Mikio Shimada of Wood Research Institute, Kyoto University, for his helpful discussion.

Supplementary Material Available: Data of GC/MS analyses for the products of reactions of **10** and anisaldehyde-*1-d* independently prepared, molecular weight measurement of diol **1c** by a vapor pressure osmometer, and combustion analyses of the substrate and catalysts (Tables S1, S2, and S3, respectively) (5 pages). Ordering information is given on any current masthead page.

Dioxygen–Copper Reactivity. Models for Hemocyanin: Reversible O_2 and CO Binding to Structurally Characterized Dicopper(I) Complexes Containing Hydrocarbon-Linked Bis[2-(2-pyridyl)ethyl]amine Units

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Abstract: A chemical system is described that mimics to a significant extent a number of properties of the copper-containing dioxygen carrier hemocyanin (Hc), including the reversible binding of CO and O_2 and major features of the UV–vis spectroscopy. A neutral dinucleating ligand, N4PY2, in which two tridenate PY2 units (PY2 = bis[2-(2-pyridyl)ethyl]amine) are connected by a tetramethylenealkyl chain, forms tetracoordinate dicopper(I) complexes, $[Cu_2(N4PY2)(CO)_2]^{2+}$ (**1**) and $[Cu_2(N4PY2)(CH_3CN)_2]^{2+}$ (**1a**), as well as the pseudotricoordinate complex $[Cu_2(N4PY2)]^{2+}$ (**2**). Compounds **1** and **2** can be readily interconverted, indicating that **2** can bind carbon monoxide reversibly. Complexes **1a** or **2**, as ClO_4^- (i.e. **1a**-$(ClO_4)_2$ or **2**-$(ClO_4)_2$), PF_6^-, or BF_4^- salts (λ_{max} 350 nm (ϵ 3500 M^{-1} cm^{-1})), can be oxygenated at −80 °C in dichloromethane to produce intensely brown-colored solutions of dioxygen complexes, **3**, which are characterized by extremely strong and multiple electronic spectral absorptions (360 nm (ϵ 14 000–18 700 M^{-1} cm^{-1}), 458 (4500–6300), 550 (1200)) in the visible region. The reaction of **2** (or **1a**) with O_2 is reversible, and the application of a vacuum to the dioxygen adduct formed, **3**, removes the bound O_2 and regenerates the dicopper(I) complex, **2**. This *vacuum cycling* can be followed spectrophotometrically over several cycles. In addition, saturating a −80 °C solution of the dioxygen complex **3** with carbon monoxide (CO) results in the displacement of the dioxygen ligand with the formation of the dicopper(I) dicarbonyl complex, **1**. This behavior lends further support to the existence of the reversible binding equilibrium, $\mathbf{2} + O_2 \Leftrightarrow \mathbf{3}$. *Carbonyl cycling*, where **2** reacts with O_2 to produce **3**, O_2 is displaced by CO to give **1**, and **1** is decarbonylated to regenerate **2**, can also be followed spectrophotometrically over several cycles. Since (a) manometric measurements indicate that the stoichiometry of the reaction of **2** (and **1a**) with dioxygen is $Cu:O_2 = 2:1$, thus formulating **3** as $[Cu_2(N4PY2)(O_2)]^{2+}$, and (b) other evidence (e.g. the presence of a d–d band; λ_{max} 775 nm (ϵ 200 M^{-1} cm^{-1})) suggests that **3** possesses Cu(II) ions, **3** is best described as a peroxo–dicopper(II) complex. Crystallographic studies have been completed for both $[Cu_2(N4PY2)(CH_3CN)_2](ClO_4)_2$ (**1a**-$(ClO_4)_2$) and $[Cu_2(N4PY2)](ClO_4)_2$ (**2**-$(ClO_4)_2$). Compound **1a**-$(ClO_4)_2$ ($C_{36}H_{46}Cl_2Cu_2N_8O_8$) crystallizes in the monoclinic space group *A*2/*a*, with $Z = 4$ and $a = 13.755$ (4) Å, $b = 20.071$ (5) Å, $c = 18.017$ (4) Å, and $\beta = 121.39$ (2)°. Complex **2**-$(ClO_4)_2$ ($C_{32}H_{40}Cl_2Cu_2N_6O_8$) crystallizes in the monoclinic space group *A*2/*a*, with $Z = 4$, $a = 19.437$ (4) Å, $b = 10.162$ (3) Å, $c = 23.231$ (6) Å, and $\beta = 128.14$ (2)°. **1a**-$(ClO_4)_2$ possesses well-separated (Cu···Cu = 7.449 Å) equivalent Cu(I)-N_4 moieties with pseudotetrahedral ligation to the three nitrogen atoms of the PY2 unit and the acetonitrile molecule. In addition to the PY2 coordination in **2**-$(ClO_4)_2$, a weak Cu–O(ClO_4^-) interaction is observed; the bonding parameters for this complex suggest that the bonding is closer to that observed for other similar tricoordinate complexes with the Cu(I)–PY2 unit. The biological relevance of the dioxygen adducts described here and comparisons to oxy–Hc are discussed.

As part of our overall efforts in developing copper coordination chemistry of relevance to copper proteins and enzymes,[1-3] we are examining the binding, interaction, and subsequent reactivity of dioxygen (O_2) and its reduced forms at copper ion centers. Interest in such investigations stems in part from the occurrence of copper-containing proteins such as hemocyanins (Hc's), which bind and transport dioxygen,[4-6] the monooxygenases tyrosinase[1-4,5b,7] and dopamine β-hydroxylase[1-4,5b,8] which incorporate an oxygen atom from O_2 into organic substrates,[9] and copper oxidases such as galactose oxidase[10] and laccase,[11] which reduce dioxygen to either hydrogen peroxide or water, respectively. Also of relevance are cytochrome *c* oxidase,[12] which reduces O_2 to water at an iron–copper center, and the Cu/Zn-containing superoxide dismutase,[13] which effects the conversion of 2 mol of superoxide anion to hydrogen peroxide and dioxygen. Copper compounds have also been established to be essential catalysts in oxidation and O_2-

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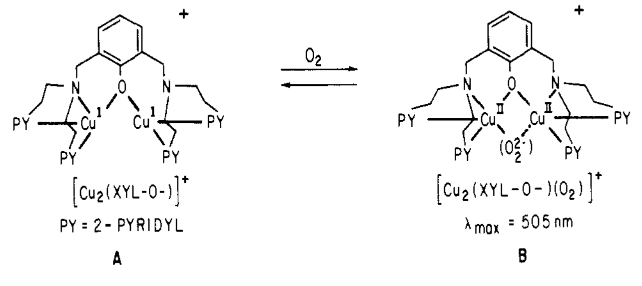
mediated reactions,[2,14] and information gained in biomimetic studies may potentially be applied to the further development of useful synthetic systems for mild and selective oxidative transformations.[14]

We recently described a system in which O_2 reacts with phenoxo-bridged dicopper(I) complex, $[Cu_2(XYL\text{-}O\text{-})]^+$ (A) (PY =

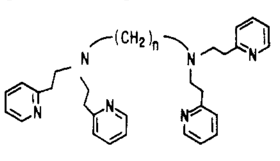


A

B

2-pyridyl), in dichloromethane at low temperature to give an intensely purple-colored (λ_{max} 505 nm (ϵ 6000 M^{-1} cm^{-1})) dioxygen complex, $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (B) (Cu:O_2 = 2:1).[15,16] Chemical studies show that the binding of dioxygen and carbon monoxide to A is reversible and cycling between deoxygenated and oxygenated forms can be carried out and followed spectrophotometrically.[16] A resonance Raman study[17] and an investigation utilizing extended X-ray absorption fine structure (EXAFS) spectroscopy[18] establish that B is best formulated as a peroxo-dicopper(II) compound (ν_{O-O} = 803 cm^{-1}) and that the binding of the peroxo ligand is asymmetric (terminal in character[17]) with a Cu···Cu distance of 3.31 Å. A protonated form of B can also be generated and this "hydroperoxo" dicopper(II) complex exhibits a greater reactivity toward oxidizable substrates (e.g. PPh_3 and RSR) compared to the parent peroxo complex.[19]

We have also been investigating the coordination chemistry of copper(I) and copper(II) using the dinucleating ligands NnPY2,



NnPY2

in which two tridentate PY2 units (PY2 = bis[2-(2-pyridyl)ethyl]amine) are connected by alkyl chains of varying length *n* (*n* = 2–5).[20] In this report, we describe the chemistry of dicopper(I) complexes of the N4PY2 (*n* = 4) ligand and their reactions with CO and O_2. Dicopper(I) compounds include the tetracoordinate complexes $[Cu_2(N4PY2)(CO)_2]^{2+}$ (**1**) and $[Cu_2(N4PY2)(CH_3CN)_2]^{2+}$ (**1a**), as well as the pseudotricoordinate complex, $[Cu_2(N4PY2)]^{2+}$ (**2**) (Figure 1). Complex **2** binds CO reversibly, and **1a** or **2** can be reversibly oxygenated at −80 °C in dichloromethane. The application of a vacuum to the dioxygen adduct formed, **3**, removes the bound O_2 and regenerates the dicopper(I) complex, **2**. Saturating the dioxygen complex **3** with CO causes displacement of the O_2 ligand with the formation of the dicopper(I) dicarbonyl complex, **1**. This latter observation lends further support to the existence of the reversible binding equilibrium, **2** + $O_2 \Leftrightarrow$ **3**; the reaction of **3** with CO shifts the equilibrium toward the dicopper(I) species, **2**, due to the ensuing reaction of **2** to give the dicarbonyl adduct **1**. Since manometric measurements indicate that the stoichiometry of the reaction of **2** (and **1a**) with dioxygen is Cu:O_2 = 2:1, the dioxygen adduct, **3**, is formulated as $[Cu_2(N4PY2)(O_2)]^{2+}$ (Figure 1).

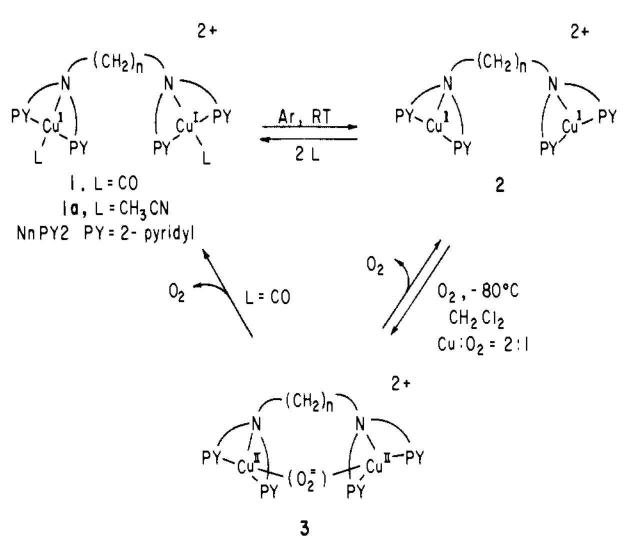


Figure 1. Scheme showing the reactions of dicationic dicopper complexes of the NnPY2 ligands, including bisadduct complexes with CO and CH_3CN, $[Cu_2(NnPY2)(L)_2]^{2+}$ (**1**, L = CO; **1a**, L = CH_3CN), tricoordinate complexes, $[Cu_2(NnPY2)]^{2+}$ (**2**), and the dioxygen adduct, $[Cu_2(NnPY2)(O_2)]^{2+}$ (**3**). The binding of CO to **2** is reversible, such that bubbling carbon monoxide through solutions of **2** readily gives **1**, while the latter can be decarbonylated through vacuum/purge cycles. $[Cu_2(NnPY2)]^{2+}$ (**2**) (or **1a**) reacts reversibly with O_2 at −80 °C in dichloromethane to give the dioxygen adduct **3**, which is best described as a peroxo–dicopper(II) complex. Carbon monoxide also reacts with **3** to give the bisadduct **1**, displacing O_2 in the process. The occurrence of the latter reaction further substantiates the reversible (equilibrium) nature of the binding of O_2 to **2**; the reaction of **2** with CO shifts the equilibrium, **2** + $O_2 \Leftrightarrow$ **3**, to the left, since **2** readily reacts with CO to produce the adduct **1**. See text for further discussion.

As part of the characterization of tricoordinate dicopper(I) complexes of N4PY2 (**2**) and the tetracoordinate dicarbonyl (**1**) and bis(acetonitrile) (**1a**) adducts, we include single-crystal X-ray structural studies of $[Cu_2(N4PY2)](ClO_4)_2$ (**2**-$(ClO_4)_2$) and $[Cu_2(N4PY2)(CH_3CN)_2](ClO_4)_2$ (**1a**-$(ClO_4)_2$). The spectral properties of the dioxygen adduct(s) **3** are also described, and the reversible CO and O_2 bindings are illustrated by following the cycling between **1**, **2**, and **3**, as monitored by UV–vis spectroscopy.

Experimental Section

Materials and Methods. Reagents and solvents used were of commercially available reagent quality unless otherwise stated. Dioxygen and carbon monoxide gases were dried by passing them through a short column of supported P_4O_{10} (Aquasorb, Mallinkrodt) and/or a copper coil tube immersed in a −80 °C cold trap. Methanol was distilled from $Mg(OMe)_2$; anhydrous diethyl ether was utilized by passing it through a 60-cm-long column of activated alumina, and/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 the acid layer was washed with water, it was removed, and the dichloromethane was washed with a KOH-KCl (satd) solution and distilled water and then dried over anhydrous $K_2CO_3/MgSO_4$ before a final reflux and distillation from CaH_2.

