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Dioxygen-Copper Reactivity: Generation, Characterization, and Reactivity of a Hydroperoxo-Dicopper(II) Complex

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Abstract: A hydroperoxo–dicopper(II) species, the protonated form of the peroxo–dicopper(II) complex derived from the reaction of O_2 with a dicopper(I) compound, is stable at −80 °C in dichloromethane solution and the methods for its generation and its properties are described. This complex, $[Cu_2(XYL\text{-}O\text{–})(OOH)]^{2+}$ (**3**), utilizes a phenolic dinucleating ligand possessing two tridentate PY2 units (PY2 = bis[2-(2-pyridyl)ethyl]amine), XYL-OH. A phenoxo-bridged dicopper(I) complex $[Cu_2(XYL\text{-}O\text{–})]^+$ (**1**) reacts with O_2 to form the previously characterized dioxygen (peroxo) adduct $[Cu_2(XYL\text{-}O\text{–})(O_2)]^+$ (**2**). As shown by a titration followed by UV–vis spectroscopy, one equivalent of H^+ can be irreversibly added to −80 °C dichloromethane solutions of **2** (isosbestic point observed) to form $[Cu_2(XYL\text{-}O\text{–})(OOH)]^{2+}$ (**3**; λ_{max} = 395 nm, ϵ = 8000 M^{-1} cm^{-1}). Complex **3** can also be generated by reaction of the phenoxo- and hydroxo-bridged dicopper(II) complex $[Cu_2(XYL\text{-}O\text{–})(OH)]^{2+}$ (**4**) with hydrogen peroxide, further substantiating its formulation as a peroxidic species. The most convenient method for forming **3** is by the addition of O_2 ($Cu{:}O_2$ = 2:1) to either $[Cu_2(XYL\text{-}OH)]^{2+}$ (**5**) or $[Cu_2(XYL\text{-}OH)(CH_3CN)_2]^{2+}$ (**6d**); these dicationic dicopper(I) compounds contain an uncoordinated phenol group. While the dioxygen complex $[Cu_2(XYL\text{-}O\text{–})(O_2)]^+$ (**2**) reacts with triphenylphosphine (PPh_3) liberating O_2 quantitatively and providing $[Cu_2(XYL\text{-}O\text{–})(PPh_3)_2]^+$ (**7**), the hydroperoxo complex $[Cu_2(XYL\text{-}O\text{–})(OOH)]^{2+}$ (**3**) reacts with PPh_3 or sulfides quantitatively to given the monooxygenated substrate ($O{=}PPh_3$ or RS(O)R) and $[Cu_2(XYL\text{-}O\text{–})(OH)]^{2+}$ (**4**), involving the transfer of a single oxygen atom to the substrate. Similar substrate oxygenation reactions can also be carried out by reacting O_2 with compounds $[Cu_2(XYL\text{-}OH)(PPh_3)_2]^{2+}$ (**6b**) or $[Cu_2(XYL\text{-}OH)(RSR)_2]^{2+}$ (**6c**, RSR = tetramethylene sulfide). Product analyses (**4** also produced quantitatively) show that only 1 mol·equiv of substrate is oxygenated, in accord with the manometric dioxygen uptake ($Cu{:}O_2$ = 2:1); labeling experiments utilizing $^{18}O_2$ show that the product phosphine oxide or sulfoxide contains a single ^{18}O atom. $[Cu_2(XYL\text{-}O\text{–})(OOH)]^{2+}$ (**3**) is proposed to contain a μ-1,1-hydroperoxo (^{-}OOH) ligand, based on (i) its structural analogy to $[Cu_2(XYL\text{-}O\text{–})(OH)]^{2+}$ (**4**), deduced from an extended X-ray absorption fine structure (EXAFS) analysis, with four N or O donors at 1.99 Å and Cu···Cu = 3.04 Å, and (ii) the chemical and spectroscopic similarities to the recently structurally described acylperoxo complex, $[Cu_2(XYL\text{-}O\text{–})(OOR)]^{2+}$ (**8**, R = $m\text{-}ClC_6H_4C(O)\text{–}$). A crystallographic study of a perchlorate salt of **6b**, $[Cu_2(XYL\text{-}OH)(PPh_3)_2](ClO_4)_2\cdot(CD_3NO_2)_2$ ($C_{74}H_{76}D_6Cl_2Cu_2N_8O_{13}P_2$), has been carried out; it crystallizes in the triclinic space group $P1$ with Z = 1 and a = 10.196 (2) Å, b = 11.715 (2) Å, c = 15.506 (3) Å, α = 94.27 (1)°, β = 90.30 (1)°, and γ = 94.53 (1)°. It contains an uncoordinated phenol group with well-separated (Cu···Cu = 9.944 (2) Å) tetracoordinate Cu(I) ions ligated to the three N atoms of the PY2 unit and a single triphenylphosphine P atom.

Copper-containing complexes are known to be important and versatile catalysts/reagents for O_2-mediated reactions in both biological and synthetic systems.[2-7] As part of our overall efforts in developing copper coordination complexes of relevance to proteins and enzymes,[5,7] we are examining the binding, interaction, and subsequent reactivity of dioxygen and its reduced forms at copper ion centers.

In particular, these biomimetic investigations have focused on the metalloproteins hemocyanin (Hc)[6-10] and tyrosinase,[6-8,10-12] which contain two copper ions in their active center. Hemocyanins bind and transport dioxygen in the hemolymph of molluscs and arthropods. A recent X-ray structural study on a deoxy-Hc indicates that in this form three imidazole groups are ligated to each copper(I) ion, and a copper–copper separation of 3.7 ± 0.4 Å is observed.[13] A variety of chemical and spectroscopic studies have shown that the addition of O_2 occurs via an inner-sphere redox reaction to give oxy-Hc, where tetragonally coordinated Cu(II) ions separated by 3.6 Å are also bridged by the "exogeneous" peroxo (O_2^{2-}) ligand which is suggested to be bound in a cis μ-1,2 fashion. An additional bridging ligand (probably OH^- or H_2O) is also suggested to be present. Tyrosinsases are ubiquitous copper-containing monooxygenases[14] that catalyze the incorporation of one oxygen atom from dioxygen into the ortho

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(2) Gampp, H.; Zuberbuhler, A. D. *Met. Ions Biol. Syst.* **1981**, *12*, 133-190.

(3) Nigh, W. G. In *Oxidation in Organic Chemistry*; Trahanovsky, W. S., Ed.; Academic: New York, 1973; Part B, pp 1-96.

(4) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981.

(5) (a) *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1983. (b) *Biological & Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1986; Vol. 1-2.

(6) (a) Karlin, K. D.; Gultneh, Y. *Prog. Inorg. Chem.* **1987**, *35*, 219-327 and references cited therein. (b) Karlin, K. D.; Gultneh, Y. *J. Chem. Educ.* **1985**, *62* (11), 983-990.

(7) Tyeklar, Z.; Ghosh, P.; Karlin, K. D.; Farooq, A.; Cohen, B. I.; Cruse, R. W.; Gultneh, Y.; Haka, M. S.; Jacobson, R. R.; Zubieta, J. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; American Chemical Society, Washington, DC, 1988; ACS Symp. Ser. Vol. 372 pp 85-104.

(8) (a) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bonding (Berlin)* **1983**, *53*, 1-57. (b) Solomon, E. I. In *Copper Coordination Chemistry: Biochemical & Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1983; pp 1-22.

(9) Lontie, R.; Witters, R. *Met. Ions Biol. Syst.* **1981**, *13*, 229-258.

(10) Lerch, K. *Met. Inos Biol. Syst.* **1981**, *13*, 143-186.

(11) Robb, D. A. In *Copper Proteins and Copper Enzymes*; Lontie, R., Ed.; CRC: Boca Raton, FL, 1984; Vol. 2, pp 207-241.

(12) (a) Wilcox, D. E.; Porras, A. G.; Hwang, Y. T.; Kerch, K.; Winkler, M. E.; Solomon, E. I. *J. Am. Chem. Soc.* **1985**, *107*, 4015-4027 and references cited therein.

(13) (a) Linzen, B.; Soeter, N. M.; Riggs, A. F.; Schneider, H.-J.; Schartau, W.; Moore, M. D.; Yokota, E.; Behrens, P. Q.; Nakashima, H.; Takagi, T.; Nemoto, T.; Vereijken, J. M.; Bak, H. J.; Beintema, J. J.; Volbeda, A.; Gaykema, W. P. J.; Hol, W. G. J. *Science* **1985**, *229*, 519-524. (b) Gaykema, W. P. J.; Volbeda, A.; Hol, W. G. J. *J. Mol. Biol.* **1985**, *187*, 255-275. (c) Gaykema, W. P. J.; Hol, W. G. J.; Vereijken, J. M.; Soeter, N. M.; Bak, H. J.; Beintema, J. J. *Nature (London)* **1984**, *309*, 23-29.

(14) Other copper-containing monooxygenases of interest are dopamine β-hydroxylase[10,15a] and a recently characterized copper phenylalanine hydroxylase.[15b]

(15) (a) Villafranca, J. J. In *Metal Ions in Biology*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1981; Vol. 3, pp 263-290. (b) Pember, S. O.; Villafranca, J. J.; Benkovic, S. J. *Biochemistry* **1986**, *25*, 6611-6619.

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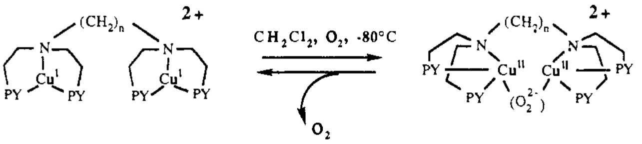
position of phenols and further oxidize the catechols formed to *o*-quinones. A comparison of spectral (i.e., EPR, electronic absorption, CD, and resonance Raman) properties of oxy-tyrosinase and its derivatives with those of oxy-Hc establishes a close similarity of the dicopper active site structures in these proteins. In tyrosinase, a peroxo–dicopper(II) intermediate is apparently accessible to substrate, which can then coordinate and undergo hydroxylation to give product.[12]

In our biomimetic studies we have recently described two types of synthetic dicopper coordination complexes that can bind O_2 (and CO) reversibly.[6,7] Both systems utilize dinucleating ligands containing two tridentate N_3 donor groups for copper, a bis[2-(2-pyridyl)ethyl]amine (PY2) unit. One set of O_2/copper complexes that may serve as good active site models for Hc, $[Cu_2(N\textit{n}PY2)(O_2)]^{2+}$, where the PY2 units are linked by variable methylene chains *n* (*n* = 3–5), are formed reversibly from the reactions of three-coordinate dicopper(I) complexes, $[Cu_2(N\textit{n}PY2)]^{2+}$, with dioxygen.[16] $[Cu_2(N\textit{n}PY2)(O_2)]^{2+}$ are characterized by multiple and strong charge-transfer bands in the visible region, with band positions and intensity patterns reminiscent of oxy-Hc. The physicochemical data suggest that the $[Cu_2(N\textit{n}PY2)(O_2)]^{2+}$ complexes are best described as peroxo–dicopper(II) complexes, with a single peroxo ligand bridging and strongly magnetically coupling the two Cu(II) ions.



We have also described a system in which O_2 reacts reversibly with a phenoxo-bridged dicopper(I) complex, $[Cu_2(XYL\text{-}O\text{-})]^+$ (**1**), in dichloromethane solution at low temperature to give an intensely purple (λ_{max} = 505 nm, ϵ = 6000 M^{-1} cm^{-1}) colored complex, $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (**2**) (Cu:O_2 = 2:1) (Figure 1).[17] Resonance Raman[18] and extended X-ray absorption fine structure (EXAFS)[19] studies have established that **2** is best formulated as a peroxo–dicopper(II) complex (ν_{O-O} = 803 cm^{-1}, Cu···Cu = 3.31 Å), possessing an effectively terminally coordinated Cu–(O_2^{2-}) unit.

More recently, we discovered that a protonated form of **2** can be prepared, a hydroperoxo dicopper(II) complex, $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**).[20] Here, we present a full report describing the generation, physical properties, and reactivity of **3** (Figure 1). $[Cu_2(XYL\text{-}O\text{-})(O_2H)]^{2+}$ (**3**) can be formed via three different routes. First, $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (**2**) can be directly protonated with 1 equiv of $HBF_4{\cdot}Et_2O$ at −80 °C in dichloromethane to give the hydroperoxo species, **3**. Second, the phenoxo and hydroxo doubly bridged dicopper(II) complex, $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ (**4**), can be directly reacted with hydrogen peroxide in a ligand displacement reaction. Third, protonated forms of the dicopper(I) complex **1**, $[Cu_2(XYL\text{-}OH)]^{2+}$ (**5**) or $[Cu_2(XYL\text{-}OH)(L)_2]^{2+}$ (**6a**, L = CO; **6d**, L = CH_3CN), can be reacted with O_2 (Cu:O_2 = 2:1) at low temperatures to directly produce solutions of $[Cu_2(XYL\text{-}O\text{-})(O_2H)]^{2+}$ (**3**). The syntheses of complexes **5** and **6** are described and an X-ray crystal structure determination of $[Cu_2(XYL\text{-}OH)(PPh_3)_2]^{2+}$ (**6b**) is presented to demonstrate the presence of the noncoordinated phenol group in these compounds (**6**). The reactivity of $[Cu_2(XYL\text{-}O\text{-})(O_2H)]^{2+}$ (**3**) toward triphenylphosphine and tetramethylene sulfide is also reported, and contrasted with the corresponding reactions of PPh_3 with $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (**2**); electrophilic activation (i.e., protonation) toward oxygen atom transfer reactions apparently occurs here, since the hydroperoxo complex $[Cu_2(XYL\text{-}O\text{-})(O_2H)]^{2+}$ (**3**) can effect the transfer of an O atom to these substrates, while the dioxygen (peroxo) complex $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (**2**) does not (Figure 1).

