Synthesis and Characterization of Copper(II) Complexes of New Tripodal Polyimidazole Ligands

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Several copper(II) complexes containing new tripodal polyimidazole ligands have been synthesized and characterized by X-ray crystallography, UV–vis and EPR spectroscopies, and cyclic voltammetry. The tripodal polyimidazole ligands have been prepared in good yields and characterized by ^1H and ^{13}C NMR and mass spectrometry. X-ray crystallographic parameters for the copper(II) compounds are as follows: compound **8**, $C_{15}H_{21}N_7PClF_6Cu$, 543.34 g/mol, monoclinic space group ($P2_1/c$), a = 16.585(3) Å, b = 12.570(3) Å, c = 10.540(3) Å, β = 105.34(2)°, V = 2118.8 Å^3, Z = 4, 3042 independent reflections with $I > 3\sigma|I|$ to a maximum 2θ scan of 50°, R = 0.040, R_w = 0.039; compound **9**, $C_{15}H_{21}N_7PClF_6Cu$, 543.34 g/mol, orthorhombic space group (*Pbca*), a = 16.487(5) Å, b = 16.246(5) Å, c = 16.555(5) Å, V = 4434.1 Å^3, Z = 8, 2240 independent reflections with $I > 3\sigma|I|$ to a maximum 2θ scan of 50°, R = 0.075, and R_w = 0.057. Both compounds have distorted trigonal bipyramidal structures. Three imidazole nitrogen atoms of each tripod occupy equatorial positions of the trigonal bipyramid, while the amine nitrogen atom and chlorine atom occupy apical sites. In both complexes the imidazole pendants are twisted from the chelate planes with torsion angles ranging from 6.7 to 22°. The Cu–N(amine) bond length in compound **8** is 0.023 Å longer than the Cu–N(amine) bond length in compound **9**. The EPR spectral data for both compounds are consistent with the retention of the solid-state structure in frozen DMF/MeOH (1:1) solution. The UV–vis spectrum of compound **8** is red-shifted relative to compound **9**, indicating that the corresponding tripod ligand in **8** is a weaker field ligand. Both compounds display quasireversible one-electron redox behavior in acetonitrile. The $E_{1/2}$ values for compound **8** and **9** are –0.193 and –0.225 V *vs* Ag/AgCl, respectively. The redox potentials of **8** and **9** are shifed cathodically compared to a related copper(II) complex, $[Cu(TMIMA)Cl]^+$ (TMIMA = tris((1-methylimidazol-2-yl)methyl)amine), which contain only 2-substituted 1-methylimidazole pendants.

Introduction

Histidine plays an important role in stabilizing the active sites of a number of metalloproteins. In particular, copper proteins such as azurin,[1,2] plastocyanin,[3,4] hemocyanin,[5–8] and tyrosinase[8–11] are known to contain several imidazole ligands per copper center. Azurin and plastocyanin contain a single copper(II) center coordinated to two histidine imidazole and two sulfur ligands in a distorted tetrahedral arrangement. Hemocyanin (Hc) and tyrosinase, on the other hand, contain two copper centers per active site unit and are thought to have at least two imidazole ligands per metal center. The X-ray crystal structure of deoxy Hc has revealed that both Cu$_I$ centers are bonded to three imidazole ligands and that the metal ions are not bridged by an endogenous ligand. The structure of oxyHc from *Limulus* has been determined to have a μ-η^2:η^2 peroxo-bridged structure with three histidine ligands per copper(II) center.[12,13] Recent inorganic modeling studies by Karlin,[14] Kitajima,[13,15–19] and Solomon[20,21] have helped clarify the mode of binding and electronic properties of Cu(II)–peroxide complexes. In general these studies have used pyridine, pyrazole, and benzimidazole ligands to model the histidine residues present in copper proteins. Only a few studies however have focused on the role of imidazole ligands in the O_2

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chemistry of copper.[22-25] As a result, little is known of the special role histidine plays in "fine-tuning" the electronic properties of metalloproteins.

In a previous study,[26] we established that tetradentate tripodal ligands containing 2-substituted pyridine and 1-methylimidazole pendants display different σ and π bonding properties and thus were useful in probing the effect of ligand donor type on the structural, electronic, and redox properties of pentacoordinate copper(II) complexes. We have extended our initial study to include ligands that contain both 2- and 4-substituted imidazole pendants. Imidazole ligands functionalized at the 4-position of the ring are of biological relevance because they are structurally more analogous to histidine. In this study, we describe the results from the synthesis and characterization of two new polyimidazole tripods and the crystal structures, electronic spectroscopies, and redox properties of their copper(II) complexes.

Experimental Section

All reagents and solvents used in this study were commercially available and were used as received. Solvents were either of reagent or spectroscopic grade and were dried by conventional procedures prior to use. 4(5)-(Hydroxymethyl)imidazole hydrochloride,[27] 2-(aminomethyl)-1-methylimidazole dihydrochloride, and bis((1-methylimidazol-2-yl)methyl)-amine (BMIMA)[28] were prepared by following previously reported procedures. Elemental analyses were performed by Midwest Analytical, Inc., Indianapolis, IN.

Ligand Synthesis. 4-(Hydroxymethyl)-1-methylimidazole Picrate (1).[29] Compound 1 was prepared by a modification of a previously reported procedure. A mixture of 14.561 g of 4(5)-(hydroxymethyl)-imidazole [27] and 3.6 g of sodium were combined with 150 mL of dry 2-propanol in a round-bottom flask under nitrogen. This mixture was stirred for 36 h after which time a solution of 9.25 mL of methyl iodide in 70 mL of 2-propanol was added and the mixture was stirred for 9 days. The solvent was removed *in vacuo* to obtain an oil containing a large amount of solid. The reacting mixture was transferred to a small flask and vacuum distilled (<1 Torr, bp ≤ 130 °C) giving 11.608 g of a nearly colorless oil. ^{1}H NMR studies revealed this oil to be a mixture of methylated 4- and 5-(hydroxymethyl)imidazole (~70 and 30%, respectively). A stock solution of 25 g of picric acid in 500 mL of absolute ethanol was prepared and used to separate the isomers. The oil obtained above was first dissolved in 58 mL of absolute ethanol. Then 5 mL of the oil solution was combined with 20 mL of the picric acid solution immediately forming a thick yellow precipitate that was quickly filtered, rinsed with ethanol, and then transferred to another container. In an identical fashion, the remainder of the stock solution of the oil was combined in 5-mL portions with a solution of picric acid resulting in the isolation of 25.905 g of picrate salt. The ^{1}H NMR spectrum of the yellow precipitate revealed the solid to be an mixture containing approximately a75/25 ratio of methylated 4- and 5-(hydroxymethyl)imidazole picrate. Recrystallization of the compound using 1.2 L of absolute ethanol affords 18.102 g (35.7%) of the hydrated 4-(hydroxymethyl)-1-methylimidazole picrate: mp 153.5–154.5 °C; ^{1}H NMR (d_6-DMSO, δ) 3.81 (s, 3H, ImN–CH_3), 4.48 (s, 2H, Im–CH_2–N), 7.54 (s, 1H, ImC(5)–H), 8.59 (s, 2H, Ar H), 8.98 (s, 1H, ImC(2)–H). The 5-substituted picrate precipitates from solution upon standing in the refrigerator overnight.

