

Cu(I) Complexes of 3,3'-Polymethylene Bridged Derivatives of 2,2'-Bi-1,10-Phenanthroline

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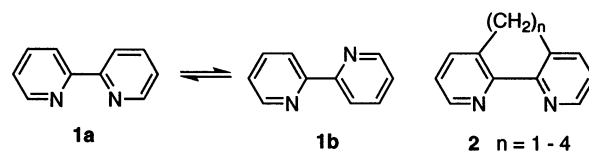
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A series of 3,3'-polymethylene-2,2'-bi-1,10-phenanthrolines coordinate with Cu(I) to form dinuclear complexes $[(CuL)_2]^{2+}$. As the 3,3'-bridge is lengthened from two to four carbons, the ligand becomes more twisted about the 2,2'-bond, favoring dinuclear coordination. The distance between the two copper atoms varies from 2.92 Å for the dimethylene-bridged system to 3.59 Å for the tetramethylene bridge. Favorable π -stacking interactions occur between opposing ligands and promote complex formation. Competition experiments indicate that self-recognition is important and only homoleptic complexes are observed. Under equilibrium conditions, formation of the tetramethylene-bridged complex appears to be the most favored while the dimethylene-bridged system is least favored. The intensity of the long wavelength metal–ligand charge-transfer absorption band decreases as the 3,3'-bridge is shortened. Interaction between the two copper centers is evidenced by a splitting of the oxidation wave, and this splitting increases as the Cu–Cu distance is decreased.

Introduction

One way in which a ligand can influence its metal complexes is by control of nuclearity. Depending on the number and disposition of binding sites, a ligand may coordinate with one or more metals.¹ For example, 2,2'-bipyridine (bpy) in its syn conformation (**1a**) is a chelating ligand and typically will bind to a single metal whereas 4,4'-bipyridine cannot form a chelate ring and more typically acts as a bridging ligand between two metals. In fact, if bpy could be constrained to its anti conformation (**1b**), chelation would become unfavorable and bridging would be much more likely. Such behavior has been demonstrated by Lehn and co-workers for an appropriately methylated derivative of quatrpyridine in which the central bpy unit is bridging rather than chelating with metals such as Cu(I) and Ag(I).² We have studied a series of bipyridines (**2**) containing a 3,3'-polymethylene bridge where $n = 2-4$. The bridge enforces noncoplanarity of the pyridines, resulting in conformations intermediate between **1a** and **1b**. For the four carbon bridged system, twisting about the 2,2'-bond is sufficiently slow at room temperature that diastereomeric methylene protons are observable in the NMR spectrum.³



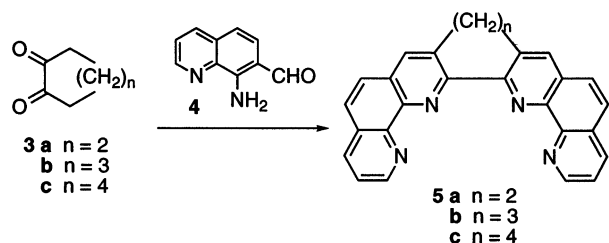
It became of interest to extend this bridging concept to other nuclei besides pyridine, and we have similarly examined analogous derivatives of 2,2'-biquinoline,⁴ 2,2'-bi[1,8]-naphthyridine,⁵ and 2,2'-biimidazole.⁶ In each of these cases, the chelating site involved two azaaryl rings joined by a 2,2'-

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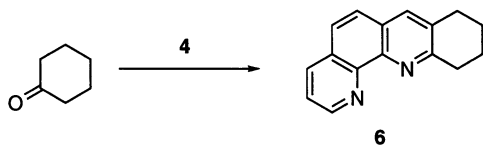
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bond. More recently, we have developed a general approach to substituted derivatives of 1,10-phenanthroline (phen) which has allowed the preparation of 3,3'-polymethylene bridged 2,2'-biphens **5a–c** by the Friedländer condensation of 8-amino-7-quinolinecarbaldehyde with cyclic 1,2-diketones.⁷ It is noteworthy that the synthesis of **5a–c** involves two sequential Friedländer condensations and thus a monocondensed species would be involved as an intermediate. This monocondensed species is not observed since the second condensation generally occurs more rapidly than the first as the initially formed phen ring activates the remaining carbonyl group toward further reaction.⁸



In this earlier work we learned that **5c** behaved as a tetradentate bridging ligand, forming a $[(\text{Cu}5\text{c})_2]^{2+}$ complex.^{7b} This binding mode is permitted and, in fact, encouraged by the large twist about the 2,2'-bond of the ligand. The $\text{N}_1\text{—C}_2\text{—C}_2'\text{—N}_1'$ dihedral angle in the complex is 64° , identical to the estimated twist of the free ligand. From this information and an inspection of models, we reasoned that the estimated twist angle in **5a** (16°) was insufficient to allow behavior as a bridging ligand and the consequent formation of a dinuclear Cu(I) complex might not be possible. We were surprised to find that both **5a** and **5b** readily formed bridged 2:2 complexes much in the same manner as the tetramethylene-bridged analogue, providing Cu(I) dimers in which the bridging ligand controlled not only the nuclearity but also the distance between the two copper centers. This paper will discuss the properties of this series of dinuclear Cu(I) complexes and compare them with a mononuclear model compound $[\text{Cu}(\mathbf{6})_2]^+$. Ligand **6** was prepared by the Friedländer condensation of cyclohexanone with aminoaldehyde **4**.



