Polynuclear Complexes of Copper(I) and the 2-(3(5)-Pyrazolyl)-6-methylpyridine Ligand: Structures and Reactivity toward Small Molecules

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Received June 27, 1997

The reactivity of trinuclear copper(I) centers vis-à-vis diagnostic diatomic and other small molecules, including carbon monoxide and dioxygen, is examined as part of an effort to unravel the pattern of dioxygen activation at multicopper sites of potential biological significance. The reaction of $[Cu(CH_3CN)_4](PF_6)$ with deprotonated 2-(3(5)-pyrazolyl),6-methylpyridine (2-(3(5)-pzH),6-Mepy, **1**) affords the trinuclear copper(I) compound $[Cu_3(py)(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_3]\cdot 0.5py$ (**2**) from pyridine solutions. Species **2** rearranges in toluene to yield a tetrameric unit that precipitates as the molecular pair $[Cu_4(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_4]_2\cdot 3tol$ (**3**). The two units are symmetry-related by virtue of a C_2 axis and are coupled via a unique Cu(I)···Cu(I) contact at 3.0045(13) Å. Compound **2** or **3** reacts with carbon monoxide to generate reversibly the trinuclear species $[Cu(CO)(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)]_3$ (**4**), featuring coordination of one CO molecule per copper ion on the same face of a nine-membered Cu_3N_6 ring framework. Compound **2** reacts with dioxygen in tetrahydrofuran to yield the dinuclear species $[Cu_2(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_4]\cdot thf$ (**5**) and an as yet uncharacterized green-brown crystalline material. In the presence of the hexafluorophosphate anion (PF_6^-) in CH_3CN, the reaction with dioxygen affords the tetranuclear compound $[Cu_4(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_6(CH_3CN)_2](PF_6)_2\cdot CH_3CN$ (**6**). An analogous dinuclear species, $[Cu_2(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_2(MeOH)_4](CF_3SO_3)_2$ (**7**), is formed in wet methanol from $Cu(CF_3SO_3)_2$ and the deprotonated ligand **1**. The nuclearity of the resulting species upon dioxygen activation and the fact that no compounds are observed containing the $Cu^{II}_3(\mu_3\text{-}O(H))$ unit are discussed.

Introduction

A remarkable series of multicopper-containing oxygenases and oxidases have been intensively studied in recent years to reveal synergism between two or more copper sites in the activation of dioxygen.[1] An important subset of this category is composed of copper enzymes that have a minimun requirement of one trinuclear copper cluster participating in their dioxygen activating apparatus. Well-characterized members of this group are the oxidases laccase,[2] ceruloplasmin,[3] and ascorbate oxidase,[4] all of which couple the four-electron reduction of dioxygen to the one-electron-at-a-time oxidation of 4 equiv of substrate. The electron-transfer cycle is conveniently mediated by four copper sites which apparently store oxidizing power upon complete reduction of dioxygen to water prior to delivering oxidizing equivalents to substrate in a sequential manner. As indicated by the crystallographic determination of ascorbate oxidase,[4] three of these copper ions are intimately engaged in a cluster arrangement considered to be the site of dioxygen reduction. The fourth copper ion is a distinct type-1 (or "blue") copper center that most likely contributes to the overall stoichiometry by long-range (~12.5 Å in ascorbate oxidase)[4] electron transfer to the trinuclear cluster. Interestingly, human ceruloplasmin, which has been recently characterized crystallographically at a 3.1-Å resolution,[3] features two additional type-1 copper sites. Typically, the trinuclear cluster of these oxidases includes a "normal", type-2 copper site in close proximity (~3.7 Å in oxidized ascorbate oxidase)[4] to an antiferromagnetically coupled, type-3 binuclear copper center.

Trinuclear copper clusters functioning in the oxygenase mode have not been unambiguously characterized, but a prominent example, which is a source of inspiration for the present work, is the putative tricopper center of particulate methane monooxygenase (pMMO).[5] By virtue of quantitative EPR and magnetic data, a ferromagnetically coupled ($S = ^3/_2$) trinuclear copper cluster has been proposed to exist in "as isolated" and ferricyanide-oxidized preparations of pMMO. Interestingly, an unusually high copper content (~70%) remains at the Cu(I) level in "as isolated" pMMO or even after extensive dioxygen treatment of dithionite-reduced preparations of pMMO (40−

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S0020-1669(97)00807-0 CCC: $15.00

50%). This finding calls into question the stoichiometry of the $Cu{:}O_2$ interaction, but without a clear knowledge of the number of copper sites that act as electron-transfer rather than catalytic centers, the issue cannot be easily resolved. If the trinuclear copper hypothesis holds (especially with respect to an alternative dinuclear copper−iron model proposed[6] and to recent reexamination[7] of the type of copper involved by low-frequency EPR), then the electronic and potentially geometric features of this cluster would be intrinsically different from those attributed to the coupled type-2/type-3 tricopper cluster found in the oxidases. In passing, we note that copper-containing ammonia monooxygenase,[8] which shows extensive sequence homology[9] with pMMO and similar chemical behavior vis-à-vis substrates[10] and inhibitors,[11] may be another good candidate for possessing an analogous copper cluster.

To systematically investigate the reactivity of reduced Cu^{I}_3 cores with respect to dioxygen and other small, diagnostic molecules, we have initiated a study to explore pathways of generating trinuclear copper sites by employing a class of ligands derived from the parent 2-(3(5)-pyrazolyl)pyridine (2-(3(5)-pzH)py)[12] structure. Reported in the present work is exploitation of one member of this group, namely, the pyridine-substituted 2-(3(5)-pzH),6-Mepy ligand. These nitrogen-rich ligands are attractive both by virtue of their pyrazolyl moiety, which has been known to stabilize multinuclear $Cu^{I}_n(pz)_n$ ($n = 3$, 4) clusters,[13] and by their ability to impose planar copper coordination that may facilitate generation of the $Cu^{II}_3(\mu_3\text{-O(H)})$ core structures upon oxidation. The latter unit has been observed in a number of complexes[14] and reported to display primarily antiferromagnetic coupling, although in rare cases population of the $S = {}^3/_2$ level has been noted.[15]

Experimental Section

General Considerations. All operations were performed under a pure dinitrogen or argon atmosphere using Schlenk techniques on an inert gas/vacuum manifold or in a drybox (O_2, H_2O < 1 ppm). Hexane, petroleum ether, and toluene were distilled over Na; THF and diethyl ether were distilled over Na/Ph_2CO. Acetonitrile and methylene chloride were distilled over CaH_2. Ethanol and methanol were distilled over the corresponding magnesium alkoxide. All solvents, besides methanol, were degassed by three freeze−pump−thaw cycles. ^{1}H and ^{13}C NMR spectra were recorded on Varian XL-400 and JEOL GSX-270 NMR spectrometers. Peaks were assigned on the basis of chemical shift, integration, and coupling patterns in 2D NMR (^{1}H observed/^{13}C (de)-coupled) and APT spectra. IR spectra were recorded on a Perkin-Elmer 1800 FT-IR instrument. UV−vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Electrospray mass spectra were recorded using a Platform II MS (Micromass Instruments, Danvers, MA). Samples were introduced from the corresponding solutions at a flow rate of 5 μL/min from a syringe pump (Harvard Apparatus). The electrospray probe capillary was maintained at a potential of 3.0 kV, and the orifice to skimmer potential ("cone voltage") was varied from 15 to 30 V. Spectra were collected in the multichannel acquisition mode. EI and CI mass spectra were obtained on a Finnigan MAT-90 mass spectrometer. Microanalyses were done by H. Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