Preparations and handling of air-sensitive materials were carried out under an argon atmosphere by standard Schlenk techniques.[21] Deoxygenation of solvents and solutions was effected either by repeated vacuum/purge cycles with 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. All column chromatography of ligands was carried out by flash chromatography[22] with silica gel (60–200 mesh, MCB); better separations and yields could be achieved with 230–400-mesh silica gel 60 (EM). Fractions from column chromatography were monitored by Baker-Flex 1B-F TLC plates. Purity of the ligands

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was judged by TLC and ^{1}H NMR. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and/or MicAnal, Tucson, AZ.

Infrared spectra were recorded as either Nujol mulls or KBr pellets on a Perkin-Elmer 283 or 710B instrument and calibrated with a polystyrene film. 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 δ values downfield from an internal standard of Me_4Si. Electrical conductivity measurements were carried out in dimethylformamide (DMF) with an Industrial Instruments Inc. Model RC16B conductivity bridge, using a 10-cm cell. The cell constant, κ, was determined with a standard aqueous KCl solution. Room-temperature magnetic moments were determined with a Johnson Matthey magnetic susceptibility balance, and the instrument was calibrated by using $Hg[Co(SCN)_4]$. 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, $g = 2.0037$). Solvents used were either CH_2Cl_2 or CH_2Cl_2/toluene (1:1, v/v). In order to faciliate the formation of glasses by rapid freezing, the samples prepared in CH_2Cl_2 were first frozen in an isopentane/N_2(l) slush bath (113 K), followed by further cooling to 77 K. Rough integration of the signals obtained was carried out by comparing the intensity observed ($I \approx h_{1/2}(w_{1/2h})^2$) with that of a known concentration of $Cu(NO_3)_2 \cdot 3H_2O$ in MeOH/EtOH (1:1, v/v at 77 K).

Synthesis of Ligands and Complexes. N4PY2. The compound 1,4-diaminobutane (6.59 g, 0.075 mol) and glacial acetic acid (22.5 g, 0.375 mol) were added to a solution of 2-vinylpyridine (78.6 g, 0.75 mol, purified by passing through a short silica gel precolumn with diethyl ether solvent, followed by removal of the ether by rotary evaporation) in reagent-grade methanol (150 mL). The mixture was allowed to stir under reflux for 10 days. The MeOH was removed by rotary evaporation, and the resulting oil was taken up in CH_2Cl_2, washed with 150 mL of 15% NaOH, and extracted with dichloromethane (3 × 75 mL). The organic extracts were dried over $MgSO_4$, and the solvent was removed to give 46 g of the crude product. This also contains the excess 2-vinylpyridine, which is largely removed by "distillation" on a rotary evaporator (vacuum pump attached, <40 °C; ligand decomposition with retroaddition and re-formation of 2-vinylpyridine occurs with too much heating). Typically, 2.0 g of the product was purified by column chromatography on silica gel by using 98% MeOH/2% NH_4OH (7.6 M) solution as eluant to give 0.50 g of the pure oily brown product (25% based on diamine). TLC: R_f 0.73. ^{1}H NMR ($CDCl_3$): δ 1.10–1.50 (4 H, br m), 2.25–2.60 (4 H, br m), 2.92 (16 H, br s), 6.65–7.45 (12 H, py-3, py-4, py-5), 8.10–8.35 (4 H, py-6, br d). ^{13}C NMR ($CDCl_3$): δ 24.9 ($\mathit{C}H_2$), 35.9 (py-$\mathit{C}H_2$), 53.8 ($\mathit{C}H_2N\mathit{C}H_2$), 120.8 (py C-5), 123.2 (py C-3), 135.9 (py C-4), 148.9 (py C-6), 160.6 (py C-2). ^{13}C NMR (CD_3NO_2): δ 20.8 ($\mathit{C}H_2$), 31.6 (py-$\mathit{C}H_2$), 49.6 ($\mathit{C}H_2N\mathit{C}H_2$), 116.8 (py C-5), 119.1 (py C-3), 131.9 (py C-4), 144.9 (py C-6), 157.0 (py C-2).

A method for the purification of N4PY2 not requiring chromatography has also been developed. Crude ligand (30 g), obtained as described above, was dissolved in 300 mL of benzene, with vigorous stirring. Solid phthalic anhydride (3.0 g, e.g. 10% by weight) was added. After 1 h, the mixture was monitored by TLC. If more than one spot (besides that corresponding to 2-vinylpyridine) was observed, additional phthalic anhydride (1 g) was added and the mixture stirred for 1 h more. When one spot was obtained, 200 mL of 10% aqueous NaOH was added and the mixture stirred for another 1 h. Separation of the organic phase after an additional water wash (300 mL) and drying with anhydrous $MgSO_4$ gave a dark brown oil. Pure product is obtained after removal of 2-vinylpyridine as above (70–80% yields).

$[Cu_2(N4PY2)(CO)_2](PF_6)_2$ (1-$(PF_6)_2$). Under an argon atmosphere, the ligand N4PY2 (0.50 g, 1.0 mmol) was dissolved in 20 mL of carbon monoxide saturated MeOH, and this solution was added dropwise with stirring to solid $[Cu(CH_3CN)_4](PF_6)$[23] (0.75 g, 2.0 mmol) under argon. The solid initially dissolved, and within a few minutes, a fine yellow-white precipitate formed. The mixture was allowed to stir for 2 h, at which time diethyl ether was added to precipitate out more product. The solution was then stirred, producing an off-white fine powder, 0.86 g (90%). Upon recrystallization from CH_2Cl_2/Et_2O (1:2 by volume), a microcrystalline material was obtained as an off-white solid (0.77 g, 80%). Anal. Calcd for ($C_{34}H_{40}Cu_2F_{12}N_6O_2P_2$): C, 41.59; H, 4.11; N, 8.56. Found: C, 41.76; H, 4.27; N, 8.61. ^{1}H NMR (CD_3NO_2): δ 1.50–1.90 (4 H, br m), 2.40–2.70 (4 H, m), 3.10 (16 H, br s), 7.10–8.0 (12 H, py-3, py-4, py-5, m), 8.20–8.40 (4 H, d, py-6). ^{13}C NMR (57.3 MHz, CD_3NO_2): δ 156.9 (py C-2), 146.4 (py C-6), 135.3 (py C-4), 121.6 (py C-3), 119.1 (py C-5), 51.5 ($N\mathit{C}H_2$), 50.5 ($N\mathit{C}H_2$), 31.1 (py-$\mathit{C}H_2$), 19.8 ($\mathit{C}H_2$), $\mathit{C}O$ resonance not observed. IR (Nujol): 2080 (CO, s), 835 (PF_6^-, s, br) cm^{-1}.

$[Cu_2(N4PY2)(CH_3CN)_2](PF_6)_2$ (1a-$(PF_6)_2$). N4PY2 (0.50 g, 0.98 mmol), in 30 mL of CH_3CN, was added dropwise with stirring to solid $[Cu(CH_3CN)_4](PF_6)$ (0.732 g, 1.96 mmol) under argon. The resulting clear golden solution was then allowed to stir for 2 h. Precipitation with diethyl ether afforded a dark yellow-brown powder, which was collected by filtration under argon, giving 0.84 g (84%). Recrystallization with CH_3CN/Et_2O (1:4, v/v) produced 0.65 g (66%) of microcrystalline material. Anal. Calcd for ($C_{36}H_{46}Cu_2F_{12}N_8P_2$): C, 42.90; H, 4.60; N, 11.12. Found: C, 43.37; H, 4.54; N, 10.78. ^{1}H NMR (CD_3NO_2): δ 1.15–1.80 (4 H, m), 2.05 (6 H, s, $C\mathit{H}_3CN$), 2.3–2.75 (4 H, m), 2.90 (16 H, s), 7.1–7.5 (8 H, m, py-3, py-5), 7.5–8.0 (4 H, m, py-4), 8.3–8.65 (4 H, d, py-6).

$[Cu_2(N4PY2)(CH_3CN)_2](ClO_4)_2$ (1a-$(ClO_4)_2$). Under an Ar atmosphere, N4PY2 (0.50 g, 0.98 mmol), in 20 mL of CH_3CN, was added dropwise with stirring to solid $[Cu(CH_3CN)_4](ClO_4)$[24] (0.642 g, 1.96 mmol). The resulting clear golden solution was then allowed to stir for 2 h. Precipitation with diethyl ether afforded dark yellow-brown crystalline material, which was collected by filtration under Ar (0.84 g, 93%). Recrystallization with CH_3CN/Et_2O (1:3, v/v) produced 0.76 g (85%) of yellow-brown crystalline material. Anal. Calcd for ($C_{36}H_{46}Cl_2Cu_2N_8O_8$): C, 47.16; H, 5.06; N, 12.22. Found: C, 47.21; H, 5.10; N, 12.16. ^{1}H NMR (CD_3NO_2): δ 1.40–1.90 (4 H, m, CH_2), 2.10–2.40 (6 H, $C\mathit{H}_3CN$), 2.50–3.20 (20 H, m), 7.05–7.50 (8 H, m, py-3, py-5), 7.50–7.90 (4 H, d, py-4), 8.30–8.60 (4 H, br d, py-6). ^{13}C NMR (57.3 MHz, CD_3NO_2): δ 156.9 (py C-2), 145.6 (py C-6), 134.3 (py C-4), 120.9 (py C-3), 118.7 (py C-5), 112.9 ($CH_3\mathit{C}N$), 52.7 ($N\mathit{C}H_2$), 50.2 ($N\mathit{C}H_2$), 30.2 (py-CH_2), 19.4 ($\mathit{C}H_2$), −3.5 ($\mathit{C}H_3CN$). IR (Nujol): 1595 (C=C, s), 1570 (C=C, m), 1050 (ClO_4^-, s, br) cm^{-1}; ν_{C-N} of the coordinated CH_3CN not observed.

$[Cu_2(N4PY2)](PF_6)_2$ (2-$(PF_6)_2$). N4PY2 (0.50 g, 0.98 mmol) dissolved in 20 mL of dichloromethane was added dropwise with stirring to solid $[Cu(CH_3CN)_4]PF_6$ (0.73 g, 1.97 mmol). The resultant clear golden solution was allowed to stir for 2 h. Precipitation with diethyl ether produced bright yellow crystalline material as long needles after filtration (0.75 g, 83%). Recrystallization with CH_2Cl_2/Et_2O (1:3, v/v) gave 0.65 g (72%) of bright yellow crystalline material. Anal. Calcd for ($C_{32}H_{40}Cu_2F_{12}N_6P_2$): C, 41.55; H, 4.36; N, 9.08. Found: C, 41.72; H, 4.32; N, 9.09. ^{1}H NMR (CD_3NO_2): δ 1.0–1.5 (4 H, m), 2.2–2.6 (4 H, m), 3.1 (16 H, br s), 7.10–7.60 (8 H, m, py-3, py-5), 7.60–8.10 (4 H, m, py-4), 8.40–8.70 (4 H, br d, py-6). ^{1}H NMR (CD_3COCD_3): δ 1.0–1.5 (4 H, m), 2.2–2.6 (4 H, m), 2.7–3.3 (16 H, br s), 7.1–8.0 (12 H, m, py), 8.5–8.7 (4 H, br d, py-6). ^{13}C NMR (57.3 MHz, CD_3NO_2): δ 157.0 (py C-2), 146.1 (py C-6), 135.2 (py C-4), 121.1 (py C-3), 119.0 (py C-5), 55.0 ($\mathit{C}H_2$), 49.8 ($N\mathit{C}H_2$), 29.3 (py-$\mathit{C}H_2$), 19.3 ($\mathit{C}H_2$). IR (Nujol): 1580 (C=C, s), 1550 (C=C, m), 860 (PF_6^-, s, br) cm^{-1}.

Complex 2-$(PF_6)_2$ can also be generated by the reduction of $[Cu_2(N4PY2)(OH)_2](PF_6)_2$ (**4**; see below). Initially, 1,2-diphenylhydrazine (0.081 g, 0.437 mmol) was placed in an evacuated and argon-purged 100-mL Kontes side-arm flask, and 40 mL of argon-purged CH_2Cl_2 was added. To this solution was added $[Cu_2(N4PY2)(OH)_2](PF_6)_2$ (**4**) (0.400 g, 0.416 mmol) dissolved in 30 mL of dichloromethane (and Ar purged) dropwise with stirring. Initially, a clear green solution formed, but within 0.5 h, a clear yellow solution was produced. After precipitation with diethyl ether and filtration under Ar, 0.233 g (81%) of yellow needles was isolated. Recrystallization from CH_2Cl_2/Et_2O (1:3, v/v) again produced 0.15 g (52%) of yellow needles. Anal. Calcd for ($C_{32}H_{40}Cu_2F_{12}N_6P_2$): C, 41.55; H, 4.36; N, 9.08. Found: C, 40.60; H, 4.37; N, 8.78. The ^{1}H NMR (CD_3COCD_3) and IR spectra of 2-$(PF_6)_2$ prepared in this manner were identical with those described above.