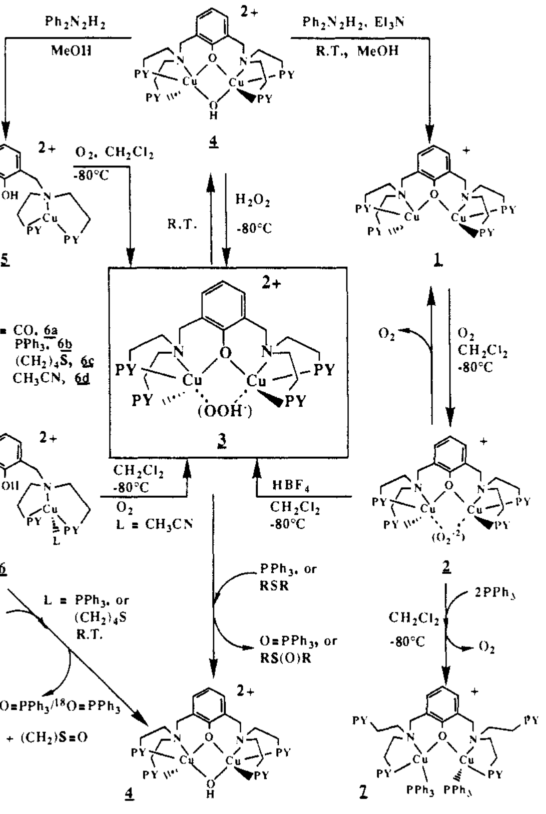


Figure 1. Scheme illustrating the copper/dioxygen chemistry and relationship between complexes leading to the generation of the hydroperoxo complex $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**) (XYL-O– is the deprotonated anionic phenoxide dinucleating ligand shown; PY = 2-pyridyl). The phenoxo-bridged dicopper(I) complex **1** can be reversibly reacted with O_2 to give the previously characterized dioxygen (peroxo) adduct **2**. This can be protonated directly to give **3**. Alternatively, $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**) can be generated by reaction of **4** with H_2O_2 or by the reaction O_2 with a phenol-containing dicopper(I) complex, either **5** or **6d** (XYL-OH is the un-deprotonated phenolic dinucleating ligand shown). While the dioxygen complex $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (**2**) reacts with triphenylphosphine-liberating O_2 quantitatively and giving **7**, the hydroperoxo complex $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**) reacts with PPh_3 or sulfides quantitatively to give the monooxygenated substrate (O=PPh_3 or RS(O)R) and $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ (**4**).

Experimental Section

Materials and Methods. Unless otherwise stated all solvents and chemicals used were of commercially available analytical grade. Dioxygen and carbon monoxide gases were dried by passing them through a short column of supported P_4O_{10} (Aquasorb, Mallinkrodt). Methanol was distilled from $Mg(OMe)_2$ and diethyl ether was obtained by passing it through a 60 cm long column of activated alumina and/or it was directly distilled from sodium/benzophenone under argon. Dry acetonitrile was prepared by refluxing it over P_4O_{10} and finally distilling it from CaH_2. In the dark, CH_2Cl_2 was stirred with concentrated sulfuric acid for several days. After being washed with $NaHCO_3$ saturated water, the acid layer was removed and the dichloromethane was washed with a KOH-KCl saturated solution and distilled water and then dried over anhydrous $K_2CO_3/MgSO_4$ before a final reflux and distillation from CaH_2.

Preparation and handling of air-sensitive materials were carried out under an argon atmosphere with standard Schlenk techniques.[21] De-

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(16) (a) Karlin, K. D.; Haka, M. S.; Cruse, R. W.; Gultneh, Y. *J. Am. Chem. Soc.* **1985**, *107*, 5828–5829. (b) Karlin, K. D.; Haka, M. S.; Cruse, R. W.; Meyer, G. J.; Farooq, A.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 1196–1207.

(17) (a) Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Farooq, A.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 2668–2679. (b) Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 3372–3374.

(18) Pate, J. E.; Cruse, R. W.; Karlin, K. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 2624–2630.

(19) Blackburn, N. J.; Strange, R. W.; Cruse, R. W.; Karlin, K. D. *J. Am. Chem. Soc.* **1987**, *109*, 1235–1237.

(20) Karlin, K. D.; Cruse, R. W.; Gultneh, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 599–600.

(21) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

oxygenation of solvents and solutions was effected either by repeated vacuum/purge cycles with argon or by bubbling (15 min) argon directly through the solutions. Crystalline solid samples were stored and the samples for IR, NMR, and UV-vis spectra were prepared in a Vacuum/Atmospheres glove box filled with argon. Column chromatography was carried out with silica gel (60–200 mesh, MCB). Fractions from column chromatography were monitored by using Baker-Flex IB-F TLC plates. All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and/or MicAnal, Tuscon, AZ.

Infrared spectra were recorded in Nujol mull on a Perkin-Elmer 283 or 710B instrument and calibrated by using a polystyrene film. NMR spectra were measured in CD_3NO_2 on either a Varian XL-300 (300 MHz) or a Varian EM360 (60 MHz) NMR spectrometer. Chemical shifts are reported as δ values downfield from an internal standard of Me_4Si. X-band EPR measurements were obtained with a Varian E-4 spectrometer equipped with a liquid nitrogen Dewar inset. The calibration was effected by using diphenylpicrylhydrazyl (DPPH). Mass spectra were recorded with a Hewlett-Packard 5970 mass selective detector interfaced to an HP gas chromatograph (12 m capillary column, cross-linked methyl silicone gum). All gas chromatographic analyses were performed on a Hewlett-Packard 5890 series gas chromatograph equipped with a capillary injector and a flame ionization detector with a 30-m HP5 (cross-linked 5% phenyl methyl silicone) capillary column 19095Z-023. Signal integration was obtained by using an HP 3392A integrator. Low-temperature UV-vis spectroscopy and O_2 uptake measurements were carried out as described elsewhere.[16b,17a] For measurements in the near-IR region (800–1100 nm) a Shimadzu 160 spectrophotometer was used.

Synthesis of Complexes. $[Cu_2(XYL\text{-}O\text{-})]PF_6$(1-($PF_6$)). Under an argon atmosphere to a solution of 2.0 g (1.99 mmol) of green crystalline complex $[Cu_2(XYL\text{-}O\text{-})(OH)](PF_6)_2$ (**4**)[22] in 50 mL of methanol was added a degassed solution of 0.80 g (4.35 mmol) of diphenylhydrazine containing 0.5 mL (3.6 mmol) of triethylamine in 50 mL of methanol. The mixture was stirred overnight at room temperature. A clear bright orange solution developed. The volume was slowly reduced under vacuum to 50 mL. An excess of degassed diethyl ether was then added to give a bright yellow precipitate. The crude product was thoroughly washed with ether to remove the last traces of unreacted diphenylhydrazine, azobenzene, and triethylammonium hexafluorophosphate. The precipitate was dried under vacuum. Crystallization was performed by slow evaporation of the methanolic solution, which had been previously filtered through a fine glass frit. The crystals were washed twice with small volumes of cold methanol and dried to give a yield of 1.1 g (65%). Anal. Calcd for ($C_{36}H_{39}Cu_2F_6N_6OP$): C, 51.24; H, 4.66; N, 9.96. Found: C, 51.21; H, 4.70; N, 9.92. UV-vis (CH_2Cl_2, −80 °C): λ_{max},(ϵ M^{-1} cm^{-1}) 320 (9100), 385 (10600). ^{1}H NMR (CD_3NO_2): δ 3.1 (br m, 16), 3.7 (s, 4), 5.94 (t, 1, J = 7 Hz), 6.6 (d, 2, J = 6 Hz), 7.5–7.8 (m, 12), 8.4 (d, 4, J = 5 Hz).

The reduction of **4** with diphenylhydrazine can be accelerated by stirring the mixture in a warm water bath (60 °C). At more elevated temperatures, the yield is poorer because of an irreversible disproportionation reaction of complex **1**.

$[Cu_2(XYL\text{-}O\text{-})(OH)](ClO_4)_2\cdot 0.25CH_2Cl_2$(4-($ClO_4$)$_2$). This was synthesized by the same hydroxylation reaction as for the hexafluorophosphate salt,[22] using $Cu(CH_3CN)_4ClO_4$[23] as the copper ion source. The reaction was carried out in dimethylformamide solvent. The green product isolated by removal of the solvent was recrystallized from CH_2Cl_2/Et_2O. Anal. Calcd for ($C_{36}H_{40}Cl_2Cu_2N_6O_{10}\cdot 0.25CH_2Cl_2$): C, 46.51; H, 4.33; N, 8.98. Found: C, 45.93; H, 4.3; N, 8.75. IR (Nujol): 3525 (O–H), 1095 (ClO_4^-, br s), 625 (ClO_4^-, m) cm^{-1}.

$[Cu_2(XYL\text{-}OH)](ClO_4)_2$ (5-(ClO_4)$_2$). Complex $[Cu_2(XYL\text{-}O\text{-})(OH)](ClO_4)_2\cdot 0.25CH_2Cl_2$ (**4-(ClO_4)$_2$**) 2.0 g; 2.13 mmol), was dissolved in 50 mL of MeOH, which was previously bubbled for 15 min with argon. To it 0.80 g (4.35 mmol) diphenylhydrazine in 50 mL oxygen-free MeOH was added with stirring. The resulting dark green solution was stirred at 60 °C for 3 h. The volume of the clear light yellow solution was slowly reduced under vacuum to 25 mL. After the solution was cooled (acetone–liquid nitrogen slush bath), 300 mL of degassed diethyl ether at −80 °C was added slowly with stirring to afford a light yellow precipitate. The supernatant solvent was removed in cold with a cannula-string transfer procedure. The precipitate was then washed twice with ether at low temperature and dried in vacuo to give a yield of 1.2 g (60%) of an extremely air sensitive product, which was stored under argon. Anal. Calcd for ($C_{36}H_{40}Cl_2Cu_2N_6O_9$): C, 48.1; H, 4.45; N, 9.35. Found: C, 48.58; H, 4.46; N, 9.46. ^{1}H NMR (CD_3NO_2): δ 3.2 (16 H, br s), 3.76 (4 H, s), 6.4–7.9 (15 H, br m), 8.45 (4 H, br d). IR (Nujol): 1095 (ClO_4^-, br s), 625 (ClO_4^-, m) cm^{-1}. The ν_{O-H} of the uncoordinated phenol was not observed in this complex; however, proof that the O–H group is there came in a deuterium-exchange experiment. When compound **5** was stirred in CH_2Cl_2 solution with MeOD, the yellow precipitate obtained by precipitation with diethyl ether, $[Cu_2(XYL\text{-}OD)](ClO_4)_2$ (**5-(ClO_4)$_2$**), also did not show a ν_{O-D}. After saturation of a methanolic solution of this complex with CO followed by precipitation, the resulting complex $[Cu_2(XYL\text{-}OD)(CO)_2](ClO_4)_2$ (see **6a** below) showed ν_{O-D} = 2450 cm^{-1} (where ν_{O-H} = 3525 cm^{-1} for **6a**) and ν_{CO} = 2050 cm^{-1}.

$[Cu_2(XYL\text{-}OH)(CO)_2](PF_6)_2$ (6a-(PF_6)$_2$). The complex was prepared by following the above procedure except that the reduction of **4** was carried out under a carbon monoxide atmosphere for 5 h. The addition of CO-saturated diethyl ether at room temperature resulted in the deposition of an off-white precipitate which was filtered under CO and recrystallized from a carbon monoxide saturated solution of CH_2Cl_2/MeOH (1:1)/Et_2O to give a cream colored microcrystalline product (yield 1.8 g, 80%). Anal. Calcd for ($C_{38}H_{40}Cu_2F_{12}N_6O_3P_2$): C, 43.63; H, 3.86; N, 8.04. Found: C, 43.58; H, 3.91; N, 8.06. ^{1}H NMR (CD_3NO_2): δ 3.2 (br s, 16), 4.5 (s, 4), 6.8–8.0 (br m, 15), 8.53 (d, 2, J = 6 Hz). IR (Nujol): 3525 (CO, s), 820 (PF_6^-, br s) cm^{-1}.

$[Cu_2(XYL\text{-}OH)(PPh_3)_2](PF_6)_2$ (6b-(PF_6)$_2$). Under an argon atmosphere diphenylhydrazine, 1.2 g (5.3 mmol) in 75 mL MeOH, was added with stirring to a degassed 50 mL methanolic solution of $[Cu_2(XYL\text{-}O\text{-})(OH)](PF_6)_2$ (**4-(PF_6)$_2$**) (3.0 g, 3.0 mmol). After 15 min solid PPh_3 (1.14 g, 6.5 mmol) was added and the mixture was stirred at 70–80 °C for 2 h. Precipitation with oxygen-free diethyl ether afforded a gray white powder that was subsequently washed with ether and a small volume of cold methanol. Recrystallization with MeOH/Et_2O (1:1 (v/v)) gave 4.33 g (95%) of small cream colored crystals, which were fairly stable in air. Anal. Calcd for ($C_{72}H_{76}Cu_2F_{12}N_6OP_4$): C, 57.08; H, 5.02; N, 5.54. Found: C, 57.01; H, 4.73; N, 5.59. ^{1}H NMR (CD_3NO_2): δ 3.0 (br s, 16), 3.9 (s, 4), 6.7–7.8 (br m, 45), 8.55 (d, 4, J = 5 Hz). IR (Nujol): 3565 (O–H, m), 820 (PF_6^-, br s) cm^{-1}.

The perchlorate salt of the complex **6b** was obtained in the same manner as above, using **4-(ClO_4)$_2$** as precursor. X-ray quality crystals were isolated in an NMR tube in deuteriated nitromethane solvent. Anal. Calcd for $[Cu_2(XYL\text{-}OH)(PPh_3)_2](ClO_4)_2\cdot(CD_3NO_2)_2$, ($C_{74}H_{76}D_6Cl_2Cu_2N_8O_{13}P_2$): C, 57.26; H, 4.9; N, 7.23. Found: C, 57.12; H, 4.88; N, 7.41. IR (Nujol): 3560 (O–H, m), 1090 (ClO_4^-, br s), 625 (ClO_4^-, m) cm^{-1}. ^{1}H NMR (CD_3NO_2): same as for **6b-(PF_6)$_2$**.

$[Cu_2(XYL\text{-}OH)(C_4H_8S)_2](PF_6)_2$ (6c-(PF_6)$_2$). The complex was synthesized following the same procedure as for **6b**, except instead of PPh_3, tetrahydrothiophene was used as the coligand. Precipitation with argon-purged diethyl ether was carried out at low temperature (−40 °C). Recrystallization of the solid obtained with MeOH/Et_2O (1:2 (v/v)) gave 2.45 g (70%) of a moderately air sensitive light yellow powder. Anal. Calcd for ($C_{44}H_{56}Cu_2F_{12}N_6S_2OP_2$): C, 45.31; H, 4.80; N, 7.21. Found: C, 46.03; H, 4.74; N, 7.39. ^{1}H NMR (CD_3NO_2): δ 2.2 (br s, 8), 3.3 (br s, 24), 4.0 (s, 4), 6.8–7.9 (m, 15), 8.43 (d, 4, J = 5 Hz). IR (Nujol): 3475 (O–H, br w), 820 (PF_6^-, br s) cm^{-1}.

