turbation theory (MP2),[14] again by using the 6-31G(d) basis set. The lowest lying triplet of **4** has been calculated at the UHF, projected UHF (PUHF), UMP2, and projected UMP2 (PUMP2) levels of theory by utilizing the MP2/6-31G(d) geometry of the singlet ground state.

The following energies (in hartrees) have been obtained: **4**, −302.509 47 (RHF/3-21G//RHF/3-21G), −304.235 74 (RHF/6-31G(d)//RHF/6-31G(d)), −305.202 56 (MP2/6-31G(d)//MP2/6-31G(d)); **5**, −302.639 67 (RHF/3-21G//RHF/3-21G), −304.335 35 (RHF/6-31G(d)//RHF/6-31G(d)).

The following energies (first entry RHF/6-31G(d) value, second entry RMP2/6-31G(d)//RHF/6-31G(d) value, both in hartrees) have been calculated to determine the strain energy of **4**: ethylene, −78.031 72, −78.294 31; ethane, −79.228 75, −79.503 97; propene, −117.071 47, −117.454 72; cyclopropene, −115.823 05, −116.218 39; propane, −118.263 65, −118.673 96; isobutene, −156.110 67, −156.645 57; isobutane, −157.277 53, −157.825 38; acetone, −191.962 24, −192.540 87; cyclopentadienone, −266.482 59, −267.301 59.

The analysis of the electron density distribution has been carried out by using MP2 response densities in the way described elsewhere.[42]

The CNDO/S method by Del Bene and Jaffe[15] has been employed to calculate the UV-vis spectrum of **4** and **14a**.

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**Registry No. 4**, 133985-05-4; **4**-$d_4$, 133985-09-8; $[^{18}O]$-**4**, 133985-10-1; **5**, 3225-37-4; **5**-$d_4$, 133985-08-7; **6**, 932-97-8; **6**-$d_4$, 113567-96-7; $[^{18}O]$-**6**, 133985-07-6; **14a**, 32264-58-7; *p*-$O_2NC_6H_4N_2^{\bullet+}BF_4^-$, 456-27-9; *p*-$O_2NC_6H_4{}^{18}OH$, 20168-37-0; *p*-$H_2NC_6H_4{}^{18}OH\cdot HCl$, 133985-06-5.

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# Reactivity Patterns and Comparisons in Three Classes of Synthetic Copper–Dioxygen $\{Cu_2–O_2\}$ Complexes: Implication for Structure and Biological Relevance

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**Abstract:** We have recently characterized three classes of peroxodicopper(II) complexes, which are formed reversibly from the reaction of Cu(I) precursors (**1–3**) with $O_2$ at −80 °C in solution. Here, we detail and compare the reactivities of $[Cu_2(XYL–O–)(O_2)]^+$ (**4**, a phenoxo-bridged peroxodicopper(II) species having terminal $Cu–O_2$ coordination), $[\{Cu(TMPA)\}_2(O_2)]^{2+}$ (**5**, a trans $\mu$-1,2-peroxo-bridged complex with a tetradentate ligand on each copper(II) atom), and $[Cu_2(N4)(O_2)]^{2+}$ (**6**, which contains a bridging peroxo moiety with tridentate groups at both copper atoms). Complexes **4** and **5** possess a basic or nulceophilic peroxo group, but **6** behaves differently, possessing a nonbasic or electrophilic peroxodicopper(II) moiety. Thus, reaction of $PPh_3$ with **4** and **5** readily causes the stoichiometric displacement of the bound $O_2$ ligad, producing $Cu(I)–PPh_3$ complexes. With **6**, slow but complete oxygen atom transfer occurs, giving triphenylphosphine oxide. Protonation (or acylation) reactions are particularly striking, as addition of $HBF_4$ or $HPF_6$ to **4** and **5** gives near-stoichiometric yields of $H_2O_2$ (from excess $H^+$; iodometric titration), but **6** is relatively insensitive to protons. Carbon dioxide reacts with **4** and **5** to give peroxycarbonato complexes at −80 °C, which decompose to carbonato compounds; **6** does not react with $CO_2$. All three complexes **4–6** react with sulfur dioxide to give sulfato products. Trityl cation ($Ph_3C^+$) reacts with all the complexes to give benzophenone, but the relative yields again support the notion that the peroxo group in **6** is a poorer nucleophile. 2,4-Di-*tert*-butylphenol acts as a protic acid toward **4** and **5**, but in the presence of **6**, hydrogen atom abstraction leads to oxidatively coupled biphenol products. The reactions of $4\text{-}X\text{-}C_6H_4MgBr$ (X = $CH_3$, F) with **4–6** produce mixtures of $4\text{-}X\text{-}C_6H_4OH$ and substituted biphenyls; product ratios again support the view that **6** is a better one-electron oxidant and electrophilic reagent. The relationship of the observed reactivity patterns and structures of **4–6** is discussed, and it suggested that the $\mu$-$\eta^2$:$\eta^2$-binding proposed for **6** confers its unique reactivity. The relationship of the structure and reactivity of **6** to a related and previously described monooxygenase model system is discussed, as well as the relevance to the active site chemistry of copper proteins involved in $O_2$ utilization.

## Introduction

Understanding the relationship between structure and reactivity is a fundamental problem and challenge in chemistry and biochemistry. In our own laboratory, attempts to elucidate the intrinsic coordination chemistry occurring at active sites of copper proteins involved in $O_2$ utilization have led to the discovery and characterization of three different classes of $\{Cu_2–O_2\}^{n+}$ complexes ($n$ = 1 or 2).[1] It is of interest to determine if these species possess varying reactivity patterns and if any of them may possess particular structures or functions seen in the copper enzymes. This has been the purpose of the present investigation.

The chemistry of peroxometal complexes is of interest in a number of disciplines, including its application to organic oxidation processes in chemical or biochemical systems.[2,3] Iron- and

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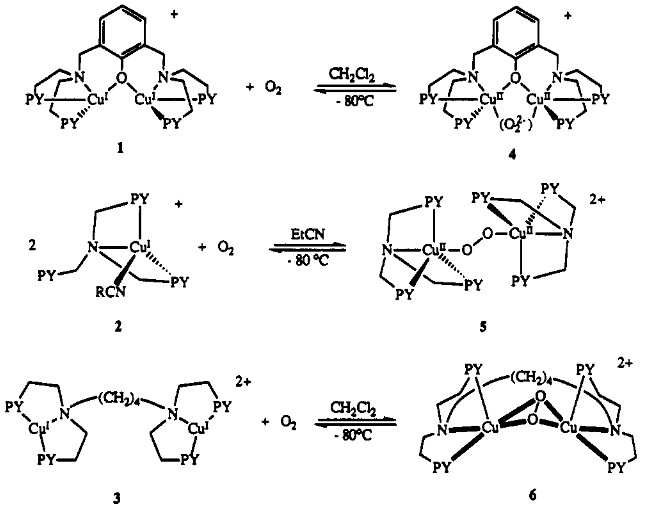
**Scheme I**



copper-containing metalloenzymes involved in $O_2$ processing often involve metal–peroxo, metal–hydroperoxo, or closely related products derived from these species. Hemerythrin and methane monooxygenase are non-heme diiron-containing metalloenzymes involved in $O_2$ transport and $O_2$ activation, respectively,[4] and non-porphyrin iron-containing chemical systems in which peroxides are bound or involved in substrate oxidation reactions are known.[5] There are manganese-dependent peroxidases,[6] while heme proteins of interest include various peroxidases[3a] and cytochrome P-450 monooxygenase.[3] Vanadium bromoperoxidases utilize $H_2O_2$,[7] dinuclear manganese catalases are known,[4c] and tetramanganese centers in photosystem II effect the oxidation of water to dioxygen.[8]

Peroxo- or hydroperoxocopper species are also implicated in copper enzymes. Hemocyanins (Hc) are molluscan and arthropodal $O_2$ carriers known to bind dioxygen via the redox process, $2Cu^I + O_2 \rightarrow Cu^{II}–(O_2^{2-})–Cu^{II}$.[1,9] Tyrosinase (Tyr)[10] is an *o*-phenol monooxygenase with an active site closely related to that for Hc, and a hydroperoxocopper active intermediate is implicated in dopamine $\beta$-hydroxylase action.[11] Peroxocopper intermediates occur during the four-electron reduction of $O_2$ by the "blue" copper oxidases laccase and ascorbate oxidase,[12,13] and a mixed-metal peroxo heme-iron/copper intermediate is generated by cytochrome *c* oxidase.[14]

Although only a few well-characterized copper–dioxygen (superoxocopper(II)[15] and peroxodicopper(II) complexes) have been described,[1,16–21] it is clear that a number of binding modes are possible, including several $\{Cu_2–O_2\}^{n+}$ species ($n$ = 1 or 2) generated in our own laboratories.[1] Complexes **4**–**6** (PY = 2-pyridyl; Scheme I) are formed reversibly at −80 °C in solution, by addition of $O_2$ to either mono- or dinuclear copper(I) complexes **1**–**3**.[1] $[Cu_2(XYL–O–)(O_2)]^+$ (**4**) is stable only at low temperature in solution, and spectroscopic analysis indicates that the peroxo moiety ($\nu_{O–O}$ = 803 cm$^{-1}$) is coordinated in an unsymmetrical manner, effectively terminally bound (i.e., $(Cu–O_2)$).[19] We were able to crystallize $[\{Cu(TMPA)\}_2(O_2)]^{2+}$ (**5**), and the X-ray structure[20] reveals a trans-$\mu$-1,2-peroxo ligand ($\nu_{O–O}$ = 831 cm$^{-1}$)[20b] connecting two mononuclear copper(II) centers. The peroxo ligand in $[Cu_2(N4)(O_2)]^{2+}$ (**6**) appears to have a rather different structure,[21] and on the basis of X-ray absorption (EXAFS and XANES) spectroscopic analyses,[21b] we suggested that it possesses a bent "butterfly" $\mu$-$\eta^2$:$\eta^2$-peroxo coordination. Kitajima and co-workers have recently confirmed the existence of such a binding mode, through an X-ray structure of a planar peroxo group found in $[\{LCu\}_2(O_2)]$ (L = hydrotris(3,5-diisopropylpyrazolyl)borato).[17]

In detailed studies reported here, we observe the peroxo group in $[Cu_2(XYL–O–)(O_2)]^+$ (**4**) and $[\{Cu(TMPA)\}_2(O_2)]^{2+}$ (**5**) to react in a manner characteristic of basic/nucleophilic $M_n–O_2$ compounds. In contrast, $[Cu_2(N4)(O_2)]^{2+}$ (**6**) behaves differently, and it appears that the $\mu$-$\eta^2$:$\eta^2$-binding confers a nonbasic/electrophilic reactivity to the peroxodicopper(II) moiety.[22] To elu-

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cidate these findings, reactions of **4**–**6** with triphenylphosphine, acid ($H^+$) and $RC(O)^+$, carbon dioxide, sulfur dioxide, triphenylcarbonium ion, 2,4-di-*tert*-butylphenol, and Grignard reagents have been carried out. The finding of relatively electrophilic behavior for the $\{Cu_2\text{–}O_2\}$ moiety in **6** has important implications for a copper monooxygenase system we have previously described[1,23] and may also be relevant to $\{Cu_n\text{–}O_2\}$ structure in $O_2$ binding or activating copper proteins.

## Experimental Section

**Materials and Methods.** Reagents and solvents used were of commercially available reagent quality unless otherwise stated. Labeled dioxygen ($^{18}O_2$, 99%) and carbon dioxide ($C^{18}O_2$, 99%) were obtained from Icon Services, Inc. Dioxygen and sulfur dioxide gases were dried by passing them through a short column of supported $P_4O_{10}$ (Aquasorb, Mallinkrodt). Oxygen was further dried by passing it through a copper coil tube immersed in a −80 °C cold trap. Carbon dioxide was dried by passing it through a 8.5-in.-long column filled with anhydrous $CaSO_4$ (Drierite). Methanol was distilled from $Mg(OMe)_2$, and anhydrous diethyl ether was utilized by passing it through a 60-cm-long column of activated alumina or it was directly distilled from sodium/benzophenone under Ar. In the dark, $CH_2Cl_2$ was stirred with concentrated sulfuric acid for several days. After being washed with water, $Na_2CO_3$(satd) solution, and water, it was dried over anhydrous $MgSO_4$ before a final reflux and distillation from $CaH_2$. Propionitrile was first distilled from $P_4O_{10}$, then refluxed, and distilled from $CaH_2$.