$[Cu_2(N4PY2)](ClO_4)_2$ (2-$(ClO_4)_2$). The ligand N4PY2 (0.50 g, 0.98 mmol), in 40 mL of dichloromethane, was added dropwise with stirring to solid $[Cu(CH_3CN)_4](ClO_4)$ (0.643 g, 1.97 mmol). The resulting clear yellow solution was allowed to stir for 2 h, after which precipitation with diethyl ether afforded a bright yellow microcrystalline powder (0.70 g, 86%). This material required multiple recrystallizations from CH_2Cl_2/Et_2O (1:2, v/v) in order to rid the product of tightly coordinated CH_3CN; the progess of these recrystallizations was followed by monitoring the $C\mathit{H}_3CN$ absorption by ^{1}H NMR. In a typical preparation involving three recrystallizations, 0.58 g (71%) of crystalline product was obtained. Anal. Calcd for ($C_{32}H_{40}Cl_2Cu_2N_6O_8$): C, 46.05; H, 4.83; N, 10.07. Found: C, 45.99; H, 4.73; N, 9.94. ^{1}H NMR (CD_3NO_2): δ 1.0–1.75 (4 H, m), 2.0–2.65 (4 H, m), 3.05 (16 H, br s), 7.1–7.5 (8 H, m, py-3, py-5), 7.55–8.2 (4 H, m, py-4), 8.4–8.8 (4 H, br d, py-6). IR (Nujol): 1580 (C=C, s), 1550 (C=C, m), 1080 (ClO_4^-, s, br).

$[Cu_2(N4PY2)(OH)_2](PF_6)_2$ (4). The ligand N4PY2 (0.25 g, 0.49 mmol), which was dissolved in 75 mL of methanol, was added dropwise,

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[23] Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90.

[24] Hemmerich, P.; Sigwart, C. *Experientia* **1963**, *19*, 488.

with stirring to solid $[Cu(CH_3CN)_4](PF_6)$ (0.37 g, 0.98 mmol). The resulting clear yellow-orange solution was cooled to 0 °C with an ice-water bath. The reaction mixture was oxygenated by the introduction of O_2 (1 atm) above the solution and was swept through a mineral oil filled bubbler. After a 2-h period, the volume of the resulting dark green solution was reduced to 50 mL, and this was placed in a refrigerator overnight. The green solid produced was filtered with a fritted funnel, giving 0.150 g of product. An additional 50 mg of product was obtained by precipitation of the filtrate with diethyl ether for a total yield of semicrystalline product of 0.200 g (43%). Anal. Calcd for $(C_{32}H_{42}Cu_2F_{12}N_6O_2P_2)$: C 40.04; H, 4.42; N, 8.76. Found: C, 39.93; H, 4.36; N, 8.43. IR (Nujol): 3635 (OH, m), 1630 (C=C, s), 1575 (C=C, m), 835 (PF_6^-, s, br) cm^{-1}. μ(RT) = 0.7 μ_B/Cu. Λ_m(DMF): 127 $cm^2\ \Omega^{-1}\ mol^{-1}$.

Gas (O_2 and CO) Uptake Measurements. Measurements of the uptake of dioxygen or carbon monoxide gases (manometry) at low temperature (0 or −80 °C) were carried out with a gas buret system as previously described.[16,25] This method applies for samples which have solids that are stable toward O_2 but which react readily with O_2 in solution. The gas uptake measurements for solutions of $[Cu_2(N4PY2)]^{2+}$ (**2**), generated by decarbonylation of $[Cu_2(N4PY2)(CO)_2]^{2+}$ (**1**), were carried out as follows. Typically, a solution of **1**-$(PF_6)_2$ (0.5 g) was prepared under an argon atmosphere in a 50-mL Kontes side-arm flask with 30–40 mL of CH_2Cl_2. Application of repeated vacuum/purging cycles with gentle heating resulted in the removal of the CO ligands, which was confirmed by recording a solution IR spectrum. Additional dichloromethane was added under Ar until the flask contained 67 mL of solution. This was accomplished by prior volume calibration of the flask, and at this point, the flask was full up to the side-arm joint. The reaction flask was then attached to the buret system while placed in the cold bath at −80 °C, and the entire system was vacuum Ar-purged, with a final application of a vacuum for 20 min. The stopcock leading to the reaction flask was closed, and the buret system was then equilibrated to 1-atm O_2 pressure by vacuum/O_2 cycles. Once equilibrium was achieved, an initial volume reading was recorded, and the stopcock leading the reaction flask (now under vacuum) was opened. "Blank" runs, to determine the volume of O_2 taken up by a solute-free reaction solution, were performed under *identical* conditions.

Reaction of CO with $[Cu_2(N4PY2)(O_2)]^{2+}$ (3) To Give $[Cu_2(N4PY2)(CO)_2]^{2+}$ (1). Crystalline $[Cu_2(N4PY2)(CH_3CN)_2](ClO_4)_2$ (**1a**-$(ClO_4)_2$) (0.100 g, 0.109 mmol) was dissolved in 30 mL of Ar-saturated CH_2Cl_2, with stirring. The solution was cooled to −85 °C, and O_2 was bubbled through the solution for 10 min as the solution changed from a yellow to a deep brown color. The system was then vacuum/purged with Ar for five cycles to remove excess uncoordinated dioxygen. Carbon monoxide was then directly bubbled through the solution and was occasionally allowed to warm by taking the reaction flask out of the cold bath for 30-s intervals. Within 1 h the solution had turned to a clear yellow color, and precipitation with diethyl ether afforded 0.98 g (89%) of slightly yellow crystalline product, $[Cu_2(N4PY2)(CO)_2](ClO_4)_2 \cdot 2CH_2Cl_2$. Anal. Calcd for $(C_{34}H_{44}Cl_6Cu_2N_6O_{10})$: C, 40.77; H, 4.29; N, 9.22. Found: C, 41.28; H, 4.10; N, 9.15. ^{1}H NMR (CD_3NO_2): 1.3–1.80 (4 H, m), 2.5–3.2 (20 H, m), 5.30 (4 H, s, CH_2Cl_2), 7.1–7.5 (8 H, py-3, py-5, m), 7.6–8.0 (4 H, m, py-4), 8.25–8.80 (4 H, br d, py-6). IR (Nujol): 2080 (C≡O, s), 1608 (C=C, s), 1570 (C=C, m), 1080 (ClO_4^-; s, br) cm^{-1}.

Qualitative Determination of Dioxygen Liberation from the Reaction of CO with $[Cu_2(N4PY2)(O_2)]^{2+}$ (3). A solution of the dioxygen complex, **3**, was prepared in the identical manner as described for the displacement reaction with carbon monoxide, except that, following passage of the CO gas stream through the copper-containing solution, it was directed through a bubbler containing an alkaline pyrogallol (1,2,3-trihydroxybenzene) solution; the latter was used to test for the presence of dioxygen.[26] The test solution was prepared as follows: Potassium hydroxide (15 g) in 150 mL of distilled water was boiled for 1 h with vigorous stirring, and this solution was then transferred to an evacuated and Ar-purged 100-mL addition funnel (Kontes K-215200) with a 50-mL side-arm Kontes flask attached to the bottom of the addition funnel via a 14/20 standard joint. A side-arm tube containing 1 g of pyrogallic acid, which had been previously evacuated and purged, was then attached to the top of the addition funnel and slowly added to the aqueous KOH solution (which had been bubbled with Ar for 1 h). By gentle shaking, the acid dissolved to produce a clear, colorless solution. After the excess O_2 was removed from the dioxygen complex solution, Ar was bubbled through both the complex and test solutions. No change in the color of the pyrogallol solution indicated that all of the excess O_2 had indeed been removed. Introduction of CO in the manner described above resulted in both a bleaching of the color in the solution containing **3** and in a darkening (tanning) of the test solution. Within 1 h, the copper-containing solution was colorless and the pyrogallol-containing solution was a dark brown. After the reaction vessel was warmed to room temperature, precipitation with diethyl ether afforded a high yield of the dicarbonyl adduct, **1**.

CO_2 Detection. The same procedure used for O_2 detection was used here except that the stream of CO gas was passed through an aqueous $Ba(OH)_2$ solution (3.0 g of $Ba(OH)_2$ in 100 mL of distilled water and filtered) after bubbling into the dichloromethane solution containing **3**. No detectable precipitate formed in the test solution upon passage of CO through the dioxygen complex solution (as above). As a crude control experiment, exposure of the test solution to air does produce a small but detectable amount of white precipitate ($BaCO_3$).

Low-Temperature UV-Vis Spectroscopy. Low-temperature electronic spectra and cycling experiments were carried out either on a Cary 14 spectrophotometer as previously described[16] or on a Perkin-Elmer Lambda Array 3840/IBM PC data system (315–900 nm) with output to an Epson FX-85 printer. The Perkin-Elmer spectrometer was equipped with a Kontes KM-611772 variable-temperature vis-UV Dewar cell, including the cuvette assembly. The latter consisted of a 10-mm quartz cuvette fused to one end of a glass tube; the other end is attached to a high-vacuum stopcock and a 14/20 ground glass joint. To maintain a low and constant temperature, a coil of copper tubing was inserted into the methanol-filled Dewar, through which cold methanol was circulated from an external source (Neslab CC-100II cryocool immersion cooler, in Agitainer A with circulating pump). The cuvette assembly with sample solution was mounted into the Dewar into the middle of the copper coil and held in place at the top with an appropriately drilled-out rubber cork.[25] Monitoring of the temperature in the Dewar was accomplished with the use of a resistance thermometer probe (Omega Model 651) placed into the Dewar immediately adjacent to the position of the cuvette. Fogging (on humid days only) of the quartz windows of the Dewar was prevented by the use of an externally applied brisk flow of nitrogen gas.

For measurements in the near-IR region (≤1100 nm), a Shimadzu UV-160 spectrometer was employed. The solution was prepared in the cuvette assembly described above and transferred quickly from a cold Dewar (−80 °C) into the spectrometer, which had been crudely fitted with cut-out cardboard coverings in order to keep out stray light and to allow insertion of the cuvette. The spectrum was recorded immediately; a spectrum of a solution of the solvent and/or of the Cu(I) complex in CH_2Cl_2, prepared and recorded in a similar fashion, was used as a blank. The UV–vis spectrum was also recorded on the Perkin-Elmer machine (<900 nm) to confirm the presence of the weak bands in the near-IR region.

The preparation and handling of samples and vacuum/heat cycling or CO cycling experiments have been previously described.[16,25]

X-ray Crystallography, Crystallization, Data Collection, and Reduction. Crystals suitable for X-ray diffraction were grown as described above. Epoxy-covered crystals of compounds **1a**-$(ClO_4)_2$ and **2**-$(ClO_4)_2$ were mounted on a Nicolet R3m four-circle automated diffractometer with a Mo X-ray source equipped with a highly ordered graphite monochromator (λ(Mo Kα) = 0.71073 Å). Automatic centering and least-squares routines were carried out on 25 reflections for both the complexes to obtain the cell dimensions that are given in Table I. A coupled θ-(crystal)–2θ(counter) scan mode was employed. The scan length was from $(2\theta(K\alpha_1 - 1.0))$ to $(2\theta(K\alpha_2 + 1.0))°$. Three check reflections were measured every 197 reflections; these exhibited no significant decay during data collection. The program XTAPE of the SHELXTL package[27] was used to process the data for both complexes. A summary of cell parameters, data collection parameters, and refinement results for complexes **1a**-$(ClO_4)_2$ and **2**-$(ClO_4)_2$ is found in Table I.

Structure Solution and Refinement. The positional parameters of the copper atoms were determined by the Patterson method for both complexes. 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. Both complexes **1a**-$(ClO_4)_2$ and **2**-$(ClO_4)_2$ crystallize in the monoclinic space group *A*2/*a* with *Z* = 4. For both complexes each asymmetric unit contains one complete molecule, with no atoms sitting at special positions. For

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(25) See also: (a) Haka, M. S. Ph.D. Thesis, State University of New York at Albany, 1987. (b) Cruse, R. W. Ph.D. Thesis, State University of New York at Albany, 1986.

(26) Gordon, A. J.; Ford, R. A. *The Chemist's Companion, A Handbook of Practiical Data, Techniques and References*; Wiley: New York, 1972; p 440.

(27) All calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words by using local versions of the Nicolet SHELXTL interaction crystallographic software package, as described in: Sheldrick, G. M. *Nicolet SHELXTL Operations Manual*; Nicolet XRD Corp.: Cupertino, CA, 1979.

