A Dicopper(I) Complex and Its Oxygenation Chemistry Using a Dinucleating Ligand with a Pendant Alkene Group

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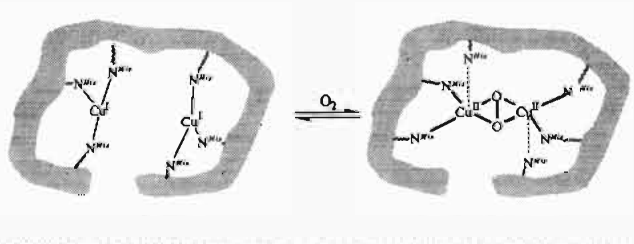
Received July 30, 1993®

A dicopper(I) complex with new dinucleating ligand has been synthesized and structurally characterized and its reactivity with dioxygen investigated. The N3OR$_1$ ligand contains two tridentate PY2 (PY2 = bis[2-(2-pyridyl)-ethyl]amine) chelating groups with connecting group possessing an appended cinnamoyl group. An X-ray structure of $[Cu_2(N3OR_1)](PF_6)_2$ (**1**) reveals unsymmetrical coordination of Cu(I) ions; one metal ion is three-coordinate, exhibiting typical ligation to the PY2 unit, while the other is tetracoordinate, also binding the cinnamoyl alkene group. ^{1}H-NMR spectroscopy confirms alkene coordination in solution, while temperature-dependent studies reveal a dynamic behavior indicating the alkene switches ligation between cuprous ions. Below ~−70 °C, binding of O_2 ($Cu/O_2 = 2{:}1$, manometry) to yellow complex **1** gives a stable adduct $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (**2**), characterized by strong charge-transfer absorptions, $\lambda_{max} = 354$ nm, $\epsilon = 26\,500$ M^{-1} cm^{-1}. By analogy to other complexes, **2** is best described as a peroxo-dicopper(II) species, most likely with a *bent* side-on μ-$\eta^2{:}\eta^2$-peroxo bridging ligand, also consistent with the observed diamagnetism (i.e., near normal ^{1}H-NMR spectrum at −90 °C and EPR silent). The binding of O_2 to **1** is reversible, as shown by the ability to cycle between **1** and **2**, via removal of dioxygen from **2** by application of a vacuum while heating. At room temperature, reaction of **1** with O_2 gives a green dicopper(II) complex, suggested to be an oxo-bridged species $[Cu_2(N3OR_1)(O)](PF_6)_2{\cdot}CH_2Cl_2$ (**3**), typical of reactions involving 4 $Cu(I)/O_2$ chemistry. The N3OR$_1$ ligand remains intact under these conditions, indicating that no oxidation or other reaction has occurred on the cinnamoyl group, in spite of its proximity to the Cu_2–O_2 which formed during the reaction. Possible reasons for this, and the relationship of dioxygen complex **2** to other protein or synthetically derived copper–dioxygen complexes is discussed.

Introduction

Dioxygen interactions with dinuclear Cu(I) species occur in both biological and inorganic chemistry.[1–3] A dicopper(I) center is readily amenable to 2e$^-$ oxidation by O_2 to generate a dicopper(II) species with concomitant 2e$^-$ reduction of dioxygen to peroxide. The resulting $Cu_2^{II}(O_2^{2-})$ species is recognized as an active intermediate or product in at least two Cu enzymes, namely, hemocyanin[2–4] and tyrosinase.[3,5] Hemocyanin is an O_2-carrier protein in arthropods and molluscs; the deoxy dicopper(I) form (Cu---Cu = 4.6 Å)[4b] reversibly binds O_2 via its 2e$^-$ reduction to O_2^{2-}. A similar active site has been identified for tyrosinase, a monooxygenase that catalyzes ortho hydroxylation of phenols to catechols with further oxidation to quinones.[3,5] Biological activation of O_2 for substrate oxygenation reactions is not limited to dinuclear copper centers. For instance, dopamine β-hydroxylase effects the oxygenation of a benzylic C–H bond but is also capable of oxidative N-dealkylation and olefin oxygenation reactions.[6] A recent study implicates a trinuclear copper center and its O_2 chemistry in alkane hydroxylation, i.e., in membrane-bound *particulate*-methane monooxygenase.[7]



A number of synthetic $\{Cu_2$–$O_2\}$ complexes have been generated by oxygenation of mono- or dinuclear copper(I) precursors.[2,8] These include two structurally characterized species, (i) one with a trans μ-1,2-peroxodicopper(II) coordination,[9] and (ii) a key

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® Abstract published in *Advance ACS Abstracts,* October 1, 1993.

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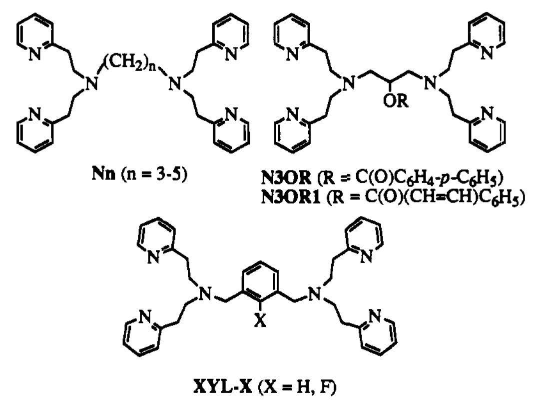
Chart I



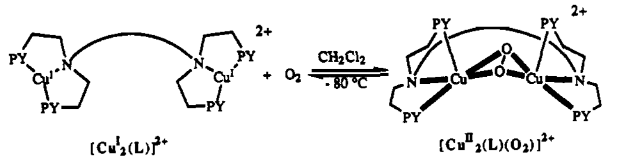
Nn (n = 3-5)

N3OR (R = $C(O)C_6H_4$-*p*-C_6H_5)
N3OR1 (R = $C(O)(CH{=}CH)C_6H_5$)

XYL-X (X = H, F)

model complex characterized by Kitajima and co-workers,[10] possessing a μ-η^2:η^2 planar side-on Cu_2–O_2 core identical to that seen in oxyhemocyanin. We have also described related series of complexes $[Cu_2(L)(O_2)]^{2+}$, where L represents a dinucleating ligand having two PY2 (PY2 = bis[2-(2-pyridyl)ethyl]amine) units connected by a hydrocarbon linker, e.g. Nn, N3OR, or XYL-X (Chart I).[2,11,12]

Binding of O_2 to the Cu(I) precursors is reversible under certain conditions and bound O_2 can be removed from $[Cu^{II}(L)(O_2)]^{2+}$ by application of a vacuum or saturation with CO. X-ray absorption spectroscopic and reactivity studies on $[Cu_2(Nn)(O_2)]^{2+}$ complex suggest that the peroxide binds in a novel *bent* μ-η^2:η^2 fashion between the two coppers.[12c,13] These complexes are characterized by strong multiple charge transfer bands in the UV–vis region, qualitatively also resembling oxyhemocyanin.



In this report, we describe a new dicopper(I) complex containing the dinucleating ligand N3OR$_1$, its structure, dynamic behavior, and its reactions with dioxygen. The ligand is the cinnamoyl analog of the ester ligand N3OR (R = $C(O)C_6H_4$-*p*-C_6H_5), for which the dicopper(I) complex has been structurally characterized[14] and for which the reversible O_2-binding behavior has been described.[12a] One reason for designing such a dincleating ligand with proximate pendant alkene group was to determine whether a $\{Cu_2$–$O_2\}$ species formed by the oxygenation of the dicopper(I) precursor would be capable of olefin oxygenation, since we have previously observed an arene hydroxylation reaction effected by related dinculear copper–dioxygen species.[15,16]

Experimental Section

Material and Methods. Reagents and solvents used were of commercially available reagent grade quality unless otherwise noted. Dioxygen, dichloromethane, and diethyl ether were dried and purified according to the published procedures.[17] THF (tetrahydrofuran) was distilled from sodium/benzophenone under Ar.

