Ligand Identity-Induced Generation of Enhanced Oxidative Hydrogen Atom Transfer Reactivity for a Cu\textsuperscript{II}\textsubscript{2}(O₂\textsuperscript{−}) Complex Driven by Formation of a Cu\textsuperscript{II}\textsubscript{2}(−OOH) Compound with a Strong O–H Bond

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Abstract

A superoxide-bridged dicopper(II) complex, [Cu\textsuperscript{II}\textsubscript{2}(XYLO)(O₂\textsuperscript{−})]\textsuperscript{2+} (1) (XYLO = binucleating \textit{m}-xylyl derivative with a bridging phenolate ligand donor and two bis(2-(2-pyridyl)ethyl)amine arms), was generated from chemical oxidation of the peroxide-bridged dicopper(II) complex [Cu\textsuperscript{II}\textsubscript{2}(XYLO)(O₂\textsuperscript{2−})]\textsuperscript{+} (2), using ferrocenium (Fc\textsuperscript{+}) derivatives, in 2-methyltetrahydrofuran (MeTHF) at −125 °C. Using Me\textsubscript{10}Fc\textsuperscript{+}, an \textit{1} ⇆ \textit{2} equilibrium was established, allowing for calculation of the reduction potential of \textit{1} as −0.525 ± 0.01 V vs Fc\textsuperscript{+}/0. Addition of 1 equiv of strong acid to \textit{2} afforded the hydroperoxide-bridged dicopper(II) species [Cu\textsuperscript{II}\textsubscript{2}(XYLO)(OOH)]\textsuperscript{2+} (3). An acid–base equilibrium between \textit{3} and \textit{2} was achieved through spectral titrations using a derivatized phosphazene base. The pK\textsubscript{a} of \textit{3} was thus determined to be 24 ± 0.6 in MeTHF at −125 °C. Using a thermodynamic square scheme and the Bordwell relationship, the hydroperoxo complex (3) O–H bond dissociation free energy (BDFE) was calculated as 81.8 ± 1.5 (BDE = 86.8) kcal/mol. The observed oxidizing capability of [Cu\textsuperscript{II}\textsubscript{2}(XYLO)(O₂\textsuperscript{−})]\textsuperscript{2+} (1), as demonstrated in H atom abstraction reactions with certain phenolic ArO–H and hydrocarbon C–H substrates, provides direct support for this experimentally determined O–H BDFE. A kinetic study reveals a very fast reaction of TEMPO–H with \textit{1} in MeTHF, with \textit{k} (−100 °C) = 5.6 M\textsuperscript{−1} s\textsuperscript{−1}. Density functional theory (DFT) calculations reveal how the structure of \textit{1} may minimize stabilization of the superoxide moiety, resulting in its enhanced reactivity. The thermodynamic insights obtained herein highlight the importance of the interplay between ligand design and the generation and properties of copper (or other metal ion) bound O₂-derived reduced species, such as pK\textsubscript{a}, reduction potential, and BDFE; these may be relevant to the capabilities (i.e., oxidizing power) of reactive oxygen intermediates in metalloenzyme chemical system mediated oxidative processes.

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Analytical details (UV–vis, \textit{r}R, and EPR spectra), \textit{E}° and pK\textsubscript{a} calculations, and DFT analysis (PDF)
INTRODUCTION

Dioxygen (O₂) reductive activation-mediated processes (e.g., the reduction of dioxygen to water, Scheme 1A) underly the functions of many essential metalloenzymes and are of interest in many research fields (e.g., catalysis, batteries, and fuel cells). While this process is well-known in (buffered) aqueous media (Scheme 1A), further intricate knowledge of chemistry requirements and mechanism(s) for O₂ reduction (or water oxidation) when mediated by metal ions in aqueous or low-polarity environments such as organic solvents may be useful or critically important in catalysis, such as in fuel cell technologies or other processes of societal energy concerns. Complementary understandings are also key to gaining a greater understanding of how coordination complexes may facilitate needed transformations and how key biological transformations are carried out by metalloenzymes involved in O₂-processing.

In nature, metalloenzymes such as cytochrome c oxidase couple the thermodynamic driving force of O₂ activation/reduction to ATP biosynthesis, while Cu-oxidases or Cu-oxygenases mediate important substrate oxidations. The reduction of dioxygen is the cathodic half-reaction of fuel cells, and metal ions (e.g., Li⁺, Mg²⁺, Fe³⁺,²⁺, and Cu²⁺,⁺) are frequently utilized in these reactions. Small-molecule copper complexes have been shown to be capable of 2- or 4-electron reduction of O₂ (with added acids/reductants) to H₂O₂ or water, respectively; their reductive abilities are dependent on the identity of the copper ligand, acid, or reductant. However, the stepwise processes involved in these reductive dioxygen-mediated catalytic cycles in metalloenzymes and fuel cells are not fully understood and require further fundamental insights, including deduction of the reduction potentials and basicity of metal-bound reduced (and possibly protonated) O₂ species (Scheme 1B).

Recent studies have provided valuable insights into the thermodynamic properties of monocopper and bimetallic (CuII₂ and NiII₂) systems containing bound reduced-oxygen moieties (e.g., superoxide and hydroperoxide). Karlin and co-workers bracketed the

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proton-coupled reduction potential of a mononuclear cupric superoxide–trifluoroacetic acid adduct using outer-sphere reductants (ferrocene derivatives) in 2-methyltetrahydrofuran (MeTHF) at −125 °C (Figure 1A). They also determined the reduction potential of a dicopper(II)–superoxide complex bearing an unsymmetrical monoanionic binucleating ligand (Figure 1B) in dichloromethane (DCM, CH₂Cl₂) at −80 °C, which was further corroborated through the use of low-temperature spectroelec-trochemistry. Using cyclic voltammetry, Meyer and co-workers have also reported on the thermodynamics of superoxide/peroxide conversion when bound to dicopper(II) or dinickel(II) complexes (Figure 1C and D) bearing pyrazolate-bridging ligands. In a significant advance, they were also able to calculate the O–H bond dissociation free energy (BDFE) for a pyrazolate-bridged dicopper(II)–hydroperoxide complex (abbreviated herein as [Cu²⁺(pyrazolate)-(OOH)]²⁺ and related to that in Figure 1C) from its pKₐ and the dicopper(II)–superoxide reduction potential using a thermodynamic square scheme and the Bordwell relationship (eq 1, where R is the gas constant, T is temperature, F is Faraday’s constant, and C_G,solv is a solvent-dependent constant).

\[ \text{BDFE} = 2.303RT(pK_a) + FE^{o} + C_{G,\text{solv}} \]  

The dicopper(II) complex, [Cu²⁺₂(XYLO)(OH)]²⁺, bearing the binucleating monoanionic ligand XYLO (a m-xylene derivative with a bridging phenolate moiety, two bis(2-{2-pyridyl}ethyl)amine chelating ligand arms) and a hydroxide bridge, has been shown to catalyze the reduction of O₂ in the presence of acid and reductant (Scheme 2). Interestingly, it was observed that either 2H⁺/2e⁻ (forming H₂O₂) or 4H⁺/4e⁻ (giving 2 equiv of H₂O) chemistry occurs, depending on the strength of acid used. With perchloric acid (HClO₄), the full reduction of O₂ to H₂O, however, with the weaker trifluoroacetic acid, partial reduction to H₂O₂ was facilitated. As revealed by the detailed studies, it is the differing species involved, dicopper(II)-bound superoxide, peroxide, and hydroperoxide, and their specific behaviors toward protons/electrons that dictate what chemistry occurs. Yet, insights into the relevant specific thermodynamic parameters (i.e., redox potentials and pKₐ values of metal–oxygen intermediates) have not been obtained. Such information and resulting fundamental insights can aid the development of biomimetic catalysts (i.e., for fuel cell technologies).

Herein, the newly described cryogenic generation, characterization, and reduction potential determination of the superoxide species [Cu²⁺₂(XYLO)(O₂⁻)]²⁺ (1, Schemes 2 and 3) are established. The pKₐ value for the hydroperoxide analogue, [Cu²⁺₂(XYLO)(OOH)]²⁺ (3, Schemes 2 and 3), is also determined. Establishing the reduction potential of 1 and the pKₐ of 3 allowed for the O–H bond dissociation free energy of the dicopper(II)–hydroperoxide species to be calculated by employing the Bordwell relationship (eqs 1 and 2 with T = 298 K in eq 2), denoted by the thermodynamic square scheme shown in Scheme 3.
\[
\text{BDFE} = 1.37(pK_a) + 23.06E^0 + C_{G,\text{solv}} \quad (2)
\]

A significant new finding is the observed abnormally elevated reactivity of 1 (versus analogous mono/dicopper–superoxo complex reactivity studies) toward H atom abstraction of phenolic O–H and hydrocarbon C–H bonds; yet this oxidative behavior is fully consistent with the observed/determined thermodynamic relationship between superoxo (1)– and hydroperoxo (3)–dicopper(II) complexes, thus highlighting the importance of ligand design in reactivity studies and for designing biomimetic catalysts.

**RESULTS AND DISCUSSION**

**Determination of the Reduction Potential of the [Cu\text{II}_2(XYLO)(O_2^{2−})]^2+ (1)/[Cu\text{II}_2(XYLO)(O_2^{2−})]^+ (2) Redox Couple.**

In accordance with previous reports,\textsuperscript{26,29} the dicopper(II)–superoxide complex 1 was formed via the addition of chemical oxidants, such as ferrocenium derivatives, to the previously described peroxide–dicopper(II) species,\textsuperscript{38} [Cu\text{II}_2(XYLO)(O_2^{2−})]^+ (2), in MeTHF at −125 °C (Figure 2). Previously, 2 was generated in CH\textsubscript{2}Cl\textsubscript{2} at −80 °C and characterized by UV–vis, resonance Raman (rR),\textsuperscript{39} and extended X-Ray absorption fine structure (EXAFS)\textsuperscript{40} spectroscopies; however, due to the incompatibility of strong bases with CH\textsubscript{2}Cl\textsubscript{2}, MeTHF was used here as the solvent system. Addition of 1 equiv of either dimethylferrocenium (Me\textsubscript{2}Fc\textsuperscript{+}) or octamethylferrocenium (Me\textsubscript{8}Fc\textsuperscript{+}) salt (\(E_{1/2} = −0.115 \text{ and } −0.430 \text{ V, respectively, vs } \text{Fc}^{+}/0 \text{ in MeTHF}\))\textsuperscript{25} to 2 at cryogenic temperatures (−125 to −80 °C) resulted in the isosbestic conversion of 2 to 1, as monitored by UV–vis spectroscopy, wherein the \(\lambda_{\text{max}}\) corresponding to the peroxide–dicopper(II) complex disappears at 523 nm and the band at 402 nm, corresponding to the superoxide–dicopper(II) complex, appears (Figure 2 and Scheme 3A). This latter species (1) is stable at cryogenic temperatures up to −80 °C, and, similar to what was observed for the peroxide–dicopper(II) complex (2),\textsuperscript{39} it decays to the hydroxo-bridged complex [Cu\text{II}_2(XYLO)(OH)]^2+ (Scheme 2) upon warming to room temperature. Interestingly, addition of the weaker oxidant, decamethylferrocenium (Me\textsubscript{10}Fc\textsuperscript{+}, \(E_{1/2} = −0.53 \text{ V vs } \text{Fc}^{+}/0 \text{ in MeTHF}\))\textsuperscript{25} to 2 resulted in the formation of an equilibrium mixture of complexes 2 and 1 (vide infra).

