Electronic and Structural Variation among Copper(II) Complexes with Substituted Phenanthrolines

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A series of copper(II) complexes with substituted phenanthroline ligands has been synthesized and characterized electronically and structurally. The compounds that have been prepared include the monosubstituted ligand complexes of the general formula $[Cu(5\text{-}R\text{-}phen)_2(CH_3CN)](BF_4)_2$, where R = NO_2, Cl, H, or Me, and the disubstituted ligand complex $[Cu(5,6\text{-}Me_2\text{-}phen)_2(CH_3CN)](BF_4)_2$. The complexes $[Cu(5\text{-}NO_2\text{-}phen)_2(CH_3CN)](BF_4)_2$ (**1**), $[Cu(5\text{-}Cl\text{-}phen)_2(CH_3CN)](BF_4)_2$ (**2**), $[Cu(o\text{-}phen)_2(CH_3CN)](BF_4)_2$ (**3**), and $[Cu(5\text{-}Me\text{-}phen)_2(CH_3CN)](BF_4)_2$ (**4**) each crystallize in the space group $C2/c$ with compounds **1**, **2**, and **4** comprising an isomorphous set. The disubstituted complex $[Cu(5,6\text{-}Me_2\text{-}phen)_2(CH_3CN)](BF_4)_2$ (**5**) crystallizes in the space group $P2_1/c$. Each structure is characterized by a distorted trigonal bipyramidal arrangement of ligands around the central copper atom with approximate or exact C_2 symmetry. The progression from electron-withdrawing to electron-donating substituents on the phenanthroline ligands correlates with less accessible reduction potentials for the bis-chelate complexes.

Introduction

Transition metal phenanthroline complexes have been studied extensively since the ligand was first reported around a century ago.[2] Phenanthroline complexes were originally developed as the basis of metal-selective analytical techniques,[3,4] but have since played a fundamental role in the development of our understanding of the ligand substitution[5−7] and electron transfer reactivities of transition metal complexes[5,8−10] and of biological systems.[11−13] Furthermore, their diverse photochemical and photophysical properties[14,15] have led to extensive studies related to the development of photonic devices such as sensors, optical switches, and photovoltaic cells.[16−18] Among many other applications, phenanthroline complexes have been used as the basis for photochemical[19−22] and chemical[23,24] probes that are used in the study of biological chemistry, for the construction of molecular devices,[25] and for the assembly of stereochemically tailored metal architectures.[26]

The copper bis-phenanthrolines, the subject of the current work, are of interest for a number of reasons. They are the basis of a widely applied chemical nuclease that causes shape-selective DNA, RNA, and protein scission,[24] and their redox and speciation behavior has been applied to the preparation of biomimetic supported catalysts.[27] The copper(I) phenanthrolines also exhibit structure-sensitive photoluminescent behavior, which has been studied in detail by McMillin and others.[28−32] The chemistry of copper bis-phenanthrolines is also of funda-

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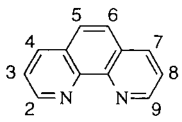

Position		
5	6	Abbreviation
NO_2	H	5-NO_2-phen
Cl	H	5-Cl-phen
H	H	o-phen
Me	H	5-Me-phen
Me	Me	5,6-Me_2-phen

Figure 1. Numbering scheme for phenanthroline ligands and substitution combinations for ligands used in this investigation.

mental and theoretical importance. In common with many other copper complexes, $[\mathrm{Cu(phen)_2}]^{n+}$ undergoes a coordination change during redox processes, from 4-coordinate in the 18-electron Cu(I) state to 5-coordinate upon oxidation to the 19-electron Cu(II) state. This large reorganization of the coordination sphere complicates the electron transfer reactivity, making the complex of significant mechanistic interest. The same coordination change plays a central role in driving a number of "molecular machines",[25] which further drives interest in the bonding and behavior of these complexes.

It has been shown repeatedly that substituents around the phenanthroline ring can have profound influence on the structure and behavior of the copper complexes, even when the substituents are placed in positions other than the stereoactive 2- and 9- (ortho) positions. For example, electron-withdrawing and -donating substituents modify interactions with nucleic acids leading to changes in shape selectivity that are not well understood,[33−37] and also affecting the kinetics of the DNA damage reaction, although the trend in rates is opposite to that expected based on simple redox arguments and electrochemical data. The influence of substituents on structure and bonding in $[\mathrm{Cu(phen)_2}]^{+}$ complexes is also apparent from significant changes in photophysical behavior.[29,31,32]

The objective of this work is a systematic examination into the influence of ring substituents on the structure, bonding, and chemistry of copper phenanthrolines. Our approach is to study a series of crystal structures of complexes with very similar compositions but with varying substitution patterns on the phenanthroline rings (see Figure 1). Our aim is to maximize the similarities among the structures in order to minimize the influences of intermolecular packing forces, so that structural trends may be correlated with changes in bonding. A number of studies have provided insight into the structural chemistry of the cuprous complexes, so we chose to examine the structural chemistry of the cupric forms. To facilitate comparison with solution studies, the complexes under study are such that the fifth ligand in the pentacoordinate Cu(II) complexes is in each case an acetonitrile solvent molecule to mimic the solution structures as closely as possible.