Results and Discussion

The ligands **5a–c** are similar to a series of 3,3'-bridged 2,2'-bi-benzo[*h*]quinolines (bi-BHQs) studied earlier which differ only in having a CH replacing the N10 and N10' nitrogens.⁹ These ligands can only bind a single Cu(I) using

Table 1. Calculated Geometric Features for Energy-Minimized Structures of Bi-1,10-phenanthrolines and Their Cu(I) Complexes^a

compound	$\text{N}_1\text{—C—C—N}_1'$ (deg) ^b	$\text{N}_1\text{—N}_1'$ (Å)	$\text{N}_1\text{—N}_{10}$ (Å)	Cu—Cu (Å)
5a	16	2.90	2.78	
5b	44	2.99	2.79	
5c	60	2.99	2.77	
$[(\text{Cu}5\text{a})_2]^{2+}$	37	2.95	2.61	3.25
$[(\text{Cu}5\text{b})_2]^{2+}$	57	3.02	2.61	3.70
$[(\text{Cu}5\text{c})_2]^{2+}$	70	3.07	2.61	3.94

^a Calculated using PC MODEL from Serena Software, Bloomington, IN.
^b Average of $\text{N}_1\text{—C}_2\text{—C}_2'\text{—N}_1'$ and $\text{C}_3\text{—C}_2\text{—C}_2'\text{—C}_3'$.

N_1 and N_1' , and such coordination is found to occur readily. The resulting $[\text{Cu}(\text{bi-BHQ})_2]^{2+}$ complexes were highly distorted due to the bulk of the BHQ ring. Intramolecular π -stacking interactions in the tetramethylene-bridged system led to a stabilization of the excited state that exhibited an unusually long lifetime.

The bisphens **5a–c** offer two competing phen sites that are much better disposed toward chelate ring formation. We treated **5a–c** with only 0.5 equiv of $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$, hoping to prepare a $[\text{Cu}(\text{L})_2]^+$ complex where the Cu(I) would be bound either at the central N_1, N_1' site or at either of the two distal phen sites. Instead, we isolated only $[(\text{CuL})_2]^{2+}$ and 0.5 equiv of unreacted ligand. Formation of the more stable dinuclear species occurs directly and immediately.

Some estimated structural features of the ligands and their complexes are summarized in Table 1. The most notable feature is the predicted dihedral angle between the two phen rings, which is controlled by the length of the polymethylene bridge. For the dimethylene-bridged system **5a**, this angle is only 16° and it increases to 44° for **5b** and to 60° for **5c**. The distance between the two central nitrogens is not much affected by these geometric variations. To achieve approximately tetrahedral coordination, the phen subunit from each of two ligands would prefer to be oriented in an approximately orthogonal sense about a single Cu(I) ion. This constraint tends to increase the central dihedral angle of the ligand by more than 20° for the complex of **5a** to about 10° for the complex of **5c**. A consequence of this variation in dihedral angle is a lengthening of the Cu—Cu distance along the series. It is also noteworthy that the twist about the central 2,2'-bond imparts helicity and, hence, inherent chirality to the ligand. Rotation about the central bond thus interconverts the two conformational enantiomers, which comprise a racemic mixture. The dinuclear complexes involve two ligands having the same helicity, and once again a racemic mixture results.

Table 2 summarizes some NMR features of the ligands and their complexes whose downfield region consisted of six readily assignable aromatic resonances and whose upfield region consisted of the polymethylene bridge protons. The protons H4 and H8 vary over only 0.05 ppm for the series of three bridged ligands. The variation is slightly more (0.13 ppm) for H9, which is more sensitive to deshielding by the adjacent phen ring. Hence for the more planar **5a**, this proton is held more in the deshielding region of the neighboring phen and its peak appears at lower field. The

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Table 2. Selected ^1H NMR Data^a for Bi-1,10-phenanthrolines and Their Cu(I) Complexes

ligand/complex	H ₄	CIS	H ₈	CIS	H ₉	CIS
5a	8.35		7.73		9.18	
5b	8.32		7.71		9.12	
5c	8.37		7.68		9.05	
6	7.99		7.63		9.05	
[Cu(5a) ₂](ClO ₄)	8.49	-0.14	7.34	+0.39	7.84	+1.34
[Cu(5b) ₂](ClO ₄)	8.14	+0.18	7.52	+0.19	8.10	+1.02
[Cu(5c) ₂](ClO ₄)	7.93	+0.44	7.69	-0.01	8.28	+0.77
[Cu(6) ₂](ClO ₄)	8.33	-0.34	7.84	-0.21	8.89	+0.16

^a Measured in CD₃CN at 25 °C and reported in ppm referenced to TMS.

