Synthesis and Characterization of Some Copper(I) Phenanthroline Complexes

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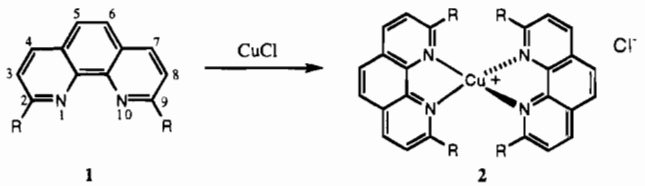
From a series of 2,9-dialkyl-1,10-phenanthrolines **1**, complexes of several structures were made with copper(I) chloride. These were examined in detail by ^{1}H NMR and X-ray crystallography. Those with stoichiometry of two phenanthrolines per copper atom have the well-known structure **2** containing a cation with distorted tetrahedral geometry about the copper atom of the general form [(2,9-dialkyl-1,10-phenanthroline)$_2$Cu]$^+$Cl$^-$. The alkyl groups of compounds **2** show a marked upfield change in the chemical shift with respect to the ligands themselves. This is ascribed to an aromatic ring current effect. The complexes with 1:1 stoichiometry can have either of two isomeric structures **3** and **4**, depending upon the bulk of the alkyl groups in the 2- and 9-positions of the phenanthroline system, how they are prepared, and whether they are in solution or solid phase. Isomer **3**, favored with bulky alkyl groups, has the copper atom in a distorted trigonal geometry with coordinated chlorine and does not exhibit the ring-current effect seen in **2**. The structures of two of these compounds were determined by X-ray crystallography. Crystals of **3f**, 2,9-di-*tert*-butyl-1,10-phenanthroline·CuCl, were tetragonal with space group $P4_2/n$ and a = 19.700(3) Å, c = 9.680(2) Å, V = 3757(2) Å^3, and Z = 8. This structure shows substantial distortion from trigonal planar geometry, due to the steric bulk of the *tert*-butyl groups. Crystals of **3g** (2,9-dineopentyl-1,10-phenanthroline·CuCl) were monoclinic with space group $P2_1/c$ and a = 9.545(2) Å, b = 18.407(3) Å, c = 12.734(2) Å, β = 107.75(2)°, V = 2130.8(11) Å^3, and Z = 4. Compounds **4** were found to have NMR identical with **2**, but are isomeric with **3**, having the structure [(2,9-dialkyl-1,10-phenanthroline)$_2$Cu]$^+$CuCl$_2^-$. The structure of **4g** ([(2,9-*n*-pentyl-1,10-phenanthroline)$_2$Cu]$^+$CuCl$_2^-$] was determined by X-ray crystallography. Crystals of **4g** were triclinic, space group $P\bar{1}$ with a = 13.861(3) Å, b = 14.108(3) Å, α = 65.35(2)°, β = 107.75 (2)°, γ = 90.05(2)°, V = 2155.2(8) Å^3, and Z = 2. This structure clearly shows the positions of the alkyl groups of each ligand directly above the face of the aromatic system of the other in a distorted tetrahedral geometry about copper.

Introduction

As part of an ongoing investigation into the biological activity of copper compounds we sought to prepare 2,9-dialkyl-1,10-phenanthrolines, **1**, and their copper(I) complexes, **2**, as shown in Figure 1. It has long been known that compound **1a** (R = methyl), often called neocuproine, is useful as an analytical reagent for the determination of copper,[2] due, in large measure to its formation of the brilliant red copper complex **2a**. Of particular significance in this regard is the fact that this compound was found to form a colored complex only with copper, among 56 metals examined.[3] While the structures of compounds like **2** have been investigated in some detail, this information applies largely to their structure in the solid phase. With the present work we have demonstrated the extent to which the stoichiometry of the complexes depends upon the size of the substituent groups R. In addition, we have shown that, in the case of the complexes containing equimolar amounts of ligand and copper, two structures are possible, and that the structures in solution can differ from that observed in the solid phase. Third, we have added a number of new phenanthrolines, and their complexes, to this group of well-characterized compounds.

The structures of compounds **2** generally exhibit pseudotetrahedral geometry about copper.[4] This has been conclusively demonstrated[5] for salts [(6,6′-dimethyl-2,2′-bipyridyl)$_2$Cu]$^+$Cl$^-$ and [(2,9-dimethyl-1,10-phenanthroline)$_2$Cu]$^+$Cl$^-$, **2a**.[6] The two



1 **2**

Figure 1. Complex of a 2,9-dialkyl-1,10-phenanthroline and cuprous chloride.

phenanthrolines per copper atom stoichiometry observed in compounds **2** appears to be the preferred state. However, it is known that the isomeric 1:1 species **3** and **4** can be made, but yields are often low,[7] with much uncomplexed copper recovered unreacted. The chloride species **3a** (R = methyl) has been reported[6] and shown to have copper in a pseudotrigonal geometry with coordinated chloride. The compound **4** (R = phenyl), of structure [(2,9-diphenyl-1,10-phenanthroline)$_2$Cu]$^+$-CuCl$_2^-$ has also been described.[8] A species analogous to **4**, in which the ligand was unsubstituted 1,10-phenanthroline, with dibromocuprate counterion, has also been reported.[9] Note that,

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(2) Smith, G. F.; McCurdy, W. H., Jr. *Anal. Chem.* **1952**, *24*, 371.

(3) Luke, C. L.; Campbell, M. E. *Anal. Chem.* **1953**, *25*, 1588.

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(5) Phillip, J. B.; McMillin, D. R.; Robertson, W. R. *Inorg. Chem.* **1980**, *19*, 1211.

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(9) Healy, P. C.; Engelhardt, L. M.; Patrick, V. A.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 2541.

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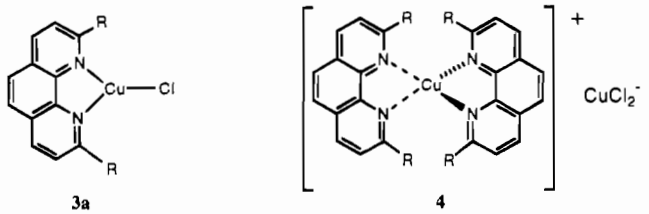

Figure 2. Isomeric copper(I) phenanthroline complexes of 1:1 net stoichiometry.