4-(Hydroxymethyl)-1-methylimidazole Hydrochloride (2). The procedure of Totter and Darby was adapted for this conversion.[27] A 4.111-g sample of 4-(hydroxymethyl)-1-methylimidazole picrate was stirred in a mixture of 10 mL of water, 4 mL of concentrated HCl, and 20 mL of benzene in a 125-mL Erlenmeyer flask. Upon gently warming the mixture, the solid was observed to dissolve. The yellow benzene layer was then decanted just before the solution began to boil. The decanted solution contains picric acid which is fairly soluble in hot benzene. The water layer was extracted five times with 13-mL portions of benzene, each time stirring the mixture just to the boiling point before decanting. The fourth and fifth extracts were nearly colorless. The combined benzene extracts were evaporated carefully (behind a blast shield) to obtain 2.768 g of picric acid, which was the theoretical amount. To the yellow aqueous solution was added 0.12 g of activated charcoal, and the mixture was allowed to cool while stirring for about 2 h. Then the mixture was filtered, the solvent removed *in vacuo*, and the resulting solid dissolved in 5 mL of hot ethanol. The yellowish solution was cooled to −20 ° C overnight, whereupon a large amount of white solid was obtained. To this mixture was added 30 mL of diethyl ether, and the solution was gently swirled and then filtered in an inert-atmosphere glovebox. The resulting precipitate was then washed with diethyl ether and dried *in vacuo*. A total of 1.790 g of white solid was obtained (100%): mp 120–123 °C; ^{1}H NMR (d_6-DMSO, δ) 3.82 (s, 3H, ImN–CH_3), 4.47 (s, 2H, Im–CH_2–N), 7.55 (s, 1H, ImC(5)–H), 9.10 (s, 1H, ImC(2)–H); ^{13}C NMR (d_6-DMSO, δ) 35.44 (ImN–CH_3), 53.19 (Im–CH_2–N), 119.75 (ImC-(5)), 134.26 (ImC(2)), 135.30 (ImC(4)).

Caution! Picric acid is known to be unstable and susceptible to explosions if shocked or dried for prolonged periods of time. Although we have not experienced any difficulty in handling picric acid or picrate salts of compound 1, we urge that extreme caution be taken in handling these compounds, and that they not be stored for prolonged periods of time. The picric salt should be immediately converted to its hydrochloride salt form.

1-Methylimidazole-4-carboxaldehyde (3).[30] A 1.52-g sample of 4-(hydroxymethyl)-1-methylimidazole hydrochloride was dissolved in a minimum amount of water, and 2.0 mL of saturated sodium carbonate solution was added. The solvent was evaporated *in vacuo*, and care was taken to ensure that the resulting white solid was very dry. The solid then was extracted with two 20-mL portions of absolute ethanol and filtered, and the filtrate was evaporated *in vacuo*. To the residue was added 22 mL of chloroform and 4.34 g of activated MnO_2. This mixture was stirred at room temperature for 16 h and filtered, and the precipitate was washed with hot chloroform. The filtrate then was evaporated to dryness and the residue dried *in vacuo* yielding 0.88 g of a white solid (78.1%): mp 63–67 °C; ^{1}H NMR ($CDCl_3$, δ) 3.74 (s, 3H, ImN–CH_3), 7.50 (s, 1H, ImC(5)–H), 7.57 (s, 1H, ImC(2)–H), 9.82 (s, 1H, Im–CHO); ^{13}C NMR ($CDCl_3$, δ) 33.86 (ImN–CH_3), 125.60 (ImC(5)), 139.36 (ImC-(2)), 142.23 (ImC(4)), 185.93 (ImCHO).

4-(Chloromethyl)-1-methylimidazole Hydrochloride (4).[30] A 1.504 g (10.1-mmol) sample of 4-(hydroxymethyl)-1-methylimidazole hydrochloride was dissolved in 5 mL of dried benzene. After the suspension was stirred for 10 min, 3–4 mL of thionyl chloride was added, whereupon two phases formed immediately. The upper level phase contains benzene and the lower phase the product. The solvent was removed *in vacuo* resulting in the isolation of 1.602 g (94.8%) of a white crystalline solid: mp 148–150 °C; ^{1}H NMR (d_6-DMSO, δ) 3.84 (s, 3H, ImN–CH_3), 4.86 (s, 2H, Im–CH_2–Cl), 7.72 (s, 1H ImC(5)–H), 9.08 (s, 1H, ImC(2)–H); ^{13}C NMR ($CDCl_3$, δ) 34.36 (ImNCH$_3$), 35.47 (ImCH_2Cl), 122.03 (ImC-(5)), 129.83 (ImC(2)), 136.65 (ImC(4)). Anal. Calcd for $C_5H_8N_2Cl_2$: C, 35.71; H, 4.76; N, 16.67. Found: C, 35.92, H; 4.82; N, 15.90.

((1-Methylimidazol-2-yl)methyl)((1-methylimidazol-4-yl)methyl)-amine Trihydrochloride, (2,4-BMIMA·3HCl) (5). A solution of 2-(-aminomethyl)- 1-methylimidazole dihydrochloride (0.782 g 4.30 mmol) in 30 mL of methanol containing KOH (0.478 g, 8.52 mmol) was added to a solution of compound **3** (0.469 g, 4.26 mmol) in 30 mL of methanol, and the resulting mixture was hydrogenated in the presence of 10% palladium–charcoal for 12 h. The catalyst was filtered from solution and the solution reduced to a volume of 20 mL *in vacuo*. KCl was filtered from the solution, and 200 mL of methanolic HCl was added with stirring. After cooling of the solution to −20 °C overnight, the resulting precipitate was filtered out and washed with 2 × 10 mL portions of methanolic HCl to give 0.776 g (57.5%) of **5**: mp 220 °C (dec); ^{1}H NMR (D_2O, δ) 3.84 (s, 3H, ImN–CH_3), 3.87 (s, 3H, ImN–CH_3), 4.38 (s, 2H, Im–CH_2–N), 4.59 (s, 2H,Im–CH_2–N), 7.45 (s, 1H,ImC–H), 7.46 (s, 1H, ImC–H), 7.59 (s, 1H, ImC–H), 8.69 (s, 1H, ImC–H); ^{13}C NMR (D_2O, δ) 37.44 (ImN–CH_3), 38.45 (ImN–CH_3), 41.60 (Im–CH_2–N), 43.64 (Im–CH_2–

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N), 122.61 (ImC), 126.70 (ImC), 127.59 (ImC), 127.73 (ImC), 139.25 (ImC), 140.57 (ImC). Anal. Calcd $C_{10}H_{18}N_5Cl_3 \cdot {}^1/_2H_2O$: C, 37.11; H, 5.88; N, 21.65. Found: C, 37.38; H, 5.83; N, 21.40.

Free base of compound **5** was made by neutralizing compound **5** with Na_2CO_3 in aqueous solution, followed by extraction with $CHCl_3$. The compound is very hydroscopic and should be used immediately after preparation.

