Reversible Reaction of O_2 (and CO) with a Copper(I) Complex. X-ray Structures of Relevant Mononuclear Cu(I) Precursor Adducts and the *trans*-(μ-1,2-Peroxo)dicopper(II) Product

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Abstract: The study of copper–dioxygen interactions and reactivity is of interest in chemical systems which involve redox activity or oxidative transformations and in biological systems where copper proteins are known to effect a variety of functions including dioxygen transport, substrate oxygenation, and O_2 reduction. Here, we describe reactions of O_2 (and CO) with a mononuclear copper(I) complex containing a tripodal tetradentate ligand L (tris(2-pyridylmethyl)-amine). Cationic copper(I) complexes $[LCu(D)]^+$ (D = RCN (**1a–c**), CO (**1d**, ν_{CO} = 2075 cm^{-1}), or PPh_3 (**1e**)) can be isolated as stable compounds, and the X-ray structures of $[LCu(PPh_3)]^+$ (**1e**) and $[L'Cu(CH_3CN)]^+$ (**1′**, L′ = bis(2-pyridylmethyl)-(5-carbomethoxy-2-pyridylmethyl)amine) are reported. Compound **1e** exhibits a pseudotetrahedral tetracoordination with ligation from two pyridines plus alkylamine and phosphine donors; the third pyridine donor is uncoordinated. Complex **1′** possesses a distorted pentacoordinate structure, resembling more closely that found for typical Cu(II) complexes with L, i.e., with a trigonal bipyramidal geometry. $[LCu(MeCN)]^+$ (**1a**) reacts to give the dioxygen complex $[(LCu)_2(O_2)]^{2+}$ (**2**) which is stable at −80 °C in EtCN or CH_2Cl_2 solution [λ_{max} = 525 nm (ϵ = 11 500 M^{-1} cm^{-1})]. The binding of O_2 and CO to **1a** is reversible, and UV–vis spectroscopy is used to demonstrate cycling between **1a** and **2** (vacuum cycling). Thermally unstable solids $[(LCu)_2(O_2)]^{2+}$ (**2**) were isolated as PF_6^- or ClO_4^- salts, and crystals suitable for X-ray diffraction were obtained. $[(LCu)_2(O_2)]^{2+}$ (**2**) stands as the *first* copper–dioxygen complex to be structurally characterized, and full details are reported and compared to structurally related peroxodicobalt(III) complexes also possessing a *trans*-(μ-1,2-peroxo) coordination. Notable features include Cu···Cu = 4.359(1) Å, and the O–O bond length is 1.432(6) Å, a typical peroxide bond distance. $[(LCu)_2(O_2)]^{2+}$ (**2**) exhibits very normal looking ^1H and ^{13}C NMR spectra, indicative of strong magnetic coupling between Cu(II) ions. This and other properties are compared to those of oxyhemocyanin (O_2 carrier) and other Cu_2O_2 complexes.

Introduction

The interaction of molecular oxygen (dioxygen, O_2) with transition metals and the formation and reactivity of dioxygen–metal compounds are subjects of importance in a variety of synthetic, industrial, and biological processes.[1,2] Discrete M_n–O_2 species, their metal complex precursors, or further reaction products may (i) mediate or catalyze organic oxidations, (ii) be used in scavenging traces of O_2 from inert atmospheres, (iii) be applied to procedures useful in the separation-purification of dioxygen (e.g., from air),[3] or (iv) be useful in fuel cells technologies, i.e., as O_2 reduction catalysts.[4] Biological systems employ either Fe or Cu for O_2 binding and transport, its utilization in substrate oxidation reactions, or in energy transduction by catalyzing the reduction of O_2 to water.

While structural and mechanistic aspects of O_2 binding and activation of by iron-containing heme proteins (e.g., myoglobin, hemoglobin, and *cyt.* P-450 monooxygenase) and model compounds[2a,b,5] are well advanced, non-heme iron-[6] and copper-containing[7–11] systems are less well understood, in spite of the fact that they mediate very similar kinds of chemical processes.

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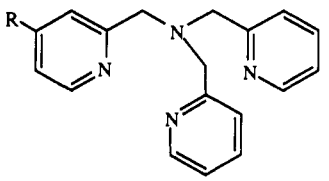
In fact, discrete copper–dioxygen complexes have remained elusive until only recently. In addition to the characterization of a variety of interesting solution species and solid materials,[7-17] there are now also *two* Cu_2O_2 complexes which have been characterized by X-ray crystallography, these being derived from reactions of copper(I) with dioxygen.[18,19] The focus here is on the chemistry and structure of one of those and the structures of mononuclear Cu(I) precursor complexes.

For some time, we have been studying the copper coordination chemistry of tripodal potentially tetradentate ligands.[20-22] These were originally employed in order to enforce a nonplanar coordination for Cu(I) or Cu(II), seen to be important and relevant to copper protein active site model studies. Here we describe the synthesis of L and L';[23] tetra- or pentacoordinate Cu(I) complexes $[LCu(D)]^+$ (D = unidentate ligand donor, **1a–e**) have been characterized. The X-ray structures of $[LCu(PPh_3)]^+$ (**1e**) and



L	R = H-	$[LCu(MeCN)]^+$	**1a**
	R = H-	$[LCu(EtCN)]^+$	**1b**
	R = H-	$[LCu(PrCN)]^+$	**1c**
	R = H-	$[LCu(CO)]^+$	**1d**
	R = H-	$[LCu(PPh_3)]^+$	**1e**
L'	R = $CH_3OC(O)$-	$[L'Cu(CH_3CN)]^+$	**1'**

$[L'Cu(MeCN)]^+$ (**1'**) are presented, and the reversible reactions

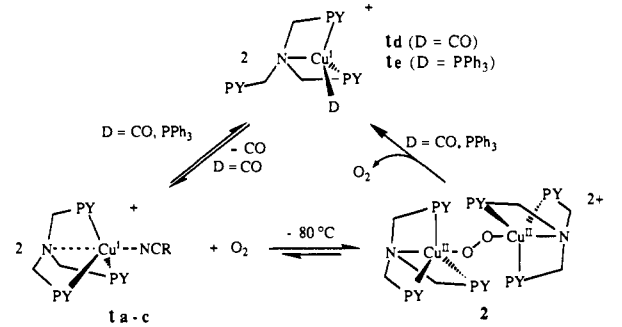


Figure 1. O_2 and CO binding behavior of complexes **1a–c** (PY = 2-pyridyl). Reversible oxygenation of **1a–c** produces the peroxo-bridged dicopper(II) complex $[(LCu)_2(O_2)]^{2+}$ (**2**), which has been characterized by X-ray crystallography. The dioxygen ligand in **2** can be displaced by CO or PPh_3 to give adducts **1d** or **1e**, respectively. See text for further explanation.

of O_2 and CO with $[LCu(MeCN)]^+$ (**1a**) are detailed (Figure 1). Reaction of **1a–c** with O_2 at –80 °C in EtCN or CH_2Cl_2 results in the reversible formation of the copper–dioxygen complex $[(LCu)_2(O_2)]^{2+}$ (**2**), isolable as a solid and best described as a peroxodicopper(II) species having a *trans*(μ-1,2-peroxo) coordination. The identity and description of **2** was confirmed in a single-crystal X-ray structural study.[18] Structural, associated spectroscopic, and other physical properties are presented, and comparisons to other peroxo–metal compounds are made.

Results and Discussion

Syntheses of Copper(I) Complexes. The general synthetic procedure for the synthesis of copper(I) complexes is to add 1 equiv of $[Cu(CH_3CN)_4]Y$ (Y = PF_6^- or ClO_4^-) to an acetonitrile solution of the appropriate ligand under argon. The synthesis and handling/study of Cu(I) complex products **1** must be carried out exclusively in organonitrile solvents, otherwise an undesirable side reaction with solvent occurs or disproportionation (e.g., to Cu metal and Cu(II), common in Cu(I) chemistry[24]) takes place. An exception is $[LCu(CO)]^+$ (**1d**), which can be formed in CO-saturated tetrahydrofuran (vide infra). In CH_2Cl_2 as solvent, **1a–c** react rapidly with abstraction of chloride, producing L–copper(II) chloride adducts in high yield. In fact, $[LCu(MeCN)]^+$ (**1a**) has been studied for its action in reductive dehalogenation of organics,[25] and Cu complexes with amine–pyridine ligands have also been demonstrated to dehalogenate CH_2Cl_2 by a mechanism involving nucleophilic attack.[25,26]

We have also synthesized and investigated compounds with ligands similar to L but varied in the number of methylene groups connecting the alkylamine and pyridine donors. Such changes cause marked effects in structure, redox properties,[20-22] and reactivity of derived Cu(I) or Cu(II) complexes, having varied chelate ring sizes; these studies will be reported elsewhere.[22,27]

Cu(I) RCN, -CO, and -PPh_3 Adducts with L. Although $[LCu(MeCN)]^+$ (**1a**) is easily prepared and a convenient starting material for various reactions, a number of other organonitrile–Cu(I) derivatives were also synthesized. Addition of $[Cu(CH_3CN)_4]^+$ to L in propionitrile or butyronitrile solution led to the isolation of $[LCu(EtCN)]^+$ (**1b**) and $[LCu(PrCN)]^+$ (**1c**), respectively. The various nitriles are also easily displaced in solution: when **1a** is dissolved in butyronitrile, precipitation with diethyl ether results in the isolation of complex **1c**. Complex **1a** also serves as a useful precursor to carbonyl or triphenylphosphine

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Table I. Crystallographic Data for Copper(I) Complexes

	$[LCu(PPh_3)]PF_6$ (1e-PF_6)	$[L'Cu(CH_3CN)]PF_6$ (1'-PF_6)
formula	$C_{36}H_{33}CuF_6N_4P_2$	$C_{22}H_{23}CuF_6N_5O_2P$
T, K	294	163
MW	761.18	597.97
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	11.823(2)	13.027(4)
b, Å	18.618(4)	15.480(4)
c, Å	16.135(3)	13.246(2)
α, deg	90.00	90.00
β, deg	99.69(1)	110.20(2)
γ, deg	90.00	90.00
V, Å^3	3501(1)	2506.9(9)
$F(000)$	1560	1216
Z	4	4
D_{calcd}, g/cm^3	1.44	1.42
absorption coefficient, cm^{-1}	7.76	10.07
reflections collected	5032	4810
independent reflections	2898 ($\geq 6\sigma\|F_o\|$)	2544 ($\geq 3\sigma(I)$)
number of refined parameters (N_v)	262	324
largest peak/hole, eÅ^{-3}	0.71/−0.41	0.87/−1.12
R^a	0.0651	0.066
$R_w{}^b$	0.0714	0.073

^{a} $R = \sum[|F_o| - |F_c|/\sum|F_o|]$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/s^2(F_o) + g^*(F_o)^2$; $g = 0.001$.

adducts; thus, $[LCu(PPh_3)]^+$ (**1e**) was prepared by addition of PPh_3 to **1a** in CH_3CN, while $[LCu(CO)]^+$ (**1d**) was isolated after dissolving **1a** in CO-saturated tetrahydrofuran:

$$[LCu(RCN)]^+ \xrightarrow{D} [LCu(D)]^+ + RCN$$

$$D = CO, PPh_3, R'CN$$

The observation that Cu(I) complexes $[LCu(D)]^+$ are only stabilized in the presence of a Cu(I)-specific ligand such as RCN, CO, or PPh_3 provides indirect evidence that these are coordinated.[28] Additional evidence for the binding of CO to Cu(I) comes from the solid-state IR spectrum of the carbonyl adduct **3**: this exhibits $\nu(CO) = 2075$ cm^{-1}, which is in the range typically observed for protein or complex terminally coordinated Cu(I)–CO.[13c,29] Infrared spectra of the various nitrile derivatives **1** show no apparent CN stretching vibration even though elemental analysis and ^{1}H NMR data clearly indicate the presence of one nitrile molecule per copper atom. This is not considered to be unusual, however, since $\nu(CN)$ associated with end-on coordinated nitriles may be very weak in intensity or undetectable in IR spectra, even in Cu(I) complexes.[13a,30]

Carbon monoxide binding to Cu(I) is also implicated on the basis of CO uptake (i.e., manometry) experiments performed on organonitrile solutions of $[LCu(MeCN)]PF_6$ (**1a**-PF_6). These investigations have shown that the uptake of CO by **1a** in propionitrile (0 °C) occurs nearly quantitatively (CO:Cu = 0.86 ± 0.05); some competition for binding to the Cu(I) ion probably occurs due to presence of the excess nitrile solvent. The carbon monoxide taken up by **1a** to form $[LCu(CO)]^+$ (**1d**) can also be recovered (>90% by manometry) by addition of 1 equiv of PPh_3 to the solution; this presumably occurs via displacement of bound CO by PPh_3 and subsequent formation of $[LCu(PPh_3)]^+$ (**1e**). To summarize, these results suggest that CO and RCN are coordinated to the cuprous ion in complexes of L, and as seen with other types of ligand–Cu(I) complexes,[12a,13a] the relative order of binding strength in solution is PPh_3 > CO > RCN.