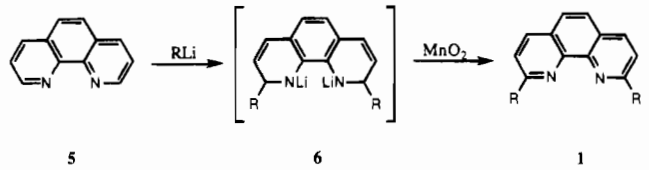

Figure 3. 2,9-Dialkyl-1,10-phenanthrolines from 1,10-phenanthroline by nucleophilic aromatic substitution followed by rearomatization.

although compound **4** is a 1:1 complex by stoichiometry and therefore isomeric with **3**, it possesses the 2:1 tetrahedral copper(I) ion as in structure **2**. Also known are structures with tetrahedral copper in a dimeric bis(μ-halide) structure[10] with bromide or iodide. In each of these cases, structures were determined for the solid phase only (by means of X-ray crystallography). In the present work, we have shown that, for many types of ligands **1**, the complexes of 1:1 stoichiometry have solution phase structures analogous to that denoted by **4** in Figure 2, while in the solid phase the compounds have the structures **3** or **4**. In other cases, in which the alkyl groups in the 2- and 9-positions of the phenanthroline system are bulky, the structures are similar to **3** in both solid and solution phases.

For this work, we required a representative series of the phenanthroline ligands **1**. Construction of the phenanthroline nucleus is impractical (for example see the original synthesis of **1a**,[11] and later, improved examples[12] of the method) we explored another alternative for obtaining a variety of compounds **1**. Higher homologues **1b**–**l** of neocuproine are available by the procedure of Sauvage[13] via the nucleophilic aromatic substitution of 1,10-phenanthroline, **5**, with the corresponding alkyllithium reagent as shown in Figure 3. The intermediate bis(dihydro) compound **6** is protonated (with water) and then rearomatized by oxidation with an excess of manganese dioxide. For these products, yields are generally in the 70–95% range. The convenience of this approach led us to pursue it as the method of choice to gain access to the series of these compounds **1**. The chief difficulty we envisioned was the limited number of commercially available alkyllithiums—requiring that all but these few be prepared in our laboratory. We have prepared a series of the ligands **1** by this nucleophilic aromatic substitution method, and their corresponding complexes **2**, **3**, and/or **4**. In the present work, the effect of variations in the geometry and size of substituents in the 2- and 9-positions of the phenanthroline ligands was examined, since these seem to exert particular influence on the geometry and stoichiometry of the complexes.

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Table 1. Stoichiometry and NMR Data of Copper Phenanthrolines **2**–**4**

			chemical shift of methyl group (δ)	
compd	R	stoichiometry	free ligand	complex
2a	methyl	2:1	2.79	2.40
4a	methyl	1:1	2.79	2.38
2b	ethyl	2:1	1.49	0.94
2c	propyl	2:1	1.07	0.31
2d	*n*-butyl	2:1	1.00	0.24
2e	*sec*-butyl	2:1	1.45, 0.99	0.35–0.15
3f	*tert*-butyl	1:1	1.58	**1.86**
2g	*n*-pentyl	2:1	0.92	0.43
4g	*n*-pentyl	1:1	0.92	0.43
2h	neopentyl	2:1	1.04	0.58
3h	neopentyl	1:1	1.04	**1.10**
2i	hexyl	2:1	0.90	0.53
2j	heptyl	2:1	0.89	0.70
2k	octyl	2:1	0.88	0.78

Results and Discussion

A wide range of phenanthrolines **1** have been prepared, where R is aliphatic with one to eight carbon atoms. Using these ligands we were able to prepare several examples of complexes **2**, **3**, and **4** as indicated in Table 1. In most cases the preparation of **2** requires nothing more than addition of $^1/_2$ equiv of cuprous chloride to a solution of the phenanthroline in an organic solvent, usually dichloromethane. In two cases, those of 2,9-di-*tert*-butyl-1,10-phenanthroline **1f** and 2,9-dineopentyl-1,10-phenanthroline **1h**, in which the phenanthrolines are sterically hindered, complex formation occurs slowly and gives products with the stoichiometry (2,9-dialkyl-1,10-phenanthroline)CuCl, the 2:1 ratio of reactants notwithstanding. Subsequent preparations of the *tert*-butyl compound **3f**, employing 1 equiv of cuprous chloride, left no significant amount of unreacted material and gave the same product. Ligand **1h** apparently afforded a mixture of products **2h** and **3h**. We prepared compound **4a** by the literature method,[7] in which the complexation is conducted in acetonitrile, with the product isolated by boiling this solution to saturation. Cooling gave a low yield of the complex along with a considerable amount of uncomplexed copper. We were able to obtain a good yield of **4g** by simply mixing equimolar amounts of cuprous chloride and **1g** in dichloromethane. In all other cases, use of $^1/_2$ equiv of cuprous chloride served to yield the complexes of stoichiometry (2,9-dialkyl-1,10-phenanthroline)$_2$CuCl.

While elemental analyses serve to distinguish compounds **2** from the 1:1 isomers **3** and **4**, all three were distinguishable by mass spectrometry. Mass spectra of compounds **3f** and **3h** both lack any significant negative ion peaks, while the positive ion FAB experiments show molecular ions (including chlorine) for the expected (2,9-dialkyl-1,10-phenanthroline)CuCl species. This stands in clear contrast to compounds **4a** and **4g**. The positive ion spectra of these compounds show the same masses as those of **2a** and **2g**: that of the [(2,9-dialkyl-1,10-phenanthroline)$_2$Cu]$^+$ cation. The negative-ion FAB mass spectra of **4a** and **4g** exhibit peaks of *m/z* 133/135/137/139 in the ratio 95:100:35:5, close to that predicted for $CuCl_2^-$ based upon isotopic abundances. The negative ion spectrum of compound **2a** shows only the *m/z* 35/37 peaks in the expected 7:3 ratio of ^{35}Cl to ^{37}Cl.