To verify the superoxide formulation of 1, electron paramagnetic resonance (EPR) and rR spectroscopies were utilized (Figures 3 and S1). The EPR spectrum at 20 K of [Cu\text{II}_2(XYLO)(O_2^{−})]^2+ (1) shows a single-line spectrum at \(g = 2.006\), typical of organic radicals, although broadened (Figure 3A). This signifies that the unpaired electron in the \(S = 1/2\) system is localized on the superoxide ligand with antiferromagnetic coupling occurring between the two copper-(II) ions (consistent with the lack of any signal due to Cu(II) ion). This finding is the same as that found for the previously published superoxide–dicopper(II) complex bearing the UNO binucleating ligand, [Cu\text{II}_2(UNO)(O_2^{−})]^2+ (Figure 1B), a close analogue of XYLO.\textsuperscript{26,41} Resonance Raman experiments confirmed the superoxide designation of 1, with the observation of two O–O stretches (1143 cm\textsuperscript{−1}, \(Δ^{18−16}\text{O}_2 = −61\); and 1103 cm\textsuperscript{−1}, \(Δ^{18−16}\text{O}_2 = −64 \text{ cm}^{-1}\)) and one Cu–O stretch (395 cm\textsuperscript{−1}, \(Δ^{18−16}\text{O}_2 = −19\)).
(Figures 3B and S1). Similar to the results reported for the superoxide–dicopper(II) complex ligated by UNO, [CuII2(UNO)-(O2•−)]2+ (Figure 1B), the two O–O vibrational frequencies are consistent with the presence of two different conformers of [CuII2(XYLO) (O2•−)]2+ (Figure 3B), in which the O2•− ligand bridges the two copper ions in either a μ-1,2 fashion (assigned as the higher-frequency ν(O–O)) or a μ-1,1 fashion (assigned as the lower-frequency ν(O–O)).

The higher-energy O–O stretch (1143 cm⁻¹) has a greater intensity than the stretch at 1103 cm⁻¹, suggesting that the 1143 cm⁻¹ conformer may be the dominant species in solution. The ratio of their intensities was identical upon generation at −125 and −80 °C (each with subsequent cooling to −196 °C for data collection), indicating that the species are very similar in both thermodynamics and formation kinetics. Additional isotope-sensitive features are observed at 505, 302, and 281 cm⁻¹ (Figure S1); however, the Δ18–16O shifts (−10, − 6, and −4 cm⁻¹, respectively) are smaller than that predicted for a pure Cu–16/18O stretch, suggesting that they may be coupled to O(phenolate) motion.

Density functional theory (DFT) calculations were carried out to evaluate the plausibility of two conformers of [CuII2(XYLO)(O2•−)]2+ in equilibrium. Geometry optimizations converged to two local minima, one exhibiting a μ1,1-bound superoxide ligand, the other exhibiting a μ-1,2 superoxide binding (Figure S17). These were calculated to be nearly isoenergetic (with the μ-1,1 favored by only 0.7 kcal/mol in ΔG). The electronic structure of both the μ-1,1 and μ-1,2 conformers involves a superoxide-localized radical; thus, both are in agreement with the EPR data. However, it was previously shown in the case of [CuII2(UNO) (O2•−)]2+ that the μ-1,2 structure yields the higher-frequency O–O stretch of the pair. The DFT-optimized structures with the XYLO ligand are comparable to those reported for the UNO ligand; thus, a similar trend in O–O stretches is assigned for the μ-1,1 and μ-1,2 structures with the XYLO ligand. In all, these findings suggest that the μ-1,2 structure is the dominant species in solution, with the μ-1,1 conformer lying close in energy.

When a weaker oxidant, Me10Fc+, was utilized to oxidize [CuII2(XYLO)(O2•−)]+, a mixture of 2 and 1 was observed by UV–vis spectroscopy, indicating that an equilibrium situation was achieved, allowing for Nernst equation analysis and determination of the reduction potential of the superoxo/peroxo–dicopper(II) complex (1/2) couple. Titration of varying amounts of Me10Fc+ into a MeTHF solution of 2 at − 125 °C resulted in differing concentrations of both 1 and 2 in solution (Figure 4), allowing for the calculation of the equilibrium constant in each instance (Figure 4 and Table S1). From these equilibrium constants and corresponding calculated E° values for each (given the known E°′ of Me10Fc+ in MeTHF),25 the reduction potential of [CuII2(XYLO)-(O2•−)]2+ was calculated to be −0.525 ± 0.01 V vs FeC+/0 (for which E°′ = 0.025 V vs saturated calomel electrode (SCE) in MeTHF). See Table S2 and eqs S1-S4 for additional details.

As mentioned earlier, the reduction potential of the superoxide–dicopper(II) complex bearing the UNO ligand (Figure 1B) was previously determined in dichloromethane to be −0.34 V vs FeC+/0 (0.13 V vs SCE) using similar methods herein.26 An interesting comparison can be made for the reduction potentials of the dicopper(II)–superoxide complexes bearing UNO and XYLO, even though the reduction potentials have been...
determined in different solvents (DCM and MeTHF, respectively). Addition of one methylene linker (going from the unsymmetrical ligand UNO to the symmetrical ligand XYLO) decreases the dicopper(II)-bound superoxide/peroxide reduction potential by ~190 mV (Figure S2) This result is corroborated by observing which ferrocene derivatives can reduce each dicopper(II)-superoxide species. For the UNO ligand, Me₈Fc can fully reduce the superoxide complex \([\text{Cu}^{II}_2(\text{UNO})(\text{O}_2^{\cdot-})]^2^+\) (Figure 1B),\(^2^6\) while multiple equivalents of the stronger reductant, Me₁₀Fc, are required to fully reduce the presently described superoxide compound bearing XYLO, \([\text{Cu}^{II}_2(\text{XYLO})(\text{O}_2^{\cdot-})]^2^+\) (1). While the exact origin of this decrease is unknown, it could be due to (i) an inherently greater thermodynamic stability of the peroxide ligand in its particular coordination to dicopper(II) within the UNO framework, compared to that for XYLO, or (ii) greater ligand donation from XYLO to the copper ions compared to that in UNO. In support of the latter as a relevant factor, we note that we previously\(^4^2\) compared the reduction potentials for copper(I) complexes with bis(2-pyridylethyl)amine (PY2) moieties possessing either a phenyl or benzyl substituent placed on the central N atom of the chelate. The copper(I) complex \([\text{Cu}^{I}(\text{Ph-PY2})]^+\), where Ph-PY2 is one of the tridentate chelates designed into the UNO unsymmetrical binucleating ligand (Figure 1B), possesses a reduction potential (measured as an \(E_{1/2}\) in dimethylformamide (DMF) solvent) that is 80 mV more positive than that for \([\text{Cu}^{I}(\text{PhCH}_2–\text{PY2})]^+\), where PhCH₂–PY2 is that tridentate chelate found in the overall symmetric binucleating ligand XYLO (Scheme 2 and Figure 2).

**Determination of the \(pK_a\) Value of \([\text{Cu}^{II}_2(\text{XYLO})(\text{OOH})]^2^+\) (3).**

To complete the thermodynamic square scheme analysis represented by Scheme 3, the \(pK_a\) value of the dicopper–hydroperoxide complex 3 was evaluated at −125 °C in MeTHF. As previously noted\(^3^7\) and observed herein, addition of stoichiometric or excess amounts of weak bases with conjugate acid \(pK_a\) values ≤19.1 (e.g., 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,8-bis(dimethylamino)naphthalene (“proton sponge”), and triethylamine) to \([\text{Cu}^{II}_2(\text{XYLO})(\text{OOH})]^2^+\) (3) did not result in formation of peroxo complex 2, even with excess base added. However, full deprotonation of 3 was accomplished via the addition of 1 equiv of the strong derivatized phosphazene base EtP₂(dma) (dma = dimethylamino) with \(pK_a\)(THF, of the conjugate acid at room temperature) = 28.1,\(^4^3,4^4\) (Chart 1) as observed via UV–vis spectroscopy wherein the hydroperoxide–dicopper(II) species (3, blue spectrum, Figure 5A, 398 nm) disappears and the peroxide–dicopper(II) complex (2, purple spectrum, Figure 5A, 523 nm) fully forms (MeTHF at −125 °C).

Most fortunately, a slightly weaker phosphazene base, that possessing a conjugate acid with a room-temperature \(pK_a\) value between 28.1 and 19, \(t\)-BuP₁(pyrr) (\(pK_a\)(THF) = 22.8, Chart 1),\(^4^3,4^4\) led to the establishment of an equilibrium between complexes 3 and 2 (Figure 5B). Spectral titration experiments in which \(t\)-BuP₁(pyrr) was incrementally added to the hydroperoxo species afforded equilibrium mixtures of 2, 3, \(t\)-BuP₁(pyrr), and \(t\)-BuP₁(pyrr)H⁺, allowing for the calculation of the \(pK_a\) of the hydroperoxide–dicopper(II) complex \([\text{Cu}^{II}_2(\text{XYLO})(\text{OOH})]^2^+\) (3) to be 24 ± 0.6 (Figure 5B, Tables S3 and S4, and eq S5).\(^4^4\) With these findings, complementary experiments could be carried out, corroborating our finding on the \(pK_a\) of 3. The conjugate acids of these two phosphazene bases (i.e., EtP₂(dma)H⁺ and...
'BuP$_1$(pyrr)H$^+$ were tested in their reactions with the peroxo complex [Cu$^{II}_2$(XYLO)(O$_2$$^\cdot$)$_2$]+ (2): Addition of EtP$_2$(dma)H$^+$, as expected, resulted in no changes in the UV–vis spectrum (Figure S3) as the $pK_a$ of EtP$_2$(dma)H$^+$ is greater than that of [Cu$^{II}_2$(XYLO)(OOH)]$^{2+}$ (3). However, 2 is protonated by 'BuP$_1$(pyrr)H$^+$ ($pK_a$(THF) = 22.8, vide supra) to give 3 (Figure S4), consistent with the experimentally determined $pK_a$ value of 24 for [Cu$^{II}_2$(XYLO)(OO–H)]$^{2+}$. Deprotonation of [Cu$^{II}_2$(XYLO)(OOH)]$^{2+}$ by EtP$_2$(pyrr) and protonation of [Cu$^{II}_2$(XYLO)(O$_2$$^\cdot$)$_2$]+ by 'BuP$_1$(pyrr)H$^+$ occurred with similar rates, qualitatively.

