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Synthesis, Structure, and Magnetic Properties of a Binuclear, Pentacoordinate Copper(II) Complex

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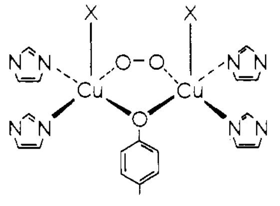
Described are the synthesis and characterization of the new binucleating ligand 2,6-bis[[bis[2-(1-pyrazolyl)ethyl]-amino]methyl]-*p*-cresol and one of its copper(II) derivatives. The ligand provides four donors, including a bridging phenoxide, to each metal ion, and an exogenous ligand completes the coordination sphere. The μ-hydroxo copper(II) complex has been characterized by X-ray crystallography, which shows that the two copper sites are nonequivalent. One copper resides in a square-pyramidal geometry while the other is closer to a trigonal-bipyramidal arrangement. Variable-temperature magnetic susceptibility measurements (6-300 K) demonstrate strong antiferromagnetic coupling ($2J = -420$ cm^{-1}) between the two copper ions. Crystal data for $C_{29}H_{38}B_2Cu_2F_8N_{10}O_2$: monoclinic, $a = 22.32$ (1) Å, $b = 9.551$ (5) Å, $c = 16.715$ (8) Å, $\beta = 95.76$ (3)°, $V = 3546.9$ (16) Å^3, $Z = 4$, space group $P2_1/c$.

Hemocyanin (Hc)[2] is a copper-containing protein whose function is to transport dioxygen in the hemolymph of several arthropods and molluscs. Spectroscopic characterization[3,4] of the binuclear active site in HcO_2 (**1**) in which both copper atoms are formally Cu(II) suggests the following structural requirements for the coordination sphere of copper: each copper is pentacoordinate with at least two of the five ligands provided by imidazolyl groups from histidine and with the peroxide ion bound in an equatorial position. A phenolate ion bridges the two coppers, which are ca. 3.6 Å apart, providing an exchange pathway that results in strong antiferromagnetic coupling between the two d^9 centers.



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The synthesis of model compounds that incorporate the structural features of the hemocyanin active site is important for understanding how dioxygen is bound by the protein since simple copper complexes usually oxidize irreversibly in the presence of O_2.[5,6] Ligands that bind two copper ions have been prepared by several groups,[7-15] but all fail to provide coordination sites that meet all of the criteria mentioned above. To date, the closest structural model for a hemocyanin derivative is one prepared by Reed[14] although, in that system, the group bridging the two copper centers is an alkoxide ion.

As alluded to above, one of the important physical properties of oxyhemocyanin is its diamagnetism, which is due to strong antiferromagnetic coupling between the two formally Cu(II) ions.[16] This phenomenon has also been observed in several other metalloproteins that are involved in oxygen reduction and electron transfer.[17,18] One of the goals in modeling the binuclear active site in hemocyanin is to mimic the strong magnetic coupling that is characteristic of these types of proteins and to obtain structural information on the binuclear bridge in order to illuminate the mechanism of propagation of magnetic coupling.

This paper reports the synthesis and characterization of a new type of binucleating ligand, N_6OH (**3**), which provides four donors to each metal in such a way so as to allow coordination of an additional "exogenous" ion in an equatorial position. A phenolate ion bridges the two metal ions. We also report the crystal structure of $[Cu_2(N_6O)OH][BF_4]_2$ (**2**) and its magnetic susceptibility over the temperature range 6-300 K.

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(2) Abbreviations used in this paper: Hc, deoxyhemocyanin; HcO_2, oxyhemocyanin; N_6O, the anion of 2,6-bis[[bis[2-(1-pyrazoyl)ethyl]-amino]methyl]-*p*-cresol; DMF, dimethylformamide; bpea, bis[2-(1-pyrazolyl)ethyl]amine.

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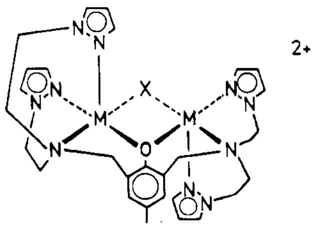
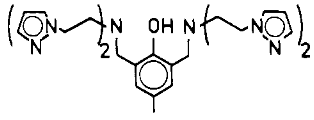


2, M = Cu, X = OH



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Experimental Section

All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise. Ethanol was distilled from magnesium ethoxide, and tetrahydrofuran was distilled from sodium–benzophenone ketyl under nitrogen. 2,6-Bis(hydroxymethyl)-*p*-cresol was prepared by the literature method.[19] Melting points were obtained with use of a Fisher-Johns apparatus and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

^{1}H NMR spectra were recorded on a Perkin-Elmer R-24B instrument at 60 MHZ with use of $CDCl_3$ as the solvent. All chemical shifts are relative to an internal standard of Me_4Si. Electronic spectra were taken on a Cary 17 spectrophotometer.

