation of $\text{LCu}(\text{CH}_3\text{CN})$ did not display any absorbance at 408 nm, indicating that, within the limits of detection, no H_2O_2 was formed.

In sum, the similarities of the UV-vis spectrum, EPR signal, and magnetic moment in solution to those reported previously for $[\text{Cu}_3\text{O}_2]^{3+}$ complexes, in combination with the spectrophotometric titration, ESI-MS, and H_2O_2 detection results, provide compelling evidence that the oxygenation of $\text{LCu}(\text{CH}_3\text{CN})$ results in the formation of $\text{L}_3\text{Cu}_3\text{O}_2$ featuring core **H** (Figure 1). This complex is novel insofar as it is supported by monoanionic rather than neutral N-donor ligands, resulting in an overall neutral rather than a +3 charge. The implications of this disparity on reactivity with exogenous substrates are explored below.

Reactivity with Exogenous Substrates

The reactions of two $[\text{Cu}_3\text{O}_2]^{3+}$ species supported by either TMCD or $\text{HPy}^{\text{Me,Me}}$ with a few substrates have been described.^{9a,10} The complex supported by TMCD was reduced by ferrocene but not acetylferrocene at -80°C and a redox potential for the complex was estimated to be between 0.48 and 0.79 V vs. SCE.^{9a} Both complexes react with 2,4-di-*tert*-butylphenol via a radical pathway to form the coupled product 3,3',5,5'-tetra-*tert*-butyl-2,2'-biphenol in high yield ($> 97\%$). Thus, they are electrophilic and are capable of performing H-atom abstractions from molecules with relatively weak O-H bonds, similar to their bis(μ -oxo)dicopper(III) relatives.^{1a,b}

For comparison, we examined the reactivity of $\text{L}_3\text{Cu}_3\text{O}_2$ toward reductants (ferrocene, decamethylferrocene) and substrates with weak O-H or C-H bonds (2,4- and 2,6-di-*tert*-butylphenols, 2,4,6-tri-*tert*-butylphenol, and 9,10-dihydroanthracene). In these experiments solutions of $\text{L}_3\text{Cu}_3\text{O}_2$ were generated by the oxygenation of $\text{LCu}(\text{CH}_3\text{CN})$ in THF at -80°C (1 mM) and then purged with argon for approximately 20 min to remove excess O_2 . Substrates were introduced at -80°C and stirred for 2 h while the reactions were monitored by UV-vis spectroscopy. The solutions were then gradually warmed to room temperature, subjected to an acidic workup to remove copper-containing species, and the residue examined by GC-MS or ^1H NMR spectroscopy. Unlike the $[\text{Cu}_3\text{O}_2]^{3+}$ species supported by TMCD or $\text{HPy}^{\text{Me,Me}}$, no reactions occurred with the aforementioned substrates; no decay of the UV-vis spectrum was seen at -80°C and no oxidized organic products were identified by GC-MS or ^1H NMR spectroscopy for the reactions with the phenols or 9,10-

dihydroanthracene. Apparently, $L_3Cu_3O_2$ is not nearly as potent an oxidant nor as electrophilic as the $[Cu_3O_2]^{3+}$ species supported by TMCD or $HPy^{Me,Me}$. Yet, $L_3Cu_3O_2$ was found to be capable of transferring an O-atom to PPh_3 , reactivity typical of electrophilic copper-oxygen complexes.^{1c} Thus, addition of 5 equivalents of PPh_3 at $-80\text{ }^\circ\text{C}$ to solutions of $L_3Cu_3O_2$ followed by warming to room temperature and examination by ^{31}P NMR spectroscopy⁴² and GC-MS led to identification of $Ph_3P=O$ in ~40% yield (based on $L_3Cu_3O_2$). On the other hand, the UV-vis spectroscopic features of $L_3Cu_3O_2$ changed instantaneously upon exposure to CO_2 . Carbonate-containing species formed according to ESI-MS and FT-IR data (Figures S9–S11), although we have been unable to unambiguously identify their structures despite repeated attempts to isolate the products from the reaction. These results are indicative of 'nucleophilic' reactivity, and contrast with the typical reaction patterns for electrophilic copper-oxygen intermediates.^{1c,43} We conclude that the strong electron donating capabilities of L^- stabilize the $[Cu_3O_2]^{3+}$ core and perturb its reactivity relative to other known examples.

