Copper(I) Complexes of 3,3′-Bridged 2,2′-Biquinoline: Synthesis, Properties, and Structure

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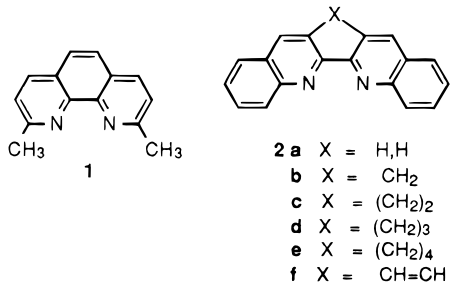
A series of 3,3′-bridged derivatives of 2,2′-biquinoline have been prepared where the bridge consists of one to four methylene units or a −CH═CH− moiety. The corresponding $[CuL_2](ClO_4)$ complexes were also prepared and their structures analyzed and confirmed by ^{1}H NMR. Electronic absorption maxima for the metal-to-ligand transition were found to move to higher energy and oxidation potentials were found to increase as the ligands became more distorted from planarity. An X-ray analysis was carried out for the most distorted system having a 3,3′-tetramethylene bridge ($C_{44}H_{36}BCuF_4N_4$: triclinic, $P\bar{1}$, $a = 11.605(2)$ Å, $b = 12.622(3)$ Å, $c = 14.524(3)$ Å, $\alpha = 106.05(1)°$, $\beta = 109.06(1)°$, $\gamma = 105.37(1)°$, $V = 1778$ Å^3, $Z = 2$). A wide variation in Cu−N bond lengths, 1.98−2.23 Å, was observed, and the two more weakly complexed quinolines were seen to be arranged in an almost parallel fashion. Ligand exchange studies with neocuproine indicated that the strength of Cu(I) binding depends on the planarity of the system as well as the *cisoid* disposition of the quinoline nitrogens.

Introduction

The complexes of copper with 1,4-diimine type ligands hold a particular interest because of the interdependence of their coordination geometry and their redox and photochemical behavior.[1] Complexes of Cu(I) adopt a tetrahedral or pseudo-tetrahedral geometry and are often deep red. In the absence of restricting steric effects, these complexes may be readily oxidized to the more stable square-planar, often green Cu(II) species. Cu(I) complexes of 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) exhibit this sort of oxidative instability.

Recent interest in Cu(I) has centered around its ability to effect the catalytic electroreduction of dioxygen[2] and to demonstrate energy transfer to anthracene which may prove useful in photocatalytic solar energy harvesting systems.[3] Complexes of Cu(I) also exhibit important biological activity.[4] From an architectural perspective, Cu(I) has been used extensively by Sauvage and co-workers as the template for the formation of tetrahedrally organized catenane derivatives.[5]

The key feature in the design of oxidatively stable Cu(I) diimine complexes of ligands such as bpy and phen is the incorporation of a substituent *ortho* to the imine nitrogen. This substituent will sterically impede the ability of the complex to become planar and thus increase the barrier for Cu(I) to Cu(II) interconversion sufficiently to allow the former species to become air stable. This effect is strong enough for $[Cu(\mathbf{1})_2]^+$ that reaction of 2,9-Me_2phen (**1**) with Cu(II) salts results ultimately in formation of the Cu(I) complex.[6] Another way to modify the coordination geometry of a chelate ring is to modulate the dihedral angle between the two diimine portions of the ligand. For bpy-type ligands, this can be accomplished by 3,3′-bridging, and we have examined the effects of such bridging on the properties of the corresponding Ru(II) complexes.[7] To examine a similar effect on Cu(I) complexes, the corresponding 3,3′-polymethylene-bridged derivatives of 2,2′-biquinoline (**2a**−**e**) were prepared and examined.[8] A closely related new ligand, dibenzo[*b*,*j*][1,10]phenanthroline (**2f**), and its Cu(I) complex are also reported.



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Experimental Section

Nuclear magnetic resonance spectra were recorded on a General Electric QE-300 spectrometer at 300 MHz, and chemical shifts are reported in parts per million downfield from Me_4Si. Electronic absorption spectra were measured on a Perkin-Elmer Lambda-3B spectrophotometer. Emission spectra were obtained on a Perkin-Elmer LS-50 luminescence spectrometer using a Hamamatsu R928 HA photomultiplier tube. Cyclic voltammograms were recorded using a BAS CV-27 voltammograph and a Houston Instruments Model 100 X-Y recorder according to a procedure which has been previously described.[9] Elemental analyses were performed by National Chemical Consulting, Inc., P.O. Box 99, Tenafly, NJ 07670. All solvents were freshly distilled reagent grade.

