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Reactions of Dioxygen (O_2) with Mononuclear Copper(I) Complexes: Temperature-Dependent Formation of Peroxo- or Oxo- (and Dihydroxo-) Bridged Dicopper(II) Complexes

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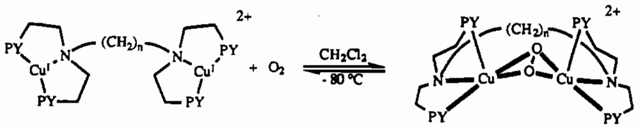
The binding of O_2 to copper(I) and its subsequent reactivity is important in a variety of chemical and biological processes. We previously studied functional models of hemocyanins (arthropodal and molluscan O_2 carriers) involving a class of O_2 adducts $[Cu_2(Nn)(O_2)]^{2+}$ (**2**) (Karlin, K. D.; et al. *Inorg. Chem.* **1992**, *31*, 1436–1451), where Nn are dinucleating ligands which employ two tridentate bis(2-pyridylethyl)amine (PY2) moieties, connected by a variable alkyl chain. Here, we report studies of O_2 reactivity using R-substituted PY2 tridentate ligands and derived mononuclear Cu(I) precursor complexes $[Cu(RPY2)]^+$ (**3a**, R = Me; **3b**, R = $PhCH_2$; **3c**, R = Ph). The X-ray structure of the nearly "T-shaped" complex **3c**(PF_6) ($C_{20}H_{21}CuN_3F_6P$) is reported; it crystallizes in the space group $P2_1/n$, $a = 10.037$ (4) Å, $b = 14.406$ (4) Å, $c = 15.210$ (5) Å, $\beta = 105.99$ (3)°, $D_{calcd} = 1.61$ g/cm^3, $Z = 4$. Electrochemical studies indicate reversible one-electron oxidations in DMF, with $E_{1/2}$ values varying between +80 and +150 mV vs NHE, depending on R. Above 0 °C, complexes **3** react with O_2 in a stoichiometry of Cu/O_2 = 4:1 (manometry) giving oxo-bridged dicopper(II) products $[Cu_2(RPY2)_2(O)]^{2+}$ (**4**). EPR spectra are consistent with the bridged dinuclear formulation; i.e., **4a,c** are EPR silent while **4b** exhibits a typical "half-field" ($g \sim 4$) line in CH_2Cl_2. In methanol, the complexes break up and exhibit normal tetragonal spectra. Oxo complexes **4** react with water (reversibly, for **4a,b**) to give dihydroxo-bridged complexes $[Cu_2(RPY2)_2(OH)_2]^{2+}$ (**5**), with "parallel-planar" structures; EPR spectroscopic and other physical measurements are consistent. However, low-temperature (−80 °C) oxygenation of complexes **3** results in the formation of O_2 adducts $[Cu_2(RPY2)_2(O_2)]^{2+}$ (**6**), as indicated by manometry (Cu/O_2 = 2:1) and EPR ("silent") and UV–vis (i.e., strong 350–360-nm absorption) spectroscopies. The latter indicates a close similarity of these complexes to **2**, with their proposed bent (μ-η^2:η^2-peroxo)dicopper(II) structures. Prolonged exposure of $[Cu(PhCH_2PY2)]^+$ (**3b**) to O_2 causes a novel N-dealkylation reaction, with oxidative cleavage of the ligand producing H-PY2 and benzaldehyde (20% yield). Isotope labeling studies reveal that the source of oxygen in the PhCHO product is O_2. The relationship of the chemistry presented here to other copper–dioxygen chemistry and copper proteins is discussed.

We are currently interested in elucidating fundamental aspects of the binding of O_2 to copper ion centers, in particular with regard to efforts in the biomimetic chemistry of copper proteins which bind or activate dioxygen.[1-6] We have recently described four classes of peroxo–dicopper(II) complexes[7] which are formed reversibly at low temperatures in solution (−80 °C) by the interaction of O_2 (Cu/O_2 = 2:1) with appropriate Cu(I) precursor complexes.[1-4,8-11] One of these systems involved the reactions of O_2 with dinuclear Cu(I) compounds $[Cu_2(Nn)]^{2+}$ (**1**) (n = 3–5; PY = 2-pyridyl).[9] The peroxo–dicopper(II) complexes $[Cu_2(Nn)(O_2)]^{2+}$ (**2**) represent a particularly interesting class of $\{Cu_2O_2\}^{n+}$ species, since a number of their physical properties are rather similar to those found for oxyhemocyanin (oxy-Hc), an



1
$[Cu_2^I(Nn)]^{2+}$

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

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(1) (a) Tyeklár, Z.; Karlin, K. D. *Acc. Chem. Res.* **1989**, *22*, 241–248. (b) Karlin, K. D.; Tyeklár, Z.; Zuberbühler, A. D. In *Bioinorganic Catalysis*; Reedijk, J., Ed.; Marcel Dekker: New York, 1992; Chapter 9. (c) Karlin, K. D.; Tyeklár, Z. *Adv. Inorg. Biochem.*, in press.

(2) Sorrell, T. N. *Tetrahedron* **1989**, *45*, 3–68.

(3) Kitajima, N. *Adv. Inorg. Chem.*, in press.

(4) (a) Solomon, E. I.; Baldwin, M. J.; Lowery, M. *Chem. Rev.* **1992**, *92*, 521–542. (b) Ross, P. K.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 3246–3259. (c) Solomon, E. I. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series 372; American Chemical Society: Washington, DC, 1988; pp 116–150.

(5) (a) Zuberbühler, A. D. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1983; pp 237–258. (b) Gampp, H.; Zuberbühler, A. D. *Met. Ions Biol. Syst.* **1981**, *12*, 133–189.

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

(7) Recent reviews on metal–dioxygen complexes include ref 6 and the following: (a) *Oxygen Complexes and Oxygen Activation by Transition Metals*, Martell, A. E., Sawyer, D. T., Eds.; Plenum: New York, 1988. (b) Gubelmann, M. H.; Williams, A. F. *Struct. Bonding (Berlin)* **1983**, *55*, 1.

(8) (a) Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Farooq, A.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 2668–2679. (b) Pate, J. E.; Cruse, R. W.; Karlin, K. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 2668–2679. (c) Blackburn, N. J.; Strange, R. W.; Cruse, R. W.; Karlin, K. D. *J. Am. Chem. Soc.* **1987**, *109*, 1235–1237.

(9) (a) Karlin, K. D.; Haka, M. S.; Cruse, R. W.; Meyer, G. J.; Farooq, A.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 1196–1207. (b) Blackburn, N. J.; Strange, R. W.; Farooq, A.; Haka, M. S.; Karlin, K. D. *J. Am. Chem. Soc.* **1988**, *110*, 4263–4272. (c) Karlin, K. D.; Tyeklár, Z.; Farooq, A.; Haka, M. S.; Ghosh, P.; Cruse, R. W.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *Inorg. Chem.* **1992**, *31*, 1436–1451.

(10) (a) Jacobson, R. R.; Tyeklár, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 3690–3692. (b) Baldwin, M. J.; Ross, P. K.; Pate, J. E.; Tyeklár, Z.; Karlin, K. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 8671–8679. (c) Tyeklár, Z.; Jacobson, R. R.; Ghosh, P.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. Submitted for publication.

(11) Sanyal, I.; Strange, R. R.; Blackburn, N. J.; Karlin, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 4692–4693.

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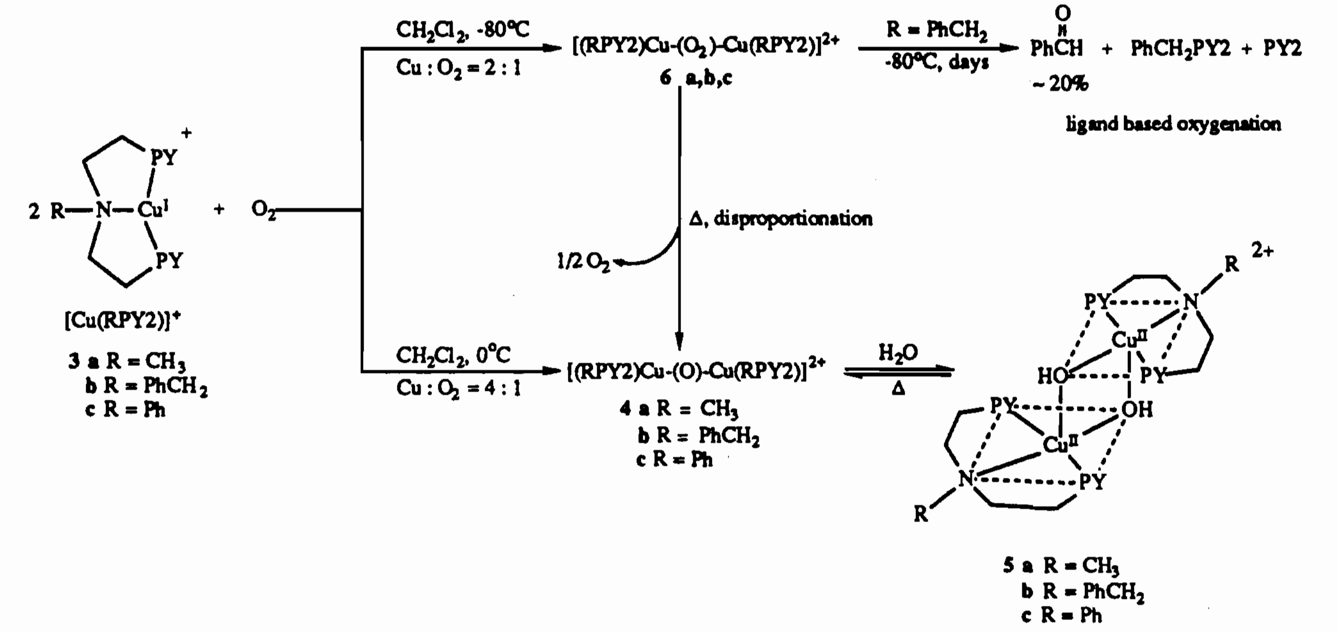
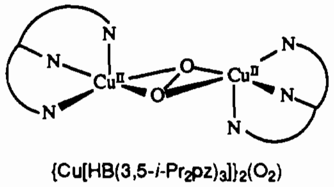
Scheme I



arthropodal and molluscan dioxygen carrier.[4,12] Such characteristics include their UV–vis spectral features (λ_{max} = 350–360 nm, $\epsilon \sim 20\,000$) and diamagnetism.[9c] EXAFS studies[9b] enabled us to suggest a bent μ-η^2:η^2-peroxo coordination in **2**, and the properties of these species are consistent with this structure. Kitajima has demonstrated the existence of this novel structural type for peroxo–copper species in a definitive X-ray structural study of {Cu[HB(3,5-*i*-Pr_2pz)$_3$]}$_2$(O_2) (HB(3,5-*i*-Pr_2pz) = a tris(pyrazolylborate) anionic ligand), possessing a planar side-on μ-η^2:η^2-peroxo coordination.[3,13] This structural type is now considered to be the likely coordination mode for hemocyanin,[1b,c,4a,9c,13] especially in light of a recent structural study of oxy-Hc.[14]



{Cu[HB(3,5-*i*-Pr_2pz)$_3$]}$_2$(O_2)
Cu···Cu = 3.56 Å, O–O = 1.41 Å, ν_{O-O} = 749 cm^{-1}

The dinucleating ligands in **1** and **2** are composed of two tridentate bis(2-pyridylethyl)amine (PY2) moieties, connected by a variable alkyl chain. When the connecting unit is a *m*-xylyl group, formation of a {Cu_2O_2}$^{2+}$ intermediate also occurs, and this is followed by hydroxylation of the arene moiety.[15] Our interest in the chemistry of Cu(I) complexes of the PY2 tridentate ligand also prompted us to study reactions of monomer units [Cu(RPY2)]$^+$ (**3**) (Scheme I), i.e. essentially "half" of the dinuclear complexes **1**. Previously we found that [Cu($PhCH_2$-PY2)]$^+$ (**3b**)[16,17] reacts with O_2 at room temperature with a stoichiometry of Cu/O_2 = 4:1. Both an oxo-bridged species **4b** and dihydroxo-bridged complex **5b** could be isolated from this reaction.[17] However, more recent investigations demonstrate that the course of reaction of **3b** with O_2 varies dramatically with temperature, since at −80 °C, manometric measurements indicate that one O_2 is taken up per two copper(I) monomer complexes (Cu/O_2 = 2:1). This suggests that a dioxygen complex [Cu_2($PhCH_2PY2$)$_2$(O_2)]$^{2+}$ forms. Furthermore, we observe an interesting further oxidation reaction when **3b** is exposed to O_2 for longer periods at −80 °C, the hydroxylation and N-dealkylation of $PhCH_2PY2$ (Scheme I).

Here, we report the details concerning these latter findings of the low-temperature chemistry. We have also synthesized and characterized newer copper(I) complex analogs [Cu(RPY2)]$^+$ (**3**) (R = Me (**3a**), Ph (**3c**)) and described their reactions with O_2 as a function of temperature. Electrochemical comparisons of complexes **3** are reported, and an X-ray structure of **3c** is described.