$[Cu_2(XYL\text{-}OH)(CH_3CN)_2](ClO_4)_2$ (6d-(ClO_4)$_2$). Reduction of $[Cu_2(XYL\text{-}O\text{-})(OH)](ClO_4)_2$ (**4-(ClO_4)$_2$**) (2.0 g; 2.2 mmol) with diphenylhydrazine (0.8 g) was carried out in an oxygen-free MeOH/CH_3CN (9:1 (v/v)) mixture for 3 h at 60 °C. A bright yellow compound precipitated at low temperature (−40 °C) upon addition of argon-purged diethyl ether. Further washing with ether and filtering under argon gave 1.6 g (80%) of yellow powder. Recrystallization from MeOH/Et_2O (1:3 (v/v)) then gave 1.1 g (55%) of microcrystalline yellow complex. Anal. Calcd for $C_{40}H_{46}Cu_2Cl_2N_8O_9$: C, 48.97; H, 4.69; N, 10.43. Found: C, 48.25; H, 4.75; N, 10.42. ^{1}H NMR (CD_3NO_2): δ 2.2 (s, 6), 3.2 (br s, 16), 3.8 (s, 4), 6.8–7.9 (m, 15), 8.45 (d, 4, J = 6 Hz). IR (Nujol): 3500 (O–H, br w), 2240 (C–N, m), 1095 (ClO_4^-, br s), 625 (ClO_4^-, s) cm^{-1}.

Complex **6d-(PF_6)$_2$** was also prepared by an analogous procedure. Anal. Calcd for $C_{40}H_{46}Cu_2F_{12}N_8OP_2$: C, 44.82; H, 4.30; N, 10.45. Found: C, 45.11; H, 4.28; N, 10.64. The proton NMR chemical shifts are the same as that of the perchlorate salt.

Compounds **6a–d** can also be prepared directly by reacting the appropriate coligand in MeOH with $[Cu_2(XYL\text{-}OH)]^{2+}$ (**5**) salts.

Formation of $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (3). The generation of the dicopper(II) –hydroperoxide species can be effected by the following procedures:

(i) Generation from $[Cu_2(XYL\text{-}O\text{-})]PF_6$ (1-(PF_6)). Protonation of $[Cu_2(XYL\text{-}O\text{-})(O_2)]PF_6$ (2-(PF_6)). In a 250-mL Schlenk flask a 100-mL oxygen-free CH_2Cl_2 solution of $[Cu_2(XYL\text{-}O\text{-})](PF_6)$ (**1-(PF_6)**) (0.125 mmol) was prepared. Oxygenation at −80 °C with stirring gave the deep violet coloration due to $[Cu_2(XYL\text{-}O\text{-})(O_2)]PF_6$.[17] To it, 1 equiv of a chilled HBF_4 (0.1 M) solution in CH_2Cl_2, prepared by adding purified dichloromethane to the commercially available etheral adduct of HBF_4

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(22) Karlin, K. D.; Hayes, J. C.; Gultneh, Y.; Cruse, R. W.; McKown, J. W.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 2121–2128.

(23) (a) Hathaway, B. J.; Holah, D. G.; Postlethwaite *J. Chem. Soc.* **1961**, 3215. (b) Hemmerich, P.; Sigwart, C. *Experimentia* **1963**, *19*, 488.

(50–52%, Aldrich), was added at −80 °C. Within a few minutes the violet color changed to deep green; this process could be monitored spectrophotometrically (see Discussion).

(ii) **Generation from $[Cu_2(XYL\text{-}O\text{-})(OH)](PF_6)_2$ ($4\text{-}(PF_6)_2$).** The displacement of the hydroxo bridge by H_2O_2 was carried out in dichloromethane. To a 100-mL chilled CH_2Cl_2 solution (−65 °C) of $[Cu_2(XYL\text{-}O\text{-})(OH)](PF_6)_2$ (**4**, 1.0 g, 10 mmol) was added 10 mL of 30% aqueous hydrogen peroxide (>100-fold excess) which quickly froze. Gradual warming of the mixture by swirling at room temperature rapidly converted the brownish green complex to a deep green solution when the temperature warmed to near the melting point of the hydrogen peroxide. This mixture was then promptly chilled to −80 °C, resulting in the formation of chunks of the frozen hydrogen peroxide–water phase and a turbid dark green solution. A clear solution was obtained by allowing it to stand at low temperature (−90 °C) for several days and carefully decanting off the clear green solution. To follow the course of the reaction spectrophotometrically *N*,*N*-dimethylformamide was used instead of CH_2Cl_2.

(iii) **Generation from $[Cu_2(XYL\text{-}OH)](ClO_4)_2$ ($5\text{-}(ClO_4)_2$).** In a 100-mL graduated schlenk tube 0.50 g (0.56 mmol) of complex **5** was weighed out inside the drybox. The tube was tightly closed under argon and was attached to the vacuum line. To it 50 mL of argon-purged dry CH_2Cl_2 was slowly added with stirring at −80 °C when a clear light yellow solution developed. With chilling (−80 °C) and stirring, dioxygen gas was passed through the solution whereupon the intense green color due to the hydroperoxo complex, $3\text{-}(ClO_4)_2$, developed. To ensure its complete formation, the purging of dioxygen was continued for 15 min.

(iv) As indicated below, the hydroperoxo complex, **3**, was generated by decarbonylation (via application of vacuum/purge cycles) of a solution of $[Cu_2(XYL\text{-}OH)(CO)_2]^{2+}$ (**6a**), followed by oxygenation at −80 °C.

Oxygen Uptake Measurement for Hydroperoxide Formation. (i) Reaction of $[Cu_2(XYL\text{-}OH)(CO)_2](PF_6)_2$ ($6a\text{-}(PF_6)_2$) with O_2. Here the gas uptake measurement of $[Cu_2(XYL\text{-}OH)](PF_6)_2$ ($5\text{-}(PF_6)_2$) generated in situ by decarbonylation of $6a\text{-}(PF_6)_2$, was carried out. A solution of $6a(PF_6)_2$ (0.455 g, 0.426 mmol) was prepared under argon in a 50-mL Kontes sidearm flask with 30 mL of dry CH_2Cl_2. Application of repeated vacuum/purging cycles with gentle heating resulted in the removal of CO ligands, which was confirmed by recording a solution IR spectrum. The dichloromethane lost by boiling was then replaced by anaerobic vacuum distillation. The exact volume of the solution was confirmed by a prior volume calibration of the flask. The reaction flask was then attached to the buret system while in the cold bath at −80 °C and the entire system was vacuum/Ar purged, with a final application of a vacuum for 15 min. The stopcock leading to the reaction flask was closed and the buret system was then equilibrated to 1 atm of O_2 pressure with vacuum/O_2 cycles. Once equilibrium was achieved, an initial volume reading was recorded and the stopcock leading to the reaction flask (now under vacuum) was opened. Blank runs were done under identical conditions to determine the volume of dioxygen taken up by the solvent itself. As a result of this, the actual volume of O_2 reacted by the copper(I) complex was 10.6 mL, which corresponded to 0.434 mmol of dioxygen by the dinuclear complex, $6a\text{-}(PF_6)_2$ (i.e., $Cu{:}O_2$ = 2:1).

(ii) Uptake of Dioxygen by $[Cu_2(XYL\text{-}OH)](ClO_4)_2$ ($5\text{-}(ClO_4)_2$). By the manometric procedure analogous to that described above, a sample of 0.683 g (0.761 mmol) of $5\text{-}(ClO_4)_2$ dissolved in CH_2Cl_2 at −80 °C was observed to take up 15.74 mL (0.644 mmol, at 24.5 °C) of O_2 while forming the green hydroperoxo complex $3\text{-}(ClO_4)_2$. This corresponds to 84.7% of that expected for $Cu{:}O_2$ = 2.1.

Oxygen Uptake Measurement: Reaction of $6b\text{-}(PF_6)_2$ with Dioxygen and Oxygenation of PPh_3. The oxygen uptake measurement for $[Cu_2(XYL\text{-}OH)(PPh_3)_2](PF_6)_2$ ($6b\text{-}(PF_6)_2$) was carried out in dry MeCN as follows. A 50-mL reaction flask with a sidearm was filled with 40 mL of dry degassed MeCN under argon and fitted with a Kontes K-218700 storage bent tube, containing a weighed amount (1.47 g; 0.97 mmol) of complex **6b**. The sidearm of this flask was attached to the buret assembly with the stopper open. The entire apparatus had been previously filled with oxygen, employing three vacuum/O_2 purge cycles. After the sidearm stopper of the reaction flask was opened the solution being stirred and the system were allowed to equilibrate to 1 atm of O_2 for 3 h at room temperature until a constant volume of the buret reading was observed. Twisting of the sidearm bent tube allowed the solid compound to fall into the dioxygen-saturated solution. Immediately, a dark green solution was generated and the dioxygen pressure in the manometer dropped. The volume of the gas was read in the buret by again adjusting the Hg-reservoir height such that the Hg levels in the two arms of the U-tube were equalized. Equilibration took place over ca. 18 h. The final reading was recorded when no further changes occurred during the last 4-h period of time. The volume of O_2 taken up was found to be 23.3 mL (0.954 mmol).

The number of moles of gas used up was calculated by following the ideal gas law with the room temperature for T and the pressure (barometric measurement) for P. Good reproducible results were found in two successive experiments. By using ca. 1.0 mmol of the dicopper(I) complex $6b\text{-}(PF_6)_2$, the $Cu{:}O_2$ ratio was found to be 2 to 1.

Precipitation of the contents of the reaction flask by addition of toluene and subsequent washing with ether afforded 0.89 g (0.88 mmol, 91%) of $[Cu_2(XYL\text{-}O\text{-})(OH)](PF_6)_2$, **4**. Chromatographic separation of PPh_3 and $O{=}PPh_3$ (yields of one mole-equivalent of each expected) was achieved on a silica gel column (30 cm × 1 cm) from the supernatant washed solvent mixture. For PPh_3, the eluent used was CH_2Cl_2, yield 0.25 g (0.95 mmol, 98%). For $O{=}PPh_3$, the eluent used was CH_2Cl_2/MeOH (20:1, v/v), to give a yield of 0.26 g (0.93 mmol, 93%). An IR spectrum (Nujol mull) showed a strong $P{=}O$ stretch at 1180 cm^{-1} and the entire spectrum was identical with that of authentic $O{=}PPh_3$.

The estimation of the amounts of PPh_3 and $O{=}PPh_3$ in the reaction mixture was also separately determined directly by GC analysis. A CH_3CN solution of 1.12 g (0.739 mmol) of $6b\text{-}(PF_6)_2$ was exposed to O_2 for 4 h, and diethyl ether was added to the product mixture to precipitate $4\text{-}(PF_6)_2$. After filtering, the solvent was removed by rotory evaporation and the residue was redissolved in CH_2Cl_2 for GC analysis. The yields of PPh_3 and $O{=}PPh_3$ were 82% and 118%, respectively. A similar experiment was carried out with $[Cu_2(XYL\text{-}OH)(C_4H_8S)_2](PF_6)_2$ ($6c\text{-}(PF_6)_2$). After reacting 2.12 g (1.82 mmol) of $6c\text{-}(PF_6)_2$ with dioxygen at room temperature in acetonitrile, subsequent GC analysis showed that a 96% yield of tetrahydrothiophene was obtained while that for tetramethylene sulfoxide was 93%. Individual authentic sample mixtures ($PPh_3/O{=}PPh_3$, $C_4H_8S/C_4H_8S{=}O$) were used to calibrate the GC analyses.

An ^{18}O-labeling experiment was performed by the analogous reaction of $[Cu_2(XYL\text{-}OH)(PPh_3)_2](PF_6)_2$ ($6b\text{-}(PF_6)_2$) in a closed system with $^{18}O_2$ (Stohler, 99% isotopic purity). The resulting dark green solution was treated as described above except the operation was carried out under argon atmosphere to eliminate the possibility of any ^{18}O exchange with atmospheric dioxygen. The supernatant toluene–ether wash was dried under vacuum and redissolved in dry CH_2Cl_2 for mass spectral analysis. The most abundant peak observed in the mass spectrum was at m/z 277 ($M^+ - H$, 100) corresponding to $O{=}PPh_3$. Other prominent peaks are 278 (M^+, 36), 201 ($M^+ - C_6H_5$, 10), 185 ($M^+ - P{=}O$, 4), and 77 (C_6H_5, 15). The mass spectral analysis of the reaction mixture isolated from the ^{18}O-labeling experiment showed a shift of the most abundant peak to m/z 279, indicating incorporation of one ^{18}O atom into the PPh_3 molecule to the extent of 72%.

Stoichiometric Oxidation of PPh_3 and/or C_4H_8S with in Situ Generated $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (3). To the green solution obtained on introducing dioxygen to the decarbonylated CH_2Cl_2 solution of $[Cu_2(XYL\text{-}OH)(CO)_2](PF_6)_2$ ($6a\text{-}(PF_6)_2$) (0.45 g, 0.43 mmol) at −80 °C, was added a slight excess of 1 equiv of PPh_3 (0.13 g, 0.5 mmol) and the solution was stirred at −80 °C overnight. The solution was then allowed to warm to room temperature and it was evaporated to dryness. The residue was thoroughly washed with ether to remove all unreacted PPh_3 and then with toluene to isolate any $O{=}PPh_3$ formed. The toluene extract was filtered and upon removal of the solvent by rotary evaporation a white powder was obtained (0.12 g, 87%) whose IR spectra was identical with that of an authentic $O{=}PPh_3$ sample. The green residue isolated after toluene extraction was dried under vacuum to give 0.42 g (97 %) of the complex whose UV–visible spectrum was exactly the same as that of $[Cu_2(XYL\text{-}O\text{-})(OH)](PF_6)_2$ ($4\text{-}(PF_6)_2$.

A similar type of oxidation resulted when tetramethylene sulfide was used as a substrate. Tetramethylene sulfoxide was isolated quantitatively as a colorless oil. The identity of the product was confirmed from its characteristic $S{=}O$ stretch at 1025 cm^{-1} in an IR (neat) spectrum. The stoichiometric organic substrate oxidation was also carried out with $[Cu_2(XYL\text{-}OH)](ClO_4)_2$ ($5\text{-}(ClO_4)_2$) as a precursor for the hydroperoxide complex (**3**).