Preparation of 2-(3(5)-Pyrazolyl)-6-methylpyridine (1). Synthesis of the ligand involved five steps, starting from commercially available 2,6-dimethyl pyridine (2,6-lutidine). 2,6-Lutidine was first oxidized to 6-methyl-2-picolinic acid (49%) by the method of Black et al.[16] The acid thus obtained was converted to ethyl 6-methyl-2-picolinate (37%) and subsequently to 2-acetyl-6-methylpyridine (69%) by a standard procedure.[17] 2-Acetyl-6-methylpyridine was then treated with *N*,*N*-dimethylformamide diethyl acetal in a ratio of 1:1.3, and the mixture was refluxed for 12 h to yield 3-(dimethylamino)-1-(6-methylpyridyl)-2-propen-1-one (80%) after solvent removal and recrystallization from ethanol. This product was then treated with hydrazine monohydrate (ratio 1:1.3) in methanol, and the mixtue was refluxed for 1 h. The solvent was removed under reduced pressure and the residue sublimed at 80−90 °C (0.001 Torr) to afford ligand **1** (95%). Mp: 118 °C. ^{1}H NMR (270 MHz, $CDCl_3$): δ 2.56 (s, 3H, CH_3), 6.74 (d, $^3J_{HH} = 2.0$ Hz, 1H, 4-*H*(pz)), 7.06 (d, $^3J_{HH} = 7.3$ Hz, 1H, 5-*H*(py)), 7.48 (d, $^3J_{HH} = 7.8$ Hz, 1H, 3-*H*(py)), 7.60 (t, $^3J_{HH} = 7.3$ Hz, 1H, 4-*H*(py)), 7.63 (d, $^3J_{HH} = 2.0$ Hz, 1H, 5-*H*(pz)), 10.5 (br, 1H, 1-*H*(pz)). ^{13}C NMR (70 MHz, $CDCl_3$): δ 24.4 (q, $^1J_{CH} = 127.4$ Hz, CH_3), 103.4 (d, $^1J_{CH} = 176.1$ Hz, 4-*C*(pz)), 117.4 (d, $^1J_{CH} = 164.1$ Hz, 3-*C*(py)), 122.4 (d, $^1J_{CH} = 162.4$ Hz, 5-*C*(py)), 136.4 (d, $^1J_{CH} = 184.6$ Hz, 5-*C*(pz)), 137.1 (d, $^1J_{CH} = 162.4$ Hz, 4-*C*(py)), 146.5 (s, 3-*C*(pz)), 149.3 (s, 2-*C*(py)), 158.3 (s, 6-*C*(py)). CI−HRMS $M-H^+$ (calcd for $C_9H_8N_3$): 158.1823. Found: 158.0723.

[Cu_3(py)(2-(3(5)-pyrazolyl)-6-methylpyridine)$_3$]·0.5py (2). Sodium ethoxide (43 mg, 0.63 mmol) dissolved in methanol (10 mL) was slowly added to a stirred solution of **1** (100 mg, 0.63 mmol) in methanol (20 mL). Stirring was continued for 10 min, followed by addition of the methanolic solution to a solution of $[Cu(CH_3CN)_4][PF_6]$ (230 mg, 0.62 mmol) in acetonitrile (20 mL). The mixture was allowed to stir for 1 h, followed by collection of the yellow-orange precipitate by filtration. The compound was crystallized as yellow rods (88 mg, 54%) from a solution of **2** in pyridine at 10 °C. Mp: 177 °C (dec). ^{1}H NMR (270 MHz, C_5D_5N): δ 2.53 (br, 3H, CH_3), 6.95 (m, 1H, 5-*H*(py)), 6.99 (d, $^3J_{HH} = 1.90$ Hz, 1H, 4-*H*(pz)), 7.53−7.61 (m, 2H, 3-*H*(py), 4-*H*(py)), 7.91 (br, 1H, 5-*H*(pz). ^{1}H NMR (270 MHz, CD_2Cl_2): δ 2.30 (br, 3H, CH_3), 6.70 (br, 1H, 4-*H*(pz)), 6.96 (d, $^3J_{HH} = 7.32$ Hz, 1H, 5-*H*(py)), 7.37 (d, $^3J_{HH} = 7.80$ Hz, 1H, 3-*H*(py)), 7.63 (t, $^3J_{HH} = 8.80$ Hz, 1H, 4-*H*(py)), 7.69 (br, 1H, 5-*H*(pz)). ^{13}C NMR (70 MHz, C_5D_5N): δ 25.2 (q, $^1J_{CH} = 127.4$ Hz, CH_3), 102.2 (d, $^1J_{CH} = 171.8$ Hz, 4-*C*(pz)), 117.4 (d, $^1J_{CH} = 163.2$ Hz, 3-*C*(py)), 122.1 (d, $^1J_{CH} = 168.4$ Hz, 5-*C*(py)), 137.9 (d, $^1J_{CH} = 161.5$ Hz, 4-*C*(py)), 141.5 (d, $^1J_{CH} = 177.8$ Hz, 5-*C*(pz)), 152.0 (s, 3-*C*(pz)), 152.6 (s, 2-*C*(py)), 157.8 (s, 6-*C*(py)). UV−vis (C_5H_5N): $\lambda_{max} = 326$ ($\epsilon_M = 21382$) nm. ES-MS (C_5H_5N): 665 ($[Cu_3L_3]^+$), 823 ($[Cu_3L_4]^+$ or $[Cu_3L_3(py)_2]^+$). Anal. Calcd for $C_{34.5}H_{31.5}N_{10.5}Cu_3$: C, 52.86; H, 4.05; N, 18.76. Found: C, 52.90; H, 4.11; N, 18.86.

[Cu_4(2-(3(5)-pyrazolyl)-6-methylpyridine)$_4$]$_2$·3tol (3). Yellow crystals of **3** were obtained by recrystallization of **2** from toluene upon cooling at 10 °C overnight. Mp: 210 °C (dec). ^{1}H NMR (270 MHz, 27 °C, CD_2Cl_2): δ 1.81 (br, 3H, CH_3), 2.65 (br, 3H, CH_3), 6.69 (br, 1H, 4-*H*(pz)), 6.75 (br, 1H, 4-*H*(pz)), 6.89 (d, $^3J_{HH} = 7.32$ Hz, 1H, 5-*H*(py)), 7.10 (d, $^3J_{HH} = 6.84$ Hz, 1H, 5-*H*(py)), 7.36 (d, $^3J_{HH} = 7.32$ Hz, 1H, 3-*H*(py)), 7.46 (d, $^3J_{HH} = 7.35$ Hz, 1H, 3-*H*(py)), 7.54−7.68 (m, 2H, 4-*H*(py)), 7.66 (br, 1H, 5-*H*(pz)), 7.84 (br, 1H, 5-*H*(pz)). ^{13}C-