Experimental Section

Materials and Methods. Unless otherwise stated the solvents and reagents were of commercially available analytical grade quality. Dioxygen was dried by passing it through a short column of P_4O_{10} (aquasorb, Mallinkrodt) and/or a copper coil immersed in dry ice (−78 °C) in a dewar. Dichloromethane was purified by first stirring it with concentrated H_2SO_4 in the dark for days. The acid layer was then removed and the dichloromethane layer was washed with a saturated water solution of Na_2CO_3. The dichloromethane layer was dried over anhydrous $MgSO_4$ before a final drying and distillation over CaH_2. Diethyl ether was passed through a 60-cm long column of activated alumina, and/or it was distilled from sodium/benzophenone under Ar.

The air-sensitive materials were handled and prepared under Ar using standard Schlenk techniques. The solvents and solutions were deoxygenated either by vacuum/purge cycles with argon or by bubbling argon (20 min) directly through the solutions. The air/moisture-sensitive solid samples were stored in a Vacuum Atmospheres drybox filled with argon, where the samples for IR, NMR, and UV-vis were prepared also. The ligands were chromatographed by flash chromatography with either silica gel (60–200 mesh, MCB) or alumina (80–200 mesh, MCB). Purity of the ligands was checked by TLC using Baker-Flex IB-F TLC plates. All elemental analyses were performed by Galbraith Laboratories Inc, Knoxville, TN, and/or Desert Analytics, Tucson, AZ.

Infrared spectra were measured in a Nujol mull or as KBr pellets on a Perkin-Elmer 283 or 710B instrument and calibrated by using a

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(12) Volbeda, A.; Hol, W. G. J. *J. Mol. Biol.* **1989**, *209*, 249–279.

(13) (a) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277–1291. (b) Kitajima, N.; Koda, T.; Iwata, Y.; Moro-oka, Y. *J. Am. Chem. Soc.* **1990**, *112*, 8833–8839.

(14) Magnus, K. Case Western Reserve University, private communication.

(15) (a) Karlin, K. D.; Hayes, J. C.; Gultneh, Y.; Cruse, R. W.; McKown, J. W.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 2121–2128. (b) Karlin, K. D.; Cohen, B. I.; Jacobson, R. R.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 6194–6196. (c) Nasir, M. S.; Cohen, B. I.; Karlin, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 2482–2494.

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

(17) Karlin, K. D.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *Inorg. Chem.* **1984**, *23*, 519–521.

polystyrene film. NMR spectra were recorded in $CDCl_3$ or CD_3NO_2 on either a Varian EM360 (60-MHz) or a Varian XL-300 (300-MHz) spectrometer. Chemical shifts are reported as δ values downfield from an internal standard Me_4Si. Electrical conductivity of the samples were measured in DMF with an Industrial Instruments Inc. Model RC16B conductivity bridge, using a 10-cm cell. The cell constant, κ, was determined with a standard aqueous KCl solution. Room temperature magnetic moments were determined by using a Johnson Matthey magnetic susceptibility balance which was calibrated by using $Hg[Co(SCN)_4]$. X-band electron paramagnetic resonance (EPR) spectra were taken using a Varian E-4 spectrometer in frozen solutions at 77K with 4-mm-o.d. quartz tubes. The field was calibrated with a powder sample of diphenylpicrylhydrazyl (DPPH, $g = 2.0037$). Solvents used were CH_2Cl_2, MeOH, or $DMF/CHCl_3$ (1:1, v/v). In order to facilitate the formation of glasses by rapid freezing the samples prepared in CH_2Cl_2 and $DMF/CHCl_3$ were first frozen in an isopentane/N_2(l) slush bath (113 K) followed by further cooling to 77 K. The signals obtained were integrated by comparing the intensity observed ($I \approx h_{1/2}(w_{1/2h})^2$) with that of a known concentration of $Cu(NO_3)_2 \cdot 3H_2O$ in MeOH (at 77 K) or with a known solution of $[Cu(tepa)(Cl)](PF_6)$[18] in $DMF/CHCl_3$ (1:1, v/v, 77 K). Room temperature electronic spectra were recorded with a Shimadzu UV-160 or a DMS 90 instrument using quartz cuvettes (1 cm). GC analysis was performed on a Hewlett-Packard HP5890 series gas chromatograph equipped with a capillary injector and a flame ionization detector using a 30-m HP-5 capillary column. Signal integration was obtained by using a HP 3392A integrator. GC/MS was performed on a Hewlett-Packard HP 5890 A series gas chromatograph (equipped with a capillary injector and a flame ionization detector using a 30 m × 0.2 mm × 0.2 μm (film thickness) methyl silicone capillary column) interfaced with a mass selected detector (MS) (HP 5970). Signal integration and MS data were obtained using a HP 10833 A integrator. Field-desorption mass spectra were obtained through the NIH sponsored Biotechnology Research Resource for mass spectrometry in the Department of Chemistry at the Massachusetts Institute of Technology, Cambridge, MA, at General Electric Company, Schenectady, NY, or at Rensselear Polytechnic Institute, Rensselear, NY.

Synthesis of Ligands and Complexes. CH_3PY2. The compounds 2-(2-(methylamino)ethyl)pyridine (6.5 g, 0.047 mol) and 2-vinylpyridine (10 g, 0.095 mol, purified by passing through a short silica gel precolumn with diethyl ether solvent, followed by removal of ether by rotary evaporation) were heated under reflux with 47 mL of distilled water and 5 mL of reagent-grade methanol for 2 days. Methanol was removed by rotary evaporation, and the resulting brown mixture was taken up in CH_2Cl_2, washed with 50 mL of 15% NaOH (aqueous), and extracted with dichloromethane (300 mL). The organic layer was dried over $MgSO_4$, and the solvent was removed to give 15.25 g of the crude product. Typically, 6.0 g of this crude oil was columned on alumina by using 98% ethyl acetate/2% MeOH as eluant to first elute 2-vinylpyridine ($R_f = 0.95$) and then CH_3PY2 ($R_f = 0.56$). A total of 7.6 g of pure product, CH_3PY2, was recovered as a brown oil (yield = 66%). ^1H NMR ($CDCl_3$): δ 2.35 (3 H, br s), 2.85 (8 H, br s), 6.80–7.55 (6 H, py-3, py-4, py-5, br m), 8.35 (2 H, py-6, br m). ^{13}C NMR ($CDCl_3$): δ 35.5 (py-CH_2), 41.3 (CH_3) 56.8 (CH_2NCH_2), 120.3 (py C-5), 122.4 (py C-3), 135.4 (py C-4), 148.3 (py C-6), 159.7 (py C-2). ^{13}C NMR (CD_3NO_2): δ 31.2 (py-CH_2), 36.9 (CH_3), 52.8 (CH_2NCH_2), 116.9 (py C-5), 119.0 (py C-3), 132.1 (py C-4), 144.8 (py C-6), 156.8 (py C-2).

$PhCH_2PY2$. Benzyl bromide (3.34 g, 0.0195 mol), was added to a solution of bis(2-(2-pyridyl)ethyl)amine (PY2)[19] (4.43 g, 0.0195 mol) and triethylamine (4.51 g, 0.0450 mol) in 75 mL of ethyl acetate. The mixture was allowed to stir at room temperature for 5 days, whereupon the solution was filtered, and the solvent was removed by rotary evaporation to give a crude oil. The oil was dissolved in 150 mL of CH_2Cl_2 and washed with 50 mL of 20% NaOH followed by 100 mL of water (twice). The organic layer was dried over $MgSO_4$, and the solvent was removed to give 3.50 g of crude oil. This oil was chromatographed on silica gel with 100% MeOH and a total of 2.80 g of the pure product, $PhCH_2PY2$, was recovered (yield = 45%). TLC: $R_f = 0.45$. ^1H NMR ($CDCl_3$): δ 2.85 (8 H, br s), 3.60 (2 H, br s), 6.70–7.40 (11 H, br m), 8.35 (2 H, br d). ^{13}C NMR ($CDCl_3$): δ 35.9 (py-CH_2), 53.2 (ph-CH_2), 58.5 (CH_2NCH_2), 120.9 (py C-5), 123.4 (py C-3), 126.7 (ph C-2), 128.1 (ph C-3), 128.7 (ph C-4), 136.1 (py C-4), 139.6 (ph C-1), 149.0 (py C-6), 160.6 (py C-2).

Ph(C=O)PY2. Benzoyl chloride (0.854 g, 6 mmol) was added to a solution of bis(2-(2-pyridyl)ethyl)amine (PY2) (1.38 g, 6 mmol) and triethylamine (1.41 g, 1.38 mmol) in 100 mL of dry CH_2Cl_2. The mixture was allowed to stir at room temperature for 5 days, whereupon the solution was added to 50 mL of water and extracted with 400 mL of CH_2Cl_2. Removal of CH_2Cl_2 by rotary evaporation gave a crude oil (2.05 g). This crude oil was chromatographed on silica gel with MeOH to yield 1.83 g (90%) of the pure product. TLC: $R_f = 0.72$. ^1H NMR ($CDCl_3$): δ 3.00 (4 H, br s), 3.65 (4 H, br s), 6.80–7.50 (11 H, br m), 8.35 (2 H, py-6, br d), IR (Neat film): 3400 (H_2O, w, br), 3000 (C–H, s, br), 1640 (amide C=O, s), 1610 (C=C, s), 1580 (C=C, w) cm^{-1}. Mass spectrum (*m/e*): 331 (M^+, 36, Ph(C=O)PY2), 252 (18), 238 (100), 226 (73, PY2), 106 (64).

$PhCD_2PY2$. Ph(C=O)PY2 (1.70 g, 2.56 mmol) was added to a slurry of $LiAlD_4$ (0.538 g, 12.8 mmol) in dry THF (40 mL) in a flask equipped with a reflux condenser and a CaH_2 drying tube, and the mixture was refluxed for 24 h. After 24 h, the mixture was cooled to room temperature and 25 mL of water was added dropwise (for 30 min) to quench any unreacted $LiAlD_4$. The solution was then filtered, and the solvent was removed to give a brown oil. This crude oil was dissolved in 300 mL of CH_2Cl_2 and extracted with 50 mL of water. Removal of the solvent from the organic layer gave a crude oil (1.50 g) which was chromatographed on silica gel with MeOH to give 0.95 g (58%) of pure $PhCD_2PY2$. TLC: $R_f = 0.48$. ^1H NMR ($CDCl_3$): δ 2.90 (8 H, br s), 6.70–7.35 (11 H, br m), 8.35 (2 H, py-6, br d). Mass spectrum (*m/e*): 319 (M^+, 25, $PhCD_2PY2$), 240 (8), 226 (100, PY2), 213 (33), 135 (25), 106 (92).

PhPY2. Aniline (5 g, 0.054 mol) and glacial acetic acid (9.7 g, 0.160 mol) were added to a stirred solution of 2-vinylpyridine (purified by passing through a silica gel column with diethyl ether as solvent) (34 g, 0.320 mol) in reagent grade methanol (100 mL). The mixture was refluxed for 5 days while stirring. Methanol was removed by rotary evaporation, and the resulting oil was dissolved in dichloromethane, washed with 100 mL of 10% NaOH (aqueous), and extracted with 150 mL of dichloromethane. The organic layer was dried over $MgSO_4$, and the solvent was removed to yield a crude oil. This oil was dried under vacuum ($P \sim 0.01$ mm) at 45 °C to remove the excess 2-vinylpyridine. The oil was purified by column chromatography on silica gel using ethyl acetate as an eluant to give 4.5 g of pure product (yield = 28%). TLC: $R_f = 0.55$ (on alumina with 20% ethyl acetate/80% CH_2Cl_2 as the solvent). ^1H NMR ($CDCl_3$): δ 2.85 (4 H, br t), 3.50 (4 H, br t), 6.20–7.60 (11 H, br m), 8.20 (2 H, py-6, br d).

$[Cu(CH_3PY2)](PF_6) \cdot 0.5CH_2Cl_2$ [3a(PF_6)]. Under an argon atmosphere, CH_3PY2 (0.50 g, 2.07 mmol) was dissolved in 25 mL of CH_2Cl_2, and this solution was added dropwise with stirring to a solution of $[Cu(CH_3CN)_4](PF_6)$ (0.77 g 2.07 mmol) in 25 mL of CH_2Cl_2 under argon. The resulting dark yellow solution was allowed to stir for 20 min, and a yellow solid was precipitated by adding 200 mL of diethyl ether. The precipitate was filtered and dissolved in 40 mL of CH_2Cl_2 and reprecipitated with 200 mL of Et_2O. The resulting solid was then washed with 30 mL of Et_2O and dried in vacuo to give 0.56 g (60%) of a yellow semicrystalline material. Anal. Calcd for ($C_{15.5}H_{20}ClCuF_6N_3P$): C, 37.82; H, 4.11; N, 8.54. Found: C, 38.27; H, 4.12; N, 8.62. ^1H NMR (CD_3NO_2): δ 2.40 (3 H, br s), 3.15 (8 H, br s), 5.45 (1 H, 0.5 CH_2Cl_2, br s), 7.30–8.00 (6 H, br m), 8.60 (2 H, py-6, br d). ^{13}C NMR (57.3 MHz, CD_3NO_2): δ 30.4 (py-CH_2), 39.2 (CH_3), 53.1 (CH_2NCH_2), 118.9 (py C-5), 121.7 (py C-3), 135.2 (py C-4), 146.8 (py C-6), 157.2 (py C-2). IR (Nujol): 1620 (C=C, s), 1580 (C=C, m), 840 (PF_6^-, s, br) cm^{-1}.