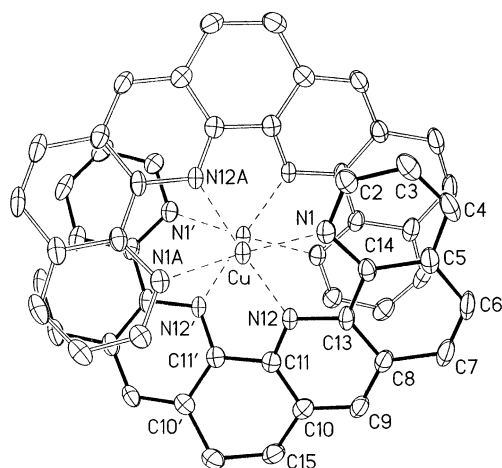
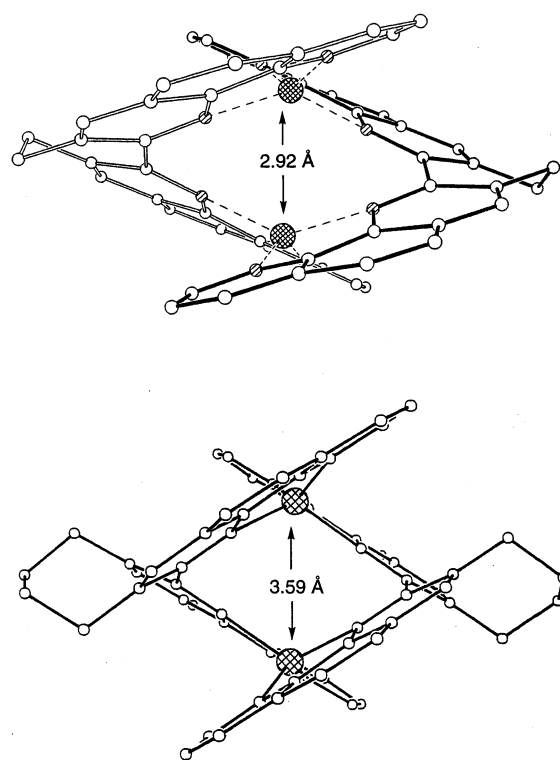
model ligand **6** most closely resembles the more highly twisted **5c** except for its H4 resonance.

Some clear trends are observed for the bridged complexes where H9 is now very diagnostic of conformation. Consider first the model complex [Cu(**6**)₂]²⁺ where one would expect that the two ligands occupy approximately orthogonal planes. This orientation would cause H9 to point into the shielding face of the opposing ligand, resulting in the small observed upfield shift of +0.16 ppm. As the tetrahedral geometry becomes flattened, the ligands are pushed closer together and H9 becomes more highly shielded with a coordination induced shift (CIS) of +0.77 for [Cu(**5c**)₂]²⁺, increasing to +1.34 for [Cu(**5a**)₂]²⁺. The same effect is observed to a lesser extent for H8 where the resonances are more evenly spaced, being separated by increments of 0.20 ppm.

The chemical shift of H4 appears to be less sensitive to geometrically controlled proximity effects as compared with the effect of charge depletion in the pyridine ring due to coordination. For the model system, a CIS of -0.34 ppm is observed, implying less electron density in the ring due to metal coordination. The deshielding effect diminishes for the bridged Cu complexes as the bridge length increases, implying less effective N-Cu binding for the more twisted systems. For [Cu(**5c**)₂]²⁺, H4 is, in fact, shielded by +0.44 ppm. The multiplicities of the bridge protons in the complexes confirmed that the coordinated ligands were conformationally rigid with regard to twisting about the 2,2'-bond.

In an earlier study we had reported the structure of [(Cu**5c**)₂]²⁺.^{7b} It was found that the tetramethylene bridge caused a twist of 64.2° about the 2,2'-bond of **5c** in the complex. In this twisted conformation, each phen moiety binds one Cu(I) so that two metals are bridged by two ligands having the same twist or chirality. The distance between the metals in [(Cu**5c**)₂]²⁺ is found to be 3.59 Å. This structure may be compared with an analogous one reported by Lehn and co-workers involving 5,5',3'',5'''-tetramethyl-2,2';6',2'';-6'',2'''-quaterpyridine as the bridging ligand.² The dinuclear Cu(I) complex of this more flexible ligand exhibited a central torsion angle of 77° and a Cu-Cu distance of 3.90 Å.