This hydroperoxo–dicopper(II) complex $pK_a$ value will be evaluated with respect to a pyrazolate bridged hydroperoxo–dicopper(II) complex, a protonated and reduced analogue of the superoxo–dicopper(II) complex shown in Figure 1C (from Meyer and co-workers), and will highlight the increased basicity of the peroxo complex [Cu$^{II}_2$(XYLO)(O$_2$$^\cdot$)$_2$]+ (2) contributing to enhanced oxidative reactivity of [Cu$^{II}_2$(XYLO)(O$_2$$^\cdot$)$_2$]+ (vide infra).

[Cu$^{II}_2$(XYLO)(OOH)]$^{2+}$ (3) can also be fully deprotonated using the strong base potassium tert-butoxide (KO'Bu); addition of 5 equiv of KO'Bu results in full deprotonation to give [Cu$^{II}_2$(XYLO)(O$_2$$^\cdot$)$_2$]+ within ~40 min (~125 °C; Figure S4). Subsequent addition of 5 equiv of the strong acid HBARF ([H(OEt)$_2$]$_2$][B(C$_6$F$_5$)$_2$]) fully reforms the dicopper(II)–hydroperoxide (Figure S6); the deprotonation of [Cu$^{II}_2$(XYLO)(OOH)]$^{2+}$ (3) is reversible. We previously showed that HBF$_4$-etherate readily protonates [Cu$^{II}_2$(XYLO)(O$_2$$^\cdot$)$_2$]+ (2) to give [Cu$^{II}_2$(XYLO)(OOH)]$^{2+}$ (3).$^{37}$ Addition of 1 equiv of the weaker acid [HDBU] [B(C$_6$F$_5$)$_2$]$_2$) ($pK_a$ = 19.1 in THF)$^{43}$ also fully protonates [Cu$^{II}_2$(XYLO)(O$_2$$^\cdot$)$_2$]+, which is in accordance with our experimentally (vide supra) calculated $pK_a$ of the hydroperoxo species 3 (i.e., the elevated basicity (relative to other (di)copper–peroxo species) of the peroxo complex 2) (Figure S7). Note that the relative rates of protonation of [Cu$^{II}_2$(XYLO)(O$_2$$^\cdot$)$_2$]+ qualitatively increase with increasing acidity of the added acid, i.e., the peroxo–dicopper(II) complex reacts much faster with HBARF (which is the strongest acid used herein) than with 'BuP$_1$(pyrr)H$^+$ or HDBU$^+$; see Figures S4, S6, and S7.

**Determination of the M–OO–H BDFE of [Cu$^{II}_2$(XYLO)-(OOH)]$^{2+}$ (3).**

Following one side of the thermodynamic square scheme shown in Scheme 3, the presently measured physical properties associated with the reduction of the superoxo complex [Cu$^{II}_2$(XYLO)(O$_2$$^\cdot$)$_2$]+ (1) to the peroxo species [Cu$^{II}_2$(XYLO)(O$_2$$^\cdot$)$_2$]+ (2) and the deprotonation of hydroperoxide [Cu$^{II}_2$(XYLO)(OOH)]$^{2+}$ (3) to give peroxide [Cu$^{II}_2$(XYLO)(O$_2$$^\cdot$)$_2$]+ (2) allow the BDFE of the Cu–O–H bond in [Cu$^{II}_2$(XYLO)(OOH)]$^{2+}$ (3) to be calculated using the Bordwell relationship, relating $pK_a$, $E^\circ$, and BDFE (eqs 1 and 2). The reduction potential for the 1/2 redox couple is $E^\circ$ = −0.525 V vs Fc$^{+}/0$ (vide supra); it can be postulated that this redox process is O$_2$$^\cdot$– fragment based, as deduced from these dicopper(II) complex’s physical properties and precedent from the closely related studies on the UNO ligand complexes [Cu$^{II}_2$(UNO)(O$_2$$^\cdot$–/O$_2$$^\cdot$–)]$^{2+}$.$^{26}$ As described, the measured apparent $pK_a$ value for [Cu$^{II}_2$(XYLO)(OOH)]$^{2+}$ of 24 and the solvent-dependent term $C_G$ (61 kcal/mol for THF),$^{46}$ and assuming that this value is similar for MeTHF solvent) have been applied to the Bordwell equation (eq 3). Thus, the BDFE of the O–H bond in [Cu$^{II}_2$(XYLO)(OO–H)]$^{2+}$ is calculated to be 81.8 ± 1.5 kcal/mol.$^{47}$ Note that O–H bonds
strengths are also commonly reported as bond dissociation enthalpies (BDEs) and that the BDE of the O–H bond in our hydroperoxide–dicopper(II) complex is 86.8 kcal/mol.

\[
BDFE = 1.37(24) + 23.06(−0.525) + 61 = 81.8 \text{ kcal/mol}
\] (3)

**Reactivity Studies between [Cu\textsuperscript{II}(XYLO)(O\textsubscript{2}•−)]\textsuperscript{2+} (1) and O–H and C–H Substrates, with Support for Our Calculated BDFE.**

Reactivity studies of [Cu\textsuperscript{II}(XYLO)−(O\textsubscript{2}•−)]\textsuperscript{2+} with substrates containing O–H bonds with various BDFEs\textsuperscript{48} were carried out to seek experimental support for the calculated O–H BDE of [Cu\textsuperscript{II}(XYLO)(OOH)]\textsuperscript{2+} (Scheme 3 and Figure 6). Because [Cu\textsuperscript{II}(XYLO)(O\textsubscript{2}•−)]\textsuperscript{2+} is stable up to −80 °C in MeTHF, reactivity studies were carried out at this temperature in order to decrease reaction times, although kinetics with TEMPO–H were conducted at −100 °C due to the very fast rate of this reaction (vide infra). For the substrates utilized herein, the O–H BDFEs were calculated in THF\textsuperscript{48} to be 66.5 kcal/mol for 2,2,6,6-tetramethylpiperdine-N-hydroxide (TEMPO–H), 75.8 kcal/mol for p-OMe-2,6-di-tert-butylphenol (p-OMe-2,6-DTBP), and 83.1 kcal/mol for p-methoxyphenol (p-OMe-phenol). From simple thermodynamic arguments, [Cu\textsuperscript{II}(XYLO)(O\textsubscript{2}•−)]\textsuperscript{2+} (1) should be able to abstract a hydrogen atom from any substrate that has a weaker O–H bond than that of the hydroperoxo–Cu\textsuperscript{II}–superoxide bond in [Cu\textsuperscript{II}(XYLO)(OOH)]\textsuperscript{2+} (3); thus, the reactivity of [Cu\textsuperscript{II}(XYLO)(O\textsubscript{2}•−)]\textsuperscript{2+} may validate our calculated O–H BDFE, determined from the Bordwell relationship and the measurements of the \(E^\prime\) and \(pK_a\) values (vide supra).

Reactivity studies were monitored by UV–vis spectroscopy because both [Cu\textsuperscript{II}(XYLO)(O\textsubscript{2}•−)]\textsuperscript{2+} and [Cu\textsuperscript{II}(XYLO)−(OOH)]\textsuperscript{2+} have distinctive UV–vis signatures. Addition of excess TEMPO–H, p-OMe-2,6-DTBP, or p-methoxyphenol to a solution of [Cu\textsuperscript{II}(XYLO)(O\textsubscript{2}•−)]\textsuperscript{2+} in MeTHF at −80 °C caused a decrease in the absorption features of the dicopper(II)–superoxide complex at 402 nm (Figures 6 and S9) and formation of the authentic [Cu\textsuperscript{II}(XYLO)(OOH)]\textsuperscript{2+} at 398 and 612 nm (blue spectrum in Figure 6). Reactions were also followed by EPR spectroscopy at 20 K; the final reaction mixtures for TEMPO–H and p-OMe-2,6-DTBP showed a sharp \(g = 2\) peak, indicative of the product TEMPO and p-OMe-2,6-di-tert-butylphenoxyl radicals, respectively, further providing evidence that a net hydrogen atom transfer (HAT) reaction had occurred (Figure 6, inset); no organic radical was observed in the EPR spectrum obtained for the reaction of p-OMe-phenol with [Cu\textsuperscript{II}(XYLO)(O\textsubscript{2}•−)]\textsuperscript{2+} due to the instability of p-methoxyphenoxyl radical. Note that the hydroperoxide – dicopper(II) complex [Cu\textsuperscript{II}(XYLO)−(OOH)]\textsuperscript{2+} (3) is EPR-silent (perpendicular mode) due to antiferromagnetic coupling between the two copper(II) ions, and thus, only the resulting organic radical product is detected by EPR spectroscopy upon completion of the reaction.

Thus, the results observed for these reactions do further support our results, leading to the calculated O–H BDFE (vide supra) for [Cu\textsuperscript{II}(XYLO)(OOH)]\textsuperscript{2+} (3) using the square scheme (Scheme 3) and the Bordwell relationship (eqs 2 and 3). Because [Cu\textsuperscript{II}(XYLO)(O\textsubscript{2}•−)]\textsuperscript{2+} (1) can react relatively quickly (i.e., the reaction goes to completion within 1 h at
−80 °C) when using 50 equiv of p-methoxyphenol (O–H BDFE of 83.1 kcal/mol, Figure S9), the O–H bond strength of \([\text{Cu}^{II}_2(\text{XYLO})(\text{OOH})]^2+\) must be similar to or greater than that of p-methoxyphenol. This demonstrates that the O–H BDFE of \([\text{Cu}^{II}_2(\text{XYLO})(\text{OOH})]^2+\) should be close to 83.1 kcal/mol; it was calculated to be 81.8 kcal/mol (vide supra). We also observe that \([\text{Cu}^{II}_2(\text{XYLO})(\text{O}_2^{-})]^2+\) (1) is not able to oxidize p-Me-phenol, for which O–H BDFE = 86.4 kcal/mol (in THF); this finding allows us to bracket our O–H BDFE for \([\text{Cu}^{II}_2(\text{XYLO})(\text{OOH})]^2+\) (3) as being <86.4 kcal/mol. Overall the results further indicate that our BDFE calculations for the hydroperoxo moiety O–H bond agree with our experimental findings on reactivity.

