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Toluene and Ethylbenzene Aliphatic C-H Bond Oxidations Initiated by a Dicopper(II)- μ -1,2-Peroxo Complex

Heather R. Lucas[†], Lei Li[†], Amy A. Narducci Sarjeant[†], Michael A. Vance[‡], Edward I. Solomon[‡], and Kenneth D. Karlin[†]

[†]Departments of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

[‡]Stanford University, Stanford, California 94305

Abstract

With an anisole containing polypyridylamine potential tetradentate ligand **OL**, a μ -1,2-peroxo-dicopper(II) complex $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ forms from the reaction of the mononuclear compound $[\text{Cu}^{\text{I}}(\text{OL})(\text{MeCN})]\text{B}(\text{C}_6\text{F}_5)_4(\text{OLCu}^{\text{I}})$ with O_2 in non-coordinating solvents at -80°C . Thermal decay of this peroxo complex in the presence of toluene or ethylbenzene leads to rarely seen C-H activation chemistry; benzaldehyde and acetophenone/1-phenylethanol mixtures, respectively, are formed. Experiments with $^{18}\text{O}_2$ confirm that the oxygen source in the products is molecular O_2 and deuterium labeling experiments indicate $k_{\text{H}}/k_{\text{D}} = 7.5 \pm 1$ for the toluene oxygenation. The O_2 -reaction of $[\text{Cu}^{\text{I}}(\text{BzL})(\text{CH}_3\text{CN})]^+$ (**BzLCu^I**) leads to a dicopper(III)-bis- μ -oxo species $[\{\text{BzLCu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2]^{2+}$ at -80°C and from such solutions, very similar toluene oxygenation chemistry occurs. Ligand **BzL** is a tridentate chelate, possessing the same moiety found in **OL**, but without the anisole O-atom donor. In these contexts, the nature of the oxidant species in or derived from $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ is discussed and likely mechanisms of reaction initiated by toluene H-atom abstraction chemistry are detailed. To confirm the structural formulations of the dioxygen-adducts, UV-vis and resonance Raman spectroscopic studies have been carried out and these results are reported and compared to previously described systems including $[\{\text{Cu}^{\text{II}}(\text{PYL})\}_2(\text{O}_2)]^{2+}$ (**PYL** = TPA = tris(2-methylpyridyl)amine). Using (**L**)**Cu^I**, CO-binding properties (i.e., $\nu_{\text{C-O}}$ values) along with electrochemical property comparisons, the relative donor abilities of **OL**, **BzL** and **PYL** are assessed.

Introduction

The topic of dioxygen activation by copper enzymes has garnered considerable recent attention due to the relevance of copper(I)-dioxygen interactions and derived species to effect or alter critical biological functions.^{1–6} For instance, a dicopper(II)- μ - η^2 : η^2 -(*side-on*)-peroxo is the structure formed in hemocyanin (Hc), the O_2 -carrier for arthropods and mollusks;⁷ a similar structure or possibly an isomeric bis- μ -oxo-dicopper(III) form is implicated in tyrosinase (Tyr), a ubiquitous binuclear copper enzyme that catalyzes the hydroxylation of phenols to catechols and/or the oxidation of catechols to quinones.^{1,8} Enzymatic copper-dioxygen derived species also effect aliphatic C-H bond hydroxylations, for example in dopamine β -monooxygenase (DBM) and peptidylglycine α -amidating monooxygenase (PHM), neurosecretory vesicular copper enzymes which play a crucial role in the biogenesis of neurotransmitters and peptide

Correspondence: Kenneth D. Karlin, karlin@jhu.edu.

Supporting Information Available. X-ray structure determination summaries, figures and X-ray data files (CIF), GC and GC/MS product analyses from experiments with isotopically labeled materials. This material is available free of charge via the Internet at <http://pubs.acs.org>.

hormones.^{9,10} DβM and PHM possess two active site copper ions, separated by about 11 Å, too far to accommodate a bridging dioxygen derived species.¹¹ Instead, a mononuclear copper (II)-superoxide ($\text{Cu}^{\text{II}}\text{-O}_2^-$) or copper(II)-hydroperoxide ($\text{Cu}^{\text{II}}\text{-OOH}$) entity is believed to be the active species which initiates C-H bond hydroxylation reactions via initial hydrogen atom abstraction chemistry.^{9,12,13} X-ray crystallographic analysis has also revealed that *particulate* methane monooxygenase (*p*-MMO), an enzyme which catalyzes the conversion of methane to methanol in bacterial methanotrophs, possesses both mono and binuclear copper centers;¹⁴ while a Cu^{I} -dioxygen derived entity is likely responsible for aliphatic C-H bond oxidation chemistry, there is as yet little insight concerning the active site identity or chemistry.

Biomimetic studies have proven to be very helpful in the development of fundamental chemistry involving copper(I)/ O_2 interactions by elucidating the nature of possible $\text{Cu}_n\text{-O}_2$ ($n = 1, 2$) species as well as for clarifying their corresponding substrate reactivity mechanisms.²⁻⁴ There has been very recent activity involving mono-copper O_2 -derived complexes and reactivity.^{6,15} Of primary interest here are copper- O_2 derived species which are binuclear and which have been demonstrated to initiate aliphatic C-H bond oxidations; four notable examples follow (a-d): Itoh and co-workers (a) discovered and then elucidated a DβM model system wherein a dicopper(III)-bis- μ -oxo $\{\text{Cu}^{\text{III}}_2(\text{O}^{2-})_2\}$ complex possessing pyridylalkylamine ligands effects an internal (i.e., ligand) benzylic hydroxylation reaction.¹⁶ Tolman and coworkers (b) detailed intramolecular ligand oxidative N-dealkylation chemistry with $\text{Cu}^{\text{III}}_2(\text{O})_2$ species that consist of alkyl substituted triazacyclononane ligands.¹⁷ Karlin and coworkers (c) described the μ - η^2 : η^2 -peroxodicopper(II)/bis- μ -oxo-dicopper(III) oxidative N-dealkylation of exogenous substrate N,N-dimethylanilines; the same complexes effect tetrahydrofuran 2-position hydroxylation.^{18,19} Lastly, Suzuki and coworkers (d) reported a dicopper(II)- μ -hydroxo- μ -hydroperoxo entity that effects *intramolecular* methylene hydroxylation of a coordinated ligand (i.e. an $\text{Ar-CH}_2\text{NR}_2$ group) and subsequent N-dealkylation.²⁰ A structurally similar dicopper(II)- μ -phenoxo- μ -hydroperoxo from Karlin and coworkers was found to not only effect ligand aliphatic $-\text{CH}_2-$ group oxidation, but also α -cyanide C-H hydroxylation of RCH_2CN solvent molecules present in solution.²¹

In the present report, a ligand-copper-complex with striking copper-dioxygen mediated C-H activation is described by utilizing a new tetradentate anisole containing ligand (**OL**; Chart 1). Generally, tetradentate chelates lead to dicopper(II)- μ -1,2-*end-on*-peroxide species which are oxidatively inert and nucleophilic in their reactivity, see Chart 1.^{2,3,22} Via a designed variation of a well known tetradentate ligand, TMPA (**PyL**; Chart 1), we here continue our broad efforts to elucidate new copper-dioxygen chemistry, unearth new structures and reactive intermediates, deduce structure-spectroscopic correlations and determine scope and mechanisms of substrate reactions.^{2,23,24} The copper(I) complex of **OL**, $[\text{Cu}^{\text{I}}(\text{OL})(\text{CH}_3\text{CN})]^+$ (**OLCu^I**) reacts with O_2 at low temperature (-80°C) in non-coordinating and non-ether containing solvents (toluene or CH_2Cl_2) leading to the formation of a dicopper(II)- μ -1,2-*end-on*-peroxide species $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$. The spectroscopic properties of $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ are compared and contrasted to those of the related and well established dicopper(II)- μ -1,2-(*end-on*)-peroxo complex $[\{\text{PyLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ (Chart 1), that has also been structurally characterized.²⁵⁻²⁷

As already suggested, the most striking element of $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ chemistry is its efficient reactivity with exogenously added alkylbenzenes. Although aliphatic C-H bond oxidations of toluene or ethylbenzene have been observed in an $\text{Fe}_2\text{-O}_2$ or Fe(IV)-oxo system,^{28,29} to the best of our knowledge, this is the first time that such chemistry has been observed by starting with a dicopper(II)- μ -1,2-*end-on*-peroxide species. Other unobservable Cu_2O_2 adducts are considered as possible active species based on parallel experiments conducted on an analogous tridentate ligand system, BzPy1 (**BzL**; Chart 1). The O_2 -reaction of the copper(I) adduct $[\text{Cu}^{\text{I}}(\text{BzL})(\text{CH}_3\text{CN})]^+$ (**BzLCu^I**) leads to a dicopper(III)-bis- μ -oxo species

$[\{^{\text{O}}\text{LCu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2]^{2+}$ that also effects C-H activation, i.e. the complex possesses electrophilic reactivity, Chart 1. Such reactivity for dicopper(III)-bis- μ -oxo species was expected based on analogous work utilizing sterically hindered tetradentate ligands that exhibit toluene oxidation chemistry.³⁰ The possible involvement of a mononuclear copper(II)-superoxide species $[(\text{L})\text{Cu}^{\text{II}}\text{-(O}_2^{\cdot-})]^+$ is also considered.

Experimental Section

Materials and Methods

Unless otherwise stated all solvents and chemicals used were of commercially available analytical grade. Dioxygen was dried by passing it through a short column of supported P₄₀₁₀ (Aquasorb, Mallinkrodt). Propionitrile was distilled over CaH₂ and acetone was distilled over Drierite. Diethyl ether, acetonitrile, toluene, THF, and methylene chloride were obtained by passing the solvents through a 60 cm long column of activated alumina under N₂ (Innovative Technology, Inc.). Toluene was dried further by distillation over lumps of sodium under an argon atmosphere. Preparation and handling of air sensitive compounds were performed under an argon atmosphere using standard Schlenk techniques or in an MBraun Labmaster 130 inert atmosphere (< 1 ppm O₂, < 1 ppm H₂O) glovebox filled with nitrogen. Deoxygenation of solvents was effected by either repeated freeze/pump/thaw cycles or bubbling with argon for 45 - 60 minutes. Elemental analyses were performed by Quantitative Technologies, Inc. (QTI, Whitehouse, NJ) or Desert Analytics (Tucson, AZ). ¹H NMR spectra were recorded at 400 MHz on a Bruker AMX-400 instrument. Chemical shifts were reported as δ values relative to an internal standard (Me₄Si) and the residual solvent proton peak.

X-ray Crystallography

Crystals of each compound were placed in the N₂ cold stream at 110 K of an O.D. Xcaliber3 system equipped with a graphite monochromator and an Enhance (Mo) X-ray Source (λ = 0.71073 Å) operated at 2 kW power (50 kV, 40 mA). The detector was placed at a distance of 50 mm from the crystal. The frames were integrated with the Oxford Diffraction *CrysAlisRED* software package. All structures were solved and refined using the Bruker *SHELXTL* (v6.1) software package. Analysis of the data showed negligible decay.

UV-visible Spectroscopy

Room-temperature UV-visible spectra were recorded with a Varian Cary-50 spectrophotometer. Low-temperature UV-visible spectra were recorded on a Hewlett-Packard Model 8453A diode array spectrophotometer equipped with a two-window quartz H.S. Martin Dewar filled with cold MeOH (25 °C to -85 °C) that was maintained and controlled by a Neslab VLT-95 low temperature circulator. Spectrophotometer cells (2 mm) were purchased from Quark Glass and equipped with a column and pressure/vacuum stopcock. The procedures are also described elsewhere.³¹ Reaction solutions were introduced to molecular oxygen via bubbling through an 18-gauge, 24-inch-long stainless steel syringe needle.

Resonance Raman (rR) Spectroscopy

rR spectra were obtained using a Princeton Instruments ST-135 back-illuminated CCD detector on a Spex 1877 CP triple monochromator with 1200, 1800, and 2400 grooves/mm holographic spectrograph gratings. Excitation was provided by Coherent 190C-K Kr⁺ and Innova Sabre 25/7 Ar⁺ CW ion lasers. Laser lines were chosen to coincide with the intense absorption transitions of $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$. The spectral resolution was < 2 cm⁻¹. Samples were run at 77 K in a liquid N₂ finger dewar (Wilmad). Isotopic substitution was achieved by oxygenating with ¹⁸O₂ (Icon).