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Table 1. Crystallographic Data[a] for $[Cu_3(py)(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_3]\cdot 0.5Py$ (**2**), $[Cu_4(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_4]_2\cdot 3Tol$ (**3**), $[Cu(CO)(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)]_3$ (**4**), $[Cu_2(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_4]\cdot thf$ (**5**), $[Cu_4(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_6(CH_3CN)_2](PF_6)_2\cdot CH_3CN$ (**6**), and $[Cu_2(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_2(MeOH)_4](CF_3SO_3)_2$ (**7**)

	2	**3**	**4**	**5**	**6**	**7**
formula	$C_{34.5}H_{31.5}Cu_3N_{10.5}$	$C_{93}H_{88}Cu_8N_{24}$	$C_{30}H_{24}Cu_3N_9O_3$	$C_{40}H_{40}Cu_2N_{12}O$	$C_{60}H_{48}Cu_4F_{12}N_{21}P_2$	$C_{24}H_{32}Cu_2F_6N_6O_{10}S_2$
formula wt	783.84	2050.19	749.20	831.92	1607.29	869.76
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$C2/c$	$C2/c$	$P2_{1/c}$	$P2/n$	$P\bar{1}$	$P\bar{1}$
Z	8	4	4	2	2	1
a, Å	42.49(3)	26.9910(2)	12.238(4)	12.4079(4)	12.4437(4)	8.238(3)
b, Å	8.877(7)	17.9254(1)	12.236(3)	8.4902(3)	12.6820(4)	9.073(2)
c, Å	10.07(2)	19.5747(2)	21.778(6)	17.6487(6)	23.2492(7)	12.025(3)
α, deg					81.433(1)	100.42(2)
β, deg	114.95(2)	108.732(1)	95.31(2)	99.725(2)	82.711(1)	96.49(2)
γ, deg					66.632(1)	95.96(2)
V, Å^3	6865(9)	8969.1(1)	3247(2)	1832.5(1)	3321.2(2)	871.2(4)
T, K	295	163	213	166	134	295
color	yellow	yellow	colorless	green	green	green
d_{calc}, g/cm^3	1.515	1.518	1.533	1.508	1.607	1.65
μ, mm^{-1}	1.883	1.919	1.992	1.213	1.402	1.43
R^b ($wR_2{}^c$), %	6.16 (14.35)	4.98 (9.86)	6.13 (8.58)	7.04 (15.15)	7.29 (16.31)	4.65 (13.25)

[a] Obtained with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2/\{\sum[w(F_o{}^2)^2]\}^{1/2}$.

{^{1}H} NMR (70 MHz, CD_2Cl_2): δ 24.7 (br, CH_3), 102.0 (4-C(pz)), 117.2 (3-C(py)), 122.3 (5-C(py)), 137.7 (4-C(py)), 142.1 (br, 5-C(pz)), 150.9 (br, 3-C(pz)), 151.6 (2-C(py)), 157.6 (6-C(py)). ES-MS (toluene): 886 ($[Cu_4L_4]^+$), 1267 ($[Cu_5L_6]^+$), 1488 ($[Cu_6L_7]^+$). Anal. Calcd for $C_{93}H_{88}N_{24}Cu_8$: C, 54.48; H, 4.33; N, 16.40. Found: C, 54.29; H, 4.32; N, 16.28.

[Cu(CO)(2-(3(5)-pyrazolyl)-6-methylpyridine)]$_3$ (4). Carbon monoxide was passed for 5 min through a yellow-orange solution of **2** (100 mg, 0.13 mmol) in toluene (20 mL) to generate a light yellow solution. Cooling the CO-saturated solution to 10 °C afforded colorless crystals of **4**. Application of reduced pressure to **4** either in the solid state or in solution should be avoided due to loss of coordinated carbon monoxide. ^{1}H NMR (270 MHz, CD_2Cl_2): δ 2.85 (s, 3H, CH_3), 6.47 (d, $^3J_{HH} = 1.95$ Hz, 1H, 4-H(pz)), 6.81 (d, $^3J_{HH} = 1.95$ Hz, 1H, 5-H(pz)), 7.21 (d, $^3J_{HH} = 8.35$ Hz, 1H, 5-H(py)), 7.42 (d, $^3J_{HH} = 7.81$ Hz, 1H, 3-H(py)), 7.72 (t, $^3J_{HH} = 7.52$ Hz, 1H, 4-H(py)). ^{13}C-{^{1}H} NMR (70 MHz, C_6D_6): δ 25.8 (CH_3), 101.8 (4-C(pz)), 116.9 (3-C(py)), 121.3 (5-C(py)), 138.2 (4-C(py)), 140.4 (5-C(pz)), 149.7 (3-C(pz)), 153.3 (2-C(py)), 157.6 (6-C(py)). IR (KBr): $\nu_{CO} = 2063$ cm^{-1}. Anal. Calcd for $C_{30}H_{24}N_9Cu_3O_3$: C, 48.09; H, 3.23; N, 16.83. Found: C, 46.75; H, 3.69; N, 16.24.

[Cu$_2$(2-(3(5)-pyrazolyl-6-methylpyridine)$_4$]·thf (5). Dioxygen was passed for 10 min through a yellow-orange solution of **2** (100 mg, 0.13 mmol) in tetrahydrofuran (10 mL) to afford a dark brown solution. The solution was filtered and the filtrate was cooled (−30 °C) to yield dark green crystals of **5** (24 mg, 15%) within a day. Dichroic green-brown crystals of unknown composition were deposited from the same solution upon prolonged cooling. Anal. Calcd for $C_{40}H_{40}N_{12}Cu_2O_1$: C, 57.75; H, 4.85; N, 20.20. Found: C, 57.81; H, 4.86; N, 20.76.

[Cu$_4$(2-(3(5)-pyrazolyl-6-methylpyridine)$_6$(CH$_3$CN)$_2$](PF$_6$)$_2$·CH$_3$CN (6). A solution of sodium ethoxide (43 mg, 0.63 mmol) in methanol (10 mL) was slowly added upon stirring to a solution of **1** (100 mg, 0.63 mmol) in methanol (20 mL). The resulting solution was added to a solution of $[Cu(CH_3CN)_4](PF_6)$ (230 mg, 0.62 mmol) in acetonitrile (20 mL). The mixture was allowed to stir for 5 min prior to dioxygen being passed through the solution. The green filtrate afforded crystals of **6** (75 mg, 44%) upon cooling at −30 °C overnight. Anal. Calcd for $C_{60}H_{57}N_{21}Cu_4F_{12}P_2$: C, 44.62; H, 3.56; N, 18.21; F, 14.12. Found: C, 44.62; H, 3.61; N, 18.11; F, 14.09.

[Cu$_2$(2-(3(5)-pyrazolyl)-6-methylpyridine)$_2$(MeOH)$_4$](CF$_3$SO$_3$)$_2$ (7). A solution of sodium ethoxide (43 mg, 0.63 mmol) in methanol (10 mL) was slowly added to a stirred solution of **1** (100 mg, 0.63 mmol) in methanol (20 mL). Stirring was continued for 10 min, followed by addition of the methanolic solution to a solution of $Cu(CF_3SO_3)_2$ (230 mg, 0.64 mmol) in methanol (20 mL). After being stirred for 1 h, the green solution was evaporated to dryness under reduced pressure, and the residue was extracted with methylene chloride. Slow diffusion of petroleum ether into the methylene chloride filtrate afforded green blocks of **7** (165 mg, 60%) at 10 °C. Mp: 225 °C (dec). UV−vis (C_5H_5N): $\lambda_{max} = 252$ (12074), 310 ($\epsilon_M = 13071$) nm. Anal. Calcd for $C_{24}H_{32}N_6Cu_2F_6N_6O_{10}S_2$: C, 33.14; H, 3.70; N, 9.66; F, 13.10; S, 7.37. Found: C, 33.08; H, 3.41; N, 9.69; F, 13.15; S, 7.28.