Conclusions

A Cu(I) complex of the hydrazine-derived β -diketiminato L^- was prepared and characterized, and the FTIR spectra of the products of its reaction with CO were analyzed. The data indicate that L^- is strongly electron donating, and support an equilibrium in solution between monomeric and dimeric forms with terminal and bridging CO ligands, respectively (Figure 3). Low temperature oxygenation of $LCu(CH_3CN)$ generated a species formulated as $L_3Cu_3O_2$ with core **H** on the basis of UV-vis and EPR spectroscopy, ESI mass spectrometry, and spectrophotometric titration, magnetic susceptibility, and H_2O_2 detection experiments. The observation of a monomer/dimer equilibrium for the Cu(I)-CO adduct and formation of core **H** upon oxygenation attest to the small steric profile of L^- relative to other β -diketiminates (cf. **1–7**) that have been used previously to study Cu/ O_2 chemistry. The anionic charge and strong electron donating characteristics of L^- result in unique reactivity for core **H** in $L_3Cu_3O_2$. Thus, unlike other reported variants supported by neutral N-donor ligands, $L_3Cu_3O_2$ is not reduced by ferrocene, does not abstract H-atoms from phenols or 1,2-dihydroanthracene, oxidizes PPh_3 to $Ph_3P=O$, and generates carbonate species upon exposure to CO_2 . The new reactivity for core **H** that results from the properties of L^- illustrate key influences of supporting ligands on the structure and function of Cu/ O_2 intermediates relevant to copper-catalyzed oxidations in catalysis and biology.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

- (1). (a) Mirica LM, Ottenwaelder X, Stack TDP. *Chem. Rev.* 2004; 104:1013–1045. [PubMed: 14871148] (b) Lewis EA, Tolman WB. *Chem. Rev.* 2004; 104:1047–1076. [PubMed: 14871149] (c) Hatcher L, Karlin KD. *J. Biol. Inorg. Chem.* 2004; 9:669–683. [PubMed: 15311336] (d) Itoh S. *Curr. Opin. Chem. Biol.* 2006; 10:115–122. [PubMed: 16504568] (e) Cramer CJ, Tolman WB. *Acc. Chem. Res.* 2007; 40:601–608. [PubMed: 17458929] (f) Himes RA, Karlin KD. *Curr. Opin. Chem. Biol.* 2009; 13:119–131. [PubMed: 19286415]
- (2). (a) Prigge ST, Eipper BA, Mains RE, Amzel LM. *Science.* 2004; 304:864–867. [PubMed: 15131304] (b) Magnus KA, Ton-That H, Carpenter JE. *Chem. Rev.* 1994; 94:727–735.(c)