Ultimately, we wish to use the information gleaned from these structural studies to help with our understanding of the physical properties and reactivities of the copper phenanthroline complexes.

Experimental Section

General Procedures. All solvents used for synthesis were dried over molecular sieves before use. All other reagents were used as received from commercial sources.

Preparation of $[\mathrm{Cu(5\text{-}NO_2\text{-}phen)_2(CH_3CN)}](\mathrm{BF_4})_2$ (1). $\mathrm{Cu(BF_4)_2}$ hydrate (122.7 mg, 0.3749 mmol) was dissolved in 10 mL of CH_3CN, resulting in a blue solution. A sample of 5-NO_2-phen (169.3 mg, 0.7517 mmol, 2.005 equiv) was dissolved in 55 mL of CH_3CN and added dropwise to the metal solution to result in a blue-green solution of **1**. Removal of the solvent on a rotary evaporator resulted in the isolation of **1** as a blue-green solid in 93.01% yield (254.1 mg). Samples for spectroscopy were recrystallized from CH_3CN/ether. IR (KBr, cm^{-1}): 3089 m, 2324 w, 2296 w, 1519 s, 1425 m, 1345 m, 1054 br, s, 840 m, 723 m. Electronic spectrum in CH_3CN: λ_{max}, nm (ϵ in $M^{-1}\ cm^{-1}$) = 691 (42), 273 (115 000), 240 (sh), 216 (sh), 196 (768 000).

Preparation of $[\mathrm{Cu(5\text{-}Cl\text{-}phen)_2(CH_3CN)}](\mathrm{BF_4})_2$ (2). The formation of **2** was achieved by the dropwise addition of 125.5 mg of 5-Cl-phen (0.5846 mmol, 1.799 equiv) dissolved in 55 mL of CH_3CN to 100.5 mg of $\mathrm{Cu(BF_4)_2}$ hydrate (0.3250 mmol) dissolved in 10 mL of CH_3CN. The 165.5 mg of the turquoise solid of **2** was isolated by removing the solvent on a rotary evaporator, resulting in a 71.97% yield. Spectroscopic samples were typically recrystallized from CH_3CN/ether. IR (KBr, cm^{-1}): 3075 m, 2328 m, 2301m, 1605 w, 1585 m, 1520 m, 1485 w, 1426 m, 1055 br, s, 970 m, 891 s, 805 m, 728 s, 521 m, 431 m. ^1H NMR for **2** (d_6-acetone): δ 4.131 ppm (full width at half-height = 83 Hz) 2.298 ppm (18 Hz). Electronic spectrum in CH_3CN: λ_{max}, nm (ϵ in $M^{-1}\ cm^{-1}$) = 704 (64), 275 (27 900), 242 (sh), 215 (sh), 196 (195 000).

Preparation of $[\mathrm{Cu(o\text{-}phen)_2(CH_3CN)}](\mathrm{BF_4})_2$ (3). Over the course of 30 min, a solution of 196.0 mg of o-phen (1.088 mmol, 2.093 equiv) dissolved in CH_3CN was slowly added to a solution of 170.1 mg of $\mathrm{Cu(BF_4)_2}$ hydrate (0.5198 mmol) dissolved in CH_3CN. After the addition was complete, ether was added to precipitate a greenish blue solid of **3**. Complex **3** was isolated in 95.89% yield (318.3 mg) by filtration under reduced pressure. Recrystallization was accomplished by slow diffusion of CCl_4 into a solution of the compound in CH_3CN and a few drops of DMSO. IR (KBr, cm^{-1}): 3070 br, m, 2293 w, 2252 w, 1520 s, 1428 s, 1056 s, 849 s, 721 s. Electronic spectrum in CH_3CN: λ_{max}, nm (ϵ in $M^{-1}\ cm^{-1}$) = 736 (96), 270 (90 300), 225 (10 100), 201 (88 100).

Preparation of $[\mathrm{Cu(5\text{-}Me\text{-}phen)_2(CH_3CN)}](\mathrm{BF_4})_2$ (4). To a solution of $\mathrm{Cu(BF_4)_2}$ hydrate (202.3 mg, 0.6542 mmol) in 10 mL of CH_3CN was added dropwise over a period of 30 min a dilute solution of 5-Me-phen (242.1 mg, 1.246 mmol, 1.905 equiv) in 55 mL of CH_3CN. The solvent was removed by placing the solution on a rotary evaporator, which produced a bluish-green solid of **4** in 85.73% yield (373.9 mg). Spectroscopic samples were recrystallized from CH_3CN/ether. IR (KBr, cm^{-1}): 3073 w, 2938 w, 2321 w, 2293 w, 1523 m, 1486 m, 1429 m, 1058 vs, 728 m. ^1H NMR for **4** (d_6-acetone): δ 3.522 ppm (full width at half-height = 15 Hz) 2.259 ppm (2.92 Hz). Electronic spectrum in CH_3CN: λ_{max}, nm (ϵ in $M^{-1}\ cm^{-1}$) = 707 (68), 274 (24 200), 240 (sh), 215 (sh), 196 (240 000).