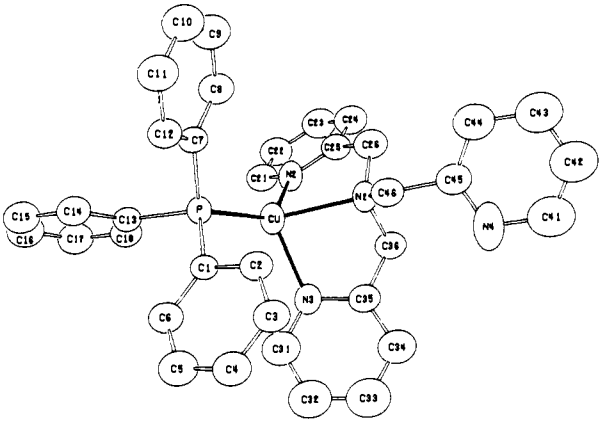

Figure 2. Perspective view of tetracoordinate $[LCu(PPh_3)]^+$ (**1e**) with dangling pyridine ligand donor, showing the atom-labeling scheme.

X-ray Structure of $[LCu(PPh_3)]PF_6$ (1e-PF_6). A summary of crystal parameters and refinement results is given in Table I, and an ORTEP drawing of the cationic portion of **1e**-PF_6 is shown in Figure 2; selected bond distances and angles appear in Table II. The structure confirms PPh_3 coordination, and it has a tetracoordinate copper(I) ion with a "dangling" uncoordinated pyridyl arm from the L ligand. Ligation occurs to the aliphatic amine nitrogen and two pyridines of the L ligand plus the phosphorous atom of the triphenylphosphine (PPh_3) unit. The copper atom is displaced ca. 0.23 Å out of the P,N2,N3 plane toward the apical amine nitrogen, resulting in a distorted tetrahedral geometry. The copper–phosphorus bond distance (Cu–P = 2.194(2) Å) is at the low end of the range usually found for Cu(I) coordinated to PR_3 but is similar to values observed for related structures possessing amine–pyridine polydentate ligands (2.21 Å average).[12a,24,32] The Cu–N_{amine} bond length is quite long at 2.248(6) Å, indicating that the aliphatic amine nitrogen binds only weakly to the Cu(I) ion. This may be a consequence of the expected strong σ-donation from the PPh_3 ligand, since this lengthening is not observed in the X-ray structures of closely related ligand complexes.[20a,22,27a] The Cu–N_{py} distances (Cu–

(28) Carbon monoxide, triphenylphosphine, and nitriles are known to stabilize the Cu(I) oxidation state and prevent disproportionation because of their strong σ-donor and π-acceptor capabilities.[24]

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Table II. Selected Bond Distances and Angles for Copper(I) Complexes

[LCu(PPh$_3$)]PF$_6$ (**1e**-PF$_6$)		[L'Cu(CH$_3$CN)]PF$_6$ (**1'**-PF$_6$)	
Interatomic Distances (Å)			
Cu–P1	2.194(2)	Cu–N1	2.439(8)
Cu–N1	2.248(6)	Cu–N2	2.093(6)
Cu–N2	2.047(6)	Cu–N3	2.130(7)
Cu–N3	2.094(6)	Cu–N4	2.108(6)
		Cu–N5	1.999(9)
Interatomic Angles (deg)			
P1–Cu–N1	127.8(2)	N1–Cu–N2	75.3(3)
N1–Cu–N2	78.1(2)	N1–Cu–N3	74.3(3)
P1–Cu–N2	130.9(2)	N1–Cu–N4	73.5(3)
N1–Cu–N3	79.8(2)	N1–Cu–N5	174.9(2)
P1–Cu–N3	112.4(2)	N2–Cu–N3	115.5(3)
N2–Cu–N3	113.0(2)	N2–Cu–N4	110.6(3)
		N2–Cu–N5	109.3(3)
		N3–Cu–N4	113.0(2)
		N3–Cu–N5	105.2(3)
		N4–Cu–N5	102.3(3)
		Cu–N5–C51	174.3(7)

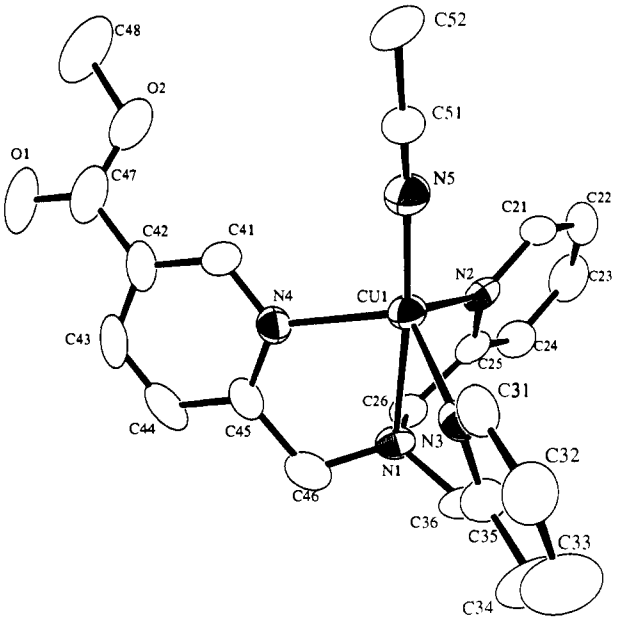
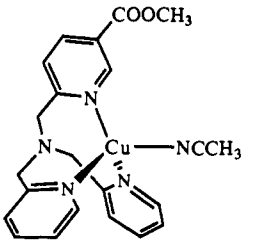


Figure 3. ORTEP drawing of pentacoordinate [L'Cu(CH$_3$CN)]$^+$ (**1'**), showing the atom-labeling scheme.

N2 = 2.047(6) Å, Cu–N3 = 2.094(6) Å) are also slightly longer than those of related tetracoordinate complexes where Cu–N$_{py}$ = 1.95–2.04 Å,[13a,20a,32] and they differ from each other by nearly 0.05 Å. This difference may result from some steric interaction between the pyridine ring containing N3 and a phenyl group of the PPh$_3$ moiety, which slightly lengthens the Cu–N3 bond. The presence of the two 5-membered chelate rings as well as the steric bulk of the triphenylphosphine group and long Cu–N$_{amine}$ bond length appear to be responsible for the extremely acute N$_{py}$–Cu–N$_{amine}$ angles (78–80°) observed for this complex.

Some of the observed structural parameters of **1e**-PF$_6$ compare favorably with those of a related dinuclear Cu(I) carbonyl complex containing the ligand *N,N,N',N'*-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN).[33] For example, [Cu$_2$(TPEN)(CO)$_2$]$^{2+}$, which possesses the identical N$_3$ tridentate ligation as in [LCu(PPh$_3$)]$^+$ (**1e**), has Cu–N$_{amine}$ distances of ca. 2.16 Å and Cu–N$_{py}$ bonds of 2.035 Å average. The N$_{py}$–Cu–N$_{amine}$ angles are also similar, ranging from 80 to 82°.

Structure of [L'Cu(CH$_3$CN)]PF$_6$ (1'-PF$_6$). X-ray structure analysis data are given in Table I, selected bond distances and angles are provided in Table II, and an ORTEP diagram of the structure is given in Figure 3. With acetonitrile as the "exogenous" donor ligand (i.e., instead of PPh$_3$), the mononuclear structure is pseudotetracoordinate but with strong bonding to all three pyridine N atoms and the CH$_3$CN donor. The dihedral angles formed by appropriate planes involving N2–N5 and Cu1 are all very close to 90°. The Cu1 atom lies 0.568 Å above the least-squares plane derived from N2,N3,N4, toward the acetonitrile N5 atom. The molecule possesses near (noncrystallographic) 3-fold symmetry with respect to the Cu–N5 (CH$_3$CN) or Cu···N1 vector, with the three pyridine rings being nearly equivalent. Small distortions may result from the inequivalence due to the ester group on the pyridine ring containing N4. There appears to be only a weak interaction with the alkylamine nitrogen N1, with Cu1···N1 = 2.439(8) Å outside the sum of their respective covalent radii. However, the lone pair on the N1 nitrogen atom is clearly directed toward the copper ion, since N1 lies on that side (by 0.346 Å) of the plane defined by the C26,C36,C46 carbon atoms (with ∠C–N1–C$_{av}$ = 114.5°).



The structure thus takes on the appearance of a trigonal bipyramidal (TBP) Cu(I) complex, exactly what is found in analogous Cu(II) complexes with this ligand.[20d,21,22] As such, the Cu–N$_{pyridine}$ bond distances are 0.05–0.06 Å longer than those found for either TBP complexes [LCu^{II}(Cl)]$^+$ or [LCu^{II}(CH$_3$CN)]$^{2+}$.[21,22] The Cu–N$_{alkylamine}$ bond lengths in these two complexes are 2.050(6) and 2.019(6) Å, respectively, considerably shorter than those observed here for [L'Cu(CH$_3$CN)]$^+$ (**1'**). The Cu–N$_{NCCH_3}$ bond distance of 1.999(9) Å in **1'** compares closely to that observed for the Cu(II) analogue [LCu^{II}(CH$_3$CN)]$^{2+}$, where this value is 1.978(7) Å. Yet, other truly four-coordinate Cu(I) complexes with one CH$_3$CN ligand have Cu–N$_{NCCH_3}$ = 1.88–1.95 Å. Thus, the Cu1–N1 interaction clearly perturbs the structure of **1'**, causing its structural parameters to be more like a pentacoordinate Cu(I) complex. It is noteworthy that the coordination geometry of Cu(I) complex **1'**, and by implication that of all complexes [LCu(RCN)]$^+$ (**1a–c**), closely resembles that of the peroxo product [(LCu)$_2$(O$_2$)]$^{2+}$ (**2**), vide infra.

Thus, the solid-state structure of derivatives [LCu(D)]$^+$ may be variable. From the present observations, one would surmise that steric factors are important, and for bulky D ligands, the tetracoordinate structure seen in [LCu(PPh$_3$)]PF$_6$ (**1e**-PF$_6$) will be observed. For smaller ligands D (e.g., CO and RCN), the structure seen for [L'Cu(CH$_3$CN)]PF$_6$ (**1'**-PF$_6$) more than likely will be found. The solution chemistry may also vary, and recent NMR spectroscopic investigations have revealed a dynamical behavior in solution.[27a] These studies may elucidate details concerning RCN coordination and the nature or exchange of uncoordinated pyridine donor groups.[27b]

Oxygenation of [LCu(MeCN)]$^+$ (1a) and Generation of the Dioxygen Adduct, [(LCu)$_2$(O$_2$)]$^{2+}$ (2). When an orange propionitrile solution of **1a** is cooled to −85 °C and exposed to dioxygen, there is a very rapid change to an intensely violet-colored solution, characteristic of the dioxygen adduct **2**. The color persists, and the solution is stable as long as it is kept cold (<−70 °C) and dry; above ca. −50 °C a green color develops which is thought to be due to the formation of more stable copper(II) decomposition

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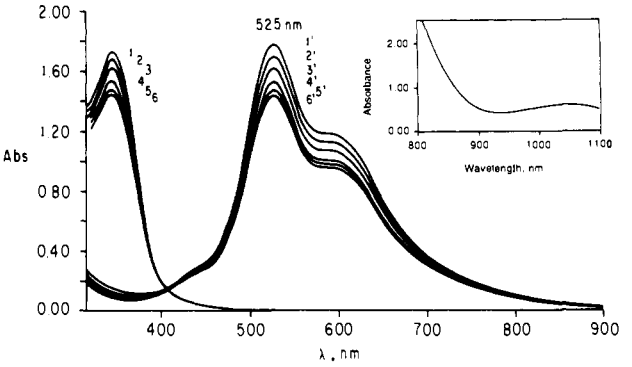

Figure 4. UV–Vis spectra demonstrating the reversible O_2-binding behavior of $[LCu(RCN)]^+$ (**1**) in EtCN to give the dioxygen adduct $[(LCu)_2(O_2)]^{2+}$ (**2**) (vacuum cycling). Reaction of **1a** (λ_{max} = 345 nm) with O_2 at –80 °C in EtCN produces an intensely violet solution of **2**, spectrum 1′, λ_{max} = 525 nm. The inset shows the d–d band in the near-IR region. Application of a vacuum and brief heating causes decoloration and regeneration of **1b**, spectrum 2. Rechilling and reoxygenation of this solution produces **2**, spectrum 2′. The process can be repeated as shown, with a small loss in absorbance due to decomposition reactions.

products, including fluoride–Cu(II) complexes.[34] A similar reaction is observed in dichloromethane; if solid **1a** is added to cold (–85 °C) oxygen-saturated CH_2Cl_2, the same (spectroscopically) violet-colored solution is also obtained. In this manner, stable solutions of **2** can be handled in dichloromethane in spite of the instability of precursor **1** in this solvent (vide supra).