The air-sensitive materials were handled and prepared under Ar using standard Schlenk techniques. The solvents and solutions were deoxygenated either by vaccuum/purge cycles with argon or bubbling argon (20 min) directly through the solutions. The air/moisture-sensitive solid samples were stored in a Vacuum Atmospheres drybox filled with argon, where the samples for IR, NMR, and UV–vis were prepared also. The ligands were chromatographed by flash chromatography on alumina (80–200 mesh, MCB). Purity of the ligands was checked by TLC using Baker-Flex IB-F TLC plates. All elemental analyses were performed by Desert Analytics, Tucson, Az.

Infrared spectra were measured in Nujol mull or as KBr pellets on a Perkin-Elmer 283 or 710B instrument and calibrated by using a polystyrene film. NMR spectra were recorded in $CDCl_3$ or CD_3NO_2 on either a Varian EM360 (60-MHz) or a Varian XL-400 (400-MHz) spectrometer. Chemical shifts are reported as δ values downfield from an internal standard Me_4Si. Electrical conductivity of the samples was measured in CH_3CN 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 by using a Johnson Matthey magnetic susceptibility balance which was calibrated by using $Hg[Co(SCN)_4]$. X-band electron paramagnetic resonance (EPR) spectra were taken using a Varian E-4 spectrometer in frozen solutions at 77 K with 4 mm o.d. quartz tubes. The field was calibrated with a powder sample of diphenylpicrylhydrazyl (DPPH, g = 2.0037). The signals obtained were integrated 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 (at 77 K) or with a known solution of $[Cu(tepa)(Cl)](PF_6)$[18] in DMF/$CHCl_3$ (1:1 (v/v), 77 K). Room temperature electronic spectra were recorded with a Shimadzu UV-160 instrument using quartz cuvettes (1 cm).

Synthesis of Ligands and Complexes: N3OR$_1$. The cinnamoyl derivative ligand N3OR$_1$ was derived from the alcohol N3OH, which was prepared by acid-catalyzed reaction of 2-vinylpyridine with 1,3-diamino-2-hydroxypropane as published elsewhere.[12a,19] To a mixture of N3OH (3.40 g, 6.70 mmol) and triethylamine (2.02 g, 20.0 mmol) in 20 mL of dry THF under argon was added dropwise a solution of cinnamoyl chloride (1.11 g, 6.70 mmol) in 10 mL of dry THF while maintaining the reaction temperature at 0 °C. The mixture was stirred overnight with slow warming to room temperature and formation of white precipitate was seen. The reaction mixture was filtered through a medium porosity filter paper and the white precipitate was washed with 20 mL of THF. The washings were collected with the filtrate and THF was removed by rotary evaporation. The resulting dark yellow oil (4.23 g) was chromatographed on an alumina column with a mixture of ethyl acetate and methanol (100:1 (v/v)) as eluant (R_f 0.31) to recover 2.80 g (67%) of a light yellow pure product. ^1H NMR ($CDCl_3$): δ 2.60 (4 H, d), 3.00 (16 H, br s), 3.80 (1 H, br m), 6.20 (1 H, br), 6.45 (1 H, br), 6.80–7.80 (17 H, py-3, py-4, py-5, Ph–, m), 8.42 (4 H, py-6, d). IR (Nujol): 1710 cm^{-1} (s, C=O).

$[Cu_2(N3OR_1)](PF_6)_2$ (1). A solution of N3OR$_1$ (0.50 g, 0.78 mmol) in 10 mL of methanol was added dropwise to a stirring suspension of $[Cu(CH_3CN)_4](PF_6)$ (0.58 g, 1.56 mmol) in 15 mL of methanol under argon. Initially, a yellow solution formed and after 15 min a dark yellow

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oil-like material came out from the solution. At this point, the yellow oil was redissolved in methanol by warming the solution to ~50 °C. Cooling to room temperature and adding diethyl ether (100 mL) to the yellow solution yielded a light yellow fine precipitate. The precipitate was washed with Et_2O (2 × 30 mL) and dried under vacuum. Under Ar, the resulting yellow powder was dissolved in 15 mL of methanol by slow warming at 45 °C over a period of 2 h. When this solution was allowed to sit at room temperature overnight, bright yellow needle-shaped crystals formed. The crystals were washed with 10 mL of cold methanol and dried under vacuum to yield 0.70 g (84%) of bright yellow crystals. Anal. Calcd for $C_{40}H_{44}Cu_2F_{12}N_6O_2P_2$: C, 45.40; H, 4.16; N, 7.95. Found: C, 45.20; H, 3.96; N, 7.68. ^1H NMR (CD_2Cl_2): δ 2.62 (4 H, d), 3.00 (16 H, br m), 4.80 (1H, br m), 5.95 (1 H, s), 6.05 (1 H, s), 7.10–7.50 (13 H, py-3, py-4, Ph–, br, m), 7.80 (4 H, py-5), 8.45 (4 H, py-6, br). IR (Nujol, cm^{-1}): 1710 (m, C=O), 1610 (s, C=C), 845 (vs, PF_6^-).

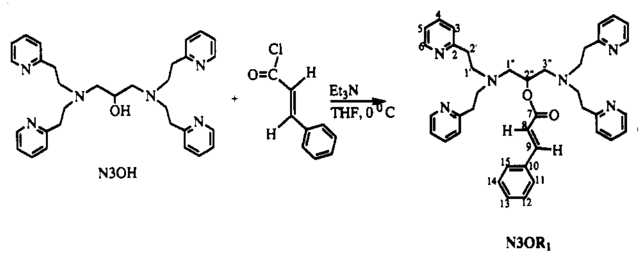
X-ray Structure Determination of $[Cu_2(N3OR_1)](PF_6)_2$ (1). Bright yellow needle-shaped crystals of $[Cu_2(N3OR_1)](PF_6)_2$ (1) suitable for X-ray crystallographic analysis were grown by slow cooling of a warm solution of 1 in methanol. A crystal having approximate dimensions of 0.1 × 0.1 × 0.2 mm was mounted on a glass fiber. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $35.15 < 2\theta < 42.21°$ corresponded to a monoclinic cell. The data were collected at a temperature using the ω–2θ scan technique to a maximum 2θ value of 50.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.37° with a take-off angle of 6.0°. Scans of $(1.15 + 0.30 \tan\theta)°$ were made at a speed of 8.0 deg/min. Of the 8683 reflections collected, 8567 were unique ($R_{int} = 0.043$). The structure was solved by direct methods.[20] The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at calculated positions. The final cycle of full-matrix least-squares refinement was based on 2936 observed reflections ($I > 3.00\sigma(I)$). All measurements were made on a Rigaku AFC6S diffractometer with graphite monochromated Mo Kα radiation (λ(Mo Kα) = 0.71073 Å) and all calculations were performed on a MicroVax-II computer using the TEXSAN crystallographic software package (Molecular Structure Corporation). The crystal data are given in Table I and positional parameters are listed in Table II.

Gas (O_2) Uptake Measurement. For complex 1, O_2-uptake measurements were carried out at –82 °C on a gas buret apparatus as described elsewhere.[11a,12b] In a typical experiment, 0.50 g (0.47 mmol) of $[Cu_2(N3OR_1)](PF_6)_2$ (1) was taken in a bent storage tube and the tube was attached to a Schlenk reaction flask containing 30 mL of CH_2Cl_2. This combination was attached to the manometer assembly and initially, a "blank" was recorded with amount of O_2 consumed by the solvent. The next step was to pour the solid copper(I) complex into the O_2-saturated solvent by slowly tapping the bent tube and uptake of O_2 by the Cu(I) complex was measured. The volume of dioxygen used up by 1 was 12.2 mL (0.49 mmol). The final stoichiometry of reaction was 2.08 ± 0.02 Cu:1 O_2 (two trials).

