Inorg. Chem. **1992**, *31*, 2255-2264 **2255**

Table IV. Crystallographic Data for $ClFe^{III}(OEPOAc)\cdot CH_2Cl_2$

$C_{39}H_{48}Cl_3FeN_4O_2$	fw = 767.0
$a = 10.238$ (2) Å	$P\bar{1}$, triclinic
$b = 13.301$ (2) Å	$T = 130$ K
$c = 15.088$ (3) Å	λ(Cu Kα) = 1.54178 Å
$\alpha = 77.610$ (2)°	μ(Cu Kα) = 5.574
$\beta = 71.820$ (2)°	d_{calcd}, Mg·m^{-3} = 1.360
$\gamma = 75.430$ (2)°	transm factors 0.63–0.87
$Z = 2$	$R^a = 0.051$
$V = 1868.5$ (6)	$R_w{}^a = 0.053$

$^a R = \sum||F_o| - |F_c||/|F_o|$ and $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o w^{1/2}|$.

purple, crystalline product obtained after recrystallization from chloroform–hexane. UV-vis (λ_{max}): 388, 506, 544, 642 nm.

X-ray Crystallographic Studies. A suitable crystal of $ClFe^{III}(OEPOAc)\cdot CH_2Cl_2$ was obtained by slow diffusion of hexane through a 2-mm layer of methanol into a dichloromethane solution of the complex in a 5 mm diameter tube. A crystal was mounted on a glass fiber with silicone grease and positioned in the cold stream of a Siemens P3/RA diffractometer. Only random fluctuations (<2%) in the intensities of two standard reflections were observed during the course of data collection. Crystal data are given in Table IV. The usual corrections for Lorentz and polarization effects were applied. Structural solution and refinement were performed with the programs of SHELXTL PLUS. Scattering factors and corrections for anomalous dispersions were taken from a standard source.[28]

The structure was solved by a Patterson synthesis and refined by full-matrix least squares. Hydrogen atoms were included at calculated positions with the use of a riding model with a C–H distance of 0.96 Å and $U_H = 0.020U_C$ Å^2. An absorption correction was applied.[29] Final refinement was carried out with anisotropic parameters for all non-hydrogen atoms. The largest feature in the final difference map was 0.52 e Å^{-3}.

Instrumentation. ^{1}H NMR spectra were recorded on a General Electric QE-300 FT spectrometer operating in the quadrature mode (^{1}H frequency is 360 MHz). The spectra were collected over a 50-kHz bandwidth with 16k data points and a 10-μs 90° pulse. For a typical spectrum, between 1000 and 5000 transients were accumulated with a 50-ms delay time. The signal-to-noise ratio was improved by apodization of the free induction decay. The residual ^{1}H spectrum of $CDCl_3$ or CD_2Cl_2 were used as a secondary reference. To obtain unambiguous methyl assignments in the diamagnetic region and T_1 values, an inversion recovery sequence was used with τ values varying between 0.5 and 100 ms.

The MCOSY spectrum was obtained after collecting a standard 1D reference spectrum. The 2D spectrum was collected by use of 1024 points in t_2 over the desired bandwidth (to include all desired peaks) with 258 t_1 blocks and 1024 scans per block. All experiments included four dummy scans prior to collection of the first block.

Figure 1 was obtained by using the program PCMODEL (Serena Software, Bloomington, IN).

Acknowledgment. We thank the National Institutes of Health (GM26226) for support, Professor G. N. La Mar and Dr. K. A. Keating for advice concerning the MCOSY spectra, and B. Sturgeon for assistance with the EPR spectrometer.

Supplementary Material Available: Tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom postions, and crystal data for $ClFe^{III}(OEPOAc)\cdot CH_2Cl_2$ (8 pages); listings of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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Contribution from the Chemistry Department,
Brookhaven National Laboratory, Upton, New York 11973

Syntheses, Structures, and Properties of Copper(II) and Copper(I) Complexes of the New Binucleating Ligand 1,3-Bis[bis(2-pyridylmethyl)amino]benzene

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The synthesis and characterization of the new copper complexes $Cu_2L'_2(H_2O)_2(ClO_4)_4\cdot 2H_2O$ (VI), $Cu_2L(H_2O)_2(ClO_4)_4\cdot 4H_2O$ (VII), $Cu_2L(CH_3CN)(PF_6)_2$ (VIII), and $Cu_2L(CO)_2(PF_6)_2$ (IX) (L = 1,3-bis[bis(2-pyridylmethyl)amino]benzene, L′ = 1-[bis(2-pyridylmethyl)amino]-3-[(2-pyridylmethyl)amino]benzene) are described. The crystal structures of the copper complexes were determined. Crystal data: complex VI, formula $Cu_2Cl_4O_{20}N_{10}C_{48}H_{54}$, triclinic space group $P\bar{1}$, $Z = 1$, $a = 11.871$ (4) Å, $b = 12.313$ (7) Å, $c = 10.441$ (14) Å, $\alpha = 108.45$ (9)°, $\beta = 102.98$ (8)°, $\gamma = 91.23$ (4)°; complex VII, formula $Cu_2Cl_4O_{22}N_6C_{30}H_{40}$, orthorhombic space group, $Pmn2_1$, $Z = 2$, $a = 23.554$ (3) Å, $b = 8.998$ (2) Å, $c = 9.863$ (2) Å. The copper(II) ions in VII are bridged by a perchlorate ion in the solid state. Complex VIII of formula $Cu_2P_2F_{12}N_7C_{32}H_{31}$ crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$, $a = 11.341$ (2) Å, $b = 17.421$ (4) Å, $c = 9.977$ (2) Å, $\alpha = 93.98$ (2)°, $\beta = 106.89$ (1)°, and $\gamma = 91.47$ (2)°. The two copper(I) ions in VIII are in different environments because acetonitrile is bound to only one copper site. Complex IX of formula $Cu_2P_2F_{12}O_2N_6C_{32}H_{28}$ crystallizes in the triclinic space group $P\bar{1}$ with Z = 2, $a = 13.465$ (2) Å, $b = 15.763$ (2) Å, $c = 9.9839$ (9) Å, $\alpha = 94.07$ (1)°, $\beta = 101.46$ (1)°, and $\gamma = 113.41$ (1)°. The dicarbonyl complex IX is formed from the addition of two molecules of carbon monoxide to VIII. The binding constant for this reaction, measured at 22 ± 2 °C in dimethylformamide by cyclic voltammetry, is 2.1×10^8 M^{-2} per copper(I) dimer. Cyclic voltammetry and differential pulse voltammetry show that the redox potentials for $Cu^{II}Cu^{II} \rightarrow Cu^{I}Cu^{II} \rightarrow Cu^{I}Cu^{I}$ are strongly solvent dependent. Reaction of the copper(I) complex with oxygen in methanol yields the same copper(II) species as is obtained independently from the reaction of Cu^{2+} with L. Hydroxylation of the benzene ring of the ligand is not observed.

Introduction

Binuclear copper complexes have been extensively studied with the aim of simulating the active sites of the copper proteins hemocyanin and tyrosinase.[2-10] Mimicry of the proteins' reactivity toward O_2 has drawn particular interest.[6,8] However, only a few copper(I) complexes manifest this reactivity,[11-24] and at present,

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(1) Permanent address: Department of Natural Sciences, Baruch College, Manhattan, NY 10010. Address questions concerning the X-ray crystallographic determinations to this author.

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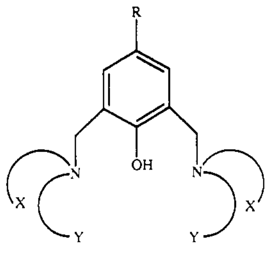
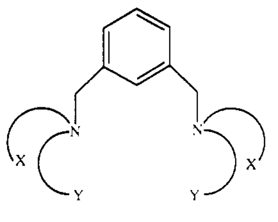
it is unclear which structural features are responsible for the ability of these copper(I) complexes to mimic the proteins' reactivity toward oxygen.[6-8,25-27]

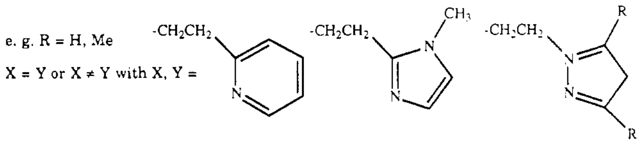
Copper complexes based on ligands of the general type I or II have been studied particularly intensively.[3,7,8,13-18,25-34] Complex III (ligand type I)[15] and derivatives[29] react quasi-reversibly with oxygen at low temperature. Complex IV (ligand type II) is the only one of this series to undergo hydroxylation of the benzene ring during reaction with oxygen.[15,26,27,29] The reasons for the differences in behavior of these complexes are not clear. The reactivity is very sensitive to small changes in the ligand system.[25,26,35] The type of nitrogen donor and the chelate ring sizes seem to play an important role in the behavior of copper complexes derived from the ligands of types I and II. Complexes based on type I ligands contain three six-membered chelate rings, while those based on type II ligands, because they lack the phenolate oxygen, contain at most two six-membered chelate rings per copper site.