Infrared spectroscopy allowed further illumination of the behavior of some of the complexes **3** and **4** by determination of copper(I)–chlorine stretching frequencies. In dichlorocuprate, such bonds are known[14] to have absorbances in the far

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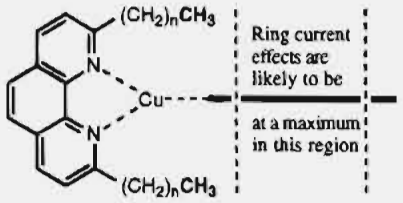

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Figure 4. Schematic of 2:1 complex of a 2,9-di-*n*-alkyl-1,10-phenanthroline with copper(I) showing how ring-current effects may be related to the length of the alkyl groups.

infrared of approximately 400−410 cm^{-1} and also at about 100 cm^{-1}, the latter of which is a region in which we were unable to make observations. However, we found that one species containing the dichlorocuprate anion, namely **4g**, had a peak at 405−410 cm^{-1} (whether in solution or in solid phase), while the compounds **3f**, **3h**, and **4a** in the solid phase (Nujol mulls) each had bands at about 330 cm^{-1}. In addition, compounds **3f** and **3h** exhibited similar bands in solution. Examination of complexes **2** as well as 2,9-dimethyl-1,10-phenanthroline **1a** (and, of course, Nujol itself) showed no significant absorbances in the range of 500−200 cm^{-1}.

Having prepared certain examples of complexes **2**, **3**, and **4**, we found several aspects of their ^1H NMR behavior rather informative (see Table 1). The first is that, for complexes **2** and **4**, the chemical shifts of the alkyl groups shifted *upfield* with respect to the ligands themselves. This seemed to stand in marked contrast to the inductive effect one would expect to observe upon complexation of these ligands with an electropositive, Lewis acidic center, such as the cuprous ion. A further important observation is that the complexes of stoichiometry 2:1, **2**, and those of stoichiometry 1:1, **4**, *had identical ^1H NMR spectra*. These observations, then, differ markedly from those of complexes **3**, where the more generally expected chemical shifts are seen.

A close examination of the ^1H NMR spectra of the complexes **2** further reveals that the extent of the upfield chemical shift in the side chain varies not simply with the number of bonds between a given atom and the metal center, but in a more subtle way with the distance from the aromatic system of the atoms in question. In particular, this upfield shift seemed to be at a maximum approximately three to four carbon atoms from the phenanthroline nucleus. Such an observation is consistent with an upfield shift due to a aromatic ring-current interaction between the two ligand molecules (Figure 4). That such an interaction is transmitted through space, rather than via chemical bonds is consistent with our observations. The lack of any appreciable difference between the ^1H NMR spectra of the complexes **2a** and **4a** (or **2g** and **4g**) suggests that their structures, in solution, contain the same $(dmp)_2Cu^+$ cation. Thus, the counterion in **2** is simply chloride, while that of **4** is dichlorocuprate. This conclusion is confirmed by the single crystal X-ray structure of (2,9-di-*n*-pentyl-1,10-phenanthroline)-CuCl, **4g** (see Figures 5 and 6), which clearly shows the $CuCl_2^-$ anion.

Further evidence for the relevance of the chemical shifts to the structure of the $[2,9\text{-dialkyl-1,10-phenanthroline}]_2Cu^+$ cation can also be seen in the single-crystal X-ray structure of the di-*n*-pentyl derivative, as shown in Figure 6. This structure clearly shows that the alkyl groups lie directly over the aromatic system, at a distance of approximately 2−3Å. Note that the alkyl groups of one of the ligands are not shown, while those of the other are shown in red. This close approach to the aromatic system

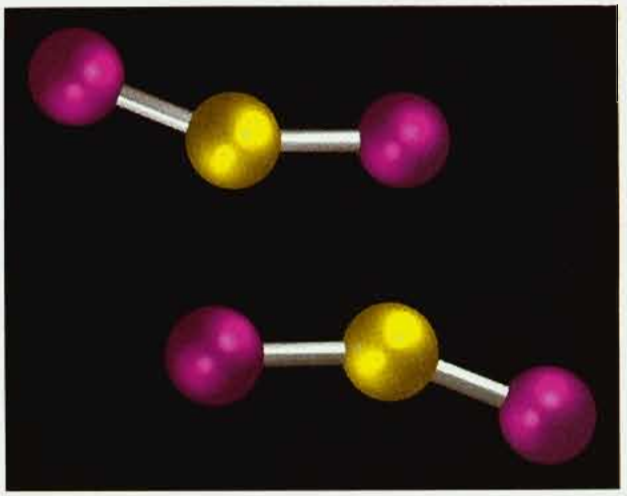

Figure 5. Dichlorocuprate ions in the single-crystal X-ray structure of compound **4g**. Note how each is distorted by its neighbor. Copper atoms are shown in gold, chlorine in purple.

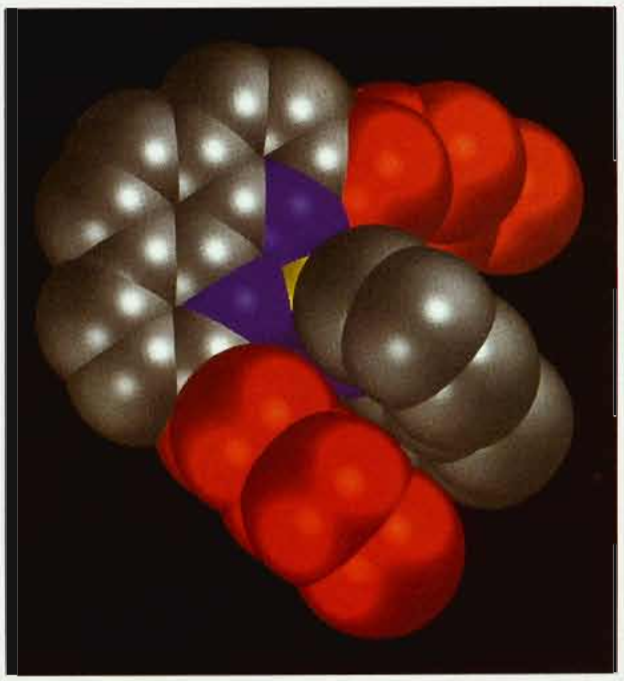

Figure 6. Cationic, pseudo-tetrahedral complex of 2,9-di-n-pentyl-1,-10-phenanthroline with copper(I), **4g**. The alkyl chains of one of the phenanthroline ligands are deleted, while those of the other ligand are shown in red. Other carbon atoms are shown in gray, and nitrogen in blue. Note proximity of these atoms to the aromatic phenanthroline system. Structure is shown with radii of 1.85 Å for the aromatic systems and 2.00 Å for the aliphatic chains.