Electrochemistry

Cyclic voltammetry was carried out with a Bioanalytical Systems BAS-100B electrochemistry analyzer. The cell was a standard three-electrode system with platinum wire auxiliary as the counter electrode. A glassy carbon electrode (GCE, BAS MF 2012) was used as the working electrode. The reference electrode was Ag/Ag⁺. Measurements were performed at room temperature in DMF solvent containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAHP) and 1 - 0.1 mM copper complex. Ferrocene (1 mM) was added as the internal standard. Solutions were deoxygenated by directly bubbling with argon.

Electron Paramagnetic Resonance (EPR) spectroscopy

EPR spectra were recorded on a Bruker EMX spectrometer controlled with a Bruker ER 041 XG microwave bridge operating at X-band (~9.4 GHz). The low-temperature EPR measurements were conducted by using either a continuous-flow liquid-helium cryostat and ITC503 temperature controller made by Oxford Instruments, Inc., or a liquid-nitrogen finger dewar.

GC and GC-MS Analysis; Determination of Solvent Oxidation Product Yields

Analysis of the toluene and/or ethylbenzene oxidation products were confirmed by comparison to commercially available standards, specifically benzaldehyde and benzyl alcohol or acetophenone and 1-phenylethanol, respectively. The yields of the corresponding product signals were calculated based on comparisons to a calibration curve; externally added decane was used as an internal standard. ¹⁸O-incorporation was determined by ^RCu^I oxygenation using ¹⁸O₂.

All GC experiments were carried out and recorded using a Hewlett-Packard 5890 Series II Gas Chromatograph. The GC conditions for the analysis of the toluene oxidation products (benzaldehyde, benzyl alcohol) were: Injector Port Temperature: 250 °C; Detector Temperature 250 °C; Column Temperature: Initial Temperature 45 °C; Initial Time, 2min; Final Temperature 250 °C, Final Time, 2 min, Gradient Rate 30 °C/min; Flow Rate: 51 mL/min. The GC conditions for the analysis of the ethylbenzene oxidation products (acetophenone, 1-phenylethanol) were as follows: Injector Port Temperature: 250 °C; Detector Temperature 250 °C; Column Temperature: Initial Temperature 50 °C; Initial Time, 2min; Final Temperature 90 °C, Final Time, 1 min, Gradient Rate 1 °C/min; Flow Rate: 51 mL/min. All GC/MS experiments were carried out and recorded using a Shimadzu GC-17A/GCMS0QP5050 Gas Chromatograph/Mass Spectrometer. The GC-MS conditions for the product analysis following toluene and ethylbenzene oxidation were: Injector Port Temperature: 220 °C; Detector Temperature 280 °C; Column Temperature: Initial Temperature 80 °C; Initial Time, 3min; Final Temperature 250 °C, Final Time, 5 min, Gradient Rate 10 °C/min; Flow Rate: 16 mL/min; Ionization voltage: 1.5 kV.

Synthetic Procedures for Ligands and Cu^{I/II} complexes

The following compounds were synthesized following procedures previously described:^{25, 27,32} [Cu^I(MeCN)₄]B(C₆F₅)₄, ^{Py}L, [Cu^I(^{Py}L)(CH₃CN)]B(C₆F₅)₄ (^{Py}LCu^I), [Cu^{II}(^{Py}L)(H₂O)](ClO₄)₂ (^{Py}LCu^{II}), [{Cu^{II}(^{Py}L)}₂(O₂)]²⁺ [{^{Py}LCu^{II}}₂(O₂²⁻)]²⁺.

^{OL}

In a 125 mL air-free addition funnel, 2-picoly chloride (4.4 g, 34.6 mmol) in 50 mL of methanol containing triethylamine (4.2 g, 41.6 mmol) was deaerated with argon for 20 min. The solution was then added dropwise to a 250 mL 3-neck flask containing a portion of 5-*tert*-butyl-o-anisidine (2.7 g, 15.1 mmol) dissolved in 100 mL methanol. The reaction solution was stirred for 3 days under an argon atmosphere at ~65 °C. The crude product was purified via column

chromatography utilizing silica gel. Elution with ethyl acetate removed the unreacted 2-picolyl chloride and elution with ethyl acetate/hexane (1:1) yielded the desired **O_L** product (3.7 g, 68%) as a brown-yellow solid, (R_f = 0.25, silica gel, ethyl acetate/hexane = 1:1). ¹H NMR (CDCl₃, 300 MHz): δ 1.10 (s, 9H), 3.83 (s, 3H), 4.53 (s, 4H), 6.77-6.90 (m, 3H), 7.06-7.10 (m, 2H), 7.48-7.59 (m, 4H), 8.48-8.51 (m, 2H). Elemental Analysis (C₂₄H₂₉N₃O): Calculated; C, 76.76; H, 7.78; N, 11.19; Found; C, 76.20; H, 7.81; N, 11.39.

Bz_L

A portion of 2-picolyl chloride (1.79 g, 14.0 mmol) was dissolved in 50 mL dichloromethane. Upon stirring, 50 mL of saturated NaOH solution was added followed by dropwise addition of benzylamine (0.5 g, 4.67 mmol). After stirring for 4 days at room temperature under an argon atmosphere, the organic layer was separated and dried with MgSO₄. The crude product was treated with 2 g phthalic anhydride in order to remove any primary or secondary amines. After four hours, the crude product was filtered and purified by column chromatography (silica gel). Elution with ethyl acetate removed the unreacted 2-picolyl chloride yielding the desired **Bz_L** product (1.1 g, 61 %) as a brown-yellow solid, (R_f = 0.25, silica gel, ethyl acetate). ¹H NMR (CDCl₃, 400 MHz): δ 3.69 (s, 2H), 3.81 (s, 4H), 7.11-7.68 (m, 11H), 8.51 (d, 2H). Elemental Analysis (C₁₉H₁₉N₃): Calculated; C, 78.86; H, 14.52; N, 6.62. Found; C, 78.11; H, 14.46; N, 6.79.

[Cu^I(O_L)**(MeCN)]B(C₆F₅)₄; **O_L**Cu^I**

Dissolution of **O_L** (109 mg, 0.3 mmol) in 8 mL of O₂-free diethyl ether followed by slow addition under an argon atmosphere to [Cu^I(MeCN)₄]B(C₆F₅)₄ (273 mg, 0.3 mmol) afforded a bright yellow solution. Precipitation by 100 mL O₂-free pentane resulted in a yellow powder. The supernatant was decanted and the yellow powder was dissolved under vacuum. The dissolution and re-precipitation process in Et₂O and pentane and vacuum drying process was repeated 3 to 5 times until a yellow microcrystalline solid was observed giving a final yield of 83 % (280 mg; 0.25 mmol). Single crystals suitable for X-ray structural analysis were obtained by recrystallization from Et₂O/Pentane. ¹H NMR (DMSO-d₆, 300 MHz): δ 1.22 (s, 9H), 2.20 (s, 3H), 4.10 (s, br, 3H), 4.87 (s, br, 4H), 6.60-6.90 (br, 3H), 7.07 (br, 2H), 7.60-7.90 (m, 4H), 8.68 (br, 2H). Elemental Analysis (C₄₉H₃₀BCuF₂₀N₄O): C, 51.39; H, 2.64; N, 4.89. Found: C, 50.66; H, 2.60; N, 4.96.

[Cu^I(Bz_L**)(MeCN)]B(C₆F₅)₄; **Bz_L**Cu^I**

Under an argon atmosphere, **Bz_L** (46 mg, 0.16 mmol) was dissolved in 8 mL of diethyl ether solution and slowly added to a 50 mL Schlenk flask containing [Cu^I(MeCN)₄]B(C₆F₅)₄ (144 mg, 0.16 mmol). Pentane (O₂-free, 100 mL) was added to the bright yellow solution obtained affording a yellow solid. The supernatant was removed via cannula and the solid was dried under vacuum. Repeated (2-3 times) dissolution and re-precipitation followed by vacuum drying afforded a fluffy yellow solid, 76 % yield (131 mg; 0.25 mmol). Single crystals suitable for X-ray crystallographic analysis were obtained by recrystallization from Et₂O/Pentane. ¹H NMR (DMSO-d₆, 300 MHz): δ 1.98 (s, 3H), 3.84 (s, 4H), 3.89 (s, 2H) 7.17-7.24 (m, 5H), 7.31 (br, 2H), 7.61 (br, 2H), 7.97 (br, 2H), 8.56 (br, 2H). Elemental Analysis (C₄₅H₂₂BCuF₂₀N₄): Calculated; C, 50.37; H, 2.07; N, 5.22. Found; C, 50.65; H, 1.89; N, 4.85.

[Cu^{II}(O_L**)(H₂O)](ClO₄)₂·H₂O; **O_L**Cu^{II}**

Under an argon atmosphere, a 10 mL EtOH solution of **O_L** (0.159 g, 0.44 mmol) was added dropwise to a 10 mL aqueous solution of Cu(ClO₄)₂·6H₂O (170 mg, 0.44 mmol). A blue crystalline solid was easily obtained by slow evaporation under vacuum (0.27 g, 78%). UV-vis: (methanol) 681 nm (80 M⁻¹ cm⁻¹); EPR (DMF/Toluene 1:1) $g_{\perp}$ = 2.05, $g_{\parallel}$ = 2.27, $A_{\parallel}$ = 169×10^{-4} cm⁻¹. Elemental Analysis (C₂₃H₃₁Cl₂CuN₃O₁₁): Calculated; C, 41.86; H, 4.73; N, 11.39.

6.37; Found: C, 42.27; H, 4.50; N, 6.24. **Warning:** While we have experienced no problems in working with perchlorate compounds, they are potentially explosive, and care must be taken not to work with large quantities.

[Cu^{II}(^{Bz}L)(MeOH)](ClO₄)₂; ^{Bz}LCu^{II}

A 15 mL EtOH solution was deoxygenated and added to a 50 mL Schlenk flask containing ^{Bz}L (45 mg, 0.44 mmol) and Cu(ClO₄)₂·6H₂O (58 mg, 0.44 mmol). The bright blue solution was slowly stirred under vacuum resulting in a blue powder. EPR (DMF/Toluene 1:1) $g_{\perp} = 2.05$, $g_{\parallel} = 2.27$, $A_{\parallel} = 169 \times 10^{-4} \text{ cm}^{-1}$. Elemental Analysis (C₂₀H₂₂Cl₂CuN₃O₉): Calculated; C, 41.21; H, 3.80; N, 7.21; Found; C, 40.88; H, 3.60; N, 7.30. Crystalline material suitable for X-ray structural analysis was obtained by repeating the slow vacuum drying process following dissolution of ^{Bz}LCu^{II} in EtOH.

[{Cu^{II}(^OL)}₂(O₂²⁻)] [B(C₆F₅)₄]₂; [{^OLCu^{II}}₂(O₂²⁻)]²⁺

Under a nitrogen atmosphere within the drybox, ^OLCu^I (11 mg, 0.01 mmol) was dissolved in 10 ml O₂-free solvent (CH₂Cl₂, toluene, ethylbenzene) giving a bright yellow solution. The reaction flask (or cuvette) was quickly removed from the dry-box and cooled to -80 °C in a dry ice/acetone bath and O₂ was gently bubbled through the reaction solution. A purple solution of complex [{^OLCu^{II}}₂(O₂²⁻)]²⁺ was formed in less than one minute. Excess dioxygen was removed by argon bubbling and the solvent oxidation products were analyzed as described above. Also, the copper(II) decay products in methylene chloride, ^OLCu^{II}-Cl, and in toluene, [{^OLCu^{II}}₂(μ-OH)₂]²⁺, were characterized as given below.