$[Cu(PhCH_2PY2)](PF_6)$ [3b(PF_6)]. To a solution of $[Cu(CH_3CN)_4](PF_6)$ (0.48 g, 1.29 mmol) in 25 mL of CH_2Cl_2 was added dropwise a solution of $PhCH_2PY2$ (0.41 g 1.29 mmol) in 25 mL of CH_2Cl_2 under Ar. The mixture was allowed to stir for 20 min, and 200 mL of Et_2O was added. The precipitate obtained was filtered and dissolved in 40 mL of CH_2Cl_2 and reprecipitated with 200 mL of Et_2O. The resulting solid was washed with 50 mL of diethyl ether and dried in vacuo to give 0.55 g (81%) of a yellow-brown semicrystalline material. Anal. Calcd for $C_{21}H_{23}CuF_6N_3P$: C, 47.93; H, 4.42; N, 8.00. Found: C, 47.77; H, 4.41; N, 8.47. ^1H NMR (CD_3NO_2): δ 3.20 (8 H, br s), 3.65 (2 H, br s), 7.10–7.90 (11 H, br m), 8.45 (2 H, py-6, d). ^{13}C NMR (57.3 MHz, CD_3NO_2): δ 30.7 (py-CH_2), 50.6 (Ph-CH_2), 55.2 (CH_2NCH_2), 118.9 (py C-6), 121.4 (py C-3), 123.9 (Ph C-2), 124.6 (Ph C-3), 125.3 (Ph C-4), 132.7 (Ph C-1), 135.2 (py C-4), 146.5 (py C-6), 156.7 (py C-2). IR (Nujol): 1610 (C=C, s), 1580 (C=C, w), 870 (PF_6^-, s, br) cm^{-1}.

$[Cu(PhPY2)](PF_6)$ [3c(PF_6)]. A solution of PhPY2 (0.40 g, 1.32 mmol) in 20 mL of CH_2Cl_2 was added dropwise with stirring to solid

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(18) Karlin, K. D.; Hayes, J. C.; Shi Juen; Hutchinson, J. P.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 4106–4108.

(19) (a) Nelson, S. M.; Rodgers, J. *Inorg. Chem.* **1967**, *7*, 1390–1395. (b) Romary, J. K.; Azchariasen, R. D.; Garger, J. D.; Schiesser, H. *J. Chem. Soc. C* **1968**, 2882–2887.

$[Cu(CH_3CN)_4](PF_6)$ (0.47 g, 1.26 mmol) under argon. The resulting light yellow solution was allowed to stir for 2 h. Precipitation with diethyl ether afforded a yellow powder upon filtration. The precipitate was dissolved in 20 mL of CH_2Cl_2 and layered with 60 mL of diethyl ether to yield bright yellow crystalline product (0.52 g, 79%). Anal. Calcd for $(C_{20}H_{21}CuF_6N_3P)$: C, 46.92; H, 4.11; N, 8.20. Found: C, 47.15; H, 4.11; N, 7.74. ^1H NMR (CD_3NO_2): δ 3.15 (4 H, br t), 3.55 (4 H, br t), 6.70–8.00 (11 H, br m), 8.55 (2 H, py-6, br d). IR (Nujol): 1605 (C=C, s), 1570 (C=C, w), 850 (PF_6^-, s, br) cm^{-1}.

$[Cu_2(CH_3PY2)_2(O)](PF_6)_2 \cdot 0.5CH_2Cl_2$ [4a(PF_6)$_2$]. $[Cu(CH_3PY2)](PF_6) \cdot 0.5CH_2Cl_2$ [3a(PF_6)] (0.529 g, 1.08 mmol) was dissolved in 70 mL of dry CH_2Cl_2, while stirring under argon. This solution was cooled to 0 °C and exposed to dry O_2 for 5 h. The resulting green solution was placed under argon, and dry Et_2O was added to make the solution cloudy (at this point some blue solid precipitated out). This mixture was then filtered under argon to give a clear green solution. Addition of 300 mL of diethyl ether to the solution yielded a green precipitate. The precipitate was recrystallized from CH_2Cl_2/Et_2O (1:5, v/v) to produce 0.44 g (92%) of a microcrystalline material. Anal. Calcd for $C_{30.5}H_{39}ClCu_2F_{12}N_6OP_2$: C, 38.27; H, 4.11; N, 8.77. Found: C, 37.97; H, 3.95; N, 8.33. IR (Nujol): 1620 (C=C, s), 1595 (C=C, m), 840 (PF_6^-, br, s) cm^{-1}.

$[Cu_2(PhCH_2PY2)_2(O)](PF_6)_2$ [4b(PF_6)$_2$]. A solution of $[Cu(PhCH_2PY2)](PF_6)$ [3b(PF_6)] (0.50 g, 0.95 mmol) was made in dry CH_2Cl_2 under argon. The solution was then exposed to an atmosphere of dry O_2 for 4 h, while stirring at 0 °C. The resulting green solution was then placed under argon and precipitated with 200 mL of dry diethyl ether. The green precipitate formed was filtered and dissolved in 40 mL of dry CH_2Cl_2 and reprecipitated with 200 mL of dry Et_2O. The resulting solid was washed with 30 mL of dry Et_2O and dried under vacuum to yield 0.34 g (68%) of a green semicrystalline material. Anal. Calcd for $C_{42}H_{46}Cu_2F_{12}N_6OP_2$: C, 47.23; H, 4.31; N, 7.87. Found: C, 46.65; H, 4.48; N, 7.83. IR (Nujol): 1605 (C=C, s), 1580 (C=C, w), 850 (PF_6^-, br, s) cm^{-1}.

$[Cu_2(PhPY2)_2(O)](PF_6)_2 \cdot 2CH_2Cl_2$ [4c(PF_6)$_2$]. $[Cu(PhPY2)](PF_6)$ [3c(PF_6)] (0.30 g, 0.59 mmol) was dissolved in 30 mL of dry CH_2Cl_2 under argon. The solution was then exposed to dry dioxygen for 12 h, while stirring at 0 °C. The resulting bluish green solution was precipitated with 200 mL of dry diethyl ether under argon. Recrystallization of the precipitate with CH_2Cl_2/Et_2O (1:3, v/v) produced 0.26 g (73%) of a bluish green microcrystalline material. Anal. Calcd for $C_{42}H_{46}Cl_4Cu_2F_{12}N_6OP_2$: C, 41.69; H, 3.38; N, 6.95. Found: C, 41.27; H, 3.72; N, 7.16. IR (Nujol): 1580 (C=C, m), 840 (PF_6^-, br, s) cm^{-1}.

$[Cu_2(CH_3PY2)(OH)_2](PF_6)_2 \cdot 0.25CH_3COCH_3$ [5a(PF_6)$_2$]. $[Cu(CH_3PY2)](PF_6) \cdot 0.5CH_2Cl_2$ (3a) (0.525 g, 1.07 mmol) was dissolved in 70 mL of CH_2Cl_2, while stirring under argon. The solution was then exposed to an atmosphere of dry dioxygen overnight at 0 °C. The resulting green solution turned immediately to blue when a few drops of water were added. This blue solution was then precipitated with 200 mL of Et_2O while standing overnight at 0 °C. The resulting blue precipitate (0.45 g, 90%) was recrystallized from acetone/Et_2O (1:5, v/v) to yield 0.41 g (82%) of a crystalline product. Anal. Calcd for $C_{30.75}H_{41.5}Cu_2F_{12}N_6O_{2.25}P_2$: C, 38.92; H, 4.21; N, 8.86. Found: C, 38.92; H, 4.15; N, 8.95. IR (Nujol): 3400 (OH, m, br), 1705 (acetone, C=O, w), 1610 (C=C, s), 1590 (C=C, s), 840 (PF_6^-, br, s) cm^{-1}.

$[Cu_2(PhCH_2PY2)_2(OH)_2](PF_6)_2 \cdot 2H_2O$ [5b(PF_6)$_2$]. $[Cu(PhCH_2PY2)](PF_6)$ (3b) (0.50 g, 0.95 mmol) was dissolved in 70 mL of CH_2Cl_2 and then exposed to dry O_2, while stirring at 0 °C. The resulting green solution turned immediately to blue upon addition of a few drops of water. Heptane (200 mL) was added, and the solution was allowed to stand overnight at 0 °C. The blue precipitate obtained was recrystallized from CH_2Cl_2 (40 mL) and heptane (150 mL), and the resulting blue crystalline product was washed with 30 mL of heptane and air dried (0.45 g, 84%). Anal. Calcd for $C_{42}H_{52}Cu_2F_{12}N_6O_4P_2$: C, 44.96; H, 4.64; N, 7.49. Found: C, 44.82; H, 4.21; N, 7.38. IR (Nujol): 3620 (OH, w, br), 3435 (H_2O, w, br), 1615 (C=C, s), 1580 (C=C, w), 850 (PF_6^-, s, br) cm^{-1}.

$[Cu_2(PhPY2)_2(OH)_2](PF_6)_2 \cdot CH_2Cl_2 \cdot (C_2H_5)_2O$ [5c(PF_6)$_2$]. A solution of $[Cu(PhPY2)](PF_6)$ (3c) (0.30 g, 0.59 mmol) was made in 30 mL of CH_2Cl_2 under argon. This was exposed to dry O_2 for 4 h, while stirring at 0 °C. The resulting bluish green solution turned to brownish green when a few drops of water were added. This solution was stirred overnight and precipitated with 100 mL of diethyl ether. Recrystallization with CH_2Cl_2/Et_2O (1:3, v/v) produced 0.25 g (69%) of a brownish green microcrystalline material. Anal. Calcd for $C_{45}H_{56}Cl_2Cu_2F_{12}N_6O_3P_2$: C, 44.41; H, 4.64; N, 6.91. Found: C, 44.97; H, 4.41; N, 7.02. IR (Nujol): 3640 (OH, w, br), 1610 (C=C, m), 840 (PF_6^-, s, br) cm^{-1}.

Oxygenation of $[Cu(PhCH_2PY2)](PF_6)$ [3b(PF_6)] at Low Temperature (−80 °C) To Generate Benzaldehyde. The complex, $[Cu(PhCH_2PY2)](PF_6)$ [3b(PF_6)] (1.08 g, 2.05 mmol) was dissolved in 50 mL of CH_2Cl_2, while stirring under argon. The yellow solution changed to a deep brown color when exposed to dry O_2 at −80 °C. After 4 days, the brown solution was allowed to warm up to the room temperature and it turned to a greenish blue color. This solution was then precipitated with 150 mL of Et_2O and the clear filtrate was saved. The resulting blue precipitate was washed with 30 mL of Et_2O and air dried (0.70 g). The blue precipitate was dissolved in 50 mL of CH_2Cl_2 and added to an equal volume of aqueous ammonia to extract the ligand. The brown CH_2Cl_2 layer was separated from the blue aqueous layer, washed with 50 mL of water and dried over $MgSO_4$. An oily brown product was isolated after the removal of the solvent by rotary evaporation (0.30 g). Ligand analysis in 90% MeOH/10% NH_4OH on a silica TLC plate showed a mixture of $PhCH_2PY2$ (R_f = 0.86) and, PY (R_f = 0.40). ^1H NMR ($CDCl_3$): δ 2.90 (8 H, br s), 3.60 (2 H, br s), 3.90 (1 H, NH-PY2, br s), 6.70–7.45 (11 H, br m), 8.35 (2 H, py-6, br d). Integration of the peaks showed a mixture of 80% $PhCH_2PY2$ and 20% PY2.

Analysis by gas chromatography and comparison to an authentic sample showed that the clear filtrate (above) contained benzaldehyde. The filtrate was added to an excess (15 mL) of dinitrophenylhydrazine reagent solution (see below). The mixture was heated at 45 °C for 20 min and evaporated in vacuo to give a reddish yellow solid. The solid was then washed with 15 mL of 95% EtOH and dried in vacuo to give 0.10 g (20%) of benzaldehyde dinitrophenylhydrazone: mp 235–237 °C. The yield of benzaldehyde was determined to be 20%, based on the starting complex **3b**.

The dinitrophenylhydrazine reagent solution was prepared by addition of 3.0 g of reagent to 15 mL of H_2SO_4 (concentrated). This mixture was added to another solution containing 20 mL of water and 70 mL of EtOH (95%).

Oxygenation of the Deuterated Analog $[Cu(PhCD_2PY2)](PF_6)$ [3b′(PF_6)] at −80 °C: Isolation of Deuteriobenzaldehyde. The deuterio analogue of 3b(PF_6), $[Cu(PhCD_2PY2)](PF_6)$ (prepared from the reaction of an equimolar amount of $[Cu(CH_3CN)_4](PF_6)$ with the ligand $PhCD_2PY2$ in CH_2Cl_2 (0.52 g, 0.986 mmol), was dissolved in 40 mL of CH_2Cl_2 while stirring under argon. This dark yellow solution changed to a brown color when exposed to an atmosphere of dry O_2 at −80 °C. The brown solution was stirred at −80 °C for 4 days and was then allowed to warm up to room temperature. The solution changed to a bluish green color, and the solvent was removed from the solution under reduced pressure (at 0 °C) leaving a bluish green solid behind. The solid was stirred with 20 mL of diethyl ether over a 3–4-h period and filtered to give 0.44 g of a bluish green solid. Analysis of the ligand in this solid (by strpping off the Cu(II) with NH_4OH) in 80% MeOH/20% NH_4OH on silica gel showed a mixture of $PhCH_2PY2$ (R_f = 0.86, 80%) and PY2 (R_f = 0.40, 20%).