Figure 1 shows an ORTEP drawing of the [(Cu**5a**)₂]²⁺ cation which lies on a 222 site such that the four quadrants of the molecule are crystallographically equivalent. Table 4 reports the structural data for one quadrant. As the polymethylene bridge is decreased to three carbons in **5b** and to two carbons in **5a**, the twist angle about the 2,2'-bond is decreased, causing the two Cu atoms to be pushed closer

**Figure 1.** ORTEP drawing of the cation [(Cu**5a**)₂](ClO₄)₂ showing the atom numbering scheme.**Figure 2.** Analogous end-on views of the cation [(Cu**5a**)₂](ClO₄)₂ (top) and [(Cu**5c**)₂](ClO₄)₂ (bottom).

together (Figure 2). Thus for [(Cu**5a**)₂]²⁺, the twist angle, taken as an average of the inner and outer dihedral angles, is 31.1°, which is almost twice the value estimated for the free ligand. The distance between the Cu(I) atoms is found to be only 2.92 Å. The strain on the bridging ligand is further reflected by nonplanarity of the phen ring where a dihedral angle of 9.9° is found between the pyridine halves of this moiety.

It is interesting to compare the Cu-Cu distances measured for [(Cu**5a,c**)₂]²⁺ (2.92 and 3.59 Å) with the distances predicted by molecular mechanics, 3.25 and 3.94 Å, respectively (Table 1). The calculated distances exceed the measured ones by 0.33–0.35 Å. This difference is likely due to the fact that the molecular mechanics approach does not account for π - π associative interactions between the

Table 3. Electronic Absorption Data for 2,2'-Bi-1,10-phenanthrolines and Their Cu(I) Complexes

compound ^a	λ_{\max} (ϵ) ^b
5a	236 (43640), 263 (29570), 303 (20900), 359 (13250), 377 (20600)
5b	236 (60480), 266 (41470), 290 (34020), 331 (13350), 348 (9610)
5c	235 (51170), 268 (36360), 283 (33710), 328 (5480), 344 (2650)
6	233 (41570), 269 (28140), 288 (12500), 327 (1600), 342 (880)
[(Cu 5a) ₂] ²⁺	318 (38700), 326 (37710), 352 (43900), 435 (4000), 600 (900)
[(Cu 5b) ₂] ²⁺	299 (41490), 326 (28940), 428 (5450), 525 (2670)
[(Cu 5c) ₂] ²⁺	270 (62010), 326 (17480), 449 (5870), 531 (3200)
[Cu(6) ₂] ⁺	230 (57240), 276 (61060), 324 (9270), 460 (8660)

^a 5×10^{-5} M in CH₂Cl₂ at 25 °C. ^b Wavelength reported in nm.

Table 4. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for [(Cu**5a**)₂](PF₆)₂^a

Cu–N1	2.047(5)	N1–Cu–N12	80.12(19)	N1–C14–C13–N12	9.8(9)
Cu–N12	2.111(5)	N1–Cu–N1a	146.5(3)	C5–C14–C13–C8	10.1(8)
C11–C11'	1.464(12)	N1–Cu–N12a	110.80(19)	N12–C11–C11'–N12'	29.5
		N12–Cu–N1a	110.80(19)	C10–C11–C11'–C10'	32.8
		N12–Cu–N12a	142.9(3)		
		N1'–Cu–N12a	80.12(19)		

^a Numbering pattern from Figure 1 with estimated standard deviations in parentheses.

opposing ligands. This interaction tends to flatten the system and decrease the Cu–Cu distance while also lending extra stability to the complex. A similar effect has been observed for the [Cu(L)₂]⁺ complexes of the analogous 3,3'-bridged bi-BHQ ligands.⁹

The distance between the mean planes defined by each pair of approximately parallel phen rings can be estimated from the X-ray data. For [(Cu**5c**)₂]²⁺ these distances are 3.65 Å for both sets of parallel phen while for [(Cu**5a**)₂]²⁺ there is some variation with one separation measuring 3.30 Å and the other 3.48 Å. The dimethylene-bridged complex shows the phen to be considerably distorted from planarity and π -stacking is limited by the less twisted, but heavily distorted, nature of the ligand as well as the preferred tetrahedral environment around Cu(I).

Coordination about Cu(I) is distorted from tetrahedral geometry. The Cu atom lies closer to the external nitrogens (N1 and N1') at 2.05 Å than it does to the internal nitrogens (N12 and N12') at 2.11 Å. The N–Cu–N bite angle internal to the chelate ring is 80.12° which compares to an angle of about 82° for the **5c** complex. Further evidence for distortion around the metal is the nonequivalence of the N–Cu–N angles external to the chelate ring which vary from 110.8 to 142.9°. Similar variation was observed for the **5c** complex. The 2,2'-bond, which connects the two phen halves of the ligand, is shorter (1.46 Å) in the **5a** complex than in the **5c** complex (1.49 Å), indicative of increased π – π interaction between these two atoms as one would expect for the more planar system.