Low Temperature UV–vis Spectroscopy and Vacuum/Heat Cycling. A solution of $[Cu_2(N3OR_1)](PF_6)_2$ (1) (6.60 mg, 0.0063 mmol) was generated under Ar in 50 mL of CH_2Cl_2 (1.25×10^{-4} M) in a 50-mL volumetric flask modified for airless work (attached with a side-arm stopcock, a 14/35 male ground glass joint and a 14/20 female ground glass joint). An aliquot of this solution was transferred into a cuvette assembly[11a] by means of an inlet adapter attached to the 14/35 male joint of the volumetric flask. The cuvette assembly was cooled to –85 °C in a Dewar filled with methanol/liquid N_2 and a spectrum of the copper(I) complex was recorded. A spectrum of the dioxygen complex 2 was recorded after oxygenating the copper(I) solution by repeatedly purging the cuvette with O_2 and vigorous shaking. The brown dioxygen complex was reconverted to 1 by applying a vacuum at low temperature and then dipping the cuvette in a boiling water bath for a few seconds until the brown color faded and the color of 1 was restored. After an exact amount of CH_2Cl_2 lost by this procedure was added to the cuvette, the solution was recooled and the spectrum of 1 was recorded. This process could be repeated several times without a significant amount of decomposition.

Low-Temperature ^1H NMR Spectroscopy of $[Cu_2(N3OR_1)](PF_6)_2$ (1) and Its Dioxygen Adduct. A solution of 1 (~50 mg) in CD_2Cl_2 was prepared in a Wilmad NMR tube (Model 528-JY, 5 mm o.d.) adapted for air-sensitive handling. A spectrum of this complex was first recorded at room temperature (20 °C) on a Varian XL-400 spectrometer. The temperature of the probe was then lowered to –90 °C while recording the spectra in intervals of 10 °C. The tube was taken out of the spectrometer and was placed in a Dewar filled with liquid N_2/methanol at –90 °C. The cap of the NMR tube was attached to a glass adapter which was further attached to Ar and O_2 lines through a three-way stopcock. The tube was purged with dioxygen repeatedly until the color of the solution changed to deep brown. A spectrum of the final dioxygen complex 2 was recorded at –90 °C.

Scheme I



Oxygenation of $[Cu_2(N3OR_1)](PF_6)_2$ (1) at Room Temperature (20 °C). (a) Isolation of $[Cu_2(N3OR_1)(O)](PF_6)_2{\cdot}CH_2Cl_2$ (3). A solution of $[Cu_2(N3OR_1)](PF_6)_2$ (1) (0.30 g, 0.28 mmol) was generated in 20 mL of dry CH_2Cl_2 under Ar, and then bubbled with dioxygen for 30 min with immediate formation of a green solution. Addition of 350 mL of ether gave a green precipitate and the mixture was left overnight in the refrigerator for complete precipitation. The ether was decanted and the green solid was washed with diethyl ether (2 × 50 mL). Recrystallization of the green solid from CH_2Cl_2/Et_2O yielded 0.21 g (69%) of a green microcrystalline product. Anal. Calcd for $C_{41}H_{45}Cl_2Cu_2F_{12}N_6O_3P_2$: C, 42.60; H, 3.91; N, 7.29. Found: C, 41.80; H, 3.89; N, 7.56. UV–vis (CH_2Cl_2); λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)]: 230 (8500), 265 (22500), 285 (16700), 685 (290). IR (Nujol, cm^{-1}): 1710 (m, C=O), 845 (vs, PF_6^-). EPR silent (CH_2Cl_2, 77 K). μ_{RT} = 1.10 BM/Cu. $\Lambda_m(CH_3CN)$ = 250 $\Omega^{-1}\,cm^2\,mol^{-1}$.

(b) Identification of CH_2Cl_2 Solvate in $[Cu_2(N3OR_1)(O)](PF_6)_2{\cdot}CH_2Cl_2$ (3). In order to confirm the presence of CH_2Cl_2 in this paramagentic complex, it was reduced (to Cu(I)) using excess KCN, allowing NMR identification of all organics in 3. To a solution of 3 (0.10 g, 0.093 mmol) in 2 mL of CD_3CN in a test tube under argon, KCN (0.05 g, 0.75 mmol) was added as a solid. The test tube was closed tightly with a rubber stopper and wrapped in Parafilm and its contents were stirred for 48 h. The dark brown solution which formed was decanted directly into a NMR tube and a NMR spectrum was recorded. Ligand analysis by TLC with ethyl acetate/methanol (100:1) as solvent showed only one spot (R_f 0.31) corresponding to the original ligand $N3OR_1$. ^1H NMR (CD_3CN): δ 2.76 (4 H, d), 3.00 (16 H, br s), 3.70 (1 H, br m), 5.25 (CH_2Cl_2, br), 6.20 (1 H, br), 6.50 (1 H, br), 6.80–7.80 (17 H, py-3, py-4, py-5, Ph–, m), 8.42 (4 H, py-6, d).

Results and Discussion

Synthesis of Ligand and Copper(I) Complex. The ligand used in the present case is an ester derivative of N3 and analogue of N3OR (Chart I) where the two PY2 units are linked by a hydrocarbon chain. The alcohol precursor (N3OH) to this ligand is synthesized by reacting excess 2-vinylpyridine with 1,3-diamino-2-hydroxypropane in acidic medium.[12a,19] The final ester ligand $N3OR_1$ is synthesized by the condensation reaction of N3OH with the cinnamoyl chloride in dry THF with triethylamine as the base (Scheme I). $N3OR_1$ exhibits a normal ^1H NMR spectrum and IR spectroscopy shows the presence of the expected $\nu_{C=O}$ carbonyl stretch.

The dicopper(I) complex of $N3OR_1$, $[Cu_2(N3OR_1)](PF_6)_2$ (1), is readily synthesized by reacting 2 equiv of the Cu(I) precursor $[Cu(CH_3CN)_4](PF_6)$ with the ligand in methanol as solvent. $[Cu_2(N3OR_1)](PF_6)_2$ (1) is air- and moisture-sensitive. An infrared spectrum of 1 gives a ν(C=O) stretch at the same place as the parent ligand (~1700 cm^{-1}) suggesting that the carbonyl oxygen does not bind to copper, a result more evident from the X-ray crystal structure (*vide infra*).

A ^1H-NMR spectrum of 1 shows minor positive (i.e., downfield) coordination induced shifts for most of the protons (except for vinyl protons) upon binding of the ligand to copper(I). However,

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(20) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42–46.

Table I. Crystallographic Data for 1

formula	$C_{40}H_{44}Cu_2$-$F_{12}N_6O_2P_2$	D_{calcd}, g/cm^3	1.53
MW	1057.85	space group	*C*2/*c*
crystal system	monoclinic	reflections collected	8683
a, Å	46.569(8)	reflections used	2936
b, Å	11.059(2)	absorption coefficient, cm^{-1}	10.81
c, Å	18.219(4)	number of refined parameters	577
β, deg	101.04(2)	R^a	0.051
V, Å^3	9209(3)	$R_w{}^b$	0.061
Z	8		

^{a} $R = \sum[|F_o| - |F_c|/\sum|F_o|]$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 4F_o{}^2/\sigma^2(F_o{}^2)$.

a very pronounced downfield shift is observed for the proton at the 2″ position (see Experimental Section). A similar notable deshielding of the 2″ proton is seen for a related complex $[Cu_2(N3OR)](PF_6)_2$ (R = –C(O)–C_6H_4–C_6H_5).[12a,19] By contrast, the vinyl protons are shifted upfield upon binding of ligands to copper in **1** (*ca.* 0.30 ppm, see Experimental Section). This can be explained based on the observed structure of **1** which shows the binding of the alkene group to one of the copper ions. This implements a significant amount of *σ*-donation by the filled alkene orbitals to the metal d-orbitals which should deshield the vinyl protons. In addition, metal to ligand *π*-back-bonding may occur, thus shielding the vinyl protons.[21] In the case of **1**, the X-ray structure shows a lengthening of the C═C bond (vide infra) suggesting a more effective back-bonding occurring here. Due to this more prominent back-bonding, there is an overall shielding effect on the vinyl protons.