2,2′-Biquinoline (**2a**) was obtained from Lancaster Synthesis, Inc. Ligands **2b**−**e** were prepared according to a previously reported procedure.[10] $[Cu(CH_3CN)_4](ClO_4)$ was prepared according to the method of Hemmerich and Sigwart,[11] and $[Cu(CH_3CN)_4](BF_4)$ was prepared according to the method of Meerwein and co-workers.[12]

Dibenzo[*b,j*][1,10]phenanthroline (2f). A mixture of 3,3′-dimethylene-2,2′-biquinoline (**2c**, 120 mg, 4.2 mmol), 10% Pd−C (50 mg), and nitrobenzene (2 g) was refluxed for 24 h, after which further 10% Pd−C (25 mg) and nitrobenzene (1 g) were added and reflux was continued another 24 h. The mixture was cooled and filtered through Celite, and the Celite was washed with CH_2Cl_2 (5 × 10 mL). The combined filtrate and washings were dried over anhydrous $MgSO_4$, and the solvent was evaporated to provide a brown solid, which was chromatographed on alumina (24 g). Eluting with hexane provided unreacted nitrobenzene and aniline; further elution with hexane/CH_2Cl_2 (1:1) provided 63 mg (53%) of **2f** as a brownish yellow solid, mp 292−4 °C: ^{1}H NMR ($CDCl_3$)[13] δ 8.73 (d, 2H, J = 8.7 Hz, H_2), 8.69 (s, 2H, H_6), 8.06 (d, 2H, J = 7.5 Hz, H_5), 7.89 (t, 2H, J = 7.7 Hz, H_3), 7.74 (s, 2H, H_7/H_8), 7.68 (t, 2H, J = 7.2 Hz, H_4); ^{13}C NMR ($CDCl_3$) δ 147.9, 147.5, 135.6, 131.2, 130.0, 127.8, 127.5, 127.3, 127.2, 126.5. Anal. Calcd for $C_{20}H_{12}N_2$: C, 85.71; H, 4.29; N, 10.00. Found: C, 85.44; H, 4.61; N, 9.64.

Preparation of the Cu(I) Complexes. Under an argon atmosphere, a solution of $[Cu(CH_3CN)_4](ClO_4)$ in CH_3CN (5 mL) was prepared in a dry, two-neck round-bottom flask equipped with a rubber septum. A solution of the ligand in CH_3CN (5 mL) was injected into the flask, and the resulting deep red solution was stirred at room temperature for 15 min. The solution was concentrated to afford the crystalline Cu(I) complex. *Caution! Perchlorate salts are potentially explosive!*

[Cu(2a)$_2$](ClO$_4$). Treatment of **2a** (63 mg, 0.25 mmol) with $[Cu(CH_3CN)_4](ClO_4)$ (38 mg, 0.12 mmol) produced 74 mg (95%) of [Cu(**2a**)$_2$](ClO_4): ^{1}H NMR (300 MHz, CD_3CN) δ 8.85 (AB quartet, 4H), 8.07 (d, 2H, J = 8.1 Hz), 7.80 (d, 2H, J = 8.4 Hz), 7.56 (t of d, 2H, J = 7.5 Hz), 7.38 (t of d, 2H, J = 7.2 Hz). Anal. Calcd for $C_{36}H_{24}ClCuN_4O_4$: C, 64.00; H, 3.56; N, 8.30. Found: C, 64.55; H, 3.93; N, 8.13.

[Cu(2c)$_2$](ClO$_4$). Treatment of **2c** (71 mg, 0.25 mmol) with $[Cu(CH_3CN)_4](ClO_4)$ (38 mg, 0.12 mmol) produced 77 mg (98%) of [Cu(**2c**)$_2$](ClO_4): ^{1}H NMR (300 MHz, CD_3CN) δ 8.56 (s, 2H), 7.99 (d, 2H, J = 7.8 Hz), 7.70 (d, 2H, J = 8.1 Hz), 7.51 (t, 2H, J = 6.9 Hz), 7.30 (t, 2H, J = 6.9 Hz), 3.34 (s, 4H, $-CH_2-$). Anal. Calcd for $C_{40}H_{28}ClCuN_4O_4\cdot 2.0H_2O$: C, 62.90; H, 4.19; N, 7.34. Found: C, 63.01; H, 4.11; N, 7.73.

[Cu(2d)$_2$](ClO$_4$). Treatment of **2d** (91 mg, 0.31 mmol) with $[Cu(CH_3CN)_4](ClO_4)$ (50 mg, 0.15 mmol) produced 99 mg (85%) of [Cu(**2d**)$_2$](ClO_4): ^{1}H NMR (300 MHz, CD_3CN) δ 8.43 (s, 2H), 7.92 (d, 2H, J = 8.1 Hz), 7.49 (d, 2H, J = 7.2 Hz), 7.45 (t, 2H, J = 8.4 Hz), 7.23 (t, 2H, J = 7.2 Hz), 3.07 (t, 4H, α-CH_2-), 2.55 (quintet, 2H, β-CH_2-). Anal. Calcd for $C_{42}H_{32}ClCuN_4O_4\cdot 0.5H_2O$: C, 65.97; H, 4.32; N, 7.33. Found: C, 65.80; H, 4.26; N, 7.64.