Preparations and handling of air-sensitive materials was carried out under an argon atmosphere with use of standard Schlenk techniques.[24] Deoxygenation of solvents and solutions was effected by either repeated vacuum/purge cycles using argon or by thorough bubbling (20 min) of Ar directly through the solutions. Solid samples were stored and transferred, and samples for IR and NMR spectra were prepared in a Vacuum Atmospheres drybox filled with argon. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Infrared spectra were recorded as Nujol mulls on either a Perkin-Elmer 710B or Mattson Galaxy 4030 FT-IR. NMR spectra were measured in $CD_3NO_2$, $CD_3COCD_3$, or $CDCl_3$ on either a Varian EM360 (60-MHz) or a Varian XL-300 (300-MHz) NMR spectrometer. Chemical shifts are reported as $\delta$ values downfield from an internal standard of $Me_4Si$. Electrical conductivity measurements were carried out in acetonitrile ($CH_3CN$) or DMF with use of an Barnstead Sybron Corp. Model PM-70CB conductivity bridge and a Yellow Springs Instrument Co. Inc. 3403 cell. The cell constant ($k$) was determined in a standard aqueous KCl solution. Room-temperature magnetic moments were determined with use of a Johnson Matthey magnetic susceptibility balance, and the instrument was calibrated against $Hg[Co(SCN)_4]$. Electron paramagnetic resonance (EPR) spectra were obtained in frozen solutions at 77 K with 4-mm-o.d. quartz tubes in a Varian Model E-4 spectrometer operating at X-band. The field was calibrated with a powder sample of diphenylpicrylhydrazyl (DPPH; $g = 2.0037$). Low-temperature electronic spectroscopic studies were carried out on either a Perkin-Elmer Lambda Array 3840 spectrophotometer driven by an IBM PC or a Hewlett-Packard 8452A diode array spectrophotometer driven by a Compaq Deskpro 386S computer using software written by On-line Instrument Systems, Inc. The spectrophotometer was equipped with a variable-temperature Dewar and a cuvette assembly as described elsewhere.[19a,21a] Gas chromatography was carried out on a Hewlett-Packard 5890 gas chromatograph fitted with a 30-m HP-5 (cross-linked 5% phenyl methyl silicone) capillary column. Electron ionization mass spectrum were obtained on a double-focusing VG Instruments 70-S gas chromatograph/mass spectrometer.

**General Method for Generating Complexes $[Cu_2(XYL\text{–}O\text{–})(O_2)]^+$ (4), $[\{Cu(TMPA)\}_2(O_2)]^{2+}$ (5), and $[Cu_2(N4)(O_2)]^{2+}$ (6).** Complexes $[Cu_2(XYL\text{–}O\text{–})]^+$ (**1**)[19a] and $[Cu_2(N4)]^{2+}$ (**3**)[21a] were dissolved in air-free, dry $CH_2Cl_2$, and the solutions were cooled to −80 to −85 °C. The solutions were oxygenated by bubbling dioxygen through it for 15 min. The removal of excess $O_2$ was accomplished either by evacuating the solution and purging with argon several times or by bubbling argon through the solution for 15 min. Complex **5** was prepared from $[Cu(TMPA)CH_3CN]^+$ (**2**)[20a] in $C_2H_5CN$ by a similar method. In order to form complex **5** in $CH_2Cl_2$, the dichloromethane was first saturated with oxygen at −80 °C. Then, solid **2** was added, followed by additional bubbling of the solution with dioxygen for 5 min. The excess oxygen was removed by using a procedure described above.

**Quantitative Determination of Hydrogen Peroxide Formed upon Protonation of Copper–Dioxygen Complexes 4–6.** Typically, to a solution of 0.3–0.5 mmol of dioxygen complex prepared in situ (dichloromethane, −80 °C) was added 10 equiv (3–5 mmol) of $HPF_6/Et_2O$. The purple (**4** and **5**) or brown (**6**) solution instantly turned blue. The reaction mixture was stirred for 15 min followed by addition of diethyl ether (60 mL) to precipitate the Cu(II) product. The precipitate was allowed to settle, and the clear supernatant solution (which, in the case of complexes **4** and **5** gave a positive test for $H_2O_2$ with EM Quant brand peroxide test paper), was transferred, with a cannula, to a flask containing a solution of KI (1.0 g) in a degassed mixture of distilled water (20 mL) and acetic acid (10 mL). The blue precipitate was washed with ether (30 mL) and the supernatant again transferred to the KI solution. The yellow KI mixture was stirred for 10 min at room temperature and then titrated with 0.05 N $Na_2S_2O_3$ solution until it became colorless. The yields of $H_2O_2$ formed were calculated from the amount of 0.05 N $Na_2S_2O_3$ solution consumed: **4**, 88%; **5**, 85% (average of three determinations); **6**, 12% (average of two determinations).

**Reaction of $[Cu_2(XYL\text{–}O\text{–})(O_2)]PF_6$ (4-$PF_6$) with $CO_2$. Synthesis of $[Cu_2(XYL\text{–}O\text{–})CO_3]PF_6\cdot{}^1/_2CH_2Cl_2$ (9-$PF_6\cdot{}^1/_2CH_2Cl_2$).** Complex **4**-$PF_6$ was generated from complex $[Cu_2(XYL\text{–}O\text{–})]PF_6$ (**1**-$PF_6$) (0.5 g, 0.60 mmol) in 50 mL of $CH_2Cl_2$. The solution was reacted with an excess of carbon dioxide gas at −80 °C, resulting in an instantaneous color change from dark purple to deep green. This was stirred at −80 °C for 1 h and then warmed to room temperature slowly, while the gas over the solution was passed through an alkaline aqueous solution of pyrogallol (which turned brown). The volume of the green solution was reduced to 25 mL by evaporation of $CH_2Cl_2$ under vacuum; argon-saturated diethyl ether (80 mL) was added to precipitate a bright green solid, which was washed with 20 mL of diethyl ether and dried under vacuum. Recrystallization from $CH_2Cl_2$/diethyl ether produced $[Cu_2(XYL\text{–}O\text{–})CO_3]PF_6\cdot{}^1/_2CH_2Cl_2$ (**9**-$PF_6\cdot{}^1/_2CH_2Cl_2$) (0.47 g, 87%). Anal. Calcd for $C_{37.5}H_{40}ClCu_2F_6N_6O_4P$: C, 47.62; H, 4.23; N, 8.88. Found: C, 47.96; H, 4.32; N, 9.12. IR (Nujol, $cm^{-1}$): 1546 (m, $CO_3^{2-}$), 840 (s, $PF_6^-$). UV–vis [$CH_2Cl_2$; $\lambda_{max}$, nm ($\epsilon$, $M^{-1}\,cm^{-1}$)]: 375 (3100), 444 sh (1150), 660 (230). $\mu_{RT} = 1.37\ \mu_B$/Cu.

In a separate experiment, complex **4**-$PF_6$ was generated in a cuvette assembly using 0.0047 g ($5.575 \times 10^{-3}$ mmol) of **1**-$PF_6$ in 17 mL of $CH_2Cl_2$. This was then bubbled with $CO_2$ gas at −80 °C until the color changed to deep green. The UV–vis spectrum was obtained at −80 °C, then the solution was allowed to warm to room temperature, and the electronic spectrum was monitored. Representative spectra are shown in Figure 1.

**Reaction of $[Cu_2(XYL\text{–}O\text{–})CO_3]PF_6\cdot{}^1/_2CH_2Cl_2$ (9-$PF_6\cdot{}^1/_2CH_2Cl_2$) with $H^+$.** Complex **9**-$PF_6\cdot{}^1/_2CH_2Cl_2$ (0.53 g, 0.57 mmol) was dissolved in 45 mL of dry $CH_2Cl_2$. To that was added $HPF_6$ (60% in water) (0.31 g, 1.27 mmol) with the aid of a syringe. Argon was bubbled through the solution, and the evolved gas was passed through a saturated solution of $Ba(OH)_2$ for 1 h. The white solid formed was filtered in a sintered crucible, washed with water, and dried overnight at 120 °C to yield 0.075 g (0.38 mmol, 67%) of $BaCO_3$. A green solid was precipitated from the $CH_2Cl_2$ solution by the addition of 95 mL of diethyl ether. This was washed with 20 mL of diethyl ether and dried under vacuum to give $[Cu_2(XYL\text{–}O\text{–})(OH)](PF_6)_2$ (**10**-$(PF_6)_2$) (0.41 g, 71.5%), identified by comparing its IR and UV–vis spectra with those of an authentic sample.

**Reaction of $[\{Cu(TMPA)\}_2(O_2)](ClO_4)_2$ (5-$(ClO_4)_2$) with $CO_2$. Synthesis of $[\{Cu(TMPA)\}_2CO_3](ClO_4)_2$ (11-$(ClO_4)_2$).** An intensely violet-colored solution of **5**-$(ClO_4)_2$ in 25 mL of propionitrile was formed from $[Cu(TMPA)CH_3CN]ClO_4$ (**2**-$ClO_4$) (0.637 g, 1.29 mmol). Reacting this solution with an excess of carbon dioxide at −85 °C immediately produced an aquamarine-colored solution. Warming this to room temperature and storage overnight under argon resulted in the formation of a blue-green X-ray-quality crystalline solid. The solution was decanted, the crystals were washed with 75 mL of degassed diethyl ether, and drying under vacuum gave 0.525 g (84%) of $[\{Cu(TMPA)\}_2CO_3](ClO_4)_2$ (**11**-$(ClO_4)_2$). Anal. Calcd for $C_{37}H_{36}Cl_2Cu_2N_8O_{11}$: C, 45.97; H, 3.75; N, 11.59. Found: C, 45.94; H, 3.68; N, 11.61. IR (Nujol, $cm^{-1}$): 1520 (s, $CO_3^{2-}$), 1340 (vs, $CO_3^{2-}$), 1080 (vs, $ClO_4$), 2000 (w, $ClO_4^-$ overtone). UV–vis [$CH_3CN$; $\lambda_{max}$, nm ($\epsilon$, $M^{-1}\,cm^{-1}$)]: 376 (3550), 695 (225), 881 (400). $\mu_{RT} = 1.73\ \mu_B$/Cu.

**Reaction of $[Cu_2(XYL\text{–}O\text{–})(O_2)]PF_6$ (4-$PF_6$) and $[\{Cu(TMPA)\}_2(O_2)](PF_6)_2$ (5-$(PF_6)_2$) with $CO_2$ in the Presence of $PPh_3$.** Solutions of **4**-$PF_6$ and **5**-$(PF_6)_2$ were generated from $[Cu_2(XYL\text{–}O\text{–})]PF_6$ (**1**-$PF_6$) (0.24 g, 0.285 mmol) in 45 mL of $CH_2Cl_2$ and $[Cu^I(TMPA)CH_3CN]PF_6$ (**2**-$PF_6$) (0.245 g, 0.452 mmol) in 40 mL of $C_2H_5CN$, respectively. After the solutions of **4**-$PF_6$ and **5**-$(PF_6)_2$ were reacted with $CO_2$ gas at −80 °C, solid $PPh_3$ (0.125 g, 0.477 mmol) and (0.15 g, 0.572 mmol), respectively, were added to the solutions of **4**-$PF_6$ and **5**-$(PF_6)_2$. The reaction mixtures were stirred at −80 °C for 2 h and then slowly warmed

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to room temperature. Green solids were precipitated by adding an excess of diethyl ether, the supernatant was decanted, and solids were washed with additional ether. The combined ether solutions were concentrated and subjected to GC analysis for determination of the yield of O═PPh$_3$ by comparing it with an external standard (a known mixture of PPh$_3$ and O═PPh$_3$). The green compounds were dried in vacuo to give **9**-PF$_6$ (68%) and **11**-(PF$_6$)$_2$ (71%), which were identified by comparing their IR and UV–vis spectra with those of the authentic samples.