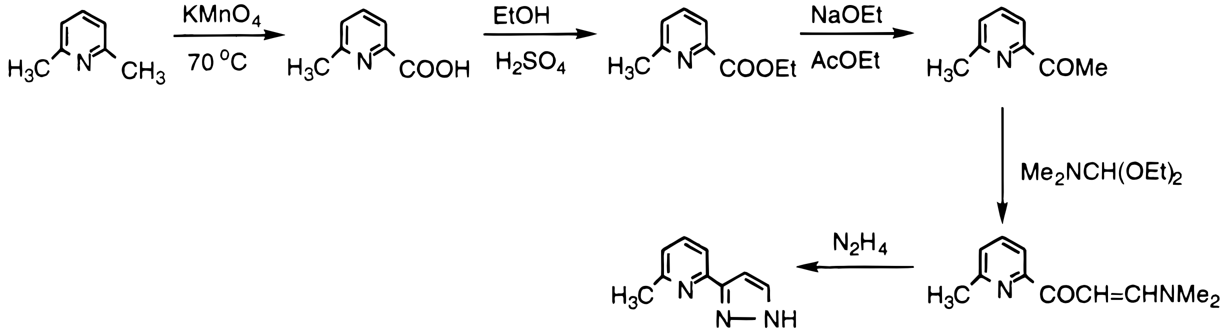
X-ray Structure Determinations. Structures were determined for the compounds listed in Table 1. Single crystals of **3**, **4**, **5**, and **6** were coated with Paratone N oil, attached to glass fibers, and transferred to a Siemens SMART diffractometer where they were cooled under a dinitrogen stream. Single crystals of **2** and **7** were mounted in sealed capillary tubes on a Nicolet P3 diffractometer. Lattice parameters were obtained from a least-squares analysis of more than 30 centered reflections. None of the crystals showed significant decay during data collection. The raw intensity data were converted (including corrections for scan speed, background, and Lorentz and polarization effects) to structure factor amplitudes and their esd's. An absorption correction based on the intensities of symmetry equivalent reflections was applied to the data sets for the crystals of **3**, **4**, **5**, and **6**.

Space group assignments were based on systematic absences, E statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and refined against all data using the SHELXTL 5.0 software package. Thermal parameters for all non-hydrogen atoms were refined anisotropically, except for those of the pyridine solvate molecule in the structure of **2**. The nitrogen atom could not be distinguished from the carbon atoms in this pyridine molecule, and each site was refined as 83% carbon and 17% nitrogen. Similarly, the oxygen atom and carbon atoms of the THF solvate molecule in the structure of **5** could not be distinguished, and each site was refined as 80% carbon and 20% oxygen. In the structure of **3**, one of the toluene solvate molecules is severely disordered within a plane bisected by a 2-fold rotational axis. The triflate anion in the structure of **7** is disordered over two sites occupied in an approximate 4:1 ratio. Hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens). Hydrogen atoms were not included for disordered solvate molecules, or for the methyl groups of the acetonitrile molecules in the structure of **6**. Further details of the structure determinations are deposited as Supporting Information.

Results and Discussion

Synthesis of the Ligand. The ligand 2-(3(5)-pzH),6-Mepy (**1**) is obtained in a five-step synthetic process (Scheme 1) starting from 2,6-dimethylpyridine. The conversion of this starting material to the intermediate 2-acetyl,6-Mepy is accomplished by following published literature procedures.[16,17] The

Scheme 1



subsequent two steps, leading to ligand **1**, are executed according to methodology implemented in the synthesis[12] of the parent compound 2-(3(5)-pzH)py from 2-acetylpyridine. The ligand can be purified by sublimation or by recrystallization from hexanes. The solubility of the ligand and its copper complexes in common organic solvents is superior to that observed for the unsubstituted 2-(3(5)-pzH)py and corresponding complexes.

Synthesis and Characterization of Complexes from Cu(I) Precursor Species. Reaction of $[Cu(CH_3CN)_4][PF_6]$ with 1 equiv of deprotonated **1** in $MeOH/CH_3CN$ leads to the formation of a yellow-orange powder, which upon recrystallization from pyridine affords yellow-orange crystals of $[Cu_3(py)(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_3]\cdot 0.5py$ (**2**). The compound is exceedingly air-sensitive, especially in solution (vide infra).

Room-temperature ^1H and ^{13}C NMR spectra of concentrated solutions of **2** in C_5D_5N or CD_2Cl_2 exhibit one set of ligand resonances, although the methyl resonance in the ^1H NMR spectrum ($\delta = 2.53$ (C_5D_5N), 2.30 (CD_2Cl_2)) is particularly broad. Under these conditions, the pyridine solvent appears to be free (noncoordinating) in solution. Variable-temperature ^1H NMR data reveal a more complex pattern at lower temperatures. Upon cooling (196−296 K) in CD_2Cl_2, gradual resolution of three methyl resonances ($\delta = 2.71$, 2.32, 1.75 (256 K)) is observed, originating from three independent species. The relative amounts of these components vary substantially with temperature, the low-field methyl resonance ($\delta = 2.65$ (s) at 196 K) dominating at low temperatures. Importantly, the 2.32- and 1.75-ppm resonances split at temperatures below 236 K into patterns composed of three ($\delta = 2.30$, 2.25, 2.22 at 216 K; relative ratio 3:1:2) and two ($\delta = 1.71$, 1.69 at 216 K; relative ratio 1:2) bands, respectively. Moreover, resonances assigned to free pyridine at room temperature lose their fine structure upon cooling, indicating coordination of pyridine to copper sites. Tentatively, we assign the aforementioned three features, from low to high field, to Cu_3L_3, Cu_6L_6, and $Cu_3L_3(py)_n$ ($n = 1$ or 2) clusters. Electrospray MS data obtained from dilute solutions of **2** in CH_2Cl_2 (dilution has an effect similar to cooling according to ^1H NMR) indicate the presence of, among others, $[Cu_3L_3]^+$ (665), $[Cu_3L_4]^+$ or $[Cu_3L_3(py)_2]^+$ (823), and $[Cu_5L_6]^+$ or $[Cu_5L_5(py)_2]^+$ (1267) fragments exhibiting appropriate isotopic patterns. The variable-temperature (240−295 K) ^1H NMR spectrum of **2** in C_5D_5N indicates that a new methyl resonance ($\delta = 1.84$ at 265 K) progressively evolves below 275 K, accompanied by a half-intensity band ($\delta = 2.79$ at 245 K) that resolves upon further cooling (<260 K). Peaks assigned to pyridine (solvent) are also broadened at lower temperatures. These features are consistent with resolution of the three- and four-coordinate copper environments in emerging **2**, although further analysis is precluded by the limits of the available temperature range. However, the single broad methyl resonance observed at room temperature remains the dominant feature in this region of the ^1H NMR spectrum, sharpening upon cooling in accord with the presence of equivalent copper sites assigned tentatively to Cu_3L_3. Electrospray MS data obtained from solutions of **2** in pyridine demonstrate the existence of $[Cu_3L_3]^+$ (665) and $[Cu_3L_4]^+$ or $[Cu_3L_3(py)_2]^+$ (823) fragments, although higher nuclearity clusters are not observed.