[Cu^{II}(^OL)(Cl)]B(C₆F₅)₄·CH₂Cl₂; ^OLCu^{II}-Cl

^OLCu^I (46 mg, 0.04 mmol) was dissolved in 10 ml O₂-free CH₂Cl₂ (under Ar) giving a bright yellow solution and this was cooled to -80 °C in a dry ice/acetone bath. Dioxygen was gently bubbled through the reaction solution resulting in a purple solution of [{^OLCu^{II}}₂(O₂²⁻)]²⁺ within a few seconds. Excess dioxygen was removed from the reaction system by purging with argon for 2 to 3 minutes. Since [{^OLCu^{II}}₂(O₂²⁻)]²⁺ was not stable at -80 °C the purple color as well as the characteristic absorption gradually bleached during the purging process. The resulting solution was then warmed to ambient temperature and the thermal decay product was kept under argon overnight resulting in a blue crystalline solid (22 mg, 45%). X-ray crystallographic analysis confirmed the identity of the cupric-chloride species, ^OLCu^{II}-Cl. UV-vis: (Methanol) 718 nm (85 M⁻¹ cm⁻¹); EPR (DMF/Toluene 1:1) $g_{\perp} = 2.05$, $g_{\parallel} = 2.26$, $A_{\parallel} = 167 \times 10^{-4} \text{ cm}^{-1}$. Elemental Analysis (C₄₈H₂₉BCl₃CuF₂₀N₃O): C, 47.08; H, 2.39; N, 3.43. Found: C, 47.46; H, 2.16; N, 3.28.

[{Cu^{II}(^OL)}₂(HO⁻)₂] [B(C₆F₅)₄]₂·0.8(C₇H₈); [{^OLCu^{II}}₂(μ-OH)₂]²⁺

Within the drybox, ^OLCu^I (46 mg, 0.04 mmol) was dissolved in 8 ml of O₂-free toluene giving a bright yellow solution. The reaction solution was removed from the drybox and cooled to -80 °C in a dry ice/acetone bath. Dioxygen was gently bubbled through the reaction solution until full formation of [{^OLCu^{II}}₂(O₂²⁻)]²⁺ (~1 min) was achieved. The solubility of [{^OLCu^{II}}₂(O₂²⁻)]²⁺ at high concentrations is poor in non-polar solvents. As a result, some of the complex existed as a purple solid that precipitated at the bottom of the Schlenk flask. Remaining excess O₂ was removed by quickly purging the solution with argon for 2 - 3 minutes. The resulting solution was then allowed to decay by warming to ambient temperature and the purple color, solution and solid, ceased to exist in ~10 second following removal from the cold bath. The resulting reaction mixture was filtered and the green precipitate subsequently obtained was characterized as [{^OLCu^{II}}₂(μ-OH)₂]²⁺ (74 % yield). Crystalline material suitable for X-ray structural analysis were obtained by allowing the dilute toluene supernatant

to remain a few days under argon until crystals fell out of solution. Elemental Analysis: Calculated; C, 51.66; H, 2.72; N, 3.64; Found: C, 51.65; H, 2.64; N, 3.19.

Under a nitrogen atmosphere within the drybox, BzLCu^{I} (25 mg, 0.024 mmol) was dissolved in 8 ml O_2 -free solvent (toluene, Et_2O , THF, acetone) giving a bright yellow solution. The reaction flask (or cuvette) was removed from the drybox and cooled to -80°C in a dry ice/acetone bath and O_2 was gently bubbled through the reaction solution. A yellow-brown solution of complex $[\{\text{BzLCu}^{\text{II}}\}_2(\mu\text{-O}_2^{2-})_2]^{2+}$ was fully formed in 5 to 30 minutes depending on the solvent. Excess dioxygen was removed by argon bubbling and the solvent oxidation products in toluene were analyzed as described above; corresponding product yields are reported within the text.

Ligand Analysis after $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ Decomposition in CH_2Cl_2

A 10 equivalent excess of KCN (520 mg, 8 mmol) in aqueous solution (10 mL) was added to the pale green reaction solution that was produced following thermal transformation of $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ (35 mg, 0.08 mmol) in CH_2Cl_2 .³³ A biphasic mixture resulted that consisted of the desired yellow organic product layer and the colorless aqueous solution layer. The products were passed through a plug of silica gel. The original, unreacted OL ligand was recovered (27 mg, 93%). ^1H -NMR spectroscopy also supported that the ligand remained intact.

Isotope Effect Determination for the Toluene Oxygenation Reaction

Under an argon atmosphere OLCu^{I} (23 mg, 0.02 mmol) was dissolved in an O_2 -free $\text{C}_6\text{H}_5\text{CH}_3$ (860 mg, 9.33 mmol)/ $\text{C}_6\text{D}_5\text{CD}_3$ (918 mg, 9.2 mmol) solvent mixture. The yellow solution was then cooled to -80°C in a dry ice/acetone bath and O_2 was gently bubbled through the reaction solution (~ 1 min) to allow full formation of the purple colored $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$. Any remaining O_2 was removed by purging argon through the solution and the resulting suspension was allowed to decay by warming to ambient temperature. The reaction mixture was then filtered and the filtrate was analyzed by GCMS. The isotope effect for the formation of benzaldehyde was calculated by comparison of the signal intensity ratios of $\text{C}_6\text{H}_5\text{CHO}$ and $\text{C}_6\text{D}_5\text{CDO}$ obtained by mass spectrometric analysis. Under the experimental conditions employed, product analysis thus gives an 'apparent' isotope effect $k_{\text{H}}/k_{\text{D}} = 7.5 \pm 1$.

Results and Discussion

Syntheses of Ligands, and Copper Complexes

The potential tetradentate N_3O ligand OL and the purely N_3 tridentate ligand BzL were straightforwardly synthesized by addition of commercially available 2-picoyl chloride to the appropriate precursors, 5-*tert*-butyl-*o*-anisidine and benzylamine, respectively. Following column purification, metallation of the ligands proceeded by dissolution of $[\text{Cu}^{\text{I}}(\text{CH}_3\text{CN})]\text{B}(\text{C}_6\text{F}_5)_4$ and the respective ligand in deoxygenated diethyl ether (Et_2O) and subsequent precipitation in pentane. Repeated dissolution and precipitation afforded yellow crystalline material that was characterized by ^1H -NMR spectroscopy and C-, H-, N- elemental analysis as $[\text{Cu}^{\text{I}}(\text{OL})(\text{CH}_3\text{CN})]\text{B}(\text{C}_6\text{F}_5)_4$ (OLCu^{I}) and $[\text{Cu}^{\text{I}}(\text{BzL})(\text{CH}_3\text{CN})]\text{B}(\text{C}_6\text{F}_5)_4$ (BzLCu^{I}). Slow diffusion of 20 equivalents by volume of pentane over an Et_2O solution of the ligand-copper (I)-complexes leads to products amenable to X-ray crystallographic analysis as will be discussed in the following section. See the Experimental Section for more details.

OL as well as an unmethylated phenol analogue were originally designed and synthesized to study their relationship to a binucleating phenol analogue referred to as $\text{PD}'\text{OH}$.^{21,34} The dicopper(I) complex $[\text{Cu}_2^{\text{I}}(\text{PD}'\text{OH})(\text{MeCN})_2]^{2+}$ reacts with O_2 to give a hydroperoxide species which effects RCN oxidation (to an aldehyde and cyanide);²¹ the dicopper(II) complex

$[\text{Cu}^{\text{II}}_2(\text{PD}'\text{O}^-)(\text{H}_2\text{O})_2]^{3+}$ can be made to mediate specific nucleobase guanine oxidation for certain DNA duplex constructs.^{10,35} As stated in the Introduction, **OL** is utilized in this study to examine the ability of the N_3O chelate to elucidate C-H bond activation, i.e. toluene and ethylbenzene oxidation, following formation of the Cu_2O_2 species; more details follow. The reactivity characteristics are compared to copper-complex systems utilizing an N_3 (**BzL**) and N_4 (TPMA; **PyL**) ligand, see Chart 1. For the purpose of structural and electrochemical investigations, the copper(II) complexes, $[\text{Cu}^{\text{II}}(\text{OL})(\text{H}_2\text{O})](\text{ClO}_4)_2$ (**OLCu^{II}**) and $[\text{Cu}^{\text{II}}(\text{BzL})(\text{ROH})](\text{ClO}_4)_2$ (**BzLCu^{II}**; ROH is EtOH or MeOH), were prepared. The ligand-copper(II)-complexes were synthesized by the slow addition of aqueous $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ to the appropriate ligand in protic solvents (EtOH, MeOH), see the Experimental Section.

X-ray Crystallographic Analysis of the Copper(I) and Copper(II) Complexes

A summary of numerical crystal and refinement data for **OLCu^I**, **BzLCu^I**, and **BzLCu^{II}** is given in Table 1, with full details given in the Supporting Information. Representative ORTEP diagrams of the copper(I) complexes, **OLCu^I** and **BzLCu^I**, are shown in Figures 1 and 2, respectively, and the ORTEP diagram of **BzLCu^{II}** is shown in Figure 3; selected bond distances and angles given in the Figure captions. The coordination spheres of all three complexes consists of the three nitrogen atoms of the bis(2-picolyl)amine (PY1) moiety of the ligands and an exogenous solvent molecule occupies the fourth position. Tetra-coordination is achieved via ligation from an acetonitrile molecule for the copper(I) complex and a neutral EtOH molecule for the cupric species.

As shown in Figure 1, the overall geometry of **OLCu^I** is highly distorted from tetrahedral. The copper ion is nearly co-planar with the $\text{N}_{\text{acetonitrile}}$ and two N_{Py} atoms, sitting slightly above the triangular plane defined by these three N-atoms in the direction of the bridgehead nitrogen. The interaction between the copper(I) ion and the central amine nitrogen atom is the weakest, as indicated by the longer bond length of 2.286(3) Å versus an average Cu- N_{Py} bond distance of 2.036(6) Å. The most noteworthy feature of the **OLCu^I** structure is that exogenous MeCN coordination is preferred over the **OL** ether oxygen atom, thus the tethered anisole moiety is rotated away from the copper(I) ion, placing the O-atom out of bonding distance at 5.072(5) Å. Of all the ligand donors, the exogenous MeCN molecule is coordinated the strongest to the copper(I) ion of **OLCu^I** as indicated by the bond length of 1.911(2) Å.

The complex **PyLCu^I** and close analogue $[\text{Cu}^{\text{I}}(\text{PyL})(\text{MeCN})]^+$ possess pseudo penta-coordination, with a distorted trigonal bipyramidal geometry; one of the three pyridyl groups of the **PyL** ligand has a 3-C(O)OCH₃ substituent.^{36,37} The interaction between the copper ion and the bridgehead nitrogen is the weakest as evidenced by the ~ 2.4 Å Cu- $\text{N}_{\text{bridgehead}}$ bond length. The four-coordinate structure of **OLCu^I** is quite different, of course due to the dangling anisole group. In fact previous work showed that for the adducts $[\text{Cu}^{\text{I}}(\text{PyL})(\text{D})]^+$ (D = CO or PPh_3), one of the pyridine arms dissociates as supported by solution ¹H-NMR data and an X-ray crystal structure of $[\text{Cu}^{\text{I}}(\text{PyL})(\text{PPh}_3)]^+$.³⁶ The copper ion of **OLCu^I** may adopt a similar coordination in solution, as demonstrated by copper(I)-carbon monoxide binding studies which are discussed in a later section.

The overall coordination environment of **BzLCu^I** is analogous to that in **OLCu^I**, yet further distorted from a tetrahedral geometry, see Figure 2. The Cu1-N2 bond distance (2.309(4) Å) in **BzLCu^I**, N2 being the central amine nitrogen atom, is longer than the corresponding value in **OLCu^I**. The average Cu- N_{Py} bond distance is shorter, 2.016(4) Å, along with the Cu- $\text{N}_{\text{acetonitrile}}$ bond distance of 1.900(4) Å. The benzyl moiety is positioned somewhat (by comparison) towards or over the copper(I) ion.

By contrast, as shown in the ORTEP diagram for **BzLCu^{II}** (Figure 3), the benzyl arm is swung away from the copper(II) ion. The Cu- N_{amine} bond distance for the cupric species is 2.035(3)

Å, approximately 0.27 Å shorter than in the copper(I) structure (vide supra). The average Cu-N_{py} bond distance is about the same, 1.983(8) Å, only about 0.03 Å shorter. The copper(II) ion is very close to the plane which includes the ethanol O-atom and other nitrogen moieties, making for an overall square planar complex.

Itoh and coworkers have investigated how cuprous ions interact with aromatic π -systems of pyridylalkylamine tridentate ligands with a phenylethylene appendage.^{38,39} The copper(I)-arene π -interactions of η^2 -type were found to alter or diminish the reactivity of the ligand-copper(I) species toward dioxygen. No copper-arene interaction is exhibited in the solid-state X-ray structure of **BzLCu^I** or **BzCu^{II}** because the benzylamine linker is shorter than the aforementioned Itoh species.