The diethyl ether filtrate was collected and the solvent was distilled off under reduced pressure, while the mixture was cooled at 0 °C. A drop of a clear yellow oil corresponding to deuteriobenzaldehyde was obtained. GC/mass spectrum (m/z): 107 (M^+, 100, PhCDO), 105 (96, PhCHO), 77 (96), 51 (56).

Oxygenation of the Deuterated Analog of $[Cu(PhCD_2PY2)](PF_6)$ [3b-(PF_6)] at −80 °C with $^{18}O_2$: Isolation of Deuteriobenzaldehyde with a ^{18}O Label. A solution of the deuterio analogue of 3b(PF_6), $[Cu(PhCD_2PY2)](PF_6)$, (0.61 g, 1.156 mmol) in 50 mL of CH_2Cl_2 was exposed to an atmosphere of dry $^{18}O_2$ (Icon Services, Inc, 98% atom ^{18}O, 100 mL) for 4 days, while stirring at −80 °C. The brown solution was then warmed up to room temperature slowly, giving a bluish green solution. The solvent was distilled off from the solution at 0 °C leaving behind a bluish green solid. The solid was stirred with 50 mL of Et_2O and filtered to give 0.56 g of a bluish green solid. Ligand analysis for the solid (by NH_4OH) showed a mixture of $PhCH_2PY2$ (80%) and PY2 (20%).

The diethyl ether filtrate was collected and the solvent was removed under reduced pressure to yield a drop of a clear yellow oil. GC/mass spectrum (m/z): 109 (M^+, 45, $PhCD^{18}O$), 107 (100, $PhCH^{18}O$), 105 (52, PhCHO), 77 (96), 51 (90). The results indicated a >65% ^{18}O atom incorporation into the organic product (deuteriobenzaldehyde) obtained.

Gas (O_2) Uptake Measurements. Measurements of the uptake of dioxygen by $[Cu(RPY2)]^+$ (3) in CH_2Cl_2 at 0 or −80 °C were carried out with the gas buret system described previously.[8a,9a] Typically, a solution of **3a** (0.30 g) was prepared in 35 mL of CH_2Cl_2 in a 25-mL Kontes side arm flask under argon. The reaction flask was then attached to the buret system and cooled to the desired temperature (0 or −80 °C) by placing it in an appropriate cold bath. The entire system was purged with argon and vacuum with a final application of vacuum for 5 min (at 0 °C) or 20 min (−80 °C). The stopcock of the flask was closed, and the buret was equilibrated with 1 atm of O_2 pressure. The initial volume reading was noted, and the stopcock of the flask was opened. "Blank" runs to determine the O_2 taken up by the solvent were performed under similar conditions.

Low-Temperature UV–Vis Spectroscopy. Low-temperature electronic spectra 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 as described previously.[8a,9a] The spectrophotometer was equipped with a Kontes KM-611772 variable-temperature UV–vis Dewar cell with quartz windows. The low temperature inside the Dewar assembly was achieved by putting a copper tubing coil inside the methanol-filled Dewar cell, through which cold methanol was circulated by an external cooling unit (Neslab CC-100II cryocool immersion cooler, in Agitainer A with circulating pump). The cuvette assembly consisted of a quartz cuvette fused to one end of a glass tube; the other end was attached to a high vacuum-stopcock and a ₸ 14/20 ground glass joint. The temperature inside the Dewar assembly was monitored by an Omega Model 651 resistance thermometer probe. For measurements in the near-IR region (≤1100 nm), a Shimadzu UV-160 spectrometer was used.

Electrochemistry. Cyclic voltammetry of the copper(I) complexes was carried out using a Bioanalytical Systems (BAS) CV-27 Voltammograph and Houston Instruments Model 100 X-Y recorder. The cell was a local modification of a standard three-chambered design equipped for handling air-sensitive solutions by utilizing high vacuum valves (Viton O-ring) seals. A glassy-carbon electrode (GCE, BAS MF 2012) was used as the working electrode. The reference electrode was a Ag/AgCl Metrohm Model 6.0724.140 electrode (stored in a 0.1 M dichloromethane solution of tetrabutylammonium hexafluorophosphate (TBAHP), saturated with LiCl). The auxiliary electrode consisted of a coiled platinum wire. The concentration of the TBAHP supporting electrolyte was 200 times (~0.2 M) that of the complex (~10^{-3} M) studied. Under the experimental conditions employed, the ferrocene/ferrocenium (Fc/Fc^+) couple used as calibrant possessed an $E_{1/2}$ value of 0.55 V vs Ag/AgCl. The measurements were taken at room temperature in DMF under argon.

Results and Discussion

Synthesis of Copper(I) Complexes. As indicated in the introduction, we have found the bis(2-pyridylethyl)amine (PY2) chelating group to be very suitable for generating tricoordinated Cu(I) species which can be handled and characterized, yet they are sensitive to dioxygen and give interesting O_2 adducts.[1,9] The methyl and phenyl mononucleating ligands CH_3PY2 and PhPY2 were both synthesized in one-step reactions from commercially available materials by pyridylethylation reactions using 2-vinylpyridine (see Experimental Section). $PhCH_2PY2$ was made by reaction of the secondary amine PY2 with benzyl bromide in the presence of triethylamine as base. The tricoordinated mononuclear Cu(I) complexes $[Cu(RPY2)]^+$ (**3a–c**) are typically formed by reaction of equimolar quantities of ligand and $[Cu(CH_3CN)_4]PF_6$ in dichloromethane. The dark yellow products were precipitated by addition of diethyl ether and recrystallized from CH_2Cl_2/Et_2O. Complexes **3a–c** are very soluble in polar organic solvents including CH_2Cl_2. Both solids and solutions are air-sensitive, especially **3a**.

The ^1H and ^{13}C NMR spectra of the ligands and their Cu(I) complexes have been obtained (Experimental Section) and correspond well with their formulation as diamagnetic (d^{10} electronic configuration) species. Sharp spectra are obtained and downfield shifting of both the ^1H and ^{13}C ligand resonances upon coordination to the positively charged Cu(I) ion is observed, as has been found for many other analogous systems.[8a,9a,c,15c] As isolated, the Cu(I) complex of the ligand CH_3PY2, $[Cu(CH_3PY2)](PF_6)\cdot{}^1/_2CH_2Cl_2$ [**3a**(PF_6)], is the only one in this series to possess a solvate molecule, the presence of which was proven by ^1H NMR spectroscopy (see Experimental Section).

X-ray Structure of [Cu(PhPY2)](PF_6) [3c(PF_6)]. The structure of **3c** has been determined by X-ray crystallography, and a view of the cation is shown in Figure 1. Experimental details, positional parameters, and selected bond lengths and distances are provided as Tables I–III, respectively. Generally, the structure of three coordinate L_3Cu^I (L = unidentate N-donor) complexes are expected to have a nearly trigonal planar geometry.[20] That for **3c** is not, but it has a coordination typical of many three-coordinate copper(I) complexes possessing linear tridentate chelating ligands, with an overall nearly T-shaped geometry.[21] The structure of **3c** compares closely with those of many of the other copper(I) complexes containing this exact PY2 tridentate group. Thus, there are two shorter Cu–$N_{pyridine}$ bonding interactions (1.91–1.92 Å), while the Cu–N_{amine} bond distance is Cu–N1 = 2.228 (8) Å. The large N_{py}–Cu–N_{py} angle of ∠N2–Cu–N3 = 159.6 (3)° makes this structure more like a linear pseudo-two-coordinate Cu(I) complex which has been perturbed by a weaker interaction with a third donor ligand. Linear pure two-coordinate Cu(I) complexes $[L_2Cu]^+$ (L = heterocyclic nitrogen donor such as

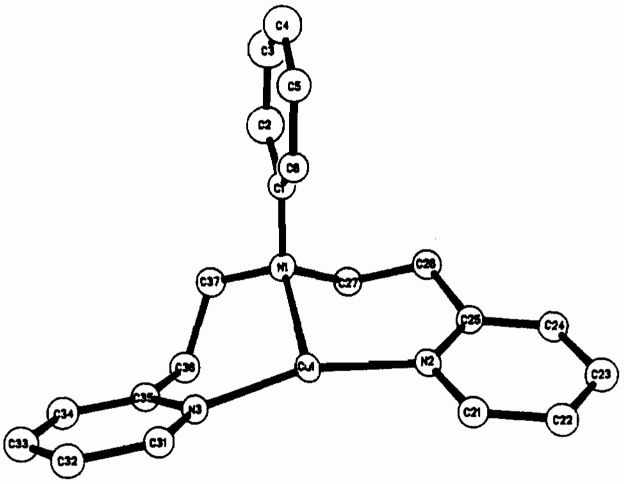

Figure 1. ORTEP diagram of the cationic portion of [Cu(PhPY2)](PF_6) [**3c**(PF_6)] showing the atom-labeling scheme.

Table I. Crystallographic Data for [Cu(PhPY2)](PF_6) [**3c**(PF_6)]

formula	$C_{20}H_{21}CuN_3F_6P$	$F(000)$	1044
temp, K	294	Z	4
MW	511.92	D_{calcd}, g/cm³	1.61
cryst syst	monoclinic	abs coeff, cm⁻¹	11.70
space group	$P2_1/n$	no. of reflcns collcd	3042
a, Å[a]	10.037 (4)	no. of indep reflcns	1941 ($\geq 6\sigma\|F_o\|$)
b, Å	14.406 (4)	no. of refined params (N_v)	180
c, Å	15.210 (5)	largest peak/hole, e Å⁻³	0.96/−0.51
α, deg	90.00	R[b]	0.0723
β, deg	105.99 (3)	R_w[c]	0.0827
γ, deg	90.00	goodness of fit[d]	1.8942
V, Å³	2114.6 (1)		

[a] All calculations were performed on a Micro-Vax II computer using local versions of the Nicolet SHELXTL interactive crystallographic software package as described in: Sheldrich, G. M. *Nicolet SHELXTL Operations Manual*: Nicolet XRD Corp.: Cupertino, CA, 1979. [b] $R = \sum[|F_o| - |F_c|/\sum|F_o|]$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o) + g^*(F_o)^2$; $g = 0.001$. [d] GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables.

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(20) Lewin, A. H.; Michl, R. J.; Ganis, P.; Lepore, U. *J. Chem. Soc., Chem. Commun.* **1972**, 661–662.

(21) A recent paper discusses T- and Y-shaped three-coordinated Cu(I) complexes. See: Munakata, M.; Maekawa, M.; Kitagawa, S.; Matsuyama, S.; Masuda, H. *Inorg. Chem.* **1989**, *28*, 4300–4302 and references cited therein.

(22) (a) Okkersen, H.; Groeneveld, W. L.; Reedijk, J. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 945–953. (b) Lewin, A. H.; Cohen, I. A.; Michl, R. *J. Inorg. Nucl. Chem.* **1974**, *36*, 1951–1957. (c) Hendriks, H. M. J.; Reedijk, J. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 95–100. (d) Agnus, Y.; Louis, R.; Weiss, R. *J. Chem. Soc., Chem. Commun.* **1980**, 867–869. (e) Sorrell, T. N.; Jameson, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 6013–6018. (f) Engelhardt, L. M.; Pakawatchai, C.; White, A. H.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* **1985**, 117–123. (g) Munakata, M.; Kitagawa, S.; Shimono, H.; Masuda, H. *Inorg. Chim. Acta* **1989**, *158*, 217–220. (h) Tan, G. O.; Hodgson, K. O.; Hedman, B.; Clark, G. R.; Garrity, M. L.; Sorrell, T. N. *Acta Crystallogr.* **1991**, *C46*, 1773–1775. (f) Habiyakare, A.; Lucken, E. A. C.; Bernardinelli, G. *J. Chem. Soc., Dalton Trans.* **1991**, 2269.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for the Compound $[Cu(PhPY2)]^+$ (**3c**)

atom	*x*	*y*	*z*	$U_{equiv/isc}$[a]
Cu	1789 (1)	1436 (1)	2908 (1)	48 (1)
N1	213 (7)	1980 (5)	3560 (5)	50 (3)
N2	750 (7)	1430 (5)	1642 (5)	46 (3)
N3	3267 (7)	1204 (5)	3988 (5)	48 (3)
C1	37 (9)	2986 (6)	3529 (6)	51 (2)
C2	−869 (16)	3429 (10)	3929 (11)	102 (5)
C3	−984 (18)	4377 (13)	3855 (12)	107 (6)
C4	−181 (12)	4902 (10)	3423 (8)	91 (4)
C5	761 (10)	4468 (7)	3099 (7)	66 (3)
C6	850 (9)	3526 (6)	3148 (6)	55 (2)
C21	1433 (10)	1270 (6)	1014 (6)	55 (2)
C22	816 (10)	1185 (7)	99 (7)	61 (3)
C23	−600 (11)	1239 (7)	−216 (7)	68 (3)
C24	−1334 (10)	1398 (7)	413 (7)	60 (2)
C25	−654 (9)	1512 (6)	1342 (6)	51 (2)
C26	−1481 (9)	1785 (7)	1999 (6)	61 (3)
C27	−1038 (9)	1480 (6)	2989 (6)	59 (2)
C31	4603 (9)	1375 (6)	4029 (6)	52 (2)
C32	5645 (10)	1364 (6)	4834 (7)	61 (3)
C33	5293 (11)	1152 (7)	5622 (8)	70 (3)
C34	3968 (10)	975 (7)	5584 (7)	65 (3)
C35	2953 (9)	995 (7)	4775 (6)	53 (2)
C36	1462 (9)	795 (7)	4703 (7)	67 (3)
C37	507 (10)	1654 (7)	4514 (7)	62 (3)
P1	9816 (3)	1690 (2)	7062 (2)	60 (1)
F1	11024 (9)	1267 (7)	6725 (5)	129 (4)
F2	10088 (10)	2628 (6)	6668 (8)	114 (5)
F3	10831 (8)	1992 (9)	7986 (5)	162 (5)
F4	8813 (8)	1438 (7)	6132 (6)	148 (5)
F5	8594 (6)	2132 (6)	7389 (5)	108 (3)
F6	9620 (17)	775 (7)	7512 (9)	82 (8)

