

Solution and Solid-State Variation of Cupric Phenanthroline Complexes

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The 1:1 cupric-phenanthroline complexes, [Cu(5,6-Me₂-phen)(MeCN)₂(BF₄)](BF₄) (**1**), [Cu(o-phen)(MeCN)₂(H₂O)](BF₄)₂ (**2**), and [Cu(5-Cl-phen)(MeCN)₂(BF₄)](BF₄) (**3**), have been prepared and characterized by X-ray crystallography. The structures of **1** and **3** are characterized by an equatorial plane about the copper center consisting of a phenanthroline ligand and two acetonitrile ligands. The copper units are connected by bridging counterions in the axial positions of the pseudo-octahedral metal centers to form one-dimensional solid-state linkages. The structure of **2** contains the same equatorial plane as **1** and **3**, but an axial water ligand completes a square pyramidal geometry for each discrete metal unit. Although the solid-state structures vary for the three complexes, characterization through electronic spectroscopy and cyclic voltammetry reveals similar behavior for all three complexes in solution.

Introduction

Copper complexes with phenanthroline ligands have been studied extensively for numerous applications including their biological activity as artificial nucleases^{2–6} and their rich photochemical and photophysical behavior.^{7–14} The substantial geometric rearrangement required for conversion between

the five- or six-coordinate cupric species and the corresponding four-coordinate cuprous complexes makes the redox properties of these systems of significant interest.^{15–20} The presence of the phenanthroline ligands offers the opportunity to tune the specific properties of a complex by adding substituents to different locations on the rings. For example, photoluminescent behavior in copper complexes requires alkyl or aryl substitutions in the stereoactive 2- and 9-positions on the phenanthroline rings.^{9–11,13,14} The nuclease activity of copper-bis-phenanthroline complexes in the presence of H₂O₂ is affected by ring substitution but requires the introduction of small substituents at the 5 or 6 position on the phenanthroline ligand to minimize the steric effects. The electronic influence of the substituents accounts for the variation in the nuclease behavior; addition of electron-withdrawing nitro or chloro groups increases the efficacy of

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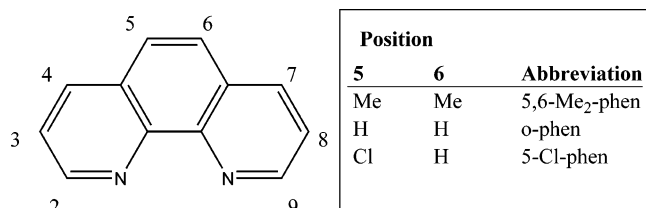


Figure 1. Phenanthroline ligand numbering scheme and list of ligands used.

the nuclease whereas electron-donating methyl groups reduce the nuclease activity.²¹

An ongoing interest in our laboratory focuses on the structural and electronic effects of substituted phenanthroline ligands in copper complexes. Similar to the nuclease studies mentioned above, we have chosen phenanthroline ligands modified with small electron-withdrawing and electron-donating groups in the 5 or 6 position so the effects on the corresponding copper complexes will result from the electronic rather than steric effects of the substituents. Metal coordination sites not occupied by phenanthroline ligands are expected to be occupied by acetonitrile; solution-state measurements are carried out in the same solvent to maximize the similarities between the solid-state and solution structures. In our Current Study, we have pursued the preparation of mono-phenanthroline copper complexes using the ligands identified in Figure 1. In the bis-phenanthroline complexes,²² both the electronic spectrum and the redox properties varied upon a change in the ring substituents; similar solution-state variations are observed for the mono-phenanthroline species discussed herein. In the solid state, the only significant effect of phenanthroline substitution in the bis-phenanthroline complexes is an elongation of the equatorial MeCN ligand in the trigonal bipyramidal structure. The mono-phenanthroline complexes, constrained by only one chelating ligand, offer the potential for greater structural variation and flexibility. As observed in the other known complexes of copper(II) with a single nitrogen chelate,^{23–27}

hydrogen-bonding and crystal-packing forces are expected to play a significant role in establishing the solid-state structures.

Experimental Section

General Procedures. Because the copper starting material is extremely hygroscopic, the Cu content in the Cu(BF₄)₂ starting material was determined by atomic absorption in conjunction with electronic spectroscopy to allow for precise stoichiometric reactions. The working molar mass of the starting material for syntheses herein was calculated to be 471.2 g/mol, corresponding to Cu(BF₄)₂•14.23 H₂O. Acetonitrile used for cyclic voltammetry was distilled from CaH₂ under an atmosphere of N₂ prior to use. CH₃CN used for reactions and CD₃CN used for NMR spectrometry was not dried or used in an anaerobic atmosphere. All other reagents were used as received from commercial sources.