Table I. Crystallographic Data for Complexes **1a**-$(ClO_4)_2$ and **2**-$(ClO_4)_2$

	1a-$(ClO_4)_2$	**2**-$(ClO_4)_2$
a, Å	13.755 (4)	19.437 (4)
b, Å	20.071 (5)	10.162 (3)
c, Å	18.017 (4)	23.231 (6)
α, deg	90.00	90.00
β, deg	121.39 (2)	128.14 (2)
γ, deg	90.00	90.00
V, Å^3	4245.6 (1.7)	3608.9 (1.4)
$F(000)$	2391	1719.63
Z	4	4
D_{calcd}, g/cm^3	1.435	1.536
space gp	$A2/a$[a]	$A2/a$[a]
cryst dimen, mm	0.40 × 0.40 × 0.40	0.35 × 0.20 × 0.20
scan rate, deg/min	15.0–30.0	7.0–30.0
scan range, deg	0.0–45.0	0.0–45.0
bkgd measmnt	stationary cryst, stationary counter, at beginning and end of each 2θ scan, each for time taken for scan	
reflcn measd	$+h,+k,\pm l$	$+h,+k,\pm l$
reflcn colld	6164	4081
indep reflcn	549, $\geq 6\sigma\lvert F_o\rvert$	1014, $\geq 6\sigma\lvert F_o\rvert$
abs coeff, cm^{-1}	3.07	13.8
redn of intens data and summary of struct soln and refinement; data corrected for bkgd, attenuators, Lorentz and polarizn effects in usual fashion[b]		
agreement between equiv reflcn	0.0071	07
abs corrn	not applied	not applied
atom-scattering factors[c]	neutral atomic scattering factors used throughout anal.	
anomalous dispersion[d]	applied to all non-hydrogen atoms	
R[e]	0.0617	0.0568
R_w[e]	0.0689	0.0544
goodness of fit[f]	2.031	1.582

[a] Alternate setting of $C2/c$. [b] Hyde, J.; Venkatasubramanian, K.; Zubieta, J. *Inorg. Chem.* **1978**, *17*, 414. [c] Cromer, D. T.; Mann, J. B., *Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *24*, 321. [d] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1962; Vol. III. [e] $R = \sum[|F_o| - |F_c|/\sum|F_o|]$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\delta^2(F_o) + g(F_o)^2$; $g = 0.001$. [f] $\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$ when NO is the number of observations and NV is the number of variables.

both complexes, anisotropic refinements were carried out only for the copper atoms, nitrogen atoms, and the atoms in the anion. The remaining atoms were refined isotropically. The carbon–hydrogen bond distance was set at 0.96 Å, and isotropic thermal parameters wer 1.2 times those of the bonded carbons. The structures of the perchlorate anions that are present in **1a**-$(ClO_4)_2$ are unexceptional. No disorder is seen, and the bond lengths and bond angles are as expected. 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 are available as supplementary material for compounds **1a**-$(ClO_4)_2$ (Tables VII–XI) and **2**-$(ClO_4)_2$ (Tables XII–XVI).

Results and Discussion

Synthesis of Dicopper Complexes. The use of the NnPY2 ligands evolved out of the chemistry developed with the *m*-XYLPY2 ligand, in which a *m*-xylyl group connects two PY2 tridentates. Here, the dicopper(I) complex containing *m*-XYLPY2 reacts with O_2, resulting in the hydroxylation of the XYL connector to form a phenoxo-bridged dicopper(II) complex; this copper-mediated hydroxylation of an arene serves as a close biomimic to the action of the copper monooxygenases.[1,2,28]

The NnPY2 ligands are a versatile class of dinucleating ligands[29] in which the consequences of structure and reactivity due to variations in the number of methylene-connecting units between the PY2 groups (e.g. metal–metal distance variability) can be investigated. We have already shown that the PY2 tridentate group is well suited to the formation of stable tricoordinate Cu(I) structures,[28,33] and we have characterized tri- and tetracoordinate dicopper(I) and pentacoordinate dicopper(II) derivatives of NnPY2 (n = 2–5).[20,25a,34,35] The Cu(I) compounds are sensitive to O_2 and are thus of interest to our studies of dioxygen–copper reactivity.

The ligand N4PY2 is synthesized straightforwardly by the acid-catalyzed reaction of an excess of 2-vinylpyridine with 1,4-diaminobutane, and it can be readily prepared and purified in large quantities (see the Experimental Section). Typically, the dicopper(I) complexes are prepared by mixing 2 equiv of $[Cu(CH_3CN)_4]Y$ ($Y = PF_6^-$ or ClO_4^-) with N4PY2 in polar organic solvents such as methanol, acetonitrile, or dichloromethane. $[Cu_2(N4PY2)(CO)_2]^{2+}$ (**1**) was prepared by carrying out the reaction in CO-saturated MeOH, and the bis(carbon monoxide) analogues for all of the NnPY2 (n = 3–5) ligands are stable crystalline solids, exhibiting typical values for ν_{C-O} in the range 2080–2095 cm^{-1}. X-ray crystallographic studies have been completed for the n = 3 and 5 analogues,[35] and they show these complexes to consist of well-separated copper ion moieties, each possessing $Cu-N_3(CO)$ tetracoordination. The $(CH_3CN)_2$ complexes, $[Cu_2(N4PY2)(CH_3CN)_2]^{2+}$ (**1a**), are formed in acetonitrile solvent, and these derivatives are convenient starting materials for the reactions with dioxygen (or other ligands) since they are quite soluble and the coordinated CH_3CN ligands are readily displaced.

The tri-coordinate complexes, $[Cu_2(N4PY2)]^{2+}$ (**2**), were formed in CH_2Cl_2, but the use of $Cu(CH_3CN)_4Y$ as the copper(I) source requires that several recrystallizations from CH_2Cl_2/Et_2O are carried out, since the CH_3CN present binds tenaciously to the Cu(I) (see the Experimental Section). Complexes of **2** are only sparingly soluble in CH_2Cl_2, but bisadducts (CO, PPh_3, CH_3CN) or oxygenation products of **2** become very soluble when subjected to the appropriate reagents. The tricoordinate compounds, $[Cu_2(N4PY2)]^{2+}$ (**2**), thus serve as useful precursors to complexes **1** or **1a** as well as to bis(triphenylphosphine) derivatives, $[Cu_2(N4PY2)(PPh_3)_2]^{2+}$:[25a]

$$[Cu_2(N4PY2)]^{2+} + 2L \rightarrow [Cu_2(N4PY2)(L)_2]^{2+}$$
$$L = CH_3CN,\ CO,\ PPh_3$$

The order of binding strength to Cu(I) in these complexes appears to be $CH_3CN < CO < PPh_3$ on the basis of the observation that CO displaces CH_3CN in **1a** ($CO:Cu_2 = 1.7 \pm 0.1$, by manometry at 0 °C in CH_2Cl_2) and PPh_3 displaces CO in **1**, and these displacement reactions can be utilized to generate nearly quantitative yields of the substituted products.[25a]

Copper(II) derivatives of N4PY2 have also been synthesized and characterized. Of relevance to the dioxygen-copper chemistry discussed here is the product of oxidation of complexes **1a** or **2** when they are allowed to react with O_2 at temperatures >0 °C or when the dioxygen adducts (**3**) are allowed to decompose by warming to ambient temperatures. Thus, in MeOH or CH_2Cl_2, a compound formulated as $[Cu_2(N4PY2)(OH)_2](PF_6)_2$ (**4**) forms, on the basis of microanalytical data, its behavior as a 2:1 electrolyte, its IR spectrum (ν_{O-H} = 3635 cm^{-1}), and the observed room-temperature magnetic moment of μ = 0.7 μ_B/Cu (EPR silent). We suggest that **4** is a bis(μ-hydroxy)-bridged dicopper(II) complex, having a structure very similar to that known for $[Cu_2(N3PY2)(OMe)_2](ClO_4)_2$.[34] As indicated in the Experi-

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Table II. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³) for Compound **1a**-$(ClO_4)_2$[a]

atom	x	y	z	$U_{equiv/iso}$
Cu(1)	3825 (1)	713 (1)	7599 (1)	55 (1)*
N(1)	5378 (6)	175 (4)	8421 (4)	59 (4)*
N(2)	4427 (6)	1353 (4)	7059 (4)	58 (4)*
N(3)	2868 (6)	−28 (4)	6789 (5)	61 (4)*
N(4)	3024 (6)	1205 (4)	8050 (5)	61 (4)*
C(1)	5713 (9)	178 (5)	9344 (6)	71 (3)
C(2)	4799 (8)	−35 (5)	9512 (6)	69 (3)
C(3)	2623 (9)	1557 (5)	8273 (6)	66 (3)
C(4)	2098 (10)	2043 (5)	8578 (7)	91 (4)
C(21)	3737 (9)	1601 (5)	6263 (6)	65 (3)
C(22)	4083 (8)	2057 (5)	5873 (6)	67 (3)
C(23)	5188 (8)	2282 (5)	6336 (6)	67 (3)
C(24)	5911 (8)	2036 (5)	7152 (6)	67 (3)
C(25)	5508 (8)	1566 (5)	7498 (6)	58 (2)
C(26)	6294 (8)	1259 (5)	8385 (6)	69 (3)
C(27)	6296 (9)	524 (5)	8362 (7)	72 (3)
C(31)	1735 (9)	−23 (5)	6382 (7)	79 (3)
C(32)	1038 (11)	−540 (6)	5825 (7)	94 (4)
C(33)	1587 (11)	−1053 (7)	5726 (8)	101 (4)
C(34)	2714 (10)	−1079 (7)	6116 (7)	97 (4)
C(35)	3374 (9)	−553 (5)	6670 (6)	68 (3)
C(36)	4644 (9)	−560 (6)	7118 (7)	89 (4)
C(37)	5242 (10)	−517 (5)	8106 (7)	87 (3)
Cl	5463 (2)	2321 (2)	1038 (2)	96 (2)*
O(1)	5664 (22)	1932 (9)	557 (11)	314 (23)*
O(2)	5802 (10)	1990 (6)	1817 (6)	169 (8)*
O(3)	4456 (10)	2448 (11)	563 (10)	296 (14)*
O(4)	6144 (16)	2808 (9)	1110 (9)	285 (14)*

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

Table III. Selected Bond Distances (Å) and Angles (deg) for $Cu_2(N4PY2)(CH_3CN)_2](ClO_4)_2$ (**1a**-$(ClO_4)_2$)

	Interatomic Distances		
Cu(1)-N(1)	2.151 (7)	Cu(1)-N(2)	2.029 (9)
Cu(1)-N(3)	2.018 (7)	Cu(1)-N(4)	1.945 (10)
Cu...Cu	7.449		
	Interatomic Angles		
N(1)-Cu(1)-N(2)	98.1 (3)	N(1)-Cu(1)-N(3)	99.7 (3)
N(1)-Cu(1)-N(4)	122.8 (3)	N(2)-Cu(1)-N(3)	113.3 (3)
N(2)-Cu(1)-N(4)	109.9 (3)	N(3)-Cu(1)-N(4)	112.2 (3)

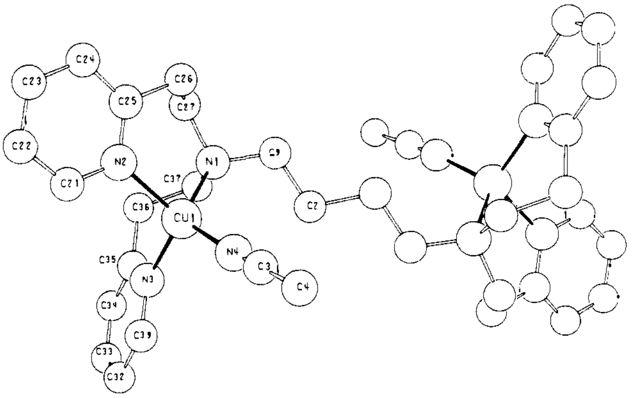

Figure 2. ORTEP diagram of the cationic portion of the bis(acetonitrile) adduct, $[Cu_2(N4PY2)(CH_3CN)_2](ClO_4)_2$ (**1a**-$(ClO_4)_2$), showing the atom-labeling scheme.

mental Section, compound **4** is also a useful precursor for the synthesis of **2**-$(PF_6)_2$; we have found that, using 1,2-diphenylhydrazine as as two-electron reductant, **4** is cleanly reduced to **2**-$(PF_6)_2$ in dichloromethane. Simply, heating complex **4** in acetonitrile under Ar also results in its reduction to **1a**-$(PF_6)_2$;[25a,36] however, the yields are low (≅30%).

Both the ^1H and ^{13}C NMR spectra of N4PY2 and the dicopper(I) complexes **1**, **1a**, and **2** have been obtained (see the Experimental Section), and on the basis of comparisons with other relevant compounds (e.g. 2-picoline[37] and Cu(I) complexes with pyridyl-containing ligands[31,38,39]), the observed resonances have been assigned. Sharp spectra typical of diamagnetic compounds are observed in all cases. As is found for other cases,[31,38,39] the predominating tendency is for a downfield shift of both the ^1H and ^{13}C ligand resonances upon coordination to the positively charged metal ion. This trend is also observed for the other Cu(I)/pyridine[31,39] and Cu(I)/bipyridine[38] systems; the phenomenon has also been observed in Cu(I) complexes with imidazole derivatives[40] although the reverse trend is observed in the recently studied case of a copper(I) adduct of bleomycin.[41] While there seems to be no obvious correlation in the observed chemical shifts (in CH_3NO_2 solvent) when the tricoordinate compounds (**2**) are compared with the tetracoordinate bisadducts (**1** and **1a**), there is a significant upfield shift for the $(CO)_2$ complex, **1**-$(PF_6)_2$, compared to the $(CH_3CN)_2$ derivative, **1a**-$(ClO_4)_2$ (135.3 versus 134.3 ppm, respectively, for the py C4 probe carbon atom[42]). This observation is consistent with a lesser degree of Cu(I) → pyridine π-back-bonding in the $(CO)_2$ complex, due to the stronger Cu(I) → L π-back-bonding for L = CO compared to L = CH_3CN.[38b] The general shift trends observed here for the ^{13}C resonances are also found in the binding of other diamagnetic metal ions to pyridines, and they are consistent with common notions of ligand basicities and M → pyridine π-back-bonding.[42]

Structure of $[Cu_2(N4PY2)(CH_3CN)_2](ClO_4)_2$ (1a-$(ClO_4)_2$). 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 of **1a**-(ClO_4) consists of the discrete $[Cu_2(N4PY2)(CH_3CN)_2]^{2+}$ dication and well-separated ClO_4^- anions; the dication is shown in Figure 2. The complex contains a crystallographic center of symmetry, and each identical Cu(I) moiety possesses ligation to two pyridyl atoms and one amino nitrogen atom of the PY2 unit and one N-bonded CH_3CN molecule in a pseudotetrahedral geometry. The dihedral angles are Cu1-N1-N2/Cu-N3-N4 = 85.3 (1)°, Cu1-N2-N3/Cu1-N1-N4 = 90.3 (1)°, and Cu1-N1-N3/Cu1-N2-N4 = 99.8 (1)°. The Cu1 atom lies 0.86 (1) Å out of the N1-N2-N3 plane, 0.60 (1) Å out of the N1-N3-N4 plane, 0.59 (1) Å out of the N2-N3-N4 plane, and 0.64 (1) Å out of the N1-N2-N4 plane. The Cu⋯Cu separation is 7.449 (2) Å.