Manometric measurements at –85 °C were carried out in order to determine the stoichiometry of the reaction with O_2 (Experimental Section). The results indicate absorption of O_2 by propionitrile solutions of **1a** occur in the ratio Cu/O_2 = 2:1, giving a complex formulated as $[(LCu)_2(O_2)]^{2+}$ (**2**):

$$2[\underset{\mathbf{1a}}{LCu(CH_3CN)}]^+ + O_2 \xrightarrow[-85\,^\circ C]{EtCN} \underset{\mathbf{2}}{[(LCu)_2(O_2)]^{2+}} + 2CH_3CN$$

This stoichiometry is consistent with the formation of a copper–dioxygen complex containing an intact O–O bond,[2d,7] and an O–O stretch (typical of the peroxide O_2^{2-} oxidation state) has been observed at 832 cm^{-1} (788 cm^{-1} with $^{18}O_2$).[18b] A 4:1 reaction stoichiometry is more typical of the reaction of low-valent metals with dioxygen[9] and could derive from (a) the disproportionation of metal–peroxo intermediates or (b) through their direct reduction to oxo–Cu(II) products, eq 1.[9,10,35]

$$Cu(II)\text{–}(O_2^{2-})\text{–}Cu(II) + 2Cu(I) \rightarrow 2[Cu(II)\text{–}O\text{–}Cu(II)] \quad (1)$$

In EtCN at –85 °C, $[LCu(EtCN)]^+$ (**1b**) exhibits a single absorption band in the UV–visible region (>315 nm), which occurs at 343 nm (ϵ = 5630 M^{-1} cm^{-1}), Figure 4. Upon exposure to O_2 (–85 °C), the intensely violet-colored solution exhibits strong $O_2^{2-} \rightarrow Cu(II)$ charge-transfer (LMCT) absorptions at 525 (ϵ = 11 500), ca. 440 (sh, ϵ = 4000 M^{-1} cm^{-1}), and ca. 590 (sh, ϵ = 7600 M^{-1} cm^{-1}) nm (Figure 4). A weaker absorption occurs in the near-IR region at 1035 nm (ϵ = 160 M^{-1} cm^{-1}), assigned as a d–d transition.[18b] The spectral features associated with the formation of $[(LCu)_2(O_2)]^{2+}$ (**2**) are observed only at low temperature (below ca. –50 °C) and only in the presence of O_2.

Reversible Binding of O_2 and CO: Vacuum and Carbonyl Cycling. The binding of dioxygen to $[LCu(RCN)]^+$ (**1**) takes place in two steps. First a 1:1 copper–dioxygen adduct forms (k_1 = 1.8 × 10^4 M^{-1} s^{-1} at –90 °C),[7,15c] which then further reacts with precursor **1** to give the dinuclear dioxygen adduct $[(LCu)_2(O_2)]^{2+}$ (**2**). In addition to the results from the kinetic study,[7,15c] the reversibility of dioxygen binding to **1** is indicated by several lines of evidence including the ability to oxygenate **1** and deoxygenate $[(LCu)_2(O_2)]^{2+}$ (**2**) through several cycles in a quasireversible manner without severe decomposition. This is accomplished by the application of a vacuum to a propionitrile solution of **2** to remove the bound dioxygen (peroxo) ligand, and this process can be followed spectrophotometrically, as shown in Figure 4. In this experiment, $[LCu(MeCN)](ClO_4)$ (**1a**-ClO_4) is dissolved in EtCN under argon, and the spectrum is recorded at –80 °C (spectrum 1). The introduction of O_2 produces the O_2 adduct $[(LCu)_2(O_2)](ClO_4)_2$ (**2**-$(ClO_4)_2$), and the spectrum with the 525-nm absorption maximum is labeled as spectrum 1′ in Figure 4. When this solution is subjected to a vacuum and then rapidly and briefly (1–5 s) heated in boiling water, the intense violet 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 2, showing the complete loss of the 525-nm absorption and the regeneration of the copper(I) complex **1a**-ClO_4. Reoxygenation at low temperature affords **2**-$(ClO_4)_2$ (spectrum 2′), showing very little loss in absorption intensity, and the cycling between oxy and deoxy forms, i.e., **1** + O_2 ⇄ **2**, can be repeated at least five times as shown, with only a small amount of decomposition (ca. 20% overall, as judged by the reduced absorbance at 525 nm, Figure 4).

As already discussed, the binding of CO to nitrile solutions of $[LCu(RCN)]^+$ (**1a–c**) readily occurs, and this is a reversible process as evidenced by UV–visible spectroscopy. The carbonylation of **1** is effected by bubbling its RCN solution with CO, while decarbonylation occurs by the application of reduced pressure (at room temperature) to solutions of $[LCu(CO)]^+$ (**1d**). Thus, compounds **1a–c** are reversible binders of both O_2 and CO. Carbon monoxide can also be used to displace the bound dioxygen ligand in $[(LCu)_2(O_2)]^{2+}$ (**2**), forming $[LCu(CO)]^+$ (**3**), and thereby allowing for "carbonyl cycling" to take place. Here, spectrophotometric monitoring of several cycles of O_2 reaction of **1** to give **2**, CO reaction of **2** producing **3**, and removal of CO (in vacuo) from **3** regenerating **1** occurs; this has been previously described.[18a] The stronger binding of CO parallels the behavior of porphyrin–iron complexes and proteins,[2d,5] as well as other O_2 carriers of copper we have studied.[7–9] Carbon monoxide is, in fact, a known inhibitor of hemocyanin and other copper proteins which react with O_2.[10–13,36]

Isolation of Solid Dioxygen Complex $[(LCu)_2(O_2)](PF_6)_2 \cdot 5Et_2O$ (2-$(PF_6)_2 \cdot 5Et_2O$). $[(LCu)_2(O_2)](PF_6)_2 \cdot 5Et_2O$ (2-$(PF_6)_2 \cdot 5Et_2O$) was obtained as a crystalline material suitable for X-ray structural analysis. It was of general interest to obtain a solid material that could be handled for various purposes, but 2-$(PF_6)_2 \cdot 5Et_2O$ was found to be inconvenient, in part because it readily lost the diethyl ether solvate. However, a perchlorate salt was found to be more suitable for these purposes. As described in the Experimental Section, slow addition of diethyl ether to cold (–85 °C) dichloromethane or propionitrile solutions of the dioxygen complex $[(LCu)_2(O_2)](ClO_4)_2$ (**2**-$(ClO_4)_2$) [generated by O_2 reaction with **1**-(ClO_4)] results in precipitation of a dark purple powder which could be collected by use of a low-temperature fritted filter. This material appears to be indefinitely stable under argon at –85 °C but turns green on standing several hours at room temperature. Spectroscopic data confirm that this compound *is* a solid form of the dioxygen complex, formulated as $[(LCu)_2(O_2)](ClO_4)_2$ (**2**-$(ClO_4)_2$), with the same properties and structure as 2-$(PF_6)_2 \cdot 5Et_2O$. Cold solid samples of **2**-$(ClO_4)_2$ can be redissolved

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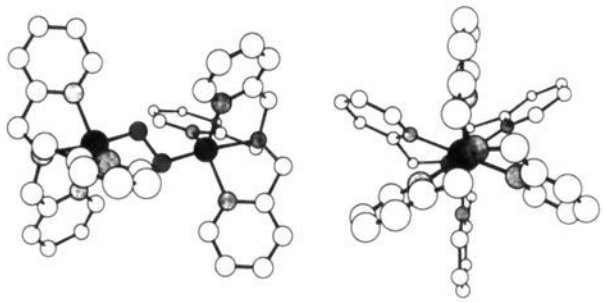
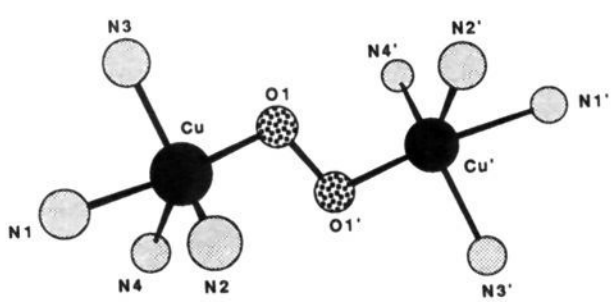


Figure 5. Chem3D drawings of the structure of $[(LCu)_2(O_2)]^{2+}$ (**2**).

(CH_2Cl_2 or EtCN, −85 °C) to give the same UV–vis spectrum observed for solutions prepared directly from $[LCu(RCN)]^+$ (**1**) and O_2. In addition, a solid-state UV–vis spectrum (taken quickly at room temperature; Nujol Mull on filter paper) of **2**-$(ClO_4)_2$ exhibited a strong broad absorption (λ_{max} 500–550 nm), in line with the solution spectrum. Similarly, ^{1}H NMR spectra (see below) of redissolved samples of **2**-$(ClO_4)_2$ (−80 °C, CD_2Cl_2) are found to be essentially identical to those obtained directly from **1** and O_2. Little or no decomposition occurs when this material is isolated and redissolved at low temperature; ϵ at 525 nm for redissolved **2**-$(ClO_4)_2$ was 11 100 ± 1160 (average, 3 trials). Analyses of the copper ion content of these solutions were also carried out to confirm and quantitate these measurements (Experimental Section).

Crystal Structure of the Copper–Dioxygen Complex $[(LCu)_2(O_2)](PF_6)_2\cdot 5Et_2O$ (2-$(PF_6)_2\cdot 5Et_2O$). An initial communication concerning this structure has been published;[18a] new comparisons of this important structure to related copper and cobalt structures are worthwhile. As a result of spectroscopic and manometric investigations which indicated formation of a dioxygen complex upon addition of O_2 to **1** at low temperature, attempts were made to obtain single crystals of this compound that would permit an X-ray crystallographic determination of the structure. Efforts in this endeavor were eventually rewarded when dark purple crystals of $[(LCu)_2(O_2)](PF_6)_2\cdot 5Et_2O$ (**2**-$(PF_6)_2\cdot 5Et_2O$) were obtained by slow diffusion of diethyl ether into a propionitrile solution of the dioxygen complex at −85 °C (Experimental Section). The structure was determined for a crystal which was maintained at −90 °C during data collection; a summary of crystal and refinement data was previously given.[18a] Chem3D drawings of the cationic portion of **2**-$(PF_6)_2\cdot 5Et_2O$ are shown in Figure 5.

The structure of **2** is of considerable interest because it represents the an unambiguous X-ray crystallographic characterization of a copper–dioxygen compound.[7-10,18] The complex is best described as a peroxo–dicopper(II) species (vide infra), and, as shown, it contains a *trans*-(μ-1,2-O_2^{2-}) group (derived from O_2) bridging the two Cu(II) ions. There is one dinuclear



Cu(II) complex per unit cell with a crystallographic inversion center between the atoms O1 and O1′. As found in other Cu(II) complexes with L,[20d,21,22] the Cu atom is pentacoordinate with a distorted trigonal bipyramidal geometry. The equatorial ligands are the pyridyl N2, N3, and N4 donors, with aliphatic amine nitrogen (N1) and peroxo oxygen (O1) atoms occupying axial sites. Analysis of the pentacoordinate geometry using the method of Addison and co-workers[37] results in a calculated τ value of 0.86, indicating only a small deviation of the complex from an idealized trigonal bipyramidal geometry (τ = 1.00). The copper(II) ion lies 0.347 Å out of the N2,N3,N4 trigonal plane and is displaced away from the aliphatic amine nitrogen atom toward the anionic peroxido ligand; the N_{py}–Cu–N_{amine} angles are rather acute and average 80.3°. The Cu–N bond lengths are typical for nitrogen ligands bonded to Cu(II)[24] and are observed to vary from 2.02 to 2.10 Å. These values are also rather typical for tetracoordinate Cu(I) complexes with pyridine ligands of this type (vide supra); shorter Cu–N_{py} are observed for three- or two-coordinate Cu(I) compounds.[38]

The peroxidic description of the bridging dioxygen ligand is further supported by the observed O–O bond length of 1.432(6) Å. This distance is somewhat shorter than the often quoted value of 1.49 Å for a peroxo species but is considerably longer than the 1.28 Å bond length reported for the superoxo moiety.[39] The Cu–O–O angle of 107.7(2)° is very close to that expected for an ideal tetrahedron (109.4°) and compares well with the 100(2)° O–O–H angle in H_2O_2.[40]

The structural parameters which arise from the binding of O_2 in **2** may be conveniently compared to those of μ-peroxo-bridged dicobalt(III) complexes for which a wealth of structural data has been amassed.[1a,2d,41,42] Table III lists bond distances and angles for the metal–O_2 units in several such 2:1 dioxygen adducts of cobalt. One trend immediately apparent from the data is that (in the absence of a second bridging group) the peroxo ligand is always found in a trans bridging mode between the two metal ions. In the majority of complexes, the M_2O_2 unit is rigorously planar with a dihedral angle of 180°; this is also the case for the present system in which the crystallographic center of symmetry necessitates the 180° torsion angle. This behavior appears to be quite reasonable since the trans geometry would tend to minimize unfavorable intermolecular contacts between adjacent polydentate ligands. The trans bridging mode additionally requires fairly long metal–metal distances for these compounds; the Co···Co separations range from 4.24 to 4.90 Å (Table III). The Cu···Cu distance of **2** (4.359(1) Å) lies at the lower end of this range as a consequence of the relatively short Cu–O bond length (1.852(5) Å) and small Cu–O–O angle (107.7(2)°).