Preparation of [Cu(5,6-Me₂-phen)(MeCN)₂(BF₄)](BF₄) (1). A 0.348 g (0.739 mmol) sample of Cu(BF₄)₂ was dissolved in 150 mL of MeCN. In a separate flask, 0.154 g of 5,6-dimethylphenanthroline (0.739 mmol, 1.00 equiv) was dissolved in 300 mL of MeCN and added dropwise to the solution of the copper starting material. As the ligand was added to the metal species, an emerald green color appeared. After the addition was complete, the resulting solution was placed on a rotary evaporator to remove the bulk of the MeCN. The pale-green complex was precipitated by the addition of anhydrous diethyl ether and isolated by vacuum filtration. The complex was obtained with a crude yield of 94.2% (0.358 g). Crystals of this complex were obtained by slow diffusion of CHCl₃ into a solution of the crude material dissolved in MeCN. IR (KBr, cm⁻¹): 3074 w, 3018 w, 2360 w, 2322 w, 1605 m, 1525 w, 1429 m, 1343 m, 1083 br, 808 m, 725 m. Electronic spectrum in MeCN: λ_{max}, nm (ε in M⁻¹ cm⁻¹) = 663 (57), 303 (sh), 284 (29300), 242 (23600), 226 (sh), 210 (35800). ¹H NMR for **1** (d₃-acetonitrile): δ 2.54 ppm (full width at half-height = 110 Hz), 3.69 ppm (full width at half-height = 32 Hz), 3.68. Anal. Calcd for C₁₈H₂₀B₂CuF₈N₄O, **1**•H₂O: C, 39.63; H, 3.67; N 10.27. Found: C, 40.06; H, 3.62; N, 9.98.

Preparation of [Cu(o-phen)(MeCN)₂(H₂O)](BF₄)₂ (2). A 0.406 g sample of Cu(BF₄)₂ (0.860 mmol) was dissolved in 200 mL of MeCN. A 0.155 g quantity of 1,10-phenanthroline (0.860 mmol, 1.00 equiv) was dissolved in 250 mL of MeCN and added dropwise to the metal starting material to form an aqua-colored solution. Excess MeCN was removed from the reaction solution by using a rotary evaporator. Anhydrous ether was used to precipitate the complex, and the pale-aqua solid was isolated by vacuum filtration. The crude yield of the solid was 86.9% (0.387 g). Samples for spectroscopy were recrystallized by using slow diffusion of toluene into a solution of the compound dissolved in MeCN. IR (KBr, cm⁻¹): 3049 w, 2362 w, 2333 w, 1587 m, 1515 m, 1425 s, 1350 m, 1106 br, 854 s, 720 s. Electronic spectrum in MeCN: λ_{max}, nm (ε in M⁻¹ cm⁻¹) = 677 (46), 295 (sh), 273 (38100), 224 (34500), 206 (36300). ¹H NMR for **2** (d₃-acetonitrile): δ 2.53 ppm (full width at half-height = 128 Hz). Anal. Calcd for C₁₆H₁₈B₂CuF₈N₄O₂, **2**•H₂O: C, 35.89; H, 3.39; N, 10.46. Found: C, 35.97; H, 3.17; N, 10.23.

Preparation of [Cu(5-Cl-phen)(MeCN)₂(BF₄)](BF₄)₂ (3). Complex **3** was formed by dropwise addition of 0.152 g of 5-chloro-

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Table 1. Experimental Details of the X-ray Diffraction Studies of [Cu(5,6-Me₂-phen)(MeCN)₂(BF₄)](BF₄) (**1**), [Cu(*o*-phen)(MeCN)₂(H₂O)](BF₄)₂ (**2**), and [Cu(5-Cl-phen)(MeCN)₂(BF₄)](BF₄) (**3**)