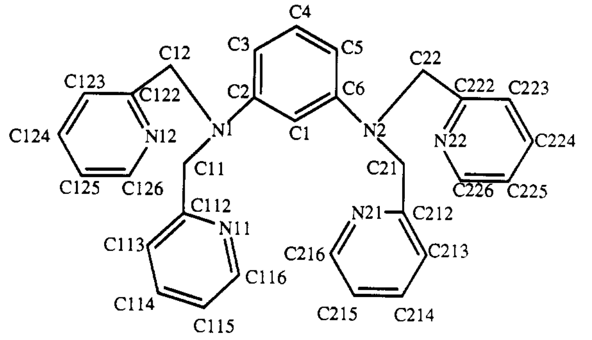


I



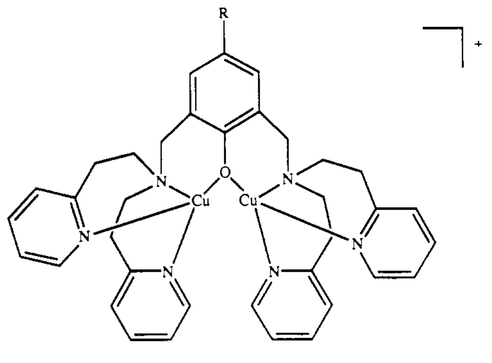
II



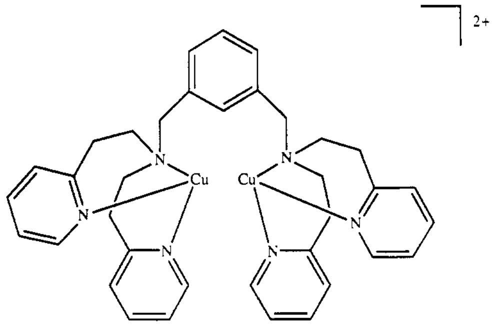


L

Figure 1. The ligand 1,3-bis[bis(2-pyridylmethyl)amino]benzene (L) and the labeling system used for the X-ray data. The numbering scheme for L′ in VI is based on that for L, but the C22-pyridyl arm of L is replaced by a hydrogen atom.



III



IV

Another phenolate-bridged complex, V, has been reported which has an inner chelate ring size of five atoms (copper, amine nitrogen, two carbons from the benzene ring, phenolate oxygen) compared

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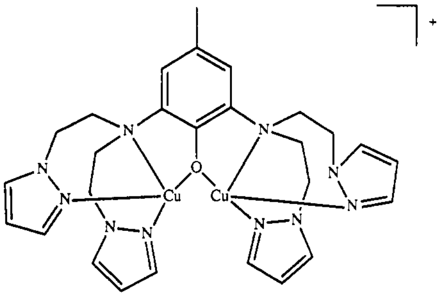

V

to complexes with ligands of type I with an inner chelate ring size of six atoms.[36,37] The azide-bridged copper(II) derivative of V exhibits some of the properties of met-hemocyanin,[36] but the reaction of V with oxygen is irreversible.[37] No reaction with oxygen was observed when the pyrazole donors were substituted in the 3- and 5-positions.[38] The non-phenolate-bridged derivative of V (lacking the 4-methyl group) formed an unidentified violet species after reaction with oxygen.[38]

Here we report the synthesis and characterization of non-phenolate-bridged pyridyl analogues of V; these derive from ligand L shown in Figure 1.

Experimental Section

Materials and Methods. Reagents and solvents used were of commercially available reagent grade quality. UV–vis spectra were measured in 1-cm quartz cells with (0.5–10) × 10^{-4} M solutions on a Cary 210 or Hewlett Packard 8452 A spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AM-300 300-MHz spectrometer. IR spectra were determined on a Mattson Polaris FT-IR spectrometer (Nujol mulls or DMF solutions in 1-mm CaF_2 cells). Emission spectra were measured on a locally built spectrofluorimeter.[39] Emission data were corrected for monochromator and PMT sensitivity variation with wavelength by use of standard spectra for a calibrated lamp purchased from the Optronic Laboratory. Carbon monoxide was determined on a Varian Model 3700 gas chromatograph equipped with a thermal conductivity detector and a molecular sieve 5-Å column at 60 °C (He carrier gas). Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY, and by E. Norton, Brookhaven National Laboratory.

1,3-Bis[bis(2-pyridylmethyl)amino]benzene (L). Sodium hydroxide (40 mL, 5 M) was added dropwise with rapid stirring (mechanical stirrer) *over 4 days* to a solution of 16.4 g (0.1 mol) of 2-(chloromethyl)pyridine hydrochloride and 2.7 g (0.025 mol) of 1,3-phenylenediamine in 20 mL of water under nitrogen. The reaction mixture was kept below pH 9 by stopping the base addition when the color of the mixture turned from orange to deep red. The addition was resumed when the solution again became green. During the reaction, an oily gum was formed, which solidified at the end of the reaction. Furthermore, it was not always possible to add the stoichometric amount of sodium hydroxide, and the reaction was stopped when the pH of the solution reached 8.5. In some early unpurified samples, the ligand L′ was present (see below). The crude solid L obtained in colors from white to red was recrystallized several times from hot toluene (sometimes with the aid of activated charcoal or by passing the hot toluene solution through a short column of alumina) and dried in vacuum to yield 3 g (25% yield) of white crystals. Anal. Calcd for $C_{30}H_{28}N_6$: C, 76.24; H, 5.98; N, 17.77. Found: C, 76.83; H, 5.95; N, 17.59. ^{1}H NMR ($CDCl_3$): δ 4.69 (8 H (CH_2), s), 6.0–6.15 (3 H (benzene), m), 6.95 (1 H (benzene), t), 7.05–7.25 (8 H (pyridine), m), 7.45–7.6 (4 H (pyridine), m), 8.4–8.55 (4 H (pyridine), m). MP: (uncorrected): 168 °C. UV–vis (methanol), λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 256 (sh, 26 000), 314 (6500).

$Cu_2L(H_2O)_2(ClO_4)_4\cdot 4H_2O$ (VII). A 1-g sample (2.1 mmol) of L was suspended in 30 mL of methanol, and 1.56 g (4.2 mmol) of $Cu(ClO_4)_2\cdot 6H_2O$ in 10 mL of water was added dropwise with stirring. The solution was left for 1 day at room temperature, and then the green crystals which had formed were filtered off and dried in air. Yield: 1.0 g (44%). Anal. Calcd for $Cu_2C_{30}H_{28}N_6Cl_4O_{16}\cdot 6H_2O$: Cu, 11.49; C, 32.59; H, 3.65; N, 7.60; Cl, 12.83. Found: Cu, 11.8; C, 33.52; H, 3.60; N, 7.67; Cl, 12.62. UV–vis (water, pH = 5.5), λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 256 (22 000) 306 (sh, 3000), 378 (1300), 686 (290). Treating an aqueous solution of VII with a K^+-loaded cation exchanger (Dowex 50W-X2) and measuring the amount of freed K^+ by atomic absorption confirmed the 4+ charge of VII in solution. When samples of L containing the impurity L′ were mixed with $Cu(ClO_4)_2$, both complexes $Cu_2L'_2{}^{4+}$ and Cu_2L^{4+} formed and crystals of both $Cu_2L'_2(H_2O)_2(ClO_4)_4\cdot 2H_2O$ (VI) and VII were obtained.

Caution! Perchlorate salts are potentially explosive and should be handled with great care.

$Cu_2L(CH_3CN)(PF_6)_2$ (VIII). Reaction of L with $Cu(CH_3CN)_4PF_6$[40] in tetrahydrofuran led to a yellow oil which solidified after several days; reaction in acetonitrile and evaporation of the solvent also gave a yellow oil which solidified after being stirred with methanol. Methanol proved the most useful solvent. The following procedure was carried out in a Vacuum/Atmospheres glovebox filled with argon. To a suspension of 0.5 g (1.05 mmol) of L in 50 mL of methanol was added with stirring 0.8 g (2.1 mmol) of $Cu(CH_3CN)_4PF_6$.[40] After 10 min of stirring, the solution was filtered. A pale yellow-green powder was obtained, washed with methanol, and dried at once in vacuum. ^{1}H NMR (CD_3CN): δ 4.41 (8 H (CH_2), s), 6.55–6.7 (3 H (benzene), m), 7.05 (1 H (benzene), t), 7.25–7.5 (8 H (pyridine), m), 7.75–7.95 (4 H (pyridine), m), 8.4–8.55 (4 H (pyridine), m). UV–vis (methanol), λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 244 (24 100), 315 (sh, 7500).

$Cu_2L(CO)_2(PF_6)_2$ (IX). A 100-mg sample of $Cu_2L(CH_3CN)(PF_6)_2$ (VIII) was suspended in 20 mL of absolute methanol in a serum bottle under argon. Under a stream of CO, the complex dissolved and the solvent was evaporated with CO (carried out in a hood). A white powder was obtained. UV–vis (methanol), λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 258 (25 500), 310 (sh, 5200). Emission (solid): 530 nm (excitation wavelength 300 nm). IR (Nujol): 2100 (CO, s), 2055 (CO, s), 820 cm^{-1} (PF_6, br s). (DMF): 2095 cm^{-1} (CO, s). The carbon monoxide content of IX was determined as follows: The solid was weighed into a serum bottle under argon and then treated with small volume of acetonitrile, which displaced CO from the copper(I). A sample of the Ar/CO gas mixture from the serum bottle was injected into a gas chromatograph. The amount of CO produced was compared with that obtained by adding known amounts of CO to an Ar-filled serum bottle under the same conditions but without complex IX. Analysis of the results gave two molecules of carbon monoxide per molecule of complex.

Electrochemistry. Cyclic voltammetry (CV) and differential-pulse voltammetry (DPV) were performed with a BAS 100 instrument at 22 ± 2 °C with CV scan rates from 2 to 1000 mV s^{-1} and DPV pulse heights from −10 to −50 mV and scan rates from 2 to 4 mV s^{-1}. The solutions studied contained 0.1–1 mM copper complex and 0.1 M tetrapropylammonium perchlorate in DMF, methanol, or acetonitrile. A conventional H-type cell was used with glassy carbon, Pt, and SCE as working, counter, and reference electrodes, respectively. Ferrocene was added as an internal standard at the end of each run. For the electrochemical determination of the CO binding constant, gas mixtures (research grade; MG Industries, Valley Forge, PA) with compositions of 20, 50, and 100% CO in Ar were used. The exit gas line for the cell was always vented to a hood.

Collection and Reduction of X-ray Data. Crystals of $Cu_2L'_2(H_2O)_2(ClO_4)_4\cdot 2H_2O$ (VI) (green prisms) were taken from the crystal mixture (recrystallized from water) obtained from the reaction of impure ligand L with $Cu(ClO_4)_2$. A crystal, 0.22 × 0.28 × 0.55 mm, was coated with petroleum jelly and mounted in a glass capillary tube. The diffraction data indicated the crystal to be triclinic. The space group was assumed to be $P\bar{1}$[41a] for the solution and refinement of the structure.