EXAFS Studies. Preparation of the Sample for EXAFS Measurements. The oxygenated complex $[Cu_2(XYL\text{-}O\text{-})(OOH)](ClO_4)_2$ ($3\text{-}(ClO_4)_2$) was prepared and transferred to the EXAFS cell in a single operation as follows. $[Cu_2(XYL\text{-}OH)](ClO_4)_2$ ($5\text{-}(ClO_4)_2$) (0.03–0.05 g) was dissolved in 1.5 mL of deoxygenated dichloromethane (redistilled over P_2O_5) in a small tube that carried a sidearm connected to the EXAFS cell via 0.2 mm thick walled capillary tubing. The resultant pale yellow solution was cooled to −78 °C by immersing the flask, tubing, and EXAFS cell in solid powdered Dry Ice. When the solution was cold, a stream of pure dioxygen was admitted via a stopcock connected to the sidearm. The solution immediately darkened to a deep green. The oxygenated solution was transferred to the EXAFS cell by application of a slight positive pressure to the apparatus, and the cells were then rapidly frozen in liquid nitrogen and stored under liquid N_2 until ready for use.

EXAFS Data Collection and Analysis. Aluminum cells with rectangular apertures (12 × 3 mm) and a sample thickness of 2 mm were used.

The frozen solution of the oxygenated complex was measured in fluorescent mode[24] on station 7.1 at the SRS, Daresbury Laboratory, under operating conditions of 2.00 GeV and maximum currents of 300 mA. The temperature was maintained at 15–25 K with an Oxford Instruments continuous flow Helium cryostat, specially designed for the EXAFS experiments. A Si 111 double crystal order-sorting monochromator was used with the second crystal detuned so as to produce harmonic rejection of 50%. The monochromator was calibrated in energy space by setting the maximum of the first feature on the absorption edge of metallic copper foil to 8982.0 eV, measured under identical conditions.

Six scans were taken for each oxygenated sample, which were later averaged. Established procedures[25,26] were used to extract EXAFS oscillations from the fluorescence data. After conversion of monochromator position to energy and normalization of the edge height, background subtraction was achieved by fitting the smoothly varying part of the absorption to polynomials below and above the absorption edge and subtracting from the experimental absorption spectrum. The background-substracted, raw EXAFS thus obtained was converted into k-space and weighted by k^3 in order to compensate for the diminishing amplitude at high k due to decay of the photoelectron wave. Analysis of the EXAFS was carried out with the nonlinear least-squares program EXCURVE[27] as previously described.[26-29] An ab initio approach was used to calculate the atomic phase shifts as described in ref 26 and 27. Multiple scatterng calculations were carried out as described in ref 26, 27, 29, and 30. The goodness of fit was judged both qualitatively and quantitatively by using a goodness of fit parameter, or "fit index" (FI) defined as

$$\mathrm{FI} = \sum_i (X(i)_{\mathrm{exptl}} - X(i)_{\mathrm{theory}})^2/N$$

where N is the number of data points in the experimental spectrum.

X-ray Crystallography. Crystallization and Reduction of X-ray Diffraction Data. Colorless crystals of $[Cu_2(XYL\text{-}OH)(PPh_3)_2](ClO_4)_2]$-$(ClO_4)_2\cdot(CD_3NO_2)_2$ (**6b-(ClO$_4$)$_2$**) suitable for X-ray crystallographic analysis were grown as described above and stored in a vacuum atmosphere dry box under argon until needed. An epoxy-covered crystal was mounted on a Nicolet R3m four-circle automated diffractometer with a Mo X-ray source equipped with a highly ordered graphite monochromator ($\lambda(\mathrm{MoK}\alpha) = 0.71073$ Å). Automatic centering and least-squares routines were carried out on 25 reflections to obtain the unit cell parameters and Bravais lattice type that are given in Table I. An ω scan mode was employed for collection of data. Three check reflections were measured in every 197 reflections; these exhibited no significant decay during data collection.

The program XTAPE of the SHELXTL package was used to process the data. A summary of cell parameters, data collection parameters, and refinement results is found in Table I.

Structure Solution and Refinement. Complex **6b-(ClO$_4$)$_2$** crystallizes in the triclinic space group $P1$ with $Z = 1$. Each asymmetric unit was found to contain one complete molecule. The positional parameters of the copper atoms were determined by the Patterson method. The remaining non-hydrogen atoms were located by subsequent difference Fourier maps and least-squares refinements. Atomic scattering factors for neutral atoms were used throughout the analysis. All atoms with the exception of hydrogen and carbon were refined anisotropically. Hydrogen atoms were included in the final stages of refinement. The carbon-hydrogen bond lengths were set at 0.96 Å, and isotropic thermal parameters were 1.2 times those of the bonded carbon atoms. The two perchlorate anions for the complex were unexceptional and no unusual bond distances or angles were observed. Two molecules of deuterated nitromethane solvent were located during the latter stages of refinement. The final R factors and refinement data appear in Table I. Structure factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors for compound **6b-(ClO$_4$)$_2$** (Tables V–IX) are available as supplementary material.

Table I. Crystallographic Data for $[Cu_2(XYL\text{-}OH)(PPh_3)_2](ClO_4)_2\cdot(CD_3NO_2)_2$ (**6b-(ClO$_4$)$_2$**)

temp, K	294
a, Å	10.196 (2)
b, Å	11.715 (2)
c, Å	15.506 (3)
α, deg	94.27 (1)
β, deg	90.30 (1)
γ, deg	94.53 (1)
V, Å^3	1841.0 (5)
MW	1550.66
$F(000)$	801
Z	1
D_{calcd}, g/cm^3	1.40
space group	P1
crystal dimns, mm	0.40 × 0.35 × 0.38
ω-scan rate, deg/min	2.0–10.0
scan type	moving crystal, stationary counter
scan width, deg	1.2
2θ range, deg	0–45.0
bckgd measurement	stationary crystal, stationary counter, at the beginning and end of each ω scan, each for half the time taken for the scan
reflcns measured	$+h,\pm k,\pm l$
reflcns collected	8934
independent reflcns	6067 ($\geq 6\sigma\vert F_o\vert$)
abs coeff, cm^{-1}	7.59
Reduction of Intensity Data and Summary of Structure Solution and Refinement[a]	
agreement between equiv reflcns	0.0264
abs corr	not applied
$T_{\mathrm{max}}/T_{\mathrm{min}}$	1.004
atom scattering factors[b]	neutral atomic scattering factors were used throughout the analysis
anomalous dispersion[c]	applied to all non-hydrogen atoms
R[d]	0.0525
R_w[d]	0.0525
goodness of fit[e]	1.311

[a] Data were corrected for background, attenuators, Lorentz, and polarization effects in the usual fashion: Hyde, J.; Venkatasubramanian, K.; Zubieta, J. *Inorg. Chem.* **1978**, *17*, 414. [b] Cromer, D. T.; Mann, J. B. *Acta Crystallogr. Sect. A: Crsyt. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *24*, 321. [c] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1962; Vol. III. [d] $R = \sum[|F_o| - |F_c|/\sum|F_o|]$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\delta^2(F_o) + g^*(F_o)^2$; $g = 0.00$. [e] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO is the number of observations and NV is the number of variables.

Results and Discussion

Synthesis. The dicopper(I) derivatives **1**, **5**, and **6** and the dicopper(II) complex **4** serve as precursors in the generation of the hydroperoxo–dicopper(II) complex **3**. The syntheses and interconversion of these species are summarized in Figure 1.

The phenoxo- and hydroxo-dicopper(II) complex, $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ (**4**), can be readily prepared in multigram quantities by the copper ion mediated hydroxylation of the "parent" XYL dinucleating ligand.[22]

$$[Cu_2(XYL)]^{2+} + O_2 \rightarrow \underset{\mathbf{4}}{[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}}$$

We previously[17] have described the synthesis of $[Cu_2(XYL\text{-}O\text{-})](PF_6)$ (**1-(PF$_6$)**) via the direct addition of the ligand XYL-OH with 2 equiv of $[Cu(CH_3CN)_4](PF_6)$ in the presence of a base. However, a superior method for its synthesis is to directly reduce $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ (**4**) to **1** by using the two-electron reductant diphenylhydrazine ($Ph_2N_2H_2$), in the presence of a base such as triethylamine (Figure 1). When the same reduction reaction of **4** with $Ph_2N_2H_2$ is carried out in the absence of base,

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(24) Hasnain, S. S.; Quinn, P. D.; Diakun, G. P.; Wardell, E. M.; Garner, C. D. *J. Phys. E: Sci. Instrum.* **1984**, *17*, 40–43.

(25) (a) Teo, B. K. In *EXAFS Spectroscopy: Techniques and Applications*; Teo, B. K., Joy, D. C., Eds.; Plenum: New York, 1981; pp 13–58. (b) Cramer, S. P.; Hodgson, K. O. *Prog. Inorg. Chem.* **1979**, *25*, 1–39.

(26) Strange, R. W.; Blackburn, N. J.; Knowles, P. F.; Hasnain, S. S. *J. Am. Chem. Soc.* **1987**, *109*, 7157–7162.

(27) (a) Gurman, S. J.; Binsted, N.; Ross, I. *J. Phys. C, Solid State Phys.* **1984**, *17*, 143–151. (b) Gurman, S. J.; Binsted, N.; Ross, I. *J. Phys. C, Solid State Phys.* **1986**, *19*, 1845–1861. (c) Lee, P. A.; Pendry, J. B. *Phys. Rev. B* **1975**, *11*, 2795–2811.

(28) Blackburn, N. J.; Hasnain, S. S.; Binsted, N.; Diakun, G. P.; Garner, C. D.; Knowles, P. F. *Biochem. J.* **1984**, *219*, 985–990.

(29) Blackburn, N. J.; Strange, R. W.; McFadden, L.; Hasnain, S. S. *J. Am. Chem. Soc.* **1987**, *109*, 7162–7170.

(30) Blackburn, N. J.; Strange, R. W.; Farooq, A.; Haka, M. S.; Karlin, K. D. *J. Am. Chem. Soc.* **1988**, *110*, 4263–4272.

(31) Blackburn, N. J.; Karlin, K. D.; Concannon, M.; Hayes, J. C.; Gultneh, Y.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1984**, 939–940.

(32) Karlin, K. D.; Hayes, J. C.; Hutchinson, J. P.; Hyde, J. R.; Zubieta, J. *Inorg. Chim. Acta* **1982**, *64*, L219–L220.

Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors (10^3 Å^2) for Compound **6b**-$(ClO_4)_2$[a]

atom	x	y	z	$U_{equiv/iso}$	atom	x	y	z	$U_{equiv/iso}$
Cu(1)	−11 (1)	5 (1)	9997 (1)	34 (1)*	C(75)	668 (8)	−1800 (6)	11643 (5)	42 (2)
Cu(2)	519 (1)	4141 (1)	4621 (1)	39 (1)*	C(80)	2894 (7)	−1331 (6)	9800 (4)	35 (1)
N(1)	−120 (6)	1575 (5)	9359 (4)	40 (2)*	C(81)	2622 (8)	−1399 (7)	8919 (5)	46 (2)
N(4)	212 (6)	4053 (5)	6027 (4)	41 (2)*	C(82)	3384 (8)	−2020 (7)	8334 (6)	53 (2)
O(1)	1662 (6)	2075 (5)	7486 (4)	57 (2)*	C(83)	4409 (9)	−2551 (8)	8635 (6)	61 (2)
C(1)	1279 (7)	2086 (6)	9271 (5)	38 (2)	C(84)	4703 (10)	−2498 (8)	9512 (6)	61 (2)
C(2)	1425 (7)	3184 (6)	8798 (4)	33 (1)	C(85)	3928 (8)	−1902 (7)	10095 (6)	53 (2)
C(3)	1475 (7)	4249 (6)	9251 (5)	41 (2)	C(90)	3122 (7)	853 (6)	10750 (4)	34 (1)
C(4)	1580 (8)	5274 (7)	8823 (5)	50 (2)	C(91)	2867 (8)	1633 (7)	11437 (5)	43 (2)
C(5)	1623 (7)	5193 (7)	7941 (5)	44 (2)	C(92)	3638 (9)	2675 (8)	11565 (6)	58 (2)
C(6)	1565 (7)	4157 (6)	7444 (5)	39 (2)	C(93)	4639 (10)	2924 (9)	10998 (6)	63 (2)
C(7)	1540 (7)	3137 (6)	7889 (4)	36 (2)	C(94)	4907 (9)	2162 (8)	10309 (6)	58 (2)
C(8)	1547 (7)	4120 (7)	6455 (5)	43 (2)	C(95)	4140 (8)	1125 (7)	10195 (5)	45 (2)
N(2)	−1462 (6)	291 (5)	10881 (4)	43 (2)*	P(2)	2611 (2)	4501 (2)	4245 (1)	35 (1)*
C(21)	−2295 (8)	−557 (8)	11142 (5)	52 (2)	C(100)	3627 (8)	3259 (7)	4188 (5)	46 (2)
C(22)	−3311 (9)	−386 (8)	11701 (6)	60 (2)	C(101)	4893 (8)	3307 (7)	3873 (5)	52 (2)
C(23)	−3524 (10)	717 (9)	11991 (7)	68 (3)	C(102)	5635 (11)	2360 (9)	3879 (7)	69 (3)
C(24)	−2683 (8)	1622 (8)	11739 (6)	55 (2)	C(103)	5096 (10)	1369 (9)	4193 (7)	69 (3)
C(25)	−1667 (7)	1394 (7)	11196 (5)	43 (2)	C(104)	3838 (10)	1296 (9)	4505 (7)	68 (3)
C(26)	−766 (8)	2347 (7)	10844 (5)	48 (2)	C(105)	3076 (9)	2244 (7)	4504 (5)	52 (2)
C(27)	−918 (8)	2380 (7)	9862 (5)	46 (2)	C(110)	2764 (7)	5056 (6)	3168 (4)	36 (2)
N(3)	−949 (7)	−1168 (6)	9112 (4)	48 (2)*	C(111)	1672 (7)	4868 (6)	2627 (5)	39 (2)
C(31)	−789 (9)	−2286 (7)	9136 (6)	54 (2)	C(112)	1748 (9)	5212 (7)	1772 (6)	53 (2)
C(32)	−1377 (10)	−3115 (9)	8534 (6)	65 (3)	C(113)	2888 (9)	5743 (8)	1501 (6)	57 (2)
C(33)	−2077 (10)	−2750 (9)	7870 (6)	66 (2)	C(114)	3961 (9)	5954 (8)	2032 (6)	57 (2)
C(34)	−2226 (10)	−1613 (8)	7821 (7)	65 (2)	C(115)	3909 (8)	5637 (7)	2885 (5)	48 (2)
C(35)	−1678 (8)	−831 (7)	8468 (5)	52 (2)	C(120)	3629 (8)	5568 (7)	4948 (5)	45 (2)
C(36)	−1943 (9)	432 (8)	8483 (6)	61 (2)	C(121)	4568 (9)	5244 (8)	5522 (6)	58 (2)
C(37)	−712 (8)	1256 (7)	8490 (5)	50 (2)	C(122)	5219 (11)	6100 (9)	6082 (7)	77 (3)
N(5)	−786 (6)	5349 (6)	4446 (4)	47 (2)*	C(123)	4967 (11)	7192 (10)	6074 (7)	80 (3)
C(51)	−1509 (8)	5327 (7)	3706 (5)	51 (2)	C(124)	4063 (11)	7553 (10)	5527 (7)	76 (3)
C(52)	−2377 (9)	6154 (8)	3575 (6)	58 (2)	C(125)	3390 (9)	6720 (8)	4966 (6)	61 (2)
C(53)	−2479 (10)	7028 (9)	4209 (6)	66 (2)	Cl(1)	7682 (2)	5515 (2)	860 (2)	58 (1)*
C(54)	−1741 (9)	7061 (8)	4959 (6)	61 (2)	O(2)	7623 (10)	4828 (7)	1581 (5)	98 (4)*
C(55)	−891 (8)	6205 (7)	5064 (5)	46 (2)	O(3)	8996 (8)	5631 (8)	572 (6)	104 (4)*
C(56)	−144 (9)	6159 (7)	5887 (6)	54 (2)	O(4)	6833 (11)	5045 (10)	212 (7)	146 (5)*
C(57)	−539 (8)	5053 (7)	6326 (5)	47 (2)	O(5)	7316 (11)	6608 (7)	1171 (8)	139 (5)*
N(6)	−375 (6)	2552 (6)	4188 (4)	45 (2)*	Cl(2)	957 (3)	9587 (2)	6099 (2)	73 (1)*
C(61)	79 (8)	1982 (7)	3480 (5)	51 (2)	O(6)	1086 (11)	8879 (7)	5327 (6)	125 (5)*
C(62)	−244 (9)	823 (8)	3265 (6)	60 (2)	O(7)	1529 (11)	9153 (9)	6809 (7)	131 (5)*
C(63)	−1025 (11)	221 (10)	3836 (7)	73 (3)	O(8)	1605 (10)	10710 (7)	5958 (5)	107 (4)*
C(64)	−1507 (9)	794 (8)	4554 (6)	60 (2)	O(9)	−385 (9)	9709 (10)	6258 (7)	130 (5)*
C(65)	−1159 (8)	1967 (7)	4727 (5)	47 (2)	N(7)	6220 (9)	3818 (8)	8130 (7)	85 (4)*
C(66)	−1653 (8)	2618 (8)	5518 (5)	55 (2)	O(10)	6528 (10)	2878 (9)	8325 (7)	127 (5)*
C(67)	−576 (8)	2966 (7)	6191 (5)	47 (2)	O(11)	6830 (13)	4396 (10)	7669 (8)	165 (6)*
P(1)	1933 (2)	−397 (2)	10509 (1)	31 (1)*	C(9)	5017 (12)	4190 (11)	8499 (8)	91 (4)
C(70)	1784 (7)	−1087 (6)	11537 (4)	37 (2)	N(8)	5094 (13)	1110 (11)	6768 (8)	113 (5)*
C(71)	2675 (8)	−868 (7)	12225 (5)	47 (2)	O(12)	4916 (15)	2101 (10)	6613 (7)	173 (7)*
C(72)	2400 (9)	−1376 (8)	13002 (6)	61 (2)	O(13)	5842 (13)	533 (12)	6373 (10)	181 (7)*
C(73)	1257 (9)	−2053 (8)	13101 (6)	55 (2)	C(10)	4408 (13)	656 (11)	7482 (8)	101 (4)
C(74)	403 (9)	−2294 (7)	12417 (6)	55 (2)					

