however, an alternative explanation was sought. Metal ions can act to increase the acidity of the macrocyclic amines, as was noted for certain metal complexes in the presence of the tetraprotonated form of **1**, as cited earlier.[14] Given that pK_{a3} for **1** is between 7 and 8, and that the presence of the electron-withdrawing $-PO_3^{2-}$ portion of the phosphoramidate would certainly make the amidate proton more acidic than the other protonated nitrogens in the macrocycle, it is reasonable to suggest that, at a pH of 5.6, a greater percentage of the phorphoramidate is actually in the deprotonated and unreactive form. This hypothesis is supported by the observed correlation of increased phosphoramidate formation (or stabilization) with increasing effective nuclear charge (or Lewis acidity) of the metal ion Mg(II) < Ca(II) < La(III).

Pyrophosphate Formation. In the presence of metal ions, the formation of pyrophosphate was observed, the net result of the metal ion "regulation". When the pH of a solution of **1**–ATP–Ca(II) was adjusted to 4 to solubilize precipitated calcium salts, pyrophosphate was observed in less than 24 h at room temperature. Without metal ion, pyrophosphate was not observed under similar conditions. The formation of pyrophosphate appears to be contingent upon reaction of the phosphoramide with inorganic phosphate present in solution.[7,8] Thus the increased concentration of the intermediate provided by magnesium(II), calcium(II), and lanthanum(III) promotes the phosphorylation reaction, provided the phosphoramidate is accessible to incoming phosphate. Indeed, the ditopic nature of **1** is such that an additional binding site is available for inorganic phosphate present in solution. The imposed proximity of the two reacting species can be considered as activation toward the transition state. A similar mechanism has been proposed by Hosseini and Lehn in the observation of pyrophosphate formation in the catalysis of acetyl phosphate dephosphorylation by **1**.[7] In that study pyrophosphate formation was inhibited by the addition of anionic species including nucleotides. Thus, removal of the nucleotides competing with incoming phosphate for the macrocyclic cavity by complexation with the metal ion may well be a factor in enhancing the rate of pyrophosphate formation.

Conclusions. In progressing from binary ATP–**1** to a ternary association by the addition of metal ions, a more complex and challenging mechanistic problem is obtained. The broad range of dephosphorylation rates includes both retardation and acceleration depending on the metal ion, as well as stabilization of the phosphoramidate intermediate and pyrophosphate synthesis for magnesium(II), calcium(II), and lanthanum(III). Increases in rate are attributed to the role of the metal ion in "structuring" the ATP molecule for a better fit of the two terminal phosphates in the macrocyclic cavity. Spectroscopic evidence indicates that the macrocycle undergoes considerable conformation changes upon reaction with ATP, which are proposed to result from repulsive interactions between the phosphate and ether oxygen atoms and attraction of the nucleophilic neutral amines by P_γ. The rate retardations observed for zinc(II) and cadmium(II) are primarily attributed to their propensity for complexation with **1**, providing competitive inhibition of the catalytic process. The stabilization of the phosphoramidate intermediate by the magnesium, calcium, and lanthanum ions is probably best explained by deprotonation of the phosphoramidate nitrogen in the presence of the metal ion. The results of complexation studies between the binary macrocycle–polyphosphate and ternary macrocycle–polyphosphate–metal ion systems will be reported in a subsequent paper.

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Registry No. **1**, 43090-52-4; PP, 14000-31-8; PPP, 14127-68-5; ATP, 56-65-5; ADP, 58-64-0; ATPase, 9000-83-3; Mg, 7439-95-4; Ca, 7440-70-2; La, 7439-91-0; Zn, 7440-66-6; Cd, 7440-43-9.

Contribution from the Departments of Chemistry, The University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27514, and University of New Orleans, New Orleans, Louisiana 70148

Binuclear Copper Complexes of Ligands Providing Three Donors to Each Metal Ion

Thomas N. Sorrell,*[1a,b] Chien-Chang Shen,[1b] and Charles J. O'Connor[1c]

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The synthesis of 2,6-bis{[2-(1-pyrazolyl)ethyl]methylamino}-*p*-cresol and its 3-*tert*-butylpyrazole derivative are described. These new chelating agents are able to provide two nitrogen donors to each metal ion in addition to a phenolate group, which bridges the metal atoms. The syntheses of the binuclear Cu(II)–azide and Cu(I)–carbonyl complexes are presented. The copper(II) dimer is diamagnetic at room temperature, and the singlet–triplet transition energy is greater than 2000 cm^{-1}. The Cu(I) dimer reacts with dioxygen irreversibly even with the steric hindrance provided by the *tert*-butyl group.