compound	1	2	3
formula	C ₁₈ H ₁₈ B ₂ CuF ₈ N ₄	C ₁₆ H ₁₆ B ₂ CuF ₈ N ₄ O	C ₁₆ H ₁₂ B ₂ ClCuF ₈ N ₄
FW, g mol ⁻¹	527.52	517.49	532.91
space group	Pmn2(1)	P2(1)/m	Pmn2(1)
<i>a</i> , Å	11.4816(19)	8.4972(16)	11.3692(13)
<i>b</i> , Å	13.517(2)	12.028(2)	13.2634(15)
<i>c</i> , Å	6.9302(11)	10.182(2)	6.9315(8)
β, deg	90	95.530(4)	90
<i>V</i> , Å ³	1075.6(3)	1035.8(3)	1044.3(2)
<i>Z</i>	2	2	2
<i>T</i> , °C	20	20	20
<i>d</i> _{calcd}	1.629 Mg/m ³	1.659 Mg/m ³	1.695 Mg/m ³
linear abs. coeff	1.097 mm ⁻¹	1.141 mm ⁻¹	1.255 mm ⁻¹
final <i>R</i> indices ^a	<i>R</i> 1 = 0.0456	<i>R</i> 1 = 0.0488	<i>R</i> 1 = 0.0517
[<i>I</i> > 2σ(<i>I</i>)]	<i>wR</i> 2 = 0.1150	<i>wR</i> 2 = 0.1400	<i>wR</i> 2 = 0.1419

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR2 = [\sum (wF_o^2 - F_c^2)^2 / \sum (wF_o^4)]^{1/2}.$$

rophenanthroline (0.708 mmol, 1.00 equiv) dissolved in 250 mL of MeCN to a solution of 0.334 g of Cu(BF₄)₂ (0.708 mmol) dissolved in 200 mL of MeCN. After formation of the pale-aqua product, the volume of the resulting solution was reduced on a rotary evaporator. Anhydrous ether was used to precipitate the blue complex that was subsequently isolated by vacuum filtration. The crude yield of the solid was 86.1% (0.330 g). Crystals of **3** were obtained by slow diffusion of toluene into a solution of complex dissolved in MeCN. IR (KBr, cm⁻¹): 3080 w, 3044 w, 2361 w, 2324 w, 1584 m, 1517 w, 1421 m, 1084 br, 962 m, 725 m. Electronic spectrum in MeCN: λ_{max}, nm (ε in M⁻¹ cm⁻¹) = 677 (58), 275 (29600), 228 (28700), 207 (29600). ¹H NMR for **3** (*d*₃-acetonitrile): δ 2.23 ppm (full width at half-height = 15 Hz). Anal. Calcd for C₁₆H₁₃B₂ClCuF₈N₄O_{0.5} · 3/2 H₂O: C, 35.46; H, 2.41; N, 10.33. Found: C, 35.93; H, 2.22; N, 9.82.

Physical Measurements. ¹H NMR spectra were obtained 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 the small quantity of NCCHD₂ in *d*₃-acetonitrile. A 100 ppm range centered at zero was scanned for each spectrum. Electronic spectra were collected on a Varian Cary 300 Bio UV–vis spectrophotometer. The Fourier transform infrared spectrum of each complex suspended in a KBr pellet was collected on an Alpha Centauri FT-IR spectrometer. Elemental analyses were performed by Galbraith Laboratories or Complete Analysis Laboratories.

Cyclic voltammetry was carried out on solutions containing 0.1 M tetrabutylammonium tetrafluoroborate ([TBA]BF₄) as the supporting electrolyte and 1 mM concentrations of the experimental compound dissolved in dry, distilled MeCN. Sonication was used to dissolve the copper compounds in the electrolyte solution. Solutions were each purged with nitrogen gas for 10 min to remove excess oxygen prior to measuring the voltammograms on a Bioanalytical Systems CV-50 electrochemical analyzer. The Ag/Ag⁺ nonaqueous reference electrode was freshly prepared each day and contained a silver wire in a solution of 0.1 M [TBA]BF₄ and 0.01 M AgNO₃ in MeCN. The working and auxiliary electrodes were platinum. The addition of TEMPO as an internal reference standard resulted in the appearance of two new couples indicating a reaction between the reference and the sample compounds, so the voltammograms were referenced to TEMPO as an external standard. Scans were carried out at a scan rate of 100 mV/sec and the potentials were scanned from +1200 to -800 mV for all samples.

X-ray Crystallography. Details of the data collection for **1–3** are included in Table 1. X-ray quality crystals of each compound were grown by slow diffusion of a precipitating solvent into a

solution of the compound dissolved in MeCN; CHCl₃ was the precipitating solvent for **1**, whereas toluene was used for **2** and **3**. Data for all three complexes were collected using a Siemens SMART CCD based diffractometer operating at room temperature. Crystals of **1–3** suitable for X-ray analysis were mounted in epoxy cement. A partial hemisphere was collected for each crystal by use of ω scans of 0.3° per frame and 30 s per frame for compounds **1–3**. A total of 1271 frames were collected for **1–3** resulting in a final resolution of 0.84 Å at a theta value of 25.05°. Decay was monitored by recollecting the first 50 frames at the end of each data collection; decay was less than 1% in all cases. Cell parameters were retrieved by using SMART³⁸ software and were subsequently refined by using SAINT³⁹ software on all observed reflections. The SAINT software was used to reduce the data and correct for Lorentzian polarization and decay. Absorption corrections were applied by using SADABS⁴⁰ supplied by George Sheldrick, for compounds **1** and **2**. Systematic absences in the data were consistent with the space groups, *Pmn*2(1), *P*2(1)/*m*, and *Pmn*2(1) for **1–3**, respectively.