Crystals of $Cu_2L(H_2O)_2(ClO_4)_4\cdot 4H_2O$ (VII) were taken from the recrystallized sample obtained from the reaction of purified ligand L with $Cu(ClO_4)_2$. A green prism, 0.20 × 0.35 × 0.45 mm, was coated with petroleum jelly and placed in a capillary tube. The diffraction data indicated orthorhombic symmetry with systematic absences $0kl$, $k + l = 2n + 1$, consistent with space group $Pnm2_1$ or $Pn2_1m$ (nonstandard settings of $Pmn2_1$[41b]) or $Pnmm$ (nonstandard setting of $Pmmn$[41c]). Solution and refinement of the structure indicated that $Pn2_1m$ was the correct space group, so the data were reindexed to conform to the standard setting $Pmn2_1$ and all subsequent results reported here refer to this standard setting for the space group.

Crystals of $Cu_2L(CH_3CN)(PF_6)_2$ (VIII) suitable for the X-ray analysis were obtained from vapor diffusion of ether into an acetone solution of the crude product. A colorless prism, 0.22 × 0.35 × 0.22 mm, was used for data collection. The crystal was coated with petroleum jelly

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Table I. Crystallographic Data from the X-ray Diffraction Study of VI–IX

compound	VI	VII	VIII	IX
formula	$Cu_2Cl_4O_{20}N_{10}C_{48}H_{54}$	$Cu_2Cl_4O_{22}N_6C_{30}H_{40}$	$Cu_2P_2F_{12}N_7C_{32}H_{31}$	$Cu_2P_2F_{12}O_2N_6C_{32}H_{28}$
a, Å	11.871 (4)	23.554 (3)	11.341 (2)	13.465 (2)
b, Å	12.313 (7)	8.998 (2)	17.421 (4)	15.763 (2)
c, Å	10.441 (14)	9.863 (2)	9.977 (2)	9.9839 (9)
α, deg	108.45 (9)		93.98 (2)	94.07 (1)
β, deg	102.98 (8)		106.89 (1)	101.46 (1)
γ, deg	91.23 (4)		91.47 (2)	113.41 (1)
V, $Å^3$	1403 (4)	2090 (1)	1879 (1)	1879 (1)
Z	1	2	2	2
fw	1359.91	1105.58	930.66	945.63
space group	$P\bar{1}$	$Pmn2_1$	$P\bar{1}$	$P\bar{1}$
ρ(calcd), g cm^{-3}	1.609	1.756	1.645	1.672
γ, Å	0.710 69 (Mo Kα)	1.5418 (Cu Kα)	0.710 69 (Mo Kα)	1.5418 (Cu Kα)
μ, cm^{-1}	10.7	44.6	13.6	31.5
transm coeff	0.7413–0.8097	0.2555–0.4737	0.6246–0.7746	0.4407–0.7587
R^a	0.092	0.048	0.087	0.059
$R_w{}^a$	0.109	0.063	0.080	0.071
max shift/error, final cycle	≤0.02	≤0.01	≤0.07; except PF_6^- ≤0.6	≤0.01
T, K	295	295	295	295

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

under argon in a glovebox and was mounted in a glass capillary tube. The diffraction data indicated that the crystal was triclinic, and space group $P\bar{1}$[41a] was assumed for the solution and refinement of the crystal structure. Over the course of the data collection, the crystal became slightly green, but no effects on the standards were observed (see supplementary Table S1).

Crystals of $Cu_2L(CO)_2(PF_6)_2$ (IX) were obtained by evaporating a solution of VIII in methanol very slowly under a stream of carbon monoxide. A colorless prism, 0.10 × 0.21 × 0.35 mm, was coated with petroleum jelly and mounted in a glass capillary tube. The diffraction data indicated triclinic symmetry, and space group $P\bar{1}$[41a] was assumed for the solution and refinement of the structure.

Crystal data and information on data collection for all four structures are given in Table I and, in detail, in Table S1.

Determination and Refinement of Structure. The structures of VI–VIII were solved by standard Patterson heavy-atom methods, while the structure of IX was solved by direct methods.[42] In the full-matrix (IX was refined in two blocks) least-squares refinement,[42] neutral-atom scattering factors[43] and corrections for anomalous dispersion were used and the quantity $\sum w(|F_o| - |F_c|)^2$ was minimized. Anisotropic temperature parameters were used for all the non-hydrogen atoms for VII and IX. For VI and VIII, isotropic temperature parameters were used for all atoms except copper and the atoms in the anions and solvent molecules, for which anisotropic temperature factors were used (except for one disordered ClO_4^- in VI). In the final cycles of refinement, hydrogen atoms were introduced in their calculated positions (X–H = 0.95 Å) and allowed to "ride"[42] on the C or N atom to which they were bound. The hydrogen atoms on the water molecules could not be located on a difference Fourier map so they were not included in the refinement with the exception of one hydrogen in $Cu_2L(H_2O)_2(ClO_4)_4{\cdot}4H_2O$ (VII) which could clearly be seen on the difference Fourier map (due to very strong hydrogen bonding; see supplementary Table S14). It was included in the refinement as a fixed contribution. A common isotropic thermal parameter was refined for all of the hydrogens in each structure. For VII, the handedness of the model was checked and the structure reported here resulted in the lower value for R_w. The atomic coordinates are listed in Tables II–V.

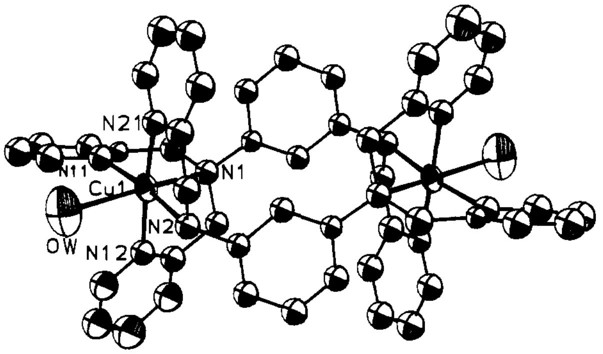


Figure 2. ORTEP view of the cation of VI ($Cu_2L'_2(H_2O)_2{}^{4+}$). The thermal ellipsoids are at the 50% probability level, and the hydrogen atoms are omitted for clarity. A crystallographic center of inversion relates the two copper centers and the two ligands.

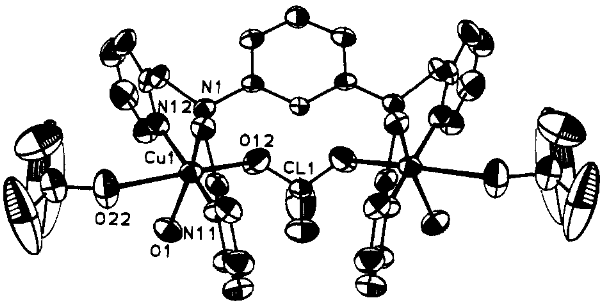
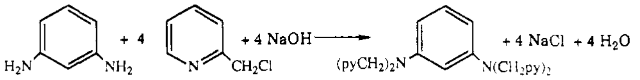


Figure 3. ORTEP view of the cation of VII ($Cu_2L(H_2O)_2(ClO_4)_3{}^+$). The thermal ellipsoids are at the 50% probability level, and the hydrogen atoms are omitted for clarity. A crystallographic mirror plane bisects the bridging benzene ring and bridging perchlorate anion.

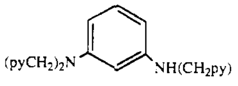
Results

Synthesis. The ligand L was prepared from the reaction of 2-(chloromethyl)pyridine with 1,3-phenylenediamine:



L

The crude product obtained had as a major impurity the compound L′, which has a hydrogen bound to N2 (see Figure 1) instead of the pyridyl arm attached to N2 by C22. It was detected by NMR spectroscopy (^1H NMR ($CDCl_3$): additional peak at δ 4.78 (CH_2)) and TLC (alumina, 2% methanol/CH_2Cl_2: shadow above the spot of ligand L). Pure L was obtained as white needles by slow evaporation of a toluene solution. In the first attempt to synthesize the complex by treating the ligand with $Cu(ClO_4)_2$ in water/methanol, a sample of L contaminated with L′ was used inadvertently. By chance, the first crystal chosen for the X-ray analysis was VI (see Figure 2), the copper(II) complex obtained



L′

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(42) Sheldrick, G. M. SHELX 76: Crystal Structure Refinement Program. Cambridge University, Cambridge, England, 1976.

(43) Neutral-atom scattering factors: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–100. Anomalous dispersion factors: Cromer, D. T.; Weiman, D. *J. Chem. Phys.* **1970**, *53*, 1891–1898.