The synthesis of ligands capable of binding two metal ions in a proximal relationship continues to attract the attention of both organic and inorganic chemists.[2-12] Our interest in this area results from the need for chelates able to bind two copper ions in a manner that mimics the active site in the type III copper proteins, most notably hemocyanin and tyrosinase.[13] While many such ligands exist, very few form stable binuclear copper(I) adducts, a prerequisite for probing reversible binding of dioxygen. We report here the synthesis of two ligands, Hpeac (**1a**) and H(*t*-Bu)peac (**1b**), and their binuclear Cu(II) (**8**) and Cu(I) (**9**) derivatives.

Experimental Section

All reagents and solvents were purchased from commercial sources and used as received. 2,6-Diacetamido-*p*-cresol (**2**) was prepared by the literature method.[2] Melting points were obtained with use of a Fisher–

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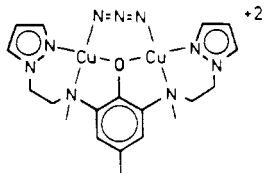

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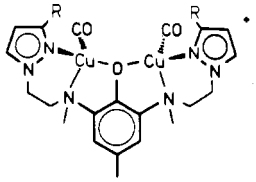

9a, R = H
b, R = *t*-Bu

Johns apparatus and are uncorrected. Flash chromatography was performed according to the general procedure of Still.[14] Analytical thin-layer chromatography was run with Analtech precoated (0.25 mm) silica gel plates. Microanalyses were performed by MicAnal Laboratories, Inc., Tucson, AZ.

^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer at 250.13 MHz using $CDCl_3$ as the solvent. All chemical shifts are reported in ppm relative to an internal standard of tetramethylsilane. Infrared spectra were recorded on a Beckman IR 4250 spectrophotometer, and peaks are reported in cm^{-1}. Absorption spectra were recorded on a Hewlett-Packard 8540A diode array spectrophotometer, and absorption bands are reported in nm with the extinction coefficient in M^{-1} cm^{-1} given in parentheses. Magnetic susceptibility studies were done as described previously.[2] The data were corrected for the diamagnetism of the bucket at each temperature, and then for the diamagnetism of the ligand, by using Pascal's constants.

4-Methyl-2,6-bis(*N*-methylacetamido)anisole (3). A magnetically stirred mixture of 10 g (22 mmol) of **2** and 5.4 g (230 mmol) of sodium hydride in 175 mL of *N,N*-dimethylformamide (DMF) was heated at 60 °C under N_2 for 3 h. The resultant mixture was treated with 64 g (450 mmol) of iodomethane and stirred at 50 °C. After 24 h, 32 g (225 mmol) of iodomethane was added. After another 24 h at 50 °C, the reaction was quenched by the addition of 95% EtOH. Volatiles were removed at reduced pressure, and 50 mL of water was added to the residue. The product was extracted with three 50-mL portions of chloroform. The combined organic extracts were successively washed with water and brine, dried over anhydrous sodium sulfate, and concentrated to give 11 g of yellowish solid. An analytical sample was further purified by flash chromatography with 1:4 hexanes–ethyl acetate as the eluent (R_f 0.32), and white crystalline solid **3** was obtained; mp 132.5–133.5 °C. IR (KBr): 1660 (C=O); 1235, 995 (C—O). ^{1}H NMR: 1.86, 1.91 (2 s, 6 H, $NCOCH_3$); 2.36 (s, 3 H, $ArCH_3$); 3.23, 3.27 (2 s, 6 H, $ArNCH_3$); 3.72 (s, 3 H, $ArOCH_3$); 7.00, 7.01 (2 s, 2 H, ArH). Anal. Calcd for $C_{14}H_{20}N_2O_3$: C, 63.62; H, 7.63; N, 10.60. Found: C, 63.84; H, 7.70; N, 10.49.

4-Methyl-2,6-bis(methylamino)anisole (4). A magnetically stirred solution of 6.22 g (23.5 mmol) of crude **3**, 70.0 g (1.25 mol) of potassium hydroxide, 70 mL of methanol, and 15 mL of water was heated under reflux for 24 h. Methanol was removed at reduced pressure, and the product was extracted into five 40-mL portions of benzene. The combined green-blue extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under vacuum. The crude mixture was purified by flash chromatography with 5:1 hexanes–ethyl acetate as the eluent (R_f 0.35). After the evaporation of solvents, 3.03 g (71%) of the product **4** was obtained as a yellow solid. Recrystallization from hexanes gave colorless crystals, mp 87.5–88 °C. IR (KBr): 3435, 3380 (N–H). ^{1}H NMR: 2.26 (s, 3 H, $ArCH_3$); 2.82 (s, 6 H, $ArNCH_3$); 3.66 (s, 3 H, $ArOCH_3$); 4.01 (s, 2 H, ArNH); 5.93 (s, 2 H, ArH). Anal. Calcd for $C_{10}H_{16}N_2O$: C, 66.64; H, 8.95; N, 15.54. Found: C, 66.88; H, 9.70; N, 15.38.