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $[Cu(PhPY2)](PF_6)$ [**3c**(PF_6)]

	Interatomic Distances		
Cu–N1	2.228 (8)	Cu–N3	1.915 (6)
Cu–N2	1.922 (6)		
	Interatomic Angles		
N1–Cu–N2	101.1 (3)	N2–Cu–N3	159.6 (3)
N1–Cu–N3	99.0 (3)		

pyridine, imidazole, benzimidazole, and pyrazole) typically have Cu–N bond lengths between 1.86 and 1.91 Å.[22,23] For comparison, four-coordinate Cu(I) complexes containing the PY2 unit plus a fourth ligand such as CO,[9c] PPh_3,[24] CH_3CN,[9a] pyridyl,[25] or phenoxo,[8a] have Cu–N_{py} bond lengths in the range 1.95–2.07 Å. Despite the distortions, the three nitrogen ligands are nearly coplanar, with the copper ion lying 0.051 Å above the plane defined by N1, N2, and N3. The structure of **3c** compares very closely with that previously determined for $[Cu(PhCH_2PY2)](PF_6)$ [**3b**(PF_6)].[16]

Electrochemical Comparisons of Copper(I) Complexes [Cu(RPY2)](PF_6) [3(PF_6)]. It is of interest to see how the ligand modification in RPY2 affects the Cu(II)/Cu(I) redox potential, since reactions of O_2 involve at least partial electron transfer,[6,7] i.e., oxidation of Cu(I) to Cu(II).

Cyclic voltammetric measurements of copper(I) complexes **3a–c** were carried out in dimethylformamide solution (Table IV). The compounds all exhibited one simple quasi-reversible wave over the potential range measured, +0.9 to −0.3 V. The $E_{1/2}$ values varied from +80 to +150 mV versus NHE (calibrated with ferrocene/ferrocenium), with the CH_3PY2 ligand complex being least positive. Current peak ratios were all unity. The peak to peak separations ΔE_p were 80–90 mV for **3a** and **3b**, but a kinetic barrier to electron transfer at the electrode surface seems to occur for **3c**, since ΔE_p was 280 mV at the scan rate used. Perhaps this is due to the phenyl group in PhPY2 which is directly attached to the coordinated amine nitrogen donor. Constant potential electrolysis (Pt guage electrode) confirmed that a one-electron oxidation occurs for **3a–c**, and a color change from light yellow to blue-green accompanies the process. Thus, the results demonstrate an effective reversibility according to the following stoichiometry:

Table IV. Cyclic Voltammetric[a] Data for the Copper(I) Complexes **3a–c**

compound	ΔE_p, mV	$E_{1/2}$, mV[b]	i_{pc}/i_{pa}
$[Cu(CH_3PY2)](PF_6)\cdot 0.5CH_2Cl_2$ [**3a**(PF_6)]	80	80	1.0
$[Cu(PhCH_2PY2)](PF_6)$ [**3b**(PF_6)]	90	120	1.0
$[Cu(PhPY2)](PF_6)$ [**3c**(PF_6)]	280	200	1.0

[a] Key: solvent, DMF; supporting electrolyte, 0.2 M TBAHP; working electrode, GCE; scan rate, 0.1 V/s; concentration, $\sim 1 \times 10^{-3}$ M. [b] Versus NHE.

$$[Cu^{II}(RPY2)]^{2+} + e^- \rightleftarrows \underset{\textbf{3}}{[Cu^{I}(RPY2)]^+}$$

The shifting of $E_{1/2}$ values to more positive potentials on going from R = CH_3 to $PhCH_2$ to Ph seems in accord with the relative electron-donating capacities of these substituents. Thus, the CH_3-PY2 ligand is expected to be the most electron donating of the three ligands and $[Cu^I(CH_3PY2)]^+$ (**3a**) is the easiest of the three complexes to oxidize. This agrees with our qualitative finding (vide infra) that **3a** is most susceptible to oxidation by O_2 and that its apparent rate of oxygenation is fastest. Detailed kinetic studies will be needed to substantiate and quantify these observations.

$LCu(I)_n/O_2$ Reactions: Formation of Oxo–Copper Complexes. It is generally assumed that dioxygen reaction with mononuclear copper(I) complexes LCu^I can proceed in steps leading to a two-electron-reduced peroxo intermediate $LCu^{II}–(O_2)–Cu^{II}L$.[2,5a,26] One-to-one $LCuO_2$ adducts are probable intermediates; we have recently detected such a species in a kinetic study,[27] and isolated "superoxo"–Cu(II) mononuclear complexes have also been previously reported.[28,29] In hemocyanin, the peroxo intermediate is stabilized and forms reversibly. However, only in the last few years have such species been stabilized in synthetic systems,[1-3] since they generally decompose rapidly, by a number of possible mechanisms.[4a,26] Included is the possibility of peroxide disproportionation, equivalent to the further reaction of $LCu–O_2–CuL$ with LCu^I, leading to an overall reaction stoichiometry of Cu/O_2 = 4:1.[2,5a,26] Thus, the most common reaction of LCu^I with O_2 is this four-electron reduction and O–O cleavage reaction to give oxo products:

$$4LCu^I + O_2 \rightarrow 2Cu_2O \text{ or } Cu_4(O)_2$$

In aprotic media using LCuX (L = amine or diamine; X = halide) compounds, Davies and co-workers[26] have studied such

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(23) Linear two-coordinate copper(I) complexes having chelating ligands are also known but the two copper ion ligands come from different ligand molecules. See: (a) Hendriks, H. M. J.; Birker, P. J. M. W. L.; van Rijn, J.; Verschoor, G. C.; Reedijk, J. *J. Am. Chem. Soc.* **1982**, *104*, 3607–3617. (b) Sorrell, T. N.; Jameson, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 2053–2054. (c) Schilstra, M. J.; Birker, P. J. M. W. L.; Verschoor, G. C.; Reedijk, J. *Inorg. Chem.* **1982**, *21*, 2637–2644.

(24) Karlin, K. D.; Ghosh, P.; Cruse, R. W.; Farooq, A.; Gultneh, Y.; Jacobson, R. R.; Blackburn, N. J.; Strange, R. W.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 6769–6780.

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

(26) (a) Davies, G.; El-Sayed, M. A. *Comments Inorg. Chem.* **1985**, *4*, 151–162. (b) Caulton, K. G.; Davies, G.; Holt, E. M. *Polyhedron* **1990**, *9*, 2319–2351.

(27) Karlin, K. D.; Wei, N.; Jung, B.; Kaderli, S.; Zuberbühler, A. D. *J. Am. Chem. Soc.* **1991**, *113*, 5868–5870.

(28) (a) Nappa, M.; Valentine, J. S.; Miksztal, A. R.; Schugar, H. G.; Isied, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 7744–7746. (b) Thompson, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 4057–4059. (c) Thompson, J. S. In *Biological & Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: Guilderland, NY, 1986; Vol. 2, pp 1–10.

(29) There is some question or controversy concerning the formulation of the $LCu(O_2)$ 1:1 species described by Thompson.[28b,c] See ref 13a.

Table V. EPR, Magnetism, UV–Vis, and Conductivity Data for the Oxo- and Dihydroxo-Bridged Dicopper(II) Complexes **4a–c** and **5a–c**

compound	EPR[a] (A, 10^{-4} cm^{-1})		μ(RT)[b] BM/Cu	UV–vis λ, nm (ϵ, M^{-1} cm^{-1})	conductivity[c] Λ_M, Ω^{-1} cm^2 mol^{-1}
	CH_2Cl_2	MeOH			
$[Cu_2(CH_3PY2)_2(O)](PF_6)_2\cdot 0.5CH_2Cl_2$ [**4a**$(PF_6)_2$]	$g_\perp = 2.06$ $g_\parallel = 2.26$ $A_\parallel = 183$ "silent"[f]	$g_\perp = 2.08$ $g_\parallel = 2.30$ $A_\parallel = 183$	1.7	260 (30 700)[e] 300 (sh, 9070)[e] 708 (190)[e]	135
$[Cu_2(CH_3PY2)_2(OH)_2](PF_6)_2\cdot 0.25CH_3COCH_3$ [**5a**$(PF_6)_2$]	$g = 4.08$[g]	$g_\perp = 2.04$ $g_\parallel = 2.26$ $A_\parallel = 182$	1.6	260 (32 000)[e] 300 (sh, 7100)[e] 714 (170)[e]	130
$[Cu_2(PhCH_2PY2)_2(O)](PF_6)_2$ [**4b**$(PF_6)_2$]	$g = 4.26$[g]	$g_\perp = 2.13$ $g_\parallel = 2.26$ $A_\parallel = 174$	1.8	660 (760)[d]	130
$[Cu_2(PhCH_2PY2)_2(OH)_2](PF_6)_2$ [**5b**$(PF_6)_2$]	$g = 4.32$[g]	$g_\perp = 2.16$ $g_\parallel = 2.32$ $A_\parallel = 169$	1.9	685 (330)[d]	130
$[Cu_2(PhPY2)_2(O)](PF_6)_2\cdot 2CH_2Cl_2$ [**4c**$(PF_6)_2$]	"silent"	$g_\perp = 2.03$ $g_\parallel = 2.21$ $A_\parallel = 155$	1.8	257 (24 400)[d] 630 (860)[d]	134
$[Cu_2(PhPY2)_2(OH)_2](PF_6)_2\cdot CH_2Cl_2\cdot(C_2H_5)_2O$ [**5c**$(PF_6)_2$]	"silent"	$g_\perp = 2.08$ $g_\parallel = 2.26$ $A_\parallel = 154$	1.9	233 (22 000)[d] 261 (27 500)[d] 683 (465)[d]	155

[a] Frozen solution at 77 K. [b] Solid-state magnetic moment at room temperature. [c] Measurements taken in DMF. [d] Measurements done in CH_2Cl_2. [e] Measured in CH_3CN. [f] Measured in DMF/$CHCl_3$ (1:1, v/v). [g] Half-field line.

reactions extensively and demonstrated that it is the reaction of the third Cu(I), i.e. the third electron, that effects the O–O bond cleavage reaction of dioxygen.[26,30,31] However, for the discrete peroxo–dicopper(II) complex $\{Cu[HB(3,5\text{-}i\text{-}Pr_2pz)_3]\}_2(O_2)$,[3,13] Kitajima suggests another mode of decomposition.[3,13b] Here, a first-order thermal decomposition is observed, proposed to be a homolytic cleavage giving a mononuclear $Cu[HB(3,5\text{-}Me_2pz)_3]$-(O) (e.g. Cu(III)–oxo or Cu(II)–O$^\bullet$) species; this reactive intermediate then combines with the Cu(I) complex which is present, giving the observed oxo–dicopper(II) final product, $\{Cu[HB(3,5\text{-}i\text{-}Pr_2pz)_3]\}_2(O)$.

While X-ray structures of μ_3-, μ_4- and μ_5-oxo–Cu(II) cluster compounds are known,[32] only one structure appears to be available for a discrete oxo- (and aqua-) bridged *di*copper(II) complex.[33] A number of interesting ones have been described[33–40] and recent reports include those which are able to fix carbon dioxide.[34,35] Oxo–Cu(II) complexes are known to oxygenate PPh_3,[13a,17,34,36,37] effect the dehydrogenation of organics,[5b,38–42] and initiate phenol oxidative coupling reactions.[26,42]

Reactions of [Cu(RPY2)](PF_6) [3(PF_6)] with Dioxygen at ≥0 °C. Characterization of Oxo–Dicopper(II) Complexes $[Cu_2(RPY2)_2(O)]^{2+}$ (4). In the absence of definitive kinetic/mechanistic information, it appears that the reaction of complexes **3** follows a behavior similar to that described above. At low temperature, oxygenation of these complexes leads to reasonably stable $LCu^{II}–(O_2)–Cu^{II}L$ species (vide infra). Either (a) the reaction with the third (and fourth) Cu(I) ion complexes does not occur at low temperature, or (b) thermal decomposition of the peroxo intermediates is suppressed. Perhaps it is the cationic nature of peroxo complexes $[Cu_2(RPY2)_2(O_2)]^{2+}$ (**6a–c**) which suppresses further reaction with cationic Cu(I) compounds **3**.