[a] Asterisks indicate values of equivalent isotropic U defined as one-third of the trace of the orthoganolized U_{11} tensor.

the phenol group of the XYL-OH ligand is not deprotonated and the three-coordinate dicopper(I) complex, $[Cu_2(XYL\text{-}OH)]^{2+}$ (**5**), or bis-adducts $[Cu_2(XYL\text{-}OH)(L)_2]^{2+}$ (**6**), are formed (Figure 1). The presence of un-coordinated phenol groups in complexes **5** and **6** is indicated by (i) analytical data that are consistent with their formulation as dicationic species, (ii) ^1H NMR data showing a broad O–H absorption at δ = 10.4 ppm for **5**-$(PF_6)_2$, and (iii) IR data showing the presence of an O–H stretching vibration in the region of 3475–3565 cm^{-1} (see Experimental Section). When deuterium was exchanged with complex $[Cu_2(XYL\text{-}OH)]^{2+}$ (**5**) by stirring it with MeOD, the intensity of the O–H band diminished significantly and a new band, $\nu_{O\text{-}D}$, at 2450 cm^{-1} was observed when the complex was isolated as the bis-carbonyl adduct, $[Cu_2(XYL\text{-}OH)(CO)_2]^{2+}$ (**6a**). Finally, X-ray quality crystals of $[Cu_2(XYL\text{-}OH)(PPh_3)]_2^{2+}$ (**6b**) were obtained, and the diffraction study (see below) confirms the proposed structures for **5** and **6**.

Although not indicated in Figure 1, $[Cu_2(XYL\text{-}O\text{-})]^+$ (**1**) and $[Cu_2(XYL\text{-}OH)]^{2+}$ (**5**) can be readily interconverted in an acid–base reaction. Thus protonation of an orange methanolic solution of $[Cu_2(XYL\text{-}O\text{-})]^+$ (**1**) with HPF_6 decolorizes the solution and produces **5**, while the addition of triethylamine to $[Cu_2(XYL\text{-}OH)]^{2+}$ (**5**) results in its deprotonation to give **1**, i.e.

$$\underset{\mathbf{1}}{[Cu_2(XYL\text{-}O\text{-})]^+} + H^+ \rightleftarrows \underset{\mathbf{5}}{[Cu_2(XYL\text{-}OH)]^{2+}}$$

Structure of $[Cu_2(XYL\text{-}OH)(PPh_3)]_2^{2+}$ (6b). X-ray quality crystals of $[Cu_2(XYL\text{-}OH)(PPh_3)_2](ClO_4)_2\cdot(CD_3NO_2)_2$ were obtained from a solution of **6b**-$(ClO_4)_2$ which was standing in an NMR tube. A summary of crystal and refinement data for this complex is given in Table I with final positional parameters provided in Table II; selected bond distances and angles are found in Table III. The structure consists of discrete $[Cu_2(XYL\text{-}OH)(PPh_3)]_2^{2+}$ cations with well-separated ClO_4^- anions and nitromethane solvent molecules; the dication is shown in Figure 2. The phenyl groups of the PPh_3 ligands are omitted in Figure 2 for clarity, but a full ORTEP drawing of the entire dication unit is available in the supplementary material.

The dicopper complex contains two crystallographically independent and well-separated copper(I) moieties, each possessing nearly identical pseudotetrahedral coordination to two pyridyl and one amino nitrogen atom of the PY2 unit and a phosphorus atom

Table III. Selected Bond Distances and Angles for $[Cu_2(XYL\text{-}OH)(PPh_3)_2](ClO_4)_2\cdot(CD_3NO_2)_2$ (**6b**-$(ClO_4)_2\cdot(CD_3NO_2)_2$)

Interatomic Distances (Å)			
Cu(1)–N(1)	2.163 (6)	Cu(2)–N(4)	2.213 (6)
Cu(1)–N(2)	2.052 (6)	Cu(2)–N(5)	2.049 (7)
Cu1)–N(3)	2.046 (6)	Cu(2)–N(6)	2.070 (6)
Cu(1)–P(1)	2.229 (2)	Cu(2)–P(2)	2.230 (2)
	Cu...Cu	9.944 (2)	
Interatomic Angles (deg)			
N(1)–Cu(1)–N(2)	96.8 (2)	N(4)–Cu(2)–N(5)	96.5 (3)
N(1)–Cu(1)–N(3)	101.2 (3)	N(4)–Cu(2)–N(6)	99.2 (2)
N(1)–Cu(1)–P(1)	118.5 (2)	N(4)–Cu(2)–P(2)	114.6 (2)
N(2)–Cu(1)–N(3)	102.3 (3)	N(5)–Cu(2)–N(6)	107.9 (3)
P(1)–Cu(1)–N(2)	117.2 (2)	P(2)–Cu(2)–N(5)	118.9 (2)
P(1)–Cu(1)–N(3)	117.5 (2)	P(2)–Cu(2)–N(6)	116.4 (2)

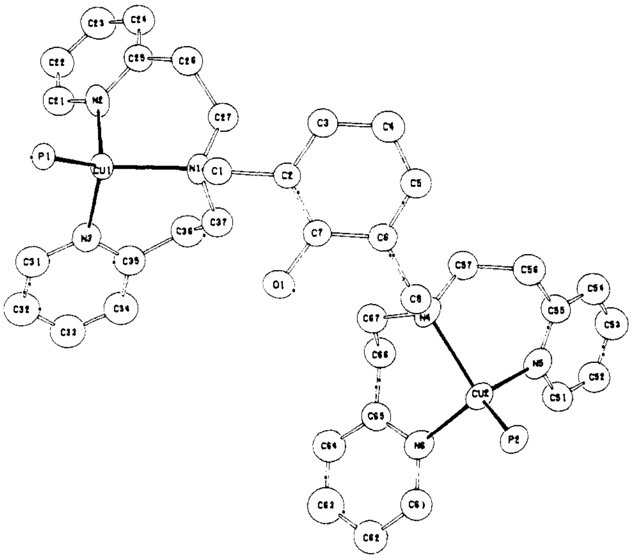

Figure 2. ORTEP diagram of the cationic portion of the bis(triphenylphosphine) adduct $[Cu_2(XYL\text{-}OH)(PPh_3)_2]^{2+}$ (**6b**), showing the atom-labeling scheme in this dicopper(I) complex containing the nondeprotonated phenol ligand, XYL-OH. The phenyl groups of the PPh_3 ligands are omitted for clarity, and a full ORTEP diagram is available as supplementary material.

of the triphenylphosphine ligand. Relevant dihedral angles are the following: Cu1,N1,N2/Cu1,N3/P1 = 75.9 (2)°; Cu1,N2,N3/Cu1,N1,P1 = 92.1 (2)°; Cu2,N4,N5/Cu2,N6,P2 = 86.9 (2)°; Cu1,N2,P1/N1,Cu1,N3 = 87.0 (2)°; Cu2,N5,N6/Cu2,N4,P2 = 92.0 (2)°; Cu2,N4,N6/Cu2,N5,P2 = 84.8 (2)°. The Cu1 atom lies 0.96 (1) Å out of the best least-squares N1,N2,N3 plane toward the phosphorus atom, P1. Similarly, Cu1 is 0.66 (1) Å out of the P1,N1,N2 plane, 0.60 (1) Å out of the P1,N1,N3 plane, and 0.60 (1) Å out of the P1,N2,N3 plane. The values observed for the dihedral angles and Cu-plane distances are very similar to those of other complexes containing the PY2 tridentate unit and a fourth ligand such as L = CH_3CN or CO, e.g., $[Cu_2(NnPY2)(L)_2]^{2+}$.[16b] The structural patterns observed also contrast and can be distinguished from tricoordinate Cu–PY2 containing structures,[22,31] or trigonal-pyramidal tetracoordinate Cu(I) moieties such as in $[Cu_2(XYL\text{-}O\text{-})]^+$ or $[Cu_2(XYL\text{-}O\text{-})(PPh_3)_2]^+$;[17a] the former contains two equitorial pyridyl nitrogens and a phenoxo oxygen atom with apical amino nitrogen coordination, while in the latter a PPh_3 ligand displaces one pyridine that remains "dangling" and uncoordinated.

The Cu–N_{PY2} bond lengths are normal (Table III), with Cu–N_{py} distances typical for tetracoordinate Cu(I) (2.0–2.05 Å[16,17,22,32]), ca. 0.1 Å longer than the Cu–N_{py} bond lengths observed in tricoordinate Cu(I) structures containing PY2, e.g., $[Cu_2(m\text{-}XYLPY2)](PF_6)_2$ (two PY2 units connected with a *m*-xylyl group, Cu–N_{py} = 1.91–1.94 Å[22]) and $[Cu(BPY2)](PF_6)$ (BPY2 = bis(2-(2-pyridyl)ethyl)benzylamine, Cu–N_{py} = 1.87–1.94 Å[31]). The "harder" amine nitrogen atom (N1 and N4) bonds more weakly to the Cu(I) ion with Cu1–N1 = 2.153 (6) Å and Cu2–N4 = 2.213 (6) Å. The Cu–PPh_3 bond distances average 2.23 Å (Table III), which is comparable to the values found in $[Cu_2(XYL\text{-}O\text{-})(PPh_3)_2]^+$ (av. 2.20 Å).[17a]

In addition to the chemical evidence (IR and NMR) and formulation of **6b** as a dicationic species indicating that the phenoxo oxygen atom is protonated, the X-ray structure shows that the phenol oxygen atom, O1, is clearly uncoordinated. The copper(I)···O1 distances are Cu1···O1 = 4.98 (1) Å and Cu2—O1 = 5.38 (2) Å, too long for any sort of interaction. The cuprous ion coordination polyhedra are well separated with Cu···Cu = 9.944 (2) Å.

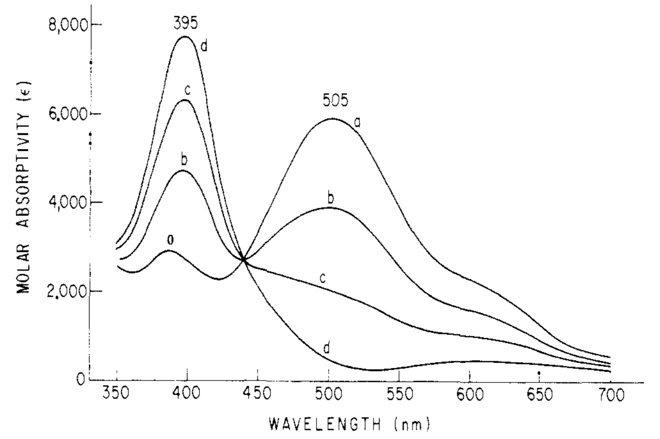

Figure 3. Protonation of the peroxo–dicopper(II) complex $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (**2**) with 0.1 M HBF_4/Et_2O in CH_2Cl_2 at −80 °C to give the hydroperoxo complex $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**): spectrum of **2** (a) at a concentration of 1.25×10^{-4} M, (b) after addition of ~$^1/_3$ equiv of the acid solution, (c) after addition of another $^1/_3$ equiv of acid, (d) after a total of 1 equiv of acid added. The volume change upon addition of acid is negligible since its concentration is 10^3 greater than that of the copper complex solution.