[Cu(2e)$_2$](ClO$_4$). Treatment of **2e** (88 mg, 0.29 mmol) with $[Cu(CH_3CN)_4](ClO_4)$ (50 mg, 0.15 mmol) produced 99 mg (89%) of [Cu(**2e**)$_2$](ClO_4): ^{1}H NMR (300 MHz, CD_3CN) δ 8.31 (s, 2H), 7.89 (d, 2H, J = 8.4 Hz), 7.63 (d, 2H, J = 8.4 Hz), 7.54 (t of d, 2H, J = 7.5, 1.2 Hz), 7.42 (t, 2H, J = 7.8 Hz), 2.70 (d of d, 4H, J = 13.8, 8.2 Hz, α-CH_2-), 2.08 (m, 4H, β-CH_2-). Anal. Calcd for $C_{44}H_{36}ClCuN_4O_4$: C, 67.43; H, 4.60; N, 7.15. Found: C, 67.61; H, 4.85; N, 6.94.

[Cu(2e)$_2$](BF$_4$). Treatment of **2e** (78 mg, 0.25 mmol) with $[Cu(CH_3CN)_4](BF_4)$ (39 mg, 0.125 mmol) produced 79 mg (84%) of [Cu(**2e**)$_2$](BF_4). A crystal suitable for X-ray analysis was grown by slow evaporation of an EtOAc solution.

[Cu(2f)$_2$](ClO$_4$). Treatment of **2f** (56 mg, 0.2 mmol) with $[Cu(CH_3CN)_4](ClO_4)$ (32.7 mg, 0.1 mmol) produced 53 mg (73%) of [Cu(**2f**)$_2$](ClO_4) as a violet solid: ^{1}H NMR (CD_3CN)[13] δ 9.29 (s, 2H, H_6), 8.25 (d, 2H, J = 8.4 Hz, H_2), 8.20 (s, 2H, H_7/H_8), 7.93 (d, 2H, J = 8.4 Hz, H_5), 7.59 (t, 2H, J = 7.4 Hz, H_3), 7.36 (t, 2H, J = 7.4 Hz, H_4). Anal. Calcd for $C_{40}H_{24}ClCuN_4O_4$: C, 66.39; H, 3.32; N, 7.75. Found: C, 66.63; H, 3.58; N, 7.06.

Crystal Structure Determination of [Cu(2e)$_2$](BF$_4$). A ruby red prismatic column having approximate dimensions 0.25 × 0.25 × 0.75 mm was mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. The crystal was placed in a stream of dry nitrogen gas at −50 °C, and the radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 5. The Laue symmetry was determined to be 1, and the space group was shown to be either $P1$ or $P\bar{1}$. Intensities were measured using the ω-scan technique, with the scan rate depending on the count obtained in rapid prescans of each reflection. Two standard reflections were monitored after every 2 h or every 100 data collected, and these showed no significant change. During data reduction, Lorentz and polarization corrections were applied; however, no correction for absorption was made because of the small absorption coefficient.

Since the unitary structure factors displayed centric statistics, space group $P\bar{1}$ was assumed from the outset. The structure was solved by interpretation of the Patterson map, which revealed the position of the Cu atom. Remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor for all of them. The tetrafluoroborate anion was found to be disordered, and this was treated by introducing two ideal rigid-body models having occupancy models of 60% for B and 40% for B′ orientations. After all shift/esd ratios were less than 0.1, convergence was reached at the agreement factors listed in Table 5. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 0.2 e/Å^3. All calculations were made using the Nicolet SHELXTL PLUS series of crystallographic programs.[14]

Results and Discussion

The bridged biquinoline ligands were prepared by the Friedländer condensation between 2 equiv of 2-aminobenzaldehyde and the appropriate 1,2-diketone as described previously.[10] The dibenzo derivative of phen was prepared by the catalytic dehydrogenation of the 3,3′-dimethylene-bridged biquinoline **2c**, using 10% Pd on carbon in refluxing nitrobenzene. The reaction of these ligands in a 2:1 fashion with $[Cu(CH_3CN)_4]^+$ as its $(ClO_4)^-$ or $(BF_4)^-$ salt in CH_3CN provided the complex as a red crystalline salt in good yield. A Cu(I) complex could not be formed with the monomethylene-bridged biquinoline **2b**. These salts were analyzed by ^{1}H NMR, and the chemical shift data for their aromatic protons are summarized in Table 1. Corresponding data for the ligands are also given,