is well within the distances known[15] to give rise to substantial upfield shifts in the ^1H NMR. Disorder was observed in the conformation of the alkyl groups in compound **4g**, largely in a direction parallel to the nearby aromatic system - that is, they can wag sideways across the phenanthroline rings. For this reason, and because the ring-current intensities in the individual rings of this system are known to be very similar,[16] we do not believe the structural disorder inherent in these molecules is reflected in the observed chemical shifts. Some key information from the X-ray data is given in Table 2.

The behavior of 2,9-di-*tert*-butyl-1,10-phenanthroline, **1f**, and its neopentyl homolog **1h** affords additional support for the ^1H

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(16) Ouellette, R. J.; van Leuwen, B. G. *J. Org. Chem.* **1969**, *34*, 62.

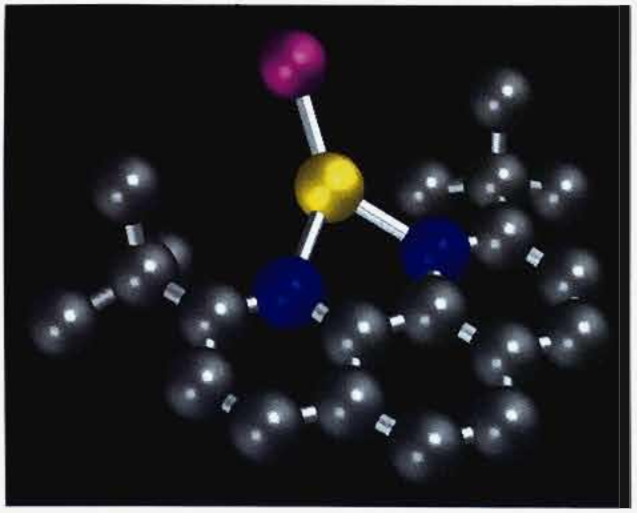

Figure 7. Structure of (2,9-di-*tert*-butyl-1,10-phenanthroline)CuCl (**3f**).

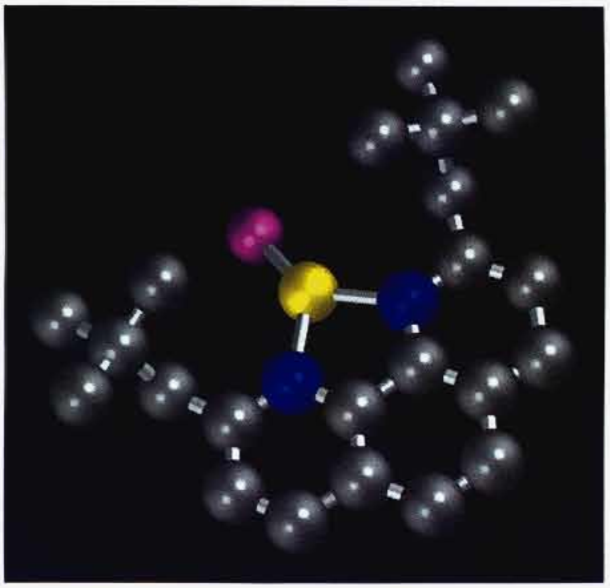

Figure 8. Structure of (2,9-dineopentyl-1,10-phenanthroline)CuCl (**3h**).

chemical shift hypothesis. At least in the presence of a coordinating chloride anion, ligand **1f** forms *only* a 1:1 complex **3f**, presumably due to its steric demand. In this case the chemical shift change upon complexation is in the downfield direction expected from the inductive effect of the copper atom acting in the absence of any ring-current phenomenon. Such behavior contrasts with that of neocuproine, **1a**, and 2,9-di-*n*-pentyl-1,10-phenanthroline, **1g**, the 1:1 complexes of which show an upfield shift in solution. Indeed, these NMR data suggest that, in compounds **3f** and **3h**, copper is not bound in a manner analogous to that of any of the compounds **2** or **4**. This was verified by single crystal X-ray crystallographic analyses of the complexes **3f** and **3h**. These clearly show that each copper atom bears only one phenanthroline ligand, with copper having a pseudotrigonal geometry as shown in Figures 7 and 8. Thus, compound **3f** is structurally similar to the known **3a**, *in the solid phase*. Unlike **4a**, however, copper complex **3f** appears to exhibit this behavior in the solid phase *and* in solution. In addition, compound **3f** is obtained in high yield as the only significant product of the reaction with cuprous chloride. We observed no trace of the copper byproducts described by White *et al.*[7] and also in our own preparations of **4a**. Compound **3f**, and to a lesser extent, **3g**, are distorted from a planar geometry in these structures (see Table 2 for the C−N−Cu−Cl dihedral angles). In compound **3f**, the chlorine atom is farther above the plane of the phenanthroline ring than any of the carbon atoms of the *tert*-butyl groups.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compounds **3f**, **3h**, and **4g**

	3f	**3h**	**4g**
Cu−Cl distance	2.147(4)	2.127(1)	2.156(4)
			2.692(6)
Cu−N distance	2.077(10)	2.068(2)	2.060(7)
	2.093(10)	2.056(2)	2.037(10)
			2.019(10)
			2.045(6)
Cα−N−Cu−Cl dihedral angle	26.0	7.7	
Cl−Cu−Cl angle		157.0(2)	
N−Cu−N angle(s)[a]	82.2(4)	81.5(1)	82.4(2)
			82.9(4)

[a] For compounds **4g**, the angles given are for two nitrogens in the same phananthroline system, as these are most nearly analogous to the angles given for the compounds **3**. The remaining angles for **4g** are 126.0(3), 119.4(3), 126.7(4), and 125.0(4)°.