Interestingly, the O–H BDFE calculated herein is considerably greater than those of organic solvent soluble derivatives of ascorbic acid, 5,6-isopropylidene ascorbic acid, and 5,6-isopropylidene ascorbate (BDFE(MeCN) = 70.5 and 65.4 kcal/mol, respectively), biologically relevant substrates. In fact, \([\text{Cu}^{II}_2(\text{XYLO})(\text{O}_2^{-})]^2+\) (1) is capable of abstracting a hydrogen atom from both of these, forming the hydroperoxide–dicopper(II) complex in 80% yield (Scheme 4 and Figures S12 and S13). While determined in an organic solvent under cryogenic conditions, the reduction potential measured and the oxidative capability of the superoxo–dicopper(II) complex 1 do seem to fall into a range that is “biologically relevant”, as, for example, ascorbic acid derivatives can reduce \([\text{Cu}^{II}_2(\text{XYLO})(\text{O}_2^{-})]^2+\) (1) (by H atom addition). As we previously discussed26 for our analogue \([\text{Cu}^{II}_2(\text{UNO})(\text{O}_2^{-})]^2+\) (Figure 1B) with a reasonably similar \(E^{'\prime}\) value (vide supra), these reduction potentials also fall in a range relatively close to a common heme protein reductant. Cytochrome c and the organic soluble ascorbate analogue possess standard reduction potentials that lie between those of the \(\text{Me}_2\text{Fc}^+/\text{Me}_2\text{Fc}\) and \(\text{Me}_8\text{Fc}^+/\text{Me}_8\text{Fc}\) couples, as measured in acetonitrile as solvent.26 Therefore, it appears that the redox and oxidative properties of these (su)peroxo–copper complexes may be compared to biological chemistries including enzymatic reactions with redox reagents, etc.

Substrates containing moderate C–H bond strengths were also utilized to support the calculated hydroperoxide–dicopper(II) O–H BDFE and monitored by UV–vis spectroscopy. Addition of excess xanthene, fluorene, or diphenylmethane (C–H BDFEs of 72.2, 76.8, and 78.7 kcal/mol in THF, respectively)48 resulted in a slow decay of \([\text{Cu}^{II}_2(\text{XYLO})(\text{O}_2^{-})]^2+\), as observed by the decrease of the 402 nm band, eventually affording the spectrum corresponding to \([\text{Cu}^{II}_2(\text{XYLO})(\text{OOH})]^2+\) (3, \(\lambda_{\text{max}} = 398 \text{ nm, Figures 7, S14, and S15). These reactions were also monitored via EPR spectroscopy, resulting in silent EPR spectra due to the instability of the carbon radicals formed. Thus, the XYLO superoxo–dicopper(II) complex (1) is capable of reacting with substrates containing moderate O–H and C–H bond strengths.

**Comparison of this Work with Pyrazolate-Bridged Dicopper Bound Reduced-O₂ Intermediates.**

There is limited knowledge of thermodynamic parameters of copper-bound superoxide, peroxide, and hydroperoxide complexes. The only other report using a thermodynamic square scheme to determine the O–H BDFE of a (di)copper-bound hydroperoxide complex comes from the laboratories of Meyer and co-workers, utilizing a binucleating pyrazolate-
bridged ligand framework (Figure 1B). Their reported hydroperoxo–dicopper(II) O–H BDFE is 71.7 kcal/mol, >10 kcal/mol less than the O–H BDFE that was calculated for [CuII2(XYLO)(OOH)]2+ (3) (vide supra, Scheme 5). It is of considerable interest, we posit, that a deeper understanding of the origins of this difference in oxidizing capability of the two systems is of fundamental importance. Specifically important are what factors, pertaining to the ligand and coordination environment and geometry, the CuII redox properties imparted by the coordination, and the reduced O2 fragment binding geometries, give rise to the variations in E°' (superoxide/peroxide) and hydroperoxide pKa (–OO–H). It will require future research to provide critical insights, but we can herein delineate a number of points of comparison arising from the present study. 

First, it is noteworthy to mention that, while experiments were carried out in MeTHF for the XYLO system, the thermodynamic parameters for the pyrazolate-bridged system were obtained in either CH3CN or butyronitrile as the solvent system. Solvent environment is an important consideration but would not fully explain the differences in the dicopper(II) complexes with XYLO anion versus the pyrazolate group. 

A further illustration concerning the large difference in oxidizing power of the superoxide–dicopper(II) complex [CuII2(XYLO)(O2•−)]2+ (1) compared to the [CuII2(pyrazolate)](O2•−)]2+ complex (shown in Scheme 5 and Figure 1C) comes from kinetic studies with TEMPO–H monitored via UV–vis spectroscopy (Figure 8). The second-order rate constant k2 was obtained under pseudo-first-order conditions at −100 °C using 20-50 equiv of TEMPO–H (relative to complex 1) (Figure 8, inset). We find that k2 = 5.6 M−1 s−1 at −100 °C in MeTHF. This value is 43 times faster than that reported for [CuII2(pyrazolate)](O2•−)]2+, a study that was carried out at a much higher temperature, −20 °C in CH3CN.29 Again, this result supports our finding that [CuII2(XYLO)(O2•−)]2+ is very reactive, with [CuII2(XYLO)-(OOH)]2+ possessing a much higher O–H BDFE as compared to [CuII2(pyrazolate)(OOH)]2+ (Scheme 5). 

In addition to the faster reaction rate with TEMPO–H, there are other significant differences between [CuII2(XYLO)-(O2•−)]2+ and Meyer and co-workers’ superoxide–dicopper-(II) complex (Scheme 5). It is of interest to break down the observed ~10 kcal/mol difference in BDFE of [CuII2(L−)-(OOH)]2+ (L− = anionic binucleating ligand). The first prominent difference is in the reduction potentials of these two systems. The E°' (superoxide/peroxide) potential of [CuII2(XYLO)(O2•−)]2+ is ~65 mV more positive than that of the pyrazolate-bridged dicopper(II)–superoxide species,29 although the reduction potentials were measured in different solvents. From just this E°' perspective, it could be suggested that [CuII2(XYLO)(O2•−)]2+ is a slightly better oxidant than is [CuII2(pyrazolate)(O2•−)]2+ (Scheme 4).

Some physical property differences in dicopper(ii) complexes with XYLO versus pyrazolate ligands should also be highlighted. As described earlier, there are two conformers of [CuII2(XYLO)(O2•−)]2+ (1) present in solution, based on the observation of two O–O stretches by resonance Raman spectroscopy (Figure 3B), while only one O–O stretching frequency was observed in the rR spectrum of [CuII2(pyrazolate)(O2•−)]2+.29 Additionally, the EPR spectrum of [CuII2(XYLO)(O2•−)]2+ exhibits a broad g = 2 signal (indicative of
antiferromagnetic coupling between the two copper ions and with the unpaired electron residing on the bound O₂ fragment, Figure 3A), while the EPR spectrum of [CuII₂(pyrazolate)(O₂²⁻)]²⁺ resembles that of a monocopper-(II) axial signal. Thus, as Meyer and co-workers concluded, the unpaired electron in [CuII₂(pyrazolate)(O₂²⁻)]²⁺ is localized on one of the copper(II) ions and the superoxide ligand is antiferromagnetically coupled to the second copper-(II) ion. These results (obtained from rR and EPR spectroscopies) led the authors to suggest that the superoxide ligand in [CuII₂(pyrazolate)(O₂²⁻)]²⁺ bridges the two copper ions in a μ-1,2 fashion (Scheme 4), similar to the previously published dicopper(II)–peroxide complex bearing the same pyrazolate-bridged ligand. These differing properties may in some manner play a role in the superoxo–dicopper(II) complex reduction properties and especially in the oxidative reactivity of [CuII₂(pyrazolate)(O₂²⁻)]²⁺. This will also be discussed later in relation to density functional theory analysis.

In addition to these electronic differences in the superoxide–dicopper(II) complexes, another contributing factor in the 10 kcal/mol difference between the O–H BDFEs of hydroperoxide complexes [CuII₂(XYLO)(OOH)]²⁺ (3) and [CuII₂(pyrazolate)(OOH)]²⁺ is the basicity of the corresponding dicopper(II)–peroxide complexes (represented as the pKₐ values of the dicopper(II)–hydroperoxide complexes, Scheme 5). The dicopper(II)–peroxide complex bearing the phenolate-bridged XYLO ligand is substantially more basic than the dicopper(II)–peroxide with a bridging pyrazolate group (pKₐ = 24 vs 22.2, respectively, although these were determined in different solvents). Reflecting this behavior that is (perhaps) more significant than the pKₐ value difference (which were calculated), we tested and confirmed that the same organic bases that were utilized by Meyer and co-workers to deprotonate [CuII₂(pyrazolate)(OH)]²⁺ (DBU and tetramethylguanidine (TMG)) do not react with [CuII₂(XYLO)-(OOH)]²⁺. While the exact cause of this increased basicity of the peroxide O atom in [CuII₂(XYLO)(O₂²⁻)]⁺ is unknown, one possibility is the structural differences between the two complexes. [CuII₂(pyrazolate)(O₂²⁻)]⁺ has been characterized by X-ray crystallography, which shows that the peroxide ligand bridges the two copper(II) ions in a μ-1,2 fashion (Figure 9B). While an X-ray structure of [CuII₂(XYLO)(O₂²⁻)]⁺ has not been reported, previous resonance Raman analysis showed that the two O atoms of the peroxide ligand are chemically inequivalent. Because XYLO is a symmetrical ligand, this means that the peroxide ligand cannot be bridged via a μ-1,2 fashion because that would make the two O atoms chemically equivalent. Instead, and based on its charge-transfer band spectroscopic features, the binding mode of O₂²⁻ was proposed to be terminal to one copper(II) ion with only a slight (at most) interaction with the second copper(II) ion (Figure 9A). Having a “free” negatively charged O atom present in the case of [CuII₂(XYLO)(O₂²⁻)]⁺ should make this complex extremely basic, especially compared to the μ-1,2 pyrazolate-bridged peroxide ligand in [CuII₂(pyrazolate)(O₂²⁻)]⁺.