There has been considerable recent work on the self-assembly of metals and bridging ligands to afford predictable supramolecular structures.¹⁰ Cu(I) is a prime candidate for such assemblies due to the kinetic lability of its complexes. In room-temperature solution, metal–ligand exchange occurs readily, so that self-assembly of the thermodynamically most stable arrangement is favored. Lehn has demonstrated for a homologous series of poly-bpy ligands that self-recognition occurs.¹¹ We carried out a series of competition experiments in which equimolar amounts of the pairs of ligands **5a,b**; **5a,c**; and **5b,c** were combined with 2 equiv of the Cu(I)

reagent. In each case, analysis by electrospray mass spectroscopy (MS) indicated only formation of the homoleptic complexes. There was no evidence for the formation of [CuL₂]²⁺ complexes involving two ligands having different bridge lengths. Similarly a mixture of all three homologues **5a–c** and Cu(I) gave only the three symmetric complexes.

In a related experiment, we allowed pairs of ligands to compete for a deficiency of Cu(I). Judging by the intensities of both the peaks for [CuL₂]²⁺ as well as unreacted ligand, we ascertained that complex stability followed the order **5c** > **5b** > **5a**. This order is understandable in terms of the angle strain and steric compression increasing for complexes involving shorter bridge lengths. It is also consistent with our initial supposition that complex formation with **5a** would be difficult.

The electronic absorption data for **5a–c**, **6**, and [(Cu**5a–c**)₂]²⁺ are summarized in Table 4. The metal–ligand charge transfer (MLCT) absorption for Cu(I) phen complexes typically appears at about 450 nm while for Cu(I) biquinoline complexes this band appears at about 550 nm.¹² Figure 3 shows the long wavelength region of the electronic spectra for [(Cu**5a–c,6**)₂]²⁺. The spectra for the complexes of the

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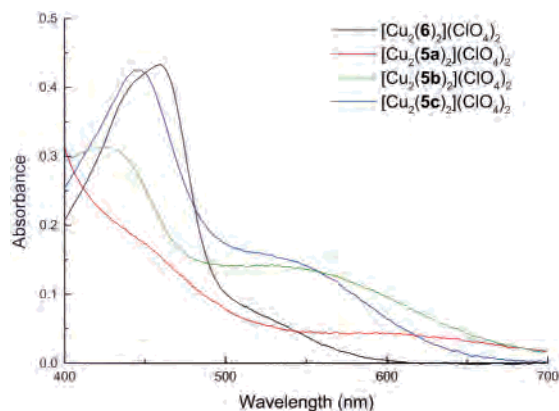


Figure 3. Long wavelength region of the electronic absorption spectra of $[(CuL)_2]^{2+}$ where $L = 5a-c$ and $[Cu(6)_2]^+$.

Table 5. Half-Wave Oxidation Potentials ($E_{1/2}$) and Comproportionation Constants (K_C) for $[(Cu5a-c)_2](ClO_4)_2$ and $[Cu(6)_2](ClO_4)_2^a$

complex	$E_{1/2}$ ($E_{pa} - E_{pc}$, mV) (V)	K_C
$[(Cu5a)_2](ClO_4)_2$	0.93 (122), 0.51 (73)	1.36×10^7
$[(Cu5b)_2](ClO_4)_2$	0.78 (62), 0.64 (94)	2.07×10^2
$[(Cu5c)_2](ClO_4)_2$	0.78 (84), 0.66 (68)	1.35×10^2
$[Cu(6)_2](ClO_4)_2$	0.61 (123)	NA

^a Potentials are in volts (V) vs SCE; solvent, CH_2Cl_2 ; electrolyte, 0.1 M TBAP; room temperature; the sweep rate = 100 mV/s; error for potentials, ± 5 mV; error for K_C , $\pm 5\%$.

trimethylene- and tetramethylene-bridged ligands show a band in each of these regions with the 450 nm (phen) band being the strongest. As expected, the mononuclear model complex $[Cu(6)_2]^+$ shows only a single band at 460 nm and most closely resembles $[(Cu5c)_2]^{2+}$. The dimethylene-bridged system $[(Cu5a)_2]^{2+}$, which holds the copper atoms closest to one another and which experiences the strongest π -stacking effect, shows almost no absorption in this region but rather just tailing of the strong absorption at 352 nm. At room temperature in acetonitrile or dichloromethane, the dinuclear systems did not evidence any luminescence.