In a finding related to that for **3f**, we found that compound **1h** forms a complex **3h** structurally analogous to **3f** (see Figure 8). However, it also forms a complex **2h** of 2:1 stoichiometry, exhibiting the upfield ring-current effect described above. Apparently, the neopentyl groups of **1h** impose sufficiently less steric demand than the *t*-butyl groups of **1f** that the formation of the pseudotetrahedral complex ion [(2,9-dineopentyl-1,10-phenanthroline)$_2$Cu]$^+$ is observed.

Conclusion

The present work has demonstrated that substituted 1,10-phenanthrolines tend to adopt structures, regardless of net stoichiometry, which contain the pseudotetrahedral [(2,9-dialkyl-1,10-phenanthroline)$_2$Cu]$^+$. Furthermore, it is relatively straightforward to tell whether a given complex possesses such a structure by a simple ^{1}H NMR experiment, due to the distinctive aromatic ring-current phenomena exhibited by these complexes. These experiments served to highlight the anomalous behavior of (2,9-dimethyl-1,10-phenanthroline)CuCl, **4a**, which appears to have a different structure in crystalline form than it does in solution in organic solvents. Hindered phenanthrolines are forced to adopt a geometry in which only one such ligand is coordinated to copper, giving the copper atom a pseudotrigonal geometry. It is our hope that this increase in the depth of understanding of these compounds will aid us in our efforts to correlate structure with activity, as we investigate the biological effects of these copper compounds.

Experimental Section

General Experimental Details. Melting point determinations are uncorrected. Tetrahydrofuran was distilled from potassium benzophenone ketyl immediately prior to use. Toluene, hexane, and dichloromethane were either distilled from an appropriate drying agent or purchased in anhydrous form. *n*-Butyl-, *sec*-butyl-, and *tert*-butyllithium were purchased from Aldrich Chemical Co. Hexyllithium, octyllithium, and 2-ethylhexyllithium were purchased from FMC Lithium Division ("Lithium Link"). Other reagents were used as received unless otherwise indicated. Flash chromatography was performed on silica gel 60 (EM Science) according to the procedure of Still.[17] Air and moisture sensitive reactions were performed under nitrogen atmosphere using flame-dried glassware and standard methods for handling air sensitive reagents. Reactions using elemental lithium were performed under argon atmosphere. Far IR spectra were measured with a Perkin-Elmer 283 instrument.

X-ray Crystallography. In each case a crystal of the compound was mounted on a glass fiber with epoxy and transferred to an Enraf-

(17) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Table 3. Crystallographic Data for Compounds **3f**, **3h**, and **4g**

	3f	**3h**	**4g**
formula	$C_{20}H_{24}ClCuN_2$	$C_{22}H_{28}ClCuN_2$	$C_{44}H_{56}Cl_2Cu_2N_4$
fw	391.4	419.5	838.9
color	orange	orange	orange-red
habit	needle	rhomb	fragment
dimens, mm	0.075 × 0.075 × 0.15	0.32 × 0.32 × 0.32	0.35 × 0.35 × 0.30
cryst syst	tetragonal	monoclinic	triclinic
space group	$P4_2/n$	$P2_1/c$	$P\bar{1}$
Z	8	4	2
a, Å	19.700(3)	9.545(2)	13.861(3)
b, Å		18.407(3)	14.108(3)
c, Å	9.680(2)	12.734(2)	14.214(3)
a, deg			65.35(2)
β, deg		107.75(2)	64.64(2)
γ, deg			90.05(2)
V, Å^3	3757(2)	2130.8(11)	2155.2(8)
μ, mm^{-1}	1.308	1.158	1.145
min/max transm	0.980/0.963	0.9124/0.9984	1.000/0.747
2θ range, deg	2.0−45.0	2.0−50.0	2.0−50.0
index ranges	$-1 \le h \le 21$	$-2 \le h \le 11$	$0 \le h \le 16$
	$-1 \le k \le 21$	$-2 \le k \le 21$	$-15 \le k \le 16$
	$-1 \le l \le 10$	$-15 \le l \le 14$	$-16 \le l \le 16$
F(000)	1632	880	880
χ, extinction cor	−0.000 10(6)	0.000 43(11)	0.0001(3)
ϱ_{calcd}, g cm^{-1}	1.384	1.308	1.293
T, K	295	298	298
λ, Å	0.710 73	0.710 73	0.710 73
no. of unique reflcns	2221	3761	7554
no. of obsd reflcns	729	2443	3291
GOF	1.00	1.06	1.12
abs cor	semiempirical	semiempirical	empirical
Δ/δ (max), (mean)	1.725, 0.027	0.007, 0.001	0.040, 0.002
R,[a] %	3.72	3.15	7.5
R_w,[b] %	4.21	4.36	8.91

[a] $R = \sum(F_o - F_c)/\sum F_o$. [b] $R_w = \sum[w^{1/2}(F_o - F_c)]/[\sum w^{1/2}F_o]$.

Nonius CAD-4 diffractometer operating with Mo Kα radiation through a graphite crystal monochromator. Scan speeds were 1.0−7.5°/min. Extinction corrections were, in each case, $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{1/4}$, where χ is given in Table 3. The structures of compounds **3f**, **3h**, and **4g** were solved by direct methods using a public-domain program called XCAD4, with further work being carried out using the PC version of Siemens SHELXTL PLUS. Refinements were performed by a full-matrix least-squares method, with riding model, calculated isotropic U hydrogen atoms. Other information for each structure is given in Table 3.

Synthesis of Phenanthroline Ligands 1. A typical procedure is shown here.