A final comparison between these two systems is made between the reactivity of the two dicopper(II)–superoxide complexes. The pyrazolate-bridged dicopper(II)–superoxide species is able to react with substrates containing weak O–H or N–H BDFEs, such as TEMPO–H and phenylhydrazine (BDFEs of 66.5 and 70.4 kcal/mol in CH₃CN, respectively),...
supporting the calculated O–H BDFE of 71.7 kcal/mol for \([\text{Cu}^{II}_2(\text{pyrazolate})(\text{OOH})]^2+\) (Scheme 5).\(^{29}\) In contrast to the pyrazolate-bridged dicopper(II)–superoxide complex, \([\text{Cu}^{II}_2(\text{XYLO})(\text{O}_2^{•−})]^2+\) is capable of oxidizing phenolic and hydrocarbon substrates with stronger O–H and C–H BDFEs such as \(p\)-OMe-2,6-di-tert-butylphenol and \(p\)-methoxyphenol (BDFEs of 75.8 and 83.1 kcal/mol in THF (Table S5),\(^{48}\) respectively) and xanthene, fluorene, and diphenylmethane (BDFEs of 72.2, 76.8, and 78.7 kcal/mol in THF (Table S6),\(^{48}\) respectively). This further supports \([\text{Cu}^{II}_2(\text{XYLO})(\text{OOH})]^2+\) having a stronger O–H BDFE than \([\text{Cu}^{II}_2(\text{pyrazolate})(\text{OOH})]^2+\) because \([\text{Cu}^{II}_2(\text{XYLO})(\text{O}_2^{•−})]^2+\) is able to react with substrates containing stronger O–H BDFEs.

BDFE calculations (using a similar thermodynamic analysis and square scheme as we have in this article) have also been reported or estimated for other copper-ligated species such as \((\text{L})\text{Cu}^{II}(\text{HO}^{•−})\), \((\text{L})\text{Cu}^{II}(\text{O}^{•−})\text{Cu}^{I}(\text{L})\), and \((\text{L})\text{Cu}^{II}(\text{OO}^{−})\) (Scheme S1).\(^{45,50-53}\) Tolman and co-workers have reported on the reactivity of copper(III) hydroxide complexes in THF with various substrates containing moderate-to-strong O–H and C–H BDEs.\(^{50,51,53}\) With slight modifications to the copper-bound ligand, a range of O–H BDEs of the resulting copper(II) aqua complex were obtained (converted to BDFEs for direct comparison herein) of 83, 85, and 86 kcal/mol.\(^{50,51}\) Kieber-Emmons and co-workers have published on the reactivity of a dicopper(II) bridging oxide complex in MeCN with substrates containing weak O–H BDFEs resulting in a copper(II)–OH–copper(I) species, whose O–H BDFE was calculated to be 77.2 kcal/mol.\(^{45}\) Most recently, Tolman and co-workers have estimated the O–H BDFE of a mononuclear copper(II)–hydroperoxide complex in THF/MeCN mixtures (predominantly THF) as being between 78 and 82 kcal/mol.\(^{52}\) As can be seen from a comparison of these previously published O–H BDFE values and that of our newly calculated O–H BDFE of \([\text{Cu}^{II}_2(\text{XYLO})(\text{OO}−)]^{2+}\), our BDFE value of 81.8 kcal/mol is on the upper end of the range of values for the mononuclear copper(II)–hydroperoxide but weaker (by 1.2–4.2 kcal/mol) than the copper(II) aqua complexes.

**Computational Evaluation of Geometric and Electronic Structure Contributions to Reactivity.**

To further investigate the greater O–H BDFE of \([\text{Cu}^{II}_2(\text{XYLO})(\text{OOH})]^2+\) relative to \([\text{Cu}^{II}_2(\text{pyrazolate})(\text{OOH})]^2+\), DFT calculations were performed for both ligand systems. By calculating the thermodynamics of abstracting an H atom from \([\text{Cu}^{II}_2(\text{XYLO})(\text{OOH})]^2+\) compared to \([\text{Cu}^{II}_2(\text{pyrazolate})(\text{OOH})]^2+\) (i.e., the energy of generating the respective \(\text{Cu}^{II}_2(\text{L})\text{OO}^{−}\) and \(\text{H}^+\) as solvated species), it was found that the XYLO complex affords an O–H BDFE that is 3.5 kcal/mol greater than that of the pyrazolate complex. This value is lower than the experimental value (10.1 kcal/mol) because the solvation model used in DFT does not adequately account for the contribution from the solvent-dependent constant \(C_G\) (which involves explicit interactions with solvent molecules); therefore, the DFT calculations reflect only the \(\text{H}^+\) affinity and ionization energy components (collectively), while they are experimentally measured as independent \(pK_a\) and \(E^\circ\) values (see eqs 1 and 2).

To understand why the phenolate-bridging XYLO ligand affords a greater O–H BDFE than the pyrazolate-bridging ligand, the geometric and electronic structures of the hydroperoxo and superoxo complexes for each ligand were examined. The geometry-optimized
hydroperoxo complex for these two ligand systems are very similar: both have the OOH ligand bound in a μ-1,1 fashion, with similar O–O bond lengths (1.437 vs 1.440 Å, respectively) and Cu–Oavg bond lengths (2.019 vs 2.025 Å, respectively) (Figure S18). In contrast, the structures of their superoxo complexes (bound in a μ-1,2 fashion) are quite different: the O–O bond is shorter in [CuII2(XYLO)(O2•−)]2+ than in [CuII2(pyrazolate)-(O2•−)]2+ (1.286 vs 1.302 Å), while the Cu–O bonds are longer in the XYLO complex (2.045 and 2.089 Å) than in the pyrazolate complex (1.968 and 1.985 Å) (Figure S19). This comparison is substantiated by the RDR data (vide supra), which reveal that the XYLO complex has a ν(O–O) ≈ 70 cm−1 higher frequency than the pyrazolate complex (predicted 55 cm−1 higher by DFT, or 61 cm−1 using Badger’s rule54); a ν(Cu–O) was not reported for the pyrazolate complex.

Additionally, the superoxide ligand with XYLO is calculated to bind in a cis fashion (∠(Cu–O–O–Cu) dihedral = 5.6°) that forms a planar 5-membered ring with the phenolate O, while it is rotated about the O–O bond in the pyrazolate complex (∠(Cu–O–O–Cu) = 74°). For comparison, the recently published phenolate-bridged analogue (UNO) had a ∠(Cu–O–O–Cu) = 8.4° in its DFT-optimized structure,26 further highlighting its similarity to XYLO and the contrast between the phenolate- and pyrazolate-bridged complexes.

In addition to their geometric dissimilarities, the μ-1,2 superoxo complexes bearing the XYLO and pyrazolate ligands possess markedly different electronic structures. Owing to the planar nature of the Cu–O–O–Cu core in [CuII2(XYLO)-(O2•−)]2+ (which also includes the phenolate O atom), the half-occupied O2•− π* orbital is out of the core plane, while the half-occupied Cu orbitals (d2−y2) are in the plane (Figure 10A). The two Cu atoms are antiferromagnetically coupled through a superexchange pathway involving the (occupied) inplane O2•− π* orbital as well as the in-plane p-orbital on the phenolate O (depicted in the a LUMO and β LUMO in Figure 10A), while the unoccupied electron on O2•− lies in an orthogonal orbital (β LUMO + 1 in Figure 10A). This electronic structure is in agreement with the EPR data (vide supra), which indicates that the unpaired e− is localized on the superoxide ligand.

In contrast, the rotation in the Cu–O–O–Cu core in the pyrazolate complex results in the half-occupied O2•− π* orbital having strong σ-overlap with one of the half-occupied Cu d2−y2 orbitals (Figure 10B). As a consequence, and as also determined by Meyer and co-workers,29 the superoxide ligand is strongly coupled to one of the Cu atoms, while the unpaired electron on the second Cu metal lies in a nearly orthogonal orbital. This electronic structure is corroborated by the published EPR data, which indicate that the unpaired electron in [CuII2(pyrazolate)(O2•−)]2+ is localized on one of the Cuions.29

Because the hydroperoxo complexes with XYLO and pyrazolate are very similar, the difference in BDPE is likely attributable to a greater stability of the superoxo complex with the pyrazolate ligand. This is supported by the DFT-optimized structures, which indicate stronger (i.e., shorter) Cu–O bonds in the pyrazolate complex. The calculations reveal that the torsion in the pyrazolate Cu–O–O–Cu core leads to greater overlap of the Cu HOMO (d2−y2) with the O2•− LUMO (π*), which enhances backbonding. Additionally, the pyrazolate donor orbitals (N lone pairs) effectively compensate donation out of the Cu d2−y2, as the ∠(N–Cu–O) angles are optimally oriented at ~94° (Figure S19). As a result,
the pyrazolate bridge donates more electron density into Cu$^{II}_{2}(O_2^{2−})$ than the phenolate bridge (Figure S19), meaning that the pyrazolate bridge better facilitates backbonding from Cu. The enhancement in backbonding in the pyrazolate complex (relative to XYLO) is therefore responsible for the longer O–O bond, shorter Cu–O bonds, and lower O–H BDFE (due to greater stability of the superoxo species). Taken together, the ability of [Cu$^{II}_{2}$(XYLO)(O$_2^{2−})$]$^{2+}$ to abstract an H atom from remarkably strong O–H substrates reported in this study is attributable to exceptionally weak backbonding in the planar (O$_{\text{phenolate}}$)Cu$^{II}_{2}(O_2^{2−})$ core, which yields one of the most reactive (L)Cu$_2$-superoxo complexes of its kind to date.

CONCLUSION

In this report, a new superoxide–dicopper(II) complex, [Cu$^{II}_{2}$(XYLO)(O$_2^{2−})$]$^{2+}$ (I), was synthesized via one-electron oxidation of a peroxide–dicopper(II) species and characterized using UV–vis, EPR, and resonance Raman spectroscopies. EPR spectroscopy suggests that the two copper(II) ions are antiferromagnetically coupled and that the unpaired electron resides on the superoxide ligand. Two O–O stretches were observed via rR spectroscopy for [Cu$^{II}_{2}$(XYLO)(O$_2^{2−})$]$^{2+}$, indicating that two conformers of the superoxide complex are present. These particular properties closely mirror the findings on the structurally similar superoxide complex [Cu$^{II}_{2}$(UNO)-(O$_2^{2−})$]$^{2+}$ (Figure 1B).