Bis[2-(1-pyrazolyl)ethyl]amine (bpea). Under a nitrogen atmosphere, 34 g (0.5 mol) of pyrazole was added slowly to a suspension of 18 g (0.75 mol) of NaH in 700 mL of dry DMF. The resulting suspension was allowed to stir for 2 h, after which 44 g (0.24 mol) of bis(2-chloroethyl)amine hydrochloride in 100 mL of dry DMF was added dropwise. The resulting mixture was allowed to stir at 60 °C for 48 h. The DMF was evaporated at reduced pressure, and the residue was dissolved in 300 mL of water. The solution was saturated with NaCl and was extracted with five 100-mL portions of benzene. The combined benzene extracts were dried over Na_2SO_4, filtered, and evaporated. The resulting yellow oil was distilled at reduced pressure to give 26 g (51%) of a pale yellow oil, bp 200 °C (0.2 torr). ^{1}H NMR: δ 2.50 (1 H, s), 2.87 (4 H, t, J = 6 Hz), 4.03 (4 H, t, J = 6 Hz), 6.02 (2 H, t, J = 2 Hz), 7.18 (2 H, d, J = 2 Hz), 7.60 (2 H, t, J = 2 Hz).

2,6-Bis(chloromethyl)-*p*-cresol. Dry HCl gas was passed through a solution of 4.2 g (0.025 mol) of 2,6-bis(hydroxymethyl)-*p*-cresol[19] dissolved in 150 mL of tetrahydrofuran for 1 h. The solution was then allowed to stir for 1 h, and the solvent was evaporated at ambient temperature and reduced pressure. The product is pure enough to be used in subsequent steps although it may be recrystallized from hexane and a small amount of dry ethyl ether. Heating the solution may cause decomposition, and even the crystals are unstable at room temperature over a period of time. The product is best stored in a tightly sealed bottle at −20 °C: yield 3.8 g (75%); mp 84 °C (lit. mp 87 °C).

2,6-Bis[[bis[2-(1-pyrazolyl)ethyl]amino]methyl]-*p*-cresol, N_6OH (3). Method A. A solution of 4.0 g (0.002 mol) of bpea, 1.1 g (0.001 mol) of *p*-cresol, 5 g (0.167 mol) of paraformaldehyde, and 5 g of barium oxide in 100 mL of ethanol was allowed to reflux for 5 days. The solvent was evaporated at reduced pressure, and the residue was acidified with 10% HCl. The solution was neutralized with $NaHCO_3$ and extracted with three 100-mL portions of ethyl acetate. The combined organic extracts were washed with saturated aqueous NaCl, dried over Na_2SO_4, filtered, and concentrated. The dark oil was purified by flash chromatography[20] using 10% methanol in ethyl acetate.

Method B. A solution of 10.3 g (0.05 mol) of bpea in 50 mL of acetonitrile was added to a solution of 5.1 g (0.025 mol) of 2,6-bis(chloromethyl)-*p*-cresol in 200 mL of acetonitrile. Enough methanol was added to dissolve the resulting hydrochloride precipitate. The solution was then allowed to stir at 50 °C for 24 h. The solvent was evaporated at reduced pressure and the residue was neutralized with saturated aqueous $NaHCO_3$. The aqueous phase was extracted with three 75-mL portions of ethyl acetate. The combined organic extracts were washed with saturated aqueous NaCl, dried over Na_2SO_4, and concentrated at reduced pressure. The resulting oil was dissolved in 100 mL of methanol and treated with 15.5 g (0.05 mol) of $Cu(BF_4)_2 \cdot 6H_2O$ dissolved in 100 mL of methanol. The resulting dark brown crystalline precipitate was dissolved in acetonitrile, and the resultant mixture was treated with aqueous EDTA.[21] The solvent was evaporated, water was added, and the ligand was extracted with ethyl acetate. The extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. ^{1}H NMR: δ 2.25 (3 H, s), 3.03 (8 H, t, J = 6 Hz), 3.79 (4 H, s), 4.23 (8 H, t, J = 6 Hz), 6.39 (4 H, t, J = 2 Hz), 6.94 (2 H, s), 7.49 (4 H, d, J = 2 Hz), 7.73 (4 H, d, J = 2 Hz).

(μ-Hydroxy)[2,6-bis[[bis[2-(1-pyrazolyl)ethyl]amino]methyl]-*p*-cresolato]dicopper(II) Tetrafluoroborate, $[Cu_2(N_6O)(OH)][BF_4]_2$ (2). A solution of 1.08 g (2 mmol) of N_6OH in 30 mL of methanol was added to a solution of 1.24 g (4 mmol) of $Cu(BF_4)_2 \cdot 6H_2O$ in 30 mL of methanol. The resulting brown solution was filtered through a medium-porosity fritted filter and was allowed to stand. Large brown-black crystals formed, which were filtered and washed with methanol to give 1.2 g (70%) of **2**.[22] UV/vis spectrum (MeOH), λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 290 (8600), 324 (4500), 390 (3200), 694 (160). Anal. Calcd for $C_{29}H_{38}B_2Cu_2F_8N_{10}O_2$: C, 40.53; H, 4.46; N, 16.30. Found: C, 40.63; H, 4.38; N, 15.26.