Electrochemistry is a powerful tool for evaluating the interaction or communication between two redox-active centers. Using cyclic voltammetry, we have measured the oxidation potentials for the dinuclear complexes $[(Cu5a-c)_2](ClO_4)_2$ and the model complex $[Cu(6)_2](ClO_4)_2$ in dichloromethane and the data are recorded in Table 5. Attempts to use DMSO or acetonitrile as the solvent were less successful, presumably due to the coordinating ability of these solvents. The model complex oxidized at +0.61 V which is similar to values reported for a series of Cu(I) complexes of 2,6-disubstituted phenes.¹³ The dinuclear complexes showed separation of their oxidation wave into two well-resolved quasi-reversible components. As the 3,3'-polymethylene bridge is lengthened, the separation between the two waves decreased from 0.42 to 0.12 V; however, the average value of the two components remained constant at +0.71–0.72 V.

Considering ligand structure, we can compare these oxidation potentials to values measured for a series of

mononuclear Cu(I) complexes with polymethylene-bridged bi-BHQ ligands identical to **5a–c** but with N10 and N10' replaced by CH.⁹ Since the oxidation of a tetrahedral Cu(I) species would flatten the coordination sphere to an approximate square planar geometry, substituents ortho to the chelating nitrogens should inhibit this flattening and thus raise the oxidation potential. Although the geometries of the dinuclear complexes are surprisingly similar to those of the analogous mononuclear series, we find that oxidation of this latter series is more difficult, occurring in the range of +0.99 to +1.17 V in dichloromethane. More interesting is the fact that bridge length does not seem to affect the (average) values for the dinuclear complexes as much as for the mononuclear ones. What does appear to be affected by bridge length is the splitting of the oxidation wave that shows two well-resolved components whose separation is a function of the degree of interaction between the two Cu(I) centers. This interaction is greatest for the dimethylene-bridged system and smallest for the tetramethylene bridge. Comproportionation constants can be calculated¹⁴ and values are also included in Table 5. The increase of almost 10^5 for the system in which the Cu atoms are held the closest is impressive and argues for considerable metal–metal interaction as well as reasonable stability for the mixed valence Cu(I)–Cu(II) species.

To probe the spectroscopic features of this mixed valence species, we submitted a dichloromethane solution of $[(Cu5a)_2]^{2+}$ to a potential of +0.7 V and measured its absorbance. The band at 352 nm diminished by about 30%, and a new band appeared at 383 nm. When the potential was raised to +1.1 V, the 352 nm band decreased even further and the new 383 nm band decreased by about 50%. The very weak MLCT absorptions at 435 and 600 nm were also diminished, but the effect was less dramatic.

In the series of complexes $[(Cu5a-c)_2]^{2+}$, we have a situation where the distance between two relatively unencumbered Cu(I) atoms is controlled by the tuning of the bridging ligand. The possibility of incorporating a small molecule between the two coppers is intriguing.¹⁵ Several initial efforts have been made to incorporate dioxygen over the temperature range of -78 to $+40$ °C; however no change was observed for any of the biphen complexes.

Experimental Section

NMR spectra were recorded on a General Electric QE-300 spectrometer at 300 MHz for 1H and 75 MHz for ^{13}C . Chemical shifts are reported in parts per million downfield from internal TMS with solvent peaks as reference. Melting points were obtained on a Hoover capillary melting point apparatus and are uncorrected. Absorption spectra were measured on a Perkin-Elmer Lambda 3B

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spectrophotometer. Emission spectra were run on a Perkin-Elmer LS-50 spectrophotometer. Mass spectra were obtained on a Hewlett-Packard 5989B mass spectrometer (59987A electrospray) using atmospheric pressure ionization at 160 °C for the complexes and atmospheric pressure chemical ionization at 300 °C for the ligands. Mass spectral analyses of competitive complexations were obtained on a Thermo-Finnigan LCQ Deca XP Plus spectrometer. Cyclic voltammograms were recorded using a BAS Epsilon potentiostat according to a procedure which has been previously described.^{6b} Elemental analyses were performed by National Chemical Consulting, P.O. Box 99, Tenafly, NJ 07670.

The 8-amino-7-quinolinecarbaldehyde,^{7a} ligands **5b**,^{7b} and the [Cu(CH₃CN)₄](ClO₄)¹⁷ were prepared according to reported procedures. An improved method is reported for ligand **5a**. CH₃CN was refluxed over CaH₂ and then distilled under Ar.

3,3'-Dimethylene-2,2'-bi-1,10-phenanthroline (5a). To a solution of 1,2-cyclohexanedione (248 mg, 1.70 mmol) and 8-amino-7-quinolinecarbaldehyde (**4**, 300 mg, 1.74 mmol) in absolute EtOH (12 mL), piperidine (7 drops) was added. The solution was refluxed under Ar for 12 h, at which time another portion of piperidine was added (4 drops) and reflux was continued for 18 h. Upon concentration of the solvent, **5a** (115 mg, 52%) precipitated as a beige solid, mp > 300 °C: ¹H NMR (CDCl₃) δ 9.52 (broad s, 2H, H₉), 8.33 (d, 2H, *J* = 9.0 Hz, H₇), 8.15 (s, 2H, H₄), 7.83 (AB quartet, 4H, H₅/H₆), 7.72 (quartet, 2H, *J* = 4.5 Hz, H₈), 4.10 (broad s, H₂O), 3.36 (s, 4H, -CH₂-).