4-Methyl-2,6-bis[(2-hydroxyethyl)methylamino]anisole (5). A solution of 3.03 g (16.8 mmol) of **4** and 15 mL of liquid ethylene oxide (cooled to −10 °C) in 40 mL of 1:1 acetic acid–water was stirred at ambient temperature under N_2. After 21 h, the solution was concentrated under reduced pressure, and 10% sodium hydroxide was added until the solution was basic. The resultant mixture was extracted with two 40-mL portions of benzene. The combined extracts were washed with water and brine, dried over anhydrous sodium sulfate, and concentrated. The product **5** was isolated by flash chromatography with 1:2 hexanes–ethyl acetate as the eluent (R_f 0.26) to afford 3.12 g (69%) of a viscous pale yellow liquid. IR (neat): 3395 (O–H); 1030 (C–OH). ^{1}H NMR: 2.27 (s, 3 H, $ArCH_3$); 2.79 (s, 6 H, $ArNCH_3$); 2.96 (s, 2 H, OH); 3.15 (t, J = 5.5 Hz, 4 H, $ArNCH_2$); 3.69 (t, J = 5.5 Hz, 4 H, OCH_2); 3.75 (s, 3 H, $ArOCH_3$); 6.56 (s, 2 H, ArH). Anal. Calcd for $C_{14}H_{24}N_2O_3$: C, 62.66; H, 9.01; N, 10.44. Found: C, 62.03; H, 9.18; N, 10.27.

4-Methyl-2,6-bis[(2-chloroethyl)methylamino]anisole (6). To a magnetically stirred solution of 12.0 g of thionyl chloride in 60 mL of methylene chloride was added a solution of 2.76 g (10.0 mmol) of **5** in 20 mL of methylene chloride. After 14 h, the solution was poured onto 80 g of ice to quench the reaction and treated dropwise with 10 N sodium hydroxide until basic. The methylene chloride layer was separated from the aqueous layer, which was extracted with 50 mL of additional methylene chloride. The combined organic extracts were washed with water and brine, dried over anhydrous sodium sulfate, and concentrated. Flash chromatography with 20:1 hexanes–ethyl acetate as the eluent (R_f 0.39) afforded 2.57 g (84%) of the product **6** as a light yellow solid, mp 57.5–58.5 °C. ^{1}H NMR: 2.25 (s, 3 H, $ArCH_3$); 2.85 (s, 6 H, $ArNCH_3$); 3.45 (t, J = 7 Hz, 4 H), 3.64 (t, J = 7 Hz, 4 H, $ArNCH_2CH_2Cl$); 3.70 (s, 3 H, $ArOCH_3$); 6.40 (s, 2 H, ArH). Anal. Calcd for $C_{14}H_{22}Cl_2N_2O$: C, 55.08; H, 7.27; N, 9.18. Found: C, 55.16; H, 7.27; N, 9.14.

4-Methyl-2,6-bis{[2-(1-pyrazolyl)ethyl]methylamino}anisole (7a). A magnetically stirred mixture of 0.630 g (9.25 mmol) of pyrazole and 0.297 g (12.4 mmol) of sodium hydride in 27 mL of DMF was heated at 60 °C under N_2. After 1 h, a solution of 1.14 g (3.73 mmol) of **6** in 10 mL of DMF was added to the sodium pyrazolate solution. Twenty-one hours later, the reaction was quenched by the addition of 95% EtOH. Volatiles were removed under reduced pressure, and 30 mL of water was added to the residue. The product was extracted into two 40-mL portions of benzene. The combined organic extracts were washed with water and brine, dried over anhydrous sodium sulfate, and concentrated to give 1.24 g (90%) of the viscous yellow liquid **7a**. An analytical sample was further purified by flash chromatography with 1:1 hexanes–ethyl acetate as the eluent (R_f 0.36). IR (neat): 3110, 3135 (pyrazolyl C–H). ^{1}H NMR: 2.244 (s, 3 H, $ArCH_3$); 2.68 (s, 6 H, $ArNCH_3$); 3.56 (s, 3 H, $ArOCH_3$); 3.58 (t, J = 6.5 Hz, 4 H, $ArNCH_2$); 4.30 (t, J = 6.5 Hz, 4 H, CH_2Pz); 6.20 (t, J = 2 Hz, 2 H, pyrazolyl C4–H); 6.33 (s, 2 H, ArH); 7.33 (d, J = 2 Hz, 2 H, pyrazolyl C5–H); 7.49 (d, J = 2 Hz, 2 H, pyrazolyl C3–H). Anal. Calcd for $C_{20}H_{28}N_6O$: C, 65.19; H, 7.66; N, 22.81. Found: C, 64.76; H, 7.62; N, 22.32.