The Cu-N_{PY2} bond lengths are normal, with Cu-N_{py} distances typical for tetracoordinate Cu(I) (2.0–2.05 Å[16,28,43]), ca. 0.1 Å longer than the Cu-N_{py} bond lengths observed in tricoordinate Cu(I) structures containing PY2, e.g. $[Cu_2(m\text{-}XYLPY2)](PF_6)_2$ (**5**; two PY2 units connected with a *m*-xylyl group, Cu-N_{py} = 1.91–1.94 Å[28]) and $[Cu(BPY2)](PF_6)$ (**6**; BPY2 = bis[2-(2-pyridyl)ethyl]benzylamine, Cu-N_{py} = 1.87–1.94 Å[33]). The "harder" amine nitrogen atom (N1) bonds more weakly to the Cu(I) ion, with Cu-N1 = 2.151 (7) Å. The nearly linearly coordinated acetonitrile ligand (Cu-N4-C3 = 170.2 (2)°) has a Cu-N4 bond length of 1.945 (10) Å, typical of other Cu-CH_3CN systems[44] but longer than the Cu-N(CH_3CN) distances of 1.85–1.88 Å observed in related dinuclear Cu(I) complexes that

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Table IV. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³) for Compound **2**-$(ClO_4)_2$[a]

atom	x	y	z	$U_{equiv/iso}$
Cu(1)	−348 (1)	100 (2)	−1896 (1)	54 (1)*
Cl(1)	328 (2)	2969 (4)	1296 (2)	70 (3)*
O(1)	−665 (6)	−3657 (9)	−1954 (5)	113 (9)*
O(2)	−1032 (5)	−2320 (9)	−1378 (5)	102 (8)*
O(3)	297 (5)	−2029 (8)	−1169 (5)	95 (7)*
O(4)	49 (7)	−3843 (11)	−738 (6)	160 (10)*
C(1)	−806 (6)	952 (10)	−895 (5)	48 (3)
C(2)	52 (6)	411 (10)	−249 (5)	48 (3)
N(1)	−806 (5)	1452 (8)	−1491 (4)	48 (6)*
N(2)	780 (6)	860 (9)	−1489 (5)	57 (7)*
C(21)	1476 (8)	108 (15)	−1266 (6)	76 (4)
C(22)	2303 (9)	645 (14)	−933 (7)	89 (4)
C(23)	2406 (9)	1939 (14)	−825 (7)	91 (5)
C(24)	1713 (8)	2720 (13)	−1044 (6)	71 (4)
C(25)	901 (7)	2167 (12)	−1370 (6)	56 (3)
C(26)	97 (7)	2940 (11)	−1636 (6)	62 (4)
C(27)	−306 (8)	2682 (11)	−1266 (7)	61 (4)
N(3)	−1394 (5)	−513 (8)	−2830 (4)	53 (6)*
C(31)	−1326 (7)	−1170 (11)	−3296 (6)	57 (3)
C(32)	−2030 (8)	−1438 (11)	−4000 (7)	68 (4)
C(33)	−2833 (8)	−1014 (11)	−4251 (7)	69 (4)
C(34)	−2923 (7)	−355 (10)	−3786 (6)	60 (3)
C(35)	−2203 (7)	−115 (12)	−3076 (6)	54 (3)
C(36)	−2281 (7)	518 (10)	−2549 (6)	61 (4)
C(37)	−1716 (7)	1724 (11)	−2142 (6)	61 (3)

[a] Asterisks indicate values of equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Selected Bond Distances (Å) and Angles (deg) for $Cu_2(N4PY2)](ClO_4)_2$ (**2**-$(ClO_4)_2$)

	Bond Distances		
Cu(1)–N(1)	2.145 (11)	Cu(1)–N(2)	1.934 (10)
Cu(1)–N(3)	1.944 (7)	Cu(1)–O(3)	2.547 (13)
Cu...Cu	6.181		
	Bond Angles		
N(1)–Cu(1)–N(2)	100.5 (4)	N(1)–Cu(1)–N(3)	105.3 (4)
N(1)–Cu(1)–O(3)	114.9 (6)	N(2)–Cu(1)–N(3)	139.6 (5)
N(2)–Cu(1)–O(3)	94.0 (6)	N(3)–Cu(1)–O(3)	102.4 (6)
Cu(1)–O(3)–Cl	115.1 (8)		

contain the Cu–$NS_2(CH_3CN)$ moiety (NS_2 = bis(2-ethylthio)ethylamine).[45]

Structure of $[Cu_2(N4PY2)](ClO_4)_2$ (2-$(ClO_4)_2$). A summary of crystal and refinement data for **2**-$(ClO_4)_2$ is also given in Table I, with final positional parameters provided in Table IV and selected bond lengths and angles listed in Table V. The compound possesses a crystallographic center of symmetry midway along the tetramethylene backbone of the N4PY2 ligand; the cuprous ion polyhedra extend away from each other, with Cu1⋯Cu1′ = 6.181 (2) Å (Figure 3).

Each copper(I) ion is tetracoordinate in the solid state, with ligation to the three nitrogen atoms of the PY2 unit and weak coordination to a single oxygen atom of the ClO_4^- anion. However, since the reactivity and solution behavior of complexes of **2** are predominantly independent of the anion, we consider that the binding of Cu(I) in **2**-$(ClO_4)_2$ is essentially that of a tricoordinate species. When compared to tetracoordinate structures such as $[Cu_2(N4PY2)(CH_3CN)_2](ClO_4)_2$ (**1a**-$(ClO_4)_2$) and $[Cu_2(NnPY2)(CO)_2](PF_6)_2$ (**7**, n = 3; **8**, n = 5),[25a,35] the bonding parameters in **2**-$(ClO_4)_2$ are closer to those observed for purely tricoordinate structures involving PY2. The Cu–N_{py} distances of 1.934 (10) and 1.944 (10) Å in **2**-$(ClO_4)_2$ are close to the bond lengths found in $[Cu_2(m\text{-XYLPY2})]^{2+}$ (**5**,[28] 1.91–1.94 Å) and $[Cu(BPY2)]^+$ (**6**,[33] 1.87–1.94 Å), contrasting with the corresponding values for tetracoordinate structures (2.0–2.5 Å). The N_{py}–Cu–N_{py} angle of 139.6 (5)° in **2**-$(ClO_4)_2$ is also somewhat closer to the values found in **5** and **6** (151–158°) compared to those observed in **1a**-$(ClO_4)_2$, **7**, or **8** (104–108°). Another indication that the coordination of Cu(I) in **2**-$(ClO_4)_2$ is only mildly distorted from tricoordination is that the copper atom is 0.42 (1) Å out of the N1–N2–N3 plane; this compares to the 0.86 (1)-Å corresponding distance in the tetracoordinate compound **1a**-$(ClO_4)_2$. This parameter is observed to be between 0.15 and 0.23 Å in $[Cu_2(m\text{-XYLPY2})]^{2+}$ (**5**). Dihedral angles (between copper-containing planes), which are of interest to compare to the structure of **1a**-$(ClO_4)_2$, are Cu1–N1–N2/Cu1–N3–O3 = 108.4°, Cu1–N1–O3/Cu1–N2–N3 = 88.0°, and Cu1–N2–O3/Cu1–N1–N3 = 107.0°.

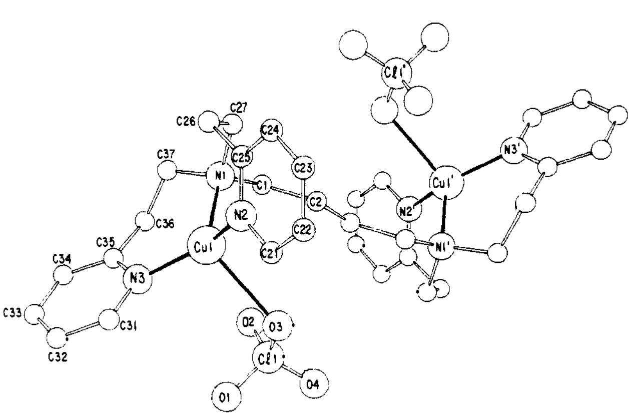

Figure 3. ORTEP diagram of the pseudotricoordinate complex, $[Cu_2(N4PY2)](ClO_4)_2$ (**2**-$(ClO_4)_2$), showing the atom-labeling scheme.

It is of some interest to compare the chemistry and structures of $[Cu_2(N4PY2)(CO)_2]^{2+}$ (**1**), $[Cu_2(N4PY2)(CH_3CN)_2]^{2+}$ (**1a**), and $[Cu_2(N4PY2)]^{2+}$ (**2**) with copper(I) complexes of *N,N,-N′,N′*-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN), reported by Gagne et al.[31] These workers have described similar complexes, i.e. $[Cu_2(TPEN)(CO)_2]^{2+}$, $[Cu_2(TPEN)(CH_3CN)_2]^{2+}$, and $[Cu_2(TPEN)]^{2+}$. Here, the solid-state structure of the $(CO)_2$ adduct is very similar to that of **1a** and $[Cu_2(NnPY2)(CO)_2]^{2+}$,[25a,35] with very similar metal–ligand bonding parameters. However, the TPEN ligand in the absence of CO or CH_3CN is apparently not able to stabilize tricoordination for Cu(I), since in addition to the ligation to three nitrogen donor groups per Cu(I) a significant Cu(I)–Cu(I) interaction is found in $[Cu_2(TPEN)]^{2+}$. The binding of CO in this Cu(I)–TPEN ligand system is also reversible.

Genesis of Dioxygen–Copper Adducts. As mentioned above, when the dicopper(I) complexes of NnPY2, e.g. **1** or **1a**, are oxygenated at ≥0 °C in MeOH or CH_2Cl_2, the irreversible oxidation of copper takes place, giving dinuclear Cu(II) complexes similar to **4**, i.e. $[Cu_2(NnPY2)(OR)_2]^{2+}$ (R = H or Me).[25a] The irreversible oxidation of Cu(I) complexes to give hydroxo or alkoxo complexes is common.[3,49a] While the mechanisms of such reactions are not well understood, it is most often presumed that they proceed through the initial formation of a dioxygen–copper (peroxo–dicopper(II)?) complex, Cu_2–(O_2), which then undergoes further reduction or reaction (e.g. disproportionation) to give oxo and/or hydroxy products derived from fully four-electron-reduced O_2.[2,16] Alternatively, the $[Cu_2(OR)_2]^{2+}$ products may result from the direct displacement of coordinated peroxide by water or alcohol.[14] In order to try to trap and characterize the intermediate Cu_2–(O_2) species, we have carried out low-temperature oxygenations of the dicoppe(I) complexes $[Cu_2(N4PY2)(CH_3CN)_2]^{2+}$ (**1a**) and $[Cu_2(N4PY2)]^{2+}$ (**2**).

When a dichloromethane-containing solution of **1a** or **2** (pale yellow-brown) is cooled to −80 °C and exposed to dioxygen, there is a very rapid change to an intensely brown-colored solution. The color persists, and the solution is stable as long as it is kept cold (<−70 °C); above ca. −40 °C, the green color of the decomposition product can be observed.

Extensive manometric measurements at −80 °C have been carried out in order to determine the stoichiometry of the reaction with O_2. The results conclusively show that the absorption of dioxygen by **1a**, **2**, or decarbonylated solutions of **1** is in the ratio

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Table VI. UV-Vis Spectral Data: Low-Temperature Oxygenation of Dicopper(I) Complexes[a]

dinucleating ligand complex	dicopper(I) complex	dioxygen–copper complex			
$[Cu_2(N4PY2)(CH_3CN)_2](ClO_4)_2$ (**1a**-$(ClO_4)_2$)	350 (3500)	360 (18 700)	458 (6300)	550 sh (1200)	*e*
$[Cu_2(N4PY2)(CH_3CN)_2](PF_6)_2$ (**1a**-$(PF_6)_2$)	350 (3500)	360 (18 700)	458 (6200)	550 sh (1200)	775 sh (160)
$[Cu_2(N4PY2)(CH_3CN)_2](BF_4)_2$ (**1a**-$(BF_4)_2$)		360 (16 500)	458 (5300)	550 sh (1200)	*e*
$[Cu_2(N4PY2)](ClO_4)_2$ (**2**-$(ClO_4)_2$)	350 (3500)	360 (16 000)	458 (4500)	550 sh (1200)	775 sh (200)
$[Cu_2(N4PY2)](PF_6)_2$ (**2**-$(PF_6)_2$[b]	350 (3500)	360 (14 000)	458 (4500)	550 sh (1200)	*e*
$[Cu_2(N4PY2)](PF_6)_2$ (**2**-$(PF_6)_2$)[c]	350 (3500)	360 (16 700)	458 (5300)	550 sh (1200)	*e*
apohemocyanin[d]		345 (20 000)	485 (CD)	570 (1000)	700 (200)

[a] Absorption maxima (λ_{max}) are given in nanometers. Extinction coefficients are based on the dicopper species and are given in parentheses (M^{-1} cm^{-1}). Extinction coefficients are calculated directly from the observed absorbance at a given λ. [b] Data obtained on PE spectrometer. [c] Data obtained via decarbonylation of **1**-$(PF_6)_2$ followed by low-temperature oxygenation. Data obtained on Cary 14 spectrometer.[20] [d] See ref 4 and 6. [e] Data not obtained.