Preparation of $[\mathrm{Cu(5,6\text{-}Me_2\text{-}phen)_2(CH_3CN)}](\mathrm{BF_4})_2$ (5). $\mathrm{Cu(BF_4)_2}$ hydrate (124.8 mg, 0.3814 mmol) was dissolved in 10 mL of CH_3CN to produce a blue solution. The slow addition of 5,6-Me_2-phen (159.8 mg, 0.7674 mmol, 2.012 equiv) dissolved in 55 mL of CH_3CN over 30 min changed the light blue solution to forest green. The solution was stirred at room temperature for 10 min after the addition of ligand was complete; subsequent solvent removal on a rotary evaporator resulted in the precipitation of a dark green solid of **5** in 77.05% yield (206.8 mg). Samples for spectroscopy were recrystallized from CH_3CN/ether. IR (KBr, cm^{-1}): 3091 w, 2923 w, 1607 m, 1587 w, 1522 w, 1482 w, 1432 m, 1055 vs, 809 m, 728 m. ^1H NMR for **5** (d_6-acetone): δ 2.032 ppm (full width at half-height = 30 Hz) 3.57 ppm (16.7 Hz). Electronic spectrum in CH_3CN: λ_{max}, nm (ϵ in $M^{-1}\ cm^{-1}$) = 715 (88), 278 (85 900), 241 (82 500), 229 (90 000), 208 (93 400).

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Table 1. Experimental Details of the X-ray Diffraction Studies of [Cu(5-NO_2-phen)$_2$(CH_3CN)](BF_4)$_2$ (**1**), [Cu(5-Cl-phen)$_2$(CH_3CN)](BF_4)$_2$ (**2**), [Cu(o-phen)$_2$(CH_3CN)](BF_4)$_2$ (**3**), [Cu(5-Me-phen)$_2$(CH_3CN)](BF_4)$_2$ (**4**), and [Cu(5,6-Me_2-phen)$_2$(CH_3CN)](BF_4)$_2$, (**5**)

compound	**1**	**2**	**3**	**4**	**5**
formula	$C_{26}H_{17}B_2CuF_8N_7O_4$	$C_{26}H_{17}B_2Cl_2CuF_8N_5$	$C_{26}H_{19}N_5B_2CuF_8$	$C_{28}H_{23}B_2CuF_8N_5$	$C_{30}H_{27}B_2CuF_8N_5O_{0.5}$
fw, g mol^{-1}	728.625	707.514	638.624	666.677	703.739
space group	*C*2/*c* (15)	*C*2/*c* (15)	*C*2/*c* (15)	*C*2/*c* (15)	$P2_1/c$ (No. 14)
a, Å	23.225(7)	24.10(1)	19.433(8)	23.94(1)	11.482(2)
b, Å	9.307(3)	8.861(4)	8.784(4)	8.904(5)	15.756(3)
c, Å	26.984(5)	16.977(8)	14.874(6)	16.850(9)	17.410(3)
β, deg	130.309(4)	131.108(7)	97.426(7)	130.380(7)	109.14(1)
V, Å^3	2800(10)	2732(2)	2518(2)	2736(2)	2975.5(9)
Z	4	4	4	4	4
T, °C	23	23	23	23	−75
ρ_{calcd}, g cm^{-1}	1.729	1.720	1.685	1.618	1.569
linear abs. coeff, cm^{-1}	8.830	10.787	9.555	8.829	8.175
R[a]	0.084	0.080	0.032	0.054	0.078
R_w[b]	0.134[c]	0.092	0.044	0.062	0.084

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 4F^2/\sigma^2(F^2)$ and $\sigma^2(F^2) = [S^2(C + 4B) + (pI)^2]/(Lp)^2$ with S = scan rate, C = peak counts, B = sum of left and right background counts, I = reflection intensity, and Lp = Lorentz−polarization factor; *p* is a constant employed to avoid overweighting of intense reflections. [c] $wR2 = [\sum(wF_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$ and $w = 1/\sigma^2(F_o^2) + (0.0482P)^2 + 0P$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$.

Physical Measurements. The Fourier transform infrared spectrum of each complex suspended in a KBr pellet was collected on an Alpha Centauri FT-IR spectrometer. The electronic spectra were collected on a Varian Cary 300 Bio UV−visible spectrophotometer. The ^{1}H NMR spectra were recorded in a 5 mm NMR tube on a 400 MHz General Electric Omega NMR spectrometer with a 10 mm variable temperature broad band probe referenced to d_6-acetone.

Cyclic voltammetry experiments were carried out using a Bioanalytical Systems CV-50 electrochemical analyzer. All sample solutions were prepared in dry acetonitrile and contained 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) as the supporting electrolyte and the experimental compound at a concentration of 1 mM. The solutions were purged with argon for 15 min prior to measurements to remove residual oxygen; during measurements, a stream of argon was passed over the sample solutions. The reaction cell for the experiments contained platinum working and auxiliary electrodes, a Ag/Ag^+ nonaqueous reference electrode, and an argon sparge tube. The reference electrode was prepared immediately prior to use by adding a solution of 0.1 M $TBABF_4$ and 0.01 M $AgNO_3$ in acetonitrile to the electrode body which contained a silver wire. All voltammograms were referenced to the Ag/Ag^+ redox couple using TEMPO as an internal standard. The scans were performed at a scan rate of 100 mV/s, unless otherwise noted. The potentials were scanned from +800 to −800 mV and back for all phenanthroline complexes and +1000 to −800 mV for Cu(BF_4)$_2$.