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Table 1. ^{1}H NMR Data for the Aromatic Protons of Biquinoline Ligands and Their Cu(I) Complexes[a]

ligand/complex	H3	H4	H5	H6	H7	H8
2a	8.84	8.19	8.01	7.82	7.65	8.47
2c		8.03	7.77	7.68	7.52	8.43
2d		8.17	7.97	7.76	7.63	8.16
2e		8.24	7.97	7.75	7.63	8.08
2f[b]		8.85	8.18	7.74	7.93	8.45
[Cu(**2a**)$_2$](ClO$_4$)	8.85[c] (−0.01)	8.85[c] (−0.66)	8.07 (−0.06)	7.56 (+0.26)	7.38 (+0.27)	7.80 (+0.67)
[Cu(**2c**)$_2$](ClO$_4$)		8.56 (−0.53)	7.99 (−0.22)	7.51 (+0.17)	7.30 (+0.22)	7.70 (+0.73)
[Cu(**2d**)$_2$](ClO$_4$)		8.43 (−0.26)	7.92 (+0.05)	7.45 (+0.31)	7.23 (+0.40)	7.49 (+0.67)
[Cu(**2e**)$_2$](ClO$_4$)		8.31 (−0.07)	7.63 (+0.34)	7.54 (+0.21)	7.42 (+0.21)	7.89 (+0.19)
[Cu(**2f**)$_2$](ClO$_4$)[b]		9.29 (−0.44)	7.93 (+0.25)	7.36 (+0.34)	7.59 (+0.34)	8.25 (+0.20)

[a] Measured in CD_3CN at 25 °C and reported in ppm referenced to CH_3CN at 1.93 ppm; complexation-induced shifts given in parentheses ($\delta_{ligand} - \delta_{complex}$). [b] Numbered to be consistent with **2a**−**e**. [c] AB quartet.

and it should be noted that the earlier ligand assignments[10] for H6 and H7 have been reversed as the result of a 2D COSY experiment which provided the connectivity of H5−H6−H7−H8. It is interesting to note the considerable deshielding of H3 for **2a** which is able to assume a *transoid* conformation in solution due to the lack of bridging, causing H3 to be proximal to the nitrogen lone pair electrons of the adjacent quinoline. Otherwise, the chemical shifts are fairly consistent throughout the ligand series although the resonances for **2f** are generally shifted downfield due to the increased delocalization of this system. For the chemical shift assignments of the complexes, a possible ambiguity could have arisen in the identification of H5 and H8. This ambiguity was resolved by an NOE experiment for [Cu(**2a**)$_2$](ClO$_4$) in which the AB quartet for H4 at 8.85 ppm was irradiated and a clear enhancement of the peak at 8.07 ppm was observed, indicating that peak to be H5. A 2D COSY experiment then verified the H5−H6−H7−H8 connectivity.

Upon complexation with Cu(I), the H4 resonance shifts downfield by 0.07−0.66 ppm. This effect, which is due to the depletion of charge at C4 that occurs upon coordination, is greatest for **2a**, **2c**, and **2f**, diminishes for **2d**, and almost disappears for **2f**. The more planar ligands are able to form less distorted tetrahedral complexes, and thus the Cu−N bond should be stronger. Electronegativity plays a role for **2f**, where H4 more resembles the central proton of acridine. For **2e**, the coordinative bond appears to be significantly weaker and the downfield shift is very small. A similar effect has been observed for the analogous Ru(II) complexes.[7]

The H6, H7, and H8 protons all experience an upfield shift which is due to shielding by the aromatic ring current of the orthogonal ligand. The H8 resonance is most sensitive to this effect, and it is interesting to note the trend along the series of complexes. Since the complexed ligand **2f** is essentially planar, tetrahedral coordination with Cu(I) causes H8 to point toward the center of the orthogonal ligand, a region of relatively low diamagnetic shielding, and the upfield shift is relatively small. Ligands **2a**, **2c**, and **2d** permit some twisting about the 2,2′-bond which causes the H8 proton to point more toward the shielding region of the orthogonal biquinoline. With an upfield shift upon coordination of only +0.19 ppm, the complex of **2e** appears inconsistent with this trend, indicating a more unusual conformation for this system.

The electronic absorption spectra of the complexes were measured in CH_3CN, and the data are recorded in Table 2. Strong absorption bands are observed in the region of 242−375 nm which correspond quite closely to the ligand π-π^* absorptions.[10] A weaker band is observed at longer wavelength which can be assigned to the metal-to-ligand charge transfer (MLCT) state. The energy of this band remains constant for the unbridged and dimethylene-bridged systems but increases for the trimethylene-bridged system while decreasing somewhat in intensity. The intensity of this band decreases considerably for the tetramethylene-bridged complex where only a weak shoulder can be observed at 500 nm (see Figure 1). These data are consistent with an MLCT state in which the energy of the receptor π^* orbital is lowered by increasing delocalization which would be found for the more planar systems. The electronic spectrum of [Cu(**2f**)$_2$]$^+$ showed an MLCT band at 565 nm (ϵ 5880) which is red-shifted from the dimethylene-bridged analogue by 17 nm with little effect on the intensity of the absorption. Irradiation into the MLCT band of these complexes