Table II. Final Positional Parameters for the Non-Hydrogen Atoms in $Cu_2L'_2(H_2O)_2(ClO_4)_4 \cdot 2H_2O$ (VI)[a]

atom	*x*	*y*	*z*
Cu1	0.20088 (19)	0.23824 (19)	0.2851 (2)
N11	0.2153 (12)	0.2541 (12)	0.4870 (14)
C112	0.1857 (12)	0.1706 (13)	0.5201 (15)
C113	0.2247 (15)	0.1595 (16)	0.6507 (17)
C114	0.2935 (16)	0.2489 (16)	0.751 (2)
C115	0.3243 (16)	0.3428 (17)	0.722 (2)
C116	0.2861 (15)	0.3441 (16)	0.5874 (18)
N12	0.3279 (12)	0.1359 (12)	0.2913 (13)
C122	0.3054 (15)	0.0270 (15)	0.2715 (17)
C123	0.3890 (16)	−0.0419 (18)	0.2883 (19)
C124	0.5059 (20)	0.0060 (19)	0.332 (2)
C125	0.5240 (18)	0.1195 (17)	0.3575 (20)
C126	0.4384 (16)	0.1814 (17)	0.3357 (18)
N1	0.0978 (11)	0.0510 (11)	0.2654 (13)
C11	0.1046 (15)	0.0673 (15)	0.4145 (17)
C12	0.1802 (13)	−0.0235 (14)	0.2126 (17)
C1	0.0555 (14)	0.0901 (4)	−0.0838 (16)
C2	0.0208 (13)	−0.0140 (14)	−0.1864 (16)
C3	0.1056 (14)	−0.0904 (15)	−0.2170 (17)
C4	0.2215 (15)	−0.0592 (15)	−0.1524 (17)
C5	0.2524 (15)	0.0470 (14)	−0.0514 (17)
C6	0.1746 (14)	0.1228 (4)	−0.0179 (16)
N2	0.2055 (11)	0.2336 (11)	0.0864 (13)
C21	0.1386 (14)	0.3286 (14)	0.0570 (17)
N21	0.0711 (11)	0.3371 (11)	0.2654 (14)
C212	0.0529 (15)	0.3580 (15)	0.1410 (18)
C213	−0.0519 (15)	0.4048 (15)	0.0948 (19)
C214	−0.1264 (16)	0.4320 (15)	0.1802 (19)
C215	−0.0988 (16)	0.4128 (16)	0.3060 (20)
C216	0.0005 (15)	0.3668 (15)	0.3436 (19)
Cl1	−0.1334 (5)	0.2886 (5)	0.6334 (6)
O11	−0.161 (3)	0.299 (2)	0.747 (2)
O12	−0.183 (2)	0.1928 (18)	0.539 (2)
O13	−0.1574 (18)	0.3828 (15)	0.5959 (20)
O14	−0.016 (2)	0.283 (2)	0.657 (2)
Cl2	0.5488 (2)	0.3106 (6)	0.0951 (7)
O21	0.593 (3)	0.386 (3)	0.246 (3)
O22	0.431 (2)	0.340 (3)	0.101 (3)
O23	0.590 (3)	0.342 (4)	−0.003 (4)
O24	0.529 (3)	0.184 (3)	0.042 (3)
O25	0.634 (6)	0.257 (6)	0.032 (7)
O26	0.551 (3)	0.405 (3)	0.040 (4)
O27	0.452 (4)	0.254 (5)	0.073 (5)
O28	0.630 (3)	0.332 (3)	0.222 (3)
OW	0.3402 (14)	0.4340 (14)	0.3476 (16)
OW2	0.343 (3)	0.576 (3)	0.177 (4)

[a] Numbers in parentheses are errors in the last significant digit(s). O21–O28 have site occupancy factors of 0.5.

Table III. Final Positional Parameters for the Non-Hydrogen Atoms in $Cu_2L(H_2O)_2(ClO_4)_4 \cdot 4H_2O$ (VII)[a]

atom	*x*	*y*	*z*
Cu1	−0.12467 (4)	0.22224 (8)	0.0000
O1	−0.1549 (2)	0.2100 (6)	−0.1875 (5)
N1	−0.1051 (2)	0.2236 (5)	0.2066 (5)
C11	−0.1050 (3)	0.0627 (6)	0.2484 (6)
C12	−0.1556 (3)	0.3017 (7)	0.2648 (7)
N11	−0.0942 (2)	0.0190 (5)	0.0061 (6)
C112	−0.0914 (3)	−0.0365 (7)	0.1324 (6)
C113	−0.0787 (3)	−0.1861 (7)	0.1520 (8)
C114	−0.0690 (3)	−0.2752 (7)	0.0425 (9)
C115	−0.0719 (4)	−0.2162 (9)	−0.0855 (8)
C116	−0.0848 (3)	−0.0678 (8)	−0.1008 (7)
N12	−0.1638 (2)	0.4105 (6)	0.0419 (6)
C122	−0.1731 (3)	0.4300 (7)	0.1756 (7)
C123	−0.1999 (3)	0.5572 (8)	0.2264 (9)
C124	−0.2174 (4)	0.6644 (9)	0.1325 (10)
C125	−0.2077 (4)	0.6430 (8)	−0.0017 (12)
C126	−0.1806 (3)	0.5138 (8)	−0.0459 (8)
C1	0.0000	0.2262 (9)	0.2058 (8)
C2	−0.0520 (2)	0.2984 (6)	0.2359 (5)
C3	−0.0519 (3)	0.4390 (6)	0.2952 (6)
C4	0.0000	0.5062 (9)	0.3232 (10)
Cl1	0.0000	0.3580 (2)	−0.1582 (2)
O11	0.0000	0.2123 (12)	−0.2041 (15)
O12	−0.0504 (2)	0.3830 (6)	−0.0770 (6)
O13	0.0000	0.4575 (17)	−0.2687 (11)
Cl2	−0.27493 (8)	0.0859 (2)	0.0583 (3)
O21	−0.2890 (6)	0.200 (2)	0.003 (4)
O22	−0.2160 (2)	0.0648 (8)	0.0592 (9)
O23	−0.2870 (7)	0.104 (4)	0.189 (2)
O24	−0.3053 (4)	−0.0387 (14)	0.047 (3)
Cl3	0.5000	0.0736 (3)	0.0373 (2)
O31	0.4503 (6)	−0.004 (2)	0.0697 (15)
O32	0.5000	0.1227 (9)	−0.0991 (8)
O33	0.5000	0.208 (3)	0.118 (2)
O31′	0.5513 (13)	0.112 (4)	0.091 (4)
O33′	0.5000	−0.089 (3)	0.016 (4)
O2	−0.3938 (3)	−0.3041 (9)	0.0924 (6)
O3	−0.3899 (4)	0.3831 (10)	0.0627 (14)

[a] Numbers in parentheses are errors in the last significant digit(s). Site occupancy factors for O31 and O31′ are 0.50 and for O33 and O33′ are 0.25.

from the impurity L′. In VI, two molecules of L′ bind two copper ions, each coordinated by a secondary and a tertiary amine nitrogen, three pyridines, and a water molecule. The use of pure ligand L led to the desired complex VII (see Figure 3), which was recrystallized from water. The copper(I) complex $Cu_2L(CH_3CN)(PF_6)_2$ (VIII) was prepared from $[Cu(CH_3CN)_4]PF_6$ and L in methanol in an argon glovebox. The compound is only slightly soluble in methanol (in which it is very air sensitive) and even less soluble in dichloromethane. As a dry solid, VIII is stable in air for several hours before it starts to turn green on the surface. The carbon monoxide complex IX derived from complex VIII is also very air sensitive in solution but is stable for at least several hours as a dry solid.

Structures. The atom-numbering scheme used for the ligand L is given in Figure 1. The numbering scheme for L′ in VI is based on that for L in Figure 1, but the C22-pyridyl arm is replaced by a hydrogen atom. A view of the cation $Cu_2L'_2(H_2O)_2^{4+}$ in VI is presented in Figure 2. The molecule is a dimer which crystallizes about a crystallographic center of inversion. Each copper(II) is "4 + 2" coordinated, with the two pyridines (N11 and N12) of the tertiary amine and the secondary amine (N2) and its pyridine (N21) from the symmetry-related ligand forming the equatorial plane (see Table VI), with the tertiary amine (N1) and a water molecule (OW) in the axial positions. The two pyridyl arms of the tertiary amine are cis to one another. The Cu1–Cu1′ distance is 7.520 (2) Å. The distances and bond angles in the coordination sphere are normal for Cu(II).

Figure 3 is a view of $Cu_2L(H_2O)_2(ClO_4)_3^+$, the cation in VII. The ligand is depicted in Figure 1. In this case, the halves of the molecule are related by a crystallographic mirror plane which bisects the bridging diaminobenzene and perchlorate units. Each copper(II) is "4 + 2" coordinate. The equatorial plane of the coordination sphere consists of the two pyridines (N11 and N12) trans to one another, the tertiary amine N1 and a water molecule O1 (see Table VI), while the axial positions are occupied by perchlorate ions. One perchlorate bridges the two copper(II) centers (Cu1–O12 = 2.395 (5) Å), while the others cap copper(II) (Cu1–O22 = 2.640 (6) Å). The Cu1–Cu1′ distance is 5.873 (1) Å.

A view of $Cu_2L(CH_3CN)^{2+}$, the cation in VIII, is shown in Figure 4. The ligand is the same as in VII but contains Cu(I) instead of Cu(II). In VIII, the coordination spheres of the two copper centers are different, and the coordination modes of the halves of the ligand differ. One copper (Cu1) is coordinated by the two pyridyl arms of the ligand (Cu1–N_{av} = 1.847 (15) Å). The N_{py}–Cu1–N_{py} angle is 164.1 (7)°. There is also a weak interaction with the tertiary amine N1, Cu1–N1 = 2.410 (12) Å, in contrast to the case of VII (Figure 3), in which this amine is strongly coordinated to copper(II). The Cu(I)–N_{py} bond lengths observed here are similar to those observed for 2-coordinate copper(I).[29] Indeed, Cu1 can be considered to be 2-coordinate since, in many linearly coordinated copper(I) structures coordinated by nitrogen atoms, a weakly interacting third atom is present at a rather long distance.[44] The site trans to the weakly coor-