- Sánchez-Ferrer A, Rodríguez-López JN, García-Cánovas F, García-Carmona F. *Biochim. Biophys. Acta*. 1995; 1247:1–11. [PubMed: 7873577] (d) Woertink JS, Smeets PJ, Groothaert MH, Vance MA, Sels BF, Schoonheydt RA, Solomon EI. *Proc. Natl. Acad. Sci. USA*. 2009; 106:18908–18913. [PubMed: 19864626] (e) Gamez P, Aubel PG, Driessen WL, Reedijk J. *Chem. Soc. Rev.* 2001; 30:376–385.
- (3). Bourget-Merle L, Lappert MF, Severn JR. *Chem. Rev.* 2002; 102:3031–3065. [PubMed: 12222981]
- (4). (a) Spencer DJE, Aboelella NW, Reynolds AM, Holland PL, Tolman WB. *J. Am. Chem. Soc.* 2002; 124:2108–2809. [PubMed: 11878952] (b) Aboelella NW, Lewis EA, Reynolds AM, Brennessel WW, Cramer CJ, Tolman WB. *J. Am. Chem. Soc.* 2002; 124:10660–10661. [PubMed: 12207513] (c) Aboelella NW, Kryatov SV, Gherman BF, Brennessel WW, Victor G, Young J, Sarangi R, Rybak-Akimova EV, Hodgson KO, Hedman B, Solomon EI, Cramer CJ, Tolman WB. *J. Am. Chem. Soc.* 2004; 126:16896–16911. [PubMed: 15612729] (d) Reynolds AM, Gherman BF, Cramer CJ, Tolman WB. *Inorg. Chem.* 2005; 44:6989–6997. [PubMed: 16180861] (e) Aboelella NW, Gherman BF, Hill LMR, York JT, Holm N, Victor G, Young J, Cramer CJ, Tolman WB. *J. Am. Chem. Soc.* 2006; 128:3445–3458. [PubMed: 16522125]
- (5). Hill LMR, Gherman BF, Aboelella NW, Cramer CJ, Tolman WB. *Dalton Trans.* 2006:4944–4953. [PubMed: 17047744]
- (6). Spencer DJE, Reynolds AM, Holland PL, Jazdzewski BA, Duboc-Toia C, Pape LL, Yokota S, Tachi Y, Itoh S, Tolman WB. *Inorg. Chem.* 2002; 41:6307–6321. [PubMed: 12444774]
- (7). DuBois JL, Mukherjee P, Stack TDP, Hedman B, Solomon EI, Hodgson KO. *J. Am. Chem. Soc.* 2000; 122:5775–5787.
- (8). Hong S, Hill LMR, Gupta AK, Naab BD, Gilroy JB, Hicks RG, Cramer CJ, Tolman WB. *Inorg. Chem.* 2009; 48:4514–4523. [PubMed: 19425614]
- (9). (a) Cole AP, Root DE, Mukherjee P, Solomon EI, Stack TDP. *Science*. 1996; 273:1848–1850. [PubMed: 8791587] (b) Root DE, Henson MJ, Machonkin T, Mukherjee P, Stack TDP, Solomon EI. *J. Am. Chem. Soc.* 1998; 120:4982–4990.
- (10). Taki M, Teramae S, Nagatomo S, Tachiu Y, Kitagawa T, Itoh S, Fukuzumi S. *J. Am. Chem. Soc.* 2002; 124:6367–6377. [PubMed: 12033867]
- (11). (a) Domnin NA, Yakimovich SI. *Zh. Organ. Khim.* 1965; 1:658–666. (b) Sedai B, Heeg MJ, Winter CH. *Organometallics*. 2009; 28:1032–1038. (c) Sedai B, Heeg MJ, Winter CH. *J. Organomet. Chem.* 2008; 693:3495–3503.
- (12). Battino, R., editor. *Oxygen and Ozone*. Vol. 7. 1981. Editor Solubility Data Series
- (13). (a) Halime Z, Kieber-Emmons MT, Qayyum MF, Mondal B, Gandhi T, Pui SC, Chufan EE, Sarjeant AAN, Hodgson KO, Hedman B, Solomon EI, Karlin KD. *Inorg. Chem.* 2010; 49:3629–3645. [PubMed: 20380465] (b) Sanyal I, Strange RW, Blackburn NJ, Karlin KD. *J. Am. Chem. Soc.* 1991; 113:4692–4693. (c) Chaudhuri P, Hess M, Mueller J, Hildenbrand K, Bill E, Weyhermueller T, Wieghardt K. *J. Am. Chem. Soc.* 1999; 121:9599–9610. (d) Eisenberg GM. *Ind. Eng. Chem., Anal. Ed.* 1943; 15:327–328.
- (14). Jacobson RR, Tyeklár Z, Farooq A, Karlin KD, Liu S, Zubieta J. *J. Am. Chem. Soc.* 1988; 110:3690–3692.
- (15). Rack JJ, Webb JD, Strauss SH. *Inorg. Chem.* 1996; 35:277–278. [PubMed: 11666204]
- (16). Zecchina A, Bordiga S, Salvalaggio M, Spoto G, Scarano D, Lamberti C. *J. Catal.* 1998; 173:540–542.
- (17). Fry HC, Lucas HR, Sarjeant AN, Karlin KD, Meyer GJ. *Inorg. Chem.* 2008; 47:241–256. [PubMed: 18052158]
- (18). Pasquali M, Floriani C, Venturi G, Gaetani-Manfredotti A, Chiesi-Villa A. *J. Am. Chem. Soc.* 1982; 104:4092–4099.
- (19). Scott AF, Wilkening LL, Rubin B. *Inorg. Chem.* 1969; 8:2533–2534.
- (20). Lupinetti AJ, Strauss SH, Frenking G. *Prog. Inorg. Chem.* 2001; 49:1–112.
- (21). Dias HVR, Lu H-L. *Inorg. Chem.* 1995; 34:5380–5382.
- (22). Haakansson M, Jagner S. *Inorg. Chem.* 1990; 29:5241–5244.
- (23). Dias RHV, Kim H-J, Lu H-L, Rajeshwar K, de Tacconi NR, Derecskei-Kovacs A, Marynick DS. *Organometallics*. 1996; 15:2994–3003.