Generation of $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (3). The hydroperoxo complex dication, **3**, can be prepared in solution by using one of three synthetic procedures: (a) direct protonation of the peroxo–dicopper(II) complex, $[Cu_2(XYL\text{-}O\text{-})(O_2)]^{2+}$ (**2**), (b) reaction of hydrogen peroxide with the hydroxo-bridged dicopper(II) complex, $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ (**4**), and (c) oxygenation of the ligand-protonated dicopper(I) precursor, i.e., $[Cu_2(XYL\text{-}OH)]^{2+}$ (**5**) (Figure 1).

The direct protonation of the well-characterized peroxo–dicopper(II) complex $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (**2**), to afford the protonated hydroperoxo complex $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**), demonstrates the direct relationship of these species. Addition of dioxygen to **2** in CH_2Cl_2 at −80 °C provides the intensely violet colored dioxygen (peroxo) adduct **2** with λ_{max} = 505 nm (spectrum a, Figure 3). The protonation reaction could be followed via a spectrophotometric titration (Figure 3) where a total of 1 equiv of chilled (−80 °C) HBF_4 (as the etherate complex diluted into dichloromethane) was added in three separate and nearly equal portions to the solution of $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (**2**). A systematic conversion of the initial peroxide spectrum a to a final, new characteristic spectrum (d, Figure 3) of the hydroperoxo complex $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**), with λ_{max} = 395 nm and ϵ = 8000 $M^{-1}\,cm^{-1}$. Other absorption bands that are characteristic of **3** but which are not readily apparent from Figure 3 are a shoulder at ca. 450 nm (ϵ = 2200 $M^{-1}\,cm^{-1}$), a peak at 620 nm (ϵ = 450 $M^{-1}\,cm^{-1}$), and another low-energy shoulder at 860 nm (ϵ = 50 $M^{-1}\,cm^{-1}$). The presence of an isosbestic point (Figure 3) indicates that only two species are involved in this protonation reaction and thus **2** is directly converted to **3**.

We note that the further addition of the HBF_4 solution to that of $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (**2**) beyond the 1 equiv required for the formation of $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**) resulted in a change causing a decrease in the intensity of the 395-nm peak. However, the subsequent addition of a base such as triethylamine resulted

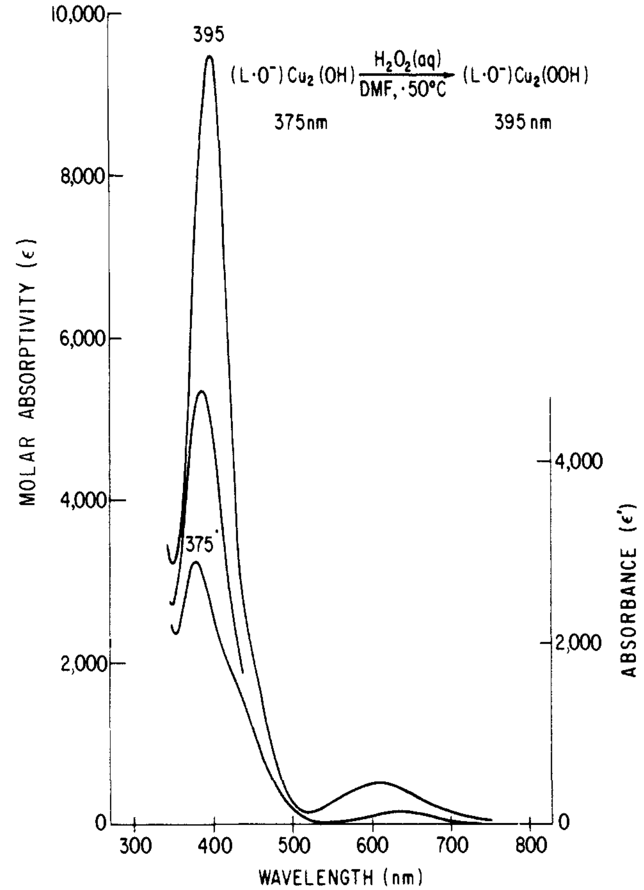

Figure 4. Spectra in DMF, at −50 °C and starting with 1.4 × 10^{-4} M hydroxo-bridged dicopper(II) complex $[Cu_2(XYL\text{-}O^-)(OH)](PF_6)_2$ (**4**-$(PF_3)_2$) and the hydroperoxo–dicopper(II) complex of $[Cu_2(XYL\text{-}O^-)(OOH)](PF_6)_2$ (**3**-$(PF_6)_2$) resulting from the addition of excess H_2O_2 to **4**-$(PF_6)_2$: (1) spectrum of **4**-$(PF_6)_2$ with λ_{max} = 375 nm (right hand ordinate), (2) incomplete conversion to **3**-$(PF_6)_2$ after addition of 1 drop of 30% H_2O_2, (3) complete conversion to **3**-$(PF_6)_2$ after addition of several drops of 30% H_2O_2.

in the regeneration of **3**, as observed by the restoration of the full intensity of the 395-nm band.[33] This observation suggests that protonation of $[Cu_2(XYL\text{-}O^-)(OOH)]^{2+}$ (**3**) either causes the release of H_2O_2 from the complex or forms a protonated form of **3**. In either case, this second protonation of $[Cu_2(XYL\text{-}O^-)(O_2)]^+$ (**2**) is reversible and the copper complex product does not absorb strongly in the 300–400 nm region.

We also tried to effect the deprotonation of green hydroperoxo complex $[Cu_2(XYL\text{-}O^-)(OOH)]^{2+}$ (**3**) to form $[Cu_2(XYL\text{-}O^-)(O_2)]^+$ (**2**), but attempts to do this met with very limited success.[33] For example, the addition of solid KO*t*Bu to a CH_2Cl_2 solution of **3** results in the loss of the 395-nm band but only partial restoration (~50%) of the 505-nm absorption characteristic of **2** takes place. Even then, the violet color of **2** faded, probably due to the presence of *tert*-butyl alcohol or oxide. Other bases were also tried, but they were either too weak to deprotonate the hydroperoxide complex (e.g., triethylamine, proton sponge) or too strong (e.g., methyllithium, lithium diisopropylamide) and caused solvent and/or copper complex decomposition.

Another way to generate $[Cu_2(XYL\text{-}O^-)(OOH)]^{2+}$ (**3**) is by the addition of an excess of aqueous hydrogen peroxide to a dichloromethane and/or dimethylformamide (DMF) solution of $[Cu_2(XYL\text{-}O^-)(OH)]^{2+}$ (**4**) (Figure 4). The reaction results in a change of the 375-nm absorption of $[Cu_2(XYL\text{-}O^-)(OH)]^{2+}$ (**4**) to produce the stronger absorption maximum at 395 nm due to **3**. This method of generating **3** provides further support that $[Cu_2(XYL\text{-}O^-)(OOH)]^{2+}$ (**3**) contains a peroxidic moiety.

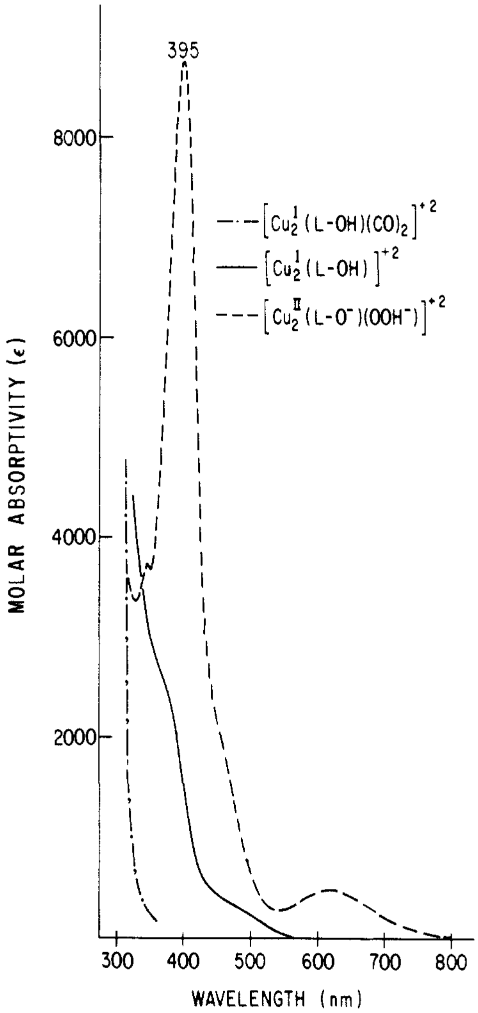

Figure 5. Spectrophotometric monitoring of the formation of $[Cu_2(XYL\text{-}O^-)(OOH)](PF_6)_2$ (**3**-$(PF_6)_2$, --- spectrum, λ_{max} = 395 nm) after bubbling O_2 (manometry, Cu:O_2 = 2:1) through a −80 °C solution of $[Cu_2(XYL\text{-}OH)](PF_6)_2$ (**5**-$(PF_6)_2$, — spectrum), which had been produced by decarbonylation (vacuum/Ar-purge cycles at room temperature) of a 2.04 x 10^{-4} M solution of $[Cu_2(XYL\text{-}OH)(CO)_2](PF_6)_2$ (**1a**-$(PF_6)_2$, ··· spectrum).

The most synthetically convenient method to produce solutions of $[Cu_2(XYL\text{-}O^-)(OOH)]^{2+}$ (**3**) is by oxygenating −80 °C dichloromethane solutions of $[Cu_2(XYL\text{-}OH)]^{2+}$ (**5**) or $[Cu_2(XYL\text{-}OH)(CH_3CN)_2]^{2+}$ (**6d**) (Figure 1). Initially,[20] **3** was produced by the in situ decarbonylation of $[Cu_2(XYL\text{-}OH)(CO)_2]^{2+}$ (**6a**) (vacuum/Ar-purge cycles of room temperature CH_2Cl_2 solutions of **6a**) and subsequent oxygenation at −80 °C of the solutions of $[Cu_2(XYL\text{-}OH)]^{2+}$ (**5**) thus produced. Manometric dioxygen uptake experiments (Experimental Section) show that Cu:O_2 = 2:1, and as shown in Figure 5, UV–vis monitoring shows that the characteristic strong λ_{max} = 395 nm absorption develops via this procedure. The development of the syntheses of salts of $[Cu_2(XYL\text{-}OH)]^{2+}$ (**5**) and $[Cu_2(XYL\text{-}OH)(CH_3CN)_2]^{2+}$ (**6d**) makes the procedure easier, since we can avoid the decarbonylation step. Manometric and spectrophotometric monitoring confirm that the same hydroperoxo complex **3** is formed. Since oxygenation of XYL and NnPY2 dicopper ligand complexes at low temperature is known to yield dioxygen adducts,[16,34] we suggest that the phenol group in $[Cu_2(XYL\text{-}OH)]^{2+}$ (**5**) or $[Cu_2(XYL\text{-}OH)(CH_3CN)_2]^{2+}$ (**6d**) serves as a stoichiometric source of H^+ and protonates the putative dioxygen

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[33] Cruse, R. W. Ph.D. Thesis, State University of New York at Albany, 1986.

[34] Karlin, K. D.; Cruse, R. W.; Haka, M. S.; Gultneh, Y.; Cohen, B. I. *Inorg. Chim. Acta* **1986**, *125*, L43–L44.

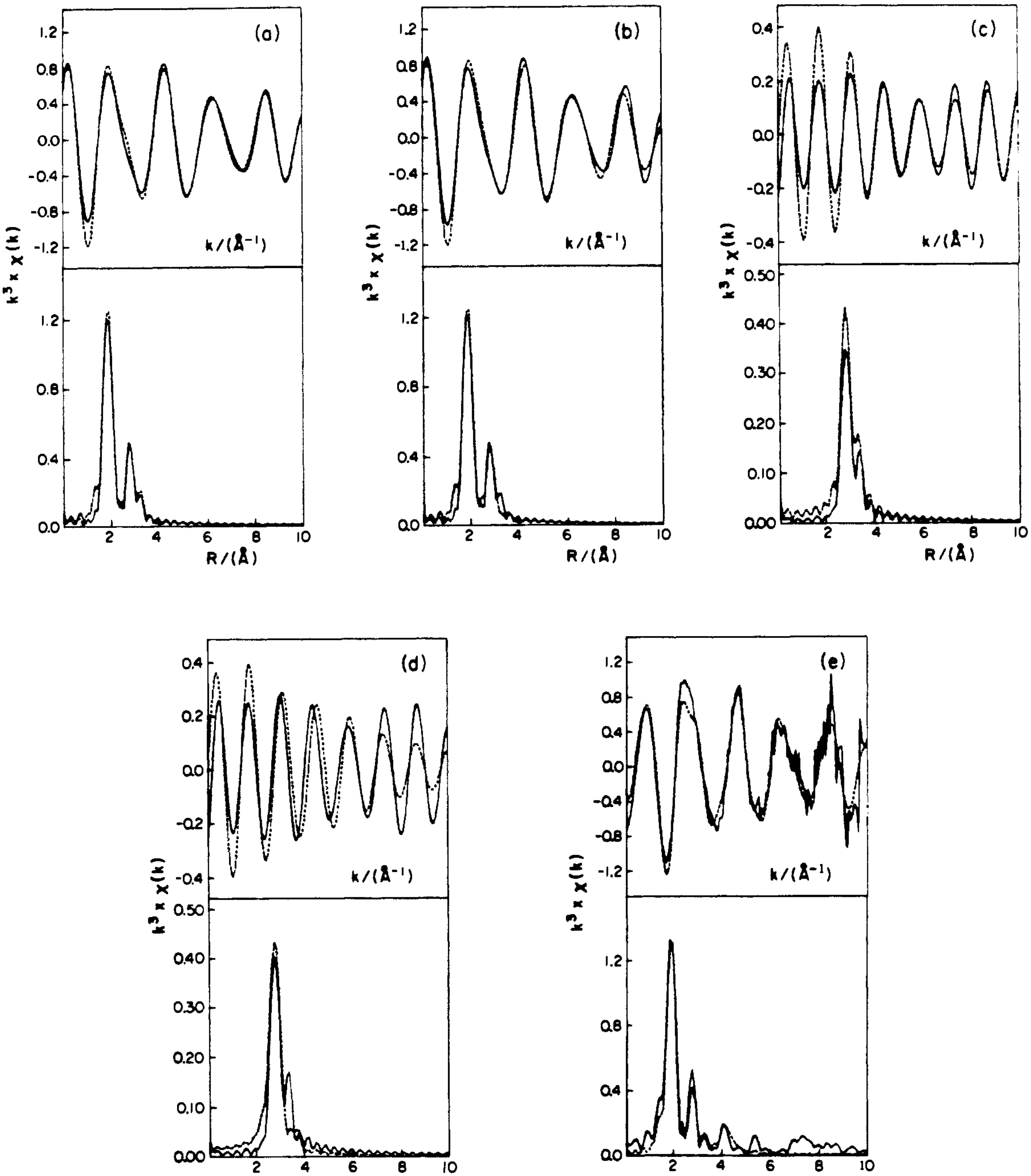
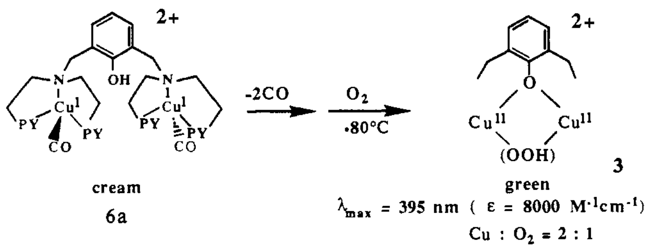


Figure 6. Experimental (—) and calculated (---) EXAFS and Fourier transforms used to fit the data for the hydroperoxo complex $[Cu_2(XYL-O-)(OOH)]^{2+}$ (3). (a) First- and second-shell Fourier filtered data, no Cu scatterer present; (b) first- and second-shell Fourier filtered data simulated with a Cu scatterer at 3.04 Å; (c) second-shell Fourier filtered data with 4 C atoms at 2.86 Å and a Cu scatterer at 3.04 Å; (d) second-shell Fourier filtered data with 4 C atoms at 2.86 Å and no Cu scatterer; (e) final fit including multiple scattering from a single pyridine group, using the parameters given in Table IV.

adduct formed by oxygenation of **5** or **6d** to give the hydroperoxo complex **3**.