An interesting feature of the structure of **2** is the localization of the peroxo ligand within a hydrophobic pocket formed by the pyridine rings of the two L ligands (Figure 5). These rings appear to form an interdigitating network about the dioxygen moiety, effectively isolating it from interaction with the surrounding medium. Perhaps such an arrangement may contribute somewhat to the stability of the complex, possibly by slowing an irreversible bimolecular reaction (e.g., **2** + $[LCu(I)]^+$) which could lead to the formation of (μ-oxo)Cu(II) products, e.g., eq 1. By way of

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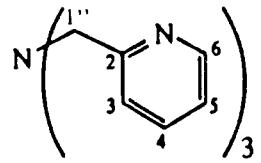
Table III. Structural Comparison of $[(LCu)_2(O_2)](PF_6)_2 \cdot 5Et_2O$ (**2**-$(PF_6)_2 \cdot 5Et_2O$) with μ-Peroxo-Bridged Dicobalt(III) Complexes

complex	O-O, Å	M-O-O, deg	M-O, Å	M-O-O-M, deg[a]	M···M, Å	ref
$[(H_3N)_5Co(O_2)Co(NH_3)_5](SCN)_4$	1.469	110.8	1.879	180	4.495	41
$[(H_3N)_5Co(O_2)Co(NH_3)_5](SO_4)(HSO_4)_3$	1.312	117.7	1.849	175.3	4.562	42a
[(dien)(en)Co(O$_2$)Co(en)(dien)](ClO$_4$)$_4$[b]	1.488	110.0	1.896	180	4.523	42b
[(tren)(H$_3$N)Co(O$_2$)Co(NH$_3$)(tren)](SCN)$_4 \cdot 2H_2O$[c]	1.511	111.5	1.889	180	4.545	42c
$[O_2N(en)_2Co(O_2)Co(en)_2(NO_2)](NO_3)_2 \cdot 4H_2O$	1.529	110.0	1.887	180	4.54	42d
[(pydpt)Co(O$_2$)Co(pydpt)]I$_4 \cdot 3H_2O$[d]	1.456	114.3	1.891	162	4.554	42e
[(pydien)Co(O$_2$)Co(pydien)]I$_4$[e]	1.489	112.5	1.876	180	4.532	42f
[(papd)Co(O$_2$)Co(papd)]$^{4+}$	1.486	111.9	1.924	180	4.612	42g
$K_3[(NC)_5Co(O_2)Co(CN)_5](NO_3)_2 \cdot 4H_2O$	1.447	118.8	1.985	180	4.899	42h
[(DMF)(salen)Co(O$_2$)Co(salen)DMF)][g]	1.339	120.3	1.910	110.1	4.241	42i
[(salen)Co(O$_2$)Co(salen)]$\cdot^2/_3$(CH$_3$)$_2$CO$\cdot^1/_3$piperidine	1.383	120.0	1.911	121.9	4.386	42j
[(salprtr)Co(O$_2$)Co(salprtr)]$\cdot$(toluene)[h]	1.45	118.5	1.93	149.3	4.65	42k
$[LCu(O_2)CuL](PF_6)_2 \cdot 5Et_2O$	1.432	107.7	1.852	180	4.359	this work

[a] Torsion angle. [b] en = ethylenediamine; dien = diethyleneamine. [c] tren = tris(2-aminoethyl)amine. [d] pydpt = 1,11-bis(2-pyridyl)-2,6,10-triazaundecane. [e] pydien = 1,9-bis(2-pyridyl)-2,5,8-triazanonane. [f] papd = 1,5,8,11,15-pentaazapentadecane. [g] salen = *N,N'*-bis(salicylidene)ethylenediamine. [h] salprtr = *N,N''*-bis(salicylidene)dipropanetriamine.

Table IV. NMR Chemical Shift Data for the Ligand L, the **1a**-ClO_4 Cu(I) Complex, and the **2**-$(ClO_4)_2$ Dioxygen Adduct at −88 °C[a]

L =



^{1}H NMR

ligand or complex	solvent	py-H^6	py-H^5	py-H^4	py-H^3	1''-CH$_2$	CH$_3$CN
L	CD_2Cl_2	8.55	7.24	7.84	7.79	3.87	
[LCu(CH$_3$CN)]ClO$_4$ (**1a**-ClO$_4$)	EtCN	8.60	7.32	7.84	7.42	3.73	2.09
$[(LCu)_2(O_2)](ClO_4)_2$ (**2**-$(ClO_4)_2$)	CD_2Cl_2	9.94	7.65	8.06[b]	7.82[b]	4.78	2.07

^{13}C NMR

ligand or complex	solvent	2-py	3-py	4-py	5-py	6-py	1''-CH$_2$
L	CD_2Cl_2	159.76	122.55	137.25	122.12	149.37	60.15
[LCu(CH$_3$CN)]ClO$_4$ (**1a**-ClO$_4$)	EtCN	156.50	124.59	137.95	124.45	149.05	56.67
$[(LCu)_2(O_2)](ClO_4)_2$ (**2**-$(ClO_4)_2$)	CD_2Cl_2	152.97	127.91	139.77	125.29	149.09	ca. 55

[a] In ppm from TMS. [b] Assignments may be interchanged.

analogy, site isolation has previously been demonstrated to be important in preventing irreversible oxidation in synthetic analogs of hemoglobin, e.g., the further reaction of $PFeO_2$ to give μ-oxo dimer complexes PFe(III)OFe(III)P (P = porphyrin ligand).[5]

In summary, this copper–dioxygen complex, best described as a peroxodicopper(II) compound, indicates that it possesses no unusual structural features. The coordination geometry is typical for Cu(II) complexes in a pentacoordinate trigonal bipyramidal environment, including those with the L ligand. The peroxo ligation to Cu(II) is also unexceptional, with close similarities to the well-established peroxodicobalt(III) compounds known.

Physical and Spectroscopic Properties of $[(LCu)_2(O_2)]^{2+}$ (2). It is worthwhile to briefly summarize these, also introducing aspects not described elsewhere, such as the NMR spectroscopic properties, which bear on the magnetic properties of **2**. Magnetic susceptibility measurements in solution (Faraday and Evans methods) and in solid state ($-2J > 600$ cm^{-1}, based on $H_{ex} = -2JS_1S_2$)[22,43] indicated that in spite of their rather large separation (4.36 Å) the paramagnetic d^9 copper(II) centers in compound **2** are very strongly antiferromagnetically coupled, and as a consequence, the compound is EPR silent. The Evans method measurements are detailed in the Experimental Section. With an unambiguous X-ray structure of **2** in hand, this study afforded an experimental opportunity to assess the ability of a peroxo ligand to mediate electronic coupling between paramagnetic copper centers, showing that it is quite efficient. Recent theoretical studies[44] carried out for Cu_2O_2 complexes in a variety of possible coordination geometries also conclude that such species will be antiferromagnetically coupled (i.e., singlet ground state). Balch and La Mar[45] have previously shown the peroxo-bridged iron–porphyrins are also strongly magnetically coupled.

The singlet ground state ascribed to $[(LCu)_2(O_2)]^{2+}$ (**2**) by its EPR and magnetic properties suggest that NMR spectra may be observed, as seen for other moderately or strongly coupled Cu(II) dinuclear compounds.[18a,19,46] Indeed this is the case, and well-resolved ligand resonances were observed in the ^{1}H and ^{13}C spectra of **2** at −88 °C in CD_2Cl_2 (Table IV and Figure 6). Solutions of $[(LCu)_2(O_2)](ClO_4)_2$ (**2**-$(ClO_4)_2$) were prepared by addition of solid [LCu(MeCN)](ClO_4) (**1a**-ClO_4) to cold, oxygenated CD_2Cl_2 contained within 10-mm-od NMR tubes (Experimental Section). Figure 6 shows the ^{1}H NMR spectrum of a sample prepared in this fashion; in addition to those of the ligand, the resonances for CH_2Cl_2 (residual from CD_2Cl_2), CH_3CN (from **1a**), and TMS are clearly observed. In the ^{13}C spectrum, the resonances of CH_3CN appear at ca. 3 and 118 ppm; however, the CH_2 peak of the ligand (1''-CH_2) is buried under the intense CD_2Cl_2 multiplet (at ca. 55 ppm). Table IV compares the ^{1}H and ^{13}C resonances of the dioxygen complex with those of the free ligand under identical conditions (CD_2Cl_2, −88 °C). Chem-

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(44) (a) Maddaluno, J.; Giessner-Prettre, C. *Inorg. Chem.* **1991**, *30*, 3439-3445. (b) Ross, P. K.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 3246-3259.

(45) Chin, D.-H.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 4344-4349.

(46) Maekawa, M.; Kitagawa, S.; Munakata, M.; Masuda, H. *Inorg. Chem.* **1989**, *28*, 1904-1909, and references cited therein.

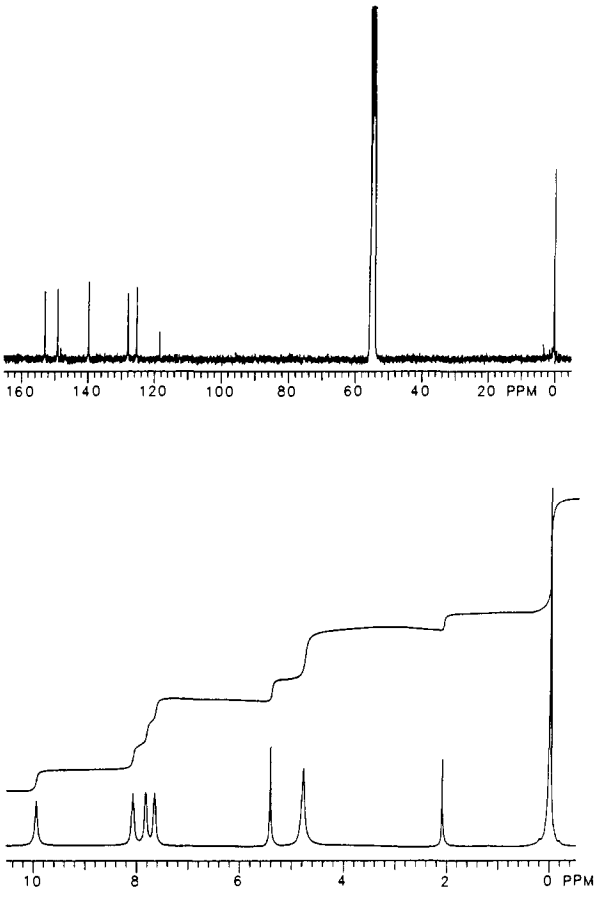


Figure 6. ^1H and ^{13}C NMR spectra of $[(LCu)_2(O_2)](ClO_4)_2$ (**2**-$(ClO_4)_2$) in CD_2Cl_2 at −88 °C.

ical shifts for $[LCu^I(MeCN)](ClO_4)$ (**1a**-ClO_4) are also provided, but these must be interpreted with caution since the spectra were recorded in EtCN solvent.

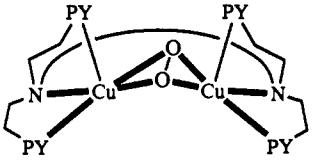
For the ^1H NMR spectra, the general trend is for a downfield shift of the resonances when comparing the dioxygen complex to the free ligand. This phenomenon is most pronounced for the methylene protons and those occupying the 6-position of the pyridine rings. The remaining protons appear to behave similarly, although the chemical shift differences are not as large. The downfield shift of the proton resonances appears to reflect the expected deshielding of these nuclei as a consequence of σ-donation to the positively charged Cu(II) ions in **2**. The relatively large changes in chemical shift observed for the methylene and py-H^6 protons (0.91 and 1.37 ppm, respectively, from the free ligand) probably result from their proximity to the nitrogen donor atoms; these protons would be expected to experience the strongest σ-effects. Additionally, magnetic anisotropy of the O–O bond in the negatively charged peroxide ligand may contribute to the enhanced downfield shift of the nearby py-H^6 protons. Molecular motions of the complex in solution could also lead to some steric interactions between py-H^5 protons on opposing L ligands resulting in moderate deshielding of these nuclei.

The ^{13}C spectral data (Table IV) show a somewhat more complicated behavior, with the methylene, 2-pyridyl, and 6-pyridyl carbon resonances of the dioxygen complex exhibiting an upfield shift relative to the ligand while the remaining resonances are shifted downfield. Shielding of nuclei can occur as a result of favorable π-back-donation from Cu into adjacent nitrogen π^* orbitals. Thus, carbon resonances which are shifted upfield (1″-CH_2, py-2, and py-6) are expected to have π-bonding contributions which outweigh any σ-donation effects. In contrast, resonances which are shifted downfield are identified with nuclei for which the predominant effect is deshielding via σ-donation.

The sharpness and lack of extensive broadening of NMR resonances in $[(LCu)_2(O_2)]^{2+}$ (**2**) is consistent with its near-diamagnetic behavior. On the other hand, the ^1H and ^{13}C resonance shifts described above, are sufficiently variable that their origin may well depend on paramagnetic effects, perhaps due to the $S = 1$ paramagnetic excited state in this dinuclear Cu(II) complex. Possible mechanisms and ligand dependencies (e.g., in pyridine-containing systems) of paramagnetically induced chemical shifts are not that well developed in copper chemistry.[46] We plan to further explore this issue, in **2**, and in other Cu_2O_2 or dinuclear Cu(II) species.