The structures were solved by direct methods using the SHELXS-90 program⁴¹ and refined by least-squares methods on *F*² by using SHELXL-93,⁴² incorporated in SHELXTL-PC V 5.03.⁴³ The space groups of **1** and **3** were the same with very similar unit cell parameters, but the packing of the BF₄⁻ anion was somewhat different between the two structures. Considering that the structural data were collected at room temperature, the disordered counterions were somewhat to be expected. In the structure of **1**, three of the fluorine atoms F2, F3, and F4 on B1 and three of the fluorine atoms F22, F23, and F24 on B2 were each disordered 50:50 over two positions. In the structure of **3**, F1, F2, and F3 were disordered with 50% occupancy in each of two positions on B1, but for B2 only a single fluorine atom, F8, displayed the 50:50 disorder. The chlorine atom substituent on the phenanthroline ligand was also disordered equally over two crystallographic sites in **3** as a result

(38) SMART V 4.043 Software for the CCD Detector System; Siemens Analytical Instruments Division: Madison, WI, 1996.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for [Cu(5,6-Me₂-phen)(MeCN)₂(BF₄)](BF₄) (**1**), [Cu(*o*-phen)(MeCN)₂(H₂O)](BF₄)₂ (**2**), and [Cu(5-Cl-phen)(MeCN)₂(BF₄)](BF₄) (**3**)

	1	2	3
Bonds			
Cu–N(phen)	1.983(4)	1.995(3)	1.974(2)
Cu–N(MeCN)	1.980(4)	1.992(3)	1.989(4)
Cu–O(H ₂ O)		2.254(5)	
Cu–F(BF ₄)	2.406(15)		2.363(11), 2.389(14)
Angles			
N(phen)–Cu–N(phen)	82.4(2)	82.80(17)	81.96(16)
N(MeCN)–Cu–N(MeCN)	86.0(2)	87.1(2)	85.9(2)
<i>cis</i> N(phen)–Cu–N(MeCN)	96.78(16)	94.86(13)	96.07(15)
<i>trans</i> N(phen)–Cu–N(MeCN)	177.4(5)	175.10(12)	177.7(4)
Cu–N–C in MeCN	168.4(4)	165.7(3)	166.6(8)
N–C–C (in MeCN)	173(2)	179.8(5)	174(2)

of the mirror plane bisecting the copper center and phenanthroline ligand. For **1–3**, all non-hydrogen atoms were refined anisotropically; the hydrogen atoms were included in calculated positions with the exception of the hydrogen atoms on the water molecule in structure **2**, which were determined from the difference map.

Results and Discussion

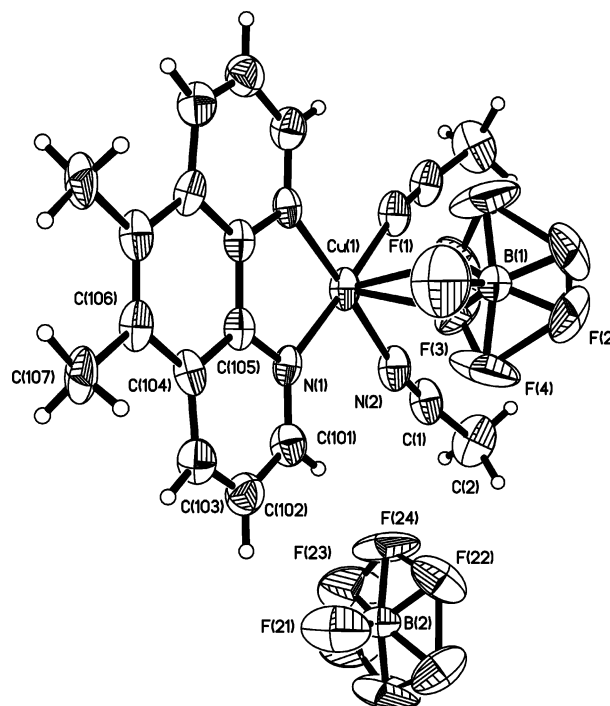
Although speciation of the copper-phenanthroline complexes is assumed to be under equilibrium control, slow addition of the ligand to the metal was used in preparation of the products. We have observed that an excess of three equivalents of ligand results in the formation of an unidentified yellow species; slow ligand addition minimizes the possibility that large localized phenanthroline concentrations could potentially form an irreversible byproduct.