X-ray Crystallography. Details of the data collection for **1**−**5** are included in Table 1. Data for complexes **1**−**4** were collected using a Siemens SMART CCD (charge coupled device) based diffractometer operating at room temperature. Suitable crystals of **1**−**4** were chosen and mounted in glass capillaries in the mother liquor. Data for compounds **1**, **2**, **3**, and **4** were measured using ω scans of 0.3° per frame for 35, 90, 15, and 40 s, respectively, such that a partial hemisphere was collected for each crystal. A total of 1271 frames for **1**, 1041 frames for **2**, 1271 frames for **3**, and 836 frames for **4** were collected with a final resolution of 0.84 Å. The first 50 frames were re-collected at the end of each data collection to monitor for decay, which was negligible in all cases. Cell parameters were retrieved by using SMART[38] software and refined by using SAINT software on all observed reflections. Data reduction was performed by using the SAINT software[39] which corrected for Lorentzian polarization and decay. Absorption corrections were applied by using SADABS[40] supplied by George Sheldrick.

[Cu(5-NO_2-phen)$_2$(CH_3CN)](BF_4)$_2$ (1). A solution of **1** dissolved in CH_3CN and a few drops of DMSO was layered with CH_2Cl_2 to yield X-ray quality crystals. Analysis of the systematic absences revealed the space group to be *C*2/*c*. The structure was solved by direct methods using the SHELXL-90[41] program and refined by the least-squares method on F^2, SHELXL-93,[42] incorporated in SHELXTL-PC software package.[43] A crystallographic C_2 axis bisecting the copper and the CH_3CN ligand rendered only half of the metal complex unique. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were included in calculated positions. In the final difference map, the maximum residual electron density was 0.96 e$^-$/Å^3.

[Cu(5-Cl-phen)$_2$(CH_3CN)](BF_4)$_2$ (2). X-ray quality crystals of complex **2** were grown by vapor diffusion of chloroform into a solution of **2** dissolved in CH_3CN and a few drops of DMSO. The space group *C*2/*c* was determined by analysis of systematic absences. The positions of the metal atom and the majority of the non-hydrogen atoms were determined by using the SIR-92[44] structure solution option within the teXsan software package.[45] Alternating least-squares cycles and Fourier maps were used to locate the remaining atoms. The copper atom and CH_3CN ligand resided on a crystallographic 2-fold axis rendering only half of the metal complex unique. The BF_4^- counterion was disordered and was refined as two rigid bodies, each at 50% occupancy, sharing a mutual B atom. This disordered counterion plus C(1)−C(3) and C(8)−C(10) were refined isotropically; the remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions. The maximum residual electron density was 0.6 e$^-$/Å^3 near the disordered BF_4^-.

[Cu(o-phen)$_2$(CH_3CN)](BF_4)$_2$ (3). Good quality crystals of complex **3** were grown by diffusion of ether into a solution of **3** dissolved in CH_3CN and a few drops of DMSO. Systematic absences were used to determine the *C*2/*c* space group. The positions of all the non-hydrogen atoms in the structure were revealed upon application of SIR-92 within the teXsan software package. Least-squares cycles were used for subsequent refinement. The asymmetric unit contained only half of the formula unit since the center of the complex ion resided on a C_2 special position. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions. The highest peak in the final difference map was 0.39 e$^-$/Å^3 between Cu(1) and N(2).

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(45) *teXsan for Windows*, version 1.05; Molecular Structure Corporation: 1997−1998.

[Cu(5-Me-phen)$_2$(CH$_3$CN)](BF$_4$)$_2$ (4). Small X-ray quality blue-green blocks of complex **4** were grown by vapor diffusion of chloroform into a solution of **4** dissolved in CH$_3$CN and a few drops of DMSO. Analysis of systematic absences led to the choice of *C*2/*c* for the space group. The teXsan software package[45] was used to solve the structure; the metal atom and most of the non-hydrogen atoms were revealed by application of the SIR-88 structure solution program.[46] The remaining atoms were located by alternating least-squares refinement and difference Fourier maps. Because of a crystallographic 2-fold axis bisecting the metal cluster, only half of the formula unit was present in the asymmetric unit. Hydrogens were included in calculated positions, and the non-hydrogen atoms were refined anisotropically with the exception of B, C(1)−C(3), and C(8)−C(10). The largest peak in the final difference map was 0.5 e$^-$/Å^3 near the BF$_4^-$ counterion.