Table 2. Electronic Absorption Data for Cu(I) Biquinoline Complexes[a]

complex	λ_{max}, nm (ϵ)
[Cu(**2a**)$_2$](ClO$_4$)	299 (27 400), 313 (24 800), 325 (32 880), 338 (30 650), 355 (26 870), 546 (3690)
[Cu(**2c**)$_2$](ClO$_4$)	357 (32 200), 373 (31 620), 548 (5160)
[Cu(**2d**)$_2$](ClO$_4$)	316 (21 740), 330 (24 790), 349 (19 940), 502 (1870), 584 (1100)
[Cu(**2e**)$_2$](ClO$_4$)	296 (16 820), 310 (19 690), 323 (19 670), 500 (s, 307)
[Cu(**2f**)$_2$](ClO$_4$)	322 (48 160), 327 (30 600), 344 (31 260), 393 (5970), 565 (5980)

[a] Measured in acetonitrile at 22 °C.

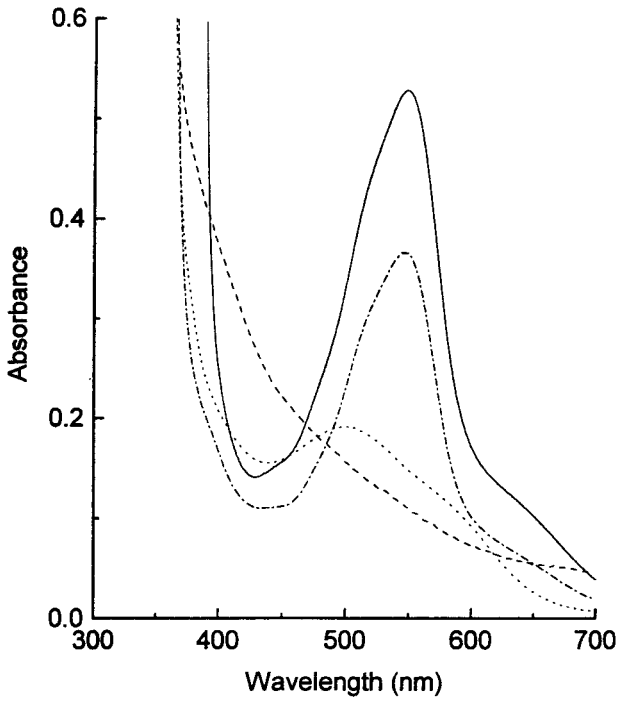

Figure 1. Long-wavelength region of the electronic absorption spectra of Cu(I) complexes (1 cm path length, 1.02 × 10^{-4} M in CH_3CN): [Cu(**2a**)$_2$](ClO$_4$) (− · −); [Cu(**2c**)$_2$](ClO$_4$) (—); [Cu(**2d**)$_2$](ClO$_4$) (···); [Cu(**2e**)$_2$](ClO$_4$) × 5 (- - -).

Table 3. Half-Wave Potentials for Cu(I) Biquinoline Complexes[a]

complex	$E_{1/2}$(oxidn)	$E_{1/2}$(redn)
$[Cu(\mathbf{2a})_2](ClO_4)$	+0.88 (90)	−1.26 (110)
$[Cu(\mathbf{2c})_2](ClO_4)$	+0.92 (110)	−1.23 (120)
$[Cu(\mathbf{2d})_2](ClO_4)$	+0.96 (110)	−1.41 (120)
$[Cu(\mathbf{2e})_2](ClO_4)$	+1.07 (110)	
$[Cu(\mathbf{2f})_2](ClO_4)$[b]	+0.77 (62)	−1.10 (70)

[a] Potentials are in volts vs SCE. Solutions were 0.1 M TBAP in CH_2Cl_2; $T = 25 \pm 1$ °C; the sweep rate was 200 mV/s. The number in parentheses is the difference between the anodic and cathodic waves. [b] Measured using a glassy carbon electrode.

did not produce any luminescence at 298 K (CH_2Cl_2 or CH_3OH/EtOH, 1:4) and only a weak emission at 77 K (CH_3OH/EtOH, 1:4).