2,6-Bis{[2-(1-pyrazolyl)ethyl]methylamino}-*p*-cresol (Hpeac, 1a). A magnetically stirred mixture of 3.52 g (9.55 mmol) of **7a** and 1.73 g (24.7 mmol) of sodium methylmercaptide in 70 mL of DMF was heated at reflux under N_2. After 2 h, the mixture was evaporated to dryness at reduced pressure and 50 mL of water was added to the residue. After neutralization with 5% hydrochloric acid, the product was extracted into two 70-mL portions of benzene. The combined extracts were washed with water and brine, dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by flash chromatography with 2:3 hexanes–ethyl acetate as the eluent (R_f 0.33) to afford 3.17 g (94%) of a viscous yellow liquid, which was stored under N_2 since it turns blue in the air after a few days. IR (neat): 3275 (broad, O–H). ^{1}H NMR: 2.24 (s, 3 H, $ArCH_3$); 2.65 (s, 6 H, $ArNCH_3$); 3.45 (t, J = 6 Hz, 4 H, $ArNCH_2$); 4.24 (t, J = 6 Hz, 4 H, CH_2Pz); 6.22 (t, J = 2 Hz, 2 H, pyrazolyl C4–H); 6.55 (s, 2 H, ArH); 7.35 (d, J = 2 Hz, 2 H, pyrazolyl C5–H); 7.43 (s, 1 H, ArOH); 7.52 (d, J = 2 Hz, 2 H, pyrazolyl C3–H). Anal. Calcd for $C_{19}H_{26}N_6O$: C, 64.38; H, 7.39; N, 23.71. Found: C, 64.00; H, 7.48; N, 23.47.

3-*tert*-Butylpyrazole. Under a nitrogen atmosphere, a mixture of 37.5 g (0.438 mol) of pinacolone and 31.5 g (0.381 mol) of ethyl formate was added to a slurry of 19.5 g (0.381 mol) of sodium methoxide in 750 mL of anhydrous ether. The reaction mixture was heated under reflux for 6 h, cooled, and extracted with three 100-mL portions of water. To the sodium salt of 1-hydroxy-4,4-dimethyl-1-pentene-3-one in the aqueous extracts was added 29.3 g (0.375 mol) of a 64% aqueous solution of hydrazine hydrate. The solution was slowly acidified with concentrated sulfuric acid. A yellow oil separated, which subsequently redissolved as the pH of the solution changed from neutral to acidic. The solution was readjusted to pH 7 with aqueous sodium hydroxide, and 3-*tert*-butylpyrazole was extracted with three 100-mL portions of ether. The combined organic phase was dried over $MgSO_4$, filtered, and concentrated to give 20.5 g (44%) of product. Small amounts of the compound were distilled by bulb-to-bulb distillation at reduced pressure just prior to use. ^{1}H NMR: 1.35 (s, 9 H, t-C_4H_9); 6.1 (d, 1 H, J = 2 Hz, pyrazole C4–H); 7.5 (d, 1 H, J = 2 Hz, pyrazole C5–H).

4-Methyl-2,6-bis{[2-(3-*tert*-butyl-1-pyrazolyl)ethyl]methylamino}anisole (7b). A magnetically stirred mixture of 4.14 g (33.3 mmol) of 3-*tert*-butylpyrazole and 1.07 g (44.6 mmol) of sodium hydride in 150 mL of DMF was heated at 60 °C under N_2. After 1 h, a solution of 2.55 g (8.35 mmol) of **6** in 20 mL of DMF was added to the sodium 3-*tert*-butylpyrazolate solution and stirred for 46 h at 60 °C. The reaction was quenched by the addition of 95% EtOH. Volatiles were removed under reduced pressure, and 50 mL of water was added to the residue. The product was extracted into two 80-mL portions of benzene. The combined organic extracts were washed with water and brine, dried over anhydrous sodium sulfate, and concentrated under vacuum. The product (**7b**) was isolated by flash chromatography with 5:1 hexanes–ethyl acetate as the eluent (R_f 0.30) to afford 3.07 g (77%) of a viscous light yellow

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liquid. IR (neat): 3100, 3110 (pyrazolyl C–H). ^{1}H NMR: 1.30 (s, 18 H, t-C_4H_9); 2.23 (s, 3 H, $ArCH_3$); 2.63 (s, 6 H, $ArNCH_3$); 3.56 (s, 3 H, $ArOCH_3$); 3.56 (t, J = 6 Hz, 4 H, $ArNCH_2$); 4.22 (t, J = 6 Hz, 4 H, CH_2 attached to the pyrazolyl ring); 6.03 (d, J = 2 Hz, 2 H, pyrazolyl C4–H); 6.31 (s, 2 H, ArH); 7.18 (d, J = 2 Hz, 2 H, pyrazolyl C5–H). Anal. Calcd for $C_{28}H_{44}N_6O$: C, 69.96; H, 9.16; N, 17.48. Found: C, 70.04; H, 9.32; N, 17.33.