Bis((1-methylimidazol-2-yl)methyl)((1-methylimidazol-4-yl)methyl)-amine (L^1) (6). Method A. A very dry acetonitrile solution (20 mL) of the free base of compound **4** (0.39 g, 2.34 mmol) and triethylamine (0.43 g, 4.3 mmol) was stirred for 1 h under an atmosphere of dry nitrogen at 0 °C. Bis((1-methylimidazol-2-yl)methyl)amine,[28] BMIMA, (0.40 g, 1.95 mmol) was then added to the solution, and the mixture was stirred for 24 h at 0 °C. The resulting triethylamine hydrochloride salt was filtered out, and the filtrate was reduced to dryness *in vacuo*. The residue was then dissolved in 10 mL of saturated NaCl solution and extracted with 4 × 15 mL portions of chloroform. The combined extracts were dried with anhydrous $MgSO_4$, and the chloroform was removed under reduced pressure giving 0.18 g (30%) of **6**.

Method B. A solution of BMIMA (0.50 g, 2.44 mmol) in 40 mL of methanol containing 0.75 mL of glacial acetic acid was added to a solution of compound **3** (0.334 g, 3.31 mmol) in 20 mL of methanol. $NaBH_3CN$ (0.69, 10.9 mmol) was added to the reaction mixture under a nitrogen atmosphere, and the solution was stirred overnight. Prior to working up the reaction mixture, the pH of the solution was adjusted to 2.0 by careful addition of concentrated HCl, resulting in the formation of a white precipitate. The mixture was filtered, and the precipitated was discarded immediately due to the presence of cyanide ion in the residue. (*Caution! Cyanide is extremely toxic, and appropriate safety precautions should be followed at this initial stage of the workup procedure.*) The filtrate was reduced to dryness under reduced pressure, and the resulting oil was redissolved in 15 mL of water. The aqueous solution then was washed several times with 20-mL aliquots of diethyl ether, and then the pH of the solution was adjusted to about 8 by addition of Na_2CO_3. The resulting basic solution then was extracted four times using 15-mL aliquots of chloroform. The extracts were combined and dried over anhydrous $MgSO_4$ and the solvent removed *in vacuo* to give 0.712 g (69.5%) of a white powder: mp 147–150 °C; ^{1}H NMR ($CDCl_3$, δ) 3.42 (s, 6H, 2ImN–CH_3), 3.59 (s, 2H, 4Im–CH_2–N), 3.65 (s, 4H, 2Im–CH_2–N), 3.67 (s, 3H, 4ImN–CH_3), 6.78 (s, 2H, 2ImC–H), 6.89 (s, 2H, 2ImC–H), 6.95 (s, 1H, 4ImC–H), 7.35 (s, 1H, 4ImC–H); ^{13}C NMR ($CDCl_3$, δ) 32.5 (2ImN–CH_3), 33.4 (4ImN–CH_3), 49.0 (2Im–CH_2–N), 50.8 (4Im–CH_2–N), 120.1 (4ImC), 121.4 (2ImC), 127.0 (2ImC), 137.3 (4ImC), 137.5 (4ImC), 145.6 (2ImC); MS (EI) m/z 299, $[M^o]^+$ (0.8); 218, [M – (MeIm)]$^+$ (0.2); 204, [M – (MeIm)]$^+$ (64.8).

Bis((1-methylimidazol-4-yl)methyl)((1-methylimidazol-2-yl)methyl)-amine (L^2) (7). Method A. Compound **7** was prepared following the same procedure described above in method A for compound **6**, except that the free base of compound **5** was substituted for BMIMA. The overall yield for this reaction was found to be 22%.

Method B. The free base of compound **5** was substituted for BMIMA in this reaction, and the procedure is as outlined above for compound **6**. The product was isolated as a semisolid in 72.5% yield: ^{1}H NMR ($CDCl_3$, δ) 3.52 (s, 4H, 4Im–CH_2–N), 3.57 (s, 3H, 2ImN–CH_3), 3.58 (s, 6H, 4ImN–CH_3), 3.61 (s, 2H, 2Im–CH_2–N), 6.71 (s, 1H, 2ImC–H), 6.82 (s, 1H, 2ImC–H), 6.85 (s, 2H, 4ImC–H), 7.30 (s, 2H, 4ImC–H); ^{13}C NMR ($CDCl_3$, δ) 33.0 (2ImN–CH_3), 33.3 (4ImN–CH_3), 49.2 (2Im–CH_2–N), 50.5 (4Im–CH_2–N), 119.4 (4ImC), 121.4 (2ImC), 126.6 (2ImC), 137.2 (4ImC), 138.9 (4ImC), 145.9 (2ImC); MS (EI) m/z 299, $[M^o]^+$ (1.0); 218, [M – (MeIm)]$^+$ (0.4); 204, [M – (MeIm)]$^+$ (60.0).

Synthesis of Metal Complexes. [Cu(L^1)Cl]PF_6 (8). To a stirred solution containing 0.150 g (0.50 mmol) of compound **6** was added 0.083 g (0.49 mmol) of $CuCl_2 \cdot 2H_2O$. The resulting green solution was stirred for an additional 1 h, whereupon 0.084 g (0.52 mmol) of NH_4PF_6 was added to induce precipitation of the complex. The precipitate was filtered from the solution, and the complex was recrystallized from 1:1 CH_3OH/CH_3CN, yielding 0.170 g (63.9%) crystals of **8** which were suitable for X-ray crystallographic analysis. Anal. Calcd for $C_{15}H_{21}N_7PClF_6Cu$: C, 33.15; H, 3.87; N, 18.05. Found: C, 33.10; H, 3.90; N, 17.66. Electronic spectrum (acetonitrile, λ_{max} (ϵ_M)): 1110 (80), 830 (65), 292 (4901).

[Cu(L^2)Cl]PF_6 (9). Compound **9** was prepared by the same procedure outlined above for compound **8** with one exception; compound **7** was substituted for compound **6** in the reaction. The green precipitate was recrystallized from 1:1 CH_3OH/CH_3CN yielding crystals of **9** (46%) that were suitable for X-ray crystallographic analysis. Anal. Calcd for $C_{15}H_{21}N_7PClF_6Cu$: C, 33.15; H, 3.87; N, 18.05. Found: C, 33.24; H, 3.84; N, 17.51. Electronic spectrum (acetonitrile, λ_{max} (ϵ_M)): 1070 (86), 827 (57), 296 (4026).

Table 1. Crystallographic Data for Compounds **8** and **9**

	8	**9**
formula	$C_{15}H_{21}N_7PClF_6Cu$	$C_{15}H_{21}N_7PClF_6Cu$
mol wt	543.34	543.34
a, Å	16.585(3)	16.487(5)
b, Å	12.570(3)	16.246(5)
c, Å	10.540(3)	16.555(5)
α, deg	90	90
β, deg	105.34(2)	90
γ, deg	90	90
V, Å^3	2118.8	4434.1
Z	4	8
space group	$P2_1/c$	$Pbca$
ρ_{calc}, g/cm^3	1.70	1.63
ρ_{exp}, g/cm^3	1.69(1)	1.60(1)
radiation (λ, Å)	Mo Kα (0.7107)	Mo Kα (0.7107)
temp, K	298 K	298 K
abs coeff, cm^{-1}	13.0	12.4
R^a	0.040	0.075
R_w^b	0.039	0.057
GOF	1.04	1.446

^{a} $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = [\sigma(F)^2 + (0.01F)^2 + 1.5]^{-1}$.