2,9-Di-*n*-pentyl-1,10-phenanthroline (1g). Under an argon atmosphere, lithium dispersion (30% in mineral oil, 0.5% sodium, 25.0 g, 1.08 mol) was washed with anhydrous hexane (3 × 25 mL) and suspended in hexane (25 mL). The suspension was cooled to −20 °C and freshly distilled 1-chloropentane (50 mL, 0.41 mol diluted with hexane (25 mL)) was added dropwise over 1.5 h. The reaction mixture was allowed to warm to room temperature and stirring was continued for 3 h. The resulting purple-gray mixture was then transferred to a filter funnel via cannula and found, after filtration, to be 1.8 M in pentyllithium by titration with *N*-benzylbenzamide. The solution of pentyllithium in hexane (ca. 150 mL, 0.27 mol) was added to a stirred suspension of 1,10-phenanthroline (12.2 g, 0.068 mol) in toluene (500 mL) cooled to 0 °C. The resulting deep-red solution was stirred overnight at room temperature. Water (150 mL) was then added. The layers were separated and the aqueous phase was extracted with dichloromethane (3 × 100 mL). The combined extracts were stirred with activated manganese dioxide (147.0 g, 1.69 mol) for 6 h, by which time the intense yellow color of the solution had discharged. This mixture was dried over magnesium sulfate, filtered, and evaporated to give 29.27g of an amber oil. Flash chromatography of this material on silica (0 → 10% methanol in dichloromethane) gave 15.43 g (71%) of the product as an amber oil: IR (film) 3040, 2955, 2927, 2870, 2856, 1591, 1495, 1365, 1143, 856 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (2H, d, J = 8.2), 7.64 (2H, s), 7.48 (2H, d, J = 8.2), 3.20 (4H, t, J = 8.2), 1.92 (4H, p, J = 7.7), 1.47 (4H, p, J = 7.7), 1.40 (4H, br p, J = 7.1), 0.92 (6H, t, J = 7.2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 145.3, 136.1, 126.9, 125.3, 122.2, 39.4, 31.9, 29.4, 22.5, 14.0; MS *m/z* (relative intensity) 321 (M + H)$^+$ (100), 291 (5), 277 (15), 264 (15), 233 (5), 221 (15), 208 (15), 194 (10). HRMS calcd for $C_{22}H_{28}N_2$ 321.2331, found 321.2346.

Other examples of compounds **1** were made by similar means, except that, as described above, commercially available alkyllithiums were used in place of those made in our laboratory. Analytical information for the remainder of compounds **1a**−**l** is as follows.

Neocuproine Hydrate (1a). Material was used as received from Aldrich Chemical Company, having the following properties: mp 161−163 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.32 (2H, d, J = 8.2), 7.85 (2H, s), 7.60 (2H, d, J = 8.1), 2.79 (6H, s); ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.0, 144.6, 136.1, 126.4, 125.3, 123.1, 24.9.

2,9-Diethyl-1,10-phenanthroline (1b):[18] amber semisolid; IR (film) 3040, 2969, 2930, 2871, 1591, 1495, 1364, 1145, 1051, 859 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (2H, d, J = 8.3), 7.70 (2H, s), 7.54 (2H, d, J = 8.2), 3.27 (4H, q, J = 7.6), 1.49 (6H, t, J = 7.6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 145.1, 136.3, 127.0, 125.4, 121.7, 32.3, 13.7.

2,9-Di-*n*-propyl-1,10-phenanthroline (1c):[18] yield 71% as a yellow crystalline solid; mp 69−70 °C; IR (film) 3038, 2958, 2927, 2864, 1590, 1504, 1365, 865, 750 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (2H, d, J = 8.2), 7.64 (2H, s), 7.47 (2H, d, J = 8.2), 3.18 (4H, t, J = 8.0), 1.94 (4H, m, J = 7.6), 1.07 (6H, t, J = 7.3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 145.1, 135.8, 126.7, 125.1, 121.9, 41.1, 22.7, 13.9.

2,9-Di-*n*-butyl-1,10-phenanthroline (1d): yield 70% as a white crystalline solid; mp 54−55 °C; IR (KBr) 3050, 2950, 2920, 1600, 1495, 855 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (2H, d, J = 8.2), 7.68 (2H, s), 7.50 (2H, d, J = 8.3), 3.21 (4H, br t, J = 8.1), 1.94−1.87

(18) Known compound: Pijper, Piet J.; Van der Goot, Henk; Timmerman, Henk; Nauta, Wijbe T. *Eur. J. Med. Chem.—Chim. Ther.* **1984**, *19*, 399.

(4H, m), 1.52 (4H, hex, $J = 7.4$), 1.00 (6H, t, $J = 7.4$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 145.4, 136.1, 127.0, 125.4, 122.3, 39.2, 31.9, 22.9, 14.0. Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58. Found: C, 82.10; H, 8.33; N, 9.27.

2,9-Di-*sec*-butyl-1,10-phenanthroline (1e): yield 61% as an amber oil, consisting of a mixture of diastereomers; IR (film) 3040, 2963, 2930, 2873, 1619, 1609, 1591, 1495, 1461, 1379, 1365, 854 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (2H, d, $J = 8.3$), 7.68 (2H, s), 7.49 (2H, d, $J = 8.3$), 3.32 (2H, hex, $J = 7.1$), 1.99−1.72 (4H, m), 1.45 (6H, d, $J = 7.0$), 0.99 (6H, 2t, $J = 7.4$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.24, 167.21, 145.39, 136.20, 127.23, 125.39, 120.45, 120.43, 44.20, 30.20, 30.07, 20.15, 20.06, 12.16. MS *m/z* 293 $(M + H)^+$ (100), 237 (45); HRMS calcd for $C_{20}H_{25}N_2$ 293.2018, found 293.2007.

2,9-Di-*tert*-butyl-1,10-phenanthroline (1f). Yield: 28% as a white solid. Recrystallization of this material from 2-propanol/water gave white prisms: mp 156−157 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (2H, d, $J = 8.8$), 7.69 (2H, d, $J = 7.8$), 7.68 (2H, s), 1.58 (18H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 144.7, 135.9, 126.8, 125.3, 119.6, 38.6, 30.2. Anal. Calcd for $C_{20}H_{24}N_2$: C, 82.15; H, 8.27; N, 9.58. Found: C, 82.05; H, 8.17; N, 9.55.