In addition to the coordination induced shifts, the ^{1}H NMR spectra of $[Cu_2(N3OR_1)](PF_6)_2$ (**1**) show significant line broadening at room temperature. One possible reason is the exchange of the alkene arm between the two copper ions. A variable temperature ^{1}H-NMR spectroscopic study was undertaken for $[Cu_2(N3OR_1)](PF_6)_2$ (**1**) to shed more light on this issue and this is discussed below.

Structure of $[Cu_2(N3OR_1)](PF_6)_2$ (1). The structure consists of one discrete complex dication and two well-separated anions per asymmetric unit. A summary of crystal parameters and refinement results is given in Table I, positional and thermal parameters are found in Table II, while selected bond lengths and angles are compiled in Table III. An ORTEP view of the cationic portion is depicted in Figure 1, including the atom labeling scheme. The structure of $[Cu_2(N3OR_1)](PF_6)_2$ (**1**) is distinctive and shows that two coppers are in unsymmetrical ligand environments. One of the coppers is in a trigonal three-coordinate environment with ligation to two pyridine and one tertiary amine nitrogens. The other copper is four-coordinate with the same N_3 ligation to the PY2 tridenate, plus it is symmetrically bonded to the alkene moiety. The geometry around this copper is pseudotetrahedral.

The two copper coordination units are separated from each other with Cu···Cu = 5.654(2) Å. This distance is significantly smaller than the other closely related ester–ligand complex $[Cu_2(N3OR)](PF_6)_2$ (Cu···Cu = 6.262 Å), where R is a biphenyl group and the three-coordinate Cu(I) moieties extend away from each other.[14] In the present case, one of the tridentate Cu(I) arms (i.e., Cu1, Figure 1) is constricted due to olefin binding, pulling the Cu1–PY2 unit toward the center of the ligand molecule resulting in a shorter Cu···Cu distance. Cu(I)···Cu(I) distances in other PY2-containing ligand complexes such as $[Cu_2(L)(D)]^{2+}$ (L = Nn or XYL; D = CH_3CN, CO) are also significantly larger (6.181–9.944 Å) than that seen in **1**.[12a,b,15b] The structure of **2** also shows that the carbonyl oxygen lies away from the copper ions and does not coordinate (C4–O2) = 1.20(1) Å).

Table II. Positional Parameters and *B*(eq) for 1

atom	*x*	*y*	*z*	*B*(eq)
Cu(1)	0.33100(3)	0.1249(1)	0.00481(8)	4.11(8)
Cu(2)	0.43577(4)	–0.0914(1)	–0.04378(8)	4.77(8)
P(1)	0.07661	0.2200(4)	0.1988(2)	5.7(2)
P(2)	0.1887(1)	0.1395(5)	0.6217(3)	6.9(3)
F(1)	0.2146(3)	0.228(1)	0.6207(5)	13.8(8)
F(2)	0.2090(3)	0.032(1)	0.6155(6)	13.1(8)
F(3)	0.1975(2)	0.133(1)	0.7089(4)	10.4(6)
F(4)	0.1630(2)	0.0532(9)	0.6226(5)	10.9(7)
F(5)	0.1681(3)	0.249(1)	0.6272(6)	13.4(8)
F(6)	0.1809(2)	0.1495(8)	0.5334(5)	10.4(6)
F(7)	0.0707(2)	0.1249(7)	0.2578(5)	10.1(6)
F(8)	0.0497(2)	0.2949(8)	0.2119(5)	10.4(6)
F(9)	0.0564(2)	0.1454(9)	0.1371(5)	12.1(7)
F(10)	0.0832(2)	0.3169(8)	0.1413(4)	9.4(6)
F(11)	0.1030(2)	0.1422(9)	0.1854(5)	11.1(6)
F(12)	0.0954(2)	0.2944(8)	0.2621(5)	10.6(6)
O(1)	0.3830(2)	–0.0496(7)	–0.0057(4)	3.9(4)
O(2)	0.4022(2)	0.1230(8)	0.0508(5)	4.9(5)
N(1)	0.3389(2)	–0.0211(9)	0.0917(6)	3.9(5)
N(2)	0.2872(2)	0.111(1)	–0.0257(5)	4.5(6)
N(3)	0.3418(2)	0.267(1)	0.0777(6)	4.1(6)
N(4)	0.4268(2)	–0.236(1)	0.0285(5)	4.3(6)
N(5)	0.4624(2)	0.010(1)	0.0257(6)	4.9(7)
N(6)	0.4260(2)	–0.158(1)	–0.1441(6)	4.3(6)
C(1)	0.3854(3)	–0.117(1)	0.0630(6)	3.9(6)
C(2)	0.3551(3)	–0.133(1)	0.0802(6)	4.0(6)
C(3)	0.3973(3)	–0.239(1)	0.0474(6)	3.9(7)
C(4)	0.3852(3)	0.073(1)	0.0023(7)	3.9(7)
C(5)	0.3644(3)	0.135(1)	–0.0572(7)	3.7(6)
C(6)	0.3413(3)	0.077(1)	–0.1045(7)	4.1(7)
C(7)	0.3207(3)	0.132(1)	–0.1668(7)	4.1(7)
C(8)	0.2971(3)	0.062(1)	–0.1999(7)	4.6(7)
C(9)	0.2753(3)	0.113(2)	–0.2538(8)	5.9(9)
C(10)	0.2772(4)	0.233(2)	–0.2730(8)	7(1)
C(11)	0.3003(4)	0.301(1)	–0.2423(9)	7(1)
C(12)	0.3222(3)	0.252(1)	–0.1894(8)	5.4(8)
C(21)	0.2729(4)	0.205(1)	–0.0652(8)	5.4(9)
C(22)	0.2440(4)	0.198(2)	–0.1005(8)	7(1)
C(23)	0.2293(4)	0.092(2)	–0.094(1)	9(1)
C(24)	0.2438(4)	–0.002(2)	–0.054(1)	8(1)
C(25)	0.2725(4)	0.007(1)	–0.191(8)	5.4(9)
C(26)	0.2896(3)	–0.093(1)	0.023(1)	6.5(9)
C(27)	0.3090(3)	–0.060(1)	0.0977(7)	5.1(8)
C(31)	0.3458(3)	0.376(2)	0.0477(7)	5.5(8)
C(32)	0.3541(3)	0.480(1)	0.090(1)	7(1)
C(33)	0.3579(4)	0.470(2)	0.164(1)	8(1)
C(34)	0.3538(3)	0.363(2)	0.1951(8)	5.9(8)
C(35)	0.3458(3)	0.261(1)	0.1524(8)	4.1(7)
C(36)	0.3401(3)	0.147(1)	0.1893(7)	6.0(8)
C(37)	0.3533(3)	0.030(1)	0.1650(7)	5.4(8)
C(51)	0.4627(3)	0.132(2)	0.0229(8)	5.7(8)
C(52)	0.4801(4)	0.202(1)	0.079(1)	7(1)
C(53)	0.4969(4)	0.149(2)	0.139(1)	9(1)
C(54)	0.4970(4)	0.026(2)	0.143(1)	8(1)
C(55)	0.4798(3)	–0.041(1)	0.087(1)	5(1)
C(56)	0.4784(3)	–0.177(2)	0.0897(7)	6(1)
C(57)	0.4489(3)	–0.232(1)	0.0994(7)	5.3(8)
C(61)	0.4302(3)	–0.093(1)	–0.2026(8)	4.6(7)
C(62)	0.4315(3)	–0.138(1)	–0.2704(7)	5.1(8)
C(63)	0.4292(3)	0.256(2)	–0.2816(8)	6(1)
C(64)	0.4250(3)	–0.328(1)	–0.226(1)	6.2(9)
C(65)	0.4227(3)	–0.278(1)	–0.158(1)	5.1(8)
C(66)	0.4141(3)	–0.352(1)	–0.098(1)	6.7(9)
C(67)	0.4315(3)	–0.346(1)	–0.016(1)	6.3(9)