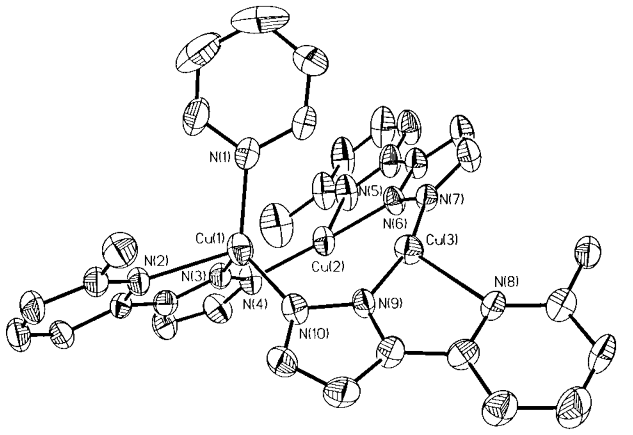


Figure 1. Structure of $[Cu_3(py)(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_3]\cdot 0.5py$ (**2**), showing 30% probability ellipsoids and the atom-labeling scheme. Selected interatomic distances (Å) and angles (deg): Cu(1)−N(10) 1.974(7), Cu(1)−N(3) 1.995(7), Cu(1)−N(1) 2.038(8), Cu(1)−N(2) 2.232(6), Cu(2)−N(4) 1.894(7), Cu(2)−N(6) 1.921(6), Cu(2)−N(5) 2.370(7), Cu(3)−N(7) 1.860(6), Cu(3)−N(9) 1.870(6), Cu(3)−N(8) 2.430(6), N(10)−Cu(1)−N(3) 116.7(3), N(10)−Cu(1)−N(1) 119.5(3), N(3)−Cu(1)−N(1) 116.3(3), N(10)−Cu(1)−N(2) 106.4(2), N(3)−Cu(1)−N(2) 78.6(2), N(1)−Cu(1)−N(2) 110.6(3), N(4)−Cu(2)−N(6) 160.3(3), N(4)−Cu(2)−N(5) 121.4(3), N(6)−Cu(2)−N(5) 76.5(3), N(7)−Cu(3)−N(9) 161.9(3), N(7)−Cu(3)−N(8) 122.6(2), N(9)−Cu(3)−N(8) 75.1(2).

Single-crystal X-ray analysis of **2** reveals a structure (Figure 1) that features an asymmetric trinuclear copper cluster composed of two three-coordinate sites and one unique four-coordinate copper site. The pyrazolyl-bridged copper ions are incorporated in a nine-member Cu_3N_6 ring that substantially deviates from planarity, especially by comparison to the framework observed in the parent $[Cu_3(2\text{-}(3(5)\text{-}pz)py)_3]$ unit.[18] This deviation is most likely due to the bulk of the methyl substituent that forces the three ligands to assume a propeller-type arrangement. The ensuing twist favors a tetrahedral rather than a T-shaped coordination of the Cu(I) sites, the latter being observed for all copper ions in the planar $[Cu_3(2\text{-}(3(5)\text{-}pz)py)_3]$ unit.[18] However, only one copper atom in **2** is tetrahedrally coordinated, presumably due to the bulk of the associated pyridine (vide infra for a carbonyl adduct). Metrical parameters for the other two three-coordinate copper sites are consistent

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[18] Singh, K.; Long, J. R.; Stavropoulos, P. *J. Am. Chem. Soc.* **1997**, *119*, 2942.

with an in-plane distortion from a T-shaped geometry, as evidenced by the deviation of the N(pz)-Cu−N(pz) angles (average 161.1(8)°) from linearity. For these copper sites the average Cu−N(pz) distance (1.89(4) Å) is shorter than the one observed for the four-coordinate site (1.985(11) Å), reflecting the difference in the coordination number, although, due to the T-shaped geometry, the Cu−N(py) distance (average 2.400(30) Å) is longer by comparison to the corresponding Cu(1)−N(2) distance (2.232(6) Å) of the tetrahedral copper atom.

Recrystallization of **2** from toluene affords yellow plates of $[Cu_4(2\text{-}(3(5)\text{-pz},6\text{-Mepy})_4]_2\cdot 3\text{tol}$ (**3**). Rearrangement has also been suggested by virtue of ^1H NMR spectra of **2** in d_8-toluene or CD_2Cl_2 (27 °C) demonstrating broad bands associated with ligand-based protons, the most discernible feature being two equally populated resonances (δ = 2.65, 1.81) assigned to the methyl substituent. Close inspection of the 6.5−8-ppm region reveals that bands assigned to pyridyl/pyrazolyl moieties are also split in appropriate patterns of equal intensity. Variable-temperature ^1H NMR data in CD_2Cl_2 suggest that both methyl resonances partly resolve in two closely spaced components. Evidence that pyridyl/pyrazolyl-centered protons also give rise to four-band resonance patterns at low temperatures is furnished by the easily detected 4-pyrazolyl hydrogen. These observations are consistent with the structural features (vide infra) of the asymmetric tetranuclear unit in **3**. However, it was not possible to determine whether the coupling of two tetranuclear units, as observed in the solid state, persists in solution, but the presence of high nuclearity fragments ($[Cu_5L_6]^+$, $[Cu_6L_7]^+$) in addition to $[Cu_4L_4]^+$ ions in the electrospray MS spectra of **3** in toluene does not exclude such pairing.

The structure of **3** (Figure 2) reveals an unusual molecular pair composed of two tetranuclear copper units coupled via a unique Cu−Cu interaction (Cu(1)−Cu(1′) = 3.0045(13) Å). The two units are symmetry-related by virtue of a crystallographically imposed C_2 axis. The tetranuclear $Cu_4(pz)_4$ core structure is composed of a 12-membered atom ring (Cu_4N_8) which folds into a trapezoidal or saddle-type conformation. The mean deviation from a least-squares plane defined by the tetrametallic core is 0.119 Å, although the square is somewhat puckered, such that Cu(1) and Cu(3) are 0.12 Å above the plane, while Cu(2) and Cu(4) are 0.12 Å below the plane. The average intermetallic Cu···Cu distance is 3.58(12) Å, a value that precludes any Cu−Cu interactions. A somewhat similar arrangement is found in the tetrameric $[Cu(3,5\text{-}Ph_2pz)]_4$ compound[13b] that features a strictly planar tetracopper core structure. In this compound, the exclusively two-coordinate copper sites are most likely further stabilized by Cu−Cu interactions (average distance 3.12 Å). In contrast, the coordination sphere of the copper ions in **3** is highly variable, with two copper atoms being three-coordinate and the other two being four- and two-coordinate. As in the case of **2**, the three-coordinate copper sites in **3** show an in-plane distorted T-shaped coordination geometry (N(4)−Cu(3)-N(8) = 167.4(2)°, N(7)−Cu(4)−N(11) = 164.2(2)°). The two coordination planes are oriented in a mutually orthogonal fashion. The four-coordinate copper center displays a distorted C_{2v}-type geometry involving a $CuN(pz)_2N(py)_2$ local environment. This unusual "seesaw" configuration accommodates two planar T-shaped coordination geometries which are orthogonal with respect to each other but are otherwise similarly distorted (N(5)−Cu(2)−N(6) = 76.8(2)°, N(2)−Cu(2)−N(3) = 78.3(2)°). The preference for the N(3) atom of the pyridyl moiety to associate with Cu(2) rather than Cu(1), thus interrupting a potentially symmetric coordination, may be partially assigned to stabilization achieved due to the Cu(1)−Cu(1′) contact. The latter interaction is solely responsible for the pairing of the two tetrameric units, since neither is ligand−ligand π-stacking overlap observed viewing down the Cu(1)−Cu(1′) vector nor are long-range Cu···N contacts anticipated (Cu(1)···N(1′) = 3.625 Å, Cu(1)···N(10′) = 3.599 Å). As such, the presently documented Cu···Cu interaction adds to the rare class of ligand-unsupported $d^{10}-d^{10}$ contacts realized for copper(I) coordination compounds.[18] This is also the first example in which the resulting molecular pair within this family of compounds resides on a C_2 rotational axis rather than on an inversion center.