X-ray Data Collection. A regular parallelepiped approximately 0.35 mm on a side was mounted on the end of a glass fiber, and a preliminary diffractometer search revealed monoclinic symmetry. Systematic absences were observed consistent with the space group $P2_1/c$. Diffraction data were collected at 293 K on an Enraf-Nonius CAD-4 computer-controlled diffractometer using Mo Kα radiation (0.7107 Å) from a graphite crystal monochromator. The unit cell constants were derived from a least-squares refinement of the setting angles of 25 reflections. The ω–2θ scan technique was used to record the intensities for a unique set of reflections for which $2° \leq 2\theta \leq 55°$ and which covered the ranges $\pm h$, $+k$, and $+l$. Peak counts were corrected for background counts that were obtained by extending the final scan by 25% at each end to yield net intensities, I, that were assigned standard deviations calculated with a conventional ρ factor selected as 0.01. Intensities were corrected for Lorentz and polarization effects and showed no decay during the data collection. The data were further corrected for absorption effects with an empirical correction based on ψ scans. The linear absorption coefficient, μ, was 13.396 cm^{-1} and the transmission factors ranged from 0.812 to 0.996. A total of 2988 independent reflections had $I \geq 3\sigma(I)$ out of a total of 6300 reflections. Crystal data: space group $P2_1/c$, a = 22.32 (1) Å, b = 9.551 (5) Å, c = 16.715 (8) Å, β = 95.76 (3)°, V = 3546.9 (16) Å^3, d(obsd) = 1.61 (flotation in CCl_4–CH_3I), d(calcd) = 1.61, Z = 4.

Structure Determination and Refinement. A three-dimensional Patterson synthesis was used to locate the copper atom positions, and a series of difference Fourier maps revealed the remaining non-hydrogen atoms. The refinement was effected by full-matrix least-squares techniques. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and the weight, w, is $4F_o^2/\sigma^2(F_o^2)$. Programs used for the structure solution and isotropic refinement were supplied as a package by Enraf-Nonius. Atomic scattering factors for the non-hydrogen atoms were taken from ref 23 and those for hydrogen atoms from Stewart et al.[24]

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(21) If only the copper(II) complex and not the free ligand is desired, this and subsequent steps may be eliminated and the complex recrystallized as described.

(22) A green form is obtained by recrystallizing the copper complex from acetonitrile–ethanol or acetonitrile–THF. Upon standing, it converts slowly to the brown form. Its electronic absorption spectrum in methanol is identical with that observed for the brown form in methanol, and the brown form can be regenerated by crystallization of the green complex from methanol. The analytical samples were obtained from acetonitrile–THF and contained a THF of solvation (confirmed by gas chromatography of redissolved crystals). Anal. ($C_{33}H_{46}B_2Cu_2F_8N_{10}O_3$) C, H, N. The coupling constant for this compound, $2J$, is −300 cm^{-1}, and we are currently trying to grow crystals for a structure determination so that we can understand the difference between the green and brown forms.

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Table I. Final Positional Parameters for $[Cu_2(N_6O)(OH)][BF_4]_2$

Cu1	0.2159 (1)	0.1614 (2)	0.1788 (1)
Cu2	0.3291 (1)	0.3059 (2)	0.2566 (1)
O1	0.3020 (3)	0.1743 (7)	0.1722 (4)
O2	0.2432 (4)	0.3057 (9)	0.2614 (5)
N1	0.2225 (6)	−0.0433 (12)	0.1605 (7)
N2	0.1293 (4)	0.1605 (11)	0.2063 (6)
N3	0.1993 (5)	0.2786 (12)	0.0726 (6)
N4	0.4032 (5)	0.3371 (12)	0.2057 (6)
N5	0.3540 (5)	0.1432 (12)	0.3423 (7)
N6	0.3416 (4)	0.4672 (10)	0.3374 (6)
N1A	0.1822 (5)	−0.1401 (15)	0.1794 (7)
N3A	0.1442 (5)	0.3256 (13)	0.0445 (6)
N4A	0.4334 (5)	0.4622 (12)	0.2058 (6)
N5A	0.3723 (5)	0.1661 (12)	0.4212 (7)
C1	0.2902 (7)	0.5691 (13)	0.3173 (8)
C2	0.1323 (5)	0.1970 (16)	0.2949 (7)
C2A	0.0908 (5)	0.2669 (15)	0.1621 (8)
C2B	0.0907 (6)	0.2688 (15)	0.0694 (8)
C2C	0.0980 (6)	0.0229 (16)	0.1919 (8)
C2D	0.1342 (7)	−0.1043 (16)	0.2270 (9)
C6A	0.3990 (6)	0.5454 (14)	0.3294 (8)
C6B	0.4118 (6)	0.5803 (14)	0.2464 (9)
C6C	0.3394 (6)	0.4167 (13)	0.4226 (8)
C6D	0.3855 (6)	0.3100 (16)	0.4499 (7)
CBP	0.0932 (6)	0.6538 (17)	0.4380 (9)
C1A	0.2612 (7)	−0.1085 (19)	0.1223 (10)
C1B	0.2491 (8)	−0.2504 (19)	0.1135 (11)
C1C	0.1979 (9)	−0.2655 (18)	0.1515 (12)
C3A	0.2380 (6)	0.3534 (18)	0.0355 (9)
C3B	0.2071 (8)	0.4480 (17)	−0.0178 (9)
C3C	0.1479 (7)	0.4256 (17)	−0.0099 (9)
C4A	0.4344 (6)	0.2488 (14)	0.1629 (8)
C4B	0.4825 (6)	0.3128 (16)	0.1337 (8)
C4C	0.4805 (6)	0.4459 (17)	0.1623 (8)
C5A	0.3472 (6)	0.0035 (17)	0.3368 (9)
C5B	0.3633 (7)	−0.0578 (15)	0.4119 (10)
C5C	0.3784 (6)	0.0466 (18)	0.4619 (8)
CB1	0.2088 (6)	0.3862 (14)	0.3034 (7)
CB2	0.2292 (6)	0.5148 (14)	0.3356 (8)
CB3	0.1912 (7)	0.5977 (14)	0.3773 (8)
CB4	0.1341 (7)	0.5575 (17)	0.3909 (9)
CB5	0.1153 (6)	0.4278 (18)	0.3621 (8)
CB6	0.1517 (5)	0.3411 (15)	0.3200 (7)
B1	0.9762 (9)	0.1257 (26)	0.3697 (15)
F1	0.9736 (5)	0.1559 (14)	0.2882 (6)
F2	0.9224 (4)	0.0893 (10)	0.3825 (8)
F3	0.0185 (4)	0.0251 (11)	0.3818 (7)
F4	0.9939 (5)	0.2442 (13)	0.4052 (7)
B2	0.565	0.333	0.413
F5	0.516 (1)	0.284 (1)	0.370 (1)
F6	0.608 (1)	0.234 (1)	0.425 (1)
F7	0.551 (1)	0.384 (2)	0.480 (1)
F8	0.588 (1)	0.422 (2)	0.371 (1)