Physical Measurements. Absorption spectra were recorded using a Shimadzu UV-160 and Perkin-Elmer 330 UV–vis–near-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra of the ligands were obtained using a Varian XL-300 spectrometer. Mass spectra were recorded on a VG-7035 GC-MS mass spectrometer in th EI mode at 20 eV. EPR spectra were recorded on a Varian E-190 spectrometer equipped with an Oxford Instruments, Inc., cryostat. Electrochemical measurements were obtained using dried and degassed acetonitrile solutions containing 0.1 M tetra-*n*-butylammonium perchlorate on a PAR Model 175 Universal Programmer, a PAR Model 173/178 potentiostat, and a digital coulometer interfaced with a Houston Model 2000 X-Y recorder. A three-electrode electrochemical cell, utilizing a Ag/AgCl reference electrode and Pt wire and coil working electrode, was used for all measurements. The reversibility of the electrochemical processes were evaluated by following standard procedures,[32] and the formal potentials of the redox couples were evaluated using the ferrocene/ferrocenium (Fc/Fc^+) redox couple ($E_{1/2}$ = +0.400 V versus SCE) as an internal standard.[33] Solution susceptibility measurements were obtained in CH_3CN solutions using the Evans method.[34]

X-ray Data Collection and Reduction. Green crystals of [Cu(L^1)Cl]PF_6 (**8**) and [Cu(L^2)Cl]PF_6 (**9**) were grown by slow evaporation of 1:1 CH_3OH/CH_3CN solutions. Single crystals were mounted on glass fibers and coated with epoxy. Crystals were aligned and X-ray intensity data were collected using an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo Kα radiation, λ = 0.710 73 Å). Crystallographic data are summarized in Table 1. Lattice parameters for each complex were obtained from a least-squares analysis of 25 centered reflections with $20° \le 2\theta \le 30°$. Data were collected using the ω–2θ scan technique to maximum 2θ values 50° with 3042 and 2240 independent reflections having $I > 3\sigma(I)$, for compound **8** and **9**, respectively. Crystal stability was monitored during data collection on both complexes by monitoring the intensities of three reflections every 60 min. Neither compound showed significant decay during data collection. Intensity data were corrected for Lorentz and polarization affects, and empirical absorption corrections based on difabs (SDP package[35]) were applied.

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Table 2. Positional Parameters and Their Estimated Standard Deviations for Compound **8**

atom	x	y	z	B,[a] Å²	occup[b]
Cu	0.74098(3)	0.06989(4)	0.12166(4)	2.707(8)	
Cl	0.78469(7)	−0.02531(9)	−0.0277(1)	4.55(2)	
N(1)	0.6993(2)	0.1600(2)	0.2650(3)	2.35(5)	
N(2)	0.7363(2)	−0.0464(2)	0.2597(3)	2.82(6)	
N(3)	0.7532(2)	−0.0809(3)	0.4697(3)	2.97(6)	
N(4)	0.6212(2)	0.1038(3)	0.0157(3)	2.67(6)	
N(5)	0.4942(2)	0.1518(2)	0.0167(3)	2.65(6)	
N(6)	0.8331(2)	0.1793(3)	0.1690(3)	3.33(7)	
N(7)	0.9493(2)	0.2646(3)	0.2541(3)	4.35(8)	
C(1)	0.7367(2)	0.1120(3)	0.3961(3)	2.73(7)	
C(2)	0.7405(2)	−0.0056(3)	0.3761(3)	2.56(7)	
C(3)	0.7479(2)	−0.1546(3)	0.2803(4)	3.55(9)	
C(4)	0.7579(2)	−0.1761(3)	0.4090(4)	3.52(8)	
C(5)	0.7627(3)	−0.0638(4)	0.6102(4)	4.16(9)	
C(6)	0.6067(2)	0.1566(3)	0.2328(3)	2.80(7)	
C(7)	0.5737(2)	0.1410(3)	0.0884(3)	2.31(6)	
C(8)	0.5688(2)	0.0902(3)	−0.1095(3)	2.92(7)	
C(9)	0.4910(2)	0.1192(3)	−0.1089(4)	3.08(7)	
C(10)	0.4237(2)	0.1885(4)	0.0641(4)	3.79(9)	
C(11)	0.7301(2)	0.2705(3)	0.2588(4)	2.95(8)	
C(12)	0.8171(2)	0.2610(3)	0.2449(4)	3.13(8)	
C(13)	0.9136(2)	0.1833(4)	0.1772(4)	4.04(9)	
C(14)	0.8894(3)	0.3145(4)	0.2986(4)	3.95(9)	
C(15)	1.0404(3)	0.2878(5)	0.2952(6)	6.6(1)	
P(1)	1.000	0.000	0.500	3.95(3)	0.5
P(2)	0.500	0.000	0.500	2.67(3)	0.5
F(1)	0.4327(2)	−0.0905(2)	0.4459(3)	5.32(6)	
F(2)	0.4538(2)	0.0765(2)	0.3834(2)	5.01(6)	
F(3)	0.4443(2)	0.0452(2)	0.5896(2)	4.56(5)	
F(4)	1.0827(2)	0.0152(6)	0.6087(5)	10.4(2)	0.8
F(5)	1.0442(3)	0.0181(4)	0.3869(4)	8.5(1)	0.8
F(6)	1.0245(4)	−0.1199(3)	0.5014(5)	11.2(2)	0.8
F(7)	1.0486(9)	0.104(1)	0.506(1)	5.7(3)*	0.2
F(8)	1.066(1)	−0.055(1)	0.442(2)	7.5(4)*	0.2
F(9)	1.053(1)	−0.003(1)	0.647(2)	6.6(3)*	0.2

[a] Starred *B* values are for atoms that were refined isotropically. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] If not specified, the occupancy of the atom is 1.0.