2,9-Di-*n*-pentyl-1,10-phenanthroline (1g): yield 71% as an amber oil; IR (film) 3040, 2955, 2927, 2870, 2856, 1591, 1495, 1365, 1143, 856 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (2H, d, $J = 8.2$), 7.64 (2H, s), 7.48 (2H, d, $J = 8.2$), 3.20 (4H, t, $J = 8.2$), 1.92 (4H, p, $J = 7.7$), 1.47 (4H, p, $J = 7.7$), 1.40 (4H, br p, $J = 7.1$), 0.92 (6H, t, $J = 7.2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.1, 145.3, 136.1, 126.9, 125.3, 122.2, 39.4, 31.9, 29.4, 22.5, 14.0; MS *m/z* (relative intensity) 321 $(M + H)^+$ (100), 291 (5), 277 (15), 264 (15), 233 (5), 221 (15), 208 (15), 194 (10); HRMS calcd for $C_{22}H_{28}N_2$ 321.2331, found 321.2346.

2,9-Di-neopentyl-1,10-phenanthroline (1h): yield 45% as a pale yellow low melting solid; IR (film) 3043, 2952, 2936, 2863, 1589, 1500, 1473, 1368, 851, 755 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (2H, d, $J = 8.1$), 7.69 (2H, s), 7.41 (2H, d, $J = 8.1$), 3.07 (4H, s), 1.04 (18H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 145.6, 135.1, 126.7, 125.3, 124.5, 52.3, 32.6, 29.7; MS *m/z* 321 $(M + H)^+$ (100), 264 (20), 208 (15); HRMS calcd for $C_{22}H_{29}N_2$ $(M + H)^+$ 321.2331, found 321.2331. Anal. Calcd for $C_{22}H_{28}N_2$: C, 82.45; H, 8.81; N, 8.74. Found: C, 82.48; H, 8.93; N, 8.67.

2,9-Di-*n*-hexyl-1,10-phenanthroline (1i): yield 83% as a light amber oil; IR (film) 3040, 2955, 2855, 1592, 1506, 1495, 1467, 1365, 855 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (2H, d, $J = 8.2$), 7.67 (2H, s), 7.49 (2H, d, $J = 8.3$), 3.21 (4H, br t, $J = 8.1$), 1.92 (4H, pent, $J = 7.8$), 1.49 (4H, pent, $J = 7.3$), 1.41−1.32 (8H, m), 0.90 (6H, t, $J = 7.0$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 145.4, 136.1, 127.0, 125.3, 122.2, 39.5, 31.7, 29.7, 29.4, 22.6, 14.0; MS *m/z* (relative intensity) 349 $(M + H)^+$ (100), 291 (15), 221 (15); HRMS calcd for $C_{24}H_{33}N_2$ 349.2644, found 349.2653.

2,9-Di-*n*-heptyl-1,10-phenanthroline (1j): yield 60% as a pale yellow low melting solid; IR (film) 3040, 2954, 2923, 2855, 1591, 1495, 1466, 1365, 855 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (2H, d, $J = 8.2$), 7.64 (2H, s), 7.47 (2H, d, $J = 8.2$), 3.18 (4H, t, $J = 8.0$), 1.94 (4H, m, $J = 7.6$), 1.07 (6H, t, $J = 7.3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 145.1, 135.8, 126.7, 125.1, 121.9, 41.1, 22.7, 13.9; MS *m/z* (relative intensity) 377 $(M + H)^+$ (100), 305 (15), 221 (15); HRMS calcd for $C_{26}H_{37}N_2$ 377.2957, found 321.2944.

2,9-Di-*n*-octyl-1,10-phenanthroline (1k): yield 79% as a low-melting, white crystalline solid; IR (film) 3040, 2955, 2855, 1592, 1506, 1495, 1467, 1365, 852, 731 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (2H, d, $J = 8.2$), 7.67 (2H, s), 7.49 (2H, d, $J = 8.4$), 3.21 (4H, br t, $J = 8.1$), 1.92 (4H, pent, $J = 7.8$), 1.49 (4H, pent, $J = 7.6$), 1.42−1.25 (16H, m), 0.88 (6H, t, $J = 6.8$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 145.5, 136.1, 127.0, 125.4, 122.3, 39.5, 31.9, 29.8, 29.7, 29.5, 29.2, 22.6, 14.1. Anal. Calcd for $C_{28}H_{40}N_2$: C, 83.11; H, 9.96; N, 6.92. Found: C, 83.12; H, 9.98; N, 6.78.

2,9-Di-(2-ethylhexyl)-1,10-phenanthroline (1l): yield 51% as a viscous, amber oil; IR (film) 3040, 2957, 2858, 1591, 1505, 1495, 1467, 1378, 1369, 855 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (2H, d, $J = 8.1$), 7.66 (2H, s), 7.44 (2H, d, $J = 8.1$), 3.12 (4H, d, $J = 7.2$), 2.08 (2H, hept., $J = 6.1$), 1.50−1.20 (16H, m), 0.94 (6H, t, $J = 7.4$), 0.86 (6H, t, $J = 7.2$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 145.6, 135.6, 126.8, 125.3, 123.1, 43.3, 39.8, 32.6, 28.8, 25.7, 23.0, 14.1, 10.7; MS *m/z* 404 $(M)^+$ (15), 389 (8), 375 (10), 361(15), 348 (10), 306 (100), 277 (12), 263 (8), 249 (15), 208 (20); HRMS calcd for $C_{28}H_{40}N_2$ $(M)^+$ 404.3188, found 404.3191.

Synthesis of Copper(I) Complexes 2. A typical procedure is shown here.

CuCl(Neocuproine)$_2$ (2a). A vacuum degassed solution of neocuproine hydrate (4.53 g, 20.0 mmol) in absolute ethanol (150 mL) was added to cuprous chloride (990mg, 10.0 mmol) via cannula under an atmosphere of nitrogen. The resulting bright solution was stirred at room temperature for 2 h. This mixture was filtered, to remove a small amount of insoluble matter, and evaporated to give 5.64g (100%) of bright red solid. Recrystallization from aqueous methanol gave very fine needles: mp 238−238.5 °C; IR (film) 3058, 2915, 1632, 1504, 1359, 860, 732, 548 cm^{-1}; UV−vis λ_{max} (CH_2Cl_2) 232 nm ($\epsilon = 91\,800$ M^{-1} cm^{-1}), 275 nm ($\epsilon = 70\,800$), 456 nm ($\epsilon = 6410$); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.75 (2H, br s), 8.22 (2H, s), 7.96 (2H, br s), 2.40 (6H, s); ^{13}C NMR (125 MHz, DMSO-d_6) δ 157.6, 142.2, 137.3, 127.1, 125.8, 125.6, 25.0; MS *m/z* (relative intensity) 481 $(M(^{65}Cu) - Cl^-)^+$ (50), 479 $(M(^{63}Cu) - Cl^-)^+$ (100), 273 (50), 271 (100), 209 (5); MS *m/z* (relative intensity, negative ion FAB) 37 (40), 35 (100). Anal. Calcd for $C_{28}H_{24}ClCuN_4$: C, 65.24; H, 4.69; N, 10.87; Cl, 6.88; Cu, 12.33. Found: C, 65.01; H, 4.73; N, 10.75; Cl, 6.84; Cu, 12.70.