[Cu(5,6-Me$_2$-phen)$_2$(CH$_3$CN)](BF$_4$)$_2$ (5). X-ray quality crystals were grown by vapor diffusion of ether into a solution of **5** dissolved in CH$_3$CN. A sample of approximate dimensions 0.16 × 0.21 × 0.24 mm was cut from a larger block and was mounted with Infineum Parabar 10312 oil on the end of a glass fiber at low temperature. The sample was examined on a CAD4 diffractometer equipped with graphite-monochromatized Mo K$\bar{\alpha}$ radiation ($\bar{\lambda} = 0.71073$ Å) and was judged to be of acceptable quality by several ω-scans whose average width at half-height was 0.283°. The monoclinic symmetry was confirmed by axial photographs. Three periodically monitored check reflections displayed no decay during data collection. The data were corrected for absorption based on data from three ψ scans. The structure was solved by using the teXsan software package.[45] The copper atom and most of the non-hydrogen atoms were located in the initial structure solution by using the program SIR-92.[44] The rest of the structure was revealed by alternating least-squares refinement cycles and difference Fourier maps. One of the BF$_4^-$ counterions was disordered and was refined as two independent interlocking rigid bodies with occupancies of 75% and 25%, respectively. All non-hydrogen atoms except for the atoms in the rigid groups B(1), C(1)−C(3), and C(8)−C(10) were refined anisotropically. Examination of an ORTEP diagram of the refined structure revealed an elongated ellipsoid for C(30) of the CH$_3$CN ligand. An attempt was made to model this disorder, but it was not possible to refine two carbon positions with reasonable distances to C(29). A persistently high peak of electron density over 1.0 e$^-$/Å^3 was modeled as a water molecule with half-occupancy hydrogen bonded to a F of the well-refined BF$_4^-$. The hydrogen atoms were included in calculated positions. The largest peak in the final difference map was 0.9 e$^-$/Å^3.

Results and Discussion

Since the 3:1 ligand:copper species are quite stable, each 2:1 complex was prepared by the slow addition of ligand into a dilute solution of the copper starting material in order to eliminate high localized concentrations of ligand that would lead to formation of the tris-ligated species. The complexes were then isolated by removing the solvent or by adding diethyl ether to induce precipitation. The ^{1}H NMR spectra are very well-defined for paramagnetic complexes and clearly display resonances due to CH$_3$CN and phenanthroline protons. The infrared spectra also display bands due to the CH$_3$CN and phenanthroline ligands as well as the typical intense feature common to the BF$_4^-$ counterion. The slight variation of color in the complexes ranging from the blue of **1** to green for **5** is reflected by accompanying shifts in the broad d−d transition around 700 nm in the visible region of the electronic spectrum.[47] All of the complexes share a well-defined maximum just above 270 nm in the ultraviolet region. In addition to two shoulders at 240 and 215 nm in each spectrum, the complexes with asymmetric phenanthrolines, **1**, **2**, and **4**, share an additional maximum at 196 nm whose molar absorptivity is 10-fold higher than the 270 nm feature. The complexes with symmetrical phenanthroline ligands, **3** and **5**, are both characterized by well-resolved maxima in the ultraviolet region between 200 and 240 nm whose molar absorptivities are comparable to the 270 nm absorption.

Table 2. The Values Obtained from Analysis of the Cyclic Voltammograms for Compounds **1**−**5**

compd	$E_{1/2}$ (mV)	ΔE (mV)	$I_{p,c}/I_{p,a}$
1	−168	189	1.12
2	−225	266	1.00
3	−284	213	0.85
4	−302	225	0.94
5	−384	318	1.13
Cu(BF$_4$)$_2$	+719	148	1.02

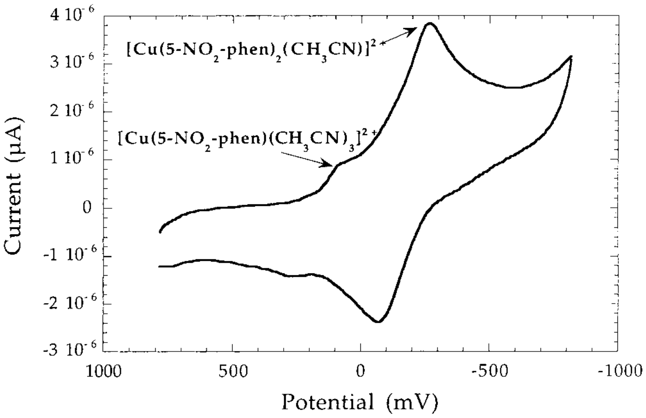

Figure 2. The cyclic voltammogram of [Cu(5-NO$_2$-phen)$_2$(CH$_3$CN)](BF$_4$)$_2$. The voltammogram is referenced to the Ag/Ag$^+$ couple.

Electrochemistry. The cyclic voltammograms for all phenanthroline complexes were measured in the potential range from −0.8 to +0.8 V and show a quasi-reversible, one-electron wave corresponding to the Cu(II)/Cu(I) couple (Table 2). A typical voltammogram is shown in Figure 2. Spectroelectrochemical titrations[48] have been used to determine that the minor wave corresponds to the reduction of the mono-phenanthroline-cupric species. The peak separation, ΔE, increases slowly with increasing scan rate (ν), and the cathodic peak currents are proportional to $\nu^{1/2}$, indicating that the data are consistent with a simple E$_r$ mechanism.[35,49,50] A plot of log($I_{p,c}$) vs log(ν) yields a slope equal to 0.5, which corresponds to a diffusion-controlled process rather than an adsorption mechanism and is consistent with transfer of a single electron.[49] The ΔE and $I_{p,c}/I_{p,a}$ values imply that there is some irreversibility to the electron transfer reaction, which suggests that a coordination change takes place at the copper ion upon oxidation or reduction on the electrochemical time scale.[50,51] Most probably the trigonal bipyramidal Cu(II) species loses an acetonitrile ligand upon reduction to Cu(I) to produce a cuprous species with the preferred tetrahedral coordination geometry.[51]