The reduction potential of the superoxo/peroxo–dicopper-(II) complex ([Cu$^{II}_{2}$(XYLO)(OOH)$]^{2+}$ (1/2) couple was determined to be −0.525 V (vs Fe$^{3+/2}$ in MeTHF) through chemical titrations of the oxidant Me$_{10}$Fc$^+$ into a solution of the peroxide–dicopper(II) [Cu$^{II}_{2}$(XYLO)(O$_2^{2−})$]$^{+}$ (2) complex, which resulted in formation of equilibrium mixtures of both dicopper(II)–superoxide and dicopper(II)–peroxide species (Figure 4). The pK$_a$ of [Cu$^{II}_{2}$(XYLO)(OOH)$]^{2+}$ was found to be 24 from chemical titrations of the base tBuP$_1$(pyrr) into a solution of the dicopper(II)–hydroperoxide complex, resulting in equilibrium mixtures of both dicopper(II)–peroxide and dicopper-(II)–hydroperoxide species (Figure 5). Using these two values and the Bordwell equation, the O–H BDFE of [Cu$^{II}_{2}$(XYLO)-(OOH)$]^{2+}$ was calculated to be 81.8 kcal/mol (Scheme 3). A BDFE value close to this has been verified experimentally, through the observations of reactions of [Cu$^{II}_{2}$(XYLO)-(O$_2^{2−})$]$^{2+}$ (1) with substrates containing weak-to-moderate O–H BDFEs (66.5, 75.8, and 83.1 kcal/mol in THF; see Figures 6, 8, and S9) as well as substrates containing moderate C–H BDFEs (72.2, 76.8, and 78.7 kcal/mol in THF; see Figures 7, S14, and S15).

Finally, comparison of the phenolate-bridged and the previously reported (by Meyer and co-workers)$^{29}$ pyrazolate-bridged dicopper(II)–hydroperoxide O–H BDFEs provided possible insight into their observed differences (Scheme 5). The chemical reasons for why [Cu$^{II}_{2}$(XYLO)(OOH)$]^{2+}$ has a 10 kcal/mol higher O–H BDFE involve the more positive reduction potential of the superoxide–dicopper(II) complex and the higher basicity of the peroxide–dicopper(II) species. As discussed, the difference in basicity between the phenolate- and pyrazolate-bridged dicopper(II)–peroxide compounds may be due to the difference in binding modes of the peroxide ligand in the two different dicopper(II)–peroxide complexes (Figure 9). DFT calculations revealed that a structural difference in the superoxide–dicopper(II) core may yield a more stable superoxide species in the pyrazolate-
bridged complex compared to the phenolate-bridged complex, which would result in a greater hydroperoxo ligand O–H BDFE in the latter.

However, to fully understand the drastic difference in the O–H BDFEs of the phenolate-bridged versus pyrazolate-bridged hydroperoxide–dicopper(II) species described, broader examples are needed, and systematic investigations are required. It is imperative to elucidate what coordination chemistry factors, those coming about through ligand design and resulting tuning, lead to the resulting redox and thermodynamic properties observed. Examples of such factors are (i) ligand donor atom type, which affects ligand-donating ability, (ii) coordination geometric factors resulting from chelation, (iii) resulting metal-complex reduction potentials (which will influence the electronic properties of bound dioxygen-derived fragments), and (iv) Cu⋯Cu distances possible from coordination constraints, arising from ligand design/architecture (in the case of these dicopper complexes) and how this factor influences or controls the electronic/redox and basicity properties of the metal- or dimetal-bound Cu-oxygen fragment. There exists a significant amount of literature emphasizing the positive influences (on efficiency, selectivity, etc.) that ligand design has in coordination/inorganic and organometallic complex reactivity not only for copper or other metal ion oxidative chemistries but for C–H activation catalysis, specific analyte-sensing detection, and many other applications. There exists considerable room and the need for new research efforts aimed to design complexes and new chemistry to enhance our fundamental understanding and our (practical) ability to maximize the potential of utilizing molecular oxygen as an energy source and/or source of O atoms in the facile and selective oxidation of organic compounds.

**EXPERIMENTAL SECTION**

**General.**

All chemicals and solvents were of commercially available quality and used without further purification unless otherwise specified. Inhibitor-free tetrahydrofuran (THF) and 2-methyltetrahydrofuran (MeTHF) were distilled over Na/benzophenone under Ar and deoxygenated with Ar before use. Pentane was distilled over calcium hydride under Ar and deoxygenated with Ar before use. All of the substituted phenols used for substrate-reactivity studies were purified according to published procedures. Air-free manipulations were performed using Schlenk techniques or a Vacuum Atmospheres OMNI-LAB glovebox. Low-temperature UV–vis spectroscopy experiments were carried out on a Cary Bio-50 spectrophotometer equipped with an Unisoku USP-203A cryostat using a 1 cm modified Schlenk cuvette. NMR spectra were collected using a Bruker Advance 400 MHz FT-NMR spectrometer at 25 °C. EPR spectra were collected with an ER 073 magnet equipped with a Bruker ER041 X-Band microwave bridge and a Bruker EMX 081 power supply: microwave frequency = 9.42 GHz, microwave power = 0.201 mW, attenuation = 30 db, modulation amplitude = 10 G, modulation frequency = 100 kHz, temperature = 20 K. The EPR spectrum of the superoxide–dicopper(II) complex I was fit using EasySpin v.5.1.12 (http://www.easyspin.org/). Resonance Raman spectra were obtained using an Andor Newton charge-coupled device (CCD) detector cooled to –80 °C on a Spex 1877 CP triple monochromator with 1200, 1800, and 2400 grooves/mm holographic spectrograph gratings.
Laser excitation (406.7 nm) was provided by a Kr+ ion (Coherent I90C-K) laser with 20 mW of incident power at the sample in a ~135° backscattering configuration. Resonance Raman spectra were collected for 5 min on samples cooled to 77 K in a liquid nitrogen finger Dewar (Wilmad). Elemental analyses were performed by Midwest Microlab, Indianapolis, IN.

Synthesis.

The organic compounds and metal complexes XYL,69 HBArF,70 [CuI(CH3CN)4]BARF,71 [CuII2(XYLO)(OH)](BARF),17 Me8FcBARF,72 and Me10FcBARF72 were synthesized according to literature procedures. The complex [CuI2(XYLO)]BARF was synthe-sized according to modified literature procedures, using EtOH and pentane instead of MeOH and Et2O.17,37

[HDBU][B(C6F5)4] was synthesized by adding 1 equiv of HBArF to the base DBU in dichloromethane, followed by 30 min of stirring. The product, a white powder, was precipitated by addition of pentane, collected, and dried. Calculated for C33H17N2BF20: C, 47.62; H, 2.06; N, 3.37. Found: C, 47.06; H, 2.10; N, 3.52.

Spectroscopic Sample Preparations.

UV–Vis Spectroscopy. Formation and Characterization of [CuII2(XYLO)(OOH)]2+ and [CuII2(XYLO)(O2−)]2+.—In an inert atmosphere glovebox, a solution of [CuII2(XYLO)]+ was prepared in MeTHF at 0.14 mM. Typically, 2.5 mL of a [CuII2(XYLO)]+ solution was added to a Schlenk cuvette capped with a septum. The cuvette was allowed to equilibrate temperature inside the cryostat for 10 min at −125 °C. After a spectrum of [CuII2(XYLO)]+ was taken, O2 (purchased from Airgas and dried through a column of ascarite) was bubbled through the [CuII2(XYLO)]BARF solution for 15 s to immediately form the dicopper(II)–peroxide complex, [CuII2(XYLO)(O2−)]2+, and spectra were recorded. Then, 50 μL of a 7 mM solution of either Me8FcBARF or Me3FcBARF was added to the cuvette, with stirring, and spectra were recorded every 30 s. Full formation of [CuII2(XYLO)(O2−)]2+ typically took 10–20 min, as indicated by full formation of the absorption feature at 402 nm. Addition of 1 equiv of acid (e.g., HBArF or [HDBU][B(C6F5)4]) to [CuII2(XYLO)(O2−)]2+ resulted in the full formation of [CuII2(XYLO)(OOH)]2+. Formation of the hydroperoxo complex typically took 10 min as indicated by the absorption feature at 398 nm.

[CuII2(XYLO)(O2−)]2+: UV–vis, λmax (molar absorptivity) in MeTHF at −125 °C: 402 nm (ε = 18 750 M−1 cm−1), 480 nm (sh, e = 4380 M−1 cm−1), 580 nm (e = 2800 M−1 cm−1).

[CuII2(XYLO)(O2−)]2+: UV–vis, λmax (molar absorptivity) in MeTHF at −125 °C: 402 nm (ε = 18 750 M−1 cm−1), 480 nm (sh, e = 4380 M−1 cm−1), 580 nm (ε = 2800 M−1 cm−1).

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[CuII2(XYLO)(OOH)]2+: UV–vis, λmax (molar absorptivity) in MeTHF at −125 °C: 398 nm (ε = 10 725 M−1 cm−1), 612 nm (ε = 1250 M−1 cm−1).

Determination of the Reduction Potential of [CuII2(XYLO)(O2−)]2+.—In a Schlenk cuvette equilibrated at −125 °C, [CuII2(XYLO)(O2−)]2+ was generated at 0.15 mM as described above. Titrations of 25–30 μL (0.25–0.30 equiv) of a 3.5 mM Me10Fc+ solution were carried out, up to the addition of 2.09 equiv total of Me10Fc+. After each addition of...
Me$_{10}$Fc$^+$ to the cuvette, there was a 15 min waiting period to ensure that equilibrium was reached. For each equilibrium mixture, the concentration of each species in solution was calculated using the absorption of Me$_{10}$Fc$^+$ at 784 nm and the mass balance (Table S1). From these equilibrium constants, the reduction potential was calculated using the Nernst equation (eqs S1, S2, S3, and S4 and Table S2). See Supporting Information for further details.

**Determination of the pK$_a$ of [CuII$_2$(XYLO)(OOH)]$^{2+}$.**—In a Schlenk cuvette equilibrated at −125 °C, [CuII$_2$(XYLO)(OOH)]$^{2+}$ was generated as previously described. Titration of 10–15 μL (0.67 or 1.01 equiv, respectively) of a 19.6 mM tBuP$_1$(pyrr) solution were carried out, up to the addition of 1.5 equiv total of tBuP$_1$(pyrr). After each addition of tBuP$_1$(pyrr) to the cuvette, there was a 15 min waiting period to ensure that equilibrium was reached. For each equilibrium mixture, the concentration of each species in solution was calculated using the absorptions at 398 and 523 nm and the mass balance (Table S3). From these equilibrium constants, the pK$_a$ was calculated (eq S5 and Table S4). Under similar reaction conditions, addition of 1 equiv of EtP$_2$(dma) to 3 fully formed 2. See Supporting Information for further details.