The half-wave oxidation and reduction potentials for the complexes were measured by cyclic voltammetry in CH_2Cl_2, and these data are reported in Table 3. The oxidation waves are quasi-reversible and show a small but steady increase in potential upon going from $[Cu(\mathbf{2a})_2]^+$ to $[Cu(\mathbf{2e})_2]^+$. Oxidation of these systems is considerably more difficult than that of the corresponding neocuproine complex $[Cu(\mathbf{1})_2]^+$, which gives an $E_{1/2}$(ox) of +0.67 V.[15] It is well established that Cu(I) complexes are stabilized toward oxidation by ligands which will inhibit the ability of the system to become planar. The 2,9-methyl groups of neocuproine are apparently less effective in this regard than the fused benzo rings of 2,2′-biquinoline. As the biq ligand becomes more distorted from planarity, this stablizing effect becomes even stronger so that the highly distorted tetramethylene-bridged complex $[Cu(\mathbf{2e})_2]^+$ is the most difficult to oxidize. The oxidation potential for $[Cu(\mathbf{1f})_2]^+$ is lower than that of any of the other biquinoline derivatives. One might have expected a higher oxidation potential since the rigid, planar structure of this ligand should inhibit planarization better than the more flexible biquinolines. This steric effect is apparently moderated by the electronic nature of **1f**, lending it properties intermediate between those of phenanthroline and biquinoline.

Reduction of these complexes is generally ligand based and thus reflects the electronegativity of the ligand. Reduction of $[Cu(\mathbf{1})_2]^+$ occurs irreversibly at −1.89 V, which is about 0.5 V more negative than the values for the complexes of **2a**−**d**, indicating that these biq ligands are better electron acceptors than **1**. The trimethylene-bridged system, being less planar, is more difficult to reduce than its dimethylene-bridged or unbridged counterparts. A reduction potential for $[Cu(\mathbf{2e})_2]^+$ could not be measured while $[Cu(\mathbf{2f})_2]^+$, having the most electronegative ligand, reduces at −1.10 V.

Since the properties of the tetramethylene-bridged complex appeared to be the most unusual, an X-ray analysis of its tetrafluoroborate salt was undertaken. Figure 2 shows the structure of the cation while Figure S2 (Supporting Information) shows the crystal packing diagram and the unit cell. Selected molecular features are summarized in Table 4.

The free ligand **2e** severely twists about the 2,2′-bond in order to avoid eclipsing interactions in the tetramethylene bridge. Molecular mechanics estimates the dihedral angle between the two quinoline rings of **2e** to be about 70°.[16] Although some flattening of the ligand occurs upon complexation, each bound ligand shows a dihedral angle of about 42° and some unusual distortions are evident in the crystal structure. Not surprisingly, both ligands show the same chirality. Although **2e** possesses a symmetry axis passing through the 2,2′-bond, it does not bind

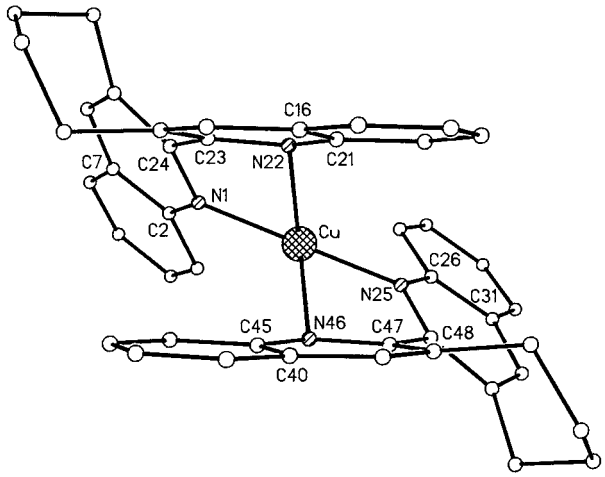

Figure 2. ORTEP diagram of the cation of $[Cu(\mathbf{2e})_2](BF_4)$ with atomic numbering for key atoms.

in a symmetrical fashion to the metal, which is found to be considerably closer to one nitrogen than the other. One Cu−N distance is 1.98 Å while the other is about 0.22 Å longer (2.23 and 2.19 Å). The typical Cu−N bond length for a variety of related Cu(I) complexes of various phen derivatives varies from about 2.02 to 2.07 Å.[17] Hence this complex reveals both an unusually short and an unusually long Cu−N bond. The N−Cu−N bond angles involving a unique ligand are both about the same and close to what is observed for other phen systems (80−81°), but the N−Cu−N angles involving both ligands indicate again that these ligands are not symmetrically disposed about the metal. One set of angles (N1−Cu−N46 and N22−Cu−N25) are quite similar at about 120°. However, the other set of angles (N22−Cu−N46 and N1−Cu−N25) are very dissimilar, 93.5 and 152.1°.

Figure 2 illustrates the unusual geometry of the complex. The quinoline rings involving N22 and N46 lie almost parallel to one another. The mean planes through these two quinolines show a dihedral angle of only 4°, and the distance of any atom in one ring to the mean plane of the other ring varies over 3.20−3.48 Å, giving a mean distance between the planes of 3.35 Å, which is approximately the optimal π-stacking distance between two parallel aromatic rings. That two nearly parallel quinolines can, in fact, bind to the same metal is quite surprising. We can evaluate the degree of distortion in the coordinative bond by examining the C_a-C_b-N-Cu dihedral angle where C_a and C_b denote the two central fused carbons of the quinoline ring. For the parallel quinolines containing N22 and N46, these angles are very severe, 124 and 127°, respectively, where an unstrained optimal angle would be 180°. The quinolines containing N1 and N25 are less strained with C_a-C_b-N-Cu angles of 163 and 167°, respectively.