In all cases, the reduction potentials of the Cu−phen complexes were shifted to more negative values relative to the Cu(II)/Cu(I) couple of Cu(BF$_4$)$_2$ dissolved in acetonitrile. This result indicates that the phenanthroline ligand stabilizes the oxidized form of the compound relative to coordination by the

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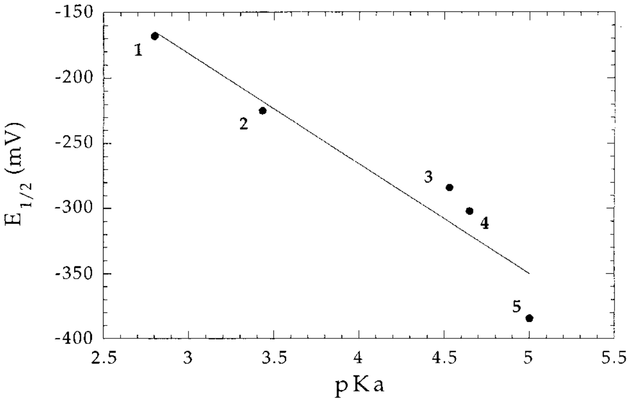

Figure 3. The dependence of the 1:2 copper−phenanthroline reduction potentials on the basicity of the ligands, $R = 0.97$. The R and R′ groups of the ligands are (**1**) NO_2, H; (**2**) Cl, H; (**3**) H, H; (**4**) CH_3, H; and (**5**) CH_3, CH_3. The pK_a values were taken from ref 52.

acetonitrile solvent alone. As the substituents on the phenanthroline ligands become more electron withdrawing, the values of $E_{1/2}$ are seen to shift to more positive values compared to the unsubstituted phenanthroline complex, **3**, which reflects the increased ease of reduction of the copper center due to the more positive formal charge. Figure 3 shows a plot of reduction potential vs pK_a, and as expected, there is a good correlation ($R = 0.97$) between the basicity of the ligand and the reduction potential of the copper center. These results are similar to those reported by James and Williams[52] and show that the basicity of the ligand can tune the Lewis acidity of the metal center to stabilize the Cu(I) state relative to the Cu(II) state with ligands having lower pK_a values.

Description of the Structures. Selected average bond distances and angles are presented in Table 3, and Figures 4, 5, and 6 display ORTEP views of **3**, **4**, and **5**, respectively; complexes **1** and **2** are isomorphous with **4** and have atom-numbering schemes corresponding to the structure of **3**, so separate views of these complexes are omitted. Each of the complexes has a distorted trigonal bipyramidal (tbp) arrangement about the copper atom with the two phenanthroline ligands each occupying one axial and one equatorial position. The third equatorial position is occupied by CH_3CN. The bond distances between the copper atom and the phenanthroline nitrogens are approximately 2.0 Å in all of the structures. The N−Cu−N angle formed by the nitrogens of one phenanthroline ligand and the central atom is smaller than the ideal value of 90° for a tbp geometry, but the values of approximately 80° are typical for copper−phenanthroline complexes.[50,53−59] In all of the structures, the axial Cu−N distances are always slightly compressed, consistent with other known trigonal bipyramidal Cu(II)−bis-phenanthroline crystal structures.[50,53−55,58] In each of the mono-substituted phenanthroline structures, the R group is located off C(6), which is closer to the axial position than the equatorial plane. Each of the first four compounds has a hydrogen atom bonded to C(5), which is the position closer to the equatorial plane, and in each of these compounds, the Cu−$NCCH_3$ distance is close to 2.0 Å. By contrast, in the 5,6-dimethylphenanthroline complex, which has methyls bound to both C(5) and C(6), the Cu−$NCCH_3$ distance is significantly elongated to 2.201(7) Å. This observation suggests that although a single substituent off C(6) does not significantly distort the complex, as judged by the similarities among structures **1**−**4**, an electron-donating substituent closer to the equatorial plane off C(5) causes a more substantial structural change as the complex adjusts to accommodate the increased electron density in the plane.