Table IV. Positional Parameters for the Non-Hydrogen Atoms in $Cu_2L(CH_3CN)(PF_6)_2$ (VIII)[a]

atom	*x*	*y*	*z*
Cu1	0.0511 (2)	0.03716 (15)	0.7123 (3)
N11	0.1093 (14)	0.1020 (9)	0.6047 (15)
C112	0.2201 (16)	0.0890 (10)	0.5885 (19)
C113	0.2728 (18)	0.1283 (12)	0.503 (2)
C114	0.2064 (20)	0.1848 (13)	0.431 (2)
C115	0.0951 (19)	0.2005 (12)	0.447 (2)
C116	0.0471 (18)	0.1597 (12)	0.533 (2)
C11	0.2932 (16)	0.0244 (10)	0.6634 (19)
N1	0.2633 (11)	0.0027 (8)	0.7907 (14)
C12	0.2319 (16)	−0.0785 (11)	0.7951 (20)
N12	0.0279 (13)	−0.0441 (8)	0.8132 (14)
C122	0.1215 (16)	−0.0932 (11)	0.8500 (19)
C123	0.1134 (18)	−0.1547 (12)	0.922 (2)
C124	0.0091 (18)	−0.1691 (12)	0.963 (2)
C125	−0.0859 (18)	−0.1198 (12)	0.929 (2)
C126	−0.0731 (17)	−0.0596 (11)	0.8519 (19)
C1	0.3636 (13)	0.1217 (10)	0.9187 (18)
C2	0.3261 (14)	0.0462 (10)	0.9179 (18)
C3	0.3450 (14)	0.0138 (10)	1.0454 (19)
C4	0.4016 (15)	0.0598 (11)	1.165 (2)
C5	0.4438 (14)	0.1340 (10)	1.1711 (19)
C6	0.4230 914)	0.1659 (10)	1.0405 (19)
Cu2	0.2889 (2)	0.32238 (16)	0.9569 (3)
N1A	0.130 (2)	0.3181 (12)	0.840 (2)
C1A	0.043 (3)	0.3373 (15)	0.778 (3)
C2A	−0.077 (2)	0.3678 (15)	0.690 (3)
N2	0.4622 (12)	0.2439 (9)	1.0322 (16)
C21	0.5293 (15)	0.2582 (10)	0.9292 (19)
N21	0.4108 (14)	0.3707 (10)	0.8768 (16)
C212	0.5160 (18)	0.3379 (11)	0.8781 (19)
C213	0.613 (2)	0.3722 (13)	0.845 (2)
C214	0.590 (2)	0.4450 (14)	0.794 (2)
C215	0.487 (2)	0.4786 (13)	0.785 (2)
C216	0.398 (2)	0.4408 (14)	0.826 (2)
C22	0.5241 (15)	0.2892 (10)	1.1712 (18)
N22	0.3247 (15)	0.3366 (9)	1.1661 (17)
C222	0.4340 (17)	0.3165 (10)	1.245 (2)
C223	0.468 (2)	0.3290 (12)	1.391 (2)
C224	0.385 (2)	0.3608 (13)	1.451 (3)
C225	0.278 (2)	0.3794 (14)	1.374 (3)
C226	0.245 (2)	0.3684 (12)	1.232 (2)
P1	0.6892 (7)	0.1506 (4)	0.6345 (8)
F11	0.6523 (18)	0.1260 (9)	0.7623 (18)
F12	0.7789 (17)	0.2106 (10)	0.7315 (20)
F13	0.5915 (14)	0.0925 (11)	0.5402 (19)
F14	0.5887 (17)	0.2089 (10)	0.6147 (17)
F15	0.7206 (14)	0.1731 (9)	0.5049 (15)
F16	0.7823 (14)	0.0879 (9)	0.6524 (16)
P2	0.8780 (14)	0.3977 (9)	0.244 (2)
F21	0.843 (3)	0.318 (2)	0.281 (5)
F22	0.945 (3)	0.349 (2)	0.163 (6)
F23	0.7624 (19)	0.3924 (17)	0.152 (3)
F24	0.912 (5)	0.4669 (18)	0.186 (5)
F25	0.984 (2)	0.397 (2)	0.372 (5)
F26	0.825 (4)	0.440 (3)	0.344 (3)

[a] Numbers in parentheses are errors in the last significant digit(s).

dinated nitrogen N1 is occupied by a fluorine atom from PF_6^- (Cu–F = 3.096 (14) Å). The copper lies 0.06 Å out of the plane of these four atoms. The other copper center in VIII (Cu2) can be considered to have distorted trigonal-planar coordination geometry. The trigonal plane consists of the two pyridyl arms (N21 and N22, $Cu-N_{av}$ = 1.994 (16) Å) and a strongly bound nitrogen from acetonitrile (Cu–N = 1.835 (23) Å). The average Cu–N distance of 1.94 (2) Å and the N–Cu–N angles (Table VI) are consistent with a distorted trigonal-planar geometry.[29] Cu2 lies 0.33 Å above the plane formed by three nitrogen atoms toward weakly interacting N2. Thus the coordination geometry could also be considered to be extended to a very distorted tetrahedron by the weak interaction with the tertiary amine N2, Cu–N = 2.391 (13) Å. The Cu1–Cu2 distance is 5.632 (3) Å. The closest Cu–Cu contact in the crystal is an intermolecular one, the Cu1–Cu1′ distance of 4.156 (3) Å, which results from the stacking of the pyridine rings of the 2-coordinate copper Cu1 across an inversion center. The stacked pyridine–pyridine distance is 3.2 Å (see supplementary Figure S1). The stacking interaction could be responsible for the complex crystallizing with the two copper centers having different coordination geometries.

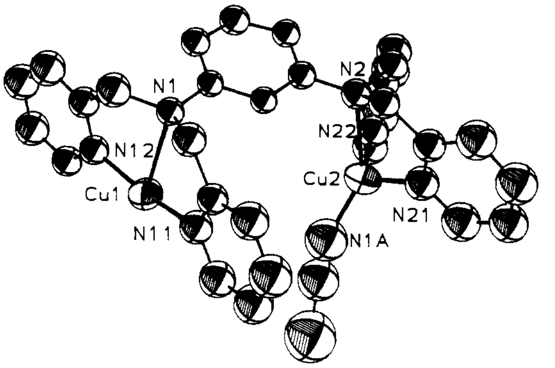

Figure 4. ORTEP view of the cation of VIII ($(Cu_2L(CH_3CN)^{2+}$). The thermal ellipsoids are at the 50% probability level, and the hydrogen atoms are omitted for clarity. Cu1 is formally 2-coordinate with a long Cu1–N1 interaction. Cu2 is trigonal planar (N21, N22, and N1A) with a long Cu2–N2 interaction.

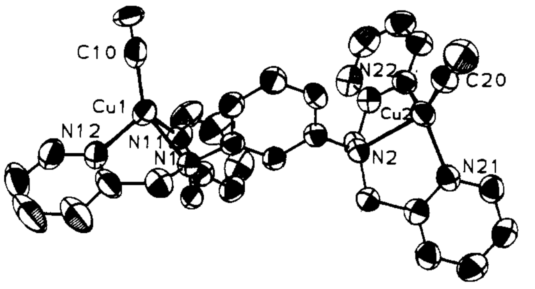

Figure 5. ORTEP view of the cation of IX ($(Cu_2L(CO)_2^{2+}$). The thermal ellipsoids are at the 50% probability level, and the hydrogen atoms are omitted for clarity.

Figure 5 is a view of $Cu_2L(CO)_2^{2+}$, the cation of IX. The two copper(I) centers in IX have a coordination geometry similar to that of 3-coordinate Cu2 in VIII (Figure 4). The trigonal plane consists of the two pyridyl arms of L and a carbon monoxide. The coordination can be considered to be extended to tetrahedral by stronger interaction with the tertiary amine (see Table VI) than was found in VIII. The intramolecular Cu1–Cu2 distance is 8.157 (1) Å. The shortest Cu–Cu distances in the crystal are between inversion-related complexes: Cu1–Cu1′ = 5.123 (1) Å and Cu2–Cu2′ = 5.664 (1) Å.

Spectral Properties. The ^1H NMR spectrum of the diamagnetic dicopper(I) complex VIII is shifted with respect to that of the free ligand but is otherwise essentially identical, as has also been found for other copper(I) complexes.[15] The solid dicarbonyl IX has two carbonyl stretching bands at 2050 and 2100 cm^{-1}, with the band at 2050 cm^{-1} being about half as intense as that at 2100 cm^{-1}. By contrast, solutions of IX in DMF exhibit a single band at 2095 cm^{-1}. Solutions of VII in water have absorption maxima at 378 and 686 nm (at pH = 5.5). The 378-nm absorption is very sensitive to pH. Below pH 3 and above pH 6.5, and 378-nm peak shifts to shorter wavelengths. The 378-nm molar absorptivity drops about 20% between pH 5.5 and pH 2 or between pH 5.5 and pH 7. The same spectra are obtained when Cu^{II}_2L is assembled from L and other copper(II) salts (PF_6^-, BF_4^-). In methanol and DMF, the UV–vis spectra are the same as in water at pH 5.5. The solid (Nujol mull) has absorption maxima at 395 and 645 nm. In acetonitrile, the absorption peaks are shifted and more intense (λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 394 (1655), 640 (470)). VII itself is not emissive, but an impurity present in aged samples or in acetonitrile solutions exposed to air gives rise to emission at 535

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[44] (a) Schilstra, M. J.; Birker, P. J. M. W. L.; Verschoor, G. C.; Reedijk, J. *Inorg. Chem.* **1982**, *21*, 2637–2644. (b) Sorrell, T. N.; Jameson, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 6013–6018.