**Reaction of [Cu$_2$(XYL–O–)($^{18}$O$_2$)]PF$_6$ (4-PF$_6$) with CO$_2$.** A flask containing 0.50 g (0.593 mmol) of complex **1**-PF$_6$ in 40 mL of CH$_2$Cl$_2$ at −80 °C was attached to a bulb containing 100 mL of $^{18}$O$_2$ gas (1 atm, 99%) and was evacuated. The glass seal on the bulb was broken to let the gas enter the flask. The solution was stirred for 15 min, and excess oxygen was removed as described earlier. After this solution was reacted with CO$_2$ and 0.159 g (0.606 mmol) of PPh$_3$ was added, the reaction was worked up in the manner described above. The green solid, [Cu$_2$(XYL–O–)C$^{18}$OO$_2$]PF$_6$·$^1/_2$CH$_2$Cl$_2$ was obtained in 70% yield. IR (Nujol): $\nu_{CO}$ = 1544 cm$^{-1}$. The ether layer was concentrated to produce an off-white solid (0.15 g) on which mass spectroscopic analysis was performed (1.2K resolution, 180 °C, electron energy 70 eV). The most abundant peak corresponds to *m/e* 279 (M − 1) with other peaks at *m/e* 281, 280, 278, and 277. Comparing this spectrum with that of O═PPh$_3$ shows that the $^{18}$O has been incorporated (>85%) in the PPh$_3$ used in the reaction.

**Reaction of [Cu$_2$(XYL–O–)(O$_2$)]PF$_6$ (4-PF$_6$) with C$^{18}$O$_2$.** A similar reaction was performed with use of 0.42 g (0.498 mmol) of complex **1**-PF$_6$ in 35 mL of CH$_2$Cl$_2$. The oxygenation was performed with $^{16}$O$_2$, but C$^{18}$O$_2$ (99%) was used, followed by addition of PPh$_3$ (0.13 g, 0.496 mmol). The off-white solid obtained from the ether layer was subjected to mass spectrometric analysis, which showed that there was no $^{18}$O incorporation into O═PPh$_3$. The green solid [Cu$_2$(XYL–O–)(O)(C$^{18}$O$_2$)]PF$_6$·$^1/_2$CH$_2$Cl$_2$ was isolated in 72% yield. IR (Nujol): $\nu_{C^{18}O}$ = 1521 cm$^{-1}$.

**Reaction of [Cu$_2$(XYL–O–)(O$_2$)]PF$_6$ (4-PF$_6$) with SO$_2$. Synthesis of [Cu$_2$(XYL–O–)SO$_4$]PF$_6$·$^1/_4$CH$_2$Cl$_2$ (12-PF$_6$·$^1/_4$CH$_2$Cl$_2$).** A solution of complex **4**-PF$_6$ was obtained by oxygenating 0.69 g (0.818 mmol) of compound **1**-PF$_6$ in 55 mL of CH$_2$Cl$_2$. To this purple solution was added SO$_2$ gas (100 mL) at −80 °C, resulting in an immediate color change to green. The mixture was stirred at −80 °C for 1 h, then warmed to room tempeature, and filtered. A green solid was precipitated by adding 150 mL of diethyl ether to the filtrate, which was redissolved in 30 mL of CH$_3$CN, filtered, and precipitated again by adding 90 mL of diethyl ether. The microcrystalline solid was washed twice with 20 mL of ether and dried in vacuo to give 0.56 g (70%) of complex **12**-PF$_6$·$^1/_4$CH$_2$Cl$_2$. Anal. Calcd for C$_{36.25}$H$_{39.5}$Cl$_{0.5}$Cu$_2$F$_5$N$_6$O$_5$PS: C, 45.30; H, 4.14; N, 8.68. Found: C, 44.94; H, 4.24; N, 8.68. IR (Nujol, cm$^{-1}$): 1230 (s, SO$_4^{2-}$), 1130 (vs, SO$_4^{2-}$), 970 (s, SO$_4^{2-}$), 843 (vs, PF$_6$). UV–vis [CH$_3$CN; $\lambda_{max}$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$)]: 293 (3400), 320 sh (2700), 415 (1800), 671 (210). $\mu_{RT}$ = 1.17 $\mu_B$/Cu. Molar conductivity (CH$_3$CN): $\Lambda_M$ = 147 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Reaction of [{Cu(TMPA)}$_2$(O$_2$)](PF$_6$)$_2$ (5-PF$_6$)$_2$ with SO$_2$. Synthesis of [{Cu(TMPA)}$_2$SO$_4$](PF$_6$)$_2$·$^1/_4$Et$_2$O (13-(PF$_6$)$_2$·$^1/_4$Et$_2$O).** A solution of **5**-(PF$_6$)$_2$ was prepared from [Cu(TMPA)CH$_3$CN]PF$_6$ (**2**-PF$_6$) (0.400 g, 0.74 mmol) in 35 mL of dichloromethane at −80 °C as described earlier. The purple solution immediately turned to dark brown upon addition of 100 mL of sulfur dioxide. The color of the solution changed to green when it was warmed to room temperature. The solution was filtered, and 75 mL of dry diethyl ether was added to the filtrate, resulting in the precipitation of a green solid that was washed twice with 15 mL of diethyl ether. Recrystallization from CH$_2$Cl$_2$/diethyl ether produced **13**-(PF$_6$)$_2$·$^1/_4$Et$_2$O in 63% yield (0.26 g). Anal. Calcd for C$_{37}$H$_{38.5}$Cu$_2$F$_{12}$N$_8$O$_{4.25}$P$_2$S: C, 39.94; H, 3.46; N, 10.07. Found: C, 40.49; H, 3.62; N, 10.24: IR (Nujol, cm$^{-1}$): 1220 (s, SO$_4^{2-}$), 1125 (s, SO$_4^{2-}$), 1005 (s, SO$_4^{2-}$). UV–vis [DMF; $\lambda_{max}$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$)]: 272 (6250), 305 sh (4300), 722 sh( 210), 915 (430). $\mu_{RT}$ = 1.73 $\mu_B$/Cu. Molar conductivity (DMF): $\Lambda_M$ = 138 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Reaction of [Cu$_2$(N4)(O$_2$)](PF$_6$)$_2$ (6-(PF$_6$)$_2$) with SO$_2$. Synthesis of [Cu$_2$(N4)(CH$_3$CN)$_2$](PF$_6$)$_2$SO$_4$·Et$_2$O (14-(PF$_6$)$_2$SO$_4$·Et$_2$O).** Oxygenation of compound **3**-(PF$_6$)$_2$ (0.67 g, 0.724 mmol) dissolved in 55 mL of CH$_2$Cl$_2$ produced a dark brown solution of complex **6**-(PF$_6$)$_2$, which was reacted with sulfur dioxide (100 mL) at −80 °C, resulting in an immediate color change to green. After the reaction mixture was stirred for 0.5 h at −80 °C, it was warmed up to room temperature, resulting in the precipitation of a blue-green solid. The supernatant liquid was removed with the help of a cannula. The solid was dried under vacuum and was dissolved in 40 mL of CH$_3$CN. The solution was filtered to remove a small amount of insoluble material, and the filtrate was concentrated to 20 mL by evaporation under vacuum. A blue microcrystalline solid was precipitated by adding 100 mL of diethyl ether. Washing twice with 25 mL of ether and drying under vacuum gave 0.4 g (54%) of **14**-(PF$_6$)$_2$SO$_4$·Et$_2$O. Anal. Calcd for C$_{40}$H$_{56}$Cu$_2$F$_{12}$N$_8$O$_5$P$_2$S: C, 40.78; H, 4.79; N, 9.51. Found: C, 41.03; H, 4.69; N, 9.77. IR (Nujol, cm$^{-1}$): 1100 (s, br, SO$_4^{2-}$), 839 (vs, PF$_6^-$). UV–vis [CH$_3$CN; $\lambda_{max}$, nm ($\epsilon$, M$^{-1}$ cm$^{-1}$)]: 286 (4720), 708 (180). $\mu_{RT}$ = 1.68 $\mu_B$/Cu. Molar conductivity (CH$_3$CN), $\Lambda_M$ = 351 $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

**Reactions of [Cu$_2$(XYL–O–)(O$_2$)]$^+$ (4), [{Cu(TMPA)}$_2$(O$_2$)]$^{2+}$ (5), and [Cu$_2$(N4)(O$_2$)]$^{2+}$ (6) with Ph$_3$C$^+$BF$_4^-$. Formation of Benzophenone.** In a typical reaction, 0.4 mmol of complex **4**, **5**, or **6** was formed by oxygenating complex **1** (0.4 mmol), **2** (0.8 mmol), or **3** (0.4 mmol), respectively, in 40 mL of CH$_2$Cl$_2$. To these solutions was added 0.8 mmol of solid Ph$_3$C$^+$BF$_4^-$. The reaction mixtures were stirred at −80 °C for 4 h during which time the color changed to brownish green. The resulting solutions were warmed slowly to room temperature and were subjected to GC analysis. The amount of benzophenone formed was quantified by using benzil as an internal standard. The yields of benzophenone were found to be 37%, 49%, and 30% for dioxygen complexes **4**, **5**, and **6**, respectively.

**Reaction of [Cu$_2$(XYL–O–)(O$_2$)]PF$_6$ (4-PF$_6$) with 2,4-Di-*tert*-butylphenol.** Solid 2,4-di-*tert*-butylphenol (0.124 g, 0.60 mmol) was added to a solution of **4**-PF$_6$ generated from [Cu$_2$(XYL–O–)(O$_2$)]PF$_6$ (**1**-PF$_6$) (0.505 g, 0.60 mmol) in 50 mL of dichloromethane at −80 °C as described above. The initial purple color immediately turned to dark green, and the reaction mixture was left to warm to room temperature whereupon it was hydrolyzed with 10% aqueous H$_2$SO$_4$ (10 mL). The phases were separated, the dichloromethane layer was dried over MgSO$_4$, and then the solvent was evaporated in vacuo to give a light orange viscous oil (0.12 g) that solidified upon standing. TLC (silica/CHCl$_3$) and $^1$H NMR showed that it was the starting 2,4-di-*tert*-butylphenol.

**Reaction of [{Cu(TMPA)}$_2$(O$_2$)](PF$_6$)$_2$ (5-PF$_6$)$_2$) with 2,4-Di-*tert*-butylphenol.** A solution of **5**-(PF$_6$)$_2$ was prepared from [Cu(TMPA)-CH$_3$CN]PF$_6$ (**2**-PF$_6$) (0.540 g, 1.00 mmol) in 50 mL of dichloromethane at −80 °C, as described earlier. The purple solution immediately turned to light blue when solid 2,4-di-*tert*-butylphenol (0.103 g, 0.50 mmol) was added. The reaction mixture was left to warm to room temperature and worked up as described above. The off-white residue (0.1 g) formed was the unchanged starting phenol as judged by TLC (silica/CHCl$_3$) and $^1$H NMR.

**Reaction of [Cu$_2$(N4)(O$_2$)](ClO$_4$)$_2$ (6-(ClO$_4$)$_2$) with 2,4-Di-*tert*-butylphenol.** To a solution of **6**-(ClO$_4$)$_2$ generated from [Cu$_2$(N4)-(CH$_3$CN)$_2$](ClO$_4$)$_2$ (**3**-(ClO$_4$)$_2$) (1.279 g, 1.53 mmol) in 70 mL of CH$_2$Cl$_2$ as described earlier was added 2,4-di-*tert*-butylphenol (0.316 g, 1.53 mmol). The dark brown color of the solution instantaneously turned to green. The reaction mixture was left to warm to room temperature and worked up as described above. The pale yellow residue formed was columned on Kieselgel 60/CCl$_4$, giving white microcrystalline 3,3′,5,5′-tetra-*tert*-butyl-2,2′-dihydroxybiphenyl (0.29 g, 93%). TLC (silica/CCl$_4$): $R_f$ 0.66. $^1$H NMR (CCl$_4$): $\delta$ 1.33 (s, 18 H), 1.42 (s, 18 H), 6.73 (d, $J$ = 2.4 Hz, 2 H), 7.03 (d, $J$ = 2.4 Hz, 2 H). Mp: 200 °C (lit.[25] mp 199 °C). Mass spectrometry: 410 (M$^+$).

**Catalytic Oxidation of 2,4-Di-*tert*-butylphenol in the Presence of Copper(I) Complexes 1–3.** Typically, 0.05–1.5 mmol of complexes [Cu$_2$(XYL–O–)]PF$_6$ (**1**-PF$_6$), [Cu(TMPA)CH$_3$CN]PF$_6$ (**2**-PF$_6$), and [Cu$_2$(N4)(CH$_3$CN)$_2$](ClO$_4$)$_2$ (**3**-(CH$_3$CN)$_2$(ClO$_4$)$_2$) and a 20–100-fold excess of 2,4-di-*tert*-butylphenol were dissolved in CH$_2$Cl$_2$ (EtCN in the case of **1**-PF$_6$) and stirred under an O$_2$ atmosphere at 25 °C for 10, 72, and 90 h, respectively. The reaction mixtures were hydrolyzed with 10% aqueous H$_2$SO$_4$ (10 mL). The phases were separated, the CH$_2$Cl$_2$ layers were dried over MgSO$_4$, and then the solvent was evaporated in vacuo. The relative amounts of starting material and 3,3′,5,5′-tetra-*tert*-butyl-2,2′-dihydroxybiphenyl were determined by $^1$H NMR, and the turnover number was calculated (31, 3, and 55 for complexes **4**, **5**, and **6**, respectively).