The three-coordinate copper atom Cu2 is ligated to PY2 tridentate group. Significant distortion from idealized trigonal-planar geometry is observed since the N_{amine}–Cu–N_{py} angles are acute (101–105°), resulting in a large N_{py}–Cu–N_{py} angle (146.6(4)°). Also, the Cu2 atom lies 0.28 Å below the plane of N4, N5, and N6 distorting the unit slightly from planarity. The Cu–N_{py} bond lengths are on the order of ~1.94 Å and comparable to the Cu–N_{py} bond distances found in other three-coordinate copper(I) complexes (1.88–1.94 Å).[12,14,15,22] This distance is ca. 0.1 Å shorter than that found in four-coordinate complexes which

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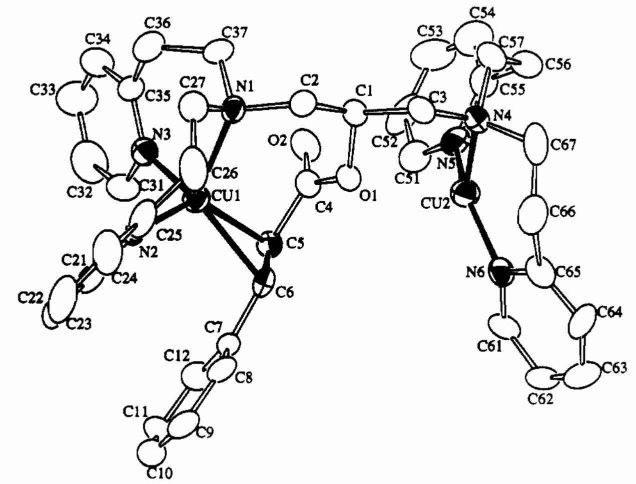

Figure 1. ORTEP diagram of the cationic portion of $[Cu_2(N3OR_1)](PF_6)_2$ (**1**), showing the atom labeling scheme.

Table III. Selected Bond Distances and Angles for **1**

	Interatomic Distances (Å)		
Cu(1)–N(1)	2.242(9)	Cu(2)–N(4)	2.166(10)
Cu(1)–N(2)	2.016(10)	Cu(2)–N(5)	1.949(11)
Cu(1)–N(3)	2.054(10)	Cu(2)–N(6)	1.943(10)
Cu(1)–C(5)	2.091(10)	C(5)–C(6)	1.398(15)
Cu(1)–C(6)	2.201(11)	Cu(1)···Cu(2)	5.654(2)
	Interatomic Angles (deg)		
N(1)–Cu(1)–N(2)	99.3(5)	N(3)–Cu(1)–C(5)	101.2(5)
N(1)–Cu(1)–N(3)	96.1(4)	N(3)–Cu(1)–C(6)	96.7(4)
N(1)–Cu(1)–C(5)	112.4(4)	C(5)–Cu(1)–C(6)	37.9(4)
N(1)–Cu(1)–C(6)	115.5(4)	N(4)–Cu(2)–N(5)	101.8(5)$(PF_6)_2$
N(2)–Cu(1)–N(3)	110.2(4)	N(4)–Cu(2)–N(6)	104.6(4)
N(2)–Cu(1)–C(5)	132.3(4)	N(5)–Cu(2)–N(6)	146.6(4)
N(2)–Cu(1)–C(6)	96.7(4)		

also contain the PY2 tridentate unit.[12a,12b,23] The Cu2–N_{amine} bond is long (2.17(1) Å) and the copper atom can be thought of being in a pseudo-two-coordinate environment, although perturbed by the N_{amine} ligation.

The Cu1 atom is in a pseudotetrahedral environment (PY2 and alkene ligation) with dihedral angles being near the expected value of 90° (e.g. N1–Cu1–C6/N2–Cu1–N3 = 83.19°; N1–Cu1–N3/N2–Cu1–C6 = 92.10°). The copper atom sits below (i.e. toward the olefin) the N1, N2, N3 plane by 0.92 Å. The Cu1–N_{py} bond lengths (>2.00 Å) are comparable to those seen in other four-coordinate complexes such as $[Cu(tepa)]^+$ (tepa = tris(2-(2-pyridyl)ethyl)amine),[23] $[Cu_2(N4)(CH_3CN)_2]^{2+}$, and $[Cu_2(N3)(CO)_2]^{2+}$.[12a,b] However, the Cu1–N_{amine} distance is ca. 0.05 Å longer than the other similar compounds. As far as binding of Cu1 to the alkene moiety is concerned, the Cu–C contact distances are typical for η^2-Cu(I)-coordinated alkenes.[24–30] The C═C bond distance is 1.40(2) Å and is significantly larger than that found in free cinnamic acid derivatives (1.31–1.34 Å).[31] In most other Cu(I)–alkene complexes a significant lengthening of C═C is not observed except for the case of Cu(I)–cyclohexene complexes reported by Thompson *et al.*[25–27] However, significant lengthening of this bond is generally observed upon olefin coordination to other d^{10} metal ions (1.41–1.46 Å).[32] This lengthening of the C═C bond suggests that other than the σ-bonding, there is significant amount of π back-bonding taking place between the metal and alkene. This result is also evident from the observed ^1H-NMR spectra (*vide supra*) where net shielding of the vinyl protons occurs.

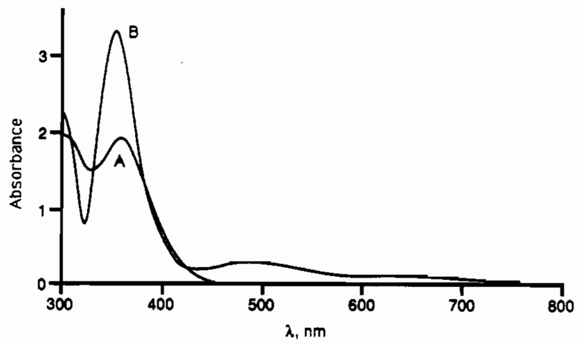

Figure 2. UV–vis spectra of the dicopper(I) complex $[Cu_2(N3OR_1)]^{2+}$ (**1**) (spectrum A) and its dioxygen adduct $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (**2**) (spectrum B) at –80 °C in CH_2Cl_2.

Oxygenation of $[Cu_2(N3OR_1)](PF_6)_2$ (1) and Generation of a $\{Cu_2\text{-}O_2\}$ Adduct $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (2). A yellow solution of $[Cu_2(N3OR_1)](PF_6)_2$ (**1**) in dichloromethane reacts rapidly with dioxygen at –80 °C to produce a dark brown species. The brown color persists at low temperature (<–70 °C) and decomposes to a green product upon warming. The stoichiometry of O_2 binding at –80 °C is measured by manometry and found to be Cu:O_2 = 2:1. This shows that one dioxygen is consumed by the dinuclear unit and the dioxygen adduct can be formulated as $[Cu_2(N3OR_1)(O_2)]^{2+}$ (**2**).