The dihedral angles of the five complexes span the range of known values for similar copper complexes. The dihedral angles between the phenanthroline planes for **2** and **4** are 72° and 71°, respectively, similar to the values of 72° observed for the crystal structure of the 2,9-Me_2-phen copper complex[19] and 67° for the unsubstituted complexes of **3**, $[Cu(o\text{-}phen)_2(O_2CCH_3)]ClO_4$,[57] and $[Cu(o\text{-}phen)_2Cl]ClO_4$.[59] The dihedral angle of 45° in **5** is at the more acute range of the possible values, but it agrees well with the NO_3^- and BF_4^- salts of $[Cu(o\text{-}phen)_2(H_2O)]^{2+}$, which display angles of 40° and 47°, respectively.[60,61] Each of these three complexes displays a N−Cu−N angle involving equatorial phenanthroline nitrogens that is substantially larger than the other equatorial angles with values of 132.3° for **5**, 139.6° for $[Cu(o\text{-}phen)_2(H_2O)](NO_3)_2$,[60] and 137° for $[Cu(o\text{-}phen)_2(H_2O)](BF_4)_2$;[61] no other complexes for which dihedral angles have been measured or calculated exhibit this extremely large bond angle. The other extreme of 82° for the dihedral angles is represented by structures of the nitrate salts of Cu(II)−bis-o-phen with either cyanide or imidazole as the additional ligand,[53,58] but is also observed for the structure of **1** which displays a dihedral angle of 79°. The range of dihedral angles for the variety of o-phen complexes from the literature, as well as the absence of significant steric differences around the Cu center between these literature examples and the substituted phenanthroline complexes included in the present study, suggests that differences in dihedral angles are predominantly due to crystal packing forces rather than electronic effects, although among the complexes presented here, there is a general trend for larger dihedral angles with more electron withdrawing substituents on the 5- and 6-positions of the chelating ligands.

Focusing on the geometry of the CH_3CN ligand, the Cu−N−C and N−C−C bond angles are constrained to be 180° by the crystallographic C_2 symmetry in **1**, **2**, **3**, and **4**. In the structure of **5**, the Cu−N−C angle is 157° and the N−C−C angle is 173°. An analysis of the closest contacts in the structures reveals consistently short contacts between the fluorines of the counterions and the atoms of the bound solvent ligand. In compound **2**, there are F−C(13) and F−C(14) contacts of between 3.03(2) and 3.06(2) Å. The analogous distances in compound **3** are 3.088(3) and 3.172(3) Å whereas the distances in **4** are each 3.08 Å, and in **1**, the shortest distance is slightly longer at 3.119 Å between F(3) and C(14). In compound **5**, the solvent ligand is bent toward the counterion with short contacts including distances between the disordered BF_4^- and the acetonitrile ligand of 3.06(2) Å to N(5), 2.86(2) Å to C(29), and 3.07(2) Å to C(30). These short packing contacts are a more probable cause for the alteration in dihedral angle and angle of binding between Cu and CH_3CN than the change in electron-donating ability of the ligand.

Although their origins are not yet fully understood, the current

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Table 3. Selected Bond Distances (Å) and Angles (deg) for [Cu(5-NO$_2$-phen)$_2$(CH$_3$CN)](BF$_4$)$_2$ (**1**), [Cu(5-Cl-phen)$_2$(CH$_3$CN)](BF$_4$)$_2$ (**2**), [Cu(o-phen)$_2$(CH$_3$CN)](BF$_4$)$_2$ (**3**), [Cu(5-Me-phen)$_2$(CH$_3$CN)](BF$_4$)$_2$ (**4**), and [Cu(5,6-Me$_2$-phen)$_2$(CH$_3$CN)](BF$_4$)$_2$ (**5**)

	1	**2**	**3**	**4**	**5**
			Bonds		
Cu−N (CH$_3$CN)	1.98(1)	1.99(1)	2.048(4)	2.02(1)	2.201(7)
Cu−N (phen, axial)	2.001(7)	1.986(8)	1.986(2)	1.968(6)	1.992(7), 1.984(7)
Cu−N (phen, equatorial)	2.098(7)	2.05(1)	2.094(2)	2.064(7)	2.051(6), 2.015(6)
			Angles		
N(phen)−Cu−N(phen)	80.1(3)	81.3(4)	81.63(9)	81.5(3)	82.0(3), 81.3(3)
N(ax)−Cu−N(ax)	172.5(4)	174.5(5)	176,2(1)	175.1(4)	176.9(2)
N(eq)−Cu−N(eq)	101.5(3)	107.5(5)	113.4(1)	109.0(3)	136.3(2)
N(eq)−Cu−N(CH$_3$CN, eq)	129.3(2)	126.2(3)	123.29(6)	125.5(2)	107.2(3), 116.5(3)
Cu−N−C (in CH$_3$CN)	180	180	180	180	157.1(9)
N−C−C (in CH$_3$CN)	180	180	180	180	173(1)
phen−phen dihedral angles	79	72	67	71	45

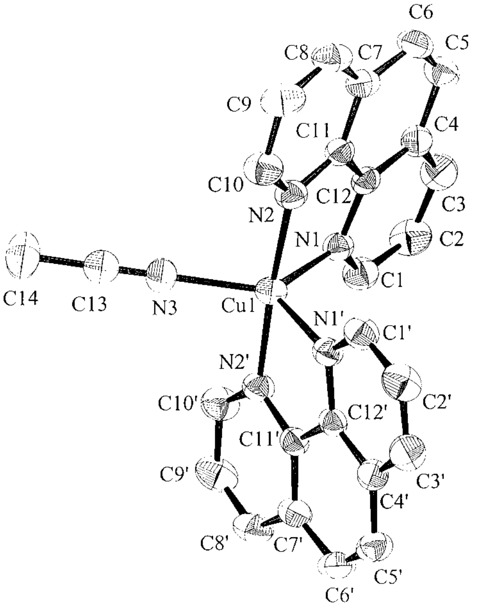

Figure 4. ORTEP diagram of [Cu(o-phen)$_2$(CH$_3$CN)](BF$_4$)$_2$, **3**, showing 50% probability ellipsoids. The hydrogen atoms and counterions are omitted for clarity. The numbering scheme of the carbon atoms is the same as for the structures of **1** and **2**.