**Catalytic Oxidation of 2,4-Di-*tert*-butylphenol in the Presence of [Cu$_2$(N4)](ClO$_4$)$_2$ (3-(ClO$_4$)$_2$) at −80 °C.** Complex **3**-(ClO$_4$)$_2$ (0.48 g, 0.58 mmol) and 2,4-di-*tert*-butylphenol (1.19 g, 5.8 mmol) were dissolved in freshly distilled dichloromethane (50 mL), and the solution was cooled to −80 °C. The yellow solution turned green instantaneously when upon dry oxygen gas was bubbled through it. The reaction mixture was stirred under dioxygen atmosphere for 6 h, the excess dioxygen was removed by bubbling the solution with argon, and then the mixture was warmed to room temperature. The copper complex(es) formed were precipitated with diethyl ether and then filtered. The solvent was removed by rotary evaporation, yielding 1.15 g of white residue, which was subjected to $^1$H NMR spetroscopic analysis. From the 3,3′,5,5′-tetra-*tert*-butyl-2,2′-dihydroxybiphenyl/2,4-di-*tert*-butylphenol ratio, the turnover number was calculated to be 1.9.

**Reactions of [Cu$_2$(XYL–O–)(O$_2$)]$^+$ (4), [{Cu(TMPA)}$_2$(O$_2$)]$^{2+}$ (5), and [Cu$_2$(N4)(O$_2$)]$^{2+}$ (6) with (4-Methylphenyl)- and (4-Fluorophenyl)mag-**

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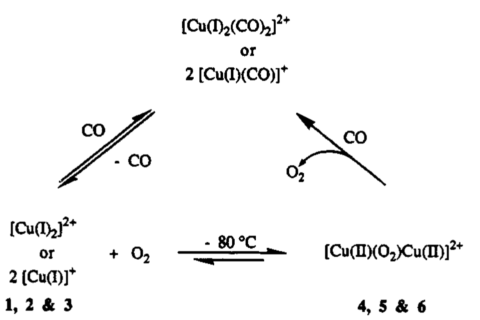
(25) Hay, A. S.; Becker, H. D. German Patent 1,900,680, 1969; *Chem. Abstr.* **1969**, *71*, 91077k.

**Table I.** Reaction of Copper–Dioxygen Complexes with Grignard Reagents

| complex | X | 4,4′-$X_2(C_6H_4)_2$, % | Me/F | 4-X-$C_6H_4OH$, % | Me/F |
|---|---|---|---|---|---|
| $[Cu_2(XYL–O–)(O_2)]PF_6$ (**4**-$PF_6$) | $CH_3$ | 22 | 0.80 | 36 | 0.75 |
| | F | 26 | | 48 | |
| $[\{Cu(TMPA)\}_2(O_2)](PF_6)_2$ (**5**-$(PF_6)_2$) | $CH_3$ | 19 | 0.60 | 53 | 0.75 |
| | F | 30 | | 70 | |
| $[Cu_2(N4)(O_2)](PF_6)_2$ (**6**-$(PF_6)_2$) | $CH_3$ | 46 | 1.20 | 28 | 2.30 |
| | F | 38 | | 12 | |

**Scheme II**



**nesium Bromide.** In a typical reaction, complexes **4** and **6** were generated from 0.5 mmol of **1** and **3**, respectively, in 40 mL of $CH_2Cl_2$. To these solutions were added 0.1 mmol of (4-methylphenyl)magnesium bromide (1.0 M solution in diethyl ether, Aldrich) and (4-fluorophenyl)magnesium bromide (2.0 M solution in diethyl ether, Aldrich) slowly at -80 °C with the aid of a syringe. The color of the solution changed to green in few minutes. After being stirred for 2 h at -80 °C and then warmed slowly to room temperature, the solution was hydrolyzed with 15–20 mL of 10% $H_2SO_4$. The $CH_2Cl_2$ layer was separated, dried with $MgSO_4$, and subjected to GC analysis to quantify the yields of 4,4′-dimethylbiphenyl, 4,4′-difluorobiphenyl, 4-methylphenol, and 4-fluorophenol, formed in the reaction (octane used as internal standard). For reaction of **5**, 1 mmol of complex **2** was used in 40 mL of $CH_2Cl_2$ before addition of 0.1 mmol of reagent. Products and yields of reactions are given in Table I.

## Results and Discussion

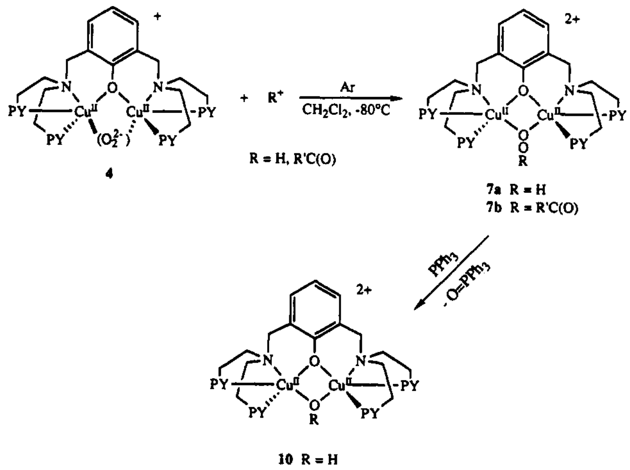
As stated, our goal was to study the reactivity of three types of peroxocopper complexes in order to elucidate reactivity features of the peroxo moiety in $\{Cu_2–O_2\}$ complexes. We also wanted to correlate possible differences in reactivity with the variations in ligand environment and $\{Cu_2–O_2\}$ structure.

It is well established that the dioxygen binding with complexes **1**–**3** is reversible.[19–21] All three Cu(I) complexes also react with carbon monoxide to form Cu(I)–CO adducts, and the CO binding is reversible (Scheme II). The peroxocopper complexes **4**–**6** also react with carbon monoxide to form the Cu(I)–CO adducts with concomitant liberation of dioxygen (Scheme II). This behavior indicates that CO is a better ligand for copper(I) than $O_2$, as is found for heme iron proteins.

Below, we discuss the reactions of **4**–**6** with a variety of reagents intended to probe reactivity characteristics of the copper–peroxo moiety. Due to the thermal instability of the $\{Cu_2–O_2\}$ complexes **4**–**6**, they were generated in situ in $CH_2Cl_2$ at -80 °C; in some cases, species **5** was made in propionitrile. Through the application of a vacuum to the -80 °C $\{Cu_2–O_2\}$ solutions, excess $O_2$ was rigorously removed. All the interactions of inorganic or organic substrates with complexes **4**–**6** were carried out initially at -80 °C, and the solutions were allowed to warm to room temperature when completion of any low-temperature reaction was indicated.

**$PPh_3$.** Triphenylphosphine is a simple reagent, often used in the characterization of reactivity of $M_n–O_2$ complexes.[2c,d] $PPh_3$ is a $\pi$-acid ligand like CO also known to be a good ligand donor in Cu(I) complexes.[26] Complexes $[Cu_2(XYL–O–)(O_2)]^+$ (**4**) and $[\{Cu(TMPA)\}_2(O_2)]^{2+}$ (**5**) react with triphenylphosphine in a fashion similar to carbon monoxide, and copper(I)–$PPh_3$ complexes are formed with concomitant liberation of dioxygen (eqs 1 and 2), as determined quantatively by manometry.[19a,20a] These reactions occur rapidly at −80 °C, in spite of the strong binding of $O_2$ (e.g., for **4**, $K_{eq} = 7.6 \times 10^7$),[27] indicating displacement and other reactions of the $\{Cu_2–O_2\}$ species can readily occur at these reduced temperatures. By contrast, complex $[Cu_2(N4)(O_2)]^{2+}$ (**6**) does not react with triphenylphosphine under the same conditions, but triphenylphosphine oxide and $[Cu_2(N4)(PPh_3)_2]^{2+}$ complex are formed (eq 3) when the reaction mixture is left to warm to room temperature. These observations suggest a clear difference in the nature of the peroxo moiety in **4** and **5** by comparison to **6**.

**Scheme III**



$$\underset{\mathbf{4}}{[Cu_2(XYL\text{-}O\text{-})(O_2)]^+} + 2\,PPh_3 \xrightarrow[CH_2Cl_2,\ -80°C]{Ar} [Cu_2(XYL\text{-}O\text{-})(PPh_3)_2]^+ + 1/2\,O_2\uparrow \quad (1)$$

$$\underset{\mathbf{5}}{[\{Cu(TMPA)\}_2(O_2)]^{2+}} + 2\,PPh_3 \xrightarrow[EtCN,\ -80°C]{Ar} 2\,[Cu(TMPA)PPh_3]^+ + 1/2\,O_2\uparrow \quad (2)$$

$$\underset{\mathbf{6}}{[Cu_2(N4)(O_2)]^{2+}} + 4\,PPh_3 \overset{Ar}{\underset{CH_2Cl_2,\ -80°C}{\not\longrightarrow}} \xrightarrow[-80°C \rightarrow RT]{Ar} [Cu_2(N4)(PPh_3)_2]^{2+} + 2\,O{=}PPh_3 \quad (3)$$

**$H^+$ and $RCO^+$.** We find that while the dioxygen (peroxo) ligand in $[Cu_2(XYL–O–)(O_2)]^+$ (**4**) and $[\{Cu(TMPA)\}_2(O_2)]^{2+}$ (**5**) are readily protonated (eqs 4 and 5) (or acylated), the corresponding reaction of $[Cu_2(N4)(O_2)]^{2+}$ (**6**) indicates that the peroxo ligand in **6** is not basic and does not react similarly with protons. Addition of 1 equiv of $HBF_4$ or $HPF_6$ at −80 °C to **4** gives a hydroperoxodicopper(II) complex, $[Cu_2(XYL–O–)(OOH)]^{2+}$ (**7a**; Scheme

$$\underset{\mathbf{4}}{[Cu_2(XYL\text{-}O\text{-})(O_2)]^+} + 2\,HPF_6 \xrightarrow[CH_2Cl_2,\ -80°C]{Ar} \text{Copper Complex(es)} + H_2O_2 \quad (4)$$

$$\underset{\mathbf{5}}{[\{Cu(TMPA)\}_2(O_2)]^{2+}} + 2\,HPF_6 \xrightarrow[CH_2Cl_2,\ -80°C]{Ar} \text{Copper Complex(es)} + H_2O_2 \quad (5)$$

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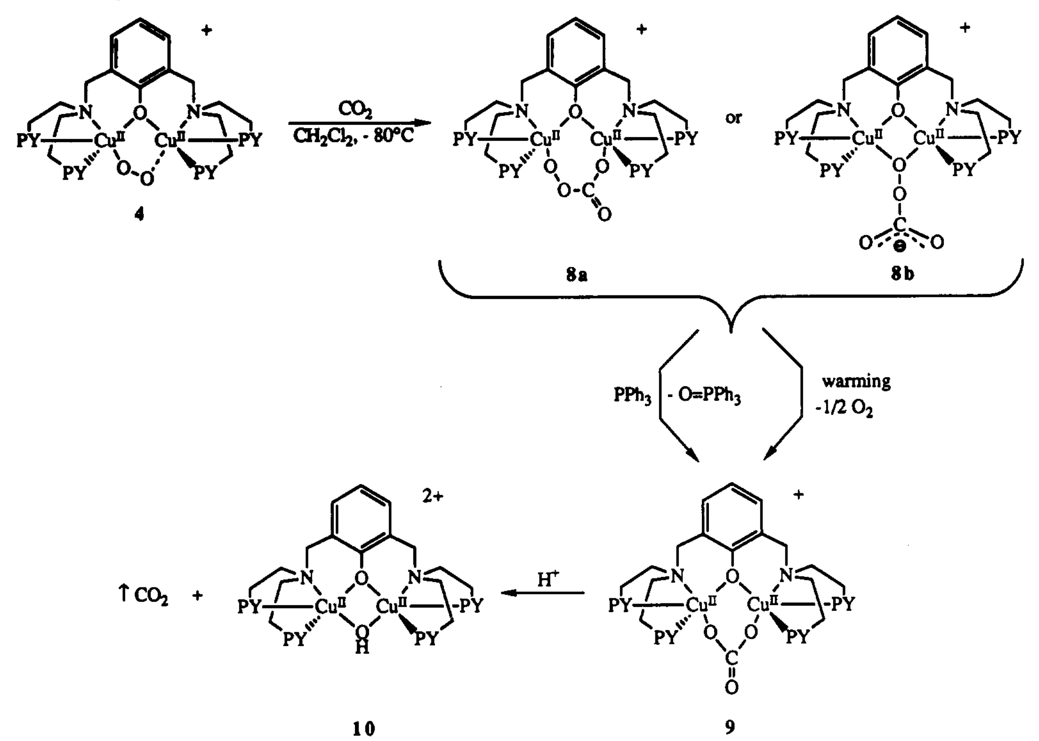
(26) Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1987; Vol. 5, Chapter 53, pp 533–774.