Low Temperature (–80 °C) UV–vis Spectroscopy. The dicopper(I) complex $[Cu_2(N3OR_1)](PF_6)_2$ (**1**) in dichloromethane exhibits a single absorption band in the UV–vis region (>300 nm) occurring at 360 nm with molar extinction coefficient (ϵ) value of 15 300 M^{-1} cm^{-1} (Figure 2). The intensity of this absorption is significantly higher than that observed in other dicopper(I) complexes having PY2 donor ligands. Perhaps this is due to Cu(I)–pyridyl coordination (MLCT?) altered by alkene coordination; Cu^I–olefins do not normally exhibit such absorptions.

When this bright yellow solution is exposed to O_2 at –80 °C, the resulting brown solution of **2** shows multiple absorption bands in the 300–700 nm region. The strongest occurs at 354 nm (ϵ = 26 500 M^{-1} cm^{-1}) while there is another band at 485 nm (ϵ = 2700 M^{-1} cm^{-1}) and a distinct shoulder at *ca.* 608 nm (ϵ = 1100 M^{-1} cm^{-1}) (Figure 2). In addition, a weaker shoulder seen at 676 nm (ϵ = 540 M^{-1} cm^{-1}) is tentatively assigned as the d–d transition, thus confirming the presence of the Cu(II) oxidation state. The dioxygen adduct **2** has the largest absorption intensities compared to any other O_2-binding copper proteins (e.g., hemocyanin, tyrosinase) or synthetically derived Cu_2–O_2 adducts known.[2,3,8] Spectroscopically, complex **2** is stable for at least 24 h at –80 °C.

Reversible Binding of Dioxygen: Vacuum Cycling. The reversibility of dioxygen binding to $[Cu_2(N3OR_1)](PF_6)_2$ (**1**) is demonstrated by a vacuum cycling experiment, which can be followed spectrophotometrically (Figure 3). In this experiment, an initial solution of $[Cu_2(N3OR_1)](PF_6)_2$ (**1**) is generated in dichloromethane under Ar and its spectrum recorded at –80 °C (Figure 3, spectrum 1). Oxygenation of this solution generates

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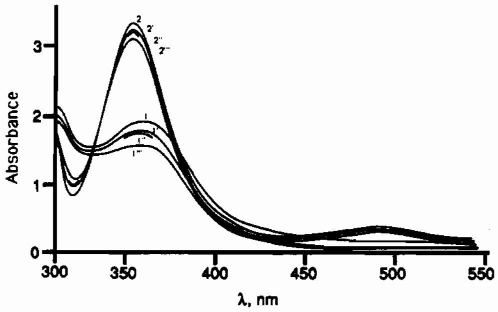

Figure 3. UV–vis spectra demonstrating the reversible dioxygen binding behavior of $[Cu_2(N3OR_1)](PF_6)_2$ (1) in CH_2Cl_2 (*vacuum cycling*). See text for details.

a deep brown solution with spectrum typical of the dioxygen adduct $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (2) with maximum absorption at 354 nm (Figure 3, spectrum 2). When this solution is subjected to a static vacuum and rapidly and briefly (1–5 s) heated to 100 °C, the brown color is lost. At this point, any lost solvent is replaced, the solution is again cooled to −80 °C, and spectrum 1′ is acquired, showing a complete loss of the 354-nm band and regeneration of the Cu(I) complex 1. Reoxygenation at −80 °C generates 2, showing little loss in spectral intensity (Figure 3). The cycling between the oxy and deoxy forms, i.e., $1 + O_2 \leftrightarrow 2$ can be repeated at least four times, with only a small amount of decomposition (*ca.* 15% based on the reduced absorbance at 354 nm).

Low Temperature NMR (−90 °C) Spectroscopy of $[Cu_2(N3OR_1)](PF_6)_2$ (1) and $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (2). As mentioned earlier, the ^1H NMR spectra of $[Cu_2(N3OR_1)](PF_6)_2$ (1) in CD_2Cl_2 show broad peaks at room temperature (Figure 4), in particular, for the protons on the PY2 moiety, including pyridyl and methylene protons. However, the vinyl protons and those on the bridging alkyl chain exhibit sharp signals. The py-5 and py-6 protons (Scheme I) show one set each of broad peaks and are nicely separated from the rest of the aromatic absorptions. Since the crystal structure of 1 shows that the two PY2 arms are inequivalent due to the interaction of the alkene moiety with one of the copper ions, this makes the two halves of the molecule magnetically inequivalent and one should expect to see two sets of resonances for each proton on the PY2 unit. In solution, at room temperature, there is a possibility of dynamic exchange of the alkene binding between the two coppers. This process may proceed through a pathway where both copper ions are three-coordinate, i.e. with uncoordinated alkene moiety. If this exchange rate is faster than the NMR time scale, the two PY2 units will be seen as equivalent and only one set of broad peaks should be observed, which appears to be the case here. By lowering the temperature, this exchange rate should decrease. When the temperature is lowered to 0 °C, the py-5 and py-6 proton resonances become even broader and further lowering of temperature splits these into doublets (Figure 4). Splitting of the other pyridine and methylene protons is also observed at still lower temperatures. At −90 °C (Figures 4 and 5), the peaks become sharper and show a finer splitting pattern due to the further inequivalence between the two pyridylethyl arms on each PY2 unit.

A ^1H-NMR spectrum of the Cu_2–O_2 complex $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (2), formed in an NMR tube at −90 °C, is shown in Figure 5 along with that of its Cu(I) precursor 1. The spectrum of the dioxygen complex is fairly sharp and is virtually unshifted from the copper(I) complex 1. In general, NMR spectra of Cu(II) complexes are not expected to exhibit sharp signals due to direct and indirect interaction between electron and nuclear spins. However, in the case of a dicopper(II) system, strong antiferromagnetic coupling through a peroxo bridging ligand can extend a near-diamagnetic character,[9,10,12] and studies of other ligand bridges (i.e., oxo[10b] and phenoxo[33]) have been described.

The strong antiferromagnetic coupling between the two Cu(II) ions in $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (2) is further evidenced by EPR spectroscopy. A solution of $[Cu_2(N3OR_1)](PF_6)_2$ (1) in CH_2Cl_2 displays no EPR signal at 77 K. The brown solution of $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (2) generated by the oxygenation of 1 at −80 °C is also EPR silent (*ca.* 2% paramagnetic impurity compared to the mononuclear complex $[Cu(TEPA)Cl)](PF_6)$).[18] This suggests that the two Cu(II) ions are strongly magnetically coupled, presumably through a bridging peroxo ligand.[9,10,33] Warming up of the EPR tube to room temperature decomposes the brown solution of 2 to an EPR silent green species, as judged by an only slightly enhanced signal (~7% compared to $[Cu(TEPA)Cl)](PF_6)$).

Comparison of $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (2) with Other Synthetic Cu_2–O_2 Adducts and Oxyhemocyanin. As alluded to, the UV–vis, ^1H-NMR, and EPR spectroscopic characteristics of the dioxygen adduct $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (2) (Chart II) are very similar to the already well-characterized $[Cu_2(Nn)(O_2)]^{2+}$ and $[Cu_2(N3OR)(O_2)]^{2+}$ complexes.[12] In fact, the UV–vis spectrum is virtually identical to that of $[Cu_2(N3OR)(O_2)]^{2+}$.[12a] Based on EXAFS and reactivity studies performed on $[Cu_2(Nn)(O_2)]^{2+}$ and $[Cu_2(N3OR)(O_2)]^{2+}$, it has been proposed that the peroxo group is bridging between the two copper(II) ions in a side-on *bent* μ-η^2:η^2 fashion.[12,13] Thus, we propose that the peroxo group in $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (2) has a similar structure. This type of bonding explains the diamagnetic behavior (sharp ^1H-NMR, EPR silence) of 2 in terms of strong antiferromagnetic coupling mediated by the peroxo group (*vide infra*). Other Cu_2O_2 geometries, such as terminal (O_2)–Cu···Cu, or *trans*-μ-1,2-peroxo ligation display distinctly different UV–vis spectroscopic properties.[2,9]