Structural Characterization of the Reaction Products following CH₂Cl₂ and Toluene Oxidation by [{Cu^{II}(^OL)}₂(O₂²⁻)]²⁺

ORTEP diagrams of [Cu^{II}(^OL)(Cl)]⁺ and [{^OLCu^{II}}₂(μ -OH)₂]²⁺ are given in Figures 4 and 5 respectively, with selected bond distances and angles given in the Figure captions. The complexes were obtained as reaction products following the thermal transformation of the dicopper(II)- μ -1,2-(*end-on*)-peroxo species [{Cu^{II}(^OL)}₂(O₂²⁻)]²⁺ that forms upon oxygenation of **^OLCu^I** in CH₂Cl₂ or toluene appropriately; further details are given below. A summary of crystal and refinement data for the solvent oxidation reaction products are given in Table 2 with full details given in the Supporting Information.

In contrast to the four-coordinate structure of **^OLCu^I** but common in copper(I) ion chemistry, the copper atom in [Cu^{II}(^OL)(Cl)]⁺ is pentacoordinate, see Figure 4. The structure of [Cu^{II}(^OL)(Cl)]⁺ is distorted square pyramidal where $\tau = 0.22$, the latter value is based on a method defined by Reedijk and Addison for structural comparison of five-coordinate copper (II) species; $\tau = 0.0$ for a square pyramidal geometry and $\tau = 1.0$ for a trigonal bipyramidal geometry.^{40,41} The three nitrogen atoms of the PY1 unit and the ligated Cl⁻ constitute the basal plane with the anisole oxygen atom O_{anisole} occupying the axial position. The average bond distance between the copper(II) center and the nitrogen atoms are 2.017(9) Å. The distances for Cu-Cl and Cu-O_{anisole} are longer, 2.242(6) Å and 2.317(5) Å, respectively, indicating a weak interaction between the copper(II) ion and the ether-oxygen ligand. The two pyridyl moieties from the PY1 unit of [Cu^{II}(^OL)(Cl)]⁺ are nearly coplanar (Figure 4); the bridgehead nitrogen sits by ~0.5 Å above the best least-squares plane defined by N1, N2, N3, Cl and Cu, towards the anisole moiety. The chloride atom sits ~0.62 Å below the plane.

The O_{anisole} is also coordinated to the copper(II) ion of the toluene oxidation dicopperdihydroxy reaction product, [{^OLCu^{II}}₂(μ -OH)₂]²⁺, see Figure 5. The Cu-O_{anisole} bond distance is 2.369(2) Å, approximately 0.05 Å longer than that in the cupric-chloride species. The average Cu-N_{py} bond distance and the Cu-N_{amine} bond distance of approximately 2.123 Å are all about the same, yet somewhat longer than in the cupric chloride species. The increased bond distance is expected because [{^OLCu^{II}}₂(μ -OH)₂]²⁺ possesses hexacoordinate copper(II), unlike that in [Cu^{II}(^OL)(Cl)]⁺ (vide supra).

If the dicopper-dihydroxy species is stored for over one-week then the binuclear structure falls apart, likely forming the mononuclear copper(II)-hydroxy species [{^OLCu^{II}}(OH)]²⁺, as indicated by a change in the EPR signal from silent to an intensity of ~100 times greater (but still ~15 times smaller than **^OLCu^{II}**, see Experimental Section for values); further characterization was not carried out. If a toluene solution of [{^OLCu^{II}}₂(μ -OH)₂]²⁺ was opened to air then after a few days the green color changed to blue, and a tetranuclear carbonate species [{^OLCu^{II}}₄(CO₃)₂]⁴⁺, formed. See Table 2 and the Supporting Information for details of the X-ray structure.

CO stretching Frequencies for the Ligand-Copper(I)-Carbonyl Complexes

Copper(I)-CO complexes were obtained by dissolution of the corresponding copper(I) species in CO saturated diethyl ether and the products could be isolated as solids by addition of CO saturated pentane. Evidence for CO binding was confirmed by observation of a single IR-band (Table 3) within the expected range for synthetic copper(I)-carbonyl complexes (ν_{CO} : 2045 - 2110 cm^{-1}).

The ν_{CO} values for ligand-copper(I)-carbonyl species are often used to deduce the complex coordination number as also related to the electron-donating ability of the corresponding ligand.⁴⁶⁻⁴⁹ It has been previously established for $[\text{Cu}^{\text{I}}(\text{PyL})(\text{CO})]^+$ that the solid-state geometry is five-coordinate, however the predominate species in solution is four-coordinate, i.e. one pyridyl arm is “dangling” or de-ligated as shown in Chart 2.⁵⁰ The CO vibrational frequency (ν_{CO}) of the solid-state five-coordinate species (thus with all N donors bound) is 2077 cm^{-1} and a shift to higher energy is observed in solution: ν_{CO} = 2090 cm^{-1} in THF and ν_{CO} = 2092 cm^{-1} in CH_3CN .⁵¹ Dissociation of a pyridyl nitrogen-donor so only three N-donors are metal bound is consistent with weaker π -backbonding resulting in a stronger C-O bond and thus a higher ν_{CO} value. A solution-state structure similar to $[\text{Cu}^{\text{I}}(\text{PyL})(\text{PPh}_3)]^+$ is expected for $[\text{Cu}^{\text{I}}(\text{PyL})(\text{CO})]^+$ as has also been exhibited by $[\text{Cu}^{\text{I}}(\text{PyL}^{\text{NMe}_2})(\text{CO})]^+$; the $\text{PyL}^{\text{NMe}_2}$ ligand has NMe_2 -substituents at the *para*-position of all three pyridyl donors.^{25,51}

The CO stretching frequency of $[\text{Cu}^{\text{I}}(\text{OL})(\text{CO})]^+$ and $[\text{Cu}^{\text{I}}(\text{BzL})(\text{CO})]^+$ were investigated in CH_3CN and THF, as having an average ν_{CO} value of 2094 cm^{-1} , essentially the same as that found for the solid-state complex with ν_{CO} = 2093 cm^{-1} . The similar CO stretching frequencies for $[\text{Cu}^{\text{I}}(\text{OL})(\text{CO})]^+$, $[\text{Cu}^{\text{I}}(\text{BzL})(\text{CO})]^+$ and the solution-state form of $[\text{Cu}^{\text{I}}(\text{PyL})(\text{CO})]^+$ demonstrates that the $\text{O}_{\text{anisole}}$ of ligand OL does not coordinate to copper(I) in $[\text{Cu}^{\text{I}}(\text{OL})(\text{CO})]^+$. Similarly, the $\text{O}_{\text{anisole}}$ likely does not coordinate in the solution-state form of OLCu^{I} , consistent with the solid-state X-ray crystal structure, see Chart 2.

Electrochemical Investigation of the Ligand-Copper(II)-Complexes, LCu^{II}

The variable dynamics of the tripodal ligand-copper systems, i.e., the fact that anisole ‘arm’ of OL does not bind copper(I) in solution (Chart 2), precludes the use of the cuprous-carbonyl adducts in electrochemical studies for the purpose of delineating the difference in overall electron-donating ability of PyL vs. OL vs. BzL . To obtain such insights, the RLCu^{II} complexes were examined through electrochemical analyses employing cyclic voltammetry. The redox potentials of $[\text{Cu}^{\text{II}}(\text{PyL})(\text{H}_2\text{O})](\text{ClO}_4)_2$ (PyLCu^{II}), $[\text{Cu}^{\text{II}}(\text{OL})(\text{H}_2\text{O})](\text{ClO}_4)_2$, (OLCu^{II}), and $[\text{Cu}^{\text{II}}(\text{ZL})(\text{EtOH})](\text{ClO}_4)_2$ (BzLCu^{II}) were measured in DMF solvent versus ferrocene/ferrocenium (Fc/Fc^+), which was added as an internal standard. Both PyLCu^{II} and OLCu^{II} exhibited reversible $\text{Cu}^{\text{II/I}}$ redox processes ($i_{\text{pc}}/i_{\text{pa}} \approx 1$) with $E_{1/2}$ values of -0.62 V and -0.51 V respectively, see Figure 6. However, BzLCu^{II} exhibited irreversible behavior (data not shown) indicating that the anisole oxygen atom of OL does indeed affect the redox processes of OLCu^{II} .

Copper complex redox potentials are influenced by many factors, including the type and number of donor atoms as well as the coordination geometry.⁵²⁻⁵⁴ The copper(II) coordination geometry of OLCu^{II} and PyLCu^{II} likely contributes to the $\Delta E_{1/2} = 0.11$ redox potential difference, assuming that the coordination environments of LCu^{II} are analogous to their corresponding cupricchloride species. $[\text{Cu}^{\text{II}}(\text{OL})(\text{Cl})]^+$ ($\tau = 0.23$) adopts a slightly distorted square pyramidal geometry, see above, while $[\text{Cu}^{\text{II}}(\text{tmpa})(\text{Cl})]^+$ exhibits a nearly perfect trigonal bipyramidal coordination ($\tau = 1.00$).⁵⁵ However, the primary effect is related to the difference in electron-donating ability of the O_{ether} versus $\text{N}_{\text{pyridyl}}$ ligands within the two complexes.⁵⁴ The higher (more positive) redox potential for OLCu^{II} suggests that the O_{ether} is a poor electron donor relative to the $\text{N}_{\text{pyridyl}}$ donor in PyLCu^{II} .

UV-visible Spectroscopy in CH₂Cl₂; Generation of [^oLCu^{II}]₂(O₂²⁻)²⁺

ˆAddition of O₂ to ^oLCu^I at -80 °C in non-coordinating and non-ether containing solvents such as CH₂Cl₂ and toluene generates an intense purple species formulated as a dicopper(II)-μ-1,2-(*end-on*)-peroxo species [^oLCu^{II}]₂(O₂²⁻)²⁺. In methylene chloride, the LMCT absorption maxima (Figure 7) and 'apparent' absorptivities (ε) were as follows: 415 nm (sh, 1100 M⁻¹ cm⁻¹), 508 nm (2000 M⁻¹ cm⁻¹) and 630 nm (1250 M⁻¹ cm⁻¹). The ε values were calculated after about one to two minutes following introduction of O₂ and they are based on the maximum absorbance values observed at 508 nm under the conditions of UV-visible bench-top oxygenation. [^oLCu^{II}]₂(O₂²⁻)²⁺ begins decaying immediately upon reaching its maximum absorbance and has fully decayed after five minutes.

The absorptions of [^oLCu^{II}]₂(O₂²⁻)²⁺ mimic in pattern and relative intensity the very distinctive UV-visible spectrum of the dicopper(II)-μ-1,2-(*end-on*)-peroxo species [^{py}LCu^{II}]₂(O₂²⁻)²⁺, which exhibits the following characteristics: λ_{max} = 440 nm (sh, ε = 4000 M⁻¹ cm⁻¹), 525 nm (111500 M⁻¹ cm⁻¹) and 590 nm (sh, 7600 M⁻¹ cm⁻¹). Thus, by analogy, we assign the 415 and 630 nm absorptions as the triplet (O₂²⁻)π*_v → Cu^{II}(d_z²) and singlet (O₂²⁻)π*_σ → Cu^{II}(d_z²) transitions, respectively, and the relatively intense 508 nm band as the (O₂²⁻)π*_σ → Cu^{II}(d_z²) transition.²⁶ The absorptions of [^oLCu^{II}]₂(O₂²⁻)²⁺ are of relatively low intensity in comparison to [^{py}LCu^{II}]₂(O₂²⁻)²⁺, likely because the dicopper(II)-dioxygen adduct does not fully form and/or that the Cu₂O₂ species quickly decays due to solvent oxidation.

The generation of [^oLCu^{II}]₂(O₂²⁻)²⁺ following oxygenation of ^oLCu^I indicates that the anisole-ether-oxygen atom is bound to the copper(II) ion. By analogy to [^{py}LCu^{II}]₂(O₂²⁻)²⁺, which has been structurally characterized by X-ray crystallography (Chart 1), formation of a dicopper(II)-*end-on*-peroxide coordination mode requires the ligand to bind to the copper(II) ion in an η⁴-tetradentate fashion (Scheme 1). As observed for other cases, tridentate ligation always leads to the formation of a dicopper(II)-η²-η²-*side-on*-peroxo or dicopper(III)-bis-μ-oxo complex, which have distinctly different UV-visible and resonance Raman (rR) spectroscopic characteristics.^{2,4,56} Further supporting that the O_{anisole} coordinates to the copper(II) ion within [^oLCu^{II}]₂(O₂²⁻)²⁺ is that the X-ray crystal structure of [Cu^{II}(^oL)(Cl)]⁺ indicates that the anisole-ether-oxygen can well bind to a copper(II) center, see above.