Table II. Selected Geometric Features of the $[Cu_2(N_6O)(OH)]^{2+}$ Cation[a]

	Distances, Å		
Cu1–O1	1.942 (6)	Cu2–O2	1.927 (8)
Cu1–O2	2.002 (8)	Cu2–N4	1.959 (10)
Cu1–N1	1.987 (11)	Cu2–N5	2.148 (11)
Cu1–N2	2.032 (9)	Cu2–N6	2.049 (10)
Cu1–N3	2.100 (10)	Cu1–Cu2	3.053 (4)
Cu2–O1	1.941 (6)		
	Angles, deg		
O1–Cu1–O2	76.2 (3)	Cu1–O1–Cu2	103.6 (3)
O1–Cu2–O2	77.9 (3)	Cu1–O2–Cu2	101.9 (4)
N4–Cu2–O1	89.8 (4)	N1–Cu1–O1	87.9 (4)
N4–Cu2–O2	154.9 (4)	N1–Cu1–O2	139.6 (4)
N4–Cu2–N5	103.1 (4)	N1–Cu1–N2	96.8 (5)
N4–Cu2–N6	96.1 (4)	N1–Cu2–N3	113.7 (4)
N5–Cu2–O1	93.3 (4)	N2–Cu1–O1	169.7 (3)
N5–Cu2–O2	99.4 (4)	N2–Cu1–O2	94.4 (4)
N5–Cu2–N6	95.4 (4)	N2–Cu1–N3	95.8 (5)
N6–Cu2–O1	168.0 (3)	N3–Cu1–O1	90.5 (4)
N6–Cu2–O2	92.5 (4)	N3–Cu1–O2	103.4 (4)

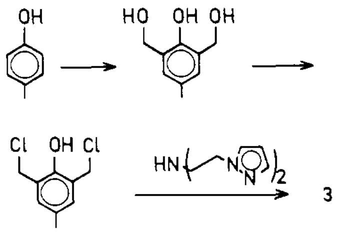
[a] Remaining bond distances and angles are included in the supplementary material.

At this point, because of the size of the structure we continued refinement at the UNC Computation Center using programs supplied by Hodgson.[25] All atoms in the cation were refined anisotropically and then calculated hydrogen atom positions were included in the structure factor calculations but were not refined. The hydrogen atoms on the aromatic methyl group were not included because of the uncertainty of their positions. When convergence of the cation atom positions was reached, the BF_4 groups were made anisotropic and were added to the refinement. We quickly discovered that the second BF_4 group would not refine properly. A final difference Fourier map revealed scattered electron density in the vicinity of the second BF_4 ion. We tried several models to resolve the disorder in that group including refinement of a twofold disordered tetrahedron generated by rotation about an axis through B2 and F5 as suggested by the difference Fourier maps. Variance of the occupancy factors from 50:50 to 80:20 resulted in no better resolution of this group, and the atoms tended to migrate to chemically unreasonable positions. Finally, in order to reach convergence, we found it necessary to refine the fluorine atoms isotropically and to fix the position and isotropic thermal parameter of B2. The remaining BF_4 group and the cation were refined anisotropically. The final weighted *R* factor (on F) was 0.073, and the unweighted *R* factor was 0.078. Clearly, the disorder in one of the BF_4 groups results in these high *R* factors. It should be noted, however, that during refinement of various models for the disordered BF_4, parameters for the converged cation positions varied very little. Final positional parameters are given in Table I, and distances and angles within the coordination sphere are tabulated in Table II. Structure factors, thermal parameters, hydrogen atom positions, and ligand and anion distances and angles are included in the supplementary material.