6a

3

EXAFS Studies and Structure of $[Cu_2(XYL-O-)(OOH)]^{2+}$ (3). To this point, we have been unable to isolate stable crystalline solid salts of $[Cu_2(XYL-O-)(OOH)]^{2+}$ (3) that would be amenable to X-ray diffraction studies. Therefore, in order to obtain structural information, Extended X-ray absorption fine structure (EXAFS) spectroscopy was carried out on low-temperature frozen solutions of $[Cu_2(XYL-O-)(OOH)](ClO_4)_2$ (3-$(ClO_4)_2$), where useful comparisons can be made to EXAFS studies carried out on structurally well defined analogues containing the XYL-O– ligand.

Initial analysis of the EXAFS for $[Cu_2(XYL-O-)(OOH)](ClO_4)_2$ (3-$(ClO_4)_2$) utilizing Fourier filtered data in the range 1.20–3.35 Å (uncorrected for the phase shift) gave a fit FI = 1.06 with four oxygen or nitrogen donors at 1.99 Å (Debye–Waller, $2\sigma^2 = 0.005$ Å²) and four carbon atoms at 2.88 Å ($2\sigma^2 = 0.012$ Å²) as shown in Figure 6a. This simulation did not reproduce the shoulder observed on the high *R* side of the second peak in the transform (Figure 6a). Inclusion of a Cu backscattering atom at 3.04 Å within a second cycle of refinement reduced the fit index to 0.77 and produced a reasonable simulation of the shoulder

Table IV. Parameters Used To Simulate the Theoretical EXAFS Fits of the Hydroperoxo Complex 3 Shown in Figure 6e[a]

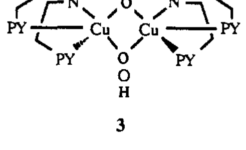
shell	R_{exafs}/Å	$2\sigma^2$/Å^2
4 N or O	1.99	0.006
2 C(py)	2.86	0.005
2 C	2.86	0.006
Cu–Cu	3.04	0.021
2 C(py)	4.18	0.013
1 C(py)	4.70	0.013

[a] Unless otherwise indicated (by parenthesis), estimated errors are ±0.03 Å for inner-shell and ±0.06 Å for outer-shell distances.[29,30] E_0 = 17.72 eV. Angles used in the multiple scattering calculations[30] were Cu–N1–C2/C6 = 120°, Cu–N1–C3/C5 = 150°, Cu–N1–C4 = 180°.

(Figure 6b). To test further the validity of the Cu–Cu interaction the second shell was isolated by backtransformation in the range 2.10–3.35 Å (uncorrected for phase shifts) and fit with either 4 C at 2.86 Å plus 1 Cu at 3.04 Å (Figure 6c, FI = 0.60) or 4 C alone at 2.86 Å (Figure 6d, FI = 0.80). The fit with only C scatterers had a higher fit index, and failed to reproduce the increasing amplitude of the EXAFS oscillations at higher *k*, maximizing at ca. *k* = 10, which is characteristic of the presence of a heavy atom scatterer such as copper.[19,35] The final fit shown in Figure 6e was obtained by inclusion of two C atoms at 4.18 Å and 1 C atom at 4.70 Å (that is at the distances expected for the outer-shell carbon atoms of a single pyridine ring), using the multiple scattering treatment described in ref 26, 27, 29, and 30. The parameters used to obtain the simulation in Figure 6e are given in Table IV.

The distances obtained from EXAFS are entirely compatible with a Cu(II) center in tetragonal geometry as is found in the majority of dicopper(II) complexes of the XYL-O– ligand system such as $[Cu_2(XYL\text{-}O\text{–})(OH)]^{2+}$ (**4**).[19,22,36] However, the Cu–Cu distance of 3.04 Å found in $[Cu_2(XYL\text{-}O\text{–})(OOH)](ClO_4)_2$ (**3**-$(ClO_4)_2$) is 0.27 shorter than the Cu–Cu distance found in the related dioxygen (peroxo) complex, $[Cu_2(XYL\text{-}O\text{–})(O_2)]^+$ (**2**),[19] and is in the range expected for a μ-1,1-bridged complex like **4** (see further discussion below).[19,22,36] Since multiple scattering from only a single pyridine group is required to simulate the outermost shell in the Fourier transform, it is likely (by analogy to the detailed studies we have carried out on the multiple scattering contributions in $[Cu_2(XYL\text{-}O\text{–})(OH)]^{2+}$ (**4**) and other complexes of related ligand systems[30]) that only a single pyridine is coordinated in the equatorial plane of each Cu(II) center. The data are therefore most consistent with the presence of one pyridine group and three other O or N ligands at 1.99 Å and two additional (methylene) carbon atoms at 2.86 Å and suggest formulation of $[Cu_2(XYL\text{-}O\text{–})(OOH)](ClO_4)_2$ (**3**-$(ClO_4)_2$) as having one pyridine N, one amino N, one phenoxo O, and one O from the hydroperoxo ligand as the four equatorial ligands to Cu(II), with a Cu–Cu distance of 3.04 Å. The EXAFS thus suggests considerable structural similarity between $[Cu_2(XYL\text{-}O\text{–})(OOH)]^{2+}$ (**3**) and $[Cu_2(XYL\text{-}O\text{–})(OH)]^{2+}$ (**4**).

Proposed Structure



3

We thus propose that the hydroperoxo complex $[Cu_2(XYL\text{-}O\text{–})(OOH)]^{2+}$ (**3**) possesses a structure very similar to that of $[Cu_2(XYL\text{-}O\text{–})(OH)]^{2+}$ (**4**), containing a coordinated μ-1,1-(OOH^-) ligand. Strong evidence for this comes from (i) the UV–vis spectroscopic alikeness of **3** with **4**, the observed EPR silence of both, along with the close structural relationship between these complexes as established by EXAFS spectroscopy, and (ii) the chemical and spectroscopic parallel between $[Cu_2(XYL\text{-}O\text{–})(OOH)]^{2+}$ (**3**) and the acylperoxo complex, $[Cu_2(XYL\text{-}O\text{–})(OOC(O)C_6H_4Cl)]^{2+}$ (**8**); a recent X-ray structure of the latter showed it to contain a μ-1,1-$OOC(O)C_6H_4Cl$ moiety.[37]

We have previously shown that the UV–vis spectroscopic characteristics for monoatomic phenoxo and ligand bridged (X^-) complexes of XYL-O–, e.g., $[Cu_2(XYL\text{-}O\text{–})(X)]^{2+}$, are sensitive to the size of X and therefore to the Cu···Cu distance.[36] For $X^- = OH^-$, containing square-based pyramidal (SP) Cu(II) ions with Cu···Cu = 3.08 Å, the $OPh^- \rightarrow Cu(II)$ LMCT band occurs at 380 nm and there is a d–d band at 635 nm and another weak absorption (sh) at ~900 nm[38] (sh, $\epsilon \simeq 50\ M^{-1}\ cm^{-1}$). For X^- groups such as N_3^-, Cl^-, and Br^-, where the Cu···Cu distance increases to 3.18–3.35 Å, the strong $OPh^- \rightarrow Cu(II)$ LMCT band moves to $\lambda > 450$ nm, and the 600–700 nm region d–d band moves to lower energy (e.g., 655 nm for $X = N_3^-$; 670 nm for $X = Cl^-$) as the Cu(II) coordination geometry is distorted away from purely SP geometry by the larger bridging atom or group.[36] Here, for the structurally related hydroperoxo complex $[Cu_2(XYL\text{-}O\text{–})(OOH)]^{2+}$ (**3**) (EXAFS, vide supra), the general pattern of UV–vis band positions and intensities is repeated. The presence of weak low-energy absorption bands (d–d) at 620 and 860 nm is indicative of the presence of copper in the 2+ oxidation state, consistent with our formulation of $[Cu_2(XYL\text{-}O\text{–})(OOH)]^{2+}$ (**3**) as a hydroperoxo dicopper(II) complex; such absorptions would be absent for a d^{10} Cu(I) ion. The positions of these bands also closely compare to those in $[Cu_2(XYL\text{-}O\text{–})(OH)]^{2+}$ (**4**) and are thus indicative of a short Cu···Cu distance and SP coordination geometry for Cu(II). It is also noteworthy that solutions (77 K) of both **3** and **4** are EPR silent.

While we suggest that the 395-nm absorption in **3** and possibly the lower energy underlying band (shoulder ca. 450 nm) are due to $OOH^- \rightarrow Cu(II)$ LMCT transitions, definitive assignments must await further spectroscopic analyses.[39,40] On the basis of an UV–vis spectroscopic/resonance Raman investigation, a strong 505-nm absorption and shoulder near 610 nm in $[Cu_2(XYL\text{-}O\text{–})(O_2)]^+$ (**2**) have been assigned to peroxide (O_2^{2-}) to Cu(II) LMCT transitions.[18] It is not unreasonable to expect such LMCT absorptions to undergo a "blue" shift upon protonation of the peroxide group, such as is observed. This would come about due to the effective increase of positive charge on the metal ion centers, resulting in stabilization of the metal orbitals.

The UV–vis spectrum of **3** is also very similar to that of the μ-1,1-acylperoxo bridged compound $[Cu_2(XYL\text{-}O\text{–})(m\text{-}ClC_6H_4C(O)OO\text{–})]^{2+}$ (**8**),[37] which also has λ_{max} = 395 nm (ϵ = 5700 $M^{-1}\ cm^{-1}$), with d–d absorptions at 650 (ϵ = 420 $M^{-1}\ cm^{-1}$) and 1020 (ϵ = 90 $M^{-1}\ cm^{-1}$) nm. Complex **8** is generated by methods completely analogous to that of the hydroperoxo complex, $[Cu_2(XYL\text{-}O\text{–})(OOH)]^{2+}$ (**3**). It can be made by the direct acylation (i.e., addition of $RC(O)^+$ by reacting RC(O)Cl followed by metathesis with Ag^+, instead of H^+) of the peroxo–dicopper(II) complex $[Cu_2(XYL\text{-}O\text{–})(O_2)]^+$ (**2**) or directly through the reaction of RC(O)OOH with $[Cu_2(XYL\text{-}O\text{–})(OH)]^{2+}$ (**4**). The reactivity of **8** with substrates such as PPh_3 is completely analogous to that of **3**. A stable crystalline solid form of **8** can be obtained and an X-ray crystal structure shows that the coordinated μ-1,1-acylperoxo group is found in a tetragonal coordination environment similar to the other complexes $[Cu_2(XYL\text{-}O\text{–})(X)]^{2+}$, with Cu···Cu

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(35) (a) Woolery, G. L.; Powers, L.; Winkler, M.; Solomon, E. I.; Spiro, T. G. *J. Am. Chem. Soc.* **1984**, *106*, 86–92. (b) Woolery, G. L.; Powers, L.; Peisach, J.; Spiro, T. G. *Biochemistry* **1984**, *23*, 3428–3434. (c) Woolery, G. L.; Powers, L.; Winkler, M.; Solomon, E. I.; Kerch, K.; Spiro, T. G. *Biochim. Biophys. Acta* **1984**, *788*, 155–161.

(36) Karlin, K. D.; Farooq, A.; Hayes, J. C.; Cohen, B. I.; Zubieta, J. *Inorg. Chem.* **1987**, *26*, 1271–1280.

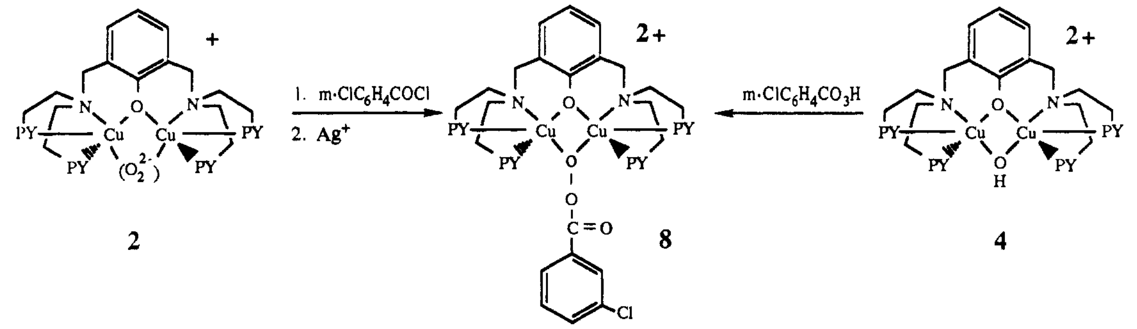
(37) Ghosh, P.; Tyeklar, Z.; Karlin, K. D.; Jacobson, R. R.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 6889–6891.