Infrared spectra of the complexes in the solid state revealed features typical of the phenanthroline, solvent, and counterion in each sample. MeCN appeared as weak $\nu(\text{C}\equiv\text{N})$ bands in each spectrum between 2365 and 2320 cm^{-1} , although the aqua ligand observed crystallographically in **2** was masked by water absorbed by the hygroscopic KBr pellet. The stretch typical of the BF_4^- counterions was observed as a broad band around 1084 cm^{-1} . ^1H NMR spectra displayed broad resonances because of the MeCN ligands in the paramagnetic complexes, but the broad signal due to the phenanthroline protons was only observed in the spectrum of the 5,6-dimethylphenanthroline complex, **1**.

Electronic spectroscopy was used to characterize the complexes in acetonitrile solution. Each of the compounds displayed a single broad d–d transition around 670 nm in the visible region, typical of cupric complexes containing a single nitrogen chelate.^{33,35,37,44} The absorbance maximum of this feature generally underwent a red shift in the progression from copper complexes containing phenanthroline ligands with electron-donating groups (5,6-Me₂-phen, $\lambda_{\text{max}} = 663$ nm; 5-Me-phen, $\lambda_{\text{max}} = 668$ nm; *o*-phen $\lambda_{\text{max}} = 677$ nm) to complexes with phenanthroline ligands with electron-withdrawing substituents (5-Cl-phen, $\lambda_{\text{max}} = 677$ nm; and 5-NO₂-phen, $\lambda_{\text{max}} = 682$),⁴⁵ although there is no consistent difference between the *o*-phen and 5-Cl-phen complexes. The correlation among the spectra of the

compounds suggests that the compounds adopt similar configurations in solution.

Description of the Structures. Selected average bond distances and angles are presented in Table 2. An ORTEP diagram of **1** is presented in Figure 2; the structure of **3** is similar except for the specific disorder of the interstitial BF_4^- . The local environment around the copper atom is similar for complexes **1** and **3**. Each displays an equatorial plane containing a single phenanthroline and two MeCN ligands. The distorted octahedral coordination sphere of the six-coordinate copper is completed by coordinated BF_4^- ions, which link the metal units into a one-dimensional chain. The core structures of complexes **1** and **3** are isomorphous, with the copper centers of each lying on a mirror plane bisecting the equatorial plane. The symmetrical nature of the phenanthroline ligand in **1** compared to the asymmetrically substituted phenanthroline ligand in **3** does not appear to be significant in the formation of the structure. In contrast to the related species, complex **2** does not display the chain structure but instead exhibits a molecular square pyramidal

**Figure 2.** ORTEP diagram of complex **1** including the coordinated and disordered BF_4^- anions.

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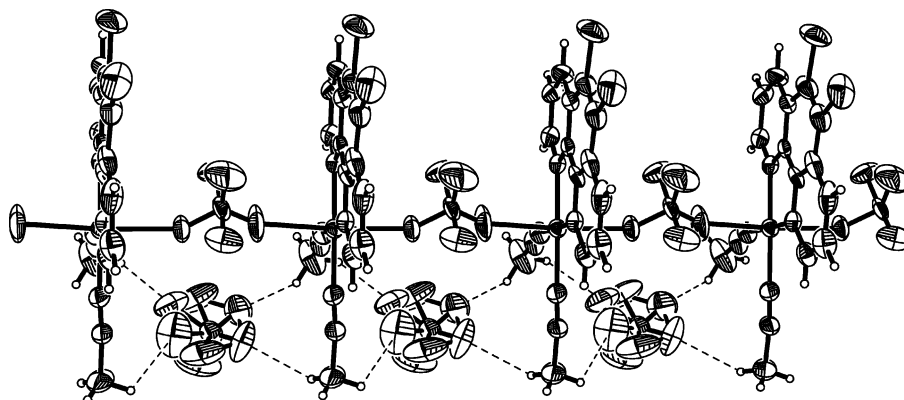


Figure 3. Packing diagram of complex **3** of the one-dimensional chains formed by alternating copper centers and BF_4^- anions. The apparent contacts between the MeCN hydrogens and the fluorines are an artifact of the calculated hydrogen positions and the anion disorder.

geometry formed by the phenanthroline/MeCN equatorial plane with H_2O occupying the axial position.