Magnetic Measurements. Magnetic susceptibility measurements were recorded on an alternating-force magnetometer. Calibration and operation techniques are described elsewhere.[17,26] Measurements were recorded on a 130-mg polycrystalline sample over the temperature range 6–300 K. The data, corrected for molecular diamagnetism with Pascal's constants,[17] are listed in the supplementary material.

Results and Discussion

(A) Synthesis. When we began this work, no ligand was available that would provide a pentacoordinate environment for two Cu(II) ions bridged by a phenolate donor. Several ligands were known, however, that bound two phenolate-bridged Cu(II) ions in a square-planar geometry,[8-12] but those were prepared by a Schiff-base condensation that could not be modified to add an additional ligating group. The first objective of this work, therefore, was to develop a general route for the synthesis of this unique ligand type, and we subsequently realized this goal using the three-step procedure shown in (1). The ligand is readily obtained by precipitation as its



(1)

copper complex (2) followed by removal of the copper with EDTA, thereby avoiding a tedious chromatographic separation. Crystals of the dicopper(II)–hydroxo complex **2** were

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(26) (a) O'Connor, C. J.; Klein, C. L.; Majeste, R. J.; Trefonas, L. M. *Inorg. Chem.* **1982**, *21*, 64–67. (b) O'Connor, C. J.; Cucaukos, E. J.; Deaver, B. S.; Sinn, E. *Inorg. Chim. Acta* **1979**, *32*, 29.

Table III. Least-Squares Planes for $Cu_2(N_6O)(OH)^{2+}$

atoms in plane	dev from plane, Å	other atoms	dev from plane, Å
O1	0.297 (7)	Cu1	0.384 (2)
O2	−0.277 (8)	N3	2.473 (10)
N1	−0.240 (12)		
N2	0.220 (10)		
O1	−0.125 (7)	Cu2	−0.269 (2)
O2	0.121 (8)	N5	−2.426 (12)
N4	0.102 (11)		
N6	−0.098 (10)		

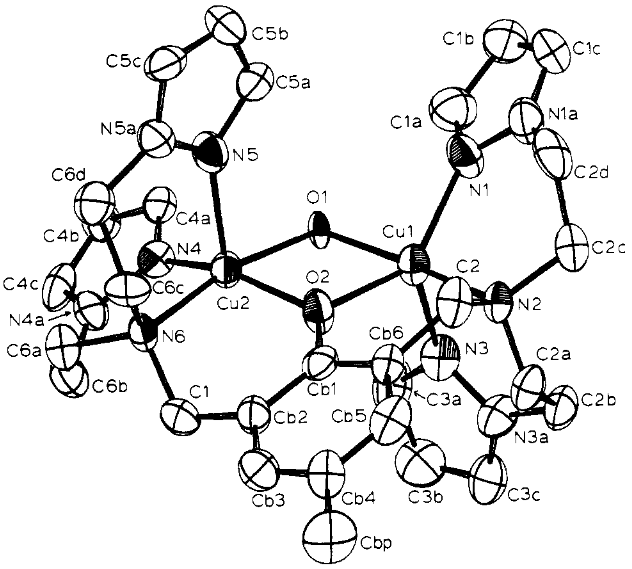


Figure 1. Structure of the $Cu_2(N_6O)(OH)^{2+}$ cation showing 40% probability thermal ellipsoids. Bond distances and angles are compiled in Table II.

obtained by slow evaporation of a methanolic solution of **2**.

(B) Molecular Structure of $[Cu_2(N_6O)(OH)][BF_4]_2$ (2). Compound **2** crystallizes from methanol in the monoclinic space group $P2_1/c$. Final parameters are listed in Table I, significant bond distances and angles are compiled in Table II, and least-squares planes are collected in Table III. The structure of the cation portion of **2** is presented in Figure 1, and the inner coordination sphere is shown in Figure 2.

The copper–ligand bond lengths are in the range of Cu–O and Cu–N bond distances observed for structures of similar complexes,[14,15] with the Cu–N(aliphatic) distances slightly longer than the equatorial Cu–N(pyrazole) bond lengths. There is, however, a significant difference in the two Cu–phenolate bond lengths that may arise from the inequivalent coordination geometry about each copper (vide infra). There are no unusual distances and angles within the ligand itself.

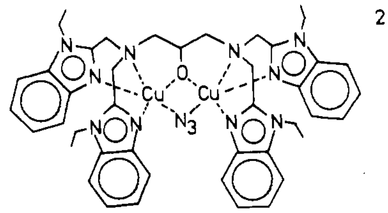
Since there are no crystallographically imposed constraints on the structure, each copper is free to adopt a different geometry. For Cu2, the geometry is best described as square pyramidal; but for Cu1, it is more distorted, bordering on trigonal bipyramidal. Our previous work with tripodal ligands[27] has shown that square-pyramidal coordination is favored by ligands that chelate the copper ion in six-membered rings, so we expected to find square-pyramidal coordination of copper in **2**.