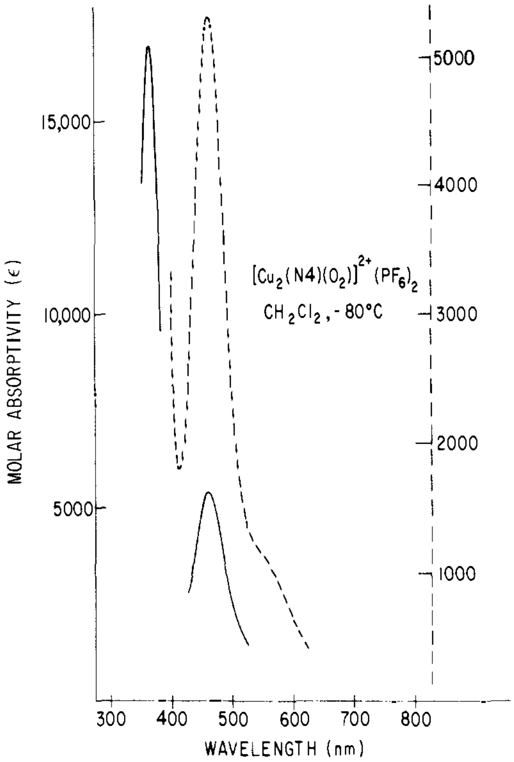

Figure 4. UV-vis spectrum of the dioxygen complex, $[Cu_2(N4PY2)(O_2)](PF_6)_2$ (**3**-$(PF_6)_2$), in CH_2Cl_2 solution at -80 °C, showing the strong bands at 360 and 458 nm and the shoulder at 550 nm. In this case, the dioxygen adduct was produced by the removal (in vacuo) of the CO ligands from $[Cu_2(N4PY2)(CO)_2](PF_6)_2$ (**1**-$(PF_6)_2$) at room temperature, followed by the addition of O_2 at -80 °C.

of Cu:O_2 = 2:1, giving complexes in solution formulated as $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**; Figure 1). Thus, in CH_2Cl_2 solution, $[Cu_2(N4PY2)(CH_3CN)_2](ClO_4)_2$ (**1a**-$(ClO_4)_2$) took up dioxygen in the ratio of 2:0.98 ± 0.02 Cu to O_2 (four trials) while the value for $[Cu_2(N4PY2)](ClO_4)_2$ (**2**-$(ClO_4)_2$) was 2:0.95 ± 0.04 Cu to O_2 (three trials). In addition, when CO was removed from $[Cu_2(N4PY2)(CO)_2](PF_6)_2$ (**1**-$(PF_6)_2$) by repeated vacuum-purging applications in a CH_2Cl_2 solution at room temperature, the resulting solution of $[Cu_2(N4PY2)](PF_6)_2$ (**2**-$(PF_6)_2$) generated in situ absorbed O_2 in the ratio of 2:0.99 Cu to O_2 (one trial) when the reaction flask was cooled to -80 °C.

Low-Temperature UV-Vis Spectra of the Dioxygen Adducts, $[Cu_2(N4PY2)(O_2)]^{2+}$ (3). When dissolved in dichloromethane, the dicopper(I) complexes of N4PY2, $[Cu_2(N4PY2)(CH_3CN)_2]^{2+}$ (**1a**) and $[Cu_2(N4PY2)]^{2+}$ (**2**), exhibit a single absorption band in the UV-vis region (>315 nm), which occurs at 350 nm and has a molar extinction coefficient of ε 3500 M^{-1} cm^{-1}. Upon exposure to O_2 at -80 °C, the intensely brown-colored solutions exhibit strong and multiple absorptions in the 315–700-nm region, with an additional weaker band being observed at still lower energy. The strongest absorption occurs at 360 nm with ε varying between 14 000 and 18 700 M^{-1} cm^{-1}, depending on the anion used (PF_6^-, ClO_4^-, or BF_4^-) and whether or not acetonitrile is present (Table VI). Another distinct absorption occurs at 458 nm (ε 4500–6300 M^{-1} cm^{-1}), and a shoulder is observed at 550 nm (ε 1200 M^{-1} cm^{-1}). A distinct shoulder is also observed at 775 nm (ε 160–200 M^{-1} cm^{-1}). A typical spectrum of the dioxygen adduct, **3**-$(PF_6)_2$, which is derived from oxygenated **2**-$(PF_6)_2$ (produced by decarbonylation of **1**-$(PF_6)_2$), is shown in Figure 4.

The known tendency of dioxygen binding to reduced metal ions to occur with at least some degree of electron transfer[46] and the observed stoichiometry of O_2 binding (Cu:O_2 = 2:1) in the present systems suggest that the dioxygen complexes formulated as $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) can best be described as peroxo–dicopper(II) complexes, i.e. $[Cu^{II}_2(N4PY2)(O_2^{2-})]^{2+}$. Strong support for this formulation comes from the observance of a weak band at 775 nm (Table VI); its intensity and occurrence at relatively low energy allow it to be assigned with confidence as a d–d absorption confirming the presence of Cu(II) with its d^9 electronic configuration. Copper(I) (d^{10}, filled shell) would not possess any ligand field absorption bands. Additional supporting evidence for the presence of Cu(II) in the dioxygen complexes (**3**) comes from X-ray absorption studies, which show that oxygenation of the dicopper(II) complexes at low temperatures results in a loss of the prominent Cu–K absorption edge feature and a shift to values typical of well-characterized dicopper(II) compounds.[47,48]

The extremely intense and multiple UV–vis absorptions observed in this system have not, to our knowledge, been observed in any other Cu(I)/(O_2) synthetic system.[2,16,49] It is also striking that the spectrum of $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) and the closely related analogues of $Cu_2(NnPY2)(O_2)]^{2+}$ (n = 3 and 5)[20] bear close similarities to the spectrum of oxyhemocyanin, for which bands are observed at 345 nm (ε 20 000 M^{-1} cm^{-1}) and 570 nm (ε 1000 M^{-1} cm^{-1}); there is also a circular dichroic (CD) feature at 485 nm (Table VI). All of these absorptions have been assigned as peroxo-to-Cu(II) ligand-to-metal charge-transfer (LMCT) transitions.[4-6] A large body of data, including extensive spectroscopic characterizations, has established that the binding of O_2 in oxy-Hc occurs via an intramolecular redox reaction to give a peroxo-bridged dicopper(II) center. The similarity of the electronic absorption spectra observed for $[Cu_2(NnPY2)(O_2)]^{2+}$ (**3**) and oxy-Hc, along with the same 2:1 Cu to O_2 binding

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(46) Gubelmann, M. H.; Williams, A. F. *Struct. Bonding (Berlin)* **1983**, *55*, 1 and references cited therein.

(47) Blackburn, N. J.; Strange, R. W.; Farooq, A.; Haka, M. S.; Karlin, K. D. *J. Am. Chem. Soc.*, in press.

(48) As yet, we have been unable to obtain a value for the O–O stretching vibration of the coordinated dioxygen moiety. Initial attempts with resonance Raman spectroscopy resulted in decomposition of the samples (observations of J. E. Pate, Stanford University).

(49) Other copper complex systems that have been reported to bind dioxygen reversibly are given in ref 2 and 3. Specific examples are: (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) Merrill, C. L.; Wilson, L. J.; Thamann, T. J.; Loehr, T. M.; Ferris, N. S.; Woodruff, W. H. *J. Chem. Soc., Dalton Trans.* **1984**, 2207–2221 and references cited therein. (d) Casella, L.; Silver, M. S.; Ibers, J. A. *Inorg. Chem.* **1984**, *23*, 1409–1418. (e) Nishida, Y.; Takahashi, K.; Kuramoto, H.; Nida, S. *Inorg. Chim. Acta* **1981**, *54*, L103–L104. (f) Bulkowski, J. E.; Burk, P. L.; Ludmann, M.-F.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 498–499.

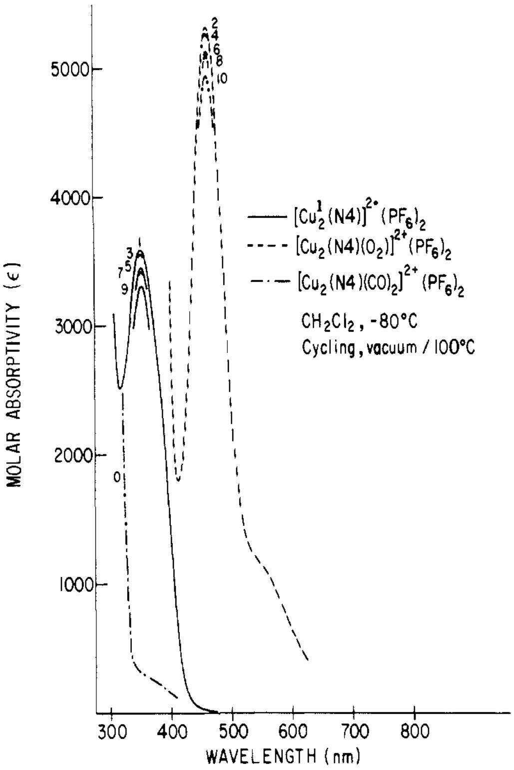

Figure 5. UV-vis spectra demonstrating the reversible dioxygen binding behavior of $[Cu_2(N4PY2)]^{2+}$ (**2**) in CH_2Cl_2 (vacuum cycling). The dicarbonyl complex, $[Cu_2(N4PY2)(CO)_2](PF_6)_2$ (**1**-$(PF_6)_2$) (spectrum 0), is used as a convenient starting material for the experiments, and it is decarbonylated in vacuo at room temperature using $[Cu_2(N4PY2)](PF_6)_2$ (**2**-$(PF_6)_2$) (spectrum 1, λ_{max} 350 nm). Oxygenation at -80 °C generates the dioxygen adduct, $[Cu_2(N4PY2)(O_2)](PF_6)_2$ (**3**-$(PF_6)_2$) (spectrum 2, λ_{max} 458 nm). Application of a vacuum to the solution and rapid warming to 100 °C remove the bound dioxygen ligand, regenerating the dicopper(I) complex, $[Cu_2(N4PY2)](PF_6)_2$ (**2**-$(PF_6)_2$) (spectrum 3). This cycling can be repeated several times, as shown. The stronger 360-nm absorption of **3**-$(PF_6)_2$ is not shown.

stoichioimetry, further suggests that the three strong absorption bands observed for **3** are also peroxo → Cu(II) LMCT transitions. The observation of more than two such absorptions indicates that these synthetic species possess a peroxo ligand that bridges two Cu(II) atoms (see futher discussion below).[4,6]

The peak positions and molar extinction coefficients (ε) listed in Table VI are derived from multiple measurements on the dioxygen adducts **3** and are probably good to at least ±10% in the value of ε. We feel that while the differences in ε observed for the different anions are relatively small, they may be significant. As also seen in Table VI, the presence of CH_3CN in the starting dicopper(I) precursor also seems to result in larger values of ε. Since each Cu(II) center in $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) is likely to be at most tetracorodinate with ligation to the three nitrogen donors of PY2 and an oxygen atom of a peroxo ligand, additional weak binding of a Lewis basic ligand such as CH_3CN or an anion seems likely, and this may be manifested in the observed anion and CH_3CN dependence of the electronic spectra of these dioxygen complexes (Table VI). The low temperature might also be a factor that favors such a binding process.

Reversible Binding of Dioxygen. Vacuum Cycling. The reversibility of dioxygen binding to solutions of **1a** and **2** is indicated by several lines of evidence including the ability to oxygenate these complexes and deoxygenate the resulting solutions of $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) in a quasi-reversible manner. This process can be repeated several times without severe decomposition, and this vacuum cycling can be followed spectrophotometrically as shown in Figure 5. In this experiment, $[Cu_2(N4PY2)(CO)_2](PF_6)_2$ (**1**-$(PF_6)_2$) is dissolved in CH_2Cl_2 under Ar and the spectrum recorded at -80 °C (featureless spectrum 0). Removal of the bound CO ligands by application of vacuum/Ar-purge cycles at room temperature gives a solution of $[Cu_2(N4PY2)](PF_6)_2$ (**2**-$(PF_6)_2$), having a spectrum with a peak at 350 nm at -80 °C (spectrum 1). The introduction of O_2 produces the dioxygen adduct, $[Cu_2(N4PY2)(O_2)](PF_6)_2$ (**3**-$(PF_6)_2$), and the band with the 458-nm absorption maximum is shown as spectrum 2 in Figure 5. When this solution is subjected to a static vacuum and rapidly and briefly (1–5 s) heated to 100 °C, the intense deep brown color is lost. At this point, any lost solvent is replaced, the solution is cooled again to -80 °C, and the spectrum now obtained is 3 (Figure 5), showing the complete loss of the 458-nm absorption and the regeneration of the dicopper(I) complex, $[Cu_2(N4PY2)](PF_6)_2$ (**2**-$(PF_6)_2$). Reoxygenation at low temperature affords **3**-$(PF_6)_2$ (spectrum 4), showing very little loss in absorption intensity, and the cycling between oxy and deoxy forms, i.e. **2** + $O_2 \Leftrightarrow$ **3**, can be repeated at least five times as shown, with only a small amount of decomposition (ca. 10%, as judged by the reduced absorbance at 458 nm, Figure 5).