(27) Cruse, R. W.; Kaderli, S.; Karlin, K. D.; Zuberbühler, A. D. *J. Am. Chem. Soc.* **1988**, *110*, 6882–6883.

**Scheme IV.** Reaction of $CO_2$ with $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ Giving Percarbonato and Carbonato Products



III) characterized by a strong CT band at 395 nm ($\epsilon$ = 8000 $M^{-1}$ $cm^{-1}$) and a Cu–Cu distance of 3.05 Å (EXAFS).[28] The proposed $\mu$-1,2-OOH coordination is based on spectroscopic comparisons to structurally characterized complexes, the acylperoxo analogue, $[Cu_2(XYL\text{-}O\text{-})\{m\text{-}ClC_6H_4C(O)O_2\}]^{2+}$ (**7b**) (vide infra),[29] and the phenoxo and hydroxo doubly bridged complex $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ (**10**).[23] One can presume that the unsymmetrically bound cis-$\mu$-1,2 peroxide group in **4** is protonated first and then rearranges to a $\mu$-1,1-OOH structure, analogous to the reaction of $[\{Co(en)\}_2O_2(NH_2)]^{3+}$ with $H^+$.[30]

Addition of 1 equiv of $H^+$ to **5** results in an immediate bleaching of the characteristic band of **5** at 525 nm, which we suggest is also due to the formation of a hydroperoxo complex. With 10 equiv of $H^+$, hydrogen peroxide is produced in 88% yield from **4** and 85% yield from **5** (iodometric titration, Experimental Section), similar to the reaction of $H^+$ with peroxocobalt complexes.[31] By contrast, addition of 3–4 equiv of $H^+$ to **6** resulted in no UV–vis change,[32] and addition of 10-fold excess acid provides a yield of only 12% $H_2O_2$ (eq 6).

$$\underset{\mathbf{6}}{[Cu_2(N4)(O_2)]^{2+}} + \le 4\,HPF_6 \xrightarrow[CH_2Cl_2,\,-80\,^\circ C]{Ar} H_2O_2 \tag{6}$$

Acylation reactions of **4**–**6** at −80 °C follow the same trend observed for protonation. Reactions of R′C(O)Cl (where R′ is alkyl or aryl group) with $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (**4**) are rapid, and they give $\mu$-1,1-acylperoxodicopper(II) complexes (**7b**; Scheme III). Using *m*-chlorobenzoyl chloride led to the isolation of $[Cu_2^{II}(XYL\text{-}O\text{-})(m\text{-}ClC_6H_4C(O)OO^-]^{2+}$ (**7b**, R′ = *m*-chlorophenyl), which was the first structurally characterized percarboxylatodicopper(II) complex.[29] Complex **4** also reacts with EtOC(O)Cl and $(CF_3CO)_2O$ to form acyl peroxo complexes and $(C_2H_5)_3OPF_6$ to produce an alkyl peroxo complex.[33] In contrast to the dioxygen adduct $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (**4**), complexes **7a** and **7b** oxidize $PPh_3$ to O=$PPh_3$ in essentially quantitative yields (Scheme III). That is, protonation (or acylation) of the dioxygencopper complex appears to activate the bound dioxygen ligand via formation of the $Cu_n$–OOR′ species; the latter is capable of transferring an oxygen atom to a substrate such as $PPh_3$. In the case of $[\{Cu(TMPA)\}_2(O_2)]^{2+}$ (**5**), benzoyl chloride reacts slowly and protonation is required to then cause oxygenation of added $PPh_3$. Surprisingly, there is *no* reaction of acyl chlorides with $[Cu_2(N4)(O_2)]^{2+}$ (**6**), again indicating a difference in the inherent reactivity of this species.

**$CO_2$.** A number of peroxometal complexes react with carbon dioxide, an electrophilic reagent, to form carbonato complexes.[2c,d] Upon addition of $CO_2$, similar reactions were also observed in the case of the dioxygen complexes $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (**4**) and $[\{Cu(TMPA)\}_2(O_2)]^{2+}$ (**5**), and these transformations appear to proceed through peroxycarbonato intermediates (vide infra). By contrast, the dioxygen complex $[Cu_2(N4)(O_2)]^{2+}$ (**6**) did *not* react with $CO_2$ under similar conditions.

The purple solution of complex **4** in $CH_2Cl_2$, characterized by a 505-nm UV–vis band, disappears immediately upon the addition of $CO_2$ at −80 °C to produce an intensely green species **8** with $\lambda_{max}$ = 340 nm ($\epsilon$ = 4350 $M^{-1}$ $cm^{-1}$), 400 nm ($\epsilon$ = 4900 $M^{-1}$ $cm^{-1}$), and 656 nm ($\epsilon$ = 350 $M^{-1}$ $cm^{-1}$), as shown in Figure 1. This complex, upon thermal decomposition, gives the carbonato complex $[Cu_2(XYL\text{-}O\text{-})CO_3]^+$ (**9**) (Scheme IV) characterized by $\lambda_{max}$ = 375 nm ($\epsilon$ = 3100 $M^{-1}$ $cm^{-1}$), 444 nm sh ($\epsilon$ = 1150 $M^{-1}$ $cm^{-1}$), and 656 nm ($\epsilon$ = 230 $M^{-1}$ $cm^{-1}$) (Figure 1). Dioxygen gas was liberated during the thermal decomposition of **8**, and this was detected (qualitatively) by sweeping the reaction mixture with Ar and passing the gases present through an alkaline pyrogallol test solution. Under the conditions used, quantitative $O_2$ determination is difficult, but we note that the accompanying yield of the carbonato complex **9** is nearly quantitative (87%).

Complex **9** is characterized by a band at 1546 $cm^{-1}$ in IR which can be assigned to C=O stretch of the bridging carbonate group by comparison to structurally characterized $[\{Cu^{II}(TMPA)\}_2(CO_3)]^{2+}$ (**11**)[22] and other bridging carbonato complexes of copper reported in the literature.[34] A somewhat reduced room-tem-

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[28] Karlin, K. D.; Ghosh, P.; Cruse, R. W.; Farooq, A.; Gultneh, Y.; Jacobson, R. R.; Blackburn, N. J.; Strange, R. W.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 6769–6780.

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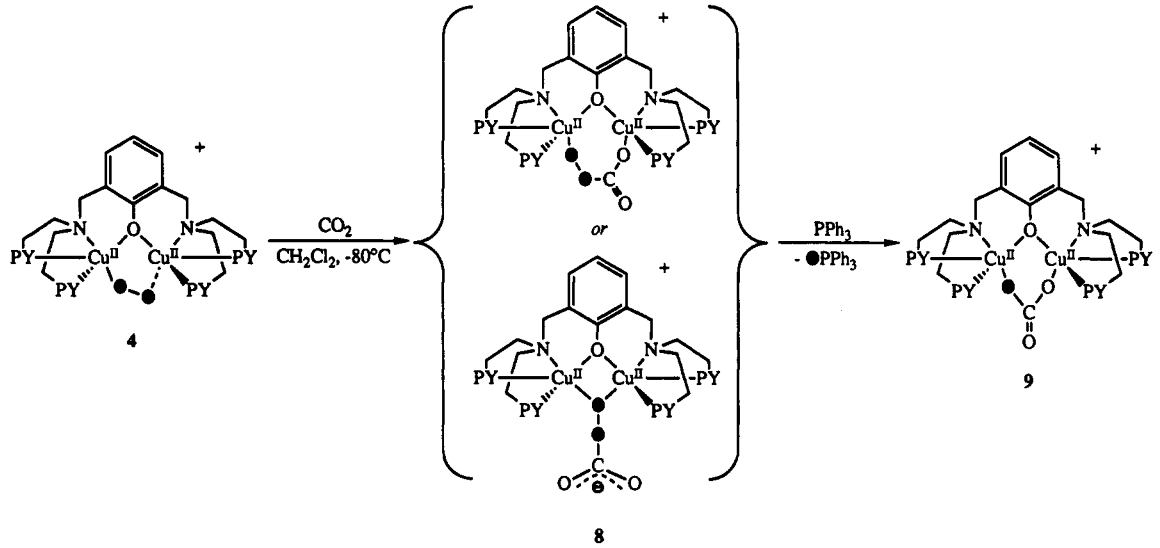
[32] (a) Haka, M. S. Ph.D. Dissertation, State University of New York at Albany, 1987. (b) Farooq, A. Ph.D. Dissertation, State University of New York at Albany, 1987.

[33] Tyeklár, Z.; Ghosh, P.; Farooq, A.; Karlin, K. D. To be published.

**Scheme V.** Reaction of $CO_2$ with Isotope-Labeled $O_2$ Complex 4



perature magnetic moment of 1.37 $\mu_B$/Cu suggests that the two coppers are antiferromagnetically coupled. Reacting complex **9** with acid causes the liberation of $CO_2$ and formation (72% yield) of the well-characterized hydroxo-bridged complex $[Cu_2(XYL–O–)(OH)]^{2+}$ (**10**). The $CO_2$ evolved was quantified by passing the gas through a saturated solution of $Ba(OH)_2$, which resulted in the precipitation of $BaCO_3$, and its yield (67%) suggests that $CO_2$ is liberated nearly stoichiometrically (Scheme IV). In a UV–vis spectroscopic experiment where 1 equiv of $PPh_3$ was added to complex **8**, it was observed that the decomposition of **8** did not go to completion at −80 °C, with a more rapid reaction occuring in the temperature range of −60 to −50 °C.

Complex **8** can be best described as a peroxycarbonato species, based on the following observations: (a) It reacts with $PPh_3$ (1 equiv added) to produce $O{=}PPh_3$, suggesting that there is an oxidizing equivalent present in **8** (Scheme IV). The moderate 65% yield observed is accounted for by the fact that warming of **8** with $PPh_3$ is required, and this then results in some $O_2$ loss through the competitive thermal disproportionation process (vide supra). As mentioned, a similar reaction was observed in the case of the hydroperoxo (**7a**)[28] and acylperoxo complex (**7b**)[29] where the coordinated peroxo in **4** is activated by electrophiles ($H^+$ and $R'CO^+$, Scheme III), suggesting that the $O_2^{2-}$ moiety in **4** is also activated by $CO_2$; in separate experiments, we determined that neither complex **4** nor **9** is capable of oxidizing $PPh_3$. The peroxycarbonato complexes $Pt(PPh_3)_2(CO_4)$[35] and $Rh(S_2CNMe_2)(CO_4)(PPh_3)_2$[36] also react with $PPh_3$ to form the carbonato complexes $Pt(PPh_3)_2(CO_3)$ and $Rh(S_2CNMe_2)(CO_3)(PPh_3)_2$, respectively. (b) The UV–vis spectrum of **8** is very similar to that of the acylperoxo complex **7b** where the two coppers are bridged by the $ArC(O)O_2^-$ group in a $\mu$-1,1 fashion. Similarities in the UV–vis spectra of peroxycarbonato- and acylperoxomanganese porphyrin complexes (obtained by reacting $CO_2$[37] or $ArC(O)Cl$,[38] with $[Mn^{II}(porphyrin)(O_2^-)]$) have been observed. Peroxycarbonato compounds have also been shown to be intermediates in reactions of $CO_2$ with other $M–O_2$ systems.[39]

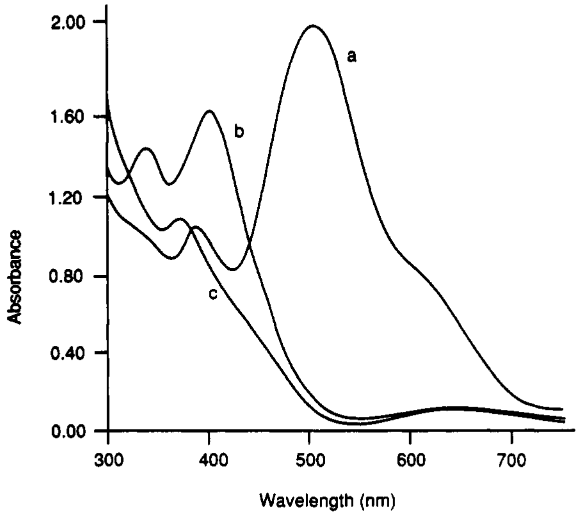


**Figure 1.** UV–vis spectra showing $[Cu_2(XYL–O–)(O_2)]^+$ (**4**) and products of reaction with carbon dioxide in dichloromethane at −80 °C: (a) spectrum of **4**, (b) percarbonato product $[Cu_2(XYL–O–)(CO_4^{2-})]^+$ (**8**) formed from reaction with $CO_2$ at −80 °C, (c) carbonato complex $[Cu_2(XYL–O–)(CO_3^{2-})]^+$ (**9**), after **8** was warmed to room temperature and recooled to take the UV–vis spectrum.