A preliminary report has appeared on the crystal structure of a closely related Cu(I) complex.[18] The ligand cyclooocta[2,1-*b*;3,4-*b*′]diquinoline (**2** where X = −CH=CHCH=CH−) was treated with $Cu(ClO_4)_2$ in refluxing EtOH, and the corresponding reduced Cu(I) complex was obtained. The complex is a "flattened tetrahedron" with approximate C_2 symmetry and fairly normal Cu−N bond lengths (2.028(4)−2.095(4)Å). The more

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(16) Calculated using the programs PC Model and MMX available form Serena Software, Bloomington, IN.
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Table 4. Selected Bond Lengths, Bond Angles, and Dihedral Angles for $[Cu(\mathbf{2e})_2](BF_4)$[a]

bond lengths, Å		bond angles, deg		dihedral angles, deg	
Cu−N1	1.979(2)	N1−Cu−N22	80.0(1)	N22−C23−C24−N1	43.6
Cu−N22	2.225(2)	N25−Cu−N46	80.4(1)	N46−C47−C48−N25	40.9
Cu−N25	1.984(2)	N1−Cu−N25	152.1(1)	C40−C45−N46−Cu	127.0
Cu−N46	2.189(3)	N22−Cu−N46	93.5(1)	C16−C21−N22−Cu	124.3
C23−C24	1.492(4)	N1−Cu−N46	120.3(1)	C31−C26−N25−Cu	167.0
C47−C48	1.493(3)	N22−Cu−N25	119.8(1)	C7−C2−N1−Cu	162.9

[a] Numbering pattern from Figure 1 with esd's in parentheses.

Table 5. Crystal Data and Data Collection and Processing Parameters for $[Cu(\mathbf{2e})_2](BF_4)$

space group	$P\bar{1}$ (triclinic)
cell constants	$a = 11.605(2)$ Å
	$b = 12.622(3)$ Å
	$c = 14.524(3)$ Å
	$\alpha = 106.05(1)°$
	$\beta = 109.06(1)°$
	$\gamma = 105.37(1)°$
	$V = 1778$ Å^3
mol formula	$(C_{44}H_{36}N_4Cu^+)(BF_4^-)$
fw	771.19
formula units/cell	$Z = 2$
density	$\rho = 1.44$ g cm^{-3}
abs coeff	$\mu = 6.72$ cm^{-1}
temp	$T = -50$ °C
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.032
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.033
weights	$w = \sigma(F)^{-2}$

rigid geometry of the tub-shaped cyclooctatetraene rings does not allow the distortion we observe for $[Cu(\mathbf{2e})_2]^+$.

The crystal packing diagram of $[Cu(\mathbf{2e})_2](ClO_4)$ (Figure S2) shows that the molecules are organized in columns with a stack of Cu(I) atoms aligned through the middle of the column. At first glance, there appears to be π-stacking between adjacent molecules, but upon closer inspection of the three-dimensional structure, we see that the parallel quinolines do not π-stack between molecules.

The evidence thus far indicates that 2,2′-biquinoline, like neocuproine **1**, is an excellent ligand for stabilizing Cu(I). Due to the considerable difference in electronegativity between these two ligands, their Cu(I) complexes exhibit MLCT absorption maxima which differ by about 100 nm. This absorption difference allows one to easily monitor the replacement of one ligand for the other, and thus we carried out spectrophotometric titrations by adding incremental amounts of neocuproine to the biquinoline complexes.[19] Figure 3 illustrates the set of curves obtained for the titration of $[Cu(\mathbf{2a})_2](ClO_4)$. One clearly observes the disappearance of the $[Cu(\mathbf{2a})_2]^+$ absorption at 550 nm and the appearance of the $[Cu(\mathbf{1})_2]^+$ absorbance at 450 nm. If no appreciable concentration of the mixed-ligand complex $[Cu(\mathbf{1})(\mathbf{2a})]^+$ were involved in this exchange, one would expect to see an isosbestic point at about 500 nm. Figure 3 demonstrates that such a mixed-ligand complex must indeed play an important role, and considering that the exchange appears to be nearly complete after the addition of 2.5 equiv of **1**, the formation constant for $[Cu(\mathbf{1})_2]^+$ must be considerably larger than that for $[Cu(\mathbf{2a})_2]^+$.