Table 3. Positional Parameters and Their Estimated Standard Deviations for Compound **9**

atom	x	y	z	B,[a] Å²	occup[b]
Cu	0.52644(5)	0.24213(5)	0.51754(5)	3.73(2)	
Cl	0.5207(2)	0.2431(2)	0.3832(1)	6.06(5)	
N(1)	0.5359(3)	0.2374(3)	0.6454(4)	3.3(1)	
N(2)	0.4703(4)	0.1322(4)	0.5391(4)	4.0(1)	
N(3)	0.4010(4)	0.0176(4)	0.5568(5)	5.3(2)	
N(4)	0.6458(3)	0.2619(4)	0.5288(4)	4.3(1)	
N(5)	0.7521(4)	0.2701(4)	0.6086(6)	5.4(2)	
N(6)	0.4537(3)	0.3434(4)	0.5470(4)	4.2(1)	
N(7)	0.3995(4)	0.4650(3)	0.5724(5)	4.9(2)	
C(1)	0.5397(5)	0.1514(4)	0.6708(5)	4.3(2)	
C(2)	0.4846(4)	0.1055(5)	0.6176(5)	4.4(2)	
C(3)	0.4210(5)	0.0772(4)	0.5058(4)	4.2(2)	
C(4)	0.4397(5)	0.0336(4)	0.6275(6)	4.7(2)	
C(5)	0.3467(6)	−0.0508(5)	0.5424(7)	5.7(2)	
C(6)	0.6102(5)	0.2824(5)	0.6712(6)	5.3(2)	
C(7)	0.6710(4)	0.2710(3)	0.6033(5)	4.0(2)	
C(8)	0.7158(5)	0.2521(6)	0.4822(7)	6.1(2)	
C(9)	0.7800(4)	0.2606(6)	0.5328(8)	6.0(2)	
C(10)	0.8024(5)	0.2772(6)	0.6803(7)	7.8(3)	
C(11)	0.4617(5)	0.2790(4)	0.6803(4)	3.9(1)	
C(12)	0.4415(5)	0.3509(5)	0.6287(6)	5.2(2)	
C(13)	0.4270(4)	0.4145(5)	0.5137(6)	5.2(2)	
C(14)	0.4077(5)	0.4256(5)	0.6437(7)	6.0(2)	
C(15)	0.3666(7)	0.5484(5)	0.5592(8)	7.4(3)	
P	0.2715(1)	0.0212(2)	0.8090(2)	5.65(6)	
F(1)	0.2877(5)	−0.0485(4)	0.7444(4)	9.7(2)	
F(2)	0.2573(4)	0.0885(3)	0.8754(5)	8.7(2)	
F(3)	0.3670(6)	0.0321(9)	0.8216(7)	10.8(3)	0.6
F(4)	0.1778(6)	0.0021(7)	0.8027(6)	8.5(2)	0.6
F(5)	0.269(1)	0.0743(8)	0.7347(8)	16.1(6)	0.6
F(6)	0.2738(7)	−0.0466(5)	0.8839(8)	9.0(3)	0.6
F(3′)	0.3533(8)	0.0667(8)	0.7909(9)	6.7(3)*	0.4
F(4′)	0.1917(9)	−0.0199(8)	0.8349(9)	7.5(3)*	0.4
F(5′)	0.233(1)	0.091(1)	0.756(2)	10.4(5)*	0.4
F(6′)	0.312(1)	−0.0344(9)	0.865(1)	8.8(4)*	0.4

[a] Starred *B* values are for atoms that were refined isotropically. *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] If not specified, the occupancy of the atom is 1.0.

The minimum absorption correction for compounds **8** and **9** are 0.877 and 0.691, respectively, while the maxima are 1.151 and 1.505. Space groups were uniquely identified by systematic absences. Compound **9** was also checked for the possibility of a tetragonal space group, but the symmetry and systematic absences were not consistent and the cation showed no internal symmetry.

Solution and Refinement of Crystal Structures. The structures were solved using direct methods (SDP package[35]) and refined by full-matrix least-squares, minimizing the function $\sum w(|F_o|-|F_c|)^2$. All non-hydrogen atoms, with exception of disordered atoms having occupancies less than 50%, were refined anisotropically. Hydrogen atoms for both complexes were calculated and included as fixed contributions (B_{iso} = 1.2B_{iso} of bonded atom). The asymmetric unit of $[Cu(L^1)Cl]PF_6$ consists of a single cation and two half-occupancy PF_6^- anions, one of which is disordered. The asymmetric unit of $[Cu(L^2)Cl]PF_6$ consists of a single cation and a disordered PF_6 anion. All non-hydrogen atomic positional parameters for the cations are given in Tables 2 and 3 for compounds **8** and **9**, respectively. Final difference Fourier maps showed no significant residual electron density.

Results and Discussion

Synthesis. There is growing interest in ligands containing multiple imidazole donors as synthetic analogues of metalloprotein active sites. In general, polyimidazole ligands reported to date[36] contain either one or two imidazole pendants as part of their ligand framework and are usually not easily derivatized. In an attempt to expand the size (number of imidazole pendants) and shape (orientation of specific pendants) of polyimidazole ligand frameworks, we have modified a previously reported synthetic protocol used to prepare polypyridine ligands. In previous studies, we have reported that 1-methylimidazole-2-carboxaldehyde is an excellent synthon for preparing polyimidazole ligands *via* Schiff base condensation reactions. Hydrogenation of the imine bond resulting from the Schiff base condensation of 1-methylimidazole-2-carboxaldehyde and 2-(aminomethyl)-1-methylimidazole affords a novel bis(imidazole) ligand, BMIMA, in good yields. BMIMA has been used as a precursor for preparing other polyimidazole ligands.[26,28,36a,36b] For example, the tetradentate tripodal ligand tris((1-methylimidazol- 2-yl)methyl)amine (TMIMA)[26] has been prepared in good yields (>60%) by either alkylation of BMIMA with 2-(chloromethyl)-1-methylimidazole or by reductive amination of BMIMA in the presence of 1-methylimidazole-2-carboxaldehyde and $NaBH_3CN$.

In order to prepare polyimidazole ligands containing biologically relevant 4-substituted imidazole pendants, we have expanded

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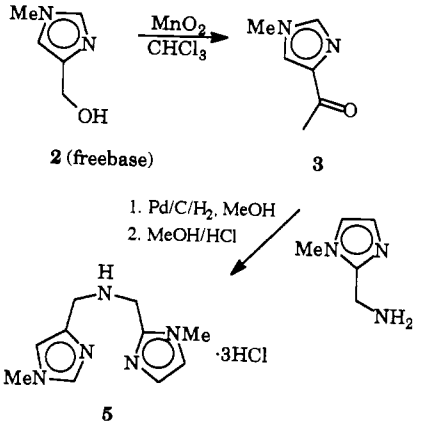
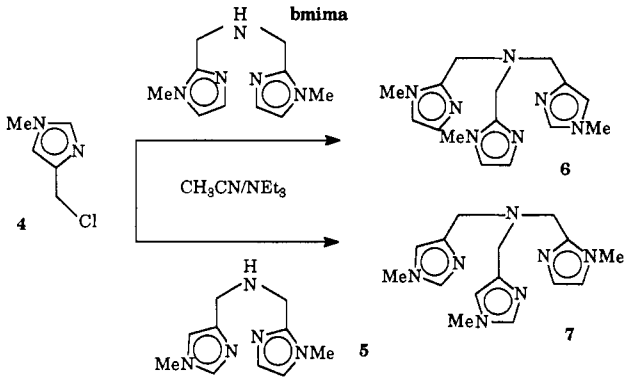
Scheme 1