UV-visible Spectroscopy in Toluene; Generation of [^oLCu^{II}]₂(O₂²⁻)²⁺ and [^{Bz}LCu^{III}]₂(μ-O₂²⁻)₂²⁺

Generation of [^oLCu^{II}]₂(O₂²⁻)²⁺ in toluene (-80 °C) reveals LMCT absorption bands and ε values at 513 nm (8300 M⁻¹ cm⁻¹), 628 nm (5200 M⁻¹ cm⁻¹). The apparent molar extinction coefficients observed are much higher than those calculated in CH₂Cl₂, yet smaller than the molar absorptivities exhibited by [^{py}LCu^{II}]₂(O₂²⁻)²⁺.^{26,36} As will be discussed in a later section, toluene oxidation also occurs during the thermal decay process of [^oLCu^{II}]₂(O₂²⁻)²⁺, possibly accounting for the low ε values. For example, approximately 50 % of the decay process has occurred after two hours, whereas [^{py}LCu^{II}]₂(O₂²⁻)²⁺ is stable for weeks at -80 °C. In addition, the absorption bands of [^oLCu^{II}]₂(O₂²⁻)²⁺ should be more intense than for [^{py}LCu^{II}]₂(O₂²⁻)²⁺ due to the poorer ligand donor ability of ^oL versus ^{py}L. Generally, a poor ligand donor results in better orbital overlap between the peroxide and copper(II), which translates into greater charge-transfer band intensity.⁵⁷

The low ε values might otherwise arise as a result of the likely small differences in coordination geometry exhibited by the copper(II) centers of [^oLCu^{II}]₂(O₂²⁻)²⁺ and [^{py}LCu^{II}]₂(O₂²⁻)²⁺. X-ray structural characterization of the latter indicates that the dicopper(II)-*end-on*-peroxo species adopts a trigonal bipyramidal geometry (τ = 0.86), consistent with

the structure of $[\text{Cu}^{\text{II}}(\text{PyL})(\text{Cl})]^+$ ($\tau = 1.00$). Assuming the same relationship exists between $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ and the corresponding cupric-chloride analogue $[\text{Cu}^{\text{II}}(\text{OL})(\text{Cl})]^+$ ($\tau = 0.23$), the t value would suggest that $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ adopts a square pyramidal geometry. In the trigonal bipyramidal coordination geometry (and d_{z^2} ground-state), the $(\text{O}_2^{2-})\pi^* \rightarrow \text{Cu}^{\text{II}}(d_{z^2})$ orbital overlap is optimized. Although we lack X-ray structural insight for $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ to fully support this assessment, if the copper(II) centers maintain a distorted square pyramidal geometry and $d_{x^2-y^2}$ ground state, this could decrease the overlap of the O_2^{2-} and Cu^{II} orbitals. Since epsilon intensity correlates to orbital overlap, the coordination geometry exhibited by $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ may, in turn, lower the inherent intensity of its LMCT bands.

A reaction of OLCu^{I} with O_2 does not occur in nitrile solvents (EtCN, MeCN), consistent with the known affinity of nitriles to suppress or compete with O_2 binding to copper(I) ions.^{46,58} Also, based on UV-visible spectroscopic criterion, a stable Cu_2O_2 species does not form in ether-containing solvents such as Et_2O and THF, nor in solvents containing an oxygen-heteroatom such as acetone. Since these solvents all possess a potential oxygen donor ligand, they most likely compete with the OMe group in OL for binding to the copper(II) ion. As a result, the 'end-on' $\text{Cu}^{\text{II}}\text{-O-O-Cu}^{\text{II}}$ peroxide structure may no longer be stable due to the lack of full tetradentate chelate ligand coordination.

Dioxygen Reactivity of BzLCu^{I}

Reaction of BzLCu^{I} with O_2 at -80°C leads to the formation of a dicopper(III)-bis- μ -oxo species $[\{\text{BzLCu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2]^{2+}$ (see diagram below) in a number of solvents examined (toluene, acetone, and Et_2O) (diagram) but not in the nitriles MeCN or EtCN.

The λ_{max} absorption feature attributed to a $\sigma^* \rightarrow d_{xy}$ transition ranged in value between 385 nm to 392 nm within the various solvents and the molar absorptivities ranged between 6500 and 9500 $\text{M}^{-1} \text{cm}^{-1}$, see Table 4. Dicopper(III)-bis- μ -oxo species typically exhibit more intense ϵ values due to the significant $\text{Cu}^{\text{III}}\text{-O}$ covalency that follows reduction of the peroxide ion and cleavage of the O-O bond. Since BzLCu^{I} possesses the same PY1 moiety as OLCu^{I} , similar competitive reactions with solvent (i.e., oxidation) may result upon addition of O_2 to the reaction solution. In dry toluene, $[\{\text{BzLCu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2]^{2+}$ slowly forms, taking almost 30 minutes to reach λ_{max} (385 nm; 7800 $\text{M}^{-1} \text{cm}^{-1}$) but is then fully stable for up to three hours, see Figure 8.⁵⁹

Resonance Raman Spectroscopy of $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ and $[\{\text{BzLCu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2]^{2+}$

In CH_2Cl_2 solvent, an O-O stretch at $\nu^{\text{O-O}} = 837\text{ cm}^{-1}$ was successfully observed in the rR spectrum for $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$; this downshifts by 45 cm^{-1} to 792 cm^{-1} upon $^{18}\text{O}_2$ substitution (Figure 9). This O-O stretch usually falls in between 820 and 840 cm^{-1} region known for dicopper(II)-*end-on*-peroxo complexes; dicopper(II)- $\mu\text{-}\eta^2\text{:}\eta^2$ -*side-on*-peroxo species exhibit much lower stretching frequencies, typically in the 730 to 760 cm^{-1} range or lower, due to an additional back-bonding interaction.^{4,26,56} In addition, a Cu-O stretch was observed for $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ at $\nu^{\text{Cu-O}} = 571\text{ cm}^{-1}$, which shifted to 545 cm^{-1} upon $^{18}\text{O}_2$ isotopic substitution. This finding also falls in line with the assignment of $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ as a dicopper(II)-*end-on*-peroxo species, as such Cu-O stretches have not been observed in dicopper(II)-*side-on*-peroxo species.⁴ Therefore, the rR spectrum of $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ is consistent with the observed UV-visible absorption features; together they clearly demonstrate that the copper-dioxygen adduct $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ is a dicopper(II)- $\mu\text{-}1,2$ -*end-on*-peroxide species, with a dicopper-dioxygen coordination mode similar to that in $[\{\text{PyLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ (Chart 1).

The $\nu_{\text{O-O}}$ and $\nu_{\text{Cu-O}}$ stretches exhibited by $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ are both centered at higher frequencies (6 and 10 cm^{-1} , respectively) than those of $[\{\text{PyLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$, which has values at 831 and 561 cm^{-1} , respectively.²⁶ The rather small changes may be simply due to environmental effects, but could also be explained by the ligand donor atom change from N_{Py} to $\text{O}_{\text{anisole}}$.⁶⁰

In toluene solvent and with $\lambda_{\text{ex}} = 407\text{ nm}$ excitation, $[\{\text{BzLCu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2]^{2+}$ exhibits a Cu=O stretch at $\nu_{\text{Cu-O}} = 595\text{ cm}^{-1}$ in the rR spectrum that downshifted by 30 cm^{-1} to 565 cm^{-1} upon $^{18}\text{O}_2$ substitution (Figure 10). The Cu-O stretch ($\sigma^* \rightarrow d_{xy}$) for dicopper(III)-bis- μ -oxo complexes are usually within the range of 580 to 650 cm^{-1} , a much higher frequency than dicopper(II)-peroxo species.⁴ Therefore, the rR spectroscopic properties of $[\{\text{BzLCu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2]^{2+}$ are consistent with the observed UV-visible spectroscopic features, conclusively demonstrating a dicopper-dioxygen coordination mode of a dicopper(III)-bis- μ -oxo species. Itoh and coworkers have previously demonstrated that copper(I) complexes derived from tridentate pyridyl alkylamine ligands similar to BzL (but with pyridyl 6-methyl substitutions) also react with dioxygen giving $[(\text{Cu}^{\text{III}})_2(\mu\text{-O}^{2-})_2]^{2+}$ complexes.^{45,62}

Dichloromethane Degradation by $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$

The most striking characteristic of the dicopper(II)- $\mu\text{-}1,2$ -(*end-on*)-peroxide species of OL is its substrate/solvent oxidative reactivity. Warming $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ to room-temperature leads to the immediate disappearance of its distinctive purple color accompanied by the formation of a blue complex $\text{OLCu}^{\text{II}}\text{-Cl}$; see earlier section for its X-ray structural characterization. Isolation of this chloride complex in $\sim 45\%$ yield suggests that CH_2Cl_2 solvent was oxidatively dechlorinated during the thermal transformation or decay of $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$; identification of CH_2Cl_2 derived oxidation products containing carbon have not been determined, but this was partially carried out in another study.⁶³ After decay of $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$, demetallation and analysis of the product solution indicates that only the starting ligand OL is present and no degradation/oxidation (e.g., O-demethylation) had occurred.

PyLCu^{I} and other copper(I) complexes are known to effect the reductive dechlorination of substrates such as dichloromethane, chloroform and benzyl and alkyl chlorides.^{36,64-66} Addition of CH_2Cl_2 to PyLCu^{I} induces an immediate color change from yellow to dark brown; $\text{PyLCu}^{\text{II}}\text{-Cl}$ has previously been isolated in such reactions. However, OLCu^{I} is stable in CH_2Cl_2 at room temperature for at least 10 minutes without obvious color change occurring,

indicating that the isolation of $^{\text{O}}\text{LCu}^{\text{II}}\text{-Cl}$ is unlikely to be a consequence of any copper(I) complex mediated reduction reaction.

Toluene Oxidation by $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$

As previously mentioned, generation of $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ in toluene ($\text{C}_6\text{H}_5\text{CH}_3$) also leads to solvent oxidation. By utilizing $\text{B}(\text{C}_6\text{F}_5)_4^-$ as the complex counteranion, $^{\text{O}}\text{LCu}^{\text{I}}$ is even soluble in such non-polar solvents as toluene. Lowering the temperature of solutions with high complex concentrations ($> 2 \text{ mM}$) to -80°C results in partial precipitation of the purple peroxide complex formed upon addition of O_2 to $^{\text{O}}\text{LCu}^{\text{I}}$. Nonetheless, standing at -80°C for a few hours results in full conversion of both the solution and solid state forms of $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ to green decay products. The dicopper(II)-dihydroxy complex $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\mu\text{-OH})_2]^{2+}$, that described above, was produced in $\sim 74\%$ yield based on the dicopperperoxo complex.

Warming low-temperature toluene solutions of $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ and carrying out subsequent GC product analyses discloses that $\sim 40\%$ benzaldehyde and $\sim 5\%$ benzyl alcohol are produced (Scheme 2). Product yields are based on the Cu_2O_2 species and excess O_2 was removed via vacuum/argon-purge cycles following formation of $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$. Considering that the generation of benzaldehyde from toluene is a four-electron oxidation process and the peroxide $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ is a two-electron oxidant (assuming no other oxidant, such as $\text{Cu}(\text{II})$ itself, is involved in this reaction), the products obtained account for an overall $\sim 90\%$ reaction yield.