2,6-Bis[[2-(3-*tert*-butyl-1-pyrazolyl)ethyl]methylamino]-*p*-cresol (H-(*t*-Bu)peac, 1b). A magnetically stirred mixture of 2.57 g (5.35 mmol) of **7b** and 1.54 g (22.0 mmol) of sodium methylmercaptide in 120 mL of DMF was heated at reflux under N_2. After 4 h, the mixture was evaporated to dryness at reduced pressure, and 70 mL of water was added to the residue. After neutralization with 5% hydrochloric acid, the product was extracted into two 120-mL portions of benzene. The combined extracts were washed with brine, dried over anhydrous sodium sulfate, and concentrated under vacuum. The crude product was purified by flash chromatography with 5:1 hexanes–ethyl acetate as the eluent (R_f 0.21) to afford 1.69 g (68%) of the light yellow solid **1b**, mp 63–65 °C, which was stored under N_2. IR (KBr): 3310 (O–H). ^{1}H NMR: 1.31 (s, 18 H, t-C_4H_9); 2.23 (s, 3 H, $ArCH_3$); 2.59 (s, 6 H, $ArNCH_3$); 3.41 (t, J = 6 Hz, 4 H, $ArNCH_2$); 4.18 (t, J = 6 Hz, 4 H, CH_2 attached to the pyrazolyl ring); 6.05 (d, J = 2 Hz, 2 H, pyrazolyl C4–H); 6.52 (s, 2 H, ArH); 7.24 (d, J = 2 Hz, 2 H, pyrazolyl C5–H); 7.62 (br s, 1 H, ArOH). Anal. Calcd for $C_{27}H_{42}N_6O$: C, 69.49; H, 9.07; N, 18.01. Found: C, 70.02; H, 9.13; N, 17.75.

(μ-1,3-Azido){2,6-bis[(2-(1-pyrazolyl)ethyl)methylamino]-*p*-cresolato}dicopper(II) Diperchlorate–Methanol (Cu_2(peac)$N_3(ClO_4)_2$·CH_3OH, 8). *Warning! Although we have experienced no problem with the handling of this compound, azide complexes and perchlorate salts should be prepared on a small scale and handled very carefully to minimize the risk of explosion.* A solution of 0.32 g (0.9 mmol) of Hpeac in 55 mL of methanol was treated with 0.68 g (1.8 mmol) of $Cu(ClO_4)_2$·$6H_2O$. To the green solution was added a solution of 0.06 g (0.9 mmol) of sodium azide in 2 mL of water. The homogeneous dark green solution was treated with 100 mL of isopropyl alcohol and allowed to stand overnight. The resulting dark green crystals were washed with isopropyl alcohol and dried; yield 0.60 g (88%). IR (KBr): 2040 (N=N=N). UV–vis (CH_3OH): 284 (10 500); 355 (8000); 430 (sh); 620 (1800). Anal. Calcd for $C_{20}H_{29}Cl_2Cu_2N_9O_{10}$: C, 31.88; H, 3.88; N, 16.72; Cl, 9.40. Found: C, 31.70; H, 3.78; N, 16.32; Cl, 8.96.

{2,6-Bis[(2-(1-pyrazolyl)ethyl)methylamino]-*p*-cresolato}dicarbonyldicopper(I) Tetrafluoroborate (Cu_2(peac)$(CO)_2BF_4$, 9a). Under a CO atmosphere, 0.42 g (1.2 mmol) of Hpeac dissolved in 10 mL of methanol was treated with 0.05 g (1.2 mmol) of KH. To that solution was added a solution of 0.75 g (2.4 mmol) of $Cu(CH_3CN)_4BF_4$ dissolved in 10 mL of methanol under CO. The solvent was evaporated under a stream of CO, a pale yellow residue dissolved in a minimum of methanol, and the solution filtered under positive CO pressure. When it stood at −20 °C, the solution deposited a small amount of white crystals. These were separated by decantation of the solvent and then dried under a stream of CO. IR (CH_2Cl_2): 2074 (C=O). Anal. Calcd for $C_{21}H_{25}BCu_2F_4N_6O_3$: C, 40.46; H, 4.04; N, 13.48. Found: C, 40.74; H, 4.00; N, 13.52. This complex can be stored under N_2 without decomposition.