Comparison to Oxyhemocyanin (Oxy–Hc) and Other Cu_2O_2 Complexes. As a potential model for hemocyanin, the present system $[LCu(RCN)]^+$ (**1a–c**) + $O_2 \rightleftarrows [(LCu)_2(O_2)]^{2+}$ (**2**) does possess certain similarities to the protein. This interconversion represents a *functional modeling* of the protein,[9a] with the ability to remove O_2 from **2** reversibly, either by application of a vacuum or by displacement using CO. Complex **2** is also strongly magnetically coupled, demonstrating that the peroxide dianion as a ligand can mediate such an interaction even when bridging in a trans arrangement at 4.36 Å. Thus, an additional hydroxo Cu(II) bridging ligand in oxyhemocyanin is not necessary to account for the observed protein diamagnetism as previously suggested.[36c,d,47]

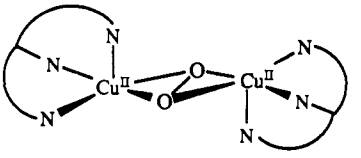
However, **2** clearly differs considerably from oxy–Hc[11,36] in its structure and spectroscopy. Such features include the long Cu···Cu distance, the trigonal (and not tetragonal) ligation about Cu(II), the UV–vis pattern, and the rather large ν_{O-O} found in **2** (832 vs ~750 cm^{-1} in oxy–Hc). Copper–dioxygen complexes which appear to be closer structural and spectroscopic models for the oxy–Hc active site include $[Cu_2(Nn)(O_2)]^{2+}$, containing



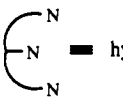
$[Cu_2(Nn)(O_2)]^{2+}$

dinucleating ligands with the bis[2-(2-pyridyl)ethyl]amine linked to the amino nitrogen by a variable hydrocarbon moiety. These are EPR silent and strongly magnetically coupled, and they possess $\lambda_{max} \sim 360$ nm with $\epsilon \sim 15000$–20000 (similar to oxy–Hc). X-ray absorption spectroscopic studies suggest that these possess a bent butterfly μ-η^2:η^2 bridging structure, as shown.[13]

However, an exceptionally good model for oxy–Hc is $\{Cu[HB(3,5\text{-}iPr_2pz)_3]\}_2(O_2)$ (**3**), the only other structurally characterized Cu_2O_2 complex, described by Kitajima and co-workers.[19]



$\{Cu[HB(3,5\text{-}iPr_2pz)_3]\}_2(O_2)$ (**3**)



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

This possesses structural (Cu···Cu = 3.56 Å), UV–vis, and vibrational spectroscopic properties (ν_{O-O} = 749 cm^{-1}) closely resembling those of oxy–Hc. The coordinated peroxide has a

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μ-η^2:η^2 binding mode, and a very recent X-ray structure of oxy-Hc confirms this to be present in the protein.[48]

Conclusion

Complex $[(LCu)_2(O_2)]^{2+}$ (**2**) was the first structurally characterized Cu_2O_2 complex, and its reversible O_2 binding nature makes it a *functional* model for hemocyanin.[9a] In fact, its three-dimensional structure indicates that it is an unexceptional coordination complex. Rather, the accomplishment here is that its generation and isolation come about by overcoming the handicaps of copper ion lability, potential peroxide disproportionation, and hydrolytic instability (i.e., moisture sensitivity), traditionally thought to be limitations in studying this type of chemistry. The use of low-temperature synthetic and spectroscopic methods has allowed us to characterize this and a variety of other Cu_2O_2 complexes in which the binding of dioxygen to a Cu(I) precursor is reversible. As seen here, in Kitajima's peroxo*di*copper(II) complexes,[19] and even when using simple unidentate imidazoles donors,[14] the use of dinucleating ligands to obtain such products is not necessary, and mononuclear Cu(I) complex precursors suffice. From considerations presented here, it can be seen how synthetic variations in appropriate ligands can be used to control the chemistry desired, in this case to stabilize a Cu_2O_2 adduct.

The lack of structural and spectroscopic similarity of $[(LCu)_2(O_2)]^{2+}$ (**2**) to the protein oxyhemocyanin active site demonstrates that nature has chosen but one of many possible means by which to bind dioxygen to copper ion. Nevertheless, important insights have been obtained, including those related to the kinetics and thermodynamics of O_2 binding to Cu(I) ion[15c] and the direct assessment of the magnetic,[43] spectroscopic,[18b] and reaction properties[49] of a peroxo ligand bound to copper ion. With the structural details now available for $[(LCu)_2(O_2)]^{2+}$ (**2**) and **3**, the rational design of other dioxygen adducts of copper will be aided, with the goals being to generate more thermally stable biomimetic copper–dioxygen complexes, O_2 carriers, and catalysts for the oxidation of organics. Such efforts are in progress.

Experimental Section

Materials and Methods. Reagents and solvents used were of commercially available reagent quality unless otherwise stated. Labeled dioxygen ($^{18}O_2$, 99%) was obtained from Icon Services, Inc. Dioxygen gas was dried by passing it through a short column of supported P_4O_{10} (Aquasorb, Mallinckrodt) and a copper coil tube immersed in a −80 °C cold trap. Methanol was distilled from $Mg(OMe)_2$, and anhydrous diethyl ether was prepared by passing it through a 60-cm-long column of activated alumina or directly distilling it from sodium/benzophenone under Ar. Dichloromethane was stirred with concentrated sulfuric acid for several days. After the mixture was washed with water, Na_2CO_3 (saturated) solution, and water, it was dried over anhydrous $MgSO_4$ before a final reflux and distillation from CaH_2. Propionitrile was first distilled from P_4O_{10} and then from CaH_2. Preparation and handling of air-sensitive materials was carried out under an argon atmosphere using standard Schlenk techniques. Deoxygenation of solvents and solutions was effected by either repeated vacuum/purge cycles using argon or by thorough bubbling (20 min) of Ar directly through the solutions. Solid samples were stored and transferred and samples for IR and NMR spectra were prepared in a Vacuum/Atmospheres drybox filled with argon.

Elemental analyses were performed by Desert Analytics, Tucson, AZ. Infrared spectra were recorded as Nujol mulls either on a Perkin-Elmer 283 or 710B instrument. NMR spectra were measured 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. Room temperature magnetic moments were determined using a Johnson-Matthey magnetic susceptibility balance, and the instrument was calibrated by using $Hg[Co(SCN)_4]$. Gas chromatography was carried out on a Hewlett-Packard 5890 gas chromatograph fitted with a 30-m HP-5 (cross-linked 5% phenylmethylsilicone) capillary column. Electron paramagnetic resonance (EPR) spectra were obtained from frozen solutions (77 K) using 4-mm-od quartz tubes in a Varian Model E-4 spectrometer operating at X-band. The field was calibrated with a powder sample of diphenylpicrylhydrazyl (DPPH, $g = 2.0037$). The solvent used was a mixture of 2-methyltetrahydrofuran (2-MeTHF) and propionitrile (EtCN) (2:1, v/v). 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 $[LCuCl]PF_6$ under identical conditions.[22]

Low-temperature electronic spectra and cycling experiments were carried out on a Perkin-Elmer Lambda Array 3840/IBM PC data system (315–900 nm) with output to an Epson FX-85 printer. The spectrophotometer was equipped with a variable temperature dewar and a cuvette assembly as described elsewhere.[12a,13a] Unless otherwise noted, samples were prepared in a 100-mL volumetric flask modified for airless work by addition of a side-arm stopcock and 14/35 male joint on the neck of the flask and a 14/20 female joint at the top. Solid samples of **1** (contained under argon in 1-mL ampules sealed with soft rubber stoppers) were weighed on an analytical balance and transferred to the argon-purged volumetric flask. Propionitrile was directly distilled from CaH_2 into the flask up to the calibration mark, and the resulting solution was stirred for 10 min with a small magnetic stirring bar. An aliquot of the solution was then transferred to the cuvette assembly by means of an inlet adapter placed onto the 14/35 male joint of the volumetric flask. The inlet adapter was constructed by attaching a 9-inch long bent glass tube to the end of a 14/35 cap (Ace 7795-06). The narrow tubing (2-mm-id) at the end of the inlet adapter was inserted into the cuvette assembly, and, with a brisk flow of Ar through the apparatus, solutions could be transferred while being protected from contact with air or moisture. After the cuvette was placed into the Dewar assembly, 30 min was allowed for temperature equilibration, and the spectrum was recorded (precooled cuvettes were allowed 5 min for temperature equilibration). Oxygenation of chilled solutions was effected by introducing O_2 into the cuvette from a vacuum line and vigorously shaking the solution. Solutions of the peroxide complex **2** could also be prepared directly in dichloromethane by an alternate procedure, whereby cold, oxygen-saturated CH_2Cl_2 was added directly to a preweighed sample of $[LCu(CH_3CN)]ClO_4$ (**1a**-ClO_4) contained within the cuvette assembly. Spectra of the solutions of the dioxygen complex in CH_2Cl_2 were identical to those obtained in EtCN. For measurements in the near-IR region (800–1100 nm), a Shimadzu UV-160 spectrophotometer was employed. A solution was prepared in the cuvette assembly described above and transferred quickly from a cold dewar (−85 °C) into the spectrometer, which had been crudely fitted with cut-out cardboard coverings in order to keep out stray light and allow insertion of the cuvette. The spectrum was recorded immediately; a spectrum of the solvent, prepared and recorded in a similar fashion, was used as a blank. The preparation and handling of samples for vacuum/heat cycling or CO cycling experiments are described below.

L. Tris[(2-pyridyl)methyl]amine. This ligand was synthesized by a modification of the procedure described by Anderegg et al.[50] A solution of 39.0 g (238 mmol) of 2-picolyl chloride hydrochloride in 100 mL of deionized water was cooled to 0 °C in an ice bath. To this solution was added, with stirring, 45 mL of a 5.3 N aqueous solution of NaOH. The resulting free amine appeared as a bright red emulsion following the neutralization. To this mixture was then added a solution of 12.8 g (119 mmol) of 2-(aminomethyl)pyridine in 200 mL of dichloromethane. The mixture was then allowed to warm to room temperature and, over a 48-h period, an additional 45-mL aliquot of 5.3 N aqueous NaOH solution was added. During addition of the NaOH solution, the pH of the aqueous portion of the reaction mixture was not allowed to exceed 9.5. The crude mixture was then washed with 100 mL of 15% NaOH, and the organic phase was dried with $MgSO_4$ and filtered. Removal of the dichloromethane yielded a brown solid mass which was extracted with boiling diethyl ether (3 × 100 mL). Evaporation of the ether extracts yielded yellow crystals of L. The ligand was purified by recrystallization from diethyl ether to give 28.1 g (81%) of white crystalline solid. ^1H NMR (CD_3CN): δ 8.48 (d, 3 H), 7.69 (t, 3 H), 7.60 (d, 3 H), 7.17 (t, 3 H), 3.81 (s, 6 H). ^{13}C NMR (CD_3CN): δ 160.51 (2-py), 149.85 (6-py), 137.25 (4-py), 123.74 (3-py), 122.94 (5-py), 60.83 (1″-CH_2).

$[LCu(CH_3CN)]ClO_4$ (1a-ClO_4). A solution of 4.04 g (13.9 mmol) of L in 45 mL of dry CH_3CN was added dropwise, with stirring, to 4.54 g (13.9 mmol) of $[Cu(CH_3CN)_4]ClO_4$ under argon. Diethyl ether (ca. 75 mL) was added to the bright orange solution until a slight cloudiness was observed to develop. The solution was filtered through a medium

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(49) Paul, P. P.; Tyeklár, Z.; Jacobson, R. R.; Karlin, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 5322–5332.
(50) Anderegg, G.; Wenk, F. *Helv. Chim. Acta* **1967**, *50*, 2330.

porosity frit, and the complex precipitated with 400 mL of dry Et_2O. The supernate was decanted, and the solid was washed with 200 mL of additional ether. Drying in vacuo yielded 6.45 g (94%) of a bright yellow-orange powder. ^1H NMR (CD_3CN): δ 8.83 (br, 3 H), 7.80 (m, 3 H), 7.47 (br, 6 H), ca. 4.3 (v br, 6 H), 2.00 (s, 3 H, CH_3CN). ^{13}C NMR (CD_3CN): δ ca. 156 (br, 2-py), ca. 148 (br, 6-py), 138.30 (4-py), 125.6 (br, 5-py, 3-py), 118.30 (5″-CN), ca. 57 (v br, 1″-CH_2), 1.30 (4″-CH_3). IR (Nujol, cm^{-1}): 2000 (w, ClO_4^- overtone), ca. 1080 (vs, ClO_4). Anal. Calcd for $C_{20}H_{21}ClCuN_5O_4$: C, 48.59; H, 4.28; N, 14.17. Found: C, 48.71; H, 4.32; N, 14.48.