The Cu2–N5 bond is significantly longer than any of the other Cu2–N or Cu2–O bonds, suggesting that N5 occupies the axial position of a tetragonal pyramid. Atoms O1, O2, N4, and N6 lie between 0.10 and 0.12 Å from a plane calculated for those four atoms, and Cu2 sits 0.269 (2) Å below that plane, toward N5. In addition, the O2–Cu2–N5 and N4–Cu2–N5 angles are significantly less than the 120° expected for a trigonal-bipyramidal structure, assuming that O1 and N6 would occupy the axial positions in the latter case.

Figure 2 shows the square-pyramidal arrangement for Cu2 quite clearly, while representing Cu1 as trigonal bipyramidal. The criteria that allowed us to assign a tetragonal geometry to Cu2 fails to provide a strong case for a tetragonal Cu1, and the trigonal-bipyramidal assignment becomes a possibility within the limitations discussed below. The principal departure from square-pyramidal coordination arises from nonplanarity of O1, O2, N1, and N2, which should define the basal plane of the pyramid. These atoms lie between 0.22 and 0.30 Å from a calculated least-squares plane (Table III); thus, the exact assignment of the geometry about Cu1 is open to interpretation.

The preceding statement notwithstanding, the unique aspect of the structure of **2** is that two different coordination geometries are observed for Cu(II) even though the ligand itself is symmetrical; to our knowledge, this phenomenon has not been observed previously. There are only two structurally characterized complexes that are similar to **2**.[14,15] The first of these is the pyridine analogue, which has two square-pyramidal copper ions bridged by a methoxide rather than a hydroxide ion.[15] Since that molecule lies on a C_2 axis, the square-pyramidal copper centers are equivalent and the two copper atoms and two oxygen atoms are coplanar. In complex **2**, Cu1, O1, and O2, and Cu2 are not coplanar and the dihedral angle between the Cu1, O1, O2 and Cu2, O1, O2 planes is 4.1°.

The other complex is [1,3-bis[bis[(1-ethyl-2-benzimidazolyl)methyl]amino]-2-propanoxy](μ-azido)dicopper(II) (tetrafluoroborate (**4**),[14] which is more substantially different,



4

having a ligand that provides benzimidazole donors, a bridging alkoxide group, and chelation within five-membered rings formed by the donor atoms. The copper ion in complex **4** has a distorted geometry much like that observed for Cu1 in the structure of **2** falling between square pyramidal and trigonal bipyramidal. Reed concludes, however, that the square-pyramidal assignment is a more accurate one for **4**. It is interesting to compare the bond distances and angles about Cu in both structures. For example, the distances from Cu1 to N1, N3, and O2[28] for **2** are 1.99 (1), 2.10 (1), and 2.002 (8) Å, respectively; the distances from Cu to N2, N4, and O2 in **4** are 1.99 (1), 2.11 (1), and 1.94 (1) Å, respectively. Similarly, the angles in **2** generated by N1, N3, and O2 with Cu1 are 113, 140, and 103°; the angles in **4** formed by N2, N4, and O2 with Cu are 114, 144, and 99°. Finally, the deviation from planarity of the atoms, which would define the basal plane of a square pyramid, is quite significant for both structures, approximately 0.3 Å. We conclude that the gross structure about Cu1 in **2** is very similar to that found for **4**. Since the strong magnetic coupling in **4** supports the assignment of square-pyramidal copper in that structure, it is rea-

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[27] Sorrell, T. N.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 1014–1019.

[28] We choose to consider only those atoms that are cis to the "exogenous" ligand in order to eliminate the trans influence of azide vs. the hydroxide ion. The atoms chosen would define the trigonal plane if the geometry were considered to be trigonal bipyramidal.

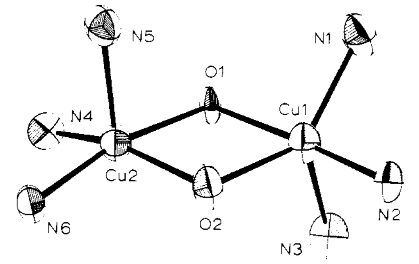

Figure 2. ORTEP plot of the inner coordination sphere about the Cu_2 core for complex **2**.

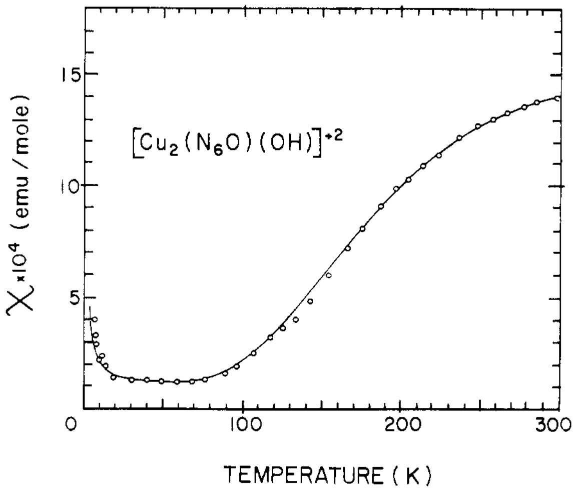

Figure 3. Magnetic susceptibility plotted as a function of temperature for $[Cu_2(N_6O)(OH)][BF_4]_2$. The smooth curve through the points is the best fit of the magnetic data to the equation as described in the text.