8,9,10,11-Tetrahydropyrido-[4,3-*b*]-acridine (6). Following the procedure described for **5a**, cyclohexanone (57 mg, 0.6 mmol) was condensed with **5** (100 mg, 0.58 mmol) in absolute EtOH (5 mL). The solvent was evaporated, and the resulting residue was chromatographed on alumina (30 g) eluting with CH₂Cl₂/hexanes (7:3) to give **6** (105 mg, 77%) as a beige solid, mp 116–117 °C: ¹H NMR (CDCl₃) δ 9.32 (d, 1H, *J* = 3.6 Hz, H₆), 8.38 (d, 1H, *J* = 7.8 Hz, H₇), 8.01 (s, 1H, H₄), 7.78 (broad s, 2H, H₅/H₆), 7.72 (quartet, 1H, *J* = 4.5 Hz, H₈), 3.58 (broad s, H₂O), 3.51 (t, 2H, *J* = 6.3 Hz, -CH₂-), 3.08 (t, 2H, *J* = 5.7 Hz, -CH₂-), 2.04 (m, 2H, -CH₂-), 1.96 (m, 4H, -CH₂-); ¹³C NMR (CDCl₃) δ 157.8, 144.4, 135.5, 133.5, 131.4, 127.8, 127.7, 126.8, 125.2, 125.0, 124.4, 124.4, 33.8, 29.2, 23.5, 23.2; MS *m/e* 235 (M⁺).

[(Cu5a)₂](ClO₄)₂.¹⁷ Solid [Cu(CH₃CN)₄](ClO₄) (34 mg, 0.1 mmol) was added to a solution of 3,3'-dimethylene-2,2'-bi-1,10-phenanthroline (**5a**, 40 mg, 0.1 mmol) in CH₃CN (10 mL). The solution became dark green and was stirred at 25 °C for 1 h under argon. The complex precipitated, and the solution was concentrated under vacuum. Recrystallization from CH₃CN gave [(Cu5a)₂](ClO₄)₂ (100 mg, 88%) as metallic green crystals: ¹H NMR (CD₃CN) δ 8.49 (s, 4H, H₄), 8.14 (d, 4H, *J* = 7.2 Hz, H₇), 7.84 (broad s, 4H, H₉), 7.73 (AB quartet, 8H, *J* = 8.1 Hz, H₅/H₆), 7.34 (broad s, 4H, H₈), 3.63 (m, 8H, -CH₂-); MS *m/e* 995 (M - ClO₄)⁺, 447 [1/2 M - (ClO₄)₂]²⁺. The analogous hexafluorophosphate salt was also prepared (79%). Anal. Calcd for C₅₂H₃₂N₈Cu₂P₂F₁₂: C, 52.66; H, 2.70; N, 9.45. Found: C, 52.81; H, 2.92; N, 9.23.

[(Cu5b)₂](ClO₄)₂.¹⁷ Following the procedure described for [(Cu5a)₂](ClO₄)₂, 3,3'-trimethylene-2,2'-bi-1,10-phenanthroline (**5b**, 40 mg, 0.1 mmol) was treated with [Cu(CH₃CN)₄](ClO₄) (35 mg, 0.1 mmol). Recrystallization from CH₃CN/toluene (1:1) gave [(Cu5b)₂](ClO₄)₂ (97 mg, 86%) as burgundy crystals: ¹H NMR (CD₃CN) δ 8.25 (dd, 4H, *J* = 9.3, 1.2 Hz, H₇), 8.14 (s, 4H, H₄), 8.10 (dd, 4H, *J* = 6.0, 1.0 Hz, H₉), 7.65 (AB quartet, 8H, *J* = 17.8, 7.2 Hz, H₅/H₆), 7.52 (dd, 4H, H₈), 3.20 (m, 4H, -CH₂-), 3.02

Table 6. Crystallographic Data for [(Cu5a)₂](ClO₄)₂

chemical formula	C ₆₀ H ₄₄ F ₁₂ N ₁₂ P ₂ Cu ₂
<i>a</i>	19.9779(13) Å
<i>b</i>	22.2432(14) Å
<i>c</i>	25.9316(17) Å
α	90.00°
β	90.00°
γ	90.00°
<i>V</i>	11523.3(13) Å ³
<i>Z</i>	8
formula weight	1350.09
space group	<i>Fddd</i>
<i>T</i>	-50 °C
λ	0.71073 Å
ρ _{calcd}	1.556 g cm ⁻³
μ	8.85 cm ⁻¹
R1 ^a	0.0667
wR2 ^b	0.1702

^a P1 = Σ||F_o| - |F_c||/Σ|F_o|. ^b wR2 = [Σw(F_o² - F_c²)²/Σw(F_o²)²]^{1/2}. w = [(σ²(F_o²) + (0.0769P)² + (186.3518P)]⁻¹, where P = (F_o² + 2F_c²)/3.