Despite having slightly different coordination environments around the copper center, the equatorial planes of complexes **1–3** are quite similar. In the case of the 5-Cl-phen ligand complex, a slight shortening of the Cu–N(phen) bond lengths is observed (1.974(2) Å) compared to 1.989(4) Å for the Cu–NCMe bond length. In the other two complexes, the Cu–N bond lengths are similar for both ligand types. For the Cu *o*-phen species, the Cu–N(phen) distance of 1.992(3) Å matches that of the Cu–NCMe at 1.995(3) Å and the 5,6-Me₂-phen complex displays the same similarity with 1.983(4) Å to N(phen) and 1.980(4) Å to NCMe. The bite angle of the phenanthroline ligand reduces the N(phen)–Cu–N(phen) angles from the ideal 90° to 82.4(2)° in **1**, 82.8(2)° in **2**, and 82.0(2)° in **3**; all of the angles are typical values for Cu-phen complexes.^{28,31,37,47–51} The opposite angles between the MeCN ligands are also consistently less than 90°, with values of 86.0(2)° for **1**, 87.1(2)° for **2**, and 85.9(2)° for **3**. These constricted angles most likely arise from steric interactions between the solvent ligands and the phenanthroline *ortho* hydrogens. The N–C–C angles of the acetonitrile ligands are approximately linear at 173(2)°, 179.8(5)°, and 174(2)° for **1**, **2**, and **3**, respectively.

The structures of complexes **1** and **3** strongly resemble the other literature examples of cupric complexes containing a single nitrogen chelate and two solvent ligands.^{26,30–33} In this class of structures, the equatorial copper plane consists of the nitrogen chelate, such as en, phen, or bpy, and two aqua ligands which are trans to the nitrogen atoms. In each of the previous literature examples, the individual copper units are linked into a one-dimensional chain through long contacts to coordinated tetrahedral SO_4^{2-} anions that bridge through the axial positions. Although BF_4^- is considered to

be less strongly binding than SO_4^{2-} , the current structures demonstrate its ability to act as a weakly coordinating anion which bridges the copper centers through the axial positions. Complexes **1** and **3** also bear a certain similarity to the one-dimensional ribbon structures commonly formed by some of the mixed organic/halide copper species.^{52–56} The elongation of the Cu–F axial bond length, 2.406(15) Å for **1** and 2.363(11) Å or 2.389(14) Å for **3**, is expected for the Jahn–Teller distortion in a six-coordinate d⁹ ion. The packing diagram displaying the extended interaction of **3** is depicted in Figure 3.

Compound **2**, shown in Figure 4, is the second reported cupric complex with a single nitrogen chelate and three solvent ligands; the structure matches that of the previous example, $[\text{Cu}(\text{bipy})(\text{H}_2\text{O})_3](\text{NO}_3)_2$,^{27,57} and strongly resembles the mixed ligand complex, $[\text{Cu}(5,6\text{-Me}_2\text{-phen})(\text{C}_2\text{H}_3\text{O}_3)(\text{H}_2\text{O})]\text{NO}_3$.⁵⁸ These four structures represent relatively rare examples of 4 + 1 geometries for copper complexes with nitrogen chelates compared to the more common 4 + 2 structures with four nitrogen containing ligands in a plane and Jahn–Teller elongated bonds to two additional ligands in the axial positions. All of the structures contain a square pyramidal arrangement of ligands with water in the axial position and phenanthroline and either two solvent molecules or the second chelating ligand in the plane. The preference for water to occupy the axial position is demonstrated in compound **2**, in which MeCN is the reaction solvent but water from the copper starting material or from the solvents is preferred for the axial position. The copper center and axial oxygen atom both lie on a crystallographic mirror plane. The bond distance of 2.254(5) Å between copper and the axial water molecule is somewhat longer than the Cu–N

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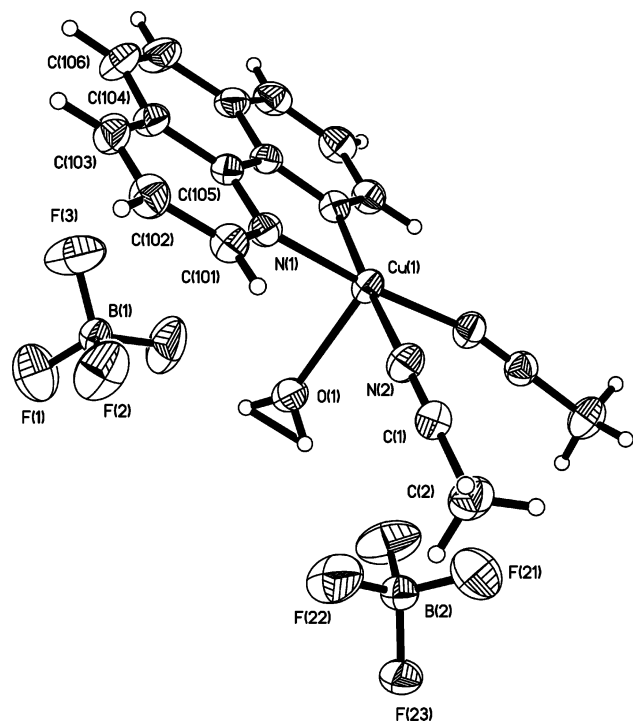