{2,6-Bis[(2-(3-*tert*-butyl-1-pyrazolyl)ethyl)methylamino]-*p*-cresolato}dicarbonyldicopper(I) Tetrafluoroborate (Cu_2[(*t*-Bu)peac]$(CO)_2BF_4$, 9b). This compound was prepared as above from H(*t*-Bu)-peac to afford a light yellow solid. It can be stored under N_2 without any decomposition. IR (KBr): 2075 (C=O). Anal. Calcd for $C_{29}H_{41}BCu_2F_4N_6O_3$: C, 47.35; H, 5.62; N, 11.42. Found: C, 47.22; H, 5.64; N, 11.22.

Results and Discussion

On the basis of the spectroscopic properties of the binuclear active site in hemocyanin,[13] available before the recently reported crystal structure,[15] we sought to prepare a ligand that was capable of providing only three donors to each copper atom with the further constraint that one of the donors, a phenolate ion, would bridge the two metal ions. Many such ligands have been reported in the literature,[3-6] and their Cu(II) complexes have been studied extensively to probe the magnetic interactions between the d^9 metal ions (vide infra). In every case, the ligand is prepared by condensation of an amine with 2,6-diformylphenol; in some instances, the resulting Schiff-base product is further treated to produce the saturated ligand.[3c,5a]

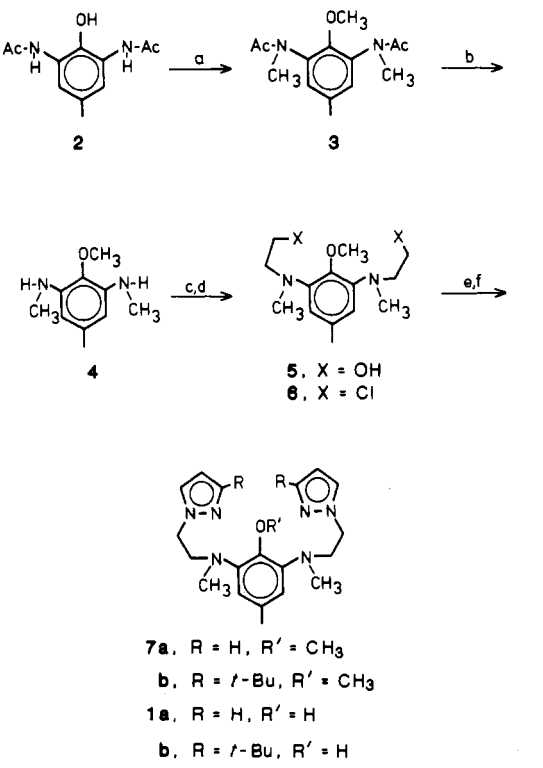

Figure 1. Reaction scheme for the synthesis of the binucleating ligands: (a) NaH, DMF, CH_3I; (b) KOH, CH_3OH, H_2O; (c) ethylene oxide, HOAc, H_2O; (d) $SOCl_2$; (e) sodium pyrazolate or sodium 3-*tert*-butylpyrazolate, DMF; (f) $NaSCH_3$, DMF.

The synthesis of Hpeac is modeled after the preparation of Hbpeac, the analogue having four side-arm pyrazolyl groups.[2] The route shown in Figure 1 begins with 2,6-diacetamido-*p*-cresol (**2**), which is completely methylated by using a large excess of methyl iodide and sodium hydride.[16] The methylated amide **3** is saponified to the amine and hydroxyethylated by using ethylene oxide. Conversion of the diol to the dichloride followed by displacement with either pyrazolate ion or its 3-*tert*-butyl derivative gives the protected ligands **7a** and **7b**. For the reaction with 3-*tert*-butylpyrazolate, we find that the steric bulk of the *tert*-butyl group prevents the nitrogen atom in the 2-position from participating in the substitution reaction. The NMR spectrum shows no evidence of mixed substitution products. The anisole derivatives (**7**) are smoothly demethylated by using $NaSCH_3$ in refluxing DMF[17] to provide the final products, which are moderately air-sensitive and must be stored under an inert atmosphere.