(m, 4H, -CH₂), 2.45 (m, 4H, -CH₂); MS *m/e* 1023 (M - ClO₄)⁺, 462 [1/2 M - (ClO₄)₂]²⁺. The analogous hexafluorophosphate salt was also prepared (70%). Anal. Calcd for C₅₄H₃₆N₈Cu₂P₂F₁₂·2.00 H₂O: C, 51.88; H, 3.20; N, 8.97. Found: C, 51.80; H, 3.29; N, 8.77.

[(Cu5c)₂](ClO₄)₂.^{7b,17} Following the procedure described for [(Cu5a)₂](ClO₄)₂, 3,3'-tetramethylene-2,2'-bi-1,10-phenanthroline (**5c**, 40 mg, 0.1 mmol) was treated with [Cu(CH₃CN)₄](ClO₄) (34 mg, 0.1 mmol). Recrystallization from CH₃CN/toluene (1:1) gave [(Cu5c)₂](ClO₄)₂ (98 mg, 90%) as dark burgundy crystals: ¹H NMR (CD₃CN) δ 8.38 (dd, 4H, *J* = 8.1 Hz, H₇), 8.28 (dd, 4H, *J* = 4.5 Hz, H₉), 7.93 (s, 4H, H₄), 7.69 (d, 4H, *J* = 9.0 Hz, H₅ or H₆), 7.69 (d, 4H, H₈), 7.65 (d, 4H, *J* = 9.0 Hz, H₅ or H₆), 3.06 (m, 4H, -CH₂-), 2.57 (m, 4H, -CH₂-), 2.20 (m, 4H, -CH₂-), 1.57 (m, 4H, -CH₂-).

[Cu(6)₂](ClO₄)₂.¹⁷ Following the procedure described for [(Cu5a)₂](ClO₄)₂, 8,9,10,11-tetrahydropyrido-[4,3-*b*]-acridine (**6**, 20 mg, 0.09 mmol) was treated with [Cu(CH₃CN)₄](ClO₄) (14 mg, 0.043 mmol) in CH₃CN (7 mL) to give [Cu(6)₂](ClO₄)₂ (22 mg, 81%) as air stable deep red crystals: ¹H NMR (CD₃CN) δ 8.82 (broad s, 2H, H₆), 8.61 (d, 2H, *J* = 8.1 Hz, H₇), 8.33 (s, 2H, H₄), 8.03 (broad s, 4H, H₅/H₆), 7.84 (quartet, 2H, *J* = 4.8 Hz, H₈), 3.08 (t, 4H, *J* = 6.0 Hz, -CH₂-), 2.71 (broad s, 4H, -CH₂-), 2.19 (s, H₂O), 1.79 (broad s, 4H, -CH₂-), 1.67 (broad s, 4H, -CH₂-); MS *m/e* 529 (M - ClO₄)⁺. Anal. Calcd for C₃₂H₂₈N₄CuClO₄: C, 60.85; H, 4.43; N, 8.87. Found: C, 60.84; H, 4.34; N, 8.70.

X-ray Determination of [(Cu5a)₂](ClO₄)₂. All measurements were made with a Siemens SMART platform diffractometer equipped with a 1K CCD area detector. A hemisphere of data (1271 frames at 5 cm detector distance) was collected using a narrow-frame method with scan widths of 0.30° in omega and an exposure time of 20 s/frame. The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability, and the maximum correction on *I* was <1%. The data were integrated using the Siemens SAINT program, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A psi scan absorption correction was applied based on the entire data set. Redundant reflections were averaged. Final cell constants were refined using 5624 reflections having *I* > 10σ(*I*), and these, along with other information pertinent to data collection and refinement, are listed in Table 6. The Laue symmetry was determined to be mmm, and from the systematic absences noted the space group was shown unambiguously to be *Fddd*. The

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(17) *Caution! Perchlorate salts are potentially explosive.*

asymmetric unit consists of $1/4$ dication situated about a crystallographic 222 site, $1/2$ anion situated on a 2-fold axis, and one acetonitrile solvent molecule in a general position. The anion is massively disordered, having a least three different orientations. These were treated as ideal rigid bodies and refined independently with isotropic temperature factors.

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Supporting Information Available: X-ray crystallographic files in CIF format for $[(\text{Cu5a})_2](\text{ClO}_4)_2$. The material is available free of charge via the Internet at <http://pubs.acs.org>.

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