To obtain additional insight into the mechanism of the $CO_2$ reaction, we generated an isotopically labeled peroxocopper complex **4** by using $^{18}O_2$ (99%) gas. After $[Cu_2(XYL–O–)(^{18}O_2)]^+$ was reacted with $CO_2$, $PPh_3$ was added at −80 °C. The more than 85% observed incorporation of labeled oxygen into $O{=}PPh_3$ suggests that the oxygen atom is transferred from the original peroxo group and not from the $CO_2$. The carbonato complex formed from $^{18}O_2$ has an IR stretching frequency at 1544 $cm^{-1}$, which is not appreciably different from that of unlabeled complex **8** (1546 $cm^{-1}$), consistent with the presence of an essentially unperturbed and unlabeled $C{=}O$ carbonato species,[40] as shown in Scheme V. In the carbonate complex derived from the reaction of $[Cu_2(XYL–O–)(^{16}O_2)]^+$ **4** with $C^{18}O_2$ in presence of $PPh_3$, the band at 1546 $cm^{-1}$ disappears while a new band at 1521 $cm^{-1}$ is generated, suggesting that this shifted band is predominantly due to the $C{=}O$ bond consisting of the external oxygen that is not coordinated to copper. The $O{=}PPh_3$ produced in this reaction has no $^{18}O$ incorporated in it. These latter observations are also in agreement with the notion that the O being transferred is derived from $O_2$; the results are also consistent with

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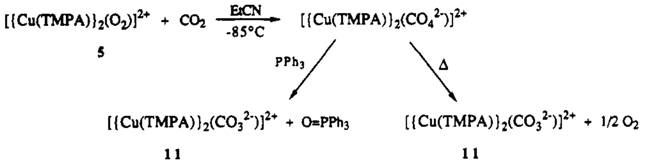
the absence of any noticeable scrambling of the oxygen atoms in either the peroxycarbonato or carbonato complex.

On the basis of these observations we can propose a possible pathway for the reaction of $[Cu_2(XYL\text{–}O\text{–})(O_2)]^+$ with $CO_2$ (Schemes IV and V). The peroxo group, which is unsymmetrically bound to copper, attacks the electrophilic carbon of the carbon dioxide, giving the peroxycarbonato species **8**. The insertion of carbon dioxide into the peroxide moiety resulting in O–O cleavage is unlikely (Scheme V). Isotopic studies carried out on reaction of $Pt(PPh_3)_2(O_2)$ with $CO_2$ also indicate that the $CO_2$ does not get inserted in the O–O bond of the peroxo group.[41] The transfer of an oxygen atom from **8** to $PPh_3$ from the peroxycarbonato species probably involves a metal complex based reaction, since (a) the low-temperature dissociation of a dianionic $CO_4^{2-}$ in $CH_2Cl_2$ seems unlikely, (b) hydrolysis of **8** to give **10** and $HCO_4^-$ or $H_2CO_4$ (which could quantitatively oxidize $PPh_3$) is unlikely to result in the isolation of **9**, since **9** itself reacts with water to give **10**, and (c) we find that neither the carbonate product of this reaction, **9**, nor the hydroxo complex **10** is capable of oxygenating triphenylphosphine. At this point, we do not understand how dioxygen gas is liberated upon warming of **8** in the absence of $PPh_3$. Weiss and co-workers have shown that the manganese porphyrin peroxycarbonato species decomposes in either a homolytic or heterolytic manner, depending on the solvent and temperature used.[37]

At this stage, we can only speculate upon the structure of the peroxycarbonato complex **8**. Two possibilities are a $\mu$-1,4-peroxycarbonato species **8a** or a $\mu$-1,1 structure **8b** (Scheme V). Structure **8a** is favored by a better stabilization of charge; it involves unsymmetrical ligation and probably is sterically demanding. The alternate structure **8b** has a dangling negative charge resulting in a charge separation, but a $\mu$-1,1 bridging coordination mode may be favorable, as indicated by the known structures found for **10** and the acylperoxo complex **7b**.[29] A $\mu$-1,1-peroxycarbonato structure may be further justified by the observation that the UV–vis spectroscopic properties of **8** are very similar to those of **7b**.[29]

Carbon dioxide reacts with complex $[\{Cu(TMPA)\}_2(O_2)]^{2+}$ (**5**) in a fashion similar to that for complex **4**. Thus, when dry $CO_2$ is reacted with a propionitrile solution of **5**-$(ClO_4)_2$ at −85 °C, bleaching of the characteristic UV–visible absorptions at 525 and 590 nm occurs. Subsequent warming of the solution to room temperature results in deposition of a green crystalline material identified as $[\{Cu(TMPA)\}_2(CO_3)](ClO_4)_2$ (**11**-$(ClO_4)_2$), which has been structurally characterized.[22] It has a bridging carbonate group joining the two Cu(TMPA) units. The reaction of complex **5** with carbon dioxide is also presumed to proceed via formation of a peroxycarbonato species. Evidence for this again comes from the reaction of $PPh_3$ with **5** with $CO_2$. Addition of 1 equiv of $PPh_3$ to a solution of **5**-$(PF_6)_2$ that has been reacted with $CO_2$ results in quantitative oxidation to $O{=}PPh_3$ (97% by GC) and formation of **11**-$(PF_6)_2$ (71%). These results indicate that the dioxygen (peroxo) ligand in both **4** and **5** can act as a nucleophile in reactions with $CO_2$.



**$SO_2$.** All three peroxo complexes $[Cu_2(XYL\text{–}O\text{–})(O_2)]^+$ (**4**), $[\{Cu(TMPA)\}_2(O_2)]^{2+}$ (**5**), and $[Cu_2(N4)(O_2)]^{2+}$ (**6**) react with $SO_2$ to form sulfato complexes. These findings are consistent with other observations that all metal–peroxo complexes tested for reaction with sulfur dioxide give sulfate as product.[2c,d,40,42,43] This kind of reaction is particularly well-known for the case of nucleophilic group 8 peroxo complexes. Sulfur dioxide also react with porphyrin iron– and titanium–peroxo complexes to produce sulfato complexes,[42] and insertion of $SO_2$ in the $M\text{–}O_2$ has been suggested from isotopic IR studies on the reaction of $SO_2$ with $Ir(O_2)Cl(PPh_3)_2$.[43] Dichloromethane solutions of complexes **4**-$PF_6$ and **5**-$(PF_6)_2$ react with dry $SO_2$ gas (eqs 7 and 8) to produce green

$$\underset{\mathbf{4}}{[Cu_2(XYL\text{-}O\text{-})(O_2)]^+} + SO_2 \xrightarrow[CH_2Cl_2,\ -80°C]{Ar} \underset{\mathbf{12}}{[Cu_2(XYL\text{-}O\text{-})(SO_4^{2-})]^+} \tag{7}$$

$$\underset{\mathbf{5}}{[\{Cu(TMPA)\}_2(O_2)]^{2+}} + SO_2 \xrightarrow[CH_2Cl_2,\ -80°C]{Ar} \underset{\mathbf{13}}{[\{Cu(TMPA)\}_2(SO_4^{2-})]^{2+}} \tag{8}$$

complexes, isolated by the addition and precipitation using diethyl ether. The bands at 1230, 1130, and 970 cm$^{-1}$ in the case of compound **12**-$PF_6$ and bands at 1220, 1125, and 1005 cm$^{-1}$ in the case of **13**-$(PF_6)_2$ can be assigned to the sulfato group. These IR bands are characteristic of a bridging bidentate sulfate possessing $C_{2v}$ local symmetry.[34b] The molar conductance values (Experimental Section) for **12**-$PF_6$ in acetonitrile and **13**-$(PF_6)_2$ in DMF suggest that they are 1/1 and 2/1 electrolytes, respectively, supporting coordinated and bridging sulfato structures in a dinuclear complex. A room-temperature magnetic moment of 1.17 $\mu_B$/Cu for **12**-$PF_6$ and 1.73 $\mu_B$/Cu for **13**-$(PF_6)_2$ are also consistent with the dinuclear formulation, where the two coppers are antiferromagnetically coupled, although **13**-$(PF_6)_2$ is rather weakly so.

The peroxo complex **6**-$(PF_6)_2$ reacts with dry $SO_2$ (eq 9) at −80 °C in $CH_2Cl_2$ to produce an insoluble solid that was recrystallized from $CH_3CN/Et_2O$ to form **14**-$(PF_6)_2$ in 54% yield. A broad

$$\underset{\mathbf{6}}{[Cu_2(N4)(O_2)]^{2+}} + SO_2 \xrightarrow[CH_2Cl_2,\ -80°C]{Ar} \underset{\mathbf{14}}{[Cu_2(N4)]^{4+}(SO_4^{2-})} \tag{9}$$

band at 1100 cm$^{-1}$ can be assigned to an uncoordinated $SO_4^{2-}$, which has a local tetrahedral symmetry[34b] and acts as a counteranion in **14**-$PF_6$. The room-temperature magnetic moment of 1.68 $\mu_B$ is a bit low but not inconsistent with the absence of a bridging ligand. The molar conductance in acetonitrile suggests that it is a 3/1 electrolyte {i.e., $[Cu_2(N4)](SO_4)(PF_6)_2$}, consistent with the formulation of the copper complex portion of **14**-$(PF_6)_2$ as a tetracation.

All three complexes **12**–**14** form a white precipitate of $BaSO_4$ when treated with $BaCl_2$ in presence of aqueous acid, confirming the presence of sulfate ion.

**$Ph_3C^+BF_4^-$.** Dioxygen complexes $[Cu_2(XYL\text{–}O\text{–})(O_2)]^+$ (**4**), $[\{Cu(TMPA)\}_2(O_2)]^{2+}$ (**5**), and $[Cu_2(N4)(O_2)]^{2+}$ (**6**) were reacted with 2 equiv of $Ph_3C^+BF_4^-$ in dichloromethane at −80 °C. In the cases of **4** and **5**, the reaction takes place within 10 min, but it takes 2–3 h in the case of **6**. For purposes of uniformity and comparisons, reaction mixtures were all stirred for 4 h at −80 °C. The solutions were warmed to room temperature, and green solids were then precipitated by adding diethyl ether. An off-white solid was obtained by concentrating the diethyl ether layer. Initially we looked for the production of trityl peroxide as this had been observed in the reaction of $Ni(O_2)(t\text{-}BuCN)_2$ with 2 equiv of trityl cation.[44] However, we could not detect any significant amount of this product, and instead, benzophenone was detected by gas chromatographic analysis.

The yields of benzophenone formed may be related to the relative nucleophilic behavior of the bound peroxide ligand. The data are consistent with the suggestion that the peroxo moieties in **4** (38% yield of benzophenone) and **5** (49%) are more nucleophilic than that in **6** (30%), although only marginally so with respect to this trityl cation substrate. The reaction of $Ph_3C^+$ with **4**, **5**, and **6** may produce an alkylperoxo intermediate (Scheme VI), which is probably similar to complex **7b**, obtained from the reaction of **4** with $m\text{-}ClC_6H_4CO^+$ (vide supra).[29] An analogous reaction was observed, where $Pt(PPh_3)_2O_2$ reacts with $Ph_3C^+$ to form $Pt(PPh_3)_2OOCPh_3$.[41] The relative ease of the formation of

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(41) Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5832.