Scheme 2

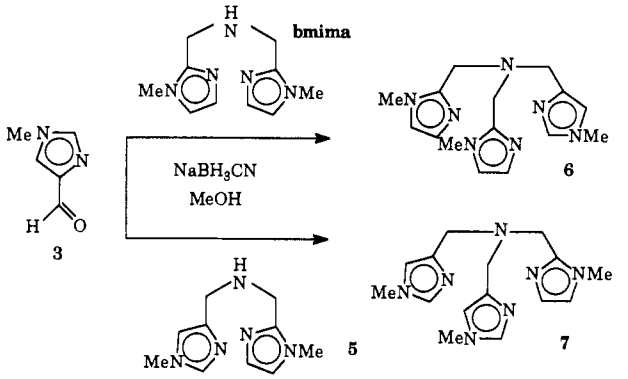


our synthetic methodology to include the use of 1-methylimidazole-4-carboxaldehyde (**3**) as a synthon. It is well-known that histidine binds to metals through imidazole ring nitrogen atoms and that the ring may be considered to be functionalized either in the 4- or 5-position depending on the position of the imidazole NH proton. Compound **3** has been prepared by the oxidation of 4-(hydroxymethyl)-1-methylimidazole (**2**) in the presence of MnO_2 in chloroform and has been used to prepare the tridentate ligand 2,4-BMIMA (**5**) *via* the procedure outlined in Scheme 1. Catalytic hydrogenation of the Schiff base formed by the condensation of compound **3** and 2-(aminomethyl)-1-methylimidazole affords compound **5** in good yields. Because the free base of **5** is very hygroscopic, it is best isolated and stored as a trihydrochloride salt.

Several mixed 2-/4-substituted polyimidazole tripods have been synthesized using BMIMA and 2,4-BMIMA as synthons. Compounds **6** and **7**, for example, have been prepared by two methods, as outlined in Schemes 2 and 3. The tetradentate tripods have been synthesized by alkylation of either compound **5** or BMIMA with 4-(chloromethyl)-1-methylimidazole (**4**) in the presence of triethylamine. At room temperature, the overall yields of the desired products are quite low (<20%). Lowering the reaction temperature to 0 °C, however, significantly improves the yields of the reactions. Apparently compound **4** is very reactive, forming substantial amounts of side products during the course of the reaction. Curiously, similar alkylating conditions at room temperature have been employed in the preparation of TMIMA, where the alkylating agent is 2-(chloromethyl)-1-methylimidazole. The overall yield of the reaction forming TMIMA typically ranges from 50 to 70%.

Scheme 3 outlines an alternative procedure for preparing compounds **6** and **7** which involves reductive-amination methods.[37]

Scheme 3



When the iminium ion resulting from the Schiff base condensation of the secondary amine of either compound **5** or BMIMA and compound **3** is reduced *in situ*, the desired tripod is isolated in good yields (>60%).

The free bases of both compounds **6** and **7** have been characterized by ^1H and ^{13}C NMR spectroscopy and by GC–mass spectrometry. Imidazole protons associated with 2- and 4-substituted tripods display different ^1H chemical shifts. For example, N–Me signals associated with 2-substituted imidazole rings in compound **6** occur at 3.42 ppm, while the N–Me resonance associated with the 4-substituted ring is shifted downfield to 3.67 ppm. The methylene signals associated with the 2-substituted ring are observed at 3.65 ppm, while the methylene signal associated with the 4-substituted ring appears at 3.59 ppm. Imidazole ring protons associated with compound **6** are observed between 6.7 and 6.9 ppm with the exception of the 2-position proton of the 4-substituted imidazole ring. This proton is observed downfield at 7.30 ppm, as a result of the greater inductive effect of the two neighboring nitrogen atoms. The same general trend in the chemical shifts of the tripod imidazole protons is observed in the ^1H NMR spectrum of compound **7**.

Copper(II) complexes of **6** and **7**, $[Cu(L)Cl]PF_6$ (where L = compounds **6** or **7**), have been prepared by mixing stoichiometric quantities of the appropriate tripod and $CuCl_2 \cdot 2H_2O$ in methanol. Addition of NH_4PF_6 to the reaction mixtures results in the formation of green precipitates, which are readily recrystallized from 1:1 CH_3OH/CH_3CN solutions.

Description of Crystal Structures. $[Cu(L^1)Cl]PF_6$ (8). An ORTEP view of the cation is shown in Figure 1. Selected bond distances and angles associated with the cation are given in Table 4. The coordination environment around the Cu atom is best described as a distorted trigonal bipyramid. The metal is bonded to three imidazole nitrogen atoms (N(2), N(4), and N(6)), which occupy equatorial sites of the bipyramid, and an amine nitrogen atom (N(1)) and chloride atom that occupy apical sites. As a result, the molecule has near mirror symmetry (C_s). The Cu–N(1) distance in **8** is 2.144(4) Å, approximately 0.02 Å shorter than the Cu–amine length reported previously for the $[Cu(TMIMA)Cl]^+$ cation.[26] This distance however is more comparable to the Cu–amine bond length reported for a related Cu^{II} complex containing a mixed pyridine/imidazole tripod, $[Cu(BPIA)Cl]^+$, where BPIA is bis(1-methylimidazol-2-yl)methyl)-(2-pyridylmethyl)amine.[26] The Cu–Cl distance in **8** is 2.245(1) Å, approximately 0.01 Å longer than the corresponding length observed in $[Cu(TMIMA)Cl]^+$.

Copper–imidazole bond lengths in **8** are considerably shorter than the Cu–amine bond distance, due in part to the greater π bonding ability of imidazole pendants compared to alkylamines,[38,39] which are exclusively σ donors, and to the constraining

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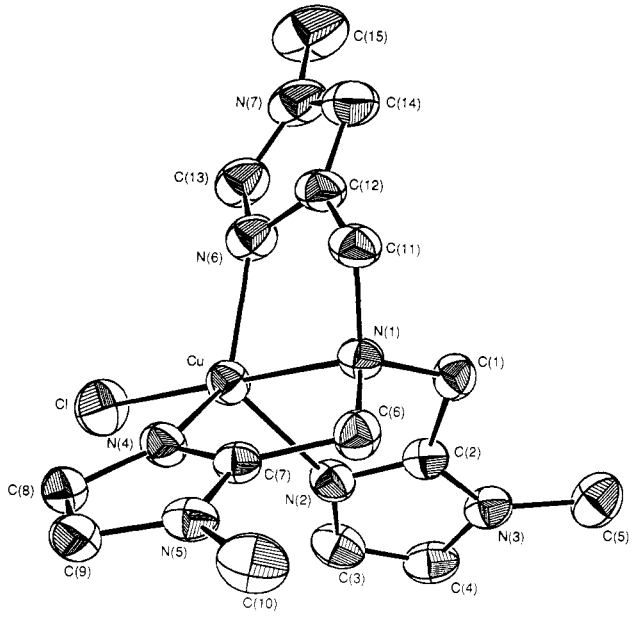

Figure 1. ORTEP drawing (50% probability ellipsoids) of compound **8** cation with atom-labeling scheme.