When the dichloromethane solution of the Cu(I) complexes **3a–c** are exposed to O_2 under very dry conditions at temperature ≥0 °C, an irreversible oxidation of copper occurs leaving a green solution in the case of **3a** and **3b** and a bluish green solution for **3c**. The stoichiometry of oxygen taken by the Cu(I) compounds has been measured by manometry and is found to occur in the mole ratio of $Cu/O_2 = 4{:}1$. This clearly suggests that a four-electron reduction of O_2 occurs giving oxo-bridged dicopper(II) complexes. These species have been isolated and characterized, i.e.

$[Cu_2(CH_3PY2)_2(O)](PF_6)_2\cdot 0.5CH_2Cl_2$ [**4a**$(PF_6)_2$],
$[Cu_2(PhCH_2PY2)_2(O)](PF_6)_2$ [**4b**$(PF_6)_2$], and
$[Cu_2(PhPY2)_2(O)](PF_6)_2\cdot 2CH_2Cl_2$ [**4c**$(PF_6)_2$].

The oxo-bridged compounds isolated were $[Cu_2(MePY2)_2(O)](PF_6)_2\cdot 0.5CH_2Cl_2$ [**4a**$(PF_6)_2$], $[Cu_2(PhCH_2PY2)_2(O)](PF_6)_2$ [**4b**$(PF_6)_2$] and $[Cu_2(PhPY2)_2(O)](PF_6)_2\cdot 2CH_2Cl_2$ [**4c**$(PF_6)_2$]. Microanalytical data indicates the presence of solvates in complexes **4a** and **4c**. Confirmation comes from ^1H NMR spectroscopy in CD_3NO_2 after these compounds were reduced by KCN, giving solutions of Cu(I) (e.g. diamagnetic) along with the ligands and solvents (see Experimental Section). No ν(O–H) in the 3300–3600-cm^{-1} region is observed in the infrared spectra of compounds **4a–c**. Spectroscopic properties are also given in Table V, and the EPR behavior also adds credence to the proposed formulations. In polar solvents such as methanol these oxo-bridged complexes break, giving monomeric species, as shown by EPR spectroscopy (Table V), since "normal" tetragonal spectra are obtained. In frozen CH_2Cl_2 solution (77 K), however, a dimeric structure for **4b** and **4c** appears to be

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(30) Davies, G.; El-Sayed, M. A. *Inorg. Chem.* **1983**, *22*, 1257–1266.

(31) Davies, G.; El-Sayed, M. A.; Henary, M. *Inorg. Chem.* **1987**, *26*, 3266–3273.

(32) (a) Agnus, Y.; Louis, R.; Metz, B.; Boudon, C.; Gisselbrecht, J. P.; Gross, M. *Inorg. Chem.* **1991**, *30*, 3155–3161 and references cited therein. (b) Butcher, R. J.; O'Connor, C. J.; Sinn, E. *Inorg. Chem.* **1981**, *20*, 537–545. (c) McKee, V.; Tandon, S. S. *Inorg. Chem.* **1989**, *28*, 2901–2902. (d) McKee, V.; Tandon, S. S. *J. Chem. Soc., Dalton Trans.* **1991**, 221–230. (e) Erdonmez, A.; van Diemen, J. H.; de Graaff, R. A. G.; Reedijk, J. *Acta Crystallogr.* **1990**, *C46*, 402–404. (f) McKillop, K. P.; Nelson, S. M.; Nelson, J.; McKee, V. *J. Chem. Soc., Chem. Commun.* **1988**, 387–389. (g) Effenberger, H. *Monatsh. Chem.* **1985**, *116*, 927–931.

(33) Chaudhuri, P.; Ventur, D.; Wieghardt, K.; Peters, E.-M.; Peters, K.; Simon, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 57–59.

(34) (a) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitagawa, T.; Moro-oko, Y. *J. Am. Chem. Soc.* **1991**, *113*, 5664–5671. (b) Kitajima, N.; Fujisawa, K.; Koda, T.; Hikichi, S.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 1357–1358. (c) Kitajima, N.; Koda, T.; Moro-oka, Y. *Chem. Lett.* **1988**, 347–350.

(35) Henary, M.; Zink, J. I. *J. Am. Chem. Soc.* **1988**, *110*, 5582–5583.

(36) Paul, P. P.; Tyeklár, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1990**, *112*, 2430–2432.

(37) Lapinte, C.; Riviere, H.; Roselli, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1109–1110.

(38) Jallabert, C.; Lapinte, C.; Riviere, H. *J. Mol. Catal.* **1980**, *7*, 127–136.

(39) Gampp, H.; Zuberbühler, A. D. *Chimia* **1978**, *32*, 54–56. (b) Gampp, H.; Zuberbühler, A. D. *J. Mol. Catal.* **1980**, *7*, 81–88.

(40) Karlin, K. D.; Gultneh, Y. *Prog. Inorg. Chem.* **1987**, *35*, 219–327.

(41) Ardizzoia, G. A.; Angaroni, M. A.; La Monica, G.; Cariati, F.; Cenini, S.; Moret, M.; Masciocchi, N. *Inorg. Chem.* **1991**, *30*, 4347–4353.

(42) El-Sayed, M. A.; Abu-Raqabah, A.; Davies, G.; El-Toukhy, A. *Inorg. Chem.* **1989**, *28*, 1909–1914.

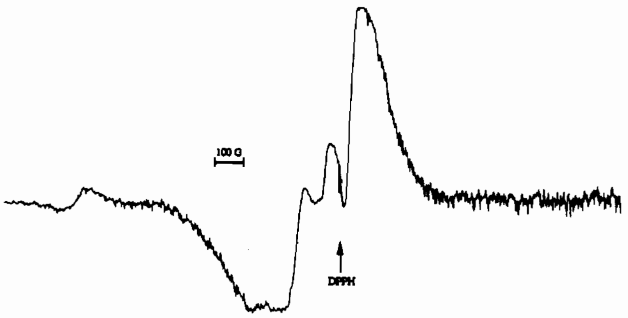

Figure 2. EPR spectrum of $[Cu_2(PhCH_2PY2)_2(O)](PF_6)_2$ [**4b**$(PF_6)_2$] in CH_2Cl_2 at 77 K. A half-field line is observed at $g \sim 4$.

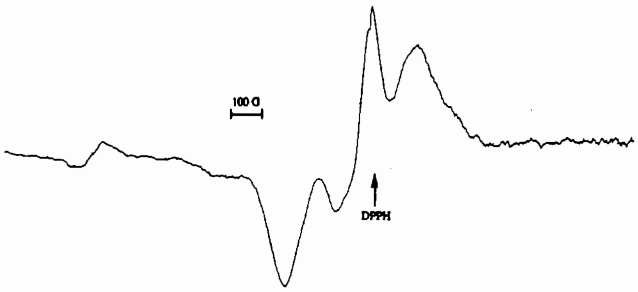

Figure 3. EPR spectrum of $[Cu_2(CH_3PY2)_2(OH)_2](PF_6)_2$·0.25$(CH_3)_2CO$ [**5a**$(PF_6)_2$] in CH_2Cl_2 at 77 K. A distinct half-field line at $g \sim 4$ is observed.

retained. For **4b**, the EPR spectrum (Figure 2) is typical[43] of those for coupled dinuclear Cu(II) complexes, including the presence of the weak signal in the $g = 4$ region (e.g. "half-field" $M_s = 2$ transition). For **4c**, sufficiently strong coupling is apparent, since the complex is EPR silent in this solvent. Complex **4a** breaks down in dichloromethane, but the dinuclear structure is retained in DMF/$CHCl_3$ (1:1) as indicated by its EPR silence (Table V). All complexes are 2:1 electrolytes in DMF, and the magnetic moments are close to the spin-only values, indicating that what magnetic coupling exists is weak at best. The solvent dependence of the EPR spectra is consistent with the notion that subtle ligand-dependent variations in structure exist for these oxo dinuclear Cu(II) complexes. The variations in Cu(II) environment are also suggested by the small but significant variation in position of the d–d bands for **4a–c**, i.e. ranging from 708 to 630 nm (Table V).

Dihydroxo-Bridged Complexes. As previously described,[17] if the oxygenation of $[Cu(PhCH_2PY2)]^+$ (**3b**) is carried out in a wet solvent, or if water is deliberately added to the green species $[Cu_2(PhCH_2PY2)_2(O)](PF_6)_2$ [**4b**$(PF_6)_2$], the blue dihydroxo-bridged dicopper(II) complex $[Cu_2(PhCH_2PY2)_2(OH)_2](PF_6)_2$ [**5b**$(PF_6)_2$] is obtained. We also found similar reactions occur with **4a** and **4c**; all dihydroxo dicopper(II) complexes show a single infrared absorption in the range 3400–3640 cm^- (Experimental Section), and the d–d band is red-shifted relative to those for their oxo–Cu(II) precursors. For **4a** and **4b**, the addition of water is reversible, and heating solid samples of **5a,b** under vacuum causes regeneration of **4a,b**, as followed by IR and UV–vis spectroscopy.

$$\underset{\textbf{4a,b}}{[Cu_2(RPY2)_2(O)]^{2+}} + H_2O \rightleftarrows \underset{\textbf{5a,b}}{[Cu_2(RPY2)_2(OH)_2]^{2+}}$$

The structure of **5b** was also previously reported,[17] and that for **5a** has also been determined and described elsewhere.[44] These consist of centrosymmetric parallel–planar dimer units (Scheme I), a structural type that is not uncommon for $Cu(II)–(X)_2–Cu(II)$ (X = halide, OR^-).[17,45,46] Each Cu(II) ion possesses a planar array of ligands consisting of the PY2 tridentate group and a hydroxide ligand (Cu–O ~ 1.93 Å). In addition, another OH^- ligand is axially coordinated (Cu–O ~ 2.25–2.30 Å). Both hydroxide ligands also bridge to the second Cu(II) ion, the equitorial OH^- ligand is axial with respect to the other Cu(II) ion, and vice versa. Cu···Cu = 3.183 (4) Å for $[Cu_2(CH_3PY2)_2(OH)_2]^{2+}$ (**5a**) and 3.271 (4) Å for $[Cu_2(PhCH_2PY2)_2(OH)_2]^{2+}$ (**5b**). This structure may be induced or stabilized by two sets of pyridine–pyridine stacking interactions clearly occurring across the halves of the dimer molecule.[17,44] This same interaction was seen a very related structure, $[\{Cu(TMPA)(F)\}_2]^{2+}$ (TMPA = tris(pyridylmethyl)amine).[47]

The axial–equitorial dibridging connectivity in these parallel–planar Cu(II) dimer structures is expected to give rise to only weak magnetic coupling, because of the $d_{x^2-y^2}$ ground state for the essentially planar coordinated Cu(II) ion. Temperature dependent magnetic measurements have not been carried out, and so attempted correlations of $Cu–O_{bridge}–Cu$ angles or other structural parameters with magnetic properties have not been attempted.[46,48,49] Never-the-less, room-temperature moments are μ_{eff}/Cu = 1.6–1.9 μ_B, consistent with weak coupling.[50]

EPR measurements are also in accord with the dimer structures. That for $[Cu_2(CH_3PY2)_2(OH)_2]^{2+}$ (**5a**) is shown in Figure 3; in frozen CH_2Cl_2, a typical dimer spectrum with half-field line is observed, and this behavior has been seen in a bis(μ-phenoxide)-bridged dicopper(II) complex with a parallel planer structure.[45b] In the more strongly coordinating solvent, methanol, the bridged structure breaks and a typical tetragonal EPR is observed (Table V). The other complexes exhibit a similar behavior, except that $[Cu_2(PhPY2)_2(OH)_2]^{2+}$ (**5c**) is EPR silent in CH_2Cl_2.

Low-Temperature Oxygenation of Cu(I) Complexes: Generation of Dioxygen–Copper Adducts. Exposing a yellow dichloromethane solution of $[Cu(RPY2)](PF_6)$ (**3a–c**) to dry O_2 at temperatures ≤–80 °C causes a relatively rapid color change to dark brown. The stoichiometry of O_2 consumed by **3a** and **3b** was determined by manometry to be Cu/O_2 = 2:1; at the concentrations and quantities required for manometry, **3c** gave inconsistent results due to its decomposition. These product solutions are EPR silent at 77 K. Thus, the course of reaction with O_2 at –80 °C is very different from that occurring at ≥0 °C, and the product of reaction at reduced temperatures is the dioxygen adduct (peroxo–dicopper(II) species, vide infra) $[Cu_2(RPY2)_2(O_2)]^{2+}$ (**6a–c**). As indicated in Table VI and Figure 4a, copper(I) complexes **3b** and **3c** exhibit a single absorption band in UV–vis region, whereas the spectrum of **3a** shows a rising absorption towards UV region with no peak maxima at >315 nm. After exposure to O_2, intense and multiple absorptions in the 315–600-nm region develop. The strongest band occurs at 355 nm (ϵ 14 700 M^{-1} cm^{-1}), 362 nm (ϵ 11 400 M^{-1} cm^{-1}) and 350 nm (ϵ 5500 M^{-1} cm^{-1}) for **6a** (Figure 4), **6b**, and **6c**, respectively. Other distinct shoulders and peaks occur in the 400–500-nm region and the 500–600-nm region. In addition, another weak absorption is present at still lower energy (600–700 nm), assigned as a d–d transition. This signifies that copper ion occurs in the Cu(II)

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(43) (a) Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: New York, 1987, Vol. 5, Chapter 53, pp 533–774. (b) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1974**, *13*, 173–278.