Figure 4. ORTEP diagram of complex **2**.

bond lengths in the equatorial plane, but this observation is consistent with the literature examples.^{27–29,47,58,59} The presence of water in this complex emphasizes the importance of hydrogen bonding in the solid-state structures of the 1:1 complexes of copper:bidentate nitrogen ligand.^{27,29–32,47,57,58,60} In this case, the axial water is hydrogen bonded to a BF_4^- counterion with H–F bond lengths of 2.40 and 2.317 Å for H1A–F2 and H1B–F22, respectively. Despite this preference for bound water in compound **2**, neither this compound nor compounds **1** and **3** are overly hygroscopic judging by the elemental analysis and particularly in comparison to the extremely hygroscopic $\text{Cu}(\text{BF}_4)_2$ starting material. Figure 5 shows the extended network of hydrogen bonds in the packing diagram of compound **2**.

The differences between the two types of solid-state structures do not have any obvious source. It is particularly curious that the weakly coordinating anion, BF_4^- , binds to the copper in the crystal structures of the complexes both with the electron-donating 5,6- Me_2 -phen ligand and with the electron-withdrawing 5-Cl-phen ligand but not in the case of the *o*-phen ligand complex, which should be intermediate between the other two. Thus, there is no obvious electronic factor driving the formation of the two different types of structures. Neither does the symmetry of the chelating ligand appear to be a factor, since one symmetrically substituted phenanthroline, 5,6- Me_2 -phen, and one asymmetrically substituted phenanthroline, 5-Cl-phen, each adopt the one-dimensional chain structure. Steric differences about the copper atoms should also be minimal since phenanthroline substitution is confined to the side of the ligand away from

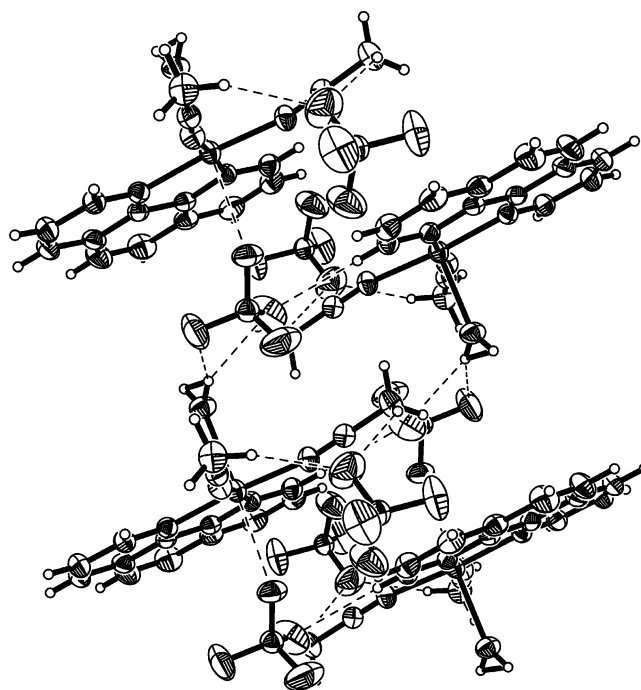


Figure 5. Packing diagram of complex **2** showing the hydrogen-bonding interactions between the axial water molecule and the tetrafluoroborate anions.

the metal centers. Considering the importance of both hydrogen bonding and packing effects in the structures of other cupric complexes with single nitrogen chelates,^{27,29–32,47,57,58,60} the different structures can probably be attributed to slight differences in crystal packing forces.