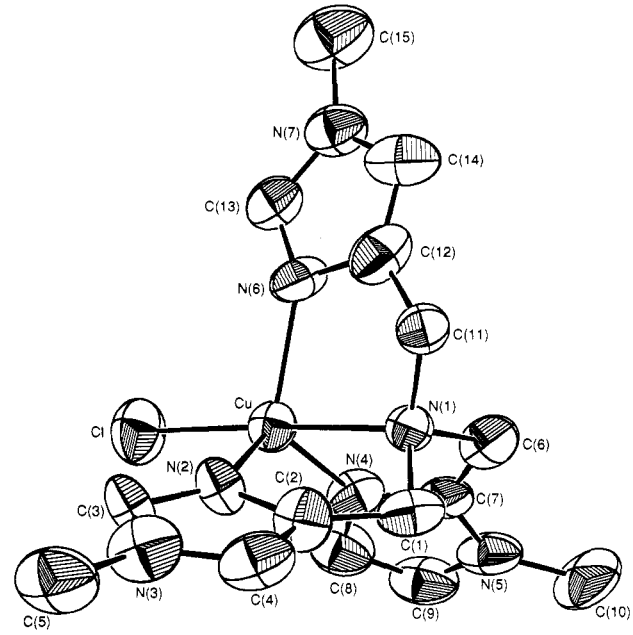

Figure 2. ORTEP drawing (50% probability ellipsoids) of compound **9** cation with atom-labeling scheme.

Table 4. Selected Bond Lengths (Å), Angles (deg), and Torsional Angles (deg) for Compounds **8** and **9**

	8	**9**	[Cu(TMIMA)Cl]$^+$
Cu–N(1)	2.144(4)	2.123(6)	2.167(3)
Cu–N(2)	2.050(3)	2.042(6)	2.062(3)
Cu–N(4)	2.078(4)	2.009(5)	2.021(4)
Cu–N(6)	2.017(3)	2.097(5)	2.011(2)
Cu–Cl	2.245(1)	2.232(2)	2.234(1)
N(1)–Cu–N(2)	80.1(2)	79.9(3)	79.0(1)
N(1)–Cu–N(4)	78.4(1)	80.5(2)	80.1(2)
N(1)–Cu–N(6)	80.2(1)	80.4(2)	79.9(1)
N(1)–Cu–Cl	179.6(8)	177.6(1)	177.9(1)
N(2)–Cu–N(4)	108.6(1)	124.1(2)	112.0(2)
N(2)–Cu–N(6)	123.7(1)	112.7(2)	116.9(1)
N(4)–Cu–N(6)	118.2(1)	114.7(2)	121.6(1)
N(1)–Cu–N(2)–C(2)	−13.1	−13.8	−17.2
N(1)–Cu–N(4)–C(7)	−22.0	−7.4	−13.9
N(1)–Cu–N(6)–C(12)	−10.2	−6.7	−14.0

nature of the tripod ligand. The Cu–N(2), Cu–N(4), and Cu–N(6) bond distances are 2.078(4), 2.050(3), and 2.017(3) Å, respectively, and are typical of Cu–imidazole distances reported for [Cu(TMIMA)Cl]$^+$ [26] and related imidazole compounds.

The distortion of the coordination environment in compound **8** is best illustrated by the deviation of the equatorial N–Cu–N bond angles from 120°. For example, the N(2)–Cu–N(4), N(2)–Cu–N(6), and N(4)–Cu–N(6) angles are 108.6(1), 118.2(1), and 123.7(1)°, respectively. The strain imposed on the metal coordination environment by the tripod ligand also is reflected in the chelate angles of the pendants, which average 79.6°, and the chelate torsion angles, N(1)–Cu–N(2)–C(2) = 22.04°, N(1)–Cu–N(4)–C(7) = 13.07° and N(1)–Cu–N(6)–C(12) = 10.17°. Interestingly, the 4-substituted imidazole pendant has the smallest torsion angle in **8**. In [Cu(TPA)Cl]$^+$, [31,40] (TPA = tris(2-pyridylmethyl)amine), the pyridine chelate torsion angles are similar to those reported for [Cu(TMIMA)Cl]$^+$, averaging 15°. The mixed pyridine/imidazole complexes,[26] on the other hand, show a greater disparity between torsion angles associated with each chelate. Again, this most likely is a result of the constraining nature of the tripod ligands and differences in σ and π bonding properties of the pyridine and imidazole pendants.

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[Cu(L^2)Cl]PF$_6$ (9). Compound **9** is structurally similar to compound **8**; however, it crystallizes in the orthorhombic space group *Pbca*. An ORTEP view of the cation is shown in Figure 2. Pertinent bond distances and angle associated with the cation are included in Table 4.

As with compound **8**, the coordination geometry around the copper center in **9** is best described as a distorted trigonal bipyramid and the molecule has approximate mirror symmetry (C_s). The copper atom is bonded to three imidazole nitrogen atoms (N2, N4, and N6), an amine nitrogen, and a chlorine atom. The Cu–N(1) bond length is 2.124(6) Å, approximately 0.02 Å shorter than the analogous bond in **8**, and 0.04 Å shorter than the Cu–N distance reported for [Cu(TMIMA)Cl]$^+$.[26]

The Cu–Cl bond distance is 2.226(2) Å, and the Cu–imidazole lengths are Cu–N(2) = 2.042(6), Cu–N(4) = 2.009(5), and Cu–N(6) = 2.097(5) Å. As with compound **8**, the chelate angles in **9** are less than 90°, averaging 80.5°. Chelate torsion angles for the complex are N(1)–Cu–N(2)-C(2) = 13.8°, N(1)–Cu–N(4)-C(7) = 7.4°, and N(1)–Cu–N(6)–C(12) = 6.7°, reflecting a less twisted configuration for the tripod ligand compared to compound **8**.

Electronic Spectroscopy. The UV–vis–near-IR spectra of compounds **8** and **9** have been recorded in acetonitrile, and the data are listed in Table 5, along with data reported previously for [Cu(TMIMA)Cl]PF$_6$.[26] The transitions in the visible–near-IR spectra of **8** and **9** are blue shifted relative to analogous transitions associated with [Cu(TMIMA)Cl]PF$_6$ (Figure 3). Similar blue shifts are observed for the optical transitions associated with a series of related [Cu(L)Cl]$^+$ and [Cu(L)(1-MeIm)]$^+$ (where 1-MeIm = 1-methylimidazole and L are tripods which containing pyridine, imidazole, and mixed pyridine/imidazole pendants),[26] suggesting that 2-substituted imidazole pendants are weaker field ligands.