sonable to suggest that a similar assignment be made for **2**. However, the one significant difference between the structures is the Cu–O distance, and the longer bond (Cu1–O2) found for **2** *might* be an indication that orbital overlap between coppers through the phenoxide oxygen is not the dominant interaction. If this is the case, then the strong antiferromagnetic coupling observed for **2** (vide infra) must result from overlap through the OH group, and this is consistent with a trigonal-bipyramidal geometry that would put the unpaired electron in the d_{z^2} orbital pointed at the OH group.[29]

(C) Magnetic Susceptibility Studies. The magnetic susceptibility data for $[Cu_2(N_6O)(OH)][BF_4]$ from Table S1 (supplementary material) is plotted as a function of temperature in Figure 3. The shape of the plot is consistent with strong antiferromagnetic coupling, and the susceptibility has not yet reached a maximum when the temperature has increased to 300 K. The slight increase in the magnetic susceptibility at the lowest temperature is attributed to the presence of a small amount of paramagnetic (monomeric) impurity (~0.2%).

The relationship that describes the magnetic coupling of two neighboring electron spins is the Heisenberg–Dirac–Van Vleck spin-exchange Hamiltonian given by eq 2. When the copper

$$\mathcal{H} = -2JS_1\cdot S_2 \qquad (2)$$

dimer model with the $S_1 = S_2 = {}^1/_2$ basis set of wave functions is used, the Van Vleck equation with the Hamiltonian in eq 2 gives the closed-form solution for the magnetic susceptibility, eq 3, where $x = 2J/kT$.

$$\chi = \frac{2Ng^2\mu_B^2}{kT}\,\frac{e^{-x}}{1 + 3e^{-x}} \qquad (3)$$

The magnetic susceptibility data were fit to eq 3 by using a least-squares fitting program, after correction for diamagnetism using Pascal's constants and for a 0.2% monomeric, paramagnetic impurity. The results of this fit gave the parameters $g = 2.30 \pm 0.03$ and $J = -210 \pm 10$ cm^{-1}. The curve drawn through the data points in Figure 3 represents the best fit of the data to eq 3 with the parameters specified above.

The magnitude of the magnetic coupling is quite large, with the excited triplet level 420 cm^{-1} above the singlet ground state. Hatfield and Hodgson[30] have tabulated the magnetic coupling and structural parameters of a series of binuclear copper(II) complexes bridged by oxygen donors, particularly hydroxide ion; and they have found a linear dependence of the Cu–O–Cu bridging angle, ϕ, on the coupling parameter J. Antiferromagnetic coupling becomes greater as ϕ increases above 98°, which is the crossover point ($J = 0$) from ferromagnetic to antiferromagnetic behavior. The complex reported herein has a bridging angle $\phi = 101.9°$ for the phenolic oxygen and $\phi = 103.6°$ for the hydroxyl oxygen. Assuming that the pathway with the stronger magnetic coupling (i.e., the larger Cu–O–Cu angle) will predominate, the Hatfield–Hodgson tabulation predicts a value of about -450 cm^{-1} for the singlet–triplet separation, in reasonable agreement with the experimentally determined value.

The different coordination geometries for the two copper(II) ions in **2** may produce electronic ground states having different electronic structures. Cu2 has a tetragonal geometry, and under a crystal field of C_{4v} symmetry, the electronic 3d orbital degeneracy splits into four energy levels, $e(d_{xz},d_{yz})$, $b_2(d_{xy})$, $a_1(d_{z^2})$, and $b_1(d_{x^2-y^2})$, listed in order of increasing energy. The unpaired electron for the 3d^9 copper(II) ion in this symmetry lies in the $b_1(d_{x^2-y^2})$ orbital. On the other hand, Cu1 has a distorted geometry falling between trigonal bipyramidal and square pyramidal (vide supra), which complicates knowing which orbital has the unpaired electron. For the square-pyramidal geometry, the same orbital splitting described for Cu2 (above) obtains, while under a crystal field of D_{3h} (trigonal-bipyramidal) symmetry, the electronic 3d orbital degeneracy splits into three energy levels, $e''(d_{xy},d_{yz})$, $e'(d_{x^2-y^2})$, and $a'(d_{z^2})$, listed in order of increasing energy. For copper(II) in this geometry, the unpaired electron thus resides in the $a'(d_{z^2})$ orbital. However, whether the local symmetry of Cu1 in **2** is tetragonal or trigonal bipyramidal, the Cu(II) orbital containing the unpaired electron has high electron density along the bond that forms the μ-hydroxo bridge and provides a pathway for magnetic exchange. This is not to say, however, that there is no possibility of exchange by way of the phenolate bridge; if Cu1 is closer to a tetragonal geometry, then the phenolate group will also be able to mediate the strong antiferromagnetic coupling.

The large magnetic coupling that is observed for this complex occurs despite a significant departure of the electronic structure of this complex from the electronic structure of the other correlated binuclears.[30] The μ-hydroxo-bridged complexes that have been cited to follow the empirical relationship between ϕ and J all fall into the category of magnetic coupling between copper(II) ions with electrons in the $d_{x^2-y^2}$ orbitals. It is not unreasonable to expect a modification of magnetic coupling when the d_{z^2} orbital is employed for one copper(II)

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(29) The square-pyramidal geometry is also consistent with coupling through the OH group; however, coupling would also be expected to occur through the phenolate ligand in this geometry. Clearly, the fact that the geometry is not one of the limiting cases, we are presenting, but rather falls between square pyramidal and trigonal bipyramidal makes the situation ambiguous and speculative.