Table V. Positional Parameters for the Non-Hydrogen Atoms in $Cu_2L(CO)_2(PF_6)_2$ (IX)[a]

atom	*x*	*y*	*z*
Cu1	0.18907 (8)	−0.00526 (7)	−0.00080 (12)
N1	0.3125 (4)	0.1164 (3)	0.1623 (6)
C11	0.3823 (5)	0.1705 (4)	0.0752 (7)
C112	0.3117 (5)	0.1780 (4)	−0.0549 (7)
C113	0.3338 (6)	0.2595 (5)	−0.1132 (9)
C114	0.2639 (8)	0.2607 (6)	−0.2314 (9)
C115	0.1708 (8)	0.1792 (7)	−0.2927 (9)
C116	0.1551 (7)	0.0981 (6)	−0.2347 (9)
N11	0.2220 (5)	0.0980 (4)	−0.1165 (6)
C12	0.3737 (6)	0.0752 (5)	0.2570 (8)
C122	0.3844 (6)	−0.0034 (6)	0.1783 (10)
C123	0.4690 (8)	−0.0294 (7)	0.2359 (11)
C124	0.4751 (10)	−0.1054 (9)	0.1687 (16)
C125	0.3955 (10)	−0.1544 (7)	0.0453 (16)
C126	0.3176 (8)	−0.1220 (5)	−0.0059 (12)
N12	0.3117 (5)	−0.0477 (4)	0.0609 (8)
C10	0.0522 (7)	−0.0898 (5)	0.0092 (8)
O10	−0.0282 (4)	−0.1427 (4)	0.0192 (7)
C1	0.2769 (5)	0.2554 (4)	0.2211 (6)
C2	0.2561 (5)	0.1627 (4)	0.2275 (7)
C3	0.1743 (5)	0.1102 (4)	0.2905 (7)
C4	0.1111 (6)	0.1491 (5)	0.3421 (7)
C5	0.1309 (5)	0.2413 (5)	0.3338 (7)
C6	0.2138 (5)	0.2943 (4)	0.2739 (7)
Cu2	0.13671 (7)	0.45198 (7)	0.35631 (10)
C20	0.0689 (6)	0.4253 (5)	0.4952 (9)
O20	0.0248 (5)	0.4125 (4)	0.5803 (7)
N21	0.2797 (4)	0.5704 (4)	0.3790 (6)
C212	0.3681 (5)	0.5549 (4)	0.3613 (7)
C213	0.4696 (6)	0.6278 (5)	0.3706 (8)
C214	0.4860 (7)	0.7185 (5)	0.4063 (9)
C215	0.3950 (6)	0.7343 (5)	0.4226 (8)
C216	0.2947 (6)	0.6590 (5)	0.4101 (7)
C21	0.3526 (5)	0.4550 (4)	0.3356 (7)
N2	0.2354 (4)	0.3916 (3)	0.2646 (5)
C22	0.2074 (5)	0.4053 (4)	0.1171 (6)
C222	0.0862 (5)	0.3846 (4)	0.0665 (7)
C223	0.0282 (7)	0.3440 (5)	−0.0686 (8)
C224	−0.0804 (8)	0.3322 (6)	−0.1114 (9)
C225	−0.1251 (7)	0.3647 (6)	−0.0178 (10)
C226	−0.0637 (6)	0.4037 (5)	0.1133 (8)
N22	0.0412 (4)	0.4148 (4)	0.1568 (6)
P1	0.1870 (2)	−0.11114 (17)	0.5169 (4)
F11	0.1019 (5)	−0.0646 (4)	0.4766 (6)
F12	0.0892 (7)	−0.2071 (5)	0.4793 (11)
F13	0.1702 (8)	−0.1052 (6)	0.6631 (8)
F14	0.2811 (5)	−0.0106 (4)	0.5437 (8)
F15	0.1917 (9)	−0.1152 (6)	0.3611 (10)
F16	0.2687 (8)	−0.1536 (6)	0.5620 (14)
P2	0.35098 (15)	0.55006 (13)	0.7997 (2)
F21	0.2679 (5)	0.5853 (5)	0.7170 (6)
F22	0.3777 (4)	0.6230 (4)	0.9322 (6)
F23	0.4431 (5)	0.6199 (4)	0.7418 (9)
F24	0.3259 (4)	0.4774 (3)	0.6655 (5)
F25	0.4295 (8)	0.5143 (8)	0.8739 (7)
F26	0.2522 (5)	0.4816 (4)	0.8452 (6)

[a] Numbers in parentheses are errors in the last significant digit(s).

nm (excitation maximum 400 nm). Mixtures of the copper(II) and -(I) complexes VII and VIII dissolved in acetonitrile exhibit no new bands ascribable to the mixed-valence species. Solutions of VII exhibit the same spectral and electrochemical properties in the presence and absence of 1 atm of carbon dioxide.

Electrochemistry. A cyclic voltammogram of $Cu_2L(H_2O)_2(ClO_4)_4·4H_2O$ (VII) in DMF is shown in Figure 6. The same voltammogram is obtained from the Cu(I) derivative $Cu_2L(CH_3CN)(PF_6)_2$ (VIII) in DMF. The average of cathodic (E_{pc}) and anodic (E_{pa}) peak potentials is 140 mV vs SCE, and the peak separation ($E_{pc} - E_{pa} = \Delta E_p$) is 116 mV with a 10 mV/s sweep rate. E_{pc}, E_{pa}, and ΔE_p increase linearly with the logarithm of the sweep rate in the range 50–1000 V/s but are independent of sweep rate in the 2–10 mV/s range. The differential-pulse voltammogram is broad (ca. 150 mV) with a peak at 140 mV vs SCE. The fact that the cyclic voltammograms exhibit only single cathodic and anodic peaks for the overall two-electron reduction of binuclear VII indicates that the two redox processes are separated by a $\Delta E_{1/2}$ smaller than 120 mV.[45] On the basis of the observed shapes at low sweep rate and the analysis of Richardson and Taube,[45] $\Delta E_{1/2}$ is ca. 80 mV. Thus $E^1{}_{1/2}$ = 178 mV and $E^2{}_{1/2}$ = 98 mV vs SCE are estimated. In methanol, the differential-pulse voltammogram is broader (ca. 200-mV width) than that in DMF, with two poorly resolved peaks separated by about 100 mV. Shoulders were evident in the cyclic voltammogram. The dependence of ΔE_p on sweep rate in methanol was similar to that in DMF. In acetonitrile, two well-resolved redox processes separated by 180 mV are evident in both the cyclic voltammogram and the differential-pulse voltammogram. These results are summarized in Table VII. Measurements at more negative potentials led to an irreversible reaction and adsorption of copper metal to the electrode, as has been observed for other binuclear copper complexes.[9,46] No redox process was observed cathodic of the Cu(II)–Cu(I) process up to +1 V vs SCE in any of the solvents used. In water, with KCF_3SO_3 as supporting electrolyte, only a cathodic peak at about −80 mV vs SCE and an anodic desorptive spike around + 700 mV were observed.

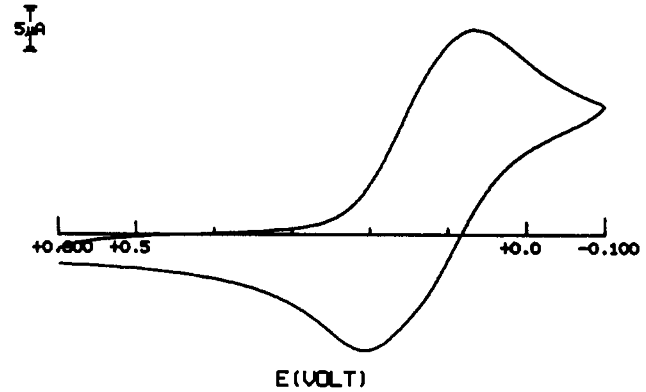

Figure 6. Cyclic voltammogram of $Cu_2L(H_2O)_2(ClO_4)_4·4H_2O$ (VII) in DMF–0.1 M tetrabutylammonium perchlorate measured with a glassy carbon electrode vs SCE at a sweep rate of 0.1 V s^{-1} (22 °C).

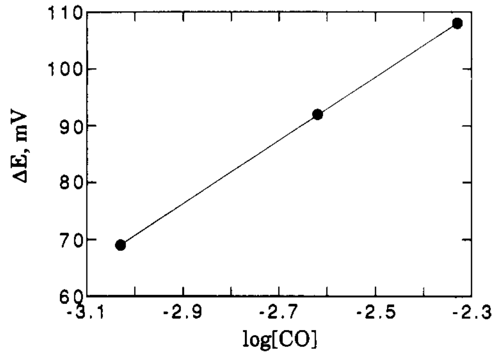

Figure 7. Plot of ΔE ($=E_{CO} - E_{Ar}$) vs log [CO].

The binding of CO to the copper(I) complex was studied in DMF according to the method of Gagnê et al.[47] Saturation of solutions of VII with CO/Ar mixtures produced a cathodic shift in the peak potentials, while the voltammogram shapes altered little. For simplicity, we treat the redox process as a net two-electron change and use the value of $E = (E_{pc} + E_{pa})/2$ as a measure of the binding of *p* CO molecules to the Cu(I) dimer. Values of ΔE ($=E_{CO} - E_{Ar}$) as a function of [CO] are given in Table VIII. A plot of ΔE vs log [CO] (Figure 7) has a slope ($=p/n$) of 56 mV and an intercept ([CO] = 1 M) of +238 mV. Since *n* = 2 electrons and *p* = 2 CO per dicopper(I) complex, *K*

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Table VI. Selected Bond Lengths and Angles for VI–IX