The ligand Hpeac (**1a**) reacts with $Cu(ClO_4)_2$ and azide ion in aqueous methanol to give the binuclear Cu(II) dimer in which N_3^- likely bridges the copper atoms in a 1,3-fashion (**8**). We base this conclusion on the similarity between the spectra for **8** and Cu(bpeac)$(N_3)^{2+}$ (**10**).[2] In the electronic absorption spectrum for each, there is a broad band with a maximum near 360 nm (**8**, 355 nm; **10**, 367 nm) and a shoulder at lower energy (**8**, 430 nm; **10**, 444 nm) that we assign as azide-to-copper CT transitions.[2] Likewise, the N_3^- stretch in the infrared region occurs at similar frequencies (**8**, 2040 cm^{-1}; **10**, 2032 cm^{-1}). Thus, even in the absence of a crystal structure for **8**, we can be reasonably certain that the azide ion forms a μ-1,3-bridge between the copper(II) ions. It is worth noting that the spectra for **8** are also similar to

(15) Linzen, B.; Soeter, N. M.; Riggs, A. F.; Schneider, H.-J.; Schartau, W.; Moore, M. D.; Yokota, E.; Behrens, P. Q.; Nakashima, H.; Takagi, T.; Nemoto, T.; Vereijken, J. M.; Bak, H. J.; Beintema, J. J.; Volbeda, A.; Gaykema, W. P. J.; Hol, W. G. J. *Science (Washington, D.C.)* **1985**, *229*, 519–524.

(16) If only a small excess of alkylating agent is used, then the dimethylated compound, having one of the amide groups unchanged, is a byproduct. We chose a methyl group to protect the phenol oxygen only after the benzyl moiety proved unsuitable. In the latter case, the benzyl group apparently migrates from the phenol oxgyen to one of the amino nitrogen atoms after the hydrolysis of the amide groups.

(17) Fieser, M.; Fieser, L. F. *Reagents for Organic Synthesis*; Wiley: New York, 1974; Vol. 4, p 465.

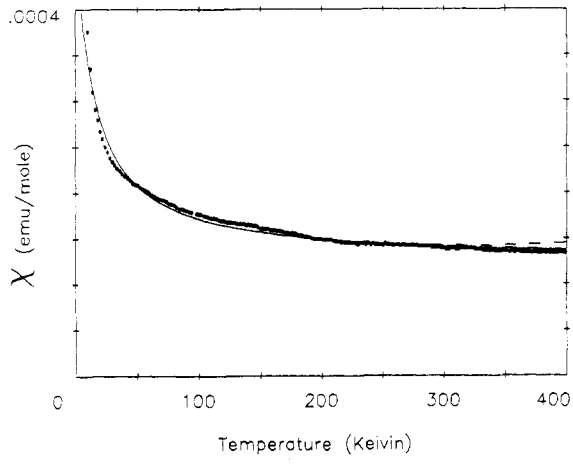

Figure 2. Plot of the corrected molar magnetic susceptibility (in cgsu) for $Cu_2(peac)(N_3)(ClO_4)_2 \cdot CH_3OH$ as a function of temperature (in K). The solid line represents the result of the least-squares fitting of the Curie–Weiss law to the data. The dashed curve represents the calculation for a singlet–triplet splitting of 2000 cm^{-1} as described in the text.

those observed for azidomethemocyanin from *Busycon*.[13] The absorption spectrum for the latter displays maxima assigned as the azide-to-Cu(II) CT bands at 380 and 430 (shoulder) nm, and the infrared spectrum has a strong band attributed to the azide stretch at 2042 cm^{-1}.

The magnetic susceptibility data plotted in Figure 2 show that the copper atoms are very strongly antiferromagnetically coupled and provide further evidence for the proposed structure. The solid line drawn through the points is a fit of the data to be Curie–Weiss law corrected for temperature-independent paramagnetism (TIP):

$$\chi = \frac{C}{T - \theta} + \text{TIP} \qquad (1)$$

The values obtained from this fit are $C = 0.0035$ (per Cu), $\theta = -24$ K, and TIP = 0.000059 (per Cu). The value for TIP is exactly that expected for a Cu(II) ion; however, the value of the Curie constant is only about 0.4% of the value expected for paramagnetic copper(II) ions. These data are readily interpreted by assuming that the copper(II) ions of the binuclear complex are very strongly antiferromagnetically coupled and that the small paramagnetic component results from a 0.4% monomeric impurity.

Since the antiferromagnetic component of the magnetic susceptibility data has no characteristic shape to fit, we can only estimate the lower limit of the singlet–triplet separation. The magnetic behavior of a Cu(II) dimer is given by eq 2. If we fix

$$\chi = \frac{2Ng^2\mu_\beta^2}{kT} \frac{e^x}{1 + 3e^x} \qquad (2)$$

the g value (=2.15) and the value for the singlet–triplet separation ($2J = 2000$ cm^{-1}) but allow the parameters for percent monomeric impurity and TIP to vary, we obtain the dashed curve in Figure 2 when the impurity is 0.4% and TIP = 0.000066. Both of these values are consistent with those obtained from the Curie–Weiss analysis above. We therefore estimate 2000 cm^{-1} as the lower limit of the singlet–triplet splitting for this binuclear complex.