A structurally characterized Cu_2–O_2 complex having a side-on peroxo bridge has been described by Kitajima and co-workers.[10] $[Cu(HB(3,5\text{-}iPr_2pz)_3]_2(O_2)$ ($HB(3,5\text{-}iPr_2pz)$ = a tris(pyrazolylborate) anionic ligand) possesses a *planar* μ-η^2:η^2 peroxo coordination mode and has properties (Cu···Cu = 3.56 Å, ν_{O-O} = 741 cm^{-1}, UV–vis: λ_{max} (ϵ, M^{-1} cm^{-1}) = 349 (21 000), 551 (800) nm) nearly identical to those of oxyhemocyanin, now shown to have the same Cu_2–O_2 coordination.[4a] Theoretical and spectroscopic analyses by Solomon and co-workers[34] indicate that the intense ~350 nm band has a peroxo-to-Cu(II) ligand-to-metal charge-transfer origin, and its strength is a consequence of the μ-η^2:η^2 peroxo dicopper(II) ligation, effectively with *two* Cu-O interactions per Cu ion. Thus, the similar side-on ligation suggested for $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (2) is supported by its very strong 354 nm absorption (*vide supra*). Complex 2 and other $[Cu_2(Nn)(O_2)]^{2+}$ species have an extra absorption band in the 400–500 nm region, not seen in Kitajima's compound nor in oxy-Hc. This charge-transfer band is not "allowed" for a planar coordination, and we suggest that the tilted or bent structures of our compounds (suggested by EXAFS spectroscopy) allow for absorption intensity.

Reactivity of $[Cu_2(N3OR_1)](PF_6)_2$ (1) with O_2 at Room Temperature. It has been shown earlier that a peroxo group in a ligand environment not too dissimilar to $N3OR_1$ is capable of hydroxylating an arene moiety which is part of the ligand.[15] Here, reaction of O_2 with $[Cu_2(XYL)]^{2+}$ results in xylyl ligand ring hydroxylation, producing the phenoxo-bridged dicopper(II) complex $[Cu_2(XYL\text{-}O^-)(OH)]^{2+}$. The intermediacy of the peroxo species $[Cu_2(XYL)(O_2)]^{2+}$ was proven by kinetics studies[35] and also by its stabilization in a slightly modified unsymmetrical

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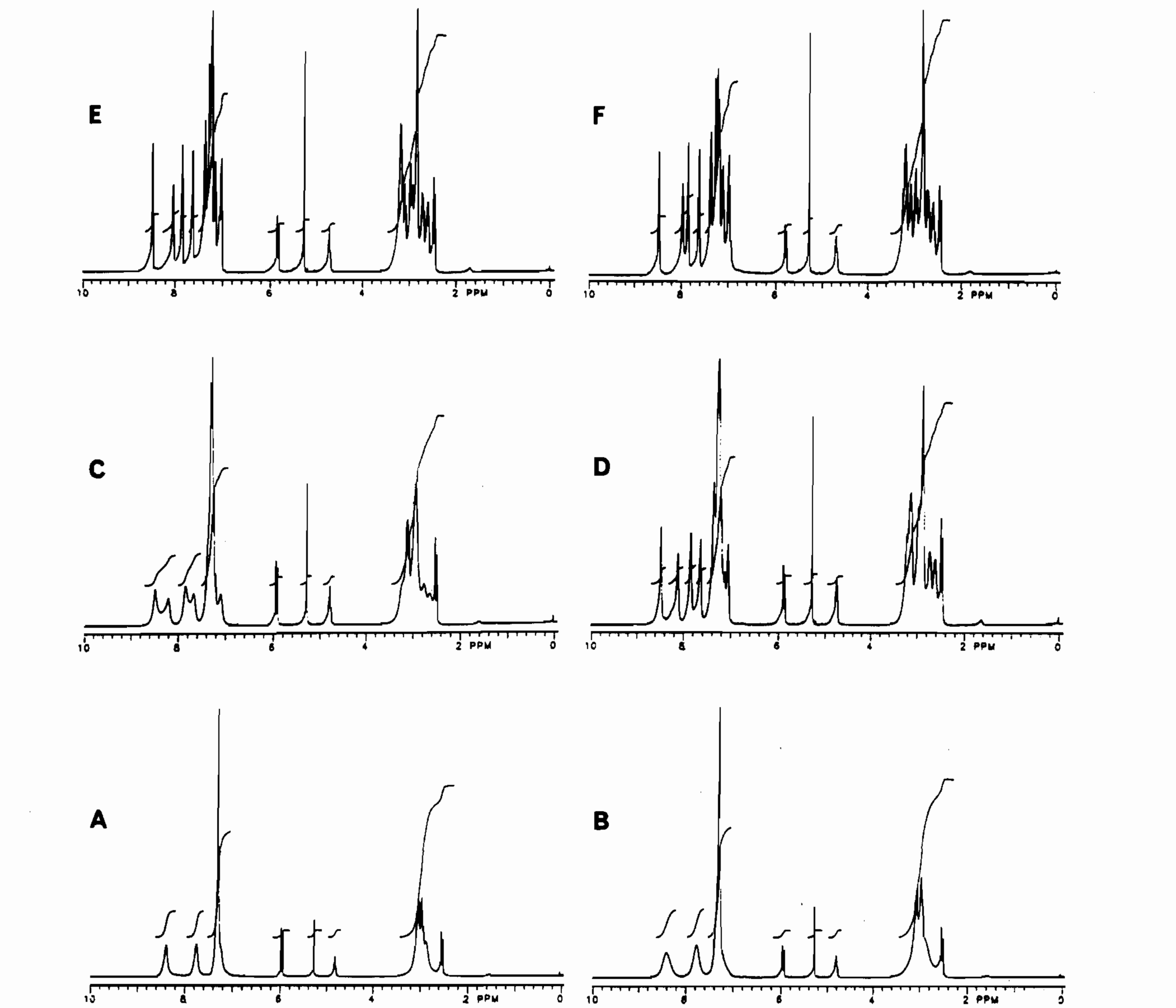
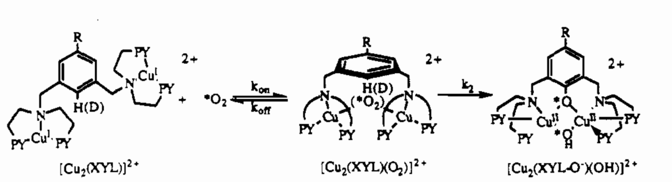


Figure 4. Variable-temperature ^{1}H-NMR spectra (400 MHz) of dicopper(I) complex $[Cu_2(N3OR_1)](PF_6)_2$ (**1**) in CD_2Cl_2: (A) +20 °C, (B) 0 °C, (C) -20 °C, (D) -40 °C, (E) -60 °C, (F) -80 °C.



ligand.[36] Spectroscopic and reactivity studies indicated that a μ-η^2:η^2-peroxo group bound to the two coppers behaves like an electrophile and is capable of hydroxylation of the proximate arene, via an NIH mechanism.[13,16] An original goal of the present study with the $N3OR_1$ dinucleating ligand was to further elaborate such chemistry, placing other substrates nearby the same type of Cu_2–O_2 moiety, investigating the scope of oxygenation reactions and their geometric and electronic requirements.

When a -80 °C solution of the Cu_2–O_2 complex $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (**2**) was allowed to warm to room temperature, a color change from brown to green took place. The ligand was stripped out by treating the reaction solution with aqueous ammonia. Analysis of the ligand by thin-layer chromatography (TLC; R_f 0.31 in 100:1 (v/v) ethyl acetate/methanol), NMR, and IR spectroscopy showed only the presence of the original unchanged ligand $N3OR_1$. Thus, no olefin oxidation or ester hydrolysis reaction appears to take place.

