# Dioxygen–Copper Reactivity. Reversible O₂ and CO Binding by a New Series of Binuclear Copper(I) Complexes

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As part of our efforts in biomimetic dioxygen–copper chemistry,[1-5] we are examining Cu(I) and Cu(II) complexes containing the ligands N*n*PY2 in which two tridentate PY2 units (PY2 =

N*n*PY2
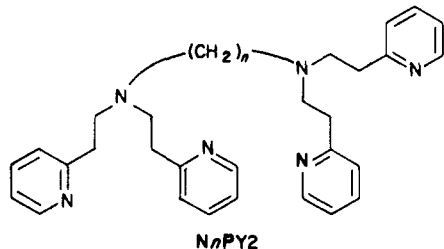
bis(2-(2-pyridyl)ethyl)amine) are connected by alkyl chains of varying length *n* (*n* = 3–5). We recently reported that the reaction of a binuclear Cu(I) complex of N3PY2 with O₂ in methanol at room temperature gives a dimethoxo-bridged Cu(II) compound.[4] Here, we report a preliminary study of the reversible binding of O₂ and CO by the Cu(I) complexes [Cu₂(N*n*PY2)]²⁺ and spectral characterization of these binuclear copper(I) and their dioxygen complexes (Scheme I).

The ligands N*n*PY2 are synthesized by the reaction of excess 2-vinylpyridine with the appropriate alkyldiamine and purified by column chromatography. Mixing 2 equiv of [Cu(CH₃CN)₄]Y (Y = ClO₄⁻ or PF₆⁻) with CO-saturated solutions of N*n*PY2 in methanol gives yellow-brown solutions of [Cu₂(N*n*PY2)(CO)₂]Y₂ which are precipitated with diethyl ether and recrystallized from CH₂Cl₂–Et₂O.[6] X-ray crystal structures show that these tetracoordinate binuclear complexes possess well-separated Cu(I)–N₃(CO) units.[7]

Decarbonylation of [Cu₂(N*n*PY2)(CO)₂]²⁺ in dichloromethane solution by vacuum–purge cycles (under argon) gives what are presumed to be [Cu₂(N*n*PY2)]²⁺.[8] Oxygenation of these faint yellow solutions at –80 °C results in the rapid formation of *intensely* colored solutions varying from deep purple to brown depending on *n*. Manometric measurements (–80 °C) confirm that the stoichiometry of the reaction is Cu:O₂ = 2:1 thus giving complexes in solution formulated as [Cu₂(N*n*PY2)(O₂)] as indicated in Scheme I. These dioxygen complexes exhibit electronic spectra with strong multiple absorptions in the visible region (300–700 nm) (Table I) that are characteristic of LMCT and/or d–d transitions for Cu(II) ions.

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(6) (a) Anal. Calcd for C₃₃H₃₈Cu₂F₁₂N₆O₂P₂: C, 40.96; H, 3.96; N, 8.68. Found: C, 40.77; H, 4.12; N, 8.17. Calcd for C₃₄H₄₀Cu₂F₁₂N₆O₂P₂: C, 41.59; H, 4.11; N, 8.56. Found: C, 41.76; H, 4.27; N, 8.61. Calcd for C₃₅H₄₂Cu₂F₁₂N₆O₂P₂: C, 42.22; H, 4.25; N, 8.44. Found: C, 41.94; H, 4.32; N, 8.35. (b) IR spectral data for [Cu₂(N*n*PY2)(CO)₂](PF₆)₂: ν(CO) (Nujol) 2075, 2095, and 2080 cm⁻¹ for *n* = 3, 4, and 5, respectively.

(7) To be published.