[LCu(CH$_3$CN)]PF$_6$ (1a-PF$_6$). This complex was prepared in a manner exactly analogous to that described for [LCu(CH_3CN)]ClO_4 (**1a**-ClO_4). Reaction of 4.02 g (13.8 mmol) of L with [Cu(CH_3CN)$_4$]PF_6 (5.14 g, 13.8 mmol) in 50 mL of CH_3CN and precipitation with diethyl ether (400 mL) resulted in the isolation of 6.91 g (93%) of a bright yellow-orange powder. ^1H NMR (CD_3CN): δ 8.91 (br, 3 H), 7.81 (t, 3 H), 7.47 (br, 6 H), ca. 4.3 (v br, 6 H), 2.01 (s, 3 H, CH_3CN). ^{13}C NMR (CD_3CN): δ ca. 157 (br, 2-py), ca. 149 (br, 6-py), 138.29 (4-py), 125.5 (br, 5-py, 3-py), 118.30 (5″-CN), ca. 58 (v br, 1″-CH_2), 1.30 (4″-CH_3). IR (Nujol, cm^{-1}): ca. 835 (vs, br, PF_6^-). Anal. Calcd for $C_{20}H_{21}CuF_6N_5P$: C, 44.49; H, 3.92; N, 12.97. Found: C, 44.67; H, 3.96; N, 12.74.

[LCu(EtCN)]PF$_6$ (1b-PF$_6$). This compound was prepared by a procedure similar to that described for [LCu(CH_3CN)]PF_6 (**1a**-PF_6) except that propionitrile was used as the solvent. Thus, reaction of L (1.02 g, 3.51 mmol) with [Cu(CH_3CN)$_4$]PF_6 (1.28 g, 3.43 mmol) in 25 mL of EtCN followed by precipitation with diethyl ether (250 mL) resulted in isolation of 1.58 g (83%) of the title compound as a bright orange powder. ^1H NMR (CD_3CN): δ 8.80 (br, 3 H), 7.80 (t, 3 H), 7.44 (br, 6 H), ca. 4.1 (v br, 6 H), 2.39 (q, 2 H, CH_3CH_2CN), 1.22 (t, 3 H, CH_3CH_2CN). ^{13}C NMR (CD_3CN): δ ca. 157 (br, 2-py), ca. 149 (br, 6-py), 138.29 (4-py), 125.4 (br, 5-py, 3-py), 118.37 (CH_3CH_2CN), ca. 58 (v br, 1″-CH_2), 11.24 (CH_3CH_2CN), 10.82 (CH_3CH_2CN). IR (Nujol, cm^{-1}): ca. 835 (vs, br, PF_6^-). Anal. Calcd for $C_{21}H_{23}CuF_6N_5P$: C, 45.53; H, 4.19; N, 12.64. Found: C, 46.56; H, 4.39; N, 12.68.

[LCu(PrCN)]PF$_6$ (1c-PF$_6$). The title complex was prepared by dissolving 0.637 g (1.18 mmol) of [LCu(CH_3CN)]PF_6 (**1a**-PF_6) in 40 mL of argon-saturated butyronitrile, followed by precipitation with diethyl ether (200 mL). This procedure led to the isolation of 0.495 g (74%) of [LCu(PrCN)]PF_6 (**1c**-PF_6) as a yellow-orange powder. ^1H NMR (CD_3CN): δ 8.71 (br, 3 H), 7.81 (t, 3 H), 7.41 (br, 6 H), ca. 4.1 (v br, 6 H), 2.36 (t, 2 H, $CH_3CH_2CH_2CN$), 1.62 (m, 2 H, $CH_3CH_2CH_2CN$), 1.01 (t, 3 H, $CH_3CH_2CH_2CN$). ^{13}C NMR (CD_3CN): δ ca. 157 (br, 2-py), ca. 149 (br, 6-py), 138.29 (4-py), 125.4 (br, 5-py, 3-py), 118.29 ($CH_3CH_2CH_2CN$), ca. 58 (v br, 1″-CH_2), 19.81 ($CH_3CH_2CH_2CN$), 19.24 ($CH_3CH_2CH_2CN$), 13.45 ($CH_3CH_2CH_2CN$). IR (Nujol, cm^{-1}): ca. 835 (vs, br, PF_6^-). Anal. Calcd for $C_{22}H_{25}CuF_6N_5P$: C, 46.52; H, 4.44; N, 12.33. Found: C, 46.68; H, 4.47; N, 12.52. Compound **1c**-PF_6 may also be prepared directly from L and [Cu(CH_3CN)$_4$]PF_6 according to the procedure for **1a**-PF_6 except that butyronitrile is used instead of acetonitrile.

[LCu(CO)]ClO$_4$ (1d-ClO$_4$). A carbon monoxide-saturated THF solution (30 mL) was added dropwise, under CO, to 0.334 g (0.676 mmol) of [LCu(CH_3CN)]ClO_4 (**1a**-ClO_4). The Cu(I) complex dissolved slowly to give a yellow solution which was stirred overnight. Addition of CO-saturated diethyl ether (75 mL) resulted in the formation of a bright yellow oil. The supernate was decanted, and the oil was dried under vacuum to give 0.271 g (83%) of a yellow solid. ^1H NMR (complex **1a**-ClO_4 in CO-saturated CD_3CN): δ 8.82 (br, 3 H), 7.83 (m, 3 H), 7.48 (br, 6 H), ca. 4.2 (v br, 6 H), 1.98 (s, 3 H, CH_3CN). ^{13}C NMR (**1a**-ClO_4 in CO-saturated CD_3CN): δ ca. 156 (br, 2-py), ca. 150 (br, 6-py), 139.07 (4-py), 125.8 (br, 5-py, 3-py), 118.32 (5″-CN), ca. 60 (v br, 1″-CH_2), 1.30 (4″-CH_3). IR (Nujol, cm^{-1}): 2000 (w, ClO_4^- overtone), ca. 1080 (vs. ClO_4^-). Anal. Calcd for $C_{19}H_{18}ClCuN_4O_5$: C, 47.41; H, 3.77; N, 11.64. Found: C, 47.73; H, 3.87; N, 11.70.

[LCu(PPh$_3$)]PF$_6$ (1e-PF$_6$). To 0.504 g (0.933 mmol) of [LCu(CH_3CN)]PF_6 (**1a**-PF_6) was added dropwise, under argon, a solution of triphenylphosphine (0.245 g, 0.934 mmol) in 50 mL of CH_3CN. The resulting light yellow solution was stirred for 1 h and then carefully layered with deoxygenated diethyl ether (200 mL). After several days, crystals were washed with diethyl ether (100 mL). Drying under vacuum yielded 0.592 g (83%) of colorless crystalline material. ^1H NMR (CD_3CN): δ 8.30 (d, 3 H), 7.71 (t, 3 H), 7.53–7.33 (m, 15 H), 7.30 (d, 3 H), 7.21 (t, 3 H), 4.06 (s, 6 H). ^{13}C NMR (CD_3CN): δ 157.23 (2-py), 150.31 (6-py), 138.73 (4-py), 134.28 (d, 8-PPh_3, $^2J_{CP}$ = 16.5 Hz), 133.78 (d, 7-PPh_3, $^1J_{CP}$ = 33.9 Hz), 131.37 (10-PPh_3), 130.06 (d, 9-PPh_3, $^3J_{CP}$ = 10.8 Hz), 125.33 (3-py), 124.66 (5-py), 60.72 (1″-CH_2). IR (Nujol, cm^{-1}): ca. 835 (vs, br, PF_6^-). Anal. Calcd for $C_{36}H_{33}CuF_6N_4P_2$: C, 56.81; H, 4.37; N, 7.36. Found: C, 57.29; H, 4.29; N, 7.46.

Methyl 6-Bromomethylnicotinate. Into a 200-mL CCl_4 solution containing 22.25 g of *N*-bromosuccinimide (NBS, 125 mmol) was added 19.0 g of methyl 6-methylnicotinate (125 mmol) with stirring, along with 0.3 g of benzoyl peroxide and 6 mL of acetic acid. The mixture was stirred under UV light for 7 h while the temperature was maintained at ~60 °C. The NBS gradually dissolved, and the color of the solution changed from colorless to yellow and finally to red. The reaction mixture was cooled to room temperature, and the reddish precipitate was filtered. The filtrate was neutralized with saturated $NaHCO_3$, and the CCl_4 layer was collected and then evaporated under reduced pressure. The resulting red oil was flushed through a short silica gel column using ethyl acetate. After the ethyl acetate was evaporated under reduced pressure, a dark brown oil was obtained. A ^1H NMR spectrum of this brown oil indicated that it was a mixture of monobromo, dibromo, and methyl 6-methylnicotinate ($CDCl_3$, δ 2.67 (CH_3), 4.61 (CH_2Br), 6.73 ($CHBr_2$)). On the basis of an integration, a yield of 38% of the methyl 6-bromomethylnicotinate was estimated. Further reaction using methyl 6-bromomethylnicotinate was also based on its NMR integration.

Ligand L′: 17.5 g of methyl 6-bromomethylnicotinate (38% of 45 g of the above mixture) (75.5 mmol) was dissolved in 20 mL of THF. Into this solution were added 15 g of bispicolylamine (75 mmol) and 10.5 g of $(iPr)_2EtN$ (81.2 mmol), and the reaction mixture was stirred at room temperature for a week, during which time a white precipitate formed and the solution color changed to brown. After the solution was filtered and the solvent was removed under reduced pressure, the resulting brown oil was column chromatographed using alumina, eluting first with hexanes followed by Et_2O (R_f = 0.6, alumina, Et_2O). After evaporating the Et_2O, a yellow solid was obtained, and recrystallization of this solid from ether gave a light yellow crystalline product (70% yield). ^1H NMR (CD_3CN): δ 3.81 (s, 3 H, CH_3COO-), 3.86 (s, 4 H, CH_2), 3.87 (s, 2 H, CH_2), 7.11–7.22 (m, 1 H), 7.52–7.70 (m, 6 H), 8.13–8.22 (d, 1 H), 8.43 (d, 2 H, 6 py), 9.05 (d, 1 H, 6 py′). Mass spectrum, EI (m/z) 348 (M^+).

[L′Cu(CH$_3$CN)]PF$_6$ (1′-PF$_6$). Dioxygen-free CH_3CN (10 mL) was added to 0.513 g (1.47 mmol) of L′ and 0.500 g (1.34 mmol) of [Cu(CH_3CN)$_4$]PF_6 under argon. Diethyl ether (~20 mL) was added to the orange solution until a slight cloudiness was observed, whereupon the solution was filtered under argon. Additional ether was added to the clear orange solution to precipitate an orange solid. The supernate was decanted, and the solid was recrystallized from acetonitrile/ether. The solid obtained was washed with ether and dried under vacuum (3 h), giving a dark orange microcrystalline material 0.70 g (87% yield). ^1H NMR (CD_3CN): δ 1.98 (s, 3 H, CH_3CN), 3.91 (s, 3 H, $CH_3C{=}O$), 7.25–8.30 (br, 7 H). Low-temperature ^1H NMR (CD_3CN/CH_3CH_2CN 1:9 v/v at −83 °C): δ 1.98 (s, 3 H, CH_3CN), 3.66–3.77 (m, 9 H), 7.20–7.30 (m, br, 5 H), 7.71 (br, 2 H), 8.11 (br, 1 H), 8.49 (s, 2 H), 8.50 (s, 1 H). IR (Nujol, cm^{-1}): 1723 (vs, C=O), 1599 (s, C=C), 841 (vs, PF_6^-). Anal. Calcd for $CuC_{22}H_{23}N_5O_2PF_6$: C, 44.19; H, 3.88; N, 11.71. Found: C, 45.38; H, 3.82; N, 11.79. Dark orange-red X-ray-quality crystals were obtained by dissolving 0.1–0.2 g of the complex in 5–10 mL of dioxygen-free CH_3CN and then carefully layering the solution with dry diethyl ether; crystals developed in two to three days.

X-ray Structure Determination of [LCu(PPh$_3$)]PF$_6$ (1e-PF$_6$) and [L′Cu(CH$_3$CN)]PF$_6$ (1′-PF$_6$). Crystals of **1e**-PF_6 and **1′**-PF_6 which were suitable for X-ray crystallographic analysis were obtained as described above. An epoxy-covered crystal of **1e**-PF_6 was mounted on a Nicolet R3m four-circle automated diffractometer with a Mo X-ray source equipped with a graphite monochromator (λ(Mo K_α) = 0.71073 Å), while an orange-red crystal of **1′**-PF_6 coated with petroleum jelly was mounted on a Rigaku AFC6S diffractometer at low temperature (−110 °C). The details of the data collection and refinement procedures are given in Table I and in the supplementary material. The copper atom positions were determined by Patterson synthesis and direct methods for **1e**-PF_6 and **1′**-PF_6 respectively; all remaining non-hydrogen atoms were located from difference Fourier maps. All atoms in the coordination sphere and hexafluorophosphate anions were refined anisotropically; hydrogen atoms were included and placed at calculated positions with C–H bond distances fixed at 0.96 Å.