- (24). Chu L, Hardcastle KI, MacBeth CE. *Inorg. Chem.* 2010; 49:7521–7529. [PubMed: 20690761]
- (25). Ebrahimpour P, Cushion M, Haddow MF, Hallett AJ, Wass DF. *Dalton Trans.* 2010; 39:10910–10919. [PubMed: 20967334]
- (26). Kitajima N, Fujisawa K, Fujimoto C, Morooka Y, Hashimoto S, Kitagawa T, Toriumi K, Tatsumi K, Nakamura A. *J. Am. Chem. Soc.* 1992; 114:1277–1291.
- (27). Polyakov OG, Ivanova SM, Gaudinski CM, Miller SM, Anderson OP, Strauss SH. *Organometallics.* 1999; 18:3769–3771.
- (28). Rack JJ, Webb JD, Strauss SH. *Inorg. Chem.* 1996; 35:277–278. [PubMed: 11666204]
- (29). Iwamoto M, Hoshino Y. *Inorg. Chem.* 1996; 35:6918–6921. [PubMed: 11666867]
- (30). Borovkov VY, Karge HG. *J. Chem. Soc., Faraday Trans.* 1995; 91:2035–2039.
- (31). (a) Lamberti C, Bordiga S, Zecchina A, Salvalaggio M, Geobaldo F, Otero Arean C. *J. Chem. Soc., Faraday Trans.* 1998; 94:1519–1525. (b) Kuroda Y, Maeda H, Yoshikawa Y, Kumashiro R, Nagao M. *J. Phys. Chem. B.* 1997; 101:1312–1316.
- (32). Another option suggested by a reviewer would be for the peak at 1968 cm^{-1} to arise from LCu(CO)THF . We view this notion to be unlikely relative to the more precedented equilibrium in Figure 3 because it is not clear why such a species would exhibit a broadened $\nu(\text{CO})$ shifted 88 cm^{-1} from the sharp peak at 2056 cm^{-1} (a much smaller shift would be anticipated; see ref. 17)
- (33). Battino, R., editor. *Oxygen and Ozone*. Vol. 7. 1981. Editor Solubility Data Series
- (34). Kang P, Bobyr E, Dustman J, Hodgson KO, Hedman B, Solomon EI, Stack TDP. *Inorg. Chem.* 2010; 49:11030–11038. [PubMed: 21028910]
- (35). Machonkin T, Mukherjee P, Henson M, Stack TDP, Solomon EI. *Inorg. Chim. Acta.* 2002; 341:39–44.
- (36). Piguet C. *J. Chem. Educ.* 1997; 74:815–816.
- (37). Sur SK. *J. Magn. Reson.* 1989; 82:169–173.
- (38). Evans DF. *J. Chem. Soc.* 1959:2003–2005.
- (39). Taktak S, Ye W, Herrera AM, Rybak-Akimova EV. *Inorg. Chem.* 2007; 46:2929–2942. [PubMed: 17335276]
- (40). Que, L. *Physical Methods in Bioinorganic Chemistry*. University Science Books; Sausalita, CA: 2000.
- (41). Yang F-A, Guo C-W, Chen Y-J, Chen J-H, Wang S-S, Tung J-Y, Hwang L-P, Elango S. *Inorg. Chem.* 2007; 46:578–585. [PubMed: 17279838]
- (42). Zeldin M, Mehta P, Vernon WD. *Inorg. Chem.* 1979; 18:463–466.
- (43). As suggested by a reviewer, reaction of $\text{L}_3\text{Cu}_3\text{O}_2$ with CO_2 may involve initial reaction with the dimethylamino group of the ligand. We cannot rule out this possibility on the basis of the available data

Chart 1.

I Selected well-characterized copper-oxygen intermediate cores derived from reactions of Cu(I) complexes with O₂.

Ligand	R	R'	R''	R'''
1	H	Me	Me	iPr
2	H	tBu	tBu	iPr
3	H	Me	CF ₃	iPr
4	H	CF ₃	CF ₃	iPr
5	H	CF ₃	CF ₃	Me
6	H	Me	Me	Me
7	Ph	H	H	iPr

Chart 2.

Selected β -diketiminato ligands used in studies of the reactivity of Cu(I) complexes with O₂.

Figure 1.

Synthesis of $\text{LCu}(\text{CH}_3\text{CN})$ and representation of its X-ray structure with nonhydrogen atoms shown as 50% thermal ellipsoids. Selected interatomic distances ($\text{\AA}$) and angles (deg): Cu(1)-N(1), 1.937(3); Cu(1)-N(2), 1.941(3); Cu(1)-N(5), 1.884(3); N(1)-N(3), 1.454(4); N(2)-N(4), 1.462(4); N(1)-Cu(1)-N(2), 98.23(12); N(5)-Cu(1)-N(1), 129.23(12); N(5)-Cu(1)-N(2), 132.54(12).

Figure 2. FTIR spectra of the product of the reaction of $\text{LCu}(\text{CH}_3\text{CN})$ in THF with CO, in the solid state (*solid line*) and in solution (*dashed line*).

Figure 3.
Proposed equilibrium between CO adducts in solution.