(8) Although we have not as yet isolated these, we would expect binuclear tricoordinate Cu(I) complexes of N*n*PY2 to be reasonably stable since we have already synthesized and crystallographically characterized several examples of Cu(I) containing the PY2 tridentate unit.[1,5]
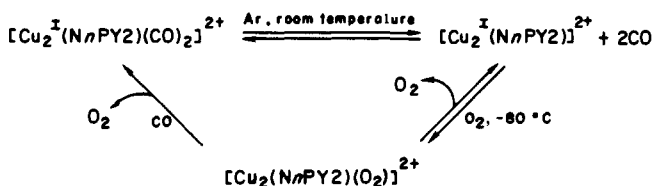
Scheme I

Table I. Spectral Data:[a] Low-Temperature Oxygenation of Copper(I) Complexes [Cu₂(L)]²⁺

	L	
N3PY2	N4PY2	N5PY2
	Copper(I) Complexes	
345 (4000)	350 (3500)	347 (3600)
	Dioxygen Complexes	
365 (15000)	360 (16700)	360 (21400)
490 (5300)	458 (5300)	423 (3600)
600 sh (1200)	550 sh (1200)	520 (1200)

[a] Absorption maximia are given in nanometers. Extinction coefficients based on [Cu₂(NnPY2)](PF₆)₂ are given in parenthesis (M⁻¹ cm⁻¹).
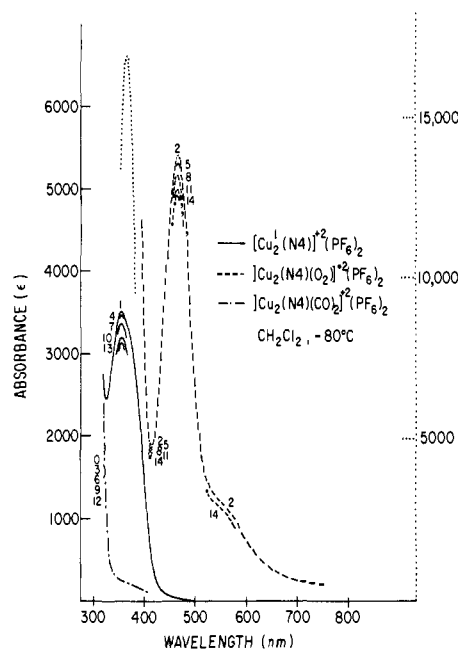

Figure 1. Electronic spectra demonstrating the reversible O₂ and CO binding behavior of the Cu(I) complexes of N4PY2. For the cycling experiments, spectrum numbers are marked on the dicarbonyl complex [Cu₂(N4PY2)(CO)₂]²⁺ (···), the 350-nm band of the decarbonylated dicopper(I) species (—), and the 458-nm absorption of the dioxygen complex [Cu₂(N4PY2)(O₂)]²⁺ (---). The 360-nm band of [Cu₂(N4PY2)(O₂)]²⁺ (···) is also shown. See text for further explanation.

Cycling experiments using [Cu₂(N4PY2)(CO)₂](PF₆)₂ that illustrate the reversible equilibria involved (Scheme I) are followed by UV–vis spectroscopy (Figure 1). The featureless spectrum 0 is that of [Cu₂(N4PY2)(CO)₂]²⁺. This is decarbonylated to give [Cu₂(N4PY2)]²⁺ (spectrum 1), which at *low temperature* is oxygenated to give the dioxygen complex [Cu₂(N4PY2)(O₂)]²⁺ (spectrum 2).[9a,b] Saturation of this solution with CO at low

(9) (a) Bubbling O₂ through solutions of the carbonyl adducts at low temperature does not result in the formation of [Cu₂(N*n*PY2)(O₂)]²⁺ due to the competitively strong binding of CO. The carbon monoxide ligand must first be removed in a separate step at room temperature. (b) The dioxygen adducts are only stable at low temperature (up to ca. –30 °C). Oxygenation of the binuclear Cu(I) precursors at room temperature or warming solutions of [Cu₂(N*n*PY2)(O₂)]²⁺ results in the irreversible oxidation to as yet uncharacterized green compounds. (c) No carbon dioxide is detected in this reaction as tested by the use of aqueous Ba(OH)₂. On a synthetic scale, the carbonylation of [Cu₂(N4PY2)(O₂)]²⁺ gives [Cu₂(N4PY2)(CO)₂]²⁺ which is isolated in yields higher than 80% without any observable ligand (N4PY2) decomposition products.