Preparation and Isolation of Solid Dioxygen Complex [(LCu)$_2$(O$_2$)](ClO$_4$) (2-(ClO$_4$)$_2$). A 250-mL Schlenk reaction vessel (Ace 7756-23) containing a magnetic stirring bar and 30 mL of freshly distilled CH_2Cl_2 under an atmosphere of argon was placed into a Neslab CB-80 cryobath maintained at −83 °C with MeOH solvent. Upon reaching low temperature, the dichloromethane was saturated with dry oxygen by

bubbling the gas through the solvent for 10 min with a stainless steel needle. Following oxygenation, the flask was flushed with argon, and $[LCu(CH_3CN)]ClO_4$ (**1a**-ClO_4) (ca. 0.5 g contained under argon in a 100-mm × 9-mm glass tube sealed with a soft rubber stopper) was added as a solid directly to the cold dichloromethane. Immediately upon contacting the solvent, the copper complex changed color from orange to violet and began to dissolve. In order to speed the dissolution process and insure that an adequate supply of oxygen was maintained, the solution was further bubbled with O_2 and stirred vigorously. After the copper complex had completely dissolved and a homogeneous solution was obtained (ca. 15 min), the flask was purged with argon, and a 250-mL additional funnel (Ace 7786-25) containing 150 mL of dry diethyl ether (under argon) was attached. The ether was added dropwise to the rapidly stirring solution of the dioxygen complex over a 6–8-h period, resulting in the precipitation of a dark purple solid. After removal of the addition funnel, the flask was stoppered and placed into a So-Low Model A13-120 Chilling Machine (maintained at −86 °C) overnight. During storage, the precipitate was allowed to settle to the bottom of the flask, resulting in the formation of a clear, colorless supernatant layer. The flask was returned to the cryobath the following day, and the supernate was decanted under a flush of argon. The solid was washed 3 times with 150 mL of cold (−85 °C) diethyl ether to remove CH_2Cl_2; during the final wash the suspended solid was quickly transferred to a low-temperature filter funnel (Kontes K-215400 with medium porosity frit modified for 200-mL capacity) and the solvent removed. The solid was washed a final time with 100 mL of Et_2O, collected on the frit of the low-temperature filter, and dried in vacuo (0.1 mm Hg) for 48 h at −83 °C. The above procedure may also be carried out with propionitrile solutions of the dioxygen complex, but, because of the relatively high boiling point of EtCN (93 °C), care must be exercised to insure that this solvent is removed completely by washing with ether as it cannot be removed in vacuo at low temperature. Since $[LCu(CH_3CN)]^+$ (**1a**) is known to react with dichloromethane to give $[LCuCl]^+$,[25] a sample of solid **2**-$(ClO_4)_2$, prepared in this solvent, was checked for the presence of chloride ion by means of a $AgNO_3$ test. The test was negative, indicating that $[LCuCl]^+$ is not formed during the preparation of **2** in CH_2Cl_2.

Crystallization and X-ray Structure Determination of $[(LCu)_2(O_2)](PF_6)_2 \cdot 5Et_2O$ (2-$(PF_6)_2 \cdot 5Et_2O$). $[LCu(CH_3CN)]PF_6$ (**1a**-PF_6) (0.25 g, 0.46 mmol) was placed into a 100-mL Schlenk reaction vessel (Ace 7756-17) and dissolved in 35 mL of dry, Ar-saturated propionitrile. The solution was cooled to −83 °C in a Neslab CB-80 cryobath and oxygenated by bubbling with dry O_2 for 10 min (resulting in a color change from bright orange to violet). A second Schlenk reaction vessel (250-mL, Ace 7756-23) containing 150 mL of dry diethyl ether (under argon) was placed into the cryobath adjacent to the flask containing the dioxygen complex. One end of a 20-in-long stainless steel cannula was inserted through a rubber septum in the female joint of the 250-mL flask and immersed in the cold ether. The opposite end of the cannula was guided through the open 14/35 joint of the 100-mL reaction vessel until it was in contact with the "far" wall of the flask. Cold diethyl ether (70 mL) was then carefully layered onto the solution of the dioxygen complex by forcing it through the cannula with argon pressure. The flask was stoppered under argon and transferred to the So-Low low-temperature freezer (−86 °C) for storage. Typically, a number of flasks were prepared in this manner with slight variations in the relative proportions of propionitrile and diethyl ether. After approximately 8 weeks at −86 °C, a flask containing a substantial quantity of violet crystals (crystals were observed to grow after storage times ranging from 5–12 weeks) was selected and placed into the cryobath (−83 °C). The purple-colored solution was carefully decanted from the crystals, which were washed and suspended in cold diethyl ether (50 mL). In preparation for mounting a crystal on the diffractometer, an aliquot of diethyl ether containing suspended crystals was transferred to a shallow dish maintained at −90 °C in an acetone/liquid N_2 slush. A crystal was selected, mounted on a glass fiber with epoxy, and positioned in the cold stream of the diffractometer. The details of the crystal data, data collection methods, and refinement procedures have been published.[18a] The structure was refined to the current residual values of $R = 0.0581$ and $R_w = 0.0580$.

Gas (O_2 and CO) Uptake Measurements. Measurements of the uptake of dioxygen or carbon monoxide gases at reduced temperature (0 or −85 °C) and constant pressure (1 atm) were carried out as previously described.[12a,13a] For four runs using ca. 1.0 mmol of the copper(I) complex $[LCu(CH_3CN)]ClO_4$ (**1a**-ClO_4) at −85 °C, the Cu:O_2 ratio was found to be 2.00 ± 0.20.

Measurements of the uptake of carbon monoxide gas were carried out in a fashion similar to that described above but at 0 °C. Typically, a propionitrile solution of **1a**-PF_6 (0.9 g) was prepared in the 25-mL calibrated flask and attached to the buret system. After equilibration at 0 °C, the flask was evacuated for 1 h to remove dissolved Ar and then allowed to take up CO gas. For two runs at 0 °C, the Cu:CO ratio was found to be 1.10 ± 0.10. For one trial, 1.1 equiv of PPh_3 was added to the solution following equilibration under CO; this resulted in the immediate (<10 min) release of a quantity of gas (CO) corresponding to 94% of that originally taken up.

Reaction of $[(LCu)_2(O_2)](ClO_4)_2$ (2-$(ClO_4)_2$) with PPh_3. Manometric Measurement of the Quantitative Release of O_2. A 25-mL side-arm flask containing a solution of $[LCu(CH_3CN)]ClO_4$ (**1a**-ClO_4) (0.514 g, 1.04 mmol) in EtCN (46 mL) was attached to the manometer system and cooled to −85 °C under argon. After evacuation of the flask for 1.5 h, the stopcock leading to the reaction flask was closed and the burette assembly was equilibrated to 1 atm O_2 pressure. Once equilibrium was achieved, oxygen from the manometer was allowed to enter the reaction flask causing the solution to become purple as the copper(I) complex reacted with the oxygen. Equilibration took ca. 20 h, and the volume of O_2 taken up (12.8 mL after accounting for the blank) corresponded to 0.526 mmol or 101% of the expected for the formation of complex **2**-$(ClO_4)_2$. At this time, a 10-mL bent storage tube (Kontes K-218700-0021) containing triphenylphosphine (0.300 g, 1.14 mmol) and filled with O_2 was attached to the reaction flask by means of a straight connecting adapter (Kontes K-274800-0030). The entire apparatus was flushed with oxygen and equilibrated to 1 atm O_2 pressure over ca. 3.5 h. The triphenylphosphine was then added to the reaction flask, whereupon, over a 2-h period, 10.7 mL of gas (O_2) was released (corresponding to 83.3% of the O_2 originally taken up). Following this initial release of O_2, the system was observed to again take up oxygen, consuming 1.10 mL of gas in a 13-h period. The experiment was stopped when no further changes occurred over a 4-h period of time. Thus, at equilibrium, a net total of 9.60 mL of oxygen was given off (corresponding to 75% of the dioxygen originally taken up). The contents of the reaction flask (green solution) were precipitated by addition of diethyl ether and filtered. The filtrate was subjected to GC analysis in order to estimate the amounts of PPh_3 and O=PPh_3 in the reaction mixture. The solvent was removed by rotary evaporation, and the residue (0.185 g) was redissolved in CH_2Cl_2 for GC analysis. The yields of PPh_3 and O=PPh_3 were determined to be 80% and 20%, respectively. An authentic sample mixture (PPh_3/O=PPh_3) was used as an external standard to calibrate the GC analyses. In a second experiment, a solution of **1b**-ClO_4 in EtCN at −85 °C took up 11.1 mL of O_2 (90.1% of theoretical) over a 20-h period. Addition of 0.291 g (1.11 mmol) of PPh_3 to the reaction mixture led to the release of 10.5 mL of O_2 over a 2-h period (following which the system again began to take up gas). The amount of O_2 released prior to reversal of the system corresponded to 95.0% of that originally taken up or 85.6% of the theoretical.

Vacuum/Heat and CO Cycling Experiments. A propionitrile solution of $[LCu(EtCN)]ClO_4$ (**1b**-ClO_4), prepared as described above, and contained within the low-temperature cuvette assembly, was cooled to −84 °C in the UV/vis Dewar cell. The spectrum of the Cu(I) species was recorded, and the solution was oxygenated to obtain the spectrum of the dioxygen complex **2**-$(ClO_4)_2$. The purple peroxide complex was reconverted to **1b**-ClO_4 by applying a vacuum at low temperature and bringing up a bath of boiling water around the cuvette for a few seconds until the purple color faded and the color of **1b**-ClO_4 was restored. After distilling into the cuvette (at room temperature) the exact amount of propionitrile that had been lost by this procedure, the solution was recooled and the spectrum of **1b**-ClO_4 was recorded. This process could be repeated several times to effect the "heat/vacuum cycling" of **1b**-ClO_4 and **2**-$(ClO_4)_2$. For the CO cycling experiments, carbon monoxide gas was used to displace the bound dioxygen and regenerate the Cu(I) complex. After recording the spectrum of the peroxide complex at −85 °C, the solution was saturated with CO by evacuating the cuvette and purging with the gas several times. The solution was slowly warmed to room temperature while continuing the evacuation/purge cycles until the color of **2**-$(ClO_4)_2$ was lost. The spectrum of the carbonyl complex **3**-ClO_4 was then recorded after the solution was recooled to −85 °C. Coordinated CO ligands in **3**-ClO_4 were removed by the application of vacuum/argon cycles to the solution at room temperature. Fresh EtCN was distilled into the cuvette to replace that lost, and the spectrum of **1b**-ClO_4 was recorded. Again the process could be repeated with approximately 12% decomposition occurring per cycle.

Reaction of $[(LCu)_2(O_2)](ClO_4)_2$ (2-$(ClO_4)_2$) with PPh_3 at −85 °C. A solution of complex **1a**-ClO_4 (0.514 g, 1.04 mmol) in 20 mL EtCN under Ar (−85 °C) was oxygenated by passing dry O_2 over the rapidly stirring

solution for 15 min. Triphenylphosphine (0.551 g, 2.10 mmol) was then added to the purple-colored solution, followed by several evacuation/purge cycles with Ar to remove excess O_2. The mixture was allowed to warm slowly (4 h) to room temperature under argon, resulting in the gradual fading of the violet color and formation of a light green solution. Stirring overnight afforded a light-yellow solution containing a substantial amount of $[LCu(PPh_3)]ClO_4$ (**4**-ClO_4) as an off-white microcrystalline solid. Additional Cu(I) complex was precipitated by addition of degassed diethyl ether (80 mL). The complex was filtered, washed with Et_2O, and dried in vacuo to give 0.741 g (99%) of **4**-ClO_4. ^1H NMR (CD_3CN): δ 8.29 (d, 3 H), 7.71 (t, 3 H), 7.53–7.33 (m, 15 H), 7.30 (d, 3 H), 7.21 (t, 3 H), 4.06 (s, 6 H). ^{13}C NMR (CD_3CN): δ 157.27 (2-py), 150.32 (6-py), 134.28 (d, 8-PPh_3, $^2J_{CP}$ = 16.5 Hz), 133.74 (d, 7-PPh_3, $^1J_{CP}$ = 33.9 Hz), 131.32 (10-PPh_3), 130.04 (d, 9-PPh_3, $^3J_{CP}$ = 10.8 Hz), 125.33 (3-py), 124.66 (5-py), 60.74 (1″-CH_2). IR (Nujol, cm^{-1}): 1075 (vs, br, ClO_4^-). Anal. Calcd for $C_{36}H_{33}ClCuN_4O_4P$: C, 60.42; H, 4.65; N, 7.83. Found: C, 60.25; H, 4.65; N, 7.85. GC analysis of the filtrate indicated that only a trace (<1%) of O=PPh_3 was formed during the reaction.