We have also confirmed that there is a gas removed when a vacuum is applied to solutions of $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**), as described, and that it is dioxygen. When the vacuum cycling is carried out on a larger scale on the bench top, it can be performed in a closed system; a static vacuum is applied to the solution of **3**, and when it is heated, the liberated gas plus some of the volatile CH_2Cl_2 solvent is trapped by placing a flask, which is attached to the system, in a cold bath at −196 °C. Bench-top cycling experiments can be performed by allowing the trapped dioxygen gas to warm up back into a rechilled (−80 °C) solution of the deoxygenated complex $[Cu_2(N4PY2)]^{2+}$ (**2**) and repeating.[25a] If, instead, the flask containing the trapped gas (O_2) is (a) closed off and separated from the reacting dicopper solution, (b) attached to a flask containing a degassed colorless alkaline pyrogallol (1,2,3-trihydroxybenzene) test solution,[16,25] and (c) allowed to warm up, the pyrogallol test solution turns brown, qualitatively identifying dioxygen as the gas that is liberated upon application of a vacuum to solutions of $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**).[50]

Reversible Binding of O_2 and CO and Displacement of O_2 by CO. Carbonyl Cycling. As has already been indicated, the binding of CO to solutions of $[Cu_2(N4PY2)]^{2+}$ (**2**) readily occurs (solution IR and manometric evidence), and this is a reversible process. The carbonylation of **2** is effected by bubbling its CH_2Cl_2 solution with CO, while decarbonylation occurs by the application of reduced pressure to dichloromethane solutions of $[Cu_2(N4PY2)(CO)_2]^{2+}$ (**1**; Figure 1).

In order to produce the dioxygen adduct, $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**), it is necessary to start with solutions of $[Cu_2(N4PY2)]^{2+}$ (**2**) or $[Cu_2(N4PY2)(CH_3CN)_2]^{2+}$ (**1a**), since we observe that, at temperatures low enough to stabilize $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) (<−60 °C), O_2 will not react with the carbonyl adduct, $[Cu_2(N4PY2)(CO)_2]^{2+}$ (**1**). It is thus apparent that at reduced temperatures the binding of CO to $[Cu_2(N4PY2)]^{2+}$ (**2**) is stronger than that of O_2, and CO can be used to displace the bound dioxygen (peroxo) ligand, thereby allowing for carbonyl cycling to take place (see also Figure 1). This process can be followed spectrophotometrically, as shown in Figure 6.

After the spectrum of $[Cu_2(N4PY2)(CO)_2]^{2+}$ (**1**; featureless spectrum 0, Figure 6) was recorded at -80 °C, the solution of this complex is decarbonylated at room temperature (vacuum/purge cycles) and rechilled to give $[Cu_2(N4PY2)]^{2+}$ (**2**, spectrum 1), which is then exposed to dioxygen to give $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**, spectrum 2). This solution is saturated with CO by directly bubbling the gas into the solution of **3** in the cuvette assembly (or by introducing CO via vacuum/purge cycles), and it is allowed to warm slightly above -80 °C in the air, with shaking, until the

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(50) We have also attempted to quantitate the amount of O_2 given off in the vacuum cycling experiment by allowing the dioxygen trapped at −196 °C (after removal from **3**) to react with a CH_2Cl_2 solution of the dicopper(I) complex $[Cu_2(QPY2)(CH_3CN)_2](PF_6)_2$ (**9**, QPY2 is a derivative of *m*-XYLPY2; Karlin, K. D.; Cohen, B. I., unpublished results), which is known to react with O_2 in the ratio of 4:1 Cu to O_2 and gives a stable precipitate of known formula weight. In this manner, it was found that 82% of the dioxygen expected to be pulled off from **3** was recovered in the form of a solid oxygenated product of **9**.[25a]

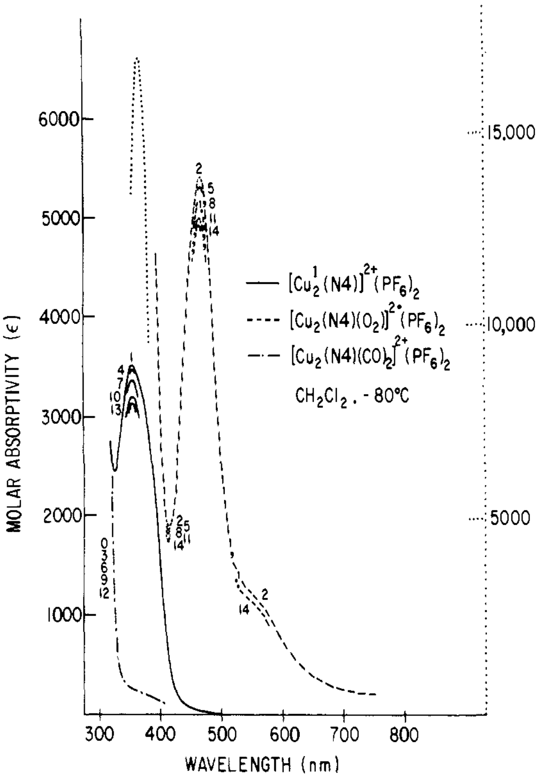

Figure 6. UV-vis spectra demonstrating the reversible O_2 and CO binding behavior of $[Cu_2(N4PY2)](PF_6)_2$ (**2**-$(PF_6)_2$) in CH_2Cl_2 (carbonyl cycling). The dicarbonyl complex, $[Cu_2(N4PY2)(CO)_2](PF_6)_2$ (**1**-$(PF_6)_2$) (featureless spectrum 0), is used as convenient starting material for the experiments and decarbonylated in vacuo at room temperature to give (**2**-$(PF_6)_2$) (spectrum 1, λ_{max} 350 nm). This solution is oxygenated at -80 °C to produce the dioxygen adduct, $[Cu_2(N4PY2)(O_2)](PF_6)_2$ (**3**-$(PF_6)_2$) (spectrum 2, λ_{max} 458 nm). This solution is then saturated with CO, and with some warming, the O_2 ligand is displaced and the dicarbonyl complex, **1**-$(PF_6)_2$, is regenerated (spectrum 3). The process can be repeated, and five cycles are shown. This figure also shows the 360-nm absorption band of **3**-$(PF_6)_2$ (···).

intense brown color due to **3** bleaches. Recooling and equilibration at -80 °C gave spectrum 3, which is characteristic of the dicarbonyl adduct, $[Cu_2(N4PY2)(CO)_2]^{2+}$ (**1**). This cycle of decarbonylation of $[Cu_2(N4PY2)(CO)_2]^{2+}$ (**1**) to give $[Cu_2(N4PY2)]^{2+}$ (**2**), oxygenation of **2** at low temperature to give $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**), and displacement of O_2 by CO to give back **1** (Figure 1) can be repeated many times, as shown in Figure 6. From the absolute decrease in the absorbance of the 485-nm peak of $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) (Figure 6), there is only a few percent loss of the dioxygen adduct per cycle, presumably due to decomposition.

As found for the vacuum cycling experiment, dioxygen is seen to be evolved from solutions of $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) when they are subjected to carbon monoxide as described above. A dichloromethane solution of $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) at -80 °C can be purged of any excess O_2 in the solvent, by either (a) alternating vacuum/purge cycles under argon or (b) flushing the solution with Ar or CO. When such a solution of **3** is bubbled continuously with carbon monoxide at -80 °C and the gas that passes through the solution is then bubbled through a clear and colorless pyrogallol test solution, no change occurs since CO does not displace O_2 from **3** under these conditions. However, when the solution of $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) is warmed up with shaking while bubbling with CO, the test solution turns brown, indicative of the presence of dioxygen.

To further confirm the integrity of the ligand and complex in the displacement reaction of O_2 in $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) by CO, it was performed on a synthetic scale in a bench-top experiment. When $[Cu_2(N4PY2)(CH_3CN)_2](ClO_4)_2$ (**1a**-$(ClO_4)_2$) is oxygenated to give the dioxygen adduct, **3**, and the O_2 is displaced by using excess carbon monoxide, an 89% yield of recovered crystalline product, $[Cu_2(N4PY2)(CO)_2](ClO_4)_2$ (**1**-$(ClO_4)_2$), is obtained (see the Experimental Section).

The possibility that CO_2 might be produced by the reaction of CO with $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) was also checked. Instead of passing the CO gas stream through a cold solution of $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) into a pyrogallol test solution, it was instead bubbled directly into an aqueous $Ba(OH)_2$ solution. No detectable precipitate of $BaCO_3$ was observed (see the Experimental Section), indicating that CO_2 is not produced in this reaction. A recent report suggests that a carbonato complex is produced when $[Cu_2(N-N)_2Im_2O_2]I_2$ is reacted with CO; the latter complex is postulated to form when $[Cu_2(N-N)_2I_2]$ is reacted with O_2 in the presence of 2-methylimidazole (Im) (N-N = 2,2′-bipyridine or 1,10-phenanthroline).[51]

It is also interesting to note the reactivity of PPh_3 with $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) compared to the corresponding reaction with the dioxygen (peroxo) adduct $[Cu_2(XYL-O-)(O_2)]^+$ (**B**). At -80 °C, the reaction of PPh_3 with **B** results in the rapid displacement of the O_2 ligand to give the bisadduct $[Cu_2(XYL-O-)(PPh_3)_2]^+$ and dioxygen gas; no oxidation of triphenylphosphine occurs.[16] However, no O_2 gas is evolved at any temperature when **3** is reacted with PPh_3. A less than stoichiometric amount of $O{=}PPh_3$ is produced in the reaction of **3** with 2 equiv of PPh_3, and even when an excess of triphenylphosphine is added, the reaction is sluggish and the yield of $O{=}PPh_3$ is low. Thus, $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) does not efficiently oxygenate a substrate as easily oxidizable as PPh_3. On the other hand, O_2 is not displaced from **3** by PPh_3 (no O_2 evolution) in spite of the fact that $[Cu_2(N4PY2)(PPh_3)_2]^{2+}$ is a stable complex.[25a]

$$[Cu_2(N4PY2)(O_2)]^{2+}\ (\mathbf{3}) + 2PPh_3 \nrightleftharpoons [Cu_2(N4PY2)(PPh_3)_2]^{2+} + O_2$$

Biological Relevance and Possible Structure of $[Cu_2(N4PY2)(O_2)]^{2+}$ (3). Extensive chemical, spectroscopic, and X-ray structural studies have contributed to a fairly detailed picture of the active site of the dioxygen-carrying arthropod and mollusc hemocyanins. Earlier studies had suggested that two or three imidazole ligands from histidine coordinate to the Cu(I) ions at a dinuclear metal center in deoxy-Hc. The recent X-ray structure of the spiny lobster Hc, *Panulirus interruptus*, shows that the two cuprous ions in this deoxy-Hc are each coordinated to three imidazole nitrogen ligands in a hydrophobic environment, with an observed Cu···Cu separation of 3.8 ± 0.4 Å.[52] As mentioned above, oxy-Hc is produced in a reaction with dioxygen to give a dinuclear Cu(II) center and a coordinated peroxo (O_2^{2-}) ligand. Detailed chemical investigations as well as spectroscopic considerations suggest that each copper(II) ion is found in a tetragonal coordination environment with ligation to either four or five donors including a *cis*(μ-1,2-peroxo) moiety. Consistent with these hypotheses are the results from extended X-ray absorption fine structure (EXAFS) measurements, which indicate a Cu···Cu separation of ca. 3.6 Å.[53] The presence of an "endogenous" bridging ligand in oxy-Hc has been proposed[4-6,54] primarily on the basis of the observations that (a) there are striking analogies between certain properties of oxy-Hc and the "met" oxidized

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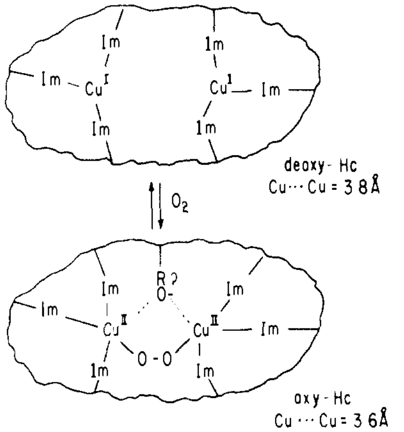
dicopper(II) forms of Hc (i.e., the N_3^- derivative[53d,55]), including the very strong magnetic superexchange coupling, and (b) there is an otherwise unassigned absorption band at 420 nm for oxy-Hc, possibly due to an "endogenous" bridging ligand-to-Cu(II) LMCT transition. The presence of a possible protein-derived bridging ligand (e.g., endogenous tyrosine or serine) is not supported by the results of the recent X-ray structural analysis,[52] such that if there is a bridging ligand (other than O_2^{2-}) at all, hydroxide[56] or water seem to be the only likely candidates.