Figure 4.

UV-vis spectra of the oxygenation of $\text{LCu}(\text{CH}_3\text{CN})$ at $-80\text{ }^\circ\text{C}$ in THF (1 mM) in a 1 cm path length cuvette (*left*) and a 0.2 cm path length cuvette (*right*). Dashed line = $\text{LCu}(\text{CH}_3\text{CN})$; dotted line = transient intermediate; solid line = final oxygenated product. The transient intermediate was not observed in the experiment using the 0.2 cm path length cuvette due to experimental difficulties associated with baseline drift and solution warming during oxygenation.

Figure 5. Data from titration of solution of $\text{LCu}(\text{CH}_3\text{CN})$ in THF (10 mM) with O_2 at -80°C , with best linear fits (solid lines). The intersection point is mapped to the x-axis (dashed line) to yield the Cu:O ratio (0.35(2) equivalents O_2 per Cu = $\sim 3:2$ Cu:O ratio).

Figure 6. Peak envelope in the ESI mass spectrum (bottom) and simulation (top) for the blue/green oxygenation product solution corresponding to $C_{32}H_{68}Cu_3N_{14}O_3$ [$L_3Cu_3O_2 + MeOH + 2CH_3CN + H^+$] $^+$. The full spectrum is presented in the supporting information (Figure S6).

Figure 7. X-Band EPR spectrum (9.3970 GHz) of the oxygenation product of $\text{LCu}(\text{NCCH}_3)$ (60 mM) in THF in parallel mode at 13 K. The inset displays an expanded view of the ~ 4 region.

Table 1

IR Data for Selected Copper(I)-CO Adducts

Entry	Compound ^a	$\nu(\text{CO})$ (cm ⁻¹)	Ref
1	Cu(CO) ₂ AsF ₆	2177, 2164	15
2	Zeolite ZSM-5 ⁻ [Cu(CO) ₂] ⁺	2178, 2151	16
3	[(TMPA)Cu(CO)] ⁺	2091, 2077	17
4	LCu(CH ₃ CN) + CO in THF	2056, 1968	this work
5	[(TMEN) ₂ Cu ₂ (μ-CO)] ²⁺ in THF	2060, 1930	18
6	[(TMPDA) ₂ Cu ₂ (μ-CO)] ²⁺ in THF	2065, 1925	18
7	Cu(CO)OTf in TfOH	2155	19
8	CO	2143	20
9	Tp ^{(CF₃)₂} Cu(CO)	2137	21
10	[Cu(CO)]Cl	2127	22
11	Tp ^{CF₃,H} Cu(CO)	2100	23
12	(5)Cu(CO)	2100	8
13	[Cu(Me ₆ Tren)CO]PF ₆ (Nujol)	2098	24
14	[(tach)Cu(CO)]PF ₆	2092	25
16	[Cu(Me ₆ Tren)CO]PF ₆ in THF	2078	24
16	(6)Cu(CO)	2071	8
17	Tp ^{ipr₂} Cu(CO)	2056	26
18	LCu(CH ₃ CN) + CO (solid)	2047	this work
19	[(TMEN) ₂ Cu ₂ (μ-CO)] ²⁺ (Nujol)	1926	18
20	[(TMPDA) ₂ Cu ₂ (μ-CO)] ²⁺ (Nujol)	1925	18

^a Abbreviations: TMPA = tris(methylpyridyl)amine; TMEN = N,N,N',N'-tetramethylethylenediamine; TMPDA = N,N,N',N'-tetramethylpropylenediamine; OTf = CF₃SO₃⁻; Tp^{R,R'} = tris(3-R, 5-R'-pyrazolyl)hydroborate; Me₆tren = tris(N,N-dimethylaminoethyl)amine; tach = 1,3,5-triazacyclohexane.

Table 2UV-vis data for [(Ligand)₃Cu₃O₂]ⁿ⁺ complexes.^a

Ligand	n	Solvent	λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹ per Cu)	Ref
TMCD	3	CH ₂ Cl ₂	355(5000), 480(470), 620(270) ^b	9a
TMEN	3	acetone	345(4200), 500(440), 620(300)	34
Hpy1 ^{Me,Me}	3	acetone	342(4000), 515(333), 685(270)	10
L	0	THF	328(10700), 420(1500), 590(835)	this work

^aTMCD = *N,N,N',N'-(R,R)*-1,2-cyclohexanediamine; TMEN = *N,N,N',N'*-tetramethylethylenediamine; Hpy1^{Me,Me} = *N,N*-dimethyl-2-(2-pyridyl)ethylamine.

^b Additional peak reported at 290 (4200).