In the UV region, both compound **8** (225 nm, ϵ = 10,531 M^{-1} cm^{-1}, and 292 nm, ϵ = 4901 M^{-1} cm^{-1}) and compound **9** (219 nm, ϵ = 11 858 M^{-1} cm^{-1}, and 296 nm, ϵ = 4026 M^{-1} cm^{-1}) display intense bands assigned to intraligand and metal-to-ligand charge-transfer transitions. As with the mixed pyridine/imidazole analogues, the bands in the visible–near-IR spectra of **8** and **9** shift progressively to higher energies as the 2-substituted 1-methylimidazole pendants of TMIMA are replaced by 4-substituted 1-methylimidazole pendants. For compound **8**, transitions are observed at 830 nm (ϵ = 65 M^{-1} cm^{-1}) and 1110 nm (ϵ = 80 M^{-1} cm^{-1}), while, for compound **9**, the transitions shift to 827 nm

Table 5. Physical Properties of $[Cu(L)Cl]PF_6$ Complexes

properties	8	9	$[Cu(TMIMA)Cl]PF_6$
λ_{max}, nm (ϵ M^{-1} cm^{-1})	1110 (80), 830 (65), 292 (4901), 225 (10 531)	1070 (86), 827 (57), 296 (4026), 219 (11 858)	1123 (112), 830 (98), 288 (4560)
frozen soln			
$g_\perp$	2.23	2.22	2.25
$A_\perp$, cm^{-1}	104×10^{-4}	104×10^{-4}	105×10^{-4}
solid state			
$g_\perp$	2.24	2.19	
$g_\parallel$	2.15	2.04	
μ_B, μ_B	1.81	1.74	1.94
$E_{1/2}$, V vs Ag/AgCl	-0.193	-0.225	-0.163
i_{pa}/i_{pc}	1.17	1.00	1.04

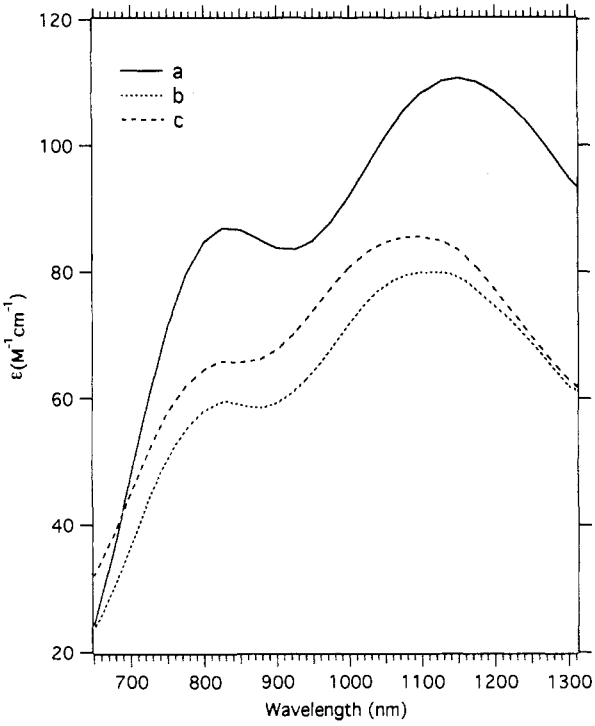

Figure 3. Electronic spectra in acetonitrile: (a) $[Cu(TMIMA)Cl]^+$; (b) compound **8**; (c) compound **9**.

(ϵ = 57 M^{-1} cm^{-1}) and 1070 nm (ϵ = 86 M^{-1} cm^{-1}), respectively. These bands are quite broad, suggesting the presence of more than two transitions at lower energies as expected for a Cu^{II} ion in a distorted trigonal bipyramidal environment.

Magnetism and EPR Spectroscopy. As with all trigonal bipyramidal copper(II) complexes containing N_4 tetradentate tripodal ligands, the effective magnetic moments for compounds **8** and **9** fall within the range of 1.7–2.0 μ_B, consistent with an $S = {}^1/_2$ ground-state configuration (Table 5). The 77 K X-band EPR spectra on powdered samples of **8** and **9** (supplementary material) clearly show $g_\perp > g_\parallel$. Frozen DMF/CH_3OH solution spectra of **8** and **9**, also recorded at 77 K, resemble spectra reported for five-coordinated copper(II) complexes with geometry intermediate between trigonal bipyramidal ($g_\perp > g_\parallel \approx 2.00$ with $|A_\parallel| \approx |A_\perp| \approx (60–100) \times 10^{-4}$ cm^{-1}) and square pyramidal ($g_\parallel > g_\perp$ with $|A_\perp| < |A_\parallel| \approx (120–150) \times 10^{-4}$ cm^{-1}).[41] Analysis of the solution spectra of the compounds gives a $g_\perp$ = 2.23 and 2.22 and $A_\perp = 104 \times 10^{-4}$ and 104×10^{-4} cm^{-1} for **8** and **9**, respectively. Due to the absence of resolvable copper hyperfine structure on the parallel component of the signal, we are unable to definitively determine $g_\parallel$ and $A_\parallel$ at this time. The frozen-solution spectra of compounds **8** and **9** however are similar in appearance to spectra reported for $[Cu(TMIMA)Cl]PF_6$ and mixed imidazole/pyridine complexes,[26,31,40] suggesting a similar ground-state configuration for the complexes.

Electrochemistry. The redox properties of compounds **8** and **9** have been studied by cyclic voltammetry in acetonitrile. Both compounds display a single quasireversible one-electron reduction processes with ratios of i_{pa}/i_{pc} equal to unity. The $Cu^{II} \rightarrow Cu^I$ reduction potentials for compounds **8** and **9** are $E_{1/2}$ = -0.193 V and -0.225 (vs Ag/AgCl), respectively. $[Cu(TMIMA)Cl]PF_6$, on the other hand, is reduced at -0.163 V vs Ag/AgCl. These results suggest that the tripodal ligands containing 4-substituted imidazole pendants are hard donors compared to the corresponding 2-substituted pendants of TMIMA and that the tripods containing 4-substituted pendants are less capable of stabilizing Cu^I forms of the complexes generated upon reduction.

Conclusion

In conclusion, we have prepared two new mixed imidazole tripods that stabilize Cu^{II} complexes having distorted trigonal bipyramidal geometries. In both cases the imidazole donors occupy equatorial sites of the trigonal bipyramid and display Cu–N(imidazole) bond lengths averaging 2.048 Å. The Cu–N(amine) bond lengths for **8** and **9**, and the related $[Cu(TMIMA)Cl]^+$ complex, differ by 0.02 Å and decrease in length according the series $[Cu(TMIMA)Cl]^+ > 8 > 9$. The length of the Cu–N(amine) bond within this series of complexes seems to be dependent on the nature of the tripod ligands. A similar trend has been observed in a series of related mixed imidazole/pyridine tripods.[26]

The visible–near-IR spectra of complexes **8** and **9** were recorded in acetonitrile and found to be blue-shifted relative to spectrum of $[Cu(TMIMA)Cl]^+$. The data suggest that the ligand field strength of the tripods increase as the 2-substituted pendants of TMIMA are replaced by 4-substituted pendants. A similar shift in the optical transitions has been observed for a series of related mixed imidazole/pyridine tripods, where pyridine pendants are substituted for 2-substituted imidazole pendants of TMIMA. Finally, there is a cathodic shift in the Cu(II) to Cu(I) reduction potentials associated with compounds **8** and **9** relative to $[Cu(TMIMA)Cl]^+$. This results suggest that the tripod ligands containing the 4-substituted pendants are less capable of stabilizing Cu(I) forms of the complexes generated upon reduction.

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Supplementary Material Available: Tables listing experimental details of the crystal structure determination, hydrogen coordinates and thermal parameters, anisotropic thermal parameters, and bond distances and angles for **8** and **9** and powdered and frozen-solution X-band EPR spectra for compound **8** and **9** (15 pages). Ordering information is given on any current masthead page.

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