**Reversibility of the Deprotonation of 3 and Protonation of 2.**—In a Schlenk cuvette equilibrated at −125 °C, [CuII$_2$(XYLO)(OOH)]$^{2+}$ was generated as described earlier. KOtBu solution (75 μL. (5.05 equiv), 19.6 mM) was added to the solution, with stirring, and spectra were taken every 30 s (Figure S3A). Full deprotonation occurred after ~40 min (Figure S3B). After the reaction was allowed to stir for 80 min at −125 °C, 75 μL (5 equiv) of a 19.6 mM HBF$_4$ solution was added to the solution, with stirring. This resulted in the immediate reformation of [CuII$_2$(XYLO)(OOH)]$^{2+}$ (Figure S4). Similarly, addition of 10 equiv of [tBuP$_1$(pyrr)H][BF$_4$] (generated in situ from addition of 1 equiv of HBF$_4$ to tBuP$_1$(pyrr) in MeTHF) to [CuII$_2$(XYLO)(O$_2$$^{2−}$)]$^+$ resulted in full protonation, affording [CuII$_2$(XYLO)(O$_2$•−)]$^{2+}$ (Figure S6). However, addition of 10 equiv of [EtP$_2$(dma)H][BF$_4$] (generated in situ from addition of 1 equiv of HBF$_4$ to EtP$_2$(dma) in MeTHF) to [CuII$_2$(XYLO)-(O$_2$•−)]$^+$ resulted in no spectral change.

**Reactivity Studies of [CuII$_2$(XYLO)(O$_2$$^{2−}$)]$^{2+}$ with Substrates of Various O–H and C–H BDFEs and with Ascorbic Acid and Ascorbate Derivatives.**—For the reactivity of [CuII$_2$(XYLO)(O$_2$$^{2−}$)]$^{2+}$, the dicopper(II)–superoxide complex was generated as previously described. Subsequently, excess O–H and C–H substrates, 5,6-isopropylidene ascorbic acid or 5,6-isopropylidene ascorbate (generated in situ from addition of 1 equiv of 5,6-isopropylidene ascorbic acid to EtP$_2$(dma) in MeTHF), were added to the cuvette, with stirring, and the reaction was monitored with a spectrum taken every 30 s. Kinetic studies were carried out, under pseudo-first-order conditions, by addition of 20–50 equiv of TEMPO–H to 0.125 mM [CuII$_2$(XYLO)(O$_2$$^{2−}$)]$^{2+}$ at −125 °C in MeTHF. See Supporting Information for further details.

**EPR Spectroscopy.**—In an inert atmosphere glovebox, 0.825 mM solutions of [CuI$_2$(XYLO)]$^+$ in MeTHF were prepared. These solutions (0.4 mL), along with 0.2 mL of MeTHF, were each added to two 5 mm EPR tubes capped with rubber septa (final [Cu] =
0.55 mM). For the EPR spectrum of [Cu\(_{2}(XYLO)\)]\(^{+}\), the tube was immediately frozen in liquid N\(_{2}\). For the EPR spectrum of [Cu\(_{2}^{II}(XYLO)(O\(_{2}^{2-}\))\]^\(+\) and [Cu\(_{2}^{II}(XYLO)(O\(_{2}^{•-}\))\]^\(2+\), tubes containing [Cu\(_{2}^{II}(XYLO)\)]\(^{+}\) were cooled to –125 °C (pentane/liquid N\(_{2}\) cold bath), and then O\(_{2}\) was bubbled through the solution for 15 s. The excess O\(_{2}\) was purged out of the tubes by bubbling Ar for 15 s, and then one of the tubes (for the spectrum of [Cu\(_{2}^{II}(XYLO)(O\(_{2}^{2-}\))\]^\(+\)) was frozen in liquid N\(_{2}\). To the second tube, 50 μL (1 equiv) of a 6.6 mM solution of Me\(_{8}\)Fc\(^{+}\) was added, followed by mixing of the solution by bubbling Ar, resulting in a color change from purple to dark green. This tube was then frozen in liquid N\(_{2}\). Similarly, addition of 1 equiv of acid (e.g., HBArF or [HDBU][B(C\(_{6}\)F\(_{5}\))\(_{4}\)]) to [Cu\(_{2}^{II}(XYLO)-(O\(_{2}^{2-}\))\]^\(+\), followed by mixing of the solution by bubbling Ar, resulted in the formation of [Cu\(_{2}^{II}(XYLO)(OOH)\]^\(2+\). This tube was then frozen in liquid N\(_{2}\). The EPR spectra of [Cu\(_{2}^{II}(XYLO)\)]\(^{+}\), [Cu\(_{2}^{II}(XYLO)(OOH)\]^\(2+\), and [Cu\(_{2}^{II}(XYLO)(O\(_{2}^{2-}\))\]^\(+\) are silent (perpendicular mode), but the EPR spectrum of [Cu\(_{2}^{II}(XYLO)-(O\(_{2}^{•-}\))\]^\(2+\) shows a broad g = 2 signal as shown in Figure 3A.

For EPR data of phenolic substrate reactivity, 5 mm rubber septa capped EPR tubes were prepared with [Cu\(_{2}^{II}(XYLO)\)]\(^{+}\) solutions (final [Cu] = 0.55 mM), without the addition of the 0.2 mL of MeTHF. Once the tubes had been cooled to –80 °C in a cold bath (dry ice and acetone), O\(_{2}\) was bubbled through the solutions for 15 s, followed by purging the solution by bubbling Ar for 15 s. Then, 100 μL (1 equiv) of a 2.9 mM solution of Me\(_{8}\)Fc\(^{+}\) was added to form [Cu\(_{2}^{II}(XYLO)(O\(_{2}^{•-}\))\]^\(2+\) followed by 50 or 100 μL (50 or 100 equiv, respectively) of a 0.29 M solution of the desired phenolic substrate in MeTHF being added to the tube, followed by mixing the solution by bubbling Ar for 30 s. The tubes were left at –80 °C for 1 h and then frozen in liquid nitrogen.

**Resonance Raman Spectroscopy.**—The dicopper(II)–superoxide complex [Cu\(_{2}^{II}(XYLO)\)]\(^{+}\) was generated at 1 mM (MeTHF) at –125 °C (pentane/liquid N\(_{2}\) bath) or –80 °C (acetone/dry ice bath) in 9 in., 5 mm NMR tubes capped with septa by addition of 5 mL of either \(^{16}\)O\(_{2}\) or \(^{18}\)O\(_{2}\) gas to solutions of [Cu\(_{2}^{II}(XYLO)\)]\(^{+}\) followed by addition of 50 μL of a 10 mM Me\(_{8}\)Fc\(^{+}\) solution and mixing by bubbling Ar through the solution. The tubes were then frozen in liquid nitrogen and flame-sealed.

**DFT Calculations.**—Density functional theory (DFT) calculations were performed with the Gaussian 16 software package. All calculations were done using the B3LYP\(^*\) functional (15% HF exchange) including GD3BJ dispersion corrections, within the spin unrestricted formalism. Geometry optimizations employed a split basis set as follows: Def2TZVP for Cu/N/O; Def2SVP for C/H. Tight self–consistent field (SCF) convergence and an ultrafine integration grid were used, as well as a polarizable continuum solvation model (PCM, THF solvent) (calculation of BDFEs in MeCN yielded similar values due to approximations of PCM; see text). Optimized structures yielded no imaginary frequencies. SCF energies were computed using single-point calculations with Def2-TZVP basis set on all atoms. Molecular orbitals were visualized using the program LUMO. Thermodynamic parameters were taken from frequency calculations. Additional details are given in the Supporting Information.

**Supplementary Material**

Refer to Web version on PubMed Central for supplementary material.
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(44) (a). It is assumed that pK$_a$ values do not vary greatly between THF and MeTHF. MeTHF has only a slightly lower dielectric constant than THF (6.97 vs 7.5, respectively), and MeTHF is a slightly weaker Lewis base than THF (donor numbers of 18 and 20.5, respectively). See: Aycock DF Solvent Applications of 2-Methyltetrahydrofuran in Organometallic and Biphasic Reactions. Org. Process Res. Dev 2007, 11, 156–159. Note, our calculations utilize room-temperature pK$_a$ values, (i) as this approach is utilized by others; $^{29,45,50,51}$ (ii) in order to use the Bordwell equation, eq 2, which requires use of a pK$_a$ value at room temperature because the “1.37(pK$_a$)” term derives from 2.303RT(pK$_a$), where R is the gas constant in kcal/(mol K) and $T$ is the temperature in Kelvin, 298 K; and (iii) as our experimental results are in accord, or self-consistent; the acid base behavior of $[\text{Cu}(\text{XYL})(\text{OOH})]$$_2^+$ (3) and $[\text{Cu}(\text{XYL})(\text{O}_2^2\text{−})]^+$ (2) follows the finding that with a pK$_a$ for complex 3 equal to 24, our experiments show that adding a base to (3) that has a room-temperature pK$_a$(THF) of <24 (e.g., DBU, proton sponge) does not lead to deprotonation, and adding an acid of room-temperature pK$_a$(THF) of >24 (e.g., EtP$_2$(dma)H$^+$) does not lead to protonation of (2).

(44) (b). The error of 1.5 kcal/mol for the calculated BDFE value comes from errors associated with the measurements of the $E''$ and pK$_a$ values reported herein and also an assumption that the approximation between THF and MeTHF is not completely accurate. We attribute 1 kcal/mol of error coming from the experimental measurements; 0.5 kcal/mol of error is estimated for the differences between THF and MeTHF. See ref 44a for a comparison of some of the properties of MeTHF vs THF.