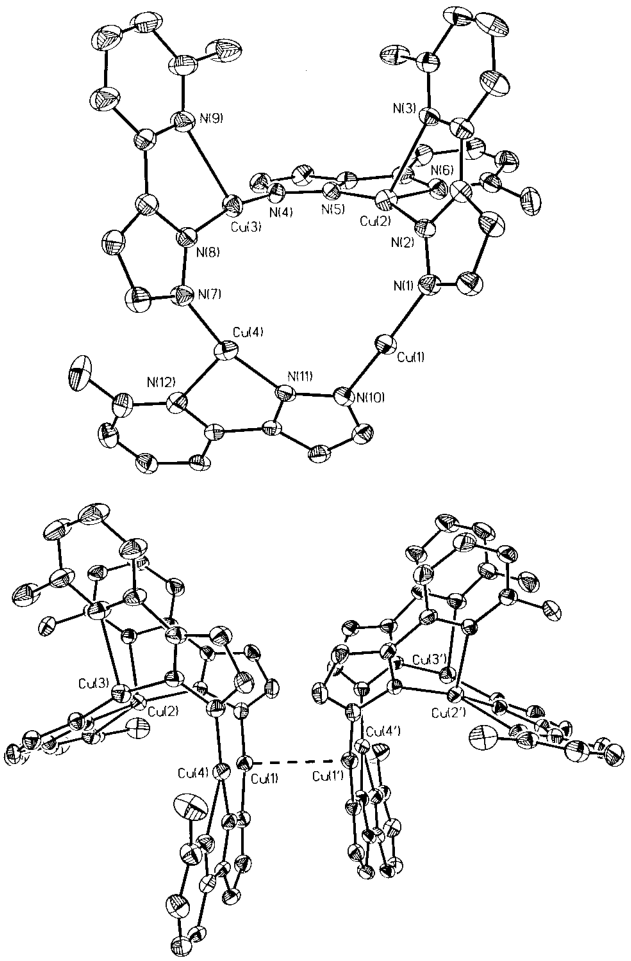

Figure 2. Structure of the tetranuclear $[Cu_4(2\text{-}(3(5)\text{-pz},6\text{-Mepy})_4]$ unit (top) and the molecular pair $[Cu_4(2\text{-}(3(5)\text{-pz},6\text{-Mepy})_4]_2\cdot 3\text{tol}$ (bottom) in **3**, showing 30% probability ellipsoids and the atom-labeling scheme. Selected interatomic distances (Å) and angles (deg): Cu(1)−N(1) 1.857(4), Cu(1)−N(10) 1.859(4), Cu(2)−N(5) 1.904(4), Cu(2)−N(2) 1.913(4), Cu(2)−N(3) 2.307(4), Cu(2)−N(6) 2.366(4), Cu(3)−N(4) 1.878(4), Cu(3)−N(8) 1.886(4), Cu(3)−N(9) 2.416(5), Cu(4)−N(7) 1.880(4), Cu(4)−N(11) 1.899(4), Cu(4)−N(12) 2.297(5), N(1)−Cu(1)−N(10) 174.1(2), N(1)−Cu(1)−Cu(1′) 93.43(13), N(10)−Cu(1)−Cu(1′) 92.41(13), N(5)−Cu(2)−N(2) 160.4(2), N(5)−Cu(2)−N(3) 116.6(2), N(2)−Cu(2)−N(3) 78.3(2), N(5)−Cu(2)−N(6) 76.8(2), N(2)−Cu(2)−N(6) 118.3(2), N(3)−Cu(2)−N(6) 87.4(2), N(4)−Cu(3)−N(8) 167.4(2), N(4)−Cu(3)−N(9) 115.9(2), N(8)−Cu(3)−N(9) 76.3(2), N(7)−Cu(4)−N(11) 164.2(2), N(7)−Cu(4)−N(12) 117.2(2), N(11)−Cu(4)−N(12) 78.5(2).

Interaction of Cu(I) Compounds with Diatomic and Other Small Molecules. The reactivity of compounds **2** and **3** has been tested with a variety of small molecules. The side-on approaching dihydrogen, ethylene, and 2-butyne have shown no signs of reactivity vis-à-vis these complexes. In contrast, the potentially end-on oriented carbon monoxide and dioxygen react readily with the Cu(I) compounds, even at low temperatures. These reactions are described in the present section.

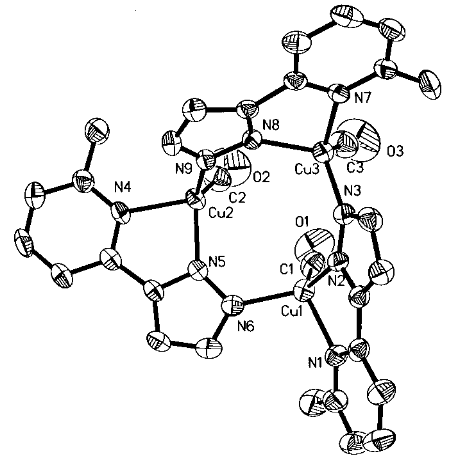

Figure 3. Structure of [Cu(CO)(2-(3(5)-pz,6-Mepy)]$_3$ (**4**), showing 50% probability ellipsoids and the atom-labeling scheme. Selected interatomic distances (Å) and angles (deg): Cu(1)−C(1) 1.779(5), Cu(1)−N(2) 2.019(3), Cu(1)−N(6) 2.014(3), Cu(1)−N(1) 2.100(3), C(1)−O(1) 1.128(5), Cu(2)−C(2) 1.778(4), Cu(2)−N(5) 2.007(3), Cu(2)−N(9) 2.003(3), Cu(2)−N(4) 2.104(3), C(2)−O(2) 1.117(5), Cu(3)−C(3) 1.778(5), Cu(3)−N(3) 1.994(3), Cu(3)−N(8) 2.005(3), Cu(3)−N(7) 2.130(3), C(3)−O(3) 1.128(5), C(1)−Cu(1)−N(6) 111.9(2), C(1)−Cu(1)−N(2) 121.2(2), C(1)−Cu(1)−N(1) 128.3(2), O(1)−C(1)−Cu(1) 172.8(4), C(2)−Cu(2)−N(5) 120.7(2), C(2)−Cu(2)−N(9) 121.4(2), C(2)−Cu(2)−N(4) 119.4(2), O(2)−C(2)−Cu(2) 177.6(5), C(3)−Cu(3)−N(3) 120.2(2), C(3)−Cu(3)−N(8) 126.3(2), C(3)−Cu(3)−N(7) 120.2(2), O(3)−C(3)−Cu(3) 176.6(5).