Benzyl alcohol to benzaldehyde oxidation chemistry has been studied by Stack and coworkers in a reactivity study of a bis- μ -oxo dicopper(III) complex.⁶⁷ Therefore, benzyl alcohol, a two-electron toluene oxidation product, was probed as the possible initial product formed following solvent oxidation by $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$, which would perhaps be further oxidized to give benzaldehyde, the major product. To determine if $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ could effect such a reaction, two equivalents of external benzyl alcohol was added to the reaction mixture. Instead of observing a 1:1 benzyl alcohol/benzaldehyde product mixture, GC analysis revealed the ratio as $\sim 5:1$, indicating that benzaldehyde has been formed in $\sim 40\%$ yield, the same yield as when no external benzyl alcohol was added. Thus, $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ does not convert benzyl alcohol to benzaldehyde. Instead, the formation of benzaldehyde and benzyl alcohol must occur at the same time during the decay process of $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ and oxidation of toluene. Such an observation is not unprecedented, Que and coworkers have also found that benzaldehyde was the sole toluene oxidation product by an iron(IV) species.²⁹ Thus, this four electron oxidation reaction may be due to the nature of the *end-on* peroxide species and its following chemistry, as discussed below.

To identify the source of the oxygen atom within the benzaldehyde product, $^{18}\text{O}_2$ was used to generate $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$. After removing excess O_2 and allowing $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ to thermally decay, GC-MS analysis of the resulting toluene supernatant revealed that $\sim 54\%$ of the generated benzaldehyde was labeled with ^{18}O .⁶⁸ This modest ^{18}O -atom incorporation may be explained by the known facility of $\text{PhC}(\text{O})\text{H}$ to undergo oxygen atom exchange with residual water present in the gas or solvent medium.^{69,70} Despite this relatively low yield, this ^{18}O labeling experiment strongly argues that the benzaldehyde oxygen atom originated from $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ following addition of $^{18}\text{O}_2$ to $^{\text{O}}\text{LCu}^{\text{I}}$.

When the formation and decay of $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ was carried out in the presence of excess O_2 the yield of benzaldehyde increased to $\sim 75\%$. The improved benzaldehyde yield not only suggests that molecular oxygen participates in the toluene oxidation reaction but also that a radical mechanism may be involved, such as toluene hydrogen atom abstraction. To garner more information about the possibility of hydrogen atom abstraction chemistry, a $\text{C}_6\text{H}_5\text{CH}_3/\text{C}_6\text{D}_5\text{CD}_3$ (1:1) mixture was adopted as the reaction solvent. Product analysis

provided an apparent $k_H/k_D = 7.5 \pm 1$ based on the yield of benzaldehyde formed, see the Experimental Section. This significant isotope effect clearly demonstrates that $\text{PhCH}_2\text{-H}$ bond cleavage is a major component of the rate-determining step for this toluene oxidation reaction.

Ethylbenzene Oxidation by $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$

If C-H bond cleavage plays a major role in the rate determining step, similar oxidation chemistry of ethylbenzene (PhCH_2CH_3) by $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ should result under the same conditions. The toluene aliphatic C-H bond energy is 90 kcal/mol while that for the α -hydrogen aliphatic C-H bond energy of ethylbenzene is 87 kcal/mol.^{29,71,72} In fact, after generation of $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ in ethylbenzene as solvent and thermal decay, GC-MS analysis indeed disclosed the formation of acetophenone and 1-phenylethanol in ~ 30 % and 25 % yield, respectively, based on the Cu_2O_2 species, see Scheme 3. Consistent with the above ^{18}O -labeling experiments, the “corresponding” acetophenone and 1-phenylethanol were produced with greater than 95% ^{18}O -atom incorporation. This confirms that $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ is the oxygen source for the products in this aliphatic ethylbenzene oxidation reaction.

Toluene Oxidation by $[\{\text{PyLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$

Since $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ exhibits an exceptional aliphatic alkylbenzene oxidation reactivity, it was of interest to see if similar reactions are induced by the analogous $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ species. Therefore, $[\{\text{PyLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ was generated in toluene by oxygenation of PyLCu^{I} and warmed to ambient temperature to facilitate the thermal decay reaction. Surprisingly, $[\{\text{PyLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ was very stable in toluene and took about one week for full completion of the thermal transformation or decay, as indicated by the disappearance of the distinctive purple color of the reaction solution and solid precipitate. This excellent thermal stability in toluene contrasts sharply with that observed for $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$, which decomposes in less than one minute upon warming. GC analysis of the reaction supernatant also led to the detection of benzaldehyde but in only ~ 8 % yield based on Cu_2O_2 species. This contrasts with the ~ 40 % yield observed following thermal decay and solvent oxidation induced by $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ (Scheme 4).

Toluene Oxidation by $[\{\text{BzLCu}^{\text{III}}\}_2(\text{O}^{2-})_2]^{2+}$

Both dicopper(III)-bis- μ -oxo and dicopper(II)- μ - η^2 : η^2 -(*side-on*)-peroxo species are known to mediate substrate hydrogen atom abstraction reactions.²⁻⁴ Therefore, the toluene oxidation chemistry of $[\{\text{BzLCu}^{\text{III}}\}_2(\text{O}^{2-})_2]^{2+}$ was tested for comparison to $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$, as well as to indirectly probe the possible involvement of such a species derived from $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ (Scheme 5). Warming the resulting reaction mixture to ambient temperature and analysis of the reaction supernatant as described in the Experimental Section resulted in yields almost identical to the products of the analogous reaction induced by $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$. GC analysis of the products disclose that if $[\{\text{BzLCu}^{\text{III}}\}_2(\text{O}^{2-})_2]^{2+}$ is allowed to decay without excess O_2 then ~ 40 % benzaldehyde and less than 5 % benzyl alcohol is produced. Thus, a putative dicopper(III)-bis- μ -oxo species derived from $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ by de-ligation of the anisole ether oxygen ligand of OL is a likely possibility for the Cu_2O_2 species responsible for toluene and/or ethylbenzene oxygenation chemistry (Scheme 5).

Possible Reaction Mechanisms

Proposed mechanisms for the alkylbenzene oxidation following oxygenation of OLCu^{I} or BzLCu^{I} in toluene are shown in Scheme 6. Pathway A follows binuclear Cu_2O_2 species initiated chemistry; its detailed structure is left intentionally vague in order to account for all possible reactive binuclear species, such as a distorted dicopper(II)-*end-on*-peroxo species. However, based on the similar benzaldehyde product yields observed following thermal decay

of either $[\{\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ or $[\{\text{BzLCu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2]^{2+}$, a bis- μ -oxo-dicopper(III) complex $[\{\text{LCu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2]^{2+}$ can be hypothesized to form during the thermal transformation process, proceeding via the equilibrium shown in Scheme 5. Another possibility for the responsible reactive species is a mononuclear copper(II)-superoxide complex $[\text{RCu}^{\text{II}}\text{-O}_2]^{+}$, a precursor to any Cu_2O_2 species formed following oxygenation of LCu^{I} or BzLCu^{I} . Pathway B, Scheme 6 starts with chemistry initiated by this, $[\text{LCu}^{\text{II}}\text{-O}_2]^{+}$. Although neither $[\{\text{LCu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2]^{2+}$ nor $[\text{RCu}^{\text{II}}\text{-O}_2]^{+}$ were detected in this work, their possible involvement can not be ruled out.⁷³

As suggested by the kinetic isotope effect results (vide supra), the first and most-likely rate determining step would be abstraction of the α -hydrogen atom of a $\text{PhCH}_2\text{-H}$ molecule to give a $\text{PhCH}_2\bullet$ moiety. Following Pathway A, this benzyl radical would rapidly react with molecular O_2 to give a benzyl peroxy radical ($\text{PhCH}_2\text{OO}\bullet$); via well known alkylperoxy radical chemistry (e.g., the Russell mechanism),^{74,75} this could disproportionate to yield a 1:1 ratio of non-radical products benzaldehyde and benzyl alcohol (Pathway A, Scheme 6). Excess or residual O_2 present in the solution could originate from the reverse oxygenation reaction of the copper(I) complex (RCu^{I}). Such a disproportionation process well explains the nearly equal yield of acetophenone and 1-phenylethanol produced from the ethylbenzene oxidation. This reaction mechanism was also reported by Que and coworkers to interpret non-heme diiron catalyzed alkylbenzene oxidation reactions.²⁸

However, as described above, benzaldehyde (the four-electron oxidation product) was found to be the dominant product following toluene oxidation. Therefore, a different process must occur in order to account for the majority benzaldehyde product formation. For example, reduction of the benzylperoxy radical ($\text{PhCH}_2\text{OO}\bullet$) by RCu^{I} present in the system may occur prior to or parallel with the disproportionation process described above. Generation of $[\text{LCu}^{\text{II}}\text{-OOCH}_2\text{Ph}]^{+}$ followed by elimination of $[\text{LCu}^{\text{II}}\text{-OH}]^{+}$ and PhC(O)H generation (Scheme 5) would in a relative manner greatly increase the benzaldehyde product yield, as is the observed situation. Support for this mechanistic pathway comes from our isolation of $[\{\text{LCu}^{\text{II}}\}_2(\mu\text{-OH})_2]^{2+}$ (74 % yield), formally a dimer of $[\text{LCu}^{\text{II}}\text{-OH}]^{+}$.

Another pathway that would lead to only benzaldehyde product is if a copper(II)-superoxide species $[\text{RCu}^{\text{II}}\text{-O}_2]^{+}$ is the actual hydrogen atom abstractor. The resulting copper-hydroperoxide $[\text{RCu}^{\text{II}}\text{-OOH}]^{+}$ moiety could further react with the benzyl radical by a formal $\text{HOO}\bullet$ rebound reaction, releasing RCu^{I} and benzylhydroperoxide product; the latter could eliminate water to give benzaldehyde (Scheme 6; Pathway B).^{76,77} Recently, experimental and theoretical mechanistic investigations of dopamine β -monooxygenase (DBM) and peptidylglycine α -amidating monooxygenase (PHM) C-H oxidation chemistry suggest a mononuclear copper(II)-superoxide species is the active hydrogen atom abstraction reagent.^{10,12,13,78} Further, recent investigations on synthetically derived copper(II)-superoxide species, $[(\text{ligand})\text{Cu}^{\text{II}}\text{-(O}_2^-)]^{+}$ {NMe₂-tmpa, tris(4-dimethyl-aminopyrid-2-ylmethyl)amine); TMG₃-tren, tris(2-(N-tetramethylguanidyl)-ethylamine)}, demonstrate that they possess some H-atom abstraction capabilities.⁷⁹

Possible Reactive Species Following Oxygenation of LCu^{I}

In prior work, the reactivity of different Cu_2O_2 species with exogenously added substrates was compared (Chart 3).²² The dicopper(II)- μ -1,2-*end-on*-peroxide complexes $[\{\text{PyLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ and $[\text{Cu}^{\text{II}}_2(\text{XYL-O}^-)(\text{O}_2^{2-})]^{2+}$ were found to exhibit nucleophilic character. As a result, interesting oxidative chemistry was not demonstrated, for instance, addition of PPh_3 led to the release of O_2 and formation of corresponding copper(I)- PPh_3 complexes. By contrast, dicopper(II)- μ - $\eta^2:\eta^2$ -(*side-on*)-peroxide species such as $[\text{Cu}^{\text{II}}_2(\text{N4})(\text{O}_2^{2-})]^{2+}$ and $[\text{Cu}^{\text{II}}_2(\text{XYL-H})(\text{O}_2^{2-})]^{2+}$ (Chart 3) exhibit electrophilic reactivity,² for example the former oxidizes externally added PPh_3 to give O=PPh_3 ,²² while the latter undergoes internal

hydroxylation of the xylyl ligand spacer.^{2,80} Thus, from this precedent, one may argue that a dicopper(II)-*end-on*-peroxide complex such as $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ may not be a good enough oxidant or electrophilic enough to effect the toluene or ethylbenzene substrate oxidation discussed herein. We thus may consider three possibilities for the reactive copper-dioxygen species involved in the present chemistry: (1) a distorted square pyramidal dicopper(II)- μ -1,2-*end-on*-peroxide species $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$, (2) an unobservable dicopper(III)-bis- μ -oxo species $[\{\text{OLCu}^{\text{III}}\}_2(\mu\text{-O}^2\text{-})_2]^{2+}$, or (3) a mononuclear copper(II)-superoxide species $[\text{OCu}^{\text{II}}\text{-O}_2]^{+}$.