Most of the previously reported binuclear compounds having four-coordinate copper(II) ions[3-6] display some degree of antiferromagnetic coupling, which is mediated either through the phenolate bridge or through another atom (usually a halide or pseudohalide ion) that bridges between the metal centers. In none of those cases, however, does the magnitude of antiferromagnetic coupling approach that observed for the azide derivative of methemocyanin, which is diamagnetic at room temperature. On the other hand, the results for **8** are similar to those obtained both for **10**, in which the magnetic coupling between the copper ions is 1800 cm^{-1},[2] and for azidomethemocyanin. We can conclude that, as expected, the absence of axial ligands to copper has little effect on the antiferromagnetic coupling which must operate through the $d_{x^2-y^2}$ orbitals in the plane of the phenolate and azide bridging ligands. The biological implication of this result is no surprise, namely that we cannot distinguish between four- and five-coordination for the oxidized derivatives of hemocyanin simply on the basis of magnetic susceptibility studies.

Previous attempts to prepare copper(I) derivatives of binuclear ligands of the type described herein (N_4ArO^- donor set) have been generally unsuccessful. The normal course of the reaction is disproportionation. Gagnè[4] was able to eliminate this problem by adding an additional ligand, such as pyrazolate ion, that could bridge between the metal ions and stabilize the Cu(I) sites. Although this approach was successful, the resulting complex lacked a cavity in which dioxygen could bind to the two metal ions. Urbach[5b] attempted to isolate the Cu(I) complex by adding CO, which is known to stabilize the reduced valence of copper. In that case, only an unstable mononuclear Cu(I) complex could be obtained.

We also tried to prepare the binuclear three-coordinated copper(I) species of our ligands but encountered only disproportionation products. However, stirring the potassium salt of each ligand with $Cu(CH_3CN)_4BF_4$ in methanol under carbon monoxide gives the copper(I) dimers $Cu_2(peac)(CO)_2BF_4$ and $Cu_2[(t\text{-}Bu)peac](CO)_2BF_4$. Both products are stable indefinitely under either CO or N_2 in the solid state. The elemental analysis for each complex is consistent with the presence of two copper ions and one BF_4^- counterion; the infrared spectrum shows a strong CO stretch at 2075 cm^{-1}. Given the known propensity of copper(I) carbonyl adducts to adopt a tetrahedral geometry, we are therefore confident of the structure illustrated in the introduction of this paper.

Despite the presence of a cavity between the metal ions that would result if CO were lost from copper(I) complex, neither **9a** nor **9b** forms a dioxygen adduct, even at low temperature. Reaction with dioxygen in CH_3CN over the temperature range −40 to +25 °C results in complete oxidation of the copper(I) ions to give greenish products similar to those observed for $Cu_2(bpeac)^+$.[18] We have not been able to characterize the products in either case, but the stoichiometry of the reaction and insolubility of the product suggest that an oligomeric μ-oxo species is formed.

The low-temperature absorption spectra for the reaction between **9b** and O_2 does show clean isosbestic behavior during the first several minutes of the reaction. Moreover, the reaction stoichiometry, determined by manometric uptake of dioxygen at −35 °C, is 2 molecules of **9b** per molecule of O_2 (4 Cu/O_2), signifying that a four-electron reduction of dioxygen occurs. The results for the oxygenation of **9a** are not as clean, and only about 28% of the theoretical amount of O_2 (assuming 1 O_2/Cu dimer) is absorbed by acetonitrile solutions of **9a** even at low temperature (−35 °C). We suggest that **9a** must decompose in solution by another pathway, perhaps by dissociation of CO followed by disproportionation. The *tert*-butylpyrazolyl group in **9b** may stabilize the Cu(I) complex so that the decarbonylated form is longer lived and can react with dioxygen before it disproportionates, resulting in a cleaner reaction.[19]

In summary, we have prepared two new ligands that are able to form stable binuclear Cu(II) and Cu(I) complexes. The μ-azido complex **8** is the first diamagnetic complex having four-coordinate Cu(II) ions bridged by a phenolate ion. The Cu(I) carbonyl adducts are the first stable binuclear species of the type having an (N_2ArO^-) donor set for each copper(I) ion.

Acknowledgment is made to the National Science Foundation for support of this research.

Supplementary Material Available: A table of magnetic susceptibility data for compound **8** (2 pages). Ordering information is given on any current masthead page.

(18) Sorrell, T. N.; Borovik, A. S. *J. Chem. Soc., Chem. Commun.* **1984**, 1489–1490.

(19) Note that the *tert*-butyl groups do not *prevent* the reaction of the Cu(I) ions with O_2 in **9b**, in contrast to the case of $Cu_2[(t\text{-}Bu)_4bpeac]^+$, which is inert to O_2 in acetonitrile, even at room temperature: Sorrell, T. N. In *Biological & Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1986; pp 41–55.