When a solution of $[Cu_2(N3OR_1)](PF_6)_2$ (**1**) in CH_2Cl_2 is oxygenated at room temperature, a deep green solution rapidly forms, and a dicopper(II) complex we formulate as $[Cu_2(N3OR_1)(O)](PF_6)_2{\cdot}CH_2Cl_2$ (**3**) was isolated from this reaction. An alternative formulation of this product could be $[Cu_2(N3OR_1)(F)_2]^{2+}$, a species with μ-F$^-$ bridging atoms (derived from decomposition of PF_6^-),[37] instead of an oxo (O^{2-}) ligand. An oxo-bridged complex could form by four-electron reduction of dioxygen (i.e. O–O bond cleavage).[17,38–41] Compound **3** is EPR silent (CH_2Cl_2, 77 K) and has low magnetic moment ($\mu_{RT} = 1.1$), suggesting that the two coppers are strongly antiferromagnetically coupled. This complex also shows ν(C═O) at 1710 cm^{-1} in IR suggesting that the ester moiety of the ligand is intact. Analysis

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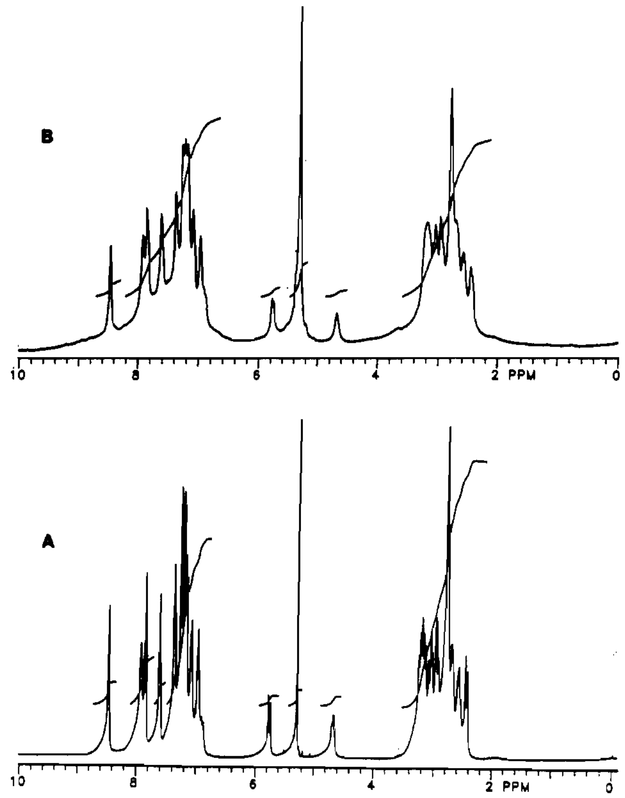
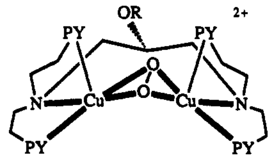


Figure 5. Proton NMR spectra (400 MHz) of the dicopper(I) precursor $[Cu_2(N3OR_1)](PF_6)_2$ (**1**) (spectrum A) and its dioxygen adduct $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (**2**) (spectrum B) at -90 °C in CD_2Cl_2.

Chart II



$[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (**2**)

of the ligand by reduction of **3** with KCN shows that there is no change in the parent $N3OR_1$ ligand, as judged by TLC and NMR spectroscopy. Also, the presence of CH_2Cl_2 as a solvate is proved by NMR spectroscopy (Experimental Section).

Under the conditions described above, it is seen that the Cu_2–O_2 complex formed here is not capable of reacting with the substrate even though it is in a dinucleating ligand environment with covalently attached alkene. This phenomenon may be explained based on steric and electronic arguments. Simple stick-type molecular modeling shows that once a peroxide ligand bridges between the two coppers, the ester group aligns itself in the opposite direction, away from the Cu_2O_2 and ligand framework (Chart II). The reason is that there are only three carbons separating the two PY2 groups and the space between them is incapable of accommodating the bulky ester group, once the dioxygen (i.e., peroxide) binds. The unreactive nature of the ligand $N3OR_1$ to O_2 could also be explained by an electronic incompatibility of the reacting Cu_2O_2 and alkene groups. Theoretical studies[34b] and our own reactivity investigations[13] have shown that a side-on peroxo group is prone to act as an electrophile in its reactions. A substrate should be more nucleophilic to be attacked by such a peroxide, such as an arene group in the *m*-xylyl hydroxylation system mentioned above.[15] The alkene group in the ligand $N3OR_1$, due to the presence of electron-withdrawing phenyl and carboxyl groups, may itself be electrophilic in nature, less likely to be attacked by a side-on peroxo dicopper(II) group.

Conclusions

Here, a new $\{Cu_2$–$O_2\}$ complex is described that is derived from a novel unsymmetrical dicopper(I) precursor $[Cu_2(N3OR_1)](PF_6)_2$ (**1**). The ligand used for the purpose of this study contains a covalently attached cinnamoyl group. The X-ray structure of **1** imparts a unique unsymmetrical dicopper(I) complex coordination. One of the copper ions is three-coordinate and binds to the PY2 (bis[2-(2-pyridyl)ethyl]amine) group, whereas the other copper is four-coordinate with coordination to the PY2 group and to the alkene moiety on the cinnamoyl derivative. Variable temperature ^1H NMR spectroscopy of **1** shows a dynamic exchange reaction occurring for the alkene unit between the two coppers at higher temperature, that can be curbed at -80 °C. Complex **1** binds O_2 at -80 °C to generate a dicopper(II)–peroxo species $[Cu_2(N3OR_1)(O_2)](PF_6)_2$ (**2**) (manometry, $Cu:O_2 = 2:1$) that is metastable at low temperature. The Cu_2–O_2 complex **2** shows multiple $O_2^{2-} \rightarrow Cu(II)$ charge transfer transitions comparable to other well-characterized $[Cu_2(Nn)(O_2)]^{2+}$ and $[Cu_2(N3OR)(O_2)]^{2+}$ compounds. A *bent* μ-η^2:η^2 peroxo bridging mode is proposed based on the spectroscopic similarity seen between **2** and $[Cu_2(Nn)(O_2)]^{2+}$ complexes, also possessing the very intense near-UV band (~350 nm) characteristic of oxyhemocyanin and $[Cu(HB(3,5\text{-}iPr_2pz)_3]_2(O_2)$. $[Cu_2(N3OR_1)](PF_6)_2$ (**1**) is a functional model for hemoxyanin; the O_2 binding to **1** is reversible and dioxygen can be pumped off by rapid application of a vacuum at 100 °C. Complex **2** is strongly magnetically coupled as shown by its EPR silent nature and a sharp ^1H NMR spectrum at -90 °C.

As we have seen with most other copper(I) complexes, the room temperature O_2 reaction with **1** proceeds in a different manner, by a likely $4e^-$ reduction pathway to afford a complex suggested to be an oxo-bridged dicopper(II) species.[17] Ligand analyses after both low and room temperature reactions of **1** with O_2 show that the alkene group is not attacked. The lack of reactivity may be explained on the basis of either a mismatch of reactivity (i.e., both the cinnamoyl and Cu_2–O_2 moieties are electrophilic, or because the Cu_2–O_2 coordination forces a ligand conformation placing the alkene away from the peroxocopper moiety. Future studies will be directed toward ligand design which can further refine our understanding and test ideas concerning the structure, orientation, and reactivity of side-on (bent) peroxodicopper(II) species.

Acknowledgment. This work was supported by Grant R01 GM28962 (K.D.K.) from the National Institutes of Health. We also thank the National Science Foundation (CHE-9000471) for aid in the purchase of the X-ray diffractometer.

Supplementary Material Available: Tables listing hydrogen atom positional parameters, anisotropic thermal parameters, bond lengths and angles, and intermolecular distances for complex **1** (10 pages). Ordering information is given on any current masthead page.