$Cu_2L'_2(H_2O)_2(ClO_4)_4 \cdot 2H_2O$ (VI)			
Metal Coordination Sphere Distances (Å)			
Cu1–N11	2.015 (13)	Cu1–N12	1.989 (13)
Cu1–N1	2.513 (13)	Cu1–N2	2.071 (12)
Cu1–N21	1.998 (13)	Cu1–OW	2.706 (15)
Cu1–Cu1′	7.520 (2)		
Metal Coordination Sphere Angles (deg)			
N11–Cu1–N12	86.2 (5)	N12–Cu1–OW	96.1 (5)
N11–Cu1–N1	78.0 (5)	N1–Cu1–N2	107.8 (5)
N11–Cu1–N2	173.0 (6)	N1–Cu1–N21	102.9 (5)
N11–Cu1–N21	97.4 (6)	N1–Cu1–OW	169.2 (4)
N11–Cu1–OW	93.6 (5)	N2–Cu1–N21	85.1 (5)
N12–Cu1–N1	76.8 (5)	N2–Cu1–OW	80.2 (5)
N12–Cu1–N2	91.4 (5)	N21–Cu1–OW	84.7 (5)
N12–Cu1–N21	176.2 (6)		
$Cu_2L(H_2O)_2(ClO_4)_4 \cdot 4H_2O$(VII)			
Metal Coordination Sphere Distances (Å)			
Cu1–N11	1.966 (5)	Cu1–N12	1.972 (5)
Cu1–N1	2.089 (5)	Cu1–O1	1.985 (5)
Cu1–O2	2.393 (5)	Cu1–O22	2.640 (6)
Cu1–Cu1′	5.873 (1)		
Metal Coordination Sphere Angles (deg)			
N11–Cu1–N12	164.5 (2)	N12–Cu1–O22	91.9 (2)
N11–Cu1–N1	84.0 (2)	N1–Cu1–O1	171.2 (2)
N11–Cu1–O1	96.2 (2)	N1–Cu1–O12	98.3 (2)
N11–Cu1–O12	107.8 (2)	N1–Cu1–O22	88.1 (2)
N11–Cu1–O22	78.0 (2)	O1–Cu1–O12	90.0 (2)
N12–Cu1–N1	83.9 (2)	O1–Cu1–O22	83.4 (2)
N12–Cu1–O1	94.3 (2)	O12–Cu1–O22	171.7 (2)
N12–Cu1–O12	83.6 (2)		
$Cu_2L(CH_3CN)(PF_6)_2$ (VIII)			
Metal Coordination Sphere Distances (Å)			
Cu1–N11	1.845 (15)	Cu2–N21	1.983 (15)
Cu1–N12	1.849 (2)	Cu2–N22	2.004 (16)
Cu1–N1	2.410 (12)	Cu2–N2	2.391 (13)
Cu1–Cu1′	4.156 (3)	Cu2–N1A	1.835 (23)
Cu1–Cu2	5.632 (3)		
Metal Coordination Sphere Angles (deg)			
N11–Cu1–N12	164.1 (7)	N21–Cu2–N22	116.4 (6)
N11–Cu1–N1	83.5 (6)	N21–Cu2–N2	77.8 (6)
N12–Cu1–N1	82.8 (6)	N21–Cu2–N1A	113.7 (8)
		N22–Cu2–N2	78.8 (6)
		N22–Cu2–N1A	121.3 (8)
		N2–Cu2–N1A	141.2 (7)
$Cu_2L(CO)_2(PF_6)_2$ (IX)			
Metal Coordination Sphere Distances (Å)			
Cu1–N11	2.019 (6)	Cu2–N21	2.038 (5)
Cu1–N12	2.019 (6)	Cu2–N22	2.038 (5)
Cu1–N1	2.245 (4)	Cu2–N2	2.197 (6)
Cu1–C10	1.823 (8)	Cu2–C20	1.793 (9)
Cu1–Cu2	8.157 (1)		
Metal Coordination Sphere Angles (deg)			
N11–Cu1–N12	116.2 (3)	N21–Cu2–N22	111.5 (2)
N11–Cu1–N1	80.2 (9)	N21–Cu2–N2	80.6 (2)
N12–Cu1–N1	78.6 (2)	N22–Cu2–N2	82.0 (2)
N1–Cu1–C10	127.1 (3)	N2–Cu2–C20	132.5 (3)
N11–Cu1–C10	127.2 (3)	N22–Cu2–C20	121.3 (3)
N12–Cu1–C10	113.2 (3)	N22–Cu2–C20	119.0 (3)

(for binding 2 CO molecules per binuclear copper(I) complex) is 2.1×10^8 M^{-2} (or 1.4×10^4 M^{-1} per Cu(I)). In methanol, VIII reacted with carbon monoxide and the adduct was isolated, but the binding constant could not be determined electrochemically because the cyclic voltammogram and differential-pulse voltammogram shapes changed in the presence of CO and the shifts of the potentials were not linear in log [CO]. In oxygen-saturated DMF, the cathodic process shifted ca. 160 mV cathodic of its position under argon and the anodic process was not observed. This has been observed for mononuclear copper complexes, with the difference that a negative potential was held for some time before running the anodic scan.[19]

Table VII. Cyclic Voltammetry of $Cu^{II}_2L(H_2O)_2(ClO_4)_4 \cdot 4H_2O$ at 22 °C[a]

solvent	E_{pc}, V vs SCE	E_{pa}, V vs SCE	$E^1_{1/2}$, V vs Fc	$E^2_{1/2}$, V vs Fc
DMF	0.08	0.2	−0.34	−0.42
methanol	0.12	0.27	−0.15	−0.25
acetonitrile	0.43	0.54	+0.09	−0.09
	0.26	0.34		

[a] All potentials measured with a glassy carbon electrode vs SCE using tetrabutylammonium perchlorate (0.1 M) as electrolyte. Results presented are limiting values in the low-sweep region in which ΔE_p is independent of sweep rate. $E^1_{1/2}$ and $E^2_{1/2}$ are derived values for the first and second reduction potentials (except for the case of acetonitrile) and are reported vs the ferrocenium/ferrocene "Fc" couple.

Table VIII. Determination of the CO Binding Constant in DMF for Complex VII at 22 °C by Cyclic Voltammetry ([VII] = 1×10^{-4} M) at a Scan Rate of 10 mV/s

[CO],[a] mM	ΔE,[b] mV	$e^{\Delta E nF/RT} - 1$
0.94	69	14.1
2.34	92	36.3
4.67	108	69.0

[a] Based on the solubility of 100% in DMF being 4.67×10^{-3} M at 22 °C measured by analyzing a CO-saturated DMF solution by gas chromatography (4.64×10^{-3} M at 25 °C[44]). [b] $\Delta E = E_{CO} - E_{Ar}$, where E_{CO} and E_{Ar} are obtained from the averages of cathodic and anodic peak potentials under carbon monoxide and in the absence of carbon monoxide, respectively.

Reaction with Oxygen. Methanol seemed an appropriate solvent for study of the reaction of the copper(I) complex VIII with oxygen.[26] Oxygen was bubbled through a solution of VIII (5×10^{-4} M) in methanol at room temperature for 5 min. The solution became green and exhibited absorption maxima at 368 nm (4000 M^{-1} cm^{-1}) and 654 nm (200 M^{-1} cm^{-1}). After water was added and the pH adjusted with dilute perchloric acid to 5.5, the UV–vis spectrum was the same as that obtained from the Cu(II) complex of L (VII) in water–methanol at pH 5.5. This suggested that hydroxylation of the benzene ring of the ligand had not occurred, which was confirmed by isolating the ligand from the oxidized Cu(I) complex: Cu(II) was removed from the organic ligand by adding aqueous NH_3, and the ligand was extracted into dichloromethane. The solid obtained after drying and evaporating the solvent has the same ^1H NMR and TLC characteristics as L. Study of the Cu(I)–oxygen reaction in dichloromethane was precluded by the very low solubility of VIII in this solvent.

Discussion

L is a new binucleating ligand which binds both Cu(II) and Cu(I). It is readily available in gram quantities and has the advantage of being a stable solid, in contrast to the highly viscous oils usually obtained. Attempts to isolate the impurity L′ have failed so far. Interestingly, treatment of a solution of the ligand mixture L and L′ with Cu^{2+} and recrystallization of the product gave a mixture of the complexes $Cu_2L'_2(H_2O)_2(ClO_4)_4 \cdot 2H_2O$ and $Cu_2L(H_2O)_2(ClO_4)_4 \cdot 4H_2O$. However, attempts to obtain more than a few crystals of VI have failed.

Pure $Cu_2L(H_2O)_2(ClO_4)_4 \cdot 4H_2O$ (VII) has the attractive feature that it is readily crystallized. This was surprising because it is usually difficult to crystallize dicopper(II) complexes of 4+ charge in the absence of "coordinating" anions.[26] However, in VII, perchlorate serves as a coordinating anion. Although bond angles and distances for VII are quite normal (Table VI), the μ-ClO_4^- dicopper(II) moiety is unusual. Other complexes containing a bridging ClO_4^- are known,[48-50] but in these, the bridge is supported by additional bridging ligands. Most commonly, ClO_4^- is coor-

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dinated to one copper or bridges copper ions intermolecularly.[35,51,52] Studies of the magnetic properties of VII would be desirable.

The structures of the copper(I) centers in $Cu_2L(CH_3CN)^{2+}$ (Figure 4) can be contrasted with that of $Cu_2L''^{2+}$ (L'' = *N*,*N*,*N'*,*N'*-tetrakis(2-methylpyridyl)ethylenediamine) reported by Gagné et al.[53] In VIII, the rigid diaminobenzene replaces the flexible ethylenediamine group, preventing the coordination of the pyridine rings from opposite ends of the ligand to the same copper center and also precluding the short Cu1–Cu2 separation found in the L'' complex. The bond distances and angles in the copper(I) coordination spheres of these two complexes also differ. In VIII, the $Cu-N_{py}$ distances for Cu1 are much shorter than those for Cu2. The coordination about Cu2 in VIII can be compared to that in complex IV,[15] in which the pyridine rings are connected to the tertiary amine nitrogen by ethylene groups. In IV, the $Cu-N_{py}$ bonds are shorter than those in VIII and there is a much stronger bond to the tertiary amine than in VIII. The copper(I) complex of the binucleating ligand $[py(CH_2)_2]_2N(CH_2)_4N[(CH_2)_2py]_2$ of Karlin et al.[18] has a much more tetrahedral geometry about the two identical copper centers than does Cu2 in VIII. In VIII, the $Cu-N_{py}$ bond lengths are about the same as those found by Karlin et al., but the $Cu-N_{NCCH_3}$ bond is much shorter and the $Cu-N_{tertiary}$ bond is much longer in VIII, leading to the more trigonal-planar geometry in VIII.

The Cu(I) bond distances in $Cu_2L(CO)_2(PF_6)_2$ (IX) are very similar to those reported for the carbon monoxide adduct of $Cu_2L''^{2+}$.[53] However, in the latter the angles about the two copper(I) centers differ by less than 2.8°, in contrast to up to 5.9° in IX.