Electrochemistry. The cyclic voltammograms for all three complexes measured between -1200 and 800 mV displayed a single irreversible one-electron wave corresponding to the Cu(II) to Cu(I) reduction. In each case, the linear relationship between cathodic peak current $I_{p,c}$ and the square root of the scan rate $\nu^{1/2}$ is in agreement with a simple E_r mechanism. The plot of $\log(I_{p,c})$ versus $\log(\nu)$ indicates a diffusion-controlled process consistent with a single electron transfer. The irreversible reduction was previously observed in the voltammograms of the 2:1 phenanthroline:copper complexes²² and was attributed to an impurity. Our current measurements verify the assignment of that feature to the mono-phenanthroline copper species. The position of $E_{p,c}$ becomes less positive with increasing scan rate, similar to the variation observed in the bis-phenanthroline cupric species.²² The complete absence of a return wave for the reduction reaction contrasts with the behavior of other Cu(II) species. The more typical quasi-reversible behavior associated with the Cu(II)/Cu(I) couple^{15,22,46} is a result of a substantial change in coordination mode between the five- or six-coordinate cupric species and the corresponding cuprous species that generally prefer a tetrahedral geometry. The irreversible behavior observed for the mono-phenanthroline complexes suggests either an even more significant change in the coordination environment of the copper center or else possible disproportionation of the Cu(I) product, which prevents any kind of reoxidation on the electrochemical time scale.

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Table 3. Reduction Potentials (in mV) of Copper Complexes

	reduction potential, $E_{1/2}^a$	reduction potential, $E_{i,c}$ mono-phen	reduction potential, $E_{1/2}$ bis-phen ²²
Cu(BF ₄) ₂	+719		
5-NO ₂ -phen			-168
5-Cl-phen		215	-225
<i>o</i> -phen		182	-284
5-Me-phen			-302
5,6-Me ₂ -phen		137	-384

^a Cyclic voltammetry of Cu(BF₄)₂ was carried out in acetonitrile under the same conditions as the other samples.

As with the bis-phenanthroline complexes, the positions of the reduction waves for the mono-phenanthroline complexes shift in the positive direction with increasing electron-withdrawing character of the phenanthroline substituents. Although phenanthroline is predominantly thought of as a π -acid, the trend in reduction potential is dominated by sigma effects; more electron-donating phenanthroline ligands impart greater stability to the cupric species. Additionally, that each compound displays a single irreversible one-electron reduction which shifts in a manner consistent with the series of bis-phenanthroline cupric complexes supports the conclusion that the solution-state structures of the three mono-phenanthroline species are not appreciably different.

The reduction potentials for the mono-phenanthroline complexes as well as the $E_{1/2}$ values for the bis-phenanthroline complexes are presented in Table 3. It is apparent from these results that addition of each phenanthroline ligand to the copper center stabilizes the cupric species by making the reduction to the cuprous species less accessible compared to Cu(BF₄)₂. The changes in reduction potential are greater when comparing the Cu(BF₄)₂ species and the mono-phen species than when comparing the mono-phen and bis-phen species. This observation suggests that slightly less stabilization results from addition of the second phenanthroline compared with the first. Some insight into this disparity may be gained by comparing the crystal structures of the two sets of phenanthroline species. In the structures of the mono-phenanthroline species discussed herein, coordination of the phenanthroline ligand produces two Cu–N(phen) distances of 1.98 Å on the average. The structures of the bis-phen species are trigonal bipyramidal, but the bond distances reveal two shorter axial Cu–N(phen) distances of 1.98 Å,

comparable to those in the mono-phen species, and two slightly longer distances of 2.07 Å in the equatorial plane. These longer distances imply slightly weaker interactions between the phenanthroline ligands and the copper centers and correlate with the smaller (60–70 mV) shift of the reduction potentials when comparing the bis-phen to the mono-phen species.

Conclusions

The similar behavior of the complexes in the electronic spectroscopy and the cyclic voltammetry suggests that regardless of differences in the solid-state structures, the three species, **1–3**, are analogous in solution. Coordination of a phenanthroline ligand to a solvated copper center imparts stability to the oxidized copper species; further stabilization of the cupric form may be obtained by using a phenanthroline ligand with electron-donating substituents such as the 5,6-Me₂-phen system. The electronic influence of the phenanthroline ligand substituents may be observed in the electronic spectroscopy as more electron-withdrawing phenanthroline ligand complexes are generally characterized by a red shift of the absorption in the visible region. The presence of only one sterically constraining chelate ligand in each complex results in structures determined largely by crystal packing forces. The existence of two distinctly different solid-state structures for the mono-phenanthroline complexes contrasts with significantly less flexible structures of the known bis-phenanthroline copper(II) species. Further investigations into the electronic and steric influences of phenanthroline substitution on cupric and cuprous complexes are ongoing in our laboratories.

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Supporting Information Available: X-ray crystallographic files in CIF format are available for complexes **1–3** as well as an ORTEP diagram of complex **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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