(44) Cohen, B. I. Ph.D. Dissertation, State University of New York (SUNY) at Albany, 1987.

(45) (a) Rojo, T.; Arriortua, M. I.; Ruiz, J.; Darriet, J.; Villeneuve, G.; Beltran-Porter, D. *J. Chem. Soc., Dalton Trans.* **1987**, 285–291 and references cited therein. (b) Calderazzo, F.; Marchetti, F.; Dell'Amico, G.; Pelizzi, G.; Colligiani, A. *J. Chem. Soc., Dalton Trans.* **1980**, 1419–1424.

(46) Hatfield, W. E. *Comments Inorg. Chem.* **1981**, *1*, 105.

(47) Jacobson, R. R.; Tyeklár, Z.; Karlin, K. D.; Zubieta, J. *Inorg. Chem.* **1991**, *30*, 2035–2040.

(48) Hatfield, W. E. In *Magneto Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; NATO ASI Series; D. Reidel: Dordrecht, The Netherlands, 1985; pp 555–602.

(49) Melnik, M. *Coord. Chem. Rev.* **1982**, *42*, 259–293.

(50) Thompson, L. K.; Ramaswamy, B. S. *Inorg. Chem.* **1986**, *25*, 2664–2665.

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

compound	copper(I) complex	dioxygen–dicopper complex			
$[Cu(CH_3PY2)](PF_6)\cdot 0.5CH_2Cl_2$ [**3a**(PF_6)]	c	355 (14 700)	405 sh (2500)	530 (400)	645 (315)
$[Cu(PhCH_2PY2)](PF_6)$ [**3b**(PF_6)]	342 (1700)	362 (11 400)	415 sh (2600)	533 (650)	625 sh (480)
$[Cu(PhPY2)](PF_6)$ [**3c**(PF_6)]	340 (1500)	350 (5500)	485 sh (310)		680 (70)
$[Cu_2(N4)](PF_6)_2$[d] [**2**$(PF_6)_2$]	350 (3500)	360 (14 000)	458 (4500)	550 sh (1200)	
$[Cu_2(N5)](PF_6)_2$[d]	347 (3600)	360 (21 400)	423 sh (3600)	520 (1200)	
apohemocyanin[e]		345 (20 000)	485 (CD)	570 (1000)	700 (200)

[a] Absorption maxima (λ_{max}) are given in nanometers. Extinction coefficients are based on the dioxygen species $[Cu_2(RPY2)_2(O_2)]^{2+}$ and are given in parentheses ($M^{-1}\ cm^{-1}$) and are calculated directly from absorbances observed. [b] Solutions were oxygenated at −80 °C, and the final spectrum was recorded until absorbances stopped increasing. See text for additional information. [c] Rising absorption toward the UV region with no maxima >315 nm. [d] Reference 9. [e] Reference 13.

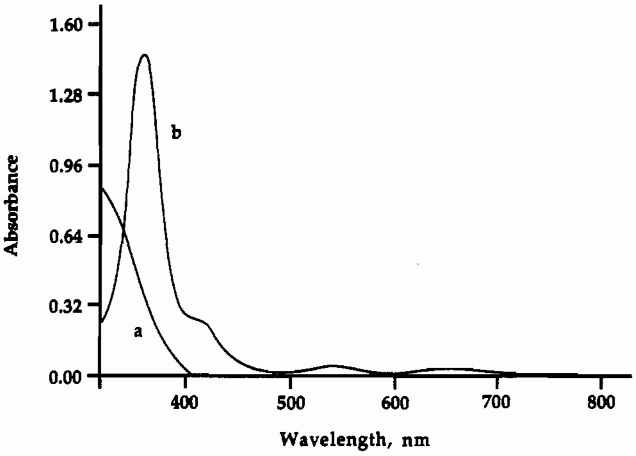
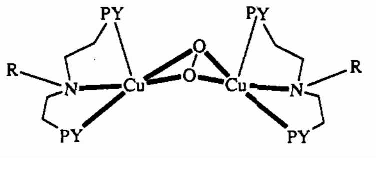


Figure 4. UV–vis spectra of the copper(I) complex $[Cu(CH_3PY2)]^+$ (**3a**) (spectrum a) and its dioxygen adduct $[Cu_2(CH_3PY2)_2(O_2)]^{2+}$ (**6a**) (spectrum b) at −80 °C in CH_2Cl_2.

oxidation state in these dioxygen complexes (**6**), thus the description as peroxo–dicopper(II) species.

The pattern and intensity of the absorption bands seen in complexes $[Cu_2(RPY2)_2(O_2)]^{2+}$ (**6a–c**) are analogous to those of the previously reported complexes $[Cu_2(Nn)(O_2)]^{2+}$ (**2**) (vide supra),[9c] with a dinucleating ligand containing two PY2 tridentate moieties. For example, $[Cu_2(N4)(O_2)]^{2+}$ (**2**) shows absorption bands at 360 nm (ϵ 14 000 $M^{-1}\ cm^{-1}$), 458 nm (ϵ 4500 $M^{-1}\ cm^{-1}$), and 550 nm (ϵ 1200 $M^{-1}\ cm^{-1}$) (Table VI). While the band position and relative intensities of $[Cu_2(RPY2)_2(O_2)]^{2+}$ (**6a–c**) are similar to **2**, the absolute intensity, particularly of the 350–360-nm absorption, is lower in **6a–c**, especially **6c**. We speculate that this could occur for two reasons: (i) subtle, as yet poorly understood structural differences cause these variations among the complexes. A large range of ϵ values are seen even among the dinuclear complexes, depending on *n* (linker in Nn dinucleating ligand), anion, and presence or absence of large R groups on the linker.[9] (ii) Although Cu/O_2 = 2:1 by manometry, it may be that the O_2 complexes of RPY2 (**6a–c**) may not be fully formed at −80 °C (i.e. lower equilibrium constant of formation), contributing to smaller apparent ϵ values. Equilibrium binding studies to determine $K_{formation}$ are planned for the future.

Complexes $[Cu_2(RPY2)_2(O_2)]^{2+}$ (**6a–c**) are proposed to have the same structure as $[Cu_2(N4)(O_2)]^{2+}$ (**2**), which from extensive spectroscopic investigations were suggested to have two Cu(II) ions bridged by a peroxo ligand in a μ-η^2-η^2 side-on fashion. As discussed for $[Cu_2(Nn)(O_2)]^{2+}$ (**2**), the strong and multiple absorptions, particularly the intense band near 350 nm bears a similarity to that observed for the O_2-carrier protein hemocyanin.



As observed by UV–vis spectroscopy at −80 °C, the oxygenation of copper(I) mononuclear complexes $[Cu(RPY2)](PF_6)$ [**3a–c**(PF_6)] to yield $[Cu_2(RPY2)_2(O_2)]^{2+}$ (**6a–c**) occurs qualitatively slower than that for reaction of $[Cu_2(Nn)]^{2+}$ (**1**) with dioxygen to give $[Cu_2(Nn)(O_2)]^{2+}$ (**2**); this latter process appears to be instantaneous. After a ~10^{-4} M solution of $[Cu(CH_3PY2)]^+$ (**3a**) was saturated with O_2 by direct bubbling for 10 min, it requires ~45 minutes for the 355 nm absorption to fully develop to its maximum intensity. For **3b** (R = $PhCH_2$) and **3c** (R = Ph), the time observed is ~65 and ~90 min, respectively. The very rapid formation of the dioxygen complexes **2** can be attributed to the forced proximity of the two copper ions when using a dinucleating ligand Nn. The reaction of two mononuclear Cu(I) complexes with O_2 is slower, as expected. It is interesting to note that the qualitatively observed reaction times for oxygenation of $[Cu(RPY2)](PF_6)$ [**3a–c**(PF_6)] roughly correlate with the observed $E_{1/2}$ value of **3a–c**. Complex **3c**, which is the most difficult to oxidize, is also the slowest to react with dioxygen. Detailed kinetic studies are needed.

On the basis of UV–vis monitoring, dioxygen complexes $[Cu_2(RPY2)_2(O_2)]^{2+}$ (**6a–c**) are stable at low temperature (≤−75 °C) with minimal decomposition observed over time (~2-4% per hour). However, upon warming, **6a–c** decompose to give absorption spectra identical to those for the oxo-bridged complexes $[Cu_2(RPY2)_2(O)]^{2+}$ (**4a,b**). In fact, we found that cycling between O_2 adducts **6** and precursors **3**, which occurred with relative facility for **1** and **2**,[9] was not possible here, presumably because of the rapid conversion to oxo complexes upon warming. Thus, the observed 2:1 $Cu:O_2$ chemistry occurring at reduced temperatures is linked to the higher temperature chemistry as discussed above and summarized in Scheme I. Dioxygen–copper (peroxo–dicopper(II)) complexes can be stabilized at low temperature. At higher temperatures, O–O bond cleavage occurs. In the case of these RPY2 copper complexes, this decomposition is clean (i.e. solvent or ligand attack is not observed), and pure oxo–Cu(II) species are formed.

With evidence for the pervasive nature of imidazole (from histidine) coordination to copper ion in hemocyanin and copper monooxygenases,[1-3,11,51] there is considerable current interest in developing ligands that possess imidazole donors. Until recently, little success has been observed in using such ligands in generating copper–dioxygen adducts. We recently observed that by employing low-temperature experimental approaches, simple unidentate imidazole ligands could be useful in generating a Cu_2O_2 adduct.[11] Sorrell and co-workers have also been developing useful synthetic approaches for making chelating ligands with one or more imidazole donor. In fact, they recently reported imidazolyl and benzimidazolyl analogues to RPY2 as well as a mixed ligand with one pyridyl and one imidazolyl donor.[52] In fact, several of the imidazolyl tridentate ligands form copper(I) mononuclear complexes which appear to bind O_2 at −80 °C. Sorrell reports that these give spectral intermediates similar to that of

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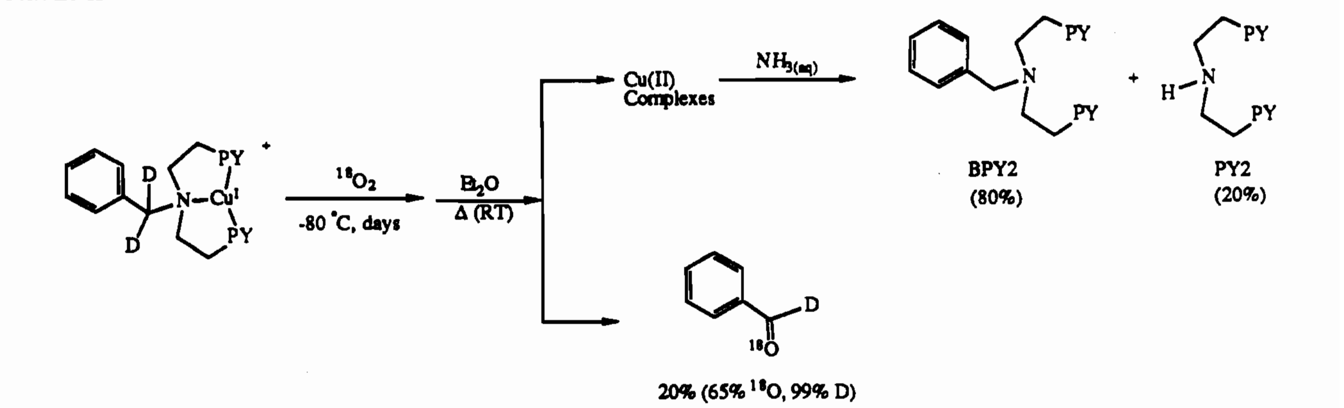
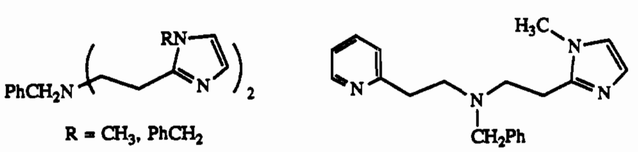
(51) Adman, E. T. *Adv. Protein Chem.* **1991**, *42*, 145–197.

(52) Sorrell, T. N.; Garrity, M. L. *Inorg. Chem.* **1991**, *30*, 210–215.