All of the L-containing species examined in this study exhibit at least two bands in the ultraviolet region. From comparison with the spectrum of the free ligand in methanol, the highest energy bands of the Cu(II) complex VII (306 and 256 nm) are ascribed to intraligand, probably $\pi-\pi^*$, transitions of the benzene and pyridine moieties, respectively. These features are retained but shifted in the dicopper(I) species VIII (313, 244 nm) and IX (310, 258 nm). Metal-to-ligand charge-transfer (MLCT) transitions are expected in the near-UV region for both VIII and IX. Probably, these are masked by the intense 313–310-nm intraligand bands. The solid-state emission observed from the dicarbonyl complex IX is either intraligand $\pi-\pi^*$ or MLCT in origin.[2,54]

The lowest energy (645–686 nm) band of Cu^{II}_2L is undoubtedly a ligand-field transition of the tetragonal copper(II) center.[55] Its shift with solvent reflects the binding of solvent molecules, with probably one bound tightly trans to the tertiary amine nitrogen and two at longer distances along the axis perpendicular to the tetragonal plane. The most striking feature of the spectrum of the Cu^{II}_2L species is the 378–395-nm band. Transitions in this spectra region have previously been observed for dicopper(II) species bridged by phenolate or by hydroxide ion and attributed to O-to-Cu(II) ligand-to-metal charge-transfer (LMCT) absorption.[28,36,56] Here, we propose that LMCT from the tertiary amine N to Cu(II) is responsible for the 378–395-nm band of Cu^{II}_2L. The band position and intensity are consistent with data for other systems[57,58] and the ionization energy of the amine nitrogen, taking *N*,*N*-diethylaniline (I = 6.99 eV[59]) as a model. This nitrogen is more oxidizable than its counterpart in complexes based on ligand types I and II because it is part of the 1,3-diaminobenzene group. Interestingly, and consistent with this interpretation, the oxidizability of *N*,*N*-diethylaniline ($E_{1/2}$ = +0.45 V vs NHE in water), a model for the tertiary amine in L, is very similar to that of 2,5-dimethylphenolate, +0.47 V vs NHE in H_2O, a model for the phenolate oxygen in III and ligands of type I.[60] An LMCT assignment is consistent with the spectral and electrochemical shifts observed for acetonitrile solvent: Binding of acetonitrile to copper(II) raises the copper(II/I) reduction potential so that an LMCT band should shift to longer wavelength, as is found.

The electrochemical behavior of binuclear copper complexes has been extensively investigated.[2,9,19,26,29,46,47,61–68] That of the Cu_2L system reveals that it (eq 1) is chemically reversible in DMF,

$$Cu^{II}_2L^{4+}(solv) + 2e^- \rightleftharpoons Cu^I_2L^{2+}(solv) \qquad (1)$$

methanol, and acetonitrile. It appears to be electrochemically reversible (mass-transport limited) at very slow sweep rates, but "electron transfer" is relatively slow at faster sweep rates, consistent with the large coordination changes required of the metal center. (These may include both changes in coordination geometry as seen in the structures of VII and VIII and desolvation of the Cu(I) center.) In contrast to those of certain macrocyclic systems,[65] the stepwise reduction processes for binuclear copper(II) complexes based on ligand types I and II are not usually well resolved. Only a single (two-electron) redox process has been reported for complex IV and its pyrazole derivative[9,29,69] and for the complexes derived from 2,5-bis(bromomethyl)pyrazine, *N*,*N*-bis(2-pyridylmethyl)amine, and *N*,*N*-bis(2-pyridylethyl)amine.[64,67] Similarly for VII, in methanol and DMF, the two reduction processes

$$Cu^{II}Cu^{II}L^{4+}(solv) + e^- \rightleftharpoons Cu^{II}Cu^{I}L^{3+}(solv) \quad E^1_{1/2} \qquad (2)$$

$$Cu^{II}Cu^{I}L^{3+}(solv) + e^- \rightleftharpoons Cu^{I}Cu^{I}L^{2+}(solv) \quad E^2_{1/2} \qquad (3)$$

are separated by only 100 mV or less. However, in acetonitrile the $E^1_{1/2}$ and $E^2_{1/2}$ values differ by 180 mV. This difference in potentials corresponds to a comproportionation constant for eq 4 of 1.2×10^3 in CH_3CN, in contrast to $\leq 2 \times 10$ in DMF. The

$$Cu^{II}_2L^{4+} + Cu^{I}_2L^{2+} \rightleftharpoons 2Cu^{II}Cu^{I}L^{3+} \qquad (4)$$

solvent dependence of the comproportionation constant is somewhat surprising. It could signify that CH_3CN asymmetrically coordinates $Cu^I_2L^{2+}$ in solution, as it does in the solid state. In any event, there is no obvious electronic interaction via the 1,3-diaminobenzene bridge which could account for enhanced stability of $Cu^{II}Cu^{I}L^{3+}$ in acetonitrile. Taking the ferrocenium/ferrocene couple as a solvent-independent reference,[9] the Cu^{II}_2L reduction potentials summarized in Table VII are seen to be rather solvent dependent, increasing by ca. 400 mV from DMF to acetonitrile. The sensitivity of these copper(II/I) couples to solvent is (except for acetonitrile, discussed above) probably chiefly a result of the

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fact that solvent serves as a ligand for Cu(II). Thus, the reduction of copper(II) to copper(I) is accompanied by a release of ligating solvent.

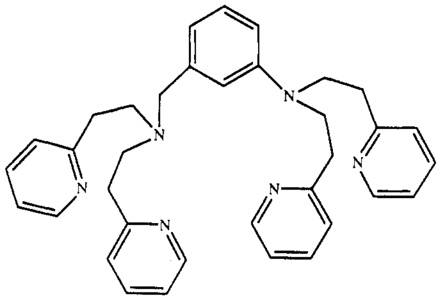
Complex IV, which contains ethylpyridyl arms, is more readily reduced than VII by ca. 140 mV.[29,69] In studies of the methyl/ethylpyridyl-based complexes above, Oshio et al. also found that ethylpyridyl complexes are reduced more easily (by ca. ~180 mV) than their methylpyridyl analogues.[64,67] The ethylpyridyl arms are more flexible than the methylpyridyl arms and, evidently, more readily accommodate the coordination geometry of copper(I). A similar pattern has been observed for mononuclear Cu(II) complexes.[2]

The dicopper(I) complex $\mathrm{Cu^I{}_2L^{2+}}$ reacts with CO in methanol to yield (eq 5) the dicarbonyl IX. The single carbonyl stretch

$$\mathrm{Cu^I{}_2L^{2+} + 2CO \rightleftharpoons Cu^I{}_2L(CO)_2{}^{2+}} \qquad (5)$$

observed at 2095 $\mathrm{cm^{-1}}$ for DMF solution suggests that the two Cu(I) sites are equivalent in solution, in contrast to their inequivalence in the solid state. The CO adduct of [(*N,N,N′,N′*-tetrakis(2-methylpyridyl)ethylenediamine)dicopper(I)](2+), which has carbonyl stretching bands at 2097 and 2107 $\mathrm{cm^{-1}}$ in the solid state and one band at 2110 $\mathrm{cm^{-1}}$ in dichloromethane solution, exhibits similar behavior.[53] The carbonyl stretching frequency is higher for IX than for most copper(I) carbonyl complexes, indicative of less Cu-to-CO π back-donation for IX.[53] The affinity of the Cu(I) for CO in the $\mathrm{Cu_2L}$ system is higher, $K_6 = 2.1 \times 10^8\ \mathrm{M^{-2}}$, particularly given the ease of Cu(II) reduction. (Note that there are actually three possible Cu(I)–CO species in this system, $\mathrm{Cu^{II}Cu^{I}L(CO)}$, $\mathrm{Cu^{I}Cu^{I}L(CO)}$, and $\mathrm{Cu^{I}(CO)Cu^{I}L(CO)}$, and that our data treatment neglects the first two.) CO-binding constants for (mononuclear) square-planar macrocyclic copper(I)[47] range from 10 to $10^6\ \mathrm{M^{-1}}$ in DMF. None with reduction potentials as positive as that of VII bind CO to a significant extent. However, the coordination sphere of Cu(I) in the $\mathrm{Cu_2L^{2+}}$ reactant differs significantly from that in the macrocyclic square-planar species. The failure of $\mathrm{Cu^I{}_2L^{2+}}$ to bind CO in acetonitrile is attributed to the well-known strong binding of acetonitrile to copper(I).

The reaction $\mathrm{Cu^I{}_2L^{2+}}$ with oxygen in methanol yields its copper(II) counterpart VII, and the 2-position of the 1,3-diaminobenzene moiety is not hydroxylated. A derivative of complex IV with methylpyridyl instead of ethylpyridyl arms also fails to undergo hydroxylation.[8,70] The phenolate-bridged derivative of the latter, synthesized by an alternative route given by Urbach et al.,[28] exhibits a high strain which leads to distortion of the complex. The different reactivity of the complexes having methylpyridyl arms toward oxygen may result from the rigidity produced by the five-membered chelate rings. As noted above, the effects of the chelate ring sizes are also seen in the electrochemistry. Karlin et al. recently reported[31] that the copper(I) complex of the unsymmetric ligand X reacts reversibly with oxygen at −80 °C in dichloromethane and undergoes hydroxylation of the benzene ring at higher temperatures. The behavior of the ethylpyridyl analogue of VIII toward oxygen is being investigated, and the first results indicate hydroxylation of the benzene ring after the reaction with oxygen at higher temperatures.[71]



X

Conclusion. With the synthesis of L, the preparation of an interesting member of a possible series of ligands similar to those obtained from ligand types I and II has been accomplished. Although reaction of $\mathrm{O_2}$ with the copper(I) complex of L results neither in reversible oxygen-binding nor in hydroxylation of the benzene ring of the ligand, copper complexes based on 1,3-phenylenediamine or 2,6-diamino-4-methylphenol may be better model compounds for the copper proteins than the complexes of ligand type I or II described so far. Preliminary results for the ethylpyridyl analogue of VIII are very promising,[71] and such complexes may better mimic the known distances in the active sites of the proteins.[36]

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Supplementary Material Available: Tables of crystallographic data collection parameters, anisotropic thermal parameters for non-hydrogen atoms, calculated hydrogen atom positions, bond distances and angles, and hydrogen-bonding parameters and an ORTEP view of the cations of VIII (38 pages); listings of final observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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