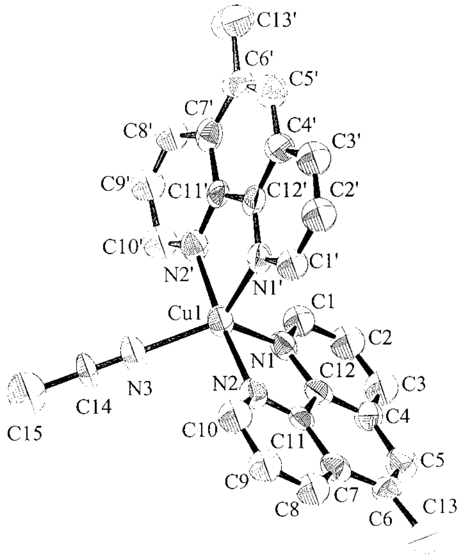

Figure 5. ORTEP diagram of [Cu(5-Me-phen)$_2$(CH$_3$CN)$_2$](BF$_4$)$_2$, **4**, showing 50% probability ellipsoids. The hydrogen atoms and counterions are omitted for clarity. Complexes **1** and **2** are isomorphous with the structure of **4**.

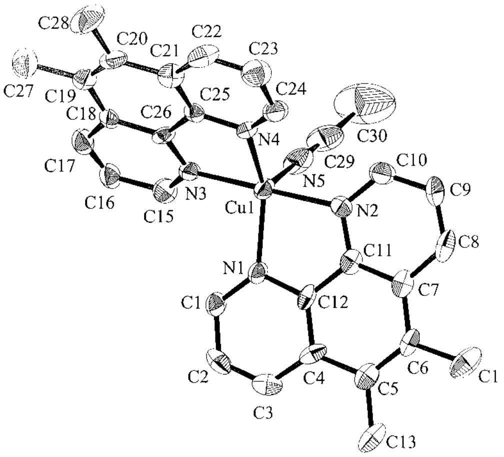

Figure 6. ORTEP diagram of [Cu(5,6-Me$_2$-phen)$_2$(CH$_3$CN)$_2$](BF$_4$)$_2$, **5**, showing 50% probability ellipsoids. The hydrogen atoms and counterions are omitted for clarity.

structural results provide clear evidence that remote substituents can play a very significant role in the chemistry of Cu(II) phenanthrolines, particularly with regard to interaction of the [Cu(5-R-phen)$_2$]$^{2+}$ fragment with additional donor ligands such as acetonitrile. In particular, the distinct elongation of the Cu−NCCH$_3$ bond in the 5,6-Me$_2$-phen derivative is a clear indication that substituents on the phenanthroline can affect binding of a fifth ligand to the Cu(II) center. These observations are related to a number of experimental phenomena involving the influence of ring substitution on the behavior of copper phenanthroline derivatives.

In the photochemistry of copper chelate complexes, McMillin has recently observed that the luminescence lifetimes of cuprous bis-phenanthrolines can be significantly enhanced in solution by remote electron-donating methyl substituents;[29] this effect was correlated with distortions of the ground state geometries. Solution luminescence lifetimes are strongly dependent on interactions between the MLCT excited state, which is largely Cu^{2+} in character, and exogenous Lewis bases such as acetonitrile.[62] A weakening of such interactions through substituent effects, as we have observed for the [Cu(5,6-Me$_2$-phen)$_2$(CH$_3$CN)]$^{2+}$, may also contribute to the extended fluorescence lifetimes of the methyl-substituted cuprous complexes.

Conclusions

Electron-withdrawing or electron-donating substituents on the phenanthroline ligands have a pronounced effect on the struc-

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tural and chemical behavior of the resulting copper(II) bischelate complexes. Electrochemical experiments have demonstrated that electron-withdrawing ligands with lower pK_a values stabilize the Cu(I) state and result in more accessible reduction potentials. In the solid state structures, substitution for a hydrogen at the phenanthroline position closer to the axial position of the copper ion causes only minor changes in the overall shape of the complex. The most significant changes in dihedral angle and equatorial bond distances are observed with the disubstituted phenanthroline ligand in which an electron-donating substituent in closer proximity to the equatorial plane causes an elongation of the Cu−solvent distance to compensate for the additional electron density on the metal center. This structural result has implications relating to the substituent influences on the behavior of copper phenanthroline complexes, particularly for processes in which coordination changes are known to play a strong role such as photochemical and redox reactions.[63] Further work aimed at determining the influence of ring substitution on the structural and chemical behavior of additional cupric and cuprous phenanthroline complexes is in progress.

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Supporting Information Available: Listings of full experimental details of X-ray crystallography, atomic coordinates, anisotropic thermal parameters, and bond lengths and distances for complexes **1**−**5**, as well as ORTEP diagrams for complexes **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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