Addressing the first proposal, perhaps it is the modified copper coordination geometry present in $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ that facilitates the remarkable exogenous substrate reactivity. It is informative to compare copper(II) ion geometries in peroxo $\text{Cu}^{\text{II}}\text{-O}_2$ compounds with simpler nonperoxidic analogues possessing the same ligand (Table 5). The O_2 -adduct coordination geometries (dicopper(II)-peroxo complexes) likely exhibit structures similar to corresponding stable mononuclear copper(II) analogs. The crystal structure of $\text{OLCu}^{\text{II}}\text{-Cl}$ indicates that within the ligand OL frame, a square pyramidal geometry is favored, and thus we suggest that such a distorted geometry (i.e., away from trigonal bipyramidal) would be retained in $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$.

To date, two *end-on* Cu_2O_2 species have been structurally characterized, $[\{\text{PyLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ (Chart 1)²⁷ and Sukuzi's complex, $[\{\text{Cy}^{\text{II}}(\text{L}^{\text{H,Bn}})\}_2(\text{O}_2^{2-})]$ ($\text{L}^{\text{H,Bn}}$ = tris (N-benzylaminoethyl)amine).⁵⁶ The copper(II) ions in both complexes adopt a nearly perfect trigonal bipyramidal (TBP) geometry, with the apical amine nitrogen of the tetradentate ligand and the oxygen from the O_2^{2-} occupying the axial positions. In contrast, the copper(II) ions of *side-on* bound peroxide complexes all adopt a (distorted) square pyramidal geometry with τ values varying from 0 to 0.44 (Table 6) based on their X-ray crystal structures. Copper(III)-bis- μ -oxo species possess structures that possess nearly perfect square pyramidal geometries, i.e., with τ approaching zero (Table 6).

Electrophilic reactivity mechanisms such as hydrogen atom abstraction reactions are well-established for dicopper(II)- μ - $\eta^2:\eta^2$ -(*side-on*)-peroxo and dicopper(III)-bis- μ -oxo species.^{3, 17,67,96} In fact, the former is a better oxygen-atom transfer reagent,⁸⁰ while the latter is a better hydrogen atom acceptor.⁹⁷ Based on the chemical evidence presented here, it may be that an unobservable dicopper(III)-bis- μ -oxo $[\{\text{OLCu}^{\text{III}}\}_2(\mu\text{-O}^2\text{-})_2]^{2+}$ species that is structurally analogous to $[\{\text{BzLCu}^{\text{III}}\}_2(\mu\text{-O}^2\text{-})_2]^{2+}$ which forms during the decay of $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$; this could explain the equivalent toluene oxidation product yields starting either with OLCu^{I} vs. BzLCu^{I} . Furthermore, the geometry changes that result upon $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ redox changes based on X-ray crystallographic analysis of OLCu^{I} and OLCu^{II} , i.e. de-ligation of the anisole-ether-oxygen, support that a tridentate ligand framework is possible for the OL ligand that could potentially lead to $[\{\text{OLCu}^{\text{III}}\}_2(\mu\text{-O}^2\text{-})_2]^{2+}$. Supporting the notions described here is what we already mentioned, that the Cu_2O_2 species observed following oxygenation of OLCu^{I} is $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$, but such dicopper(II)- μ -1,2-(*end-on*)-peroxo species typically are nucleophilic and not good oxidants.

Tolman and coworkers⁸⁴ published an observation that is perhaps relevant to the present system involving chemistry with a tridentate tri-isopropyl substituted TACN triazacyclononane ligand and with a pyridyl appendage (L^{Py}) (Scheme 7). With their tetradentate ligand L^{Py} (Scheme 7A), an *end-on* peroxide species with UV-visible and rR characteristics (Table 5) similar to those known for $[\{\text{PyLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ were obtained. Thermal decay led to a ketone product, indicating a four-electron oxidation process. The chemistry was suggested to occur via a dicopper(II)-*side-on*-peroxide species transformed from the dicopper(II)-*end-on*-peroxide primary form.⁸⁴ In a separate study, a modified L^{Py} ligand possessing a sterically hindered 2-phenyl pyridyl donor formed a dicopper(III)-bis- μ -oxo species upon oxygenation and thermal

decay instead led to a two-electron oxidative N-dealkylation reaction (Scheme 7B).⁸⁵ The latter chemistry also occurs from the dicopper(III)-bis- μ -oxo species formed in the parent tridentate tri-isopropyl substituted TACN triazacyclononane ligand.¹⁷ Thus, different reactive species were probably involved in these two different reaction scenerios (Schemes 7A vs. 7B). The work from the Tolman labs may support the view that it is a dicopper(III)-bis- μ -oxo complex leads to the four-electron oxidation product (R^1R^2C-H to $R^1R^2C=O$, e.g., toluene to benzaldehyde) in the present system.

Summary/Conclusion

By employing a new anisole containing polypyridylamine ligand **OL**, a dicopper(II)- μ -1,2-*end-on*-peroxo species $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ was obtained by reacting the copper(I) precursor **OLCu^I** with molecular oxygen at -80 °C). The UV-vis and rR spectroscopic properties of $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ closely mimic those of the analogous species $[\{\text{PyLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$, which possesses a pyridyl ligand **PyL** instead of an anisole-ether-oxygen donor as in $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$. Compared to $[\{\text{PyLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$, the $\nu_{\text{Cu-O}}$ and $\nu_{\text{O-O}}$ shift to higher energy values for $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ suggests that the $\text{O}_{\text{anisole}}$ in that complex is a poorer donor than the corresponding $\text{N}_{\text{pyridyl}}$ atom in $[\{\text{PyLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$. This conclusion is further supported by the observed redox potential difference of $\Delta E_{1/2} = 0.11$ V between **PyLCu^{II}** and **OLCu^{II}** with the former possessing a more negative value. Additionally, $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ is very unstable in solvents possessing an oxygen-heteroatom as indicated by the lack of observable Cu_2O_2 species by UV-visible spectroscopy, suggesting competitive solvent binding. The poor electron-donating ability of **OL** as a result of the anisole-ether-oxygen moiety is also illustrated by the X-ray crystal structure of **OLCu^I** and the carbon monoxide binding studies revealing that the $\text{O}_{\text{anisole}}$ does not coordinate to the cuprous ion.

The most striking characteristic of $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ is the aliphatic alkylbenzene C-H bond oxidative ability. To our knowledge, this is the first example of such oxidation reactions starting with a dicopper(II)- μ -1,2-*end-on*-peroxo species. Dioxygen ¹⁸O-labeling experiments demonstrate that the oxygen atom in the product species is derived from molecular oxygen. An apparent $k_{\text{H}}/k_{\text{D}} = 7.5 \pm 1$ isotope effect suggests that α -H-atom abstraction from the alkylbenzene to yield a corresponding organic radical is likely to be the first as well as the rate-determining step of the reaction. Benzylic radical combination with O_2 (free or derived from a copper complex) and well established $\text{ROO}\cdot$ and $\text{ROO}\cdot/\text{metal}$ (here Cu^{I}) chemistry can account for the distribution of observed organic products.

As discussed, unobservable Cu_2O_2 derived species may be the actual oxidant species. Chemical precedence suggests that substrate reactions of $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ occur via its thermal transformation to a dicopper(III)-bis- μ -oxo isomer form $[\{^{\text{O}}\text{LCu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2]^{2+}$. Such an equilibration is supported by conducting parallel toluene-oxidation reactions with $[\{\text{BzLCu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2]^{2+}$ giving identical product distributions and yields. The weakly coordinated axial $\text{O}_{\text{anisole}}$ may deligate to form a tridentate η^3 -chelate, like exhibited by the cuprous species **OLCu^I**, that would support a dicopper(III)-bis- μ -oxo coordination mode. A copper(II)-superoxo intermediate generated from the loss of loss of (**OL**)Cu^I from $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ may alternatively be responsible for the observed H-atom abstraction reactivity. Further experimental or theoretical research is needed to test the validity of these hypotheses and to shed further light on the nature of the differing reactivity of $\text{Cu}^{\text{I}}_{\text{n}}/\text{O}_2$ derived species.

Supplementary Material

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through ligand donation to the copper center leads to a compensating decrease in peroxide π^* (σ) donation to the copper Cu^{II} ion (d_{z^2} orbital in TBP geometry), thus weakening the Cu-O bond. As a result, more electron density is localized in the peroxide π^* orbitals, weakening the O-O bond.

Thus, the higher O-O and Cu-O frequencies observed in the rR spectrum of $[\{\text{OLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ suggests that the anisole-ether-oxygen atom of **OL** is a weaker donor than the “corresponding” pyridyl nitrogen within $[\{\text{PyLCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$. This conclusion is supported by the electrochemical studies carried out (vide supra). The weaker ligand donation by tetradentate ligand **OL** increases peroxide π^* (σ) donation to the copper Cu^{II} ion (d_{z^2} orbital), which strengthens the Cu-O bond and consequently strengthens the O-O bond.

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Chart 1.

Figure 1.

Representative diagram showing the cationic portion of $[\text{Cu}^{\text{I}}(\text{OL})(\text{CH}_3\text{CN})]\text{B}$ (C_6F_5)₄, OLCu^{I} ; hydrogen atoms and the $\text{B}(\text{C}_6\text{F}_5)_4$ counter-anion has been omitted for clarity. Selected bond distances are: Cu1-N1, 2.010(2) Å; Cu1-N2, 2.286(3) Å; Cu1-N3, 2.063(1) Å; Cu1-N4, 1.911(2) Å; Cu1...O1, 5.072(5) Å. Selected bond angles are: N1-Cu1-N4, 126.79(8)°; N1-Cu1-N2, 79.32(7)°; N1-Cu1-N3, 115.38(8)°; N2-Cu1-N3, 79.68(7)°; N2-Cu1-N4, 129.57(7)°; N3-Cu1-N4, 113.52(8)°.

Figure 2.

Representative diagram showing the cationic portion of $[\text{Cu}^{\text{I}}(\text{BzL})(\text{CH}_3\text{CN})]\text{B}(\text{C}_6\text{F}_5)_4$, $\text{BzL} = \text{Cu}^{\text{I}}$; the $\text{B}(\text{C}_6\text{F}_5)_4$ counteranion has been omitted for clarity. Selected bond distances are: Cu1-N1, 1.990(4) Å; Cu1-N2, 2.309(4) Å; Cu1-N3, 2.042(4) Å; Cu1-N4, 1.900(4) Å. Selected bond angles are: N1-Cu1-N4, 123.83(2)°; N1-Cu1-N2, 79.24(1)°; N1-Cu1-N3, 123.77(1)°; N2-Cu1-N3, 79.63(1)°; N2-Cu1-N4, 133.31(2)°; N3-Cu1-N4, 108.39(2)°.

Figure 3.

Representative diagram showing the cationic portion of $[\text{Cu}^{\text{II}}(\text{BzL})(\text{EtOH})](\text{ClO}_4)_2$, BzLCu^{II} the two ClO_4^- counteranions has been omitted for clarity. Selected bond distances are: Cu-N1, 1.979(3) Å; Cu-N2, 2.035(3) Å; Cu-N3, 1.988(3) Å; Cu-O, 1.965(3) Å. Selected bond angles are: N1-Cu-N3, 165.74(1)°; N1-Cu-N2, 82.85(1)°; N2-Cu-N3, 83.09(1)°; N1-Cu-O, 96.33(1)°; N2-Cu-O, 172.94(1)°; N3-Cu-O, 97.34(1)°.

Figure 4.

ORTEP diagram showing views of the cationic portion of $[\text{Cu}^{\text{II}}(\text{O'L})(\text{Cl})]^+$. Selected bond distances are: Cu-O1, 2.317(5) Å; Cu-Cl1, 2.242(6) Å; Cu1-N1, 1.984(0) Å; Cu1-N2, 2.073(6) Å; Cu1-N3, 1.996(3) Å. Selected bond angles are: N1-Cu-N3, 165.70(8)°; N1-Cu-N2, 82.65(7)°; N3-Cu-N2, 83.61(8)°; N1-Cu-Cl, 96.92(6)°; N3-Cu-Cl, 96.87(6)°; N2-Cu-Cl, 179.01(6)°; N1-Cu-O, 96.76(7)°; N3-Cu-O, 84.26(7)°; N2-Cu-O, 78.22(6)°; Cl-Cu-O, 100.95(4)°.

Figure 5.