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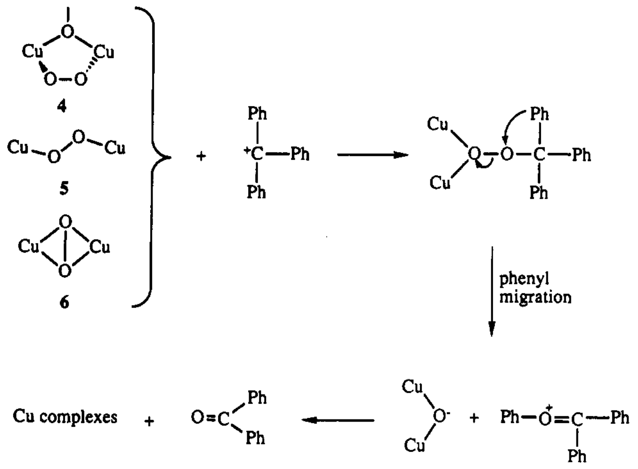
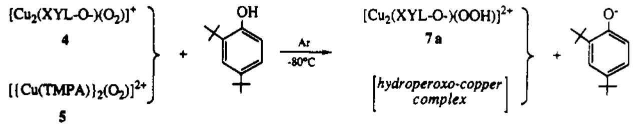
(44) Otsuka, S.; Nakamura, A.; Tatsuno, Y.; Miki, M. *J. Am. Chem. Soc.* **1972**, *94*, 3761–3767.

**Scheme VI**



the alkylperoxo complex will be dependent on the nucleophilicity of the peroxo species, which then undergoes a phenyl migration to produce benzophenone (Scheme VI). This kind of reaction has literature precedence, since tertiary carbonium ions react with $H_2O_2$ in presence of a strong acid to produce a ketone, formed through an alkyl group migration.[45]

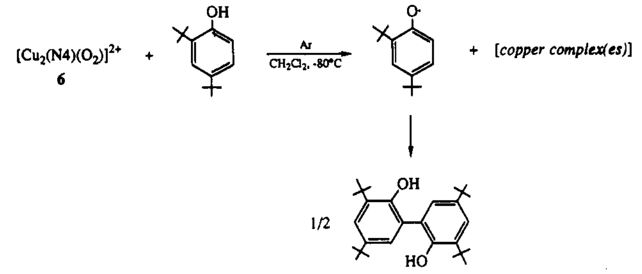
**2,4-Di-*tert*-butylphenol.** All three dioxygen complexes (**4**–**6**) react instantaneously with 2,4-di-*tert*-butylphenol at −80 °C, but the course of the reaction is very different for complexes $[Cu_2(XYL–O–)(O_2)]^+$ (**4**) and $[\{Cu(TMPA)\}_2(O_2)]^{2+}$ (**5**) compared to $[Cu_2(N4)(O_2)]^{2+}$ (**6**). This phenol acts as acid toward **4** and **5** protonates it to form a hydroperoxo complex (**7a**).[28] Thus, as followed by UV–vis spectroscopy, addition of 2,4-di-*tert*-butylphenol to a −80 °C $CH_2Cl_2$ solution of **4** in 1/1 stoichiometry showed that the intense characteristic peak at 505 nm ($\epsilon$ = 6000 $M^{-1}$ $cm^{-1}$) disappeared while a new band at 395 nm ($\epsilon$ = 8000 $M^{-1}$ $cm^{-1}$) formed, indicating that $[Cu_2(XYL–O–)(OOH)]^+$ (**7a**) had formed.[28] No further spectral change was observed when excess phenol was added, and warming the solution to room temperature resulted in the formation of phenoxocopper complexes.[46] Complex **5** reacted in a manner analogous to that seen when strong acid ($HPF_6$) is added to **5**; the characteristic absorptions [$\lambda_{max}$, nm ($\epsilon$, $M^{-1}$ $cm^{-1}$): 440 sh (2000), 525 (11 500), 590 (7600)] were bleached.



By contrast, the oxidation of 2,4-di-*tert*-butylphenol to 3,3′,5,5′-tetra-*tert*-butyl-2,2′-dihydroxybiphenyl occurred when the former was reacted with complex **6** at −80 °C and the reaction is catalytic under an $O_2$ atmosphere. An absorption at $g \approx 2$ was observed when the reaction was followed by EPR spectroscopy (−80 °C), suggesting the presence of an organic (most likely phenoxy) radical in the reaction mixture. These observations suggest that the reaction with phenol is initiated via a hydrogen atom abstraction by $[Cu_2(N4)(O_2)]^{2+}$ (**6**), giving rise to an intermediate phenoxy radical that readily dimerizes to form the dihydroxybiphenyl product (Scheme VII). Such a process is well established for the oxidative coupling of phenols.[47]

In explaining the relative reactivities of $O_2$ complexes **4**–**6**, it is worthwhile to compare the reactivity of related Cu(II) complexes of the XYL–O–, TMPA, and N4 ligands, since many copper(II) complexes themselves readily oxidize phenols. However, under anaerobic conditions, Cu(II) complexes of XYL–O– and TMPA do *not* oxidize 2,4-di-*tert*-butylphenol, rather forming stable phenoxocopper(II) complexes.[46] Under aerobic conditions at room temperature, **1** and **2** do catalyze very slow oxidation of 2,4-di-*tert*-butylphenol to give the coupled biphenol product [31 (3 days) and 3 (4 days) turnovers, respectively], while catalysis using **3** is markedly faster [110 turnovers, 1 day].

**Scheme VII**



**4-X-$C_6H_4$MgBr (X = $CH_3$, F).** All three dioxygen complexes react with 4-X-$C_6H_4$MgBr (X = $CH_3$, F) to give a mixture of 4-X-$C_6H_4$OH (X = $CH_3$, F) and substituted biphenyl X-$C_6H_4$-$C_6H_4$-X (X = $CH_3$, F). A measure of the electrophilicity of a peroxo moiety has been related to the ease of formation of lithium *n*-butoxide from the reaction of *n*-butyllithium with metal–peroxo complexes.[2d,48] Electrophilic peroxides have been used for conversion of alkyl- and arylmagnesium bromides to alcohols and phenols[49] and for the hydroxylation of enolate anions.[50] Both of these reactions are similar to the conversion of *n*-BuLi to lithium *n*-butoxide.

We carried out reactions of (4-methyl- and (4-fluorophenyl)-magnesium bromide with 5-fold excess of the peroxo complexes. An excess of dioxygen complex was used to ensure that the $Ph^-$ source reacts predominantly with the peroxo moiety in **4**–**6** and it does not become oxidized by Cu(II) ions. The products formed in the reaction have been identified with use of gas chromatography as 4,4′-dimethylbiphenyl and 4,4′-difluorobiphenyl (formed by one-electron oxidation of $Ph^-$ followed by dimerization) and 4-methylphenol and 4-fluorophenol (formed by oxygen atom transfer). No other products were detected.[51] In the cases of complexes **4** and **5** the absolute yield of phenol is higher than the biphenyl products whereas the trend is opposite in the case of **6**, suggesting that this species is a better one-electron oxidant, just as seen in the phenol reactions (vide supra).

Since there are two competing reactions for which the relative rates will dictate the product distribution (phenol, O transfer vs biphenyl, one-electron oxidation), we thought it to be useful to compare the methyl- to fluoro-substituted products ratios in order to sort out electronic preferences and eliminate the possible role of steric factors (Table I). The Me product to F product ratios for biphenyl and phenol are less than 1 in the reactions of **4** and **5**, suggesting that these complexes favor (in a relative manner) reactions with electron-poor substrates. By contrast, these ratios are greater than 1 for the case of complex **6**, demonstrating this species to be more electrophilic in its reactions.

## Chemical/Biological Relevance and Summary

The results obtained from these reactivity studies indicate that $[Cu_2(XYL–O–)(O_2)]^+$ (**4**) and $[\{Cu(TMPA)\}_2(O_2)]^{2+}$ (**5**) react quite similarly with the reagents used, and they possess a peroxo ligand which is relatively basic and has a more pronounced nucleophilic character than is found for $[Cu_2(N4)(O_2)]^{2+}$ (**6**). Species **6** is rather more electrophilic in its reactions (Chart I), which is more typical of early-transition-metal–peroxo complexes.[2d]

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(45) Olah, G. A.; Yoneda, N.; Parker, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 483–488.

(46) Tyeklár, Z.; Karlin, K. D. Unpublished observations.

(47) Gampp, H.; Zuberbühler, A. D. In *Metal Ions in Biological Systems* (*Properties of Copper*); Sigel, H., Ed.; Marcel Dekker: New York, 1981; Vol. 12, Chapter 4, pp 162–165 and references cited therein. (b) Finkbeiner, H. L.; Hay, A. S.; White, D. M. *High Polymers* **1977**, *29*, 537 and references cited therein.

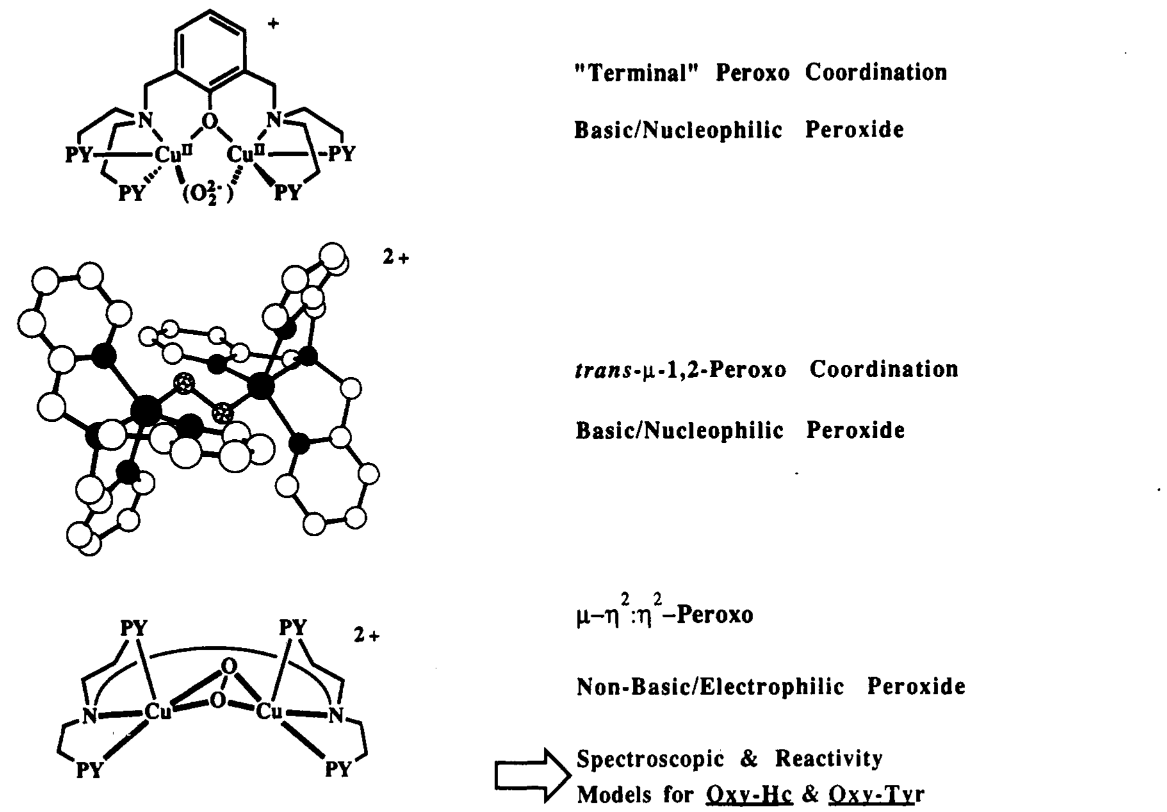
(48) Regen, S. L.; Whitesides, G. M. *J. Organomet. Chem.* **1973**, *59*, 293–297.

(49) (a) Lewis, N. J. *Aust. J. Chem.* **1978**, *31*, 2091–2094. (b) Lewis, N. J.; Gabhe, S. Y.; DeLaMater, M. *J. Org. Chem.* **1977**, *42*, 1479–1480.

(50) (a) Vedjes, E.; Engler, D. A.; Telschow, J. E. *J. Org. Chem.* **1978**, *43*, 188. (b) Vedjes, E. *J. Am. Chem. Soc.* **1974**, *96*, 5944.

(51) The possibility of $CH_2Cl_2$ solvent as a chlorine or proton source in the reaction intermediates is therefore ruled out.