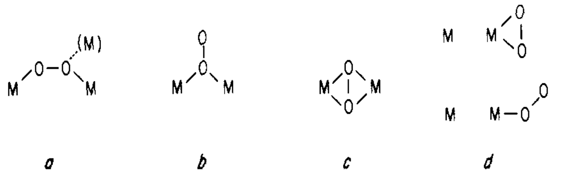


As discussed above, the dicopper(I) complexes $[Cu_2(N4PY2)]^{2+}$ (**2**) react with O_2 and CO reversibly, and in the former case the dioxygen adducts formed ($[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) possess at least three strong absorption bands in the UV–vis region, comparing closely to what is observed for oxy-Hc. In itself, the presence of more than two charge-transfer bands suggests that the peroxo ligand bridges the two Cu(II) ligands.[4,6] Since the ligands NnPY2 have no potential Cu···Cu bridging group, these results indicate that a Cu···Cu bridging ligand (besides perhaps O_2^{2-} itself) is *not* a prerequisite for systems capable of binding CO and O_2 reversibly and of exhibiting spectral features reminiscent of oxyhemocyanin.

We observe that $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) is EPR silent, based on measurements taken in frozen CH_2Cl_2 or CH_2Cl_2/toluene solutions (77 K) (see the Experimental Section). We also find that solutions of **3** at −80 °C exhibit ^1H NMR spectra essentially unchanged from those of the precursor complexes $[Cu_2(N4PY2)]^{2+}$ (**2**); the proton resonances due to the N4PY2 ligand are unshifted in **3** compared to those observed for **2**, although there is some loss (ca. 20–30%) in intensity.[25a] Although further characterization of $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) by magnetic susceptibility techniques will be necessary, the observed NMR and EPR properties suggest that **3** is either diamagnetic or strongly magnetically coupled. These observations lead us to speculate that a single peroxo bridging ligand for two Cu(II) ions may be sufficient to provide the strong antiferromagnetic coupling observed here, and possibly in oxyhemocyanin, as well. Of possible relevance to this suggestion is the observation that a number of monohydroxo-bridged dicopper(II) complexes possess strongly magnetically coupled metal centers.[56] An extension of this discussion would lead to the speculation that an endogenous bridging ligand is not required to account for the observed EPR silence and strong magnetic coupling observed in oxy-Hc. As stated above, this would be in accord with the recent crystal structure of deoxy-Hc. However, this does not rule out the possibility that, along with peroxo bridging of Cu(II) ions, a μ-aquo[49a] or μ-hydroxo[56a] ligand is present; the lack of the proposed "endogenous" bridge would not account for the presence of the absorption band at 420 nm in oxy-Hc.

The coordination environment and mode of binding of the O_2 (peroxo) ligand in $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) is of considerable interest since there is no unambigously structurally characterized dioxygen adduct of copper known at present.[2] In addition, the extremely unusual and interesting spectral features observed in $[Cu_2(NnPY2)(O_2)]^{2+}$ are of general interest in relating spectroscopic features to structure. At present, we have been unable to isolate a stable solid form of $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**), although current efforts in our laboratories are directed toward the use of modified ligands that may improve the thermal stability of these systems. Thus, we are presently using low-temperature solution techniques such as resonance Raman and EXAFS[47] spectroscopy in order to define the dioxygen (peroxo)–copper coordination.

Several possible modes of binding of a peroxo ligand to a dinuclear metal center are known (*a*–*d*).[1,2,46] The μ-1,2-peroxo coordination to Cu(II) (*cis*- or *trans*-*a*) is suggested for oxy-Hc and has been proposed (by analogy to Hc) in coordination complexes reported by Wilson[49c] and Casella.[49d] These and other model systems[49] are also reported to bind dioxygen reversibly. The μ-1,2-type of coordination (cis or trans) is well established for peroxo- and superoxocobalt(III) compounds.[46] A μ-1,1-peroxo bridging mode (*b*) had been considered and ruled out for oxy-Hc[57] and oxyhemerythrin[58] (non-heme diiron O_2 carrier), but such an entity has been proposed in cobalt systems[59] and a protonated hydroperoxodicobalt(III) complex with this binding mode has been structurally characterized.[60] Another possibility is structure *c*; a few such η^2:η^2-dioxygen complexes are known.[46] The coordination of the peroxo ligand to one copper(II) ion at a dinuclear center (*d*) would seem unlikely, but as is indicated in the introduction, the peroxo ligand in complex B is now established to be terminal in character.[16,17]



As discussed, complex $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**) is indicated to be a peroxo–dicopper(II) complex, based on (a) the presence of a d–d band, (b) the further identification of Cu(II) in **3** from X-ray absorption studies,[47] and (c) the observed Cu:O_2 = 2:1 dioxygen binding stoichiometry. Although we cannot unambiguously rule out the possibility of cluster formation (e.g. $\{[Cu_2(N4PY2)(O_2)]^{2+}\}_n$) in the present system, the rapid rate of dioxygen absorption in dilute solutions of $[Cu_2(N4PY2)]^{2+}$ (**2**) at −80 °C, and the observed marked dependence upon *n* of the CT absorption band positions in $[Cu_2(NnPY2)(O_2)]^{2+}$,[20] suggests that dioxygen binding to **2** is an intramolecular process and that **3** is a dinuclear complex.

While the UV–vis spectra of the peroxo complexes, $[Cu_2(NnPY2)(O_2)]^{2+}$ (**3**), and that observed for oxy-Hc's are very similar, a distinct difference is that a strong absorption band is seen in the 400–500-nm region in **3** (Table VI), but the corresponding band is only seen in the CD spectrum of mollusc oxy-Hc's. A nonplanar structure of the ligand/Cu_2/O_2 unit with symmetry lower than C_{2v} is thus suggested for these complexes, $[Cu_2(NnPY2)(O_2)]^{2+}$. Group-theoretical arguments by Solomon and co-workers[4,6] show that the LMCT band seen at 480 nm in the CD and not the absorption spectrum of oxy-Hc is as expected for a planar C_{2v} Cu^{II}_2–(O_2^{2-}) structure. Lowering the symmetry by tilting the coordinated peroxo group out of plane should "allow" absorption intensity into this band; this indeed occurs in arthropod oxy-Hc's compared to those of molluscs where one sees an increase

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in the absorption intensity in the region of 480 nm for the arthropods.[61]

On the basis of the UV-vis properties, model-building studies, and initial observations concerning the reactivity of these $Cu_2(NnPY2)(O_2)]^{2+}$ complexes,[62] we currently favor either a nonplanar structural type *a* or *c* for the coordinated peroxo group in $Cu_2(N4PY2)(O_2)]^{2+}$ (**3**). EXAFS spectroscopic studies on **3** and the other $[Cu_2(NnPY2)(O_2)]^{2+}$ complexes are in progress,[47] and these may be useful in distinguishing between structural possibilities.

Summary

We have presented evidence that, at low temperatures, the reaction of dioxygen with the dicopper(I) complex, $[Cu_2(N4PY2)]^{2+}$ (**2**), results in the formation of a dioxygen/copper adduct, $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**), which is best described as a peroxo–dicopper(II) species. The binding of O_2 is reversible (Figure 1), and cycling experiments can be carried out such that O_2 can be removed from **3** by the application of a vacuum, resulting in the regeneration of **2** and the recovery of dioxygen. In addition, carbon monoxide can be used to displace dioxygen from **3**, such that when CO is reacted with $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**), O_2 is liberated, and the dicarbonyl adduct, $[Cu_2(N4PY2)(CO)_2]^{2+}$ (**1**), is formed. The carbon monoxide ligands in **1** can then be removed at room temperature under a partial vacuum, with the regeneration of **2**; subsequent cooling and addition of O_2 result in the reformation of the dioxygen adduct, **3**. No oxidation product (e.g. CO_2 or carbonates or oxidized N4PY2 product) has been observed in these reactions.

The electronic absorption spectrum of the dioxygen complex **3** and the other $[Cu_2(NnPY2)(O_2)]^{2+}$ species bear a close resemblance to that observed for oxyhemocyanins. The most striking aspect of these synthetic efforts involving Cu–O_2 reactivity using NnPY2 ligands is the ability to produce a system with the multiple and exceedingly strong CT bands, particularly the near-UV band (360 nm (ϵ 14 000–19 000 M^{-1} cm^{-1}) for **3**, Table VI; 345 nm (ϵ 20 000 M^{-1} cm^{-1}) for oxy-Hc). The presence of a strong band (ϵ 3500–5500 M^{-1} cm^{-1}) in the 400–500-nm region for $[Cu_2(NnPY2)(O_2)]^{2+}$ may possibly be explained by a distortion from planarity of the $Cu(II)_2$–$(O_2{}^{2-})$ unit in these synthetic systems, a necessity which is also borne out by an examination of molecular models of possible structures of $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**).

Thus, we have been able to mimic to a significant extent a number of properties of hemocyanins, including the reversible binding of CO and O_2 and the major features of the UV-vis spectroscopy. Current efforts include further structural and spectroscopic characterization of the dioxygen complexes, examination of their reactivity, and systematic modification of the NnPY2 ligands.

Acknowledgment. We thank the National Institutes of Health for their generous support of this research. We also acknowledge Professor E. I. Solomon and J. E. Pate of Stanford University and Dr. N. J. Blackburn of UMIST, England, for helpful discussions. We also thank Brett Cohen for help in obtaining NMR spectra.

Registry No. **1**-$(PF_6)_2$, 98218-45-2; **1**-$(ClO_4)_2$, 112022-76-1; **1a**-$(PF_6)_2$, 112022-70-5; **1a**-$(ClO_4)_2$, 112022-71-6; **1a**-$(BF_4)_2$, 112022-77-2; **2**-$(PF_6)_2$, 112022-72-7; **2**-$(ClO_4)_2$, 112022-73-8; **3**, 112022-74-9; **4**, 112022-75-0; N4Py2, 98218-51-0; $[Cu(CH_3CN)_4](PF_6)$, 64443-05-6; 1,4-diaminobutane, 110-60-1; 2-vinylpyridine, 100-69-6.

Supplementary Material Available: Listings of bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors for complexes **1a**-$(ClO_4)_2$ (Tables VIII–XI) and **2**-$(ClO_4)_2$ (Tables XIII–XVI) (8 pages); listings of observed and calculated structure factors for **1a**-$(ClO_4)_2$ (Table VII) and **2**-$(ClO_4)_2$ (Table XII) (16 pages). Ordering information is given on any current masthead page.

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[62] Preliminary indications are that these dioxygen complexes are relatively unreactive, and thus we think that the O_2 is very tightly bound (e.g. possibly mode *c*). An example of this is the observation that at −80 °C *no* reaction (as followed spectroscopically) occurs upon the addition of 2 equiv of a strong acid (e.g. HPF_6) to $[Cu_2(N4PY2)(O_2)]^{2+}$ (**3**). Thus, the coordinated $O_2{}^{2-}$ moiety in **3** is not basic; this is in contrast to the corresponding result obtained with $[Cu_2(XYL\text{-}O\text{-})(O_2)]^+$ (**B**), where protonation readily produces a hydroperoxo complex, $[Cu_2(XYL\text{-}O\text{-})(O_2H)]^{+}$.[19]

A Deoxymyoglobin Model with a Sterically Unhindered Axial Imidazole

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Contribution from the Institut Curie, Section de Biologie, Centre Universitaire, 91405 Orsay, France, the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556, and the Department of Chemistry, University of Southern California, Los Angeles, California 90089-1062. *Received June 8, 1987*

Abstract: With use of an $\alpha,\alpha,\alpha,\alpha$-tetra-*o*-amido functionalized tetraphenylporphyrin having *trans*-dipivalamido pickets and a *trans*-NH–C(O)–$(CH_2)_6$–C(O)–NH– strap, a single-face hindered porphyrin is produced. Its iron(II) complex attains only five-coordination with the unhindered axial ligand 1-methylimidazole. The product has been isolated as a toluene solvate and characterized by magnetic susceptibility ($\mu_{eff}{}^{300K}$ = 5.4 μ_B), Mossbauer spectroscopy (ΔE_q = 2.3 mm/s, δ = 0.88 mm/s at 4.2 K), and single-crystal X-ray structure analysis as a five-coordinate high-spin iron(II) complex. Crystal data: $FeO_4N_{10}C_{66}H_{64}$-C_7H_8, monoclinic, space group $P2_1$, cell constants a = 13.075 (2) Å, b = 17.821 (3) Å, c = 13.862 (2) Å, and β = 89.97 (1)°, Z = 2, 2388 unique observed data (average of two forms), all measurements at 292 K. The complex has an average Fe–N_p bond distance of 2.075 Å, an axial Fe–N distance of 2.134 Å, and an iron(II) displacement of 0.34 Å from the mean plane of the 24-atom core. The structure is compared to other five-coordinate imidazole-ligated metalloporphyrin species reported in the literature. Of greatest interest is the comparison with previously characterized five-coordinate 2-methylimidazole-ligated iron(II) complexes where the 2-methyl substituent on imidazole is the means used to attain five-coordination. A smaller iron atom displacement and less imidazole tilting result from the absence of a 2-methyl group, and these results support the idea of a constrained proximal histidine in T-state deoxyhemoglobin.

Five-coordination in deoxymyoglobin and deoxyhemoglobin is a textbook example of protein control of axial ligation in hemoproteins. Of the several histidine residues in the polypeptide chain only one, the so-called proximal histidine,[4] coordinates to the

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