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site since the orbital contribution to the magnetic moment is quite different for d_{z^2}. It is interesting to note that even though the chemistry of the binuclear complex reported here shows marked differences from the complexes reported by Hatfield and Hodgson,[30] the magnetic coupling is in agreement with their prediction.

(D) Summary and Conclusions. We have prepared a new type of binucleating ligand that provides three nitrogen donors for binding each metal ion in addition to a phenolate group to bridge the two metals. When the metal ion is copper(II), an additional bridging ligand can be accommodated and each copper center is five-coordinate. We have characterized the μ-hydroxo complex **2** crystallographically and find that the copper ions are in different coordination environments. The geometry of one copper ion is square pyramidal while that for the other copper center is more distorted, falling between square pyramidal and trigonal bipyramidal. In addition, we have examined the magnetic susceptibility of **2** and find that the two copper(II) centers are strongly antiferromagnetically coupled ($2J = -420$ cm^{-1}).

The complex described herein *may* provide a structural model for the active site in type-3 copper proteins. It meets the salient structural requirements of two *pentacoordinate* Cu(II) ions bridged by an "endogenous" phenolate ion in addition to having the appropriate strong antiferromagnetically coupled metal centers. No other single complex encompasses all three of these features,[31] suggesting the need for further investigation of complexes of this type.

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Registry No. **2**, 88106-60-9; **3**, 88130-57-8; bpea, 88106-61-0; pyrazole, 288-13-1; bis(2-chloroethyl)amine hydrochloride, 821-48-7; 2,6-bis(chloromethyl)-*p*-cresol, 5862-32-8; *p*-cresol, 106-44-5; paraformaldehyde, 30525-89-4.

Supplementary Material Available: Tables S1–S6, listing magnetic susceptibility data, ligand and anion distances and angles, final hydrogen atom positions, final thermal parameters, and observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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(31) Karlin's complex[15] has the same structural features as the complex reported here, but it has not yet been magnetically characterized. We have recently prepared a new type of binucleating ligand in which the aliphatic nitrogen donors are bound directly to the phenol ring (ligand **3** minus the benzylic carbons) and the (μ-azido)dicopper(II) complex of that ligand is diamagnetic: Sorrell, T. N.; O'Connor, C. J., submitted for publication in *Inorg. Chem.*

Contribution from the Solar Energy Research Group,
The Institute of Physical and Chemical Research, Wako, Saitama 351, Japan

Wavelength-Dependent Photochemical Reaction of (μ-Tetraphenylporphinato)bis[dicarbonylrhodium(I)]. Locking of Metal Ion into Ligand

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(μ-Tetraphenylporphinato)bis[dicarbonylrhodium(I)], $\mathrm{TPP[Rh^{I}(CO)_2]_2}$, in benzene solutions undergoes photochemical reaction to produce rhodium(II) tetraphenylporphyrin, $\mathrm{Rh^{II}TPP}$, which forms its diamagnetic dimer, $\mathrm{[Rh^{II}TPP]_2}$. The quantum yields of the photoreaction depend strongly on the irradiation wavelengths: $\Phi \sim 0$ at $\lambda > 420$ nm, $\Phi = 0.025$ in the range 350 nm $< \lambda <$ 400 nm, and $\Phi = 0.057$ at $\lambda = 300$ nm. The laser photolysis study using the fundamental (694 nm) of a ruby laser and the second (532 nm) and the third (355 nm) harmonics of a Nd-YAG laser revealed that neither the lowest excited singlet nor the triplet state of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ is concerned with the photochemical reaction. Higher excited singlet states, S_n (probably $n > 2$), are assumed to be responsible for the reaction. The homolytic cleavage of one of the Rh–N bonds of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ in S_n is considered to be involved in the reaction pathway.

Introduction

In recent decades, several unusual metalloporphyrins that have two metal ions in a molecule have been detected spectroscopically[1] and sometimes isolated as stable products.[2-5] The X-ray structure analysis carried out for some of these binuclear complexes revealed that one metal ion is located on each side of the porphyrin plane.[6,7] These complexes are expected to show photochemical behavior characteristically different from usual mononuclear metalloporphyrins.

We have carried out systematic studies on the photochemistry of binuclear metalloporphyrins for an understanding of their nature in their electronically excited states. The present paper reports the photochemistry of (μ-tetraphenylporphinato)bis[dicarbonylrhodium(I)] ($\mathrm{TPP[Rh^{I}(CO)_2]_2}$) studied by steady-light and laser-flash photolysis.

Experimental Section

(μ-Tetraphenylporphinato)bis[dicarbonylrhodium(I)] was prepared according to the literature.[3] The absorption peaks of $\mathrm{TPP[Rh^{I}(CO)_2]_2}$ in benzene solution are located at 700, 460, and 370 nm with molar absorption coefficients of 6.0×10^3, 6.45×10^4, and 5.55×10^4 M^{-1} cm^{-1}, respectively. Sample solutions were degassed by freeze–pump–thaw cycles.

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