(48). See the Supporting Information for calculations of the O–H and C–H BDFEs of the substrates in THF. Similar calculations were performed by Mayer and co-workers to determine O–H BDFEs in MeCN; see: Warren JJ; Mayer JM Predicting organic hydrogen atom transfer rate constants using the Marcus cross relation. Proc. Natl. Acad. Sci U. S. A 2010, 107, 5282–5287 BDFEs of the substrates in DMSO are also given in the Supporting Information for comparison. [PubMed: 20215463]
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Figure 1.
Experimentally derived reduction potentials of the superoxide ligand ($E^\circ$ for $O_2^-/O_2^{2-}$) in metal-bound superoxide, complexes.\textsuperscript{25,26,29,30}
Figure 2.
UV–vis spectra monitoring the full oxidation of [Cu$^{II}_2$(XYLO)(O$_2$^{2−})]$^{+}$ (purple spectrum, $\lambda_{\text{max}} = 523$ nm) to [Cu$^{II}_2$(XYLO)(O$_2$^{•−})]^{2+}$ (green final spectrum, $\lambda_{\text{max}} = 402$ nm) following addition of 1 equiv of Me$_8$Fc$^+$ in MeTHF at −125 °C. Total reaction time is 20 min.
Figure 3.
EPR and rR spectroscopic characterization of [Cu$^{II}_2$(XYLO)(O$_2^-$)]$^{2+}$ (1). (A) Frozen MeTHF solution EPR (20 K, X-band) spectrum of 1 (black) and fitted spectrum (red). (B) rR spectra of [Cu$^{II}_2$(XYLO)(O$_2^-$)]$^{2+}$ (1) using $^{16}$O$_2$ (blue), $^{18}$O$_2$ (red), and difference spectrum ($^{16}$O$_2$ – $^{18}$O$_2$, green).
Figure 4.

UV–vis spectroscopy monitoring of the incremental addition of 0.25 equiv of Me$_{10}$Fc$^+$, from 0 to 2 equiv, to [Cu$^{II}_2$(XYLO)(O$_2^{2-}$)]$^+$ (2, purple) in MeTHF at −125 °C resulting in the generation of equilibrium mixtures shown in gray of Me$_{10}$Fc, [Cu$^{II}_2$(XYLO)(O$_2^{2-}$)]$^{2+}$ (1), Me$_{10}$Fc$^+$, and [Cu$^{II}_2$(XYLO)(O$_2^{2-}$)]$^+$ (2) (see the Experimental Section and Supporting Information for more details), which allowed the determination of the reduction potential of the $1/2$ couple. The low-energy feature at 784 nm is ascribed to the decamethylferrocenium cation. (Inset) Monitoring of the absorbances at 523 (purple) and 402 (green) nm, demonstrating the decrease and increase of absorbance at the $\lambda_{max}$ values for [Cu$^{II}_2$(XYLO)(O$_2^{2-}$)]$^+$ (2) and [Cu$^{II}_2$(XYLO)(O$_2^{2-}$)]$^{2+}$ (1), respectively.
Figure 5.
(A) Addition of 1 equiv of EtP$_2$(dma) to a $-125$ °C MeTHF solution of [Cu$^{II}_2$(XYLO)(OOH)]$^{2+}$ (3) resulted in full deprotonation, forming [Cu$^{II}_2$(XYLO)(O$_2$$^{2-}$)]$^+$ (2) (purple, $\lambda_{\text{max}} = 523$ nm). A spectrum was obtained every 30 s (gray spectra).
(B) Incremental titration of tBuP$_1$(pyrr) into a solution of [Cu$^{II}_2$(XYLO)(OOH)]$^{2+}$ (3) gave equilibrium mixtures (shown in gray, 15 min after each addition of tBuP$_1$(pyrr) to ensure equilibration) of tBuP$_1$(pyrr)H$^+$, [Cu$^{II}_2$(XYLO)(O$_2$$^{2-}$)]$^+$ (2) ($\lambda_{\text{max}} = 523$ nm), tBuP$_1$(pyrr), and [Cu$^{II}_2$(XYLO)(OOH)]$^{2+}$ (3) (see also Tables S3 and S4 and eq S5). (Inset) Monitoring the absorbance at 398 (blue)
and 523 (purple) nm upon addition of various amounts of $^1$BuP$_1$(pyrr), demonstrating the disappearance of 3 and concomitant formation of 2.
Figure 6.
UV–vis spectra monitoring of the reaction of $\text{[Cu}^{II}_2\text{(XYLO)}\text{(O}_2^{\cdot-})\text{]}^{2+}$ (green spectrum) with 30 equiv of $p$-OMe-2,6-DTBP in MeTHF at $-80 \, ^\circ\text{C}$ to give $\text{[Cu}^{II}_2\text{(XYLO)}\text{(OOH)}\text{]}^{2+}$ (blue final spectrum, $\lambda_{\text{max}} = 398$ and 612 nm). Spectra were taken every 5 min (gray spectra, total reaction time is 3 h). (Inset) EPR spectra (20 K) of $\text{[Cu}^{II}_2\text{(XYLO)}\text{(O}_2^{\cdot-})\text{]}^{2+}$ (1) (green spectrum, broad $g = 2$ peak) and its reaction with 30 equiv of $p$-OMe-2,6-DTBP to give $\text{[Cu}^{II}_2\text{(XYLO)}\text{(OOH)}\text{]}^{2+}$ (3) (X-band EPR silent) and the phenoxyl radical (blue spectrum, sharp $g = 2$ peak). The yield calculated based on the absorption of $\text{[Cu}^{II}_2\text{(XYLO)}\text{(OOH)}\text{]}^{2+}$ at 398 nm is 77%. The yield calculated based on spin quantification of the $p$-OMe-2,4-di-tert-buty1phenoxyl radical is 71%. See Figure S8 for a time trace of this reaction.
Figure 7.
UV–vis spectra monitoring the reaction of \([\text{Cu}^{II}_2(\text{XYLO})-(\text{O}_2^{•−})]^2+\) (green spectrum) with 500 equiv of diphenylmethane in MeTHF at −80 °C to give \([\text{Cu}^{II}_2(\text{XYLO})(\text{OOH})]^2+\) (blue final spectrum). Spectra were taken every 10 min (gray spectra, total reaction time was 8 h). Yield calculated based on the absorption of \([\text{Cu}^{II}_2(\text{XYLO})(\text{OOH})]^2+\) at 398 nm is 80%. See Figure S16 for a time trace of this reaction.
Figure 8.

UV–vis spectra monitoring the reaction of $[\text{Cu}^{II}_{2}\text{XYLO}-(\text{O}_2^*-\text{XYLO})]^{2+}$ at 402 nm (green spectrum) with 20 equiv of TEMPO–H in MeTHF at −100 °C to yield $[\text{Cu}^{II}_{2}(\text{XYLO})(\text{OOH})]^{2+}$ at 398 nm (blue final spectrum, total reaction time was 15 min). (Inset) Plot of $k_{\text{obs}}$ (s$^{-1}$) vs varying concentrations of TEMPO–H (M) to obtain the second-order rate constant, $k_2 = 5.6 \pm 0.4$ M$^{-1}$ s$^{-1}$. Yield calculated based on the absorption of $[\text{Cu}^{II}_{2}(\text{XYLO})(\text{OOH})]^{2+}$ at 398 nm is 96%. See the Supporting information for a larger version of the inset (Figure S11), which also includes the origin (0, 0).
Figure 9.
Comparison of the peroxide-binding modes in (A) $[\text{Cu}^{II}_2(\text{XYLO})(\text{O}_2^{2-})]^+$ and (B) $[\text{Cu}^{II}_2(\text{pyrazolate})(\text{O}_2^{2-})]^+$. 
Figure 10.
Lowest unoccupied molecular orbitals for $[\text{Cu}^{II}_2(XYLO)-(\text{O}_2^\cdot-)]^{2+}$ (A) and $[\text{Cu}^{II}_2(\text{pyrazolate})(\text{O}_2^\cdot-)]^{2+}$ (B), with the structure and unpaired spins (Cu = green, O$_2$ = red) for each complex shown on the left. Antiferromagnetic coupling between unpaired electrons is denoted below the structures on the left. For each complex, the singly occupied superoxo $\pi^*$ orbital (backbonding acceptor) is indicated in red. The percent of (formally) occupied orbital character mixed into the unoccupied orbitals is given for Cu atoms and chelating ligand (contributions from the bridging phenolate(Ph)/pyrazolate(Pyr) and the remaining ligand ($N_L$) are given separately); orbitals active in backbonding are bolded.
Scheme 1.
(A) Four-Electron, Four-Proton Reduction of Dioxygen to Water; (B) O₂ Addition at a Mixed-Valent Dicopper Site Giving a Bridging Superoxo Complex, Which Can Then Be Externally Reduced with or without a Proton Present to Give a Binuclear Hydroperoxo or Peroxo Complex, Respectively
Scheme 2.
Previously Deduced Catalytic Mechanism\textsuperscript{17} for the 2H\textsuperscript{+}/2e\textsuperscript{−} Reduction of O\textsubscript{2} to H\textsubscript{2}O\textsubscript{2} by [Cu\textsuperscript{II\textsubscript{2}}(XYLO)(OH)]\textsuperscript{2+} in the Presence of Acid (Trifluoroacetic Acid (TFA)) and Reductant (Decamethylferrocene)\textsuperscript{a}
\textsuperscript{a} All species depicted have been characterized in separate studies presently (vide infra) or previously.

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Scheme 3.
Thermodynamic Square Scheme Relevant to the Interconversion of Superoxo, Peroxo, and Hydroperoxo XYLO Dicopper(II) Complexes and the Present Determination of the O–H Bond Dissociation Free Energy of [Cu\textsuperscript{II}\textsubscript{2}(XYLO)(OOH)]\textsuperscript{2+} in MeTHF at −125 °C
Scheme 4.

$[\text{Cu}^{II}_2(\text{XYLO})(\text{O}_2^-)]^{2+}$ Can Abstract an H-Atom from Organic Solvent Soluble Derivatives of Ascorbic Acid (Green) and from Ascorbate (Blue)
Scheme 5.
Comparison of the Thermodynamic Parameters Determined for the Phenolate-Bridged (XYLO, Reported Herein) and the Pyrazolate-Bridged Dicopper(II) Complexes Reported \(^{28,29}\) by Meyer and Co-workers\(^a\).

\(^a\) Note that reduction potentials shown are vs \(\text{Fc}^{+/0}\).
Chart 1.
Strong, EtP₂(dma) (Left, Conjugate Acid $pK_a$(THF) = 28.1), and Weaker, $^t$BuP₁(pyrr) (Right, Conjugate Acid $pK_a$(THF) = 22.8), Phosphazene Base Derivatives Capable of Deprotonating [Cu^{II}₂(XYLO)(OOH)]^{2+} (3) To Give the Peroxo Complex [Cu^{II}₂(XYLO)(O₂²⁻)]⁺ (2)