(38) Karlin, K. D., and co-workers, unpublished results.

(39) Solomon, E. I.; Karlin, K. D., and co-workers, investigations in progress.

(40) Initial attempts to determine the O–H and O–O stretching frequencies by low-temperature solution infrared spectroscopy on $[Cu_2(XYL\text{-}O\text{–})(OOH)]^{2+}$ (**3**) have not been fruitful; resonance Raman studies[39] should allow for their determination.

Scheme I



= 3.197 Å.[37] The hydroperoxo bridging mode observed in **8** and $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**) is not unexpected based upon the previously described μ-1,1-(OOH^-) dicobalt(III) complex whose structure was determined by Thewalt and Marsh[41] (see Scheme I).

Reactions of $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (3) with Organic Substrates. Solutions of $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**) in dichloromethane which are kept at −80 °C are stable for several days. However, warming results in the irreversible decomposition and reactions with solvent apparently take place. In CH_2Cl_2, a slow but complete conversion of $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**) to the chloro-bridged complex $[Cu_2(XYL\text{-}O\text{-})(Cl)]^{2+}$ occurs.[36] In nitrile solvents (RCN, R = CH_3 or CH_3CH_2), the hydroxo-bridged complex $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ (**4**) forms and can be isolated in high yields. This suggests that the well-established copper(II)-catalyzed disproportionation of the coordinated hydroperoxide is taking place,[42,43] i.e., $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**) → $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ (**4**) + $^1/_2O_2$. However, we have tried hard to detect the dioxygen that would be expected to be liberated in this process and were unable to detect any. Thus, we conclude that here the solvent may also take part in the decomposition reaction of **3**.

However, with substrates (S) such as triphenylphosphine (PPh_3) and tetramethylene sulfide (RSR), clean oxygen atom transfer reactions take place (Figure 1). These reactions were carried out in one of two ways. The substrate could be added to −80 °C solutions of $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**) generated in situ. Workup of these solutions (see Experimental Section) resulted in the isolation of near quantitative yields of the monooxygenated substrate (S=O; O=PPh_3 or RS(O)R) as well as the hydroxo-bridged dicopper(II) complex $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ (**4**). Alternatively, reactions of the bis-adduct complexes, $[Cu_2(XYL\text{-}OH)(L)_2]^{2+}$ (**6**) (**6b**, L = PPh_3; **6c**, L = $(CH_2)_4S$), containing an uncoordinated and protonated phenol group, could be reacted with dioxygen to produce the same products. Only 1 mol of oxygenated product was formed in each case, and S, S=O, and $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ (**4**) were isolated in high yields. In addition, manometric measurements indicate that 1 mol of O_2 per dicopper(II) unit is taken up in these reactions and isotopic labeling experiments carried out with $^{18}O_2$ reveal that the monooxygenated product (S=O) contained the ^{18}O label. No dioxygenated sulfone product was detected under any conditions observed.

$$\underset{\mathbf{6}}{[Cu_2(XYL\text{-}OH)(S)_2]^{2+}} + O_2 \rightarrow \underset{\mathbf{4}}{[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}} + S{=}O + S$$

The reactivity observed with these substrates also corroborates the oxidation state assignment for the hydroperoxo complex $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**). The formation of 1 mol of S=O, even in the presence of excess S, shows that **3** possesses two oxidizing equivalents compared to $[Cu_2(XYL\text{-}O\text{-})(OH)]^{2+}$ (**4**).[44]

The observed oxygen atom transfer reactions also stand in marked contrast to the reaction observed when PPh_3 is added to −80 °C solutions of the dioxygen (peroxo) complex, $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (**2**). In this case, a simple displacement reaction occurs and O_2 is liberated quantitatively while the bis(triphenylphosphine) adduct, $[Cu_2(XYL\text{-}O\text{-})(PPh_3)_2]^+$ (**7**), is formed (Figure 1).[17a] The enhanced reactivity toward substrates exhibited by $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**) or $Cu_2(XYL\text{-}O\text{-})(OOR)]^{2+}$ (R = C(O)R′)[37] is in accord with observations on other transition-metal peroxide complexes where the oxidation of organic substrates is enhanced by the presence of electrophiles such as H^+ or $RC(O)^+$.[45] The electrophilic activation of (porphyrin)M–O_2 complexes has also been reported,[46] and studies on O–O bond-breaking in porphyrin-containing and other LM–OOR species have shown that heterolytic and/or homolytic cleavage processes can lead to active metal–oxo oxidizing agents.[46,47]

We therefore suggest that dioxygen/copper complex derivatives such as $Cu_2(XYL\text{-}O\text{-})(OOR)]^{2+}$, or O–O cleavage products derived from these, may be important intermediates in copper-mediated oxidation/oxygenation processes. The protonation of a dioxygen–copper complex may result in "activation" through the formation of a hydroperoxo complex which can transfer an oxygen atom while leaving behind a stable hydroxo–copper(II)$_n$ moiety. In the absence of further detailed mechanistic/kinetic studies, a pathway involving the displacement of $^-$OOR followed by direct attack on PPh_3 or RSR substrate cannot be ruled out; such pathways have been suggested in group 8 metal catalyzed triphenylphosphine oxidations by O_2,[48,49] especially in the presence of protic solvents or "trace protic" species. However, in aprotic nonpolar solvents which would disfavor dissociation of an anionic ligand, a metal-based reaction seems more likely.[49] Solutions of $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (**3**) do not oxygenate substrates more readily oxidizable than phosphines or sulfides; olefins are not oxygenated. The possible occurrence of metal complex based reactivity can and will be more easily tested by studying the

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(41) Thewalt, U.; Marsh, R. A. *J. Am. Chem. Soc.* **1967**, *89*, 6364–6365.

(42) (a) Thompson, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 8308–8309. (b) Thompson, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 4057–4059. (c) Thompson, J. S. In ref 5b, Vol. 2, pp 1–10.

(43) Zuberbühler, A. D. In ref 5a, pp 237–258.

(44) Smegal, J. A.; Schardt, B. C.; Hill, C. L. *J. Am. Chem. Soc.* **1983**, *105*, 3510–3515.

(45) (a) Chen, M. J. Y.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1977**, 204–205. (b) Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5832–5839. (c) Strukul, G.; Ros, R.; Michelin, R. A. *Inorg. Chem.* **1982**, *21*, 495–500. (d) Fukuzumi, S.; Ishikawa, K.; Tanaka, T. *Chem. Lett.* **1986**, 1–4. (e) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 3101–3110.

(46) (a) Schappacher, M.; Weiss, R. *Inorg. Chem* **1987**, *26*, 1190–1192. (b) Khenkin, A. M.; Shteinman, A. A. *J. Chem. Soc., Chem. Commun.* **1984**, 1219. (c) Karasevich, E. I.; Khenkin, A. M.; Shilov, A. E. *J. Chem. Soc., Chem. Commun.* **1987**, 731–732. (d) Tabushi, I.; Kodera, M.; Yokoyama, M. *J. Am. Chem. Soc.* **1985**, *107*, 4466.

(47) (a) Balasubramanian, P. N.; Bruice, T. C. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 1734–1738. (b) Sugimoto, H.; Spencer, L.; Sawyer, D. T. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 1731–1733. (c) Groves, J. T.; Watanabe, Y. *Inorg. Chem.* **1987**, *26*, 785–786. (d) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7834–7836. (e) Groves, J. T.; Watanabe, Y. *Inorg. Chem.* **1986**, *25*, 4808–4810. (f) Lee, W. A.; Bruice, T. C. *J. Am. Chem. Soc.* **1985**, *107*, 513–514. (g) Traylor, T. G.; Lee, W. A.; Stynes, D. *J. Am. Chem. Soc.* **1984**, *106*, 755–764.

(48) Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1977**, *99*, 8337–8339.

(49) Read, G.; Urgelles, M. *J. Chem. Soc., Dalton, Trans.* **1986**, 1383–1387.

(50) Parshall, G. W. *Homogeneous Catalysis. The Application of Catalysis by Soluble Transition Metal Complexes*; Wiley: New York, 1980.

reactivity of olefinic substrates that have the possibility of alternative reaction pathways and associated products. Such reactions will be carried out with the acylperoxo complexes, $[Cu_2(XYL\text{-}O\text{-})(OOR)]^{2+}$,[37] since these do react with olefins.[38]

Thus, $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (3) does not appear to display exceptional reactivity toward organic substrates and we suggest that this can be ascribed to the fact that the coordinated hydroperoxo group is bound simultaneously to two Cu(II) ions, in an environment that is essentially coordinatively saturated and that has limited steric accessibility to substrate molecules. Degradative processes, either hydroperoxide disproportionation or reactions of $(Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (3) with solvent, are also clearly important and in competition with processes involving substrate oxidation.

Summary

Transition-metal hydroperoxo species are well established as important intermediates in the oxidation of hydrocarbons,[4] and a number of recent studies have focused upon the isolation of such complexes and studies of their reactivity.[45e,51] Here, we have reported on one of the first examples of a hydroperoxo complex of copper, $[Cu_2(XYL\text{-}O\text{-})(OOH)]^{2+}$ (3), containing a μ-1,1-hydroperoxo (^-OOH) ligand. A Cu^{II}–OOH complex generated by the one-electron reduction and protonation of a superoxo–Cu(II) compound, $LCu^{II}\text{–}(O_2^-)$,[42b,c] has also recently been described.[52]

In copper biochemistry, a Cu–OOH species has been implicated by Klinman and co-workers[53] as an important intermediate in the reaction of the copper monooxygenase, dopamine β-hydroxylase. It is suggested that the reduction of O_2 at a Cu(I) center is accompanied by a proton transfer from a protein-derived group leading to the copper–hydroperoxo intermediate. This is then capable of abstracting a hydrogen atom from the benzyl dopamine substrate and subsequent oxygen atom transfer leads to products. A Cu–OOH moiety has also been proposed to be involved in the disproportionation of superoxide ($2O_2^- + 2H^+ \rightarrow O_2 + H_2O_2$) mediated by the copper–zinc superoxide dismutase (SOD) enzyme.[54,55] Since an Fe–OOH intermediate has been suggested in the oxidation of the tetrahydropterin cofactor in phenylalanine hydroxylase,[56] further descriptions of the action of the copper-dependent form of the enzyme[15b] may require the consideration of a Cu–OOH species, by analogy.

Porphyrin–M–OOR and other Fe–OOR complexes have come under recent scrutiny because of their relevance to the active oxygenating reagent in cytochrome P-450 monooxygenase.[47] In synthetic systems, powerful M–(O) oxidizing agents form from M–OOR intermediates via heterolytic and/or homolytic O–O cleavage processes.[47] In the enzyme it seems likely that protonation of an $Fe\text{–}O_2$ intermediate similarly leads to the active iron–oxo reagent. We expect that related effects may be seen in copper ion chemistry, and we are continuing to study the reactivity of both mononuclear and dinuclear Cu_n–OOR species.

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Supplementary Material Available: ORTEP diagram of the complete cation of **6b** and tables of bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors for **6b** (Tables VI–IX) (11 pages); listing of structure factors (Table V) (36 pages). Ordering information is given on any current masthead page.

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(51) Also see, for example, (a) Saussine, L.; Brazi, E.; Robina, A.; Mimoun, H.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1985**, *107*, 3534. (b) Sugimoto, H.; Sawyer, D. T. *J. Am. Chem. Soc.* **1985**, *107*, 5712. (c) Sugimoto, H.; Sawyer, D. T. *J. Org. Chem.* **1985**, *50*, 1784–1786. (d) Durand, R. R., Jr.; Bencosme, C. S.; Collman, J. P.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 2710. (e) Strukul, G.; Michelin, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 7563–7569. (f) Francis, K. D.; Cummins, D.; Oakes, J. *J. Chem. Soc., Dalton Trans.* **1985**, 493. (g) Ledon, H. J.; Varescon, F. *Inorg. Chem.* **1984**, *23*, 2735–2737.

(52) (a) Thompson, J. S., personal communication. (b) Thompson, J. S. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*(6–7), 354.

(53) Miller, S. M.; Klinman, J. P. *Biochemistry* **1985**, *24*, 2114–2127.

(54) Osman, R.; Basch, H. *J. Am. Chem. Soc.* **1984**, *106*, 5710–5714.

(55) Rosi, M.; Sgamellotti, A.; Tarantelli, F.; Bertini, I.; Luchinat, C. *Inorg. Chem.* **1986**, *25*, 1005–1008.

(56) Dix, T. A.; Benkovic, S. J. *Biochemistry* **1985**, *24*, 5839–5846.

Cobalt(II)-Facilitated Transport of Dioxygen in a Polystyrene Membrane

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Abstract: In this paper we present conclusive evidence to illustrate that reversible binding of O_2 to transition-metal O_2 carriers can be utilized to facilitate transport of O_2 through a solid membrane when such complexes are incorporated into the membrane. The key experiment to establish this concept involves the proper selection of a blank film. The polystyrene-supported CoSDPT type complexes and blanks consisting of nickel(II) derivatives are ideal for demonstrating facilitated transport because of their structural similarity. We also present a procedure for evaluating permeation data, which should find widespread use in this area since it eliminates imperfections that can exist in test and blank membranes. A transport mechanism is discussed in light of these results.

The separation of oxygen and nitrogen is of industrial significance for the production of pure oxygen and pure nitrogen. The main commercial processes for oxygen production involve cryogenic air separation[1] and pressure swing adsorption.[2] Many applications do not require high-purity oxygen but can use oxygen-enriched air. This market includes waste-water treatment facilities, the pulp and paper industry, fermentation processes, and numerous medical applications. To produce lower purity oxygen

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(1) (a) Barron, R. F. *Cryogenic Systems*, 2nd ed.; Oxford University: New York, 1985. (b) Hands, B. A. *Cryogenic Engineering*; Academic: London, 1986. (c) Braton, N. R. *Cryogenic Recycling and Processing*; CRC: Boca Raton, FL, 1980.

(2) (a) Knoblauch, K. *Chem. Eng.* (*N.Y.*) **1978**, *85*, 87. (b) Miwa, K.; Inoue, T. CEER, *Chem. Econ. Eng. Rev.* **1980**, *12*, 40. (c) Whyte, T. E., Jr.; Yon, C. M.; Wagener, E. H. *Industrial Gas Separations*; ACS Symposium Series 223; American Chemical Society: Washington, DC, 1983.

0002-7863/88/1510-6780$01.50/0