temperature and allowing the solution to warm up to room temperature converts the dioxygen adduct back to [Cu₂(N4PY2)-(CO)₂]²⁺ (spectrum 3).⁹ᶜ The process can be repeated, and as estimated from the change in absorption intensities, less than 10% decomposition occurs over the five cycles shown. The O₂ released from [Cu₂(N4PY2)(O₂)]²⁺ by reaction with CO is identified by sweeping the solution with CO and bubbling the gas into an aqueous alkaline pyrogallol test solution which forms an intense brown color in the presence of O₂.¹⁰

[Cu₂(N4PY2)]²⁺ and [Cu₂(N4PY2)(O₂)]²⁺ can also be *directly* interconverted through several cycles (without appreciable decomposition) by alternate oxygenation and deoxygenation by warming under vacuum. These experiments can be monitored spectrophotometrically. The reversible binding of CO and O₂ by Cu(I) complexes of N3PY2 and N5PY2 has also been confirmed by similar cycling experiments.⁷

The extremely intense and multiple UV–vis absorptions observed for these O₂ complexes (Table I) have not, to our knowledge, been reported in any other Cu(I)/O₂ synthetic systems.³,¹¹,¹² Also, the spectra of [Cu₂(NnPY2)(O₂)]²⁺ bear close similarities to the spectrum of the copper metalloprotein hemocyanin (Hc, an O₂ carrier); where oxy-Hc exhibits absorptions at 345 nm (ε 20 000 m⁻¹ cm⁻¹), 570 nm (ε 1000 M⁻¹ cm⁻¹), and a CD feature at 485 nm, all assigned to peroxo to Cu(II) LMCT transitions.¹³⁻¹⁶ The occurrence of strong charge-transfer transitions (suggestive of Cu(II)) in the spectra of [Cu₂-(NnPY2)(O₂)]²⁺, the observed 2:1 Cu/O₂ stoichiometry, and the reversibility of O₂ and CO binding all suggest that these dioxygen complexes are probably best described as peroxodicopper(II) compounds.

Since the ligands NnPY2 have no potential Cu···Cu bridging group, the present results indicate that a Cu···Cu bridging ligand (besides perhaps O₂²⁻ itself) is *not* a prerequisite for systems capable of binding CO and O₂ reversibly¹² and for exhibiting spectral features reminiscent of oxyhemocyanin.¹⁷ The implications of the present findings regarding the occurrence, spectroscopic effects, and functional role of the proposed "endogenous" bridge¹³,¹⁶ in oxy- or deoxy-Hc remain to be determined. While a recent X-ray structural determination of deoxy-Hc showed that each Cu(I) center appears to be coordinated by three imidazole ligands (Cu···Cu = 3.8 ± 0.4 Å), it did not, unfortunately, settle questions concerning an "endogeneous" bridging ligand.¹⁹

Furthur physical and chemical characterization of these novel dioxygen–copper complexes is in progress.

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Indirect, Negative Heteronuclear Overhauser Effect Detected in a Steady-State, Selective ¹³C{¹H} NOE Experiment at Natural Abundance†

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It has recently been shown that both selective ¹³C{¹H} NOE measurements¹⁻¹⁰ and nonselective two-dimensional (2D) NOE¹¹⁻¹³ (cross-relaxation) spectroscopy are promising techniques for the determination of carbon–proton distances in organic molecules in solution.

In the present paper we show that the quasi-simultaneous saturation¹⁴ of all ¹³C satellite lines of a proton in a ¹³C isotopomer is an efficient new technique for selective ¹³C{¹H} NOE measurements.¹⁵ More importantly, we have unambiguously detected a negative, indirect ¹³C{¹H} NOE at a protonated carbon when the lines of a not directly bound proton were saturated.

As a model system, (–)-α-hydrastine (1) (Figure 1) has been investigated. Assignments of proton and carbon resonances are supported by the basic chemical shift correlation methods.¹⁶⁻¹⁸ Nonprotonated carbons have been assigned via long-range ¹³C{¹H} spin–spin couplings in a 2D DEPT experiment.¹⁹⁻²² The preferred

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†We dedicate this manuscript to the memory of Peter Kerekes.

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