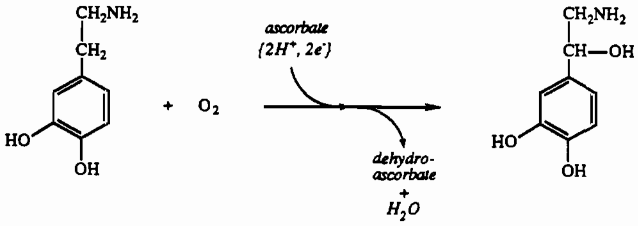
Scheme II



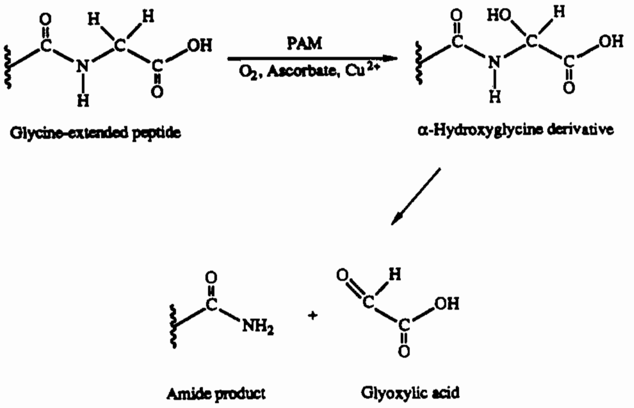
$[Cu_2(Nn)(O_2)]^{2+}$ (**2**), and thus appear likely to be analogous to $[Cu_2(RPY2)_2(O_2)]^{2+}$ (**6a–c**), reported here. These authors also report that they synthesized $PhCH_2PY2$ and give a spectrum of $[Cu_2(PhCH_2PY2)_2(O_2)]^{2+}$ (**6b**), agreeing with that described here. However, they do not mention any follow-up reactivity observed for **6b**, which we have detected (vide infra).



Reactivity of $[Cu_2(PhCH_2PY2)_2(O_2)]^{2+}$: Formation of Benzaldehyde. When a CH_2Cl_2 solution of $[Cu(PhCH_2PY2)](PF_6)$ (**3b**) is exposed to dry O_2 at -80 °C and is left stirring at low temperature under a positive dioxygen pressure for ~4 days, a ligand N-dealkylation reaction occurs; a greenish blue copper(II) complex precipitates, and benzaldehyde is produced (Scheme II). This reaction appears to come about as a result of an oxygenation process, i.e., following the reaction of O_2 with **3b** to form $[Cu_2(PhCH_2PY2)_2(O_2)]^{2+}$ (**6b**). Support for this conclusion comes from several lines of evidence: (a) Benzaldehyde was identified qualitatively by gas chromatography. Its yield (~20%) was determined by derivatization using 2,4-dinitrophenylhydrazine (see Experimental Section). (b) GC/MS is used to detect the formation of deuteriobenzaldehyde when the oxygenation reaction (-80 °C) was carried out using $[Cu(PhCH_2PY2\text{-}D_2)](PF_6)$, in which the benzylic position of the ligand is deuterated. (c) In addition, it is found that the oxygen atom in the deuteriobenzaldehyde product is derived from molecular oxygen. This was shown by running a similar reaction using $^{18}O_2$. Mass spectroscopic measurements demonstrated a >65% incorporation of ^{18}O atom, where the deuterium atom incorporation was determined to be greater than 95%. (d) With the sluggish nature of the reaction and the yield of N-dealkylated product benzaldehyde observed to be <50%, it was presumed the copper-bound dioxygen ligand (e.g. peroxide) attacks the benzylic position of $PhCH_2PY2$, and that probably only one of the two ligands in $[Cu_2(PhCH_2PY2)_2(O_2)]^{2+}$ (**6b**) is attacked. In other words, one dioxygen–copper complex may be capable of only one oxygenation/hydroxylation, as in a biological monooxygenase. Thus, a mixture of $PhCH_2PY2$ (estimated yield ~80%) and PY2 (estimated yield ~20%, based on the observed 20% yield of benzaldehyde) is expected in the Cu(II) product which precipitated. Indeed, this was the case. The ligands isolated by treatment of the copper(II) complex with aqueous NH_3 and extraction into dichloromethane revealed two distinct spots on TLC (thin-layer chromatography), corresponding to $PhCH_2PY2$ (R_f = 0.80) and PY2 (R_f = 0.40). Integration of appropriate signals in an ^1H NMR spectrum of the ligand mixture showed that 80 mol % of the material was $PhCH_2PY2$, the rest being the dealkylated secondary amine PY2.



The hydroxylation reaction at the benzylic position of the ligand $PhCH_2PY2$ in the presence of copper and dioxygen is reminiscent of the action of the copper monooxygenases such as dopamine β-hydroxylase (DβH)[53] and peptidylglycine α-amidating monooxygenase (PAM).[54] The enzyme DβH catalyzes the benzylic hydroxylation of dopamine to form norepinephrine, while PAM effects an oxidative N-dealkylation reaction, thought to proceed by an initial hydroxylation.



Oxygenation of $[Cu(CH_3PY2)](PF_6)$ [**3a**(PF_6)] and $[Cu(PhPY2)](PF_6)$ [**3c**(PF_6)] under similar reaction conditions does not result in the oxygenation of R group in the RPY2 ligand. This result seems to indicate that the $PhCH_2PY2$ system is more reactive than the other two, perhaps for electronic reasons (i.e., $PhCH_2PY2$ has benzylic C–H bonds) or possibly due to a more favorable orientation of the molecule for attack by the dioxygen complex. In possibly sheding more light on PAM mechanistic chemistry, it would be of interest to develop newer systems which are more efficient at N-dealkylation chemistry than is seen for the reaction of O_2 with $[Cu(PhCH_2PY2)](PF_6)$ [**3b**(PF_6)].

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(53) (a) Brenner, M. C.; Klinman, J. P. *Biochemistry* **1989**, *28*, 4664–4670. (b) Stewart, L. C.; Klinman, J. P. *Annu. Rev. Biochem.* **1988**, *57*, 551–592.

Sayre[54d] and Capdevielle and Maumy[55] have recently reported very interesting synthetic systems acting as models for PAM reactivity.

Summary

The results described here further demonstrate that mononuclear copper(I) complexes $[Cu(RPY2)]^+$ (**3a–c**) are perfectly capable and useful as compounds which can form dinuclear copper–dioxygen (e.g., Cu_2O_2) adducts; dinucleating ligands are not absolutely necessary. The first structurally characterized copper–dioxygen complex was derived from a mononuclear precursor $[(TMPA)Cu(RCN)]^+$ (TMPA = tris((2-pyridyl)methyl)amine), which reacts with O_2 forming a dinuclear complex $[\{(TMPA)Cu\}_2(O_2)]^{2+}$ with a μ-1,2-peroxo coordination.[10] Kinetic studies[27] reveal that a mononuclear $[(TMPA)Cu(O_2)]^+$ 1:1 adduct forms as an intermediate. As mentioned in the introduction, Kitajima's μ-η^2:η^2-peroxo complex $\{Cu[HB(3,5\text{-}i\text{-}Pr_2pz)_3]\}_2(O_2)$ was also derived from a mononuclear precursor.[3,13] Clearly, it will be of future interest to search for and characterize mononuclear 1:1 copper–dioxygen adducts involving **3a–c**. The chemistry of 1:1 Cu–O_2 species is of interest in (a) determining fundamentals of Cu(I)/O_2 interactions, e.g. kinetics, thermodynamics, structure and spectroscopy, and (b) reactivity studies, since a number of copper proteins involved in monooxygenation using O_2 or dioxygen reduction, involve single copper ion sites. Reactivity studies comparing $[Cu_2(RPY2)_2(O_2)]^{2+}$ (**6**) and dinuclear analogues $[Cu_2(Nn)(O_2)]^{2+}$ (**2**) are also worthy of future studies, since **6** are expected to possess a peroxo group more accessible to substrates.

The straightforward and high-yield decomposition of complexes $[Cu_2(RPY2)_2(O_2)]^{2+}$ (**6**) to give oxo species $[Cu_2(RPY2)_2(O)]^{2+}$ (**4**) is of interest in the elucidation of O–O cleavage mechanisms(s), of likely importance in O_2 activation. However, we observe that $[Cu_2(Nn)(O_2)]^{2+}$ (**2**) complexes do not cleanly transform to oxo–dicopper(II) species; uptake of dioxygen by the dicopper(I) complexes $[Cu_2(Nn)]^{2+}$ (**1**) at temperatures ≥ 0 °C in CH_2Cl_2 or MeOH shows that excess O_2 is absorbed,[9] probably indicating that solvent oxidation occurs. The difference in behavior of mono versus dinuclear copper(I) complexes **3** and **1** remains to be established. Oxo–Cu(II)$_n$ or oxo–Cu(III)$_n$ deserves further future investigation as possible active intermediates in systems effecting organic oxygenation reactions, either chemical or biological. Mononuclear terminal high-valent oxo–Cu species ("cupryl") are not expected to be stable,[57,58] but they have often been invoked[13a,40,59–61] as active intermediates, in large part because of the as yet *unproven* analogy to ferryl (e.g. high-valent iron–oxo) chemistry established for cytochrome P-450 and porphyrin metal complexes,[62] and even non-heme iron systems.[63]

Oxo complexes $[Cu_2(RPY2)_2(O)]^{2+}$ (**4**) undergo a facile reversible hydration to dihydroxo complexes $[Cu_2(RPY2)_2(OH)_2]^{2+}$ (**5**) possessing parallel-planar structures. Kitajima and co-workers have observed similar reaction chemistry involving $\{Cu[HB(3,5\text{-}Me_2pz)_3]\}_2(O)$ and $\{Cu[HB(3,5\text{-}Me_2pz)_3(OH)]\}_2$. These latter complexes have been useful as precursors to the peroxo complex $\{Cu[HB(3,5\text{-}Me_2pz)_3]\}_2(O_2)$, by reaction with hydrogen peroxide.[13] An acylperoxo species $Cu[HB(3,5\text{-}Me_2pz)_3](OOR)$ (R = m-$ClC_6H_4C(O)$) was also synthesized by reaction of $\{Cu[HB(3,5\text{-}Me_2pz)_3(OH)]\}_2$ with *m*-chloroperoxybenzoic acid.[56]

Finally, one main point of this paper is the observed temperature-dependent oxygenation chemistry, attesting to the thermodynamic, but not kinetic, stability of Cu_2O_2 adducts derived from dioxygen reaction with Cu(I) complexes. Recent investigations confirm the Cu_2O_2 adducts such as $[Cu_2(Nn)(O_2)]^{2+}$ (**2**) and $[\{(TMPA)Cu\}_2(O_2)]^{2+}$ are characterized by large negative enthalpies of formation, but that the unfavorable entropy precludes room-temperature stability.[1,27] As described in this report and elsewhere,[1–3,8–11] low-temperature techniques have now allowed considerable recent progress in copper–dioxygen chemistry.

Acknowledgment. We are grateful to the National Institutes of Health (GM 28962, K.D.K.) for their support of this research.

Supplementary Material Available: Tables VII–X, listing details of the structure determination, bond lengths, bond angles, and H atom coordinates and isotropic displacement parameters (4 pages). Ordering information is given on any current masthead page.

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(54) (a) Zabriskie, T. M.; Cheng, H.; Vederas, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 2270–2272. (b) Ping, D.; Katopodis, A. G.; May, S. W. *J. Am. Chem. Soc.* **1992**, *114*, 3998–4000. (c) Merkler, D. J.; Kulathila, R.; Consalvo, A. P.; Young, S. D.; Ash, D. E. *Biochemistry* **1992**, *31*, 7282–7288. (d) Reddy, K. V.; Jin, S.-J.; Arora, P. K.; Sfeir, D. S.; Feke Maloney, S. C.; Urbach, F. L.; Sayre, L. M. *J. Am. Chem. Soc.* **1990**, *112*, 2332–2340.

(55) Capdevielle, P.; Maumy, M. *Tet. Lett.* **1991**, *31*, 3831–3834.

(56) Kitajima, N.; Fujisawa, K.; Moro-oka, Y. *Inorg. Chem.* **1990**, *29*, 357–358.

(57) Bäckvall, J.-E.; Bökman, F.; Blomberg, M. R. A. *J. Am. Chem. Soc.* **1992**, *114*, 534–538.

(58) (a) Mayer, J. M. *Comments Inorg. Chem.* **1988**, *8*, 125–135. (b) Nugent, W. A.; Mayer, J. A. *Metal-Ligand Multiple Bonds* Wiley-Interscience: New York, 1988.

(59) Réglier, M.; Amadeï, E.; Tadayoni, R.; Waegell, B. *J. Chem. Soc., Chem. Commun.* **1989**, 447–450.

(60) (a) Capdevielle, P.; Sparfel, D.; Baranne-Lafont, J.; Cuong, N. M.; Maumy, M. *J. Chem. Soc., Chem. Commun.* **1990**, 565–566. (b) Reinaud, O.; Capdevielle, P.; Maumy, M. *J. Chem. Soc., Chem. Commun.* **1990**, 566–568. (c) Capdevielle, P.; Baranne-Lafont, J.; Sparfel, D.; Cuong, N. K.; Maumy, M. *J. Mol. Catal.* **1988**, *47*, 59–66.

(61) Villafranca, J. J. In *Copper Proteins: Metal Ions in Biology*; Spiro, T. G., Ed.; Wiley-Interscience, New York, 1981; Vol. 3, pp 263–290.

(62) (a) Dawson, J. H. *Science* **1988**, *240*, 433–439 and references cited therein. (b) *Cytochrome P-450*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986.

(63) (a) Que, L., Jr.; True, A. E. *Prog. Inorg. Chem.* **1991**, *38*, 97–200. (b) Leising, R. A.; Brennan, B. A.; Que, L., Jr.; Fox, B. G.; Münck, E. *J. Am. Chem. Soc.* **1991**, *113*, 3988–3990.