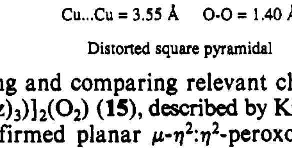
**Chart I**



Comparisons of protonation reactions are particularly striking, since they are not subject to any possible steric effects, the decidedly nonbasic and differing behavior of **6** is demonstrated by its lack of sensitivity to strong acid. $[Cu_2(N4)(O_2)]^{2+}$ (**6**) is also relatively more reactive with substrates capable of facile one-electron-transfer reactions.

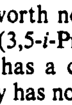
The origin of the alternate and unusual electrophilic/nonbasic reactivity behavior of the $\mu$-$\eta^2$:$\eta^2$-peroxo moiety in $[Cu_2(N4)(O_2)]^{2+}$ (**6**) is of interest. An obvious difference in the coordination environment in **4**–**6** is that there is one more donor group per copper ion in **4** and **5**, than in **6**. Aside from the peroxo group, the XYL–O– ligand in **4** and the TMPA ligand in **5** each provide four donor ligands. Thus, one can make the simplistic argument that the copper ion in **4** and **5** is more electron rich than in **6**, leaving the peroxide group more negatively charged and basic. Also, one might expect anionic phenoxo coordination in **4** to allow for facile transfer of charge from Cu(I) to dioxygen, and we have previously shown that the TMPA ligand complexes possess rather negative redox potentials, also stabilizing the Cu(II) oxidation state.[52] We have not as yet carried out direct electrochemical comparisons for copper(I) complexes of the three ligand types.

Perhaps a more important aspect to consider is the exact mode of binding and differences that may occur. The peroxo group in **4** is terminal in nature,[1,19] and the trans-$\mu$-1,2-peroxo group in **5** also has an end-on coordination mode. The binding of both oxygen atoms to both copper ions in $[Cu_2(N4)(O_2)]^{2+}$ (**6**) may occur since the N4 dinucleating ligand provides only three other donors to each copper ion. Such a coordination is likely to confer a relatively positive charge to the oxygen atoms, just based upon simple valence-bond arguments (i.e., three bonds to each oxygen atom). A more satisfying and quantitative analysis has been recently offered by Ross and Solomon,[53] where broken-symmetry SCF–X$\alpha$–scattered wave calculations were used to detail the electronic structure of peroxide-bridged copper(II) dimers; specific comparisons were made between cis-$\mu$-1,2- and planar $\mu$-$\eta^2$:$\eta^2$-peroxo species. An important finding is that there is a stronger $\Pi^*_\sigma$ donor interaction with the Cu d orbital in the $\eta^2$:$\eta^2$-peroxo complex as compared to the end-on species, suggesting that the charge on the $O_2^{2-}$ ligand is less negative in the case of the side-on peroxodicopper complex. Another novel finding was that the peroxide $\sigma^*$ orbital acted as a $\pi$ acceptor from Cu; this could account for the weak O–O peroxide bond as manifested in an unusually low $\nu_{O-O}$ observed in $[Cu(HB(3,5\text{-}i\text{-}Pr_2pz)_3)]_2(O_2)$ (**15**) and oxy-Hc (~750 cm$^{-1}$).[17] Together, these observations may account for the electrophilic behavior of a peroxide ligand bound in a $\mu$-$\eta^2$:$\eta^2$ fashion and its potential for reactions resulting in O–O cleavage.



**15**

[Cu(HB{3,5-iPr$_2$pz}$_3$)]$_2$(O$_2$)



≡ (hydrotris(3,5-diisopropyl-(pyrazolyl)borate anion

Cu...Cu = 3.55 Å  O-O = 1.40 Å

Distorted square pyramidal

It is worth noting and comparing relevant characteristics of $[Cu(HB(3,5\text{-}i\text{-}Pr_2pz)_3)]_2(O_2)$ (**15**), described by Kitajima et al.,[17,54] since it has a confirmed planar $\mu$-$\eta^2$:$\eta^2$-peroxo structure. Its reactivity has not yet been studied with many of the reagents used in the present investigation, but some comparisons can be made. In reactions with phenols, the dominant behavior is similar to that

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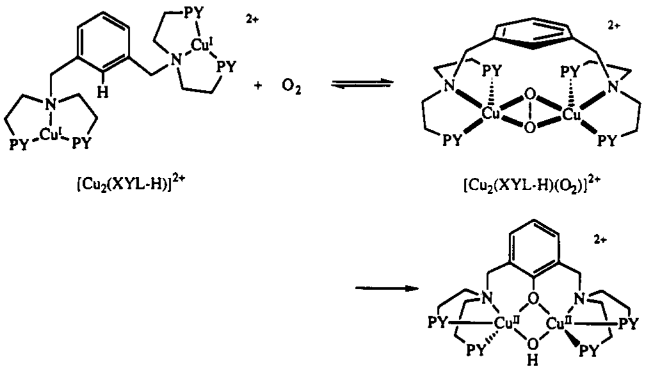
[52] (a) Karlin, K. D.; Hayes, J. C.; Shi, J.; Hutchinson, J. P.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 4106–4108. (b) Zubieta, J.; Karlin, K. D.; Hayes, J. C. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspective*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: Guilderland, NY, 1983; pp 97–108.

[53] (a) Ross, P. K.; Solomon, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 5871–5872. (b) Ross, P. K.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 3246–3259.

[54] (a) Kitajima, N.; Koda, T.; Iwata, Y.; Moro-Oka, Y. *J. Am. Chem. Soc.* **1990**, *112*, 8833–8839. (b) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitagawa, T.; Moro-Oka, Y. *J. Am. Chem. Soc.*, in press. (c) Kitajima, N.; Fujisawa, K.; Koda, T.; Hikichi, S.; Moro-Oka, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 1357–1358.

observed for $[Cu_2(N4)(O_2)]^{2+}$ (**6**), with (presumed) one-electron oxidation to phenoxy radicals leading to oxidative coupling products; a very small yield of oxygenated products is observed.[54a] The course of reaction of triphenylphosphine and carbon dioxide with $[Cu(HB(3,5\text{-}i\text{-}Pr_2pz)_3)]_2(O_2)$ (**15**) and **6** appears to differ. $PPh_3$ readily displaces $O_2$ in **15** but does not in reaction with **6**. As described, $CO_2$ does not react with **6** at temperatures where this $O_2$ complex is stable, contrasting with the behavior observed for **4** and **5**. Kitajima[54] isolates a carbonato complex after allowing $[Cu(HB(3,5\text{-}i\text{-}Pr_2pz)_3)]_2(O_2)$ to warm in the presence of $CO_2$, but it would appear that this is due to reaction of carbon dioxide with an oxo or hydroxo thermal decomposition product of **14**.[54b,55] One can speculate that some of these variations in reactivity may be due to differences in properties of a bent (i.e., in **6**) versus planar $\mu\text{-}\eta^2\text{:}\eta^2$-peroxo moiety (i.e., in **15**), steric effects (i.e., access to substrates), or temperature of reaction and solvent employed.

The proposed $\mu\text{-}\eta^2\text{:}\eta^2$-peroxo structure and its electrophilic nature in $[Cu_2(N4)(O_2)]^{2+}$ (**6**) also have important implications for a chemical system we have previously described. Here, a *m*-xylyl group rather than a $-(CH_2)_4-$ unit (as in the N4 ligand of **6**) connects two chelating bis[2-(2-pyridyl)ethyl]amine units.



$[Cu_2(XYL\text{-}H)]^{2+}$

$[Cu_2(XYL\text{-}H)(O_2)]^{2+}$

**10**

The dicopper(I) complex $[Cu_2(XYL\text{-}H)]^{2+}$ reacts with $O_2$ in a manner closely mimicking the stoichiometry and action of copper monooxygenases such as tyrosinase.[23] We have already accumulated a substantial body of evidence[1,27,56] indicating that a $\{Cu_2\text{-}O_2\}$ intermediate ($[Cu_2(XYL\text{-}H)(O_2)]^{2+}$) forms, and its spectroscopic properties indicate it has a structure similar to that found in $[Cu_2(N4)(O_2)]^{2+}$ (**6**).[56] Recent kinetic studies using 5-substituted derivatives $[Cu_2(R\text{-}XYL\text{-}H)]^{2+}$ (R = *t*-Bu, H, $NO_2$) are consistent with the hydroxylation reaction (i.e., $Cu_2(XYL\text{-}H)(O_2)]^{2+} \rightarrow$ **10**) occuring by an electrophilic attack upon the substrate.[1,57] Also in line with this conclusion is our previous finding that a 2-methyl-substituted xylyl ligand complex (e.g., $XYL\text{-}CH_3$) undergoes an oxidatively induced methyl 1,2-migration ("NIH shift"), suggestive of a carbonium ion intermediate formed from electrophilic attack of the $\{Cu_2\text{-}O_2\}$ intermediate upon the arene substrate.[58] Thus, the results of the present reactivity studies are in complete accord with the monooxygenase model system findings, further suggesting the notion that a $\mu\text{-}\eta^2\text{:}\eta^2$-peroxo unit acts as an electrophilic species capable of hydroxylation of an arene, at least when it is formed in close proximity to this substrate for this intramolecular reaction.

Further insights and details of how this copper-peroxide unit could effect an electrophilic attack of an arene substrate (i.e., in model systems and tyrosinase) have recently been discussed by Sorrell.[16a] As applied to the present case, the important point is that the copper ion binding of dioxygen may orient the coordinated peroxo O–O bond so as to align its empty $\sigma^*$ orbital with the arene substrate p–$\pi$ orbital, facilitating electrophilic attack and O–O bond cleavage to give product. Sorrell's conclusions not only provide an explanation for why a peroxo group need not be inherently highly reactive to effect the hydroxylation reaction but appear to fit this case well. Indeed, a molecular model of the $\mu\text{-}\eta^2\text{:}\eta^2$-peroxo intermediate $[Cu_2(XYL\text{-}H)(O_2)]^{2+}$ indicates a favorable orientation of the O–O bond with the p–$\pi$ orbital of the 2-carbon, which becomes hydroxylated.

Both $[Cu_2(Nn)(O_2)]^{2+}$ (e.g., **6**, *n* = 4) and $[Cu_2(XYL\text{-}X)(O_2)]^{2+}$ (X = H, F) have very distinctive UV-vis spectroscopic properties, with multiple and strong charge-transfer absorptions unlike complexes **4** and **5**. $[Cu(HB(3,5\text{-}i\text{-}Pr_2pz)_3)]_2(O_2)$ (**15**) also is reported to possess a strong 340-nm absorption ($\epsilon \sim 20000$) in solution.[17,59] All of these spectra are rather similar to those seen in oxy-Hc ($\lambda_{max}$ = 345 nm ($\epsilon \sim 20000$), 485 nm (circular dichroism), 570 nm ($\epsilon \sim 1000$)),[9b–d] especially with respect to the prominent high-energy 350–360-nm absorption. As supported by chemical and spectroscopic studies of **6**, reactivity in the closely related monooxygenase model system involving $[Cu_2(R\text{-}XYL)(O_2)]^{2+}$, studies of **15**,[17] and the recent insights into the electronic structure of the $\mu\text{-}\eta^2\text{:}\eta^2$-peroxo group,[53] a $\mu\text{-}\eta^2\text{:}\eta^2$-peroxo $\{Cu_2\text{-}O_2\}$ structure must now be strongly considered as the relevant unit present in the Hc and Tyr protein active sites.

We have shown how studies of the reactivity of these peroxo complexes, apart from spectroscopy, can be used to elucidate or discriminate between structural possibilities. The $\mu\text{-}\eta^2\text{:}\eta^2$-peroxodicopper(II) structure is a relatively new and important moiety, at least in copper chemistry and probably biochemistry; the present study demonstrates its unique nonbasic and electrophilic behavior, which has been independently seen in a copper monooxygenase model system, and predicted in theoretical studies. It is clear that the ligand environment can greatly influence the structure and reactivity of derived $\{LCu_2\text{-}O_2\}$ complexes, and this provides optimism in longer term interests to control structure and reactivity by synthetic means.

**Acknowledgment.** We are very grateful to the National Institutes of Health for support of this research.

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(55) This suggestion has now been confirmed.[54b] We also observe carbonato complex production when $CO_2$ reacts with oxo- or hydroxocopper(II) byproducts of **4**–**6**.

(56) (a) Nasir, M. S.; Karlin, K. D.; McGowty, D.; Zubieta, J. *J. Am. Chem. Soc.* **1991**, *113*, 698–700. (b) Karlin, K. D.; Tyeklár, Z.; Farooq, A.; Haka, M. S.; Ghosh, P.; Cruse, R. W.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. Submitted for publication.

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(59) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitagawa, T.; Moro-Oka, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 151–152.