ORTEP diagrams showing views of the cationic portion of $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{m-OH})_2]^{2+}$; hydrogen atoms (except for HO^-) and the $\text{B}(\text{C}_6\text{F}_5)_4$ counteranion have been omitted for clarity. Selected bond distances are: Cu1-N1, 2.245(8) Å; Cu1-N2, 2.123(3) Å; Cu1-N3, 2.002(9) Å; Cu1-O1, 2.369(2) Å; Cu1-O2, 1.954(5) Å; Cu1-O2A, 1.944(1) Å; Cu1...Cu1A, 2.889(6) Å. Selected bond angles are: O1-Cu-N1, 152.66(3)°; O1-Cu-N2, 75.23(7)°; O1-Cu-N3, 80.42(2)°; O1-Cu-O2, 86.02(3)°; N1-Cu-N3, 96.23(8)°; O2-Cu-N1, 95.93(3)°; O2-Cu-N2, 93.47(5)°; O2-Cu-N3, 166.44(2)°; N1-Cu-N2, 77.42(7)°; N3-Cu-N2, 83.37(9)°.

Chart 2.

Figure 6. Cyclic voltammograms of **OLCu^{II}** (A) and **PyLCu^{II}** in DMF with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Ferrocene was added as an internal standard; the Fc/Fc⁺ redox waves are denoted by *.

Figure 7.

UV-vis absorptions of $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+}$ (**blue**) at $-80\text{ }^{\circ}\text{C}$ in CH_2Cl_2 . Addition of CO results in the quick formation of a new absorbance at 410 nm (**red**) before complete formation of the copper(I)-carbonyl adduct (**green**).

Scheme 1.

Figure 8. UV-visible absorption of $[\{\text{BzLCu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2]^{2+}$ (purple) at $-80\text{ }^{\circ}\text{C}$ in toluene following oxygenation of BzLCu^{I} (blue).

Figure 9. rRaman spectrum of $[\{^{\text{O}}\text{LCu}^{\text{II}}\}_2(\text{O}_2^{2-})]^{2+} \{\text{B}(\text{C}_6\text{F}_5)_4^-\text{ counterion}\}$ with ¹⁶O₂ (red) and ¹⁸O₂ (blue) isotopic substitution. The samples were run at 77 K in CH₂Cl₂ with 620 nm excitation. Solvent peaks denoted by *.

Figure 10. Resonance Raman (rR) spectrum of $[\{\text{BzLCu}^{\text{III}}\}_2(\mu\text{-O}^{2-})_2]^{2+}$ $\{\text{B}(\text{C}_6\text{F}_5)_4^-\}$ as counterion with $^{16}\text{O}_2$ (red) and $^{18}\text{O}_2$ (blue) isotopic substitution. The samples were run at 77 K in toluene with 407 nm excitation.

Scheme 2.

Scheme 3.

Scheme 4.

Scheme 5.

Scheme 6.

Chart 3.

Scheme 7.

Table 1Numerical Crystal and Refinement Data for the X-ray Crystal Structures of **BzLCu^I**, **O₂LCu^I**, **BzLCu^{II}**

Complex	BzLCu^I	O₂LCu^I	BzLCu^{II}
formula (sum)	C _{48.5} H ₃₀ B Cu F ₂₀ N ₄	C ₄₉ H ₃₀ B Cu F ₂₀ N ₄ O	C _{20.24} H _{23.48} Cl ₂ Cu N ₃ O ₉
fw	1123.11	1145.12	587.22
crystal system	triclinic	triclinic	monoclinic
space group	P1 ⁻	P1 ⁻	P2 ₁ /n
<i>a</i> (Å)	13.023(3)	8.0704(10)	9.1046(5)
<i>b</i> (Å)	13.409(4)	17.337(3)	30.057(7)
<i>c</i> (Å)	15.048(3)	17.499(2)	9.6380(5)
<i>α</i> (deg)	112.14(3)	107.807(12)	90
<i>β</i> (deg)	104.071(19)	90.416(10)	91.630(4)
<i>γ</i> (deg)	97.69(2)	91.680(11)	90
<i>V</i> (Å ³)	2285.5(12)	2329.8(6)	2636.4(7)
<i>Z</i>	2	2	4
<i>μ</i> /mm ⁻¹ (Mo K α)	0.600	0.593	1.082
reflections collected (total)	19 421	27 377	37 457
<i>R</i> _{int} (no. of equiv. reflections)	7713	11 504	6088
observed reflections [<i>I</i> / <i>s</i> (<i>I</i>) > 2]	4168	7952	4353
Final <i>R</i> , <i>R</i> _w [<i>I</i> / <i>σ</i> (<i>I</i>) > 2]	0.0612, 0.1076	0.0412, 0.1195	0.0565, 0.1433

Table 2

Numerical Crystal and Refinement Data for the X-ray Crystal Structures of Solvent Oxidation Products.

Complex	$^0\text{LCu}^{\text{II}}\text{-Cl}$	$[\{^0\text{LCu}^{\text{II}}\}_2(\mu\text{-OH})_2]^{2+}$	$[\{^0\text{LCu}^{\text{II}}\}_4(\text{CO}_3)_2]^{4+}$
formula (sum)	$\text{C}_{47.47}\text{H}_{27.94}\text{Cl}_{1.94}\text{Cu}\text{F}_{20}\text{N}_3\text{O}$	$\text{C}_{94}\text{H}_{56}\text{B}_2\text{Cu}_2\text{F}_{40}\text{N}_6\text{O}_4$	$\text{C}_{195.6}\text{H}_{122}\text{B}_4\text{Cu}_4\text{F}_{80}\text{N}_{12}\text{O}_{11.4}$
fw	1179.43	1179.43	4640.05
crystal system	Triclinic	Triclinic	Triclinic
space group	$\text{P}\bar{1}$	$\text{P}\bar{1}$	$\text{P}\bar{1}$
a (Å)	12.1990(5)	12.330(2)	17.232(3)
b (Å)	12.4156(5)	12.7247(17)	18.005(6)
c (Å)	16.1018(7)	14.7999(18)	18.767(6)
α (deg)	73.056(4)	74.404(11)	115.41(3)
β (deg)	82.456(4)	84.914(12)	109.99(2)
γ (deg)	85.222(4)	80.369(12)	94.716(19)
V (Å ³)	2310.08(17)	2202.7(6)	4759(2)
Z	2	1	1
μ/mm^{-1} (Mo $K\alpha$)	0.77167	0.626	0.585
reflections collected (total)	43 084	22 767	40 552
R_{int} (no. of equiv. reflections)	11 737	10 667	16 536
observed reflections [$I/s(I) > 2$]	9297	7840	5665
Final R , R_w [$I/\sigma(I) > 2$]	0.0500, 0.1173	0.0375, 0.1050	0.0883, 0.2072

Table 3

Carbonyl stretching frequencies for the ligand-copper(I)-carbonyl complexes.

Compound	Nujol (cm ⁻¹)	THF (cm ⁻¹)	CH ₃ CN (cm ⁻¹)
[Cu ^I (^{Py} L)(CO)] ⁺	2077	2090	2092
[Cu ^I (^O L)(CO)] ⁺	2093	2093	2095
[Cu ^I (^{Bz} L)(CO)] ⁺	2093	2095	2094

Table 4
UV-visible and Resonance Raman data for the Dicopper-Dioxygen (Cu_2O_2)
Complexes.^a

Copper-Dioxygen Adducts	Solvent; Temp.	UV-visible Data	rR data; cm ⁻¹ (Δ ¹⁸ O ₂)	
		LMCT; nm (M ⁻¹ cm ⁻¹)	ν _{Cu-O}	ν _{O-O}
Dicopper(II) μ-1,2 Peroxo Species				
[{ ^{Py} LCu ^{II} }] ₂ O ₂ ²⁻) ²⁺	THF; -80°C	525 (11500) 590 (7600)	561 (-26)	831 (-44)
[{ ^O LCu ^{II} }] ₂ O ₂ ²⁻) ²⁺	CH ₂ Cl ₂ ; -80°C	508 (2000) 630 (1250)	571 (-26)	837 (-45)
[{ ^O LCu ^{II} }] ₂ O ₂ ²⁻) ²⁺	Toluene; -80°C	513 (8300) 628 (5200)		
Dicopper(III) Bis-μ-oxo Species ^a				
[{ ^{Bz} LCu ^{III} }] ₂ O ₂ ²⁻) ²⁺	Toluene; -80°C	385 (7800)	595 (-30)	
[{ ^{Bz} LCu ^{III} }] ₂ O ₂ ²⁻) ²⁺	THF; -80°C	390 (8000)		
[{ ^{Bz} LCu ^{III} }] ₂ O ₂ ²⁻) ²⁺	Acetone; -80°C	392 (9500)		
[{ ^{Bz} LCu ^{III} }] ₂ O ₂ ²⁻) ²⁺	Et ₂ O; -80°C	390 (6500)		

^a Dicopper(III)-bis- μ -oxo species do not possess O-O bonds, therefore such rR values are not listed.

Table 5

Criterion τ value) for pentacoordination^a for select dicopper(II)- μ -1,2-*end-on*-peroxo species along with related (analog) ligand-copper(II)-complexes.

Ligand	Copper(II) Complex	τ value	Ref
PyL (TMPA)	$[\{\text{Cu}^{\text{II}}(\text{PyL})\}_2(\text{O}_2^{2-})]^{2+}$	0.86	27
	$[\text{Cu}^{\text{II}}(\text{PyL})(\text{Cl})]^+$	1.00	55
	$[\text{Cu}^{\text{II}}(\text{PyL})(\text{CN})]^+$	0.90	81
	$[\text{Cu}^{\text{II}}(\text{PyL})(\text{ONO})]^+$	0.74	82
$\text{L}^{\text{H,Bn}}$	$[\{\text{Cu}^{\text{II}}(\text{L}^{\text{H,Bn}})\}_2(\text{O}_2^{2-})]^{2+}$	0.81	56
	$[\text{Cu}^{\text{II}}(\text{L}^{\text{H,Bn}})(\text{Cl})]^+$	0.93	56
	$[\text{Cu}^{\text{II}}(\text{L}^{\text{H,Bn}})(\text{H}_2\text{O})]^{2+}$	0.78	83
L^{Py} (Scheme 8)	$[\{\text{Cu}^{\text{II}}(\text{L}^{\text{Py}})\}_2(\text{O}_2^{2-})]^{2+}$	not available	84
	$[\text{Cu}^{\text{II}}(\text{L}^{\text{Py}})(\text{ONO})]^+$	0.003	85
	$[\text{Cu}^{\text{II}}(\text{L}^{\text{Py}})(\text{Cl})]^+$	0.46	86
OL	$[\{\text{Cu}^{\text{II}}(\text{OL})\}_2(\text{O}_2^{2-})]^{2+}$	not available	--
	$[\text{Cu}^{\text{II}}(\text{OL})(\text{Cl})]^+$	0.23	--

^a trigonal bipyramidal, $\tau = 1.00$; square pyramidal, $\tau = 0.00$.⁴¹

Table 6Structural descriptions (τ values)^a for five-coordinate Cu(II) in complexes with a Cu₂O₂ core.^{40,87}

Copper(II) Complex	τ value	Cu ₂ (O ₂ ²⁻) species	Ref
[Cu ^{II} (PyL)} ₂ (O ₂ ²⁻)] ²⁺	0.86	end-on peroxo	27
[{Cu ^{II} (L ^{H,Bn})} ₂ (O ₂ ²⁻)] ²⁺	0.81	end-on peroxo	56
[Cu ^{II} (HB(3,5-i-Pr ₂ pz) ₃) ₂](O ₂ ²⁻)	0.027	side-on peroxo	42,88
[Cu ^{II} ₂ (O ₂ ²⁻)(L)] ²⁺	0.16,0.44	side-on peroxo	89
[{Cu ^{II} TP ^{CF₃,CH₃})} ₂ (O ₂ ²⁻)]	0.002	side-on peroxo	90
[Cu ^{II} ₂ (O ₂ ²⁻)(iPr ₃ TACD)] ²⁺	0.30 (av)	side-on peroxo	91
[{Cu ^{III} (L ^{Bn3})} ₂ (μ-O) ₂] ²⁺	0.018	bis-μ-oxo	92,93
[{Cu ^{III} (Me ₂ -tpa)} ₂ (μ-O) ₂] ²⁺	0.017	bis-μ-oxo	94
[{Cu ^{III} (iPr ₄ dtne)} ₂ (μ-O) ₂] ²⁺	0.077,0.142	bis-μ-oxo	95

^a trigonal bipyramidal, $\tau = 1$; square pyramidal, $\tau = 0$.⁴¹