Reaction of CO with $[(LCu)_2(O_2)](ClO_4)_2$ (2-$(ClO_4)_2$). A solution of $[LCu(CH_3CN)]ClO_4$ (**1a**-ClO_4) (0.340 g, 0.688 mmol) was prepared in 40 mL of EtCN and cooled to −85 °C. Dioxygen was bubbled through the solution for 5 min, causing a color change from orange to deep violet. Immediately following the oxygenation, CO gas was bubbled through the solution, which was then allowed to warm slightly until the purple color had bleached and the solution was essentially colorless. At this point, the solution was further warmed to room temperature (over a 4-h period) while being stirred under an argon atmosphere. The solution, which had become yellow-orange in color after stirring overnight, was reduced in volume to 30 mL under vacuum; this evacuation additionally served to remove any remaining CO ligands from the complex. Precipitation with diethyl ether (200 mL) afforded a substantial quantity of orange semicrystalline powder along with a small amount of oily green product which adhered to the sides of the flask. The orange powder was separated from the green oil by decantation and dried in vacuo to yield 0.268 g (77%) of $[LCu(EtCN)]ClO_4$ (**1b**-ClO_4). IR (Nujol, cm^{-1}): ca. 1080 (vs, br, ClO_4^-). Anal. Calcd for $C_{21}H_{23}ClCuN_5O_4$: C, 49.59; H, 4.56; N, 13.77. Found: C, 49.64; H, 4.54; N, 13.70.

Qualitative Determination of Dioxygen Liberation from the Reaction of $[(LCu)_2(O_2)](ClO_4)_2$ (2-$(ClO_4)_2$) with PPh_3 or CO at −85 °C in EtCN. A 50-mL Schlenk reaction vessel (Ace 7756-11) was attached, by means of a three-way stopcock, to a vacuum line, and a 50-mL side-arm flask was fitted on top with an addition funnel (Kontes K-215200-0100). The additional funnel contained an aqueous alkaline pyrogallol solution which was used to test for the presence of dioxygen.[12a,13a] The test solution was prepared as follows: potassium hydroxide (12 g) was dissolved in 100 mL of water which had been boiled for 3 h; the hot solution was transferred to the addition funnel and bubbled with argon for 1 h. The aqueous KOH solution was then added to 0.5 g of pyrogallic acid contained (under Ar) in the attached 50-mL side-arm flask. The acid dissolved to produce a clear, colorless solution which was returned to the addition funnel by inverting the apparatus. With this system, solutions in the reaction vessel could be bubbled with a gas (Ar or CO) and swept into the pyrogallol test solution.

A solution of **2**-$(ClO_4)_2$ was prepared in the reaction vessel by dissolving 0.243 g (0.491 mmol) of $[LCu(CH_3CN)]ClO_4$ (**1a**-ClO_4) in propionitrile, cooling to −85 °C, and bubbling with O_2 for 10 min. After the excess O_2 was removed from the dioxygen complex solution, Ar was bubbled through both the complex and test solutions for 30 min. No change in the color of the pyrogallol solution indicated that all of the excess O_2 had been removed. While argon was still bubbling in this fashion, triphenylphosphine (0.131 g, 0.501 mmol) was added to the reaction vessel. After several minutes, the pyrogallol solution began to turn brown, gradually becoming darker as the purple color of the reaction mixture faded, indicating that O_2 is releated from **2**-$(ClO_4)_2$ upon addition of PPh_3. In a separate experiment, CO was bubbled through a solution of **2**-$(ClO_4)_2$, but at −85 °C only a very slight color development in the pyrogallol solution was observed over a 1-h period, indicating that O_2 is not displaced by CO at this temperature. However, when the solution of **2**-$(ClO_4)_2$ was warmed slightly (ca. 75 °C) while bubbling with CO, the purple color slowly faded and the pyrogallol test solution turned to the characteristic brown color indicative of exposure to O_2. Finally, in a control experiment, argon was continually bubbled through a solution of **2**-$(ClO_4)_2$ while the solution was warmed to room temperature; only a very slight tanning of the pyrogallol solution was observed, even after complete decomposition of the dioxygen complex (green solution). This result indicates that O_2 is not released from the peroxide complex upon thermal decomposition; it must be displaced by PPh_3 or CO.

UV–Visible Spectroscopy of Redissolved $[(LCu)_2(O_2)](ClO_4)_2$ (2-$(ClO_4)_2$) in CH_2Cl_2. A small quantity (ca. 40 mg) of solid **2**-$(ClO_4)_2$ prepared as described above) was quickly transferred to a prechilled (ca. −85 °C) 50-mL Schlenk reaction vessel (Ace 7756-11) with a cold metal spatula. Cold CH_2Cl_2 from a second 50-mL reaction flask was added to dissolve the complex until the resulting solution was judged to be sufficiently dilute for absorption spectroscopy. An aliquot of this violet-colored solution was then transferred to the precooled low-temperature cuvette assembly by means of the inlet adapter described previously. The electronic absorption spectrum was then recorded at −80 °C in the usual fashion. The spectra obtained by this method were qualitatively identical to those obtained for samples prepared in situ by addition of O_2 to **1a**. In order to quantify the absorption spectrum of the redissolved dioxygen complex, the following procedure was employed. After the volume of solution in the cuvette assembly was determined at low temperature, the solution was allowed to warm to room temperature (causing decomposition of the peroxide complex), and the volume was measured again. A 10.0-mL aliquot of this solution was transferred to a 25-mL pear-shaped flask, and the solvent was removed by rotary evaporation. To the residue was then added 10.0 mL of a solution of neocuproine (0.104 g, 0.501 mmol) and L-(+)-ascorbic acid (0.0947 g, 0.538 mmol) in 100 mL of dry MeOH, resulting in the formation of a yellow-orange-colored solution. The absorbance of the 452-nm band of this solution (arising from formation of the Cu(I)-neocuproine complex) was compared to a standard curve of concentration vs absorbance (A_{452}) prepared in a similar fashion from $[LCu(CH_3CN)](ClO_4)_2$. The concentration of the redissolved dioxygen complex at low temperature could thus be determined and, from the absorbance values, the molar extinction coefficients were calculated. For this sample, the molar extinction coefficient (ϵ, M^{-1} cm^{-1}) corresponding to the 525-nm band of the peroxide complex was found to be 10 250. Two additional samples, prepared similarly, returned values of 12 400 and 10 700 M^{-1} cm^{-1}, respectively, for ϵ at 525 nm.

Low-Temperature NMR Spectroscopy of $[(LCu)_2(O_2)](ClO_4)_2$ (2-$(ClO_4)_2$) Generated in situ. Low-temperature ^1H and ^{13}C NMR spectra of **25** were obtained at −88 °C with the Varian XL-300 spectrometer using CD_2Cl_2 as solvent. In the drybox, 5.0 g (3.7 mL) of CD_2Cl_2 was added to a 10-mm-od × 179-mm NMR tube contained within a 100-mL Schlenk flask (Kontes K-213100-1024). A connecting adapter (Kontes K-274750-254) was placed on the flask, and the apparatus was sealed under an atmosphere of argon. After removal from the drybox, the flask was connected to a vacuum argon line and immersed up to the neck in a cold bath maintained at −83 °C. After cooling, the CD_2Cl_2 was saturated with oxygen by bubbling dry O_2 through the solvent for 5 min with a stainless steel needle. The flask and NMR tube were then flushed with argon, and a quantity (ca. 100 mg) of $[LCu(CH_3CN)]ClO_4$ (**1a**-ClO_4) was quickly added from an ampule to the CD_2Cl_2 solvent in the tube. Immediately after addition of the Cu(I) complex, the solvent was bubbled with O_2 for 5 min to ensure complete oxygenation and dissolution of the solid. After oxygenation, the solvent was bubbled with argon to remove excess paramagnetic O_2. The NMR tube was then sealed with a soft rubber stopper and transferred to the probe of the spectrometer.

Low-Temperature ^1H NMR Spectroscopy of Redissolved $[(LCu)_2(O_2)](ClO_4)_2$ (2-$(ClO_4)_2$). A precooled (−85 °C) and argon-purged 50-mL Schlenk reaction vessel (Ace 7756-11) was attached, by means of a ground glass connecting adapter, to a low-temperature filter funnel containing a quantity of solid **2**-$(ClO_4)_2$, prepared as described above, and maintained at −83 °C. A small amount (ca. 100 mg) of the dioxygen complex was transferred to the cold reaction vessel by inverting the apparatus and shaking gently. The complex was dissolved in cold CD_2Cl_2 (5.0 g, ca. 3.2 mL) and, by using the previously described inlet adapter, transferred to a prechilled 10-mm-od NMR tube contained within a 100-mL Schlenk flask. The NMR tube was sealed with a soft rubber stopper and transferred to the spectrometer probe, which was set to maintain a temperature of −75 °C.

Solution Magnetic Susceptibility of $[(LCu)_2(O_2)](ClO_4)_2$ (2-$(ClO_4)_2$). Measurements of the solution magnetic susceptibility of **2**-$(ClO_4)_2$ were performed according to the Evans method[51] using coaxial NMR tubes and dichloromethane (either CD_2Cl_2 alone or mixtures of CH_2Cl_2/CD_2Cl_2) or propionitrile/toluene-d_8 as solvent. Samples were prepared by two different procedures as described below.

Method I. This procedure was used for samples of **2**-$(ClO_4)_2$ prepared in dichloromethane. For measurements in CD_2Cl_2 alone, the commercially available deuterated solvent was used (Aldrich dichloromethane-d_2, 99.6+ atom % D containing 1% (v/v) TMS). For measurements in CH_2Cl_2/

CD_2Cl_2, a mixture of 5 g of CD_2Cl_2 in 95 g of CH_2Cl_2 was prepared and refluxed over CaH_2 for 2 days. The solvent was then distilled under argon, and ca. 1–2% (v/v) of TMS was added. For preparation of the samples, 3.0 mL of dichloromethane (CD_2Cl_2 or CH_2Cl_2/CD_2Cl_2) was added, in the drybox, to a 10-mm-od NMR tube (Wilmad 513-5PP) contained within a 100-mL Schlenk flask (Kontes K-213100-1024). A connecting adapter (Kontes K-274750-254) was placed on the flask, which was then sealed under argon with a ground-glass stopper. Also in the drybox, an identical sample of the solvent was introduced into the stem portion of a coaxial insert (Wilmad WGS-10BL), which was sealed with the supplied cap. The flask containing the NMR tube was then removed from the drybox and immersed in a Neslab CB-80 cryobath maintained at –83 °C. After cooling, the dichloromethane contained within the NMR tube was saturated with oxygen by bubbling dry O_2 through the solvent for 5 min with a stainless steel needle. Air and moisture were kept away from the solvent by flushing dry argon through the open 100-mL flask. Following oxygenation, the flask and NMR tube were flushed with argon, and a weighed quantity (ca. 30–80 mg) of [LCu-(CH_3CN)]ClO_4 (**1a**-ClO_4) was quickly added from an ampule to the solvent in the tube. Immediately following addition of the Cu(I) complex, the solvent was bubbled with dioxygen for 5 min to ensure complete oxygenation and dissolution of the solid. The solution was then bubbled with argon for 5 min to remove excess O_2, and the coaxial tube containing pure solvent was slowly inserted into the sample tube. The joint between the insert and outer tube was sealed with parafilm, and the NMR tube was transferred to the probe of the Varian XL-300 which had previously been set to maintain a temperature of ca. –85 °C.

Method II. For samples prepared in propionitrile, toluene-d_8 was used as a lock solvent (Aldrich, toluene-d_8, 99+ atom % D containing 1% (v/v) TMS). A mixture of 5 g of toluene-d_8 in 45 g of propionitrile was distilled from CaH_2 under argon, and then ca. 1% (v/v) of TMS was added to it. Samples using this solvent system were prepared in the drybox by dissolving a weighed quantity of [LCu(CH_3CN)]ClO_4 (**1a**-ClO_4) in 2.00 mL of propionitrile/toluene. An aliquot of this solution was transferred to a 5-mm-od NMR tube (Wilmad 506-PP), which was then placed into a 100-mL Schlenk flask (Kontes K-274750-254) and sealed under argon. Solvent was also added to a coaxial insert (Wilmad 520-3), which was sealed with the supplied cap. The flask containing the Cu(I) sample was then transferred to a Neslab CB-80 cryobath maintained at –83 °C. After cooling, the sample was oxygenated by bubbling with dry O_2 for 5 min using a stainless steel needle. A coaxial tube containing the pure solvent was inserted slowly into the NMR tube containing the dioxygen adduct. After the joint between the two coaxial tubes was sealed with parafilm, the assembly was transferred to the probe of the spectrometer. Following temperature equilibration, ^1H NMR spectra of the samples were recorded as usual. From the spectra, the difference in chemical shift of the TMS protons in the pure solvent and the solution of **2**-$(ClO_4)_2$ was measured. The solution magnetic susceptibility was then calculated.[51]

Determination of μ_{eff} using Evans method NMR measurements of solutions of **2** were problematic[23] because of the effects of variable amounts of paramagnetic impurities, presumably caused by the large concentrations necessary in CD_2Cl_2 as solvent. The latter is a particular problem since any Cu(I) starting complex (e.g., **1**) present would react to give $[LCu^{II}(Cl)]^+$.[25] Values of μ_{eff} ranging from 0.23 to 1.18 BM/Cu were obtained,[23] but the lowest values of 0.22–0.33 observed in $EtCN/C_7D_8$ are thought to be most reliable, due to the particular stability of **2** in cold EtCN.

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Supplementary Material Available: Experimental details, listings of atom coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, hydrogen coordinates, and temperature factors for **1e**-PF_6 and **1′**-PF_6 (20 pages); listing of observed and calculated structure factors (53 pages). Ordering information is given on any current masthead page.

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