The precise determination of stability constants for the Cu(I) biquinoline complexes is complicated by the involvement of the mixed-ligand species, but qualitative evidence may be garnered from an examination of the sets of titration curves. For the trimethylene-bridged complex $[Cu(\mathbf{2d})_2]^+$ and the tetramethylene-bridged one $[Cu(\mathbf{2e})_2]^+$, the situation is similar to the unbridged system and essentially complete conversion

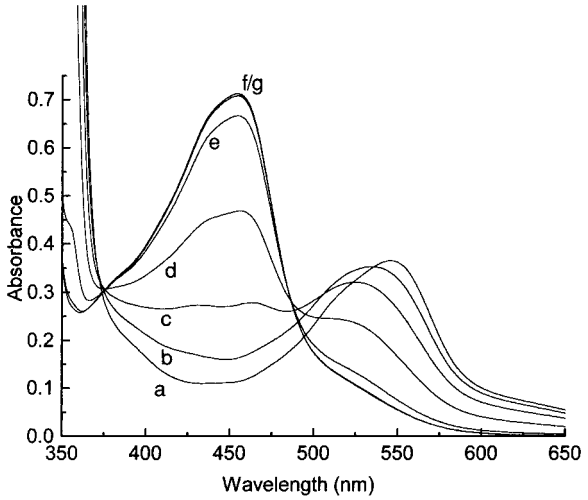

Figure 3. Electronic absortption spectra for $[Cu(\mathbf{2a})_2]^+$ (1.02×10^{-4} M in CH_3CN) with varying equiv of added neocuproine (**1**): a = pure $[Cu(\mathbf{2a})_2]^+$; b = 0.5; c = 1.0; d = 1.5; e = 2.0; f = 2.5; g = 3.0.

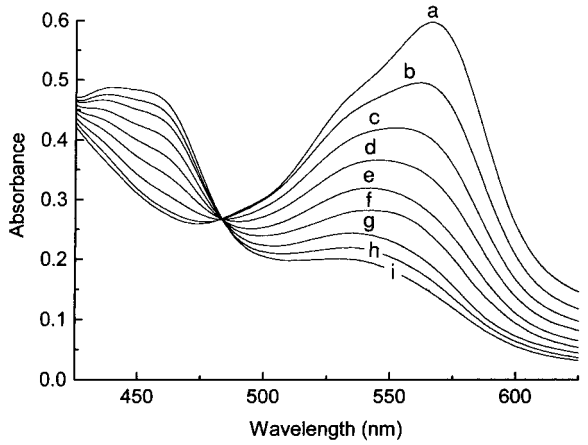

Figure 4. Electronic absortption spectra for $[Cu(\mathbf{2f})_2]^+$ (1.00×10^{-4} M in CH_3CN) with varying equiv of added neocuproine (**1**): a = pure $[Cu(\mathbf{2f})_2]^+$; b = 0.5; c = 1.0; d = 1.5; e = 2.0; f = 2.5; g = 3.0; h = 3.5; i = 4.0.

to $[Cu(\mathbf{1})_2]^+$ occurs after the addition of 2.5 equiv of neocuproine. All three of these ligands are therefore considerably weaker binders of Cu(I) than neocuproine. The situation is somewhat different for $[Cu(\mathbf{2c})_2]^+$, which, after the addition of 1.5 equiv of neocuproine, shows a curve that is nearly identical to what is observed after the addition of 1 equiv of neocuproine to $[Cu(\mathbf{2a})_2]^+$. The exchange process is clearly more difficult and is still not complete after 5 equiv of neocuproine has been added. Ligand **2c** therefore binds more strongly to Cu(I). For **2f**, the effect is considerably more pronounced, and now a clear isosbestic point is observed over the range of 0−4 equiv of added neocuproine (Figure 4). It appears that $[Cu(\mathbf{2f})_2]^+$ is being converted to a single species, which should be the mixed-ligand complex $[Cu(\mathbf{1})(\mathbf{2f})]^+$, and an equilibrium constant of 0.40 can be calculated for this process.

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These complex stablity studies are fully consistent with the ligand structures. Neocuproine is a stronger binder of Cu(I) because of its rigid planar geometry and the *cisoid* disposition of its nitrogens. The unbridged and trimethylene- and tetramethylene-bridged biquinolines have varying degrees of freedom of rotation about the 2,2′-bond, which assist in the stepwise decomplexation of these ligands, thus facilitating their replacement. For the dimethylene-bridged system this flexibility is much reduced and binding improves while dibenzophenanthroline, **2f**, which is both rigid and hindered near the binding cavity, binds Cu(I) somewhat better than neocuproine. The apparent stability of the resulting mixed-ligand species is surprising, and advantage maybe taken of this fact in the design of molecular assemblies involving various components held together by Cu(I).[20] Future work will take advantage of some of these design principles to prepare interesting structures based on these binding properties.

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Supporting Information Available: For $[Cu(\mathbf{2e})_2](BF_4)$, Figure S1, showing the complete numbering scheme for the X-ray determination, Figure S2, showing the crystal packing diagram, and tables of atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and H atom coordinates (8 pages). Ordering information is given on any current masthead page.

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