(a) Carbon Monoxide. Bubbling CO through a yellow-orange solution of **2** in toluene under ambient conditions leads to a light yellow solution from which colorless crystals of the air-sensitive [Cu(CO)(2-(3(5)-pz,6-Mepy)]$_3$ (**4**) slowly precipitate. Applying reduced pressure to solutions of **4** or solid **4** results in immediate restoration of the original yellow-orange coloration, suggesting reversible CO binding. ^{1}H and ^{13}C NMR spectra in C_6D_6 or CD_2Cl_2 indicate only one set of ligand-assigned resonances. A single ν_{CO} band (2063 cm^{-1}) observed in IR spectra is further suggestive of a symmetric coordination environment.

The structure of **4** (Figure 3) reveals a trinuclear copper compound, featuring the pyrazolyl-bridging Cu$_3$(pz)$_3$ pattern as evidenced in compound **2**. However, each copper site in **4** is tetrahedrally coordinated by virtue of a single CO molecule that is linearly attached to each copper ion on the same face of the Cu_3N_6 ring. The Cu_3N_6 core structure assumes an elongated chair-type conformation. The metrical parameters associated with the distorted tetrahedral geometry around the copper ions are very similar but not identical for each copper center. The Cu−C (average 1.778(1) Å) and C−O (average 1.124(7) Å) bond distances are typical of copper carbonyl species in a N_3Cu−CO local environment.[19]

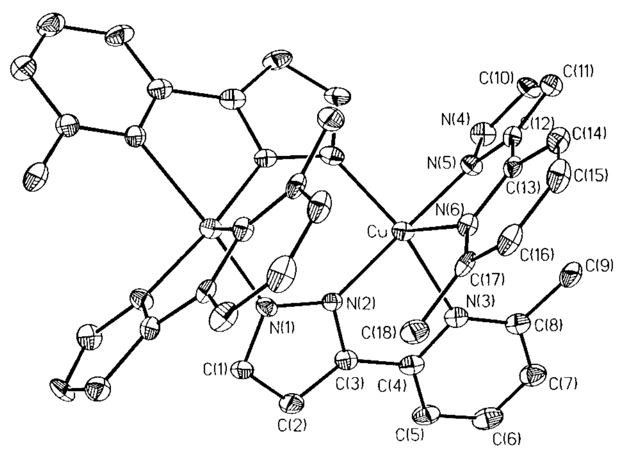

Figure 4. Structure of [Cu$_2$(2-(3(5)-pz,6-Mepy)$_4$]·thf (**5**), showing 30% probability ellipsoids and the atom-labeling scheme. Selected interatomic distances (Å) and angles (deg): Cu−N(5) 1.940(6), Cu−N(2) 1.951(6), Cu−N(1′) 2.033(6), Cu−N(3) 2.210(6), Cu−N(6) 2.287(6), N(5)−Cu−N(2) 170.5(2), N(5)−Cu−N(1′) 89.6(2), N(2)−Cu−N(1′) 92.0(2), N(5)−Cu−N(3) 95.6(2), N(2)−Cu−N(3) 79.3(2), N(1′)−Cu−N(3) 156.5(2), N(5)−Cu−N(6) 78.6(2), N(2)−Cu−N(6) 109.9(2), N(1′)−Cu−N(6) 106.2(2), N(3)−Cu−N(6) 97.3(2).

Compound **4** is also obtained from solutions of **3** in toluene upon admittance of CO. This result indicates that tetranuclear **3** rearranges in the presence of CO to afford a presumably more stable trimeric species. However, it is currently unclear whether **4** reacts directly with CO prior to rearrangement or whether it is in equilibrium with a trinuclear analogue that may have a higher affinity for CO binding. The same argument is also applicable to the reaction of **2** with CO in toluene, since this solution in the absence of CO yields compound **3** upon crystallization.

(b) Dioxygen. Bubbling dioxygen through solutions of **2** in tetrahydrofuran under ambient conditions results in an immediate change of the solution color from yellow-orange to brown-green. Crystallization affords green blocks of paramagnetic [Cu$_2$(2-(3(5)-pz,6-Mepy)$_4$]·thf (**5**) followed by deposition of dichroic green-brown crystals. The latter material cannot be easily separated from **5** by fractional crystallization, thus hampering efforts to characterize this compound. In addition, its crystals are unsuitable for X-ray analysis.

The structure of **5** (Figure 4) reveals a dinuclear copper species residing on a C_2 rotational axis. The two five-coordinate copper centers display a distorted square pyramidal geometry. They are bridged by two symmetry-related pyrazolyl moieties in the usual μ-1,2 coordination mode to generate a quasi-planar Cu_2L_2 arrangement, while each copper site is further chelated by a perpendicularly oriented ligand that surprisingly remains uncoordinated at the distal pyrazolyl nitrogen atom N(4). It is unlikely that this nitrogen is protonated, since that would reduce the formal oxidation state of the metal to Cu(I), an assignment which is not supported by the paramagnetism, color, coordination number, and Cu−N bond distances demonstrated by the present compound.

In the presence of hexafluorophosphate as a potential counteranion, solutions of [Cu(CH$_3$CN)$_4$][PF$_6$] and deprotonated ligand **1** in MeCN/MeOH which have been exposed to dioxygen afford green crystals of [Cu$_4$(2-(3(5)-pz,6-Mepy)$_6$(CH$_3$CN)$_2$](PF$_6$)$_2$·CH$_3$CN (**6**).

The structure of **6** (Figure 5) reveals that the tetranuclear compound, which is residing on an inversion center, is composed of two symmetry-related dinuclear copper units that are facially bound to each other via two pyrazolyl-derived bridges. Each dicopper unit features an asymmetric pair of five-coordinate copper ions. These copper sites are bridged in an almost planar fashion by two ligand-derived moieties arranged in a manner similar to that found in compound **5**. However, the coordination sphere of each copper site is now completed by a different set of contributing residues. In the case of Cu(1), chelation of a ligand bridging between the two dicopper units generates a distorted square pyramidal geometry with vector Cu(1)−N(6)

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(19) (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. (b) Kiani, S.; Long, J. R.; Stavropoulos, P. *Inorg. Chim. Acta* **1997**, *263*, 357.

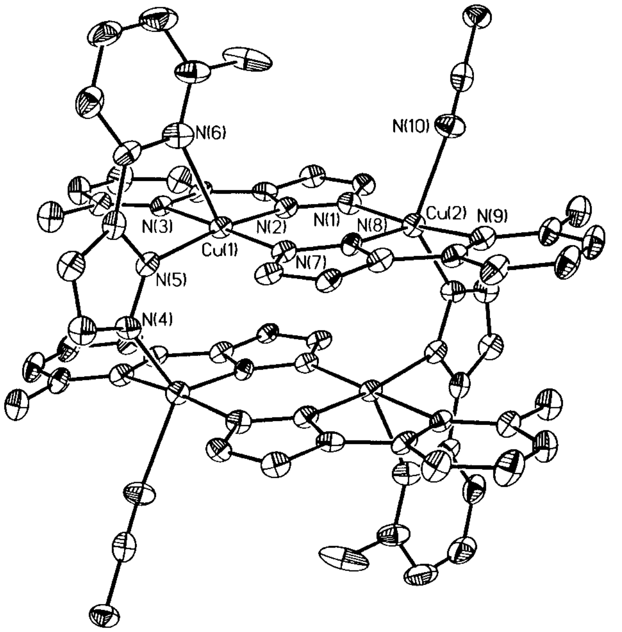

Figure 5. Structure of $[Cu_4(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_6(CH_3CN)_2](PF_6)_2 \cdot CH_3CN$ (**6**), showing 30% probability ellipsoids and the atom-labeling scheme. Selected interatomic distances (Å) and angles (deg): Cu(1)−N(5) 1.945(7), Cu(1)−N(2) 1.949(7), Cu(1)−N(7) 2.019(7), Cu(1)−N(3) 2.234(6), Cu(1)−N(6) 2.302(8), Cu(2)−N(1) 1.949(7), Cu(2)−N(8) 1.965(7), Cu(2)−N(9) 2.059(7), Cu(2)−N(4′) 2.063(7), Cu(2)−N(10) 2.222(8), N(5)−Cu(1)−N(2) 167.8(3), N(7)−Cu(1)−N(3) 175.0(3), N(5)−Cu(1)−N(7) 88.8(3), N(5)−Cu(1)−N(6) 77.4(3), N(3)−Cu(1)−N(6) 89.7(3), N(1)−Cu(2)−N(9) 172.3(3), N(1)−Cu(2)−N(10) 85.5(3), N(8)−Cu(2)−N(10) 120.0(3), N(4′)−Cu(2)−N(10) 114.6(3), N(8)−Cu(2)−N(4′) 125.1(3).

lying on the apex. On the other hand, Cu(2) is further coordinated by a single pyrazolyl nitrogen and a unique MeCN molecule to form the center of a trigonal bipyramidal geometry with vector N(1)−Cu(2)-N(9) residing on the axis.

The fact that these copper clusters did not show any tendency to trap oxo or hydroxo species upon dioxygen activation (to form, for instance, $[Cu_3O(H)]$ or $[Cu_4O]$ units) prompted us to examine the type of compounds generated upon coordination of the present ligand to Cu(II) precursor sites under wet conditions. In one attempt, the deprotonated ligand **1** reacted with $Cu(CF_3SO_3)_2$ in wet methanol to afford green blocks of $[Cu_2(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_2(MeOH)_4](CF_3SO_3)_2$ (**7**). X-ray analysis reveals a structure (Figure 6) that shows similar features to those observed in the structures of compounds **5** and **6**. The dinuclear copper core is bridged by two ligand-derived pyrazolyl residues which are symmetry-related by virtue of an inversion center. Two coordinated MeOH molecules further define a trigonal bipyramidal geometry around each copper site. That these are not methoxide ligands is suggested by the observed C−O−Cu angles which are close to 120°.

Finally, the reaction of yellow-orange **2** with NO in pyridine leads rapidly to precipitation of a green microcrystalline material. Unfortunately, all attempts to obtain crystals suitable for X-ray analysis have thus far failed.

Conclusions

Although the goal of retaining the trinuclear integrity of the copper species upon dioxygen activation has not been realized with the present ligand, some useful conclusions can be drawn from the reported results. First, the overwhelming tendency to form dinuclear or tetranuclear structures most likely arises from the requirement of four copper sites to deliver one electron per metal for the complete reduction of dioxygen to water. Further, the fact that a Cu_3O unit has not been observed in any of the present structures suggests that a strict requirement for fitting an sp^2-hybridized oxo group in the trinuclear copper cavity may be the planar arrangement of the molecular framework. This is clearly unattainable with the present methyl-substituted ligand but may be feasible with the parent nonsubstituted ligand or 4-R-pyridyl substituted derivatives thereof. The stability of the Cu_3O unit may be of importance, especially if switching from a 4:1 to a 6:1 $Cu{:}O_2$ interaction is desirable in order to activate dioxygen between two trinuclear copper clusters which retain their integrity. In addition, the 6:1 stoichiometry circumvents the need for generating a high-valent copper-oxo unit upon dioxygen cleavage, which otherwise will be required in a 3:1 stoichiometric ratio, as witnessed in a recently reported case.[20] Whether a copper(III)-oxo moiety[21] is needed for oxygenation purposes in a biological setting is a point of current debate.[22]

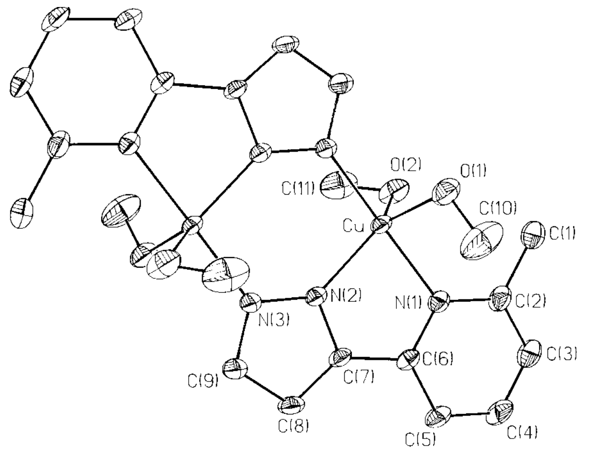

Figure 6. Structure of $[Cu_2(2\text{-}(3(5)\text{-}pz,6\text{-}Mepy)_2(MeOH)_4](CF_3SO_3)_2$ (**7**), showing 30% probability ellipsoids and the atom-labeling scheme. Selected interatomic distances (Å) and angles (deg): Cu−N(1) 2.018(3), Cu−N(2) 1.987(3), Cu−N(3′) 1.933(3), Cu−O(1) 2.166(2), Cu−O(2) 2.129(2), N(3′)−Cu−N(2) 99.32(10), N(3′)−Cu−N(1) 179.29(9), N(2)−Cu−N(1) 81.35(10), N(3′)−Cu−O(2) 89.48(11), N(2)−Cu−O(2) 121.36(11), N(1)−Cu−O(2) 89.98(10), N(3′)−Cu−O(1) 86.79(10), N(2)−Cu−O(1) 114.81(11), N(1)−Cu(1)−O(1) 93.13(10), O(2)−Cu−O(1) 123.55(11).

Acknowledgment. We thank Dr. R. J. Staples for experimental assistance and Prof. R. H. Holm for use of the X-ray diffractometer. The present work was generously supported by grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society (ACS-PRF-29383-G3), the U.S. Environmental Protection Agency (R823377-01-1) and by an Alzheimer's Association Investigator-Initiated grant (IIRG-95-087).

Supporting Information Available: Variable-temperature ^1H NMR spectra of **2** in C_5D_5N and CD_2Cl_2 and tables containing listings of crystal and data collection parameters, atomic coordinates and isotropic thermal parameters, interatomic distances, bond angles, and anisotropic displacement parameters for complexes **2** and **7** (26 pages). X-ray crystallographic files in CIF format for the structure determinations of complexes **3**, **4**, **5**, and **6** are available on the Internet only. Ordering and access information is given on any current masthead page.

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