The remaining complexes **2** were prepared by similar means, except that they were performed using dichloromethane as solvent. We obtained identical results if the cuprous chloride was simply added to the degassed solutions in solid form. Analytical information for compounds **2b**−**l** is as follows.

CuCl(2,9-diethyl-1,10-phenanthroline)$_2$ (2b). Yield: 100% of a dark red solid. Recrystallization of this material (CH_2Cl_2/hexane) gave the product as an orange solid: mp 201−204 °C; IR (film) 3042, 2971, 2925, 2875, 1586, 1498, 1365, 868 cm^{-1}; UV−vis λ_{max} (CH_2Cl_2) 232 nm ($\epsilon = 87\,900$ M^{-1} cm^{-1}), 275 nm ($\epsilon = 67\,600$), 456 nm ($\epsilon = 6550$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (2H, d, $J = 8.3$), 8.13 (2H, s), 7.83 (2H, d, $J = 8.3$), 2.74 (4H, q, $J = 7.6$), 0.94 (6H, t, $J = 7.7$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 143.0, 137.7, 127.8, 126.3, 124.2, 33.2, 13.5; MS *m/z* (relative intensity) 535 (M^+ less Cl) (75), 537 (40), 383 (10), 299 (95), 284 (20), 271 (10), 235 (5), 154 (50), 136 (50); HRMS calcd for $C_{32}H_{32}N_4{}^{63}Cu$ (M^+ less Cl) 535.1923, found, 535.1903; HRMS calcd for $C_{32}H_{32}N_4{}^{65}Cu$ (M^+ less Cl) 537.1905, found, 537.1900.

CuCl(2,9-di-*n*-propyl-1,10-phenanthroline)$_2$ (2c): yield 100% as a bright-red solid; mp 184−185 °C; IR (film) 3040, 2961, 2928, 2869, 1585, 1497, 1367, 863 cm^{-1}; UV−vis λ_{max} (CH_2Cl_2) 232 nm ($\epsilon = 94\,100$ M^{-1} cm^{-1}), 275 nm ($\epsilon = 72\,800$), 456 nm ($\epsilon = 5820$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (2H, d, $J = 8.5$), 8.14 (2H, s), 7.81 (2H, d, $J = 8.3$), 2.68 (4H, t, $J = 7.9$), 1.40 (4H, q, $J = 7.7$) 0.31 (6H, t, $J = 7.3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 143.1, 137.7, 127.8, 126.3, 124.8, 42.0, 22.7, 13.4; MS *m/z* (relative intensity) 593 (M^+ less Cl) (40), 591 (75), 329 (40), 327 (100); HRMS calcd for $C_{36}H_{40}N_4{}^{63}Cu$ (M^+ less Cl) 591.2549, found 591.2539; HRMS calcd for $C_{36}H_{40}N_4{}^{65}$-Cu (M^+ less Cl) 593.2531, found 593.2562.

CuCl(2,9-di-*n*-butyl-1,10-phenanthroline)$_2$ (2d): yield 74% as a dark-red amorphous solid; IR (KBr) 3040, 2960, 2930, 1495, 1375, 870 cm^{-1}; UV−vis λ_{max} (CH_2Cl_2) 232 nm ($\epsilon = 96\,600$ M^{-1} cm^{-1}), 275 nm ($\epsilon = 83\,200$), 456 nm ($\epsilon = 7440$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (2H, d, $J = 8.5$), 8.13 (2H, s), 7.81 (2H, d, $J = 8.2$), 2.72 (4H, br t, $J = 8.3$), 1.37−1.30 (4H, m), 0.67 (4H, hex, $J = 7.4$), 0.24 (6H, t, $J = 7.4$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 143.0, 137.7, 127.8, 126.3, 124.8, 39.9, 31.6, 22.2, 13.0; MS *m/z* (relative intensity) 649 $(M(^{65}Cu) - Cl^-)^+$ (35), 647 $(M(^{63}Cu) - Cl^-)^+$ (95), 357 (50), 355 (100); HRMS calcd for $C_{40}H_{48}N_4{}^{63}Cu$ (M^+ less Cl), 647.3175, found 647.3167; HRMS calcd for $C_{40}H_{48}N_4{}^{65}Cu$ 649.3157, found 649.3172.

CuCl(2,9-di-*sec*-butyl-1,10-phenanthroline)$_2$ (2e): yield: 82% as a dark-red amorphous solid mixture of diastereomers; IR (film) 3042, 2973, 2929, 2874, 1587, 1498, 1366, 874, 732 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (4H, m), 8.15 (4H, m), 7.77 (4H, m), 3.01 (0.9H, hex, J = 7.2), 2.90−2.76 (2H, m), 2.68 (1.1H, hex, $J = 7.0$), 1.55−1.22 (8H, m), 1.05−0.87 (12H, m), 0.35−0.15 (12H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ (166.08, 165.97), 142.89, (138.25, 138.15, 138.04), (128.20, 128.11, 128.01), (126.39, 126.35), (122.16, 122.12, 122.06), (46.15, 46.05, 45.73, 45.65, 45.33), (29.96, 29.64, 29.56, 29.46, 29.33, 29.22, 29.11, 28.89), (19.36, 19.22, 18.98, 18.66, 18.53, 18.47, 18.08), (11.61, 11.56, 11.42, 11.36, 11.30, 11.20); MS *m/z*: 649 (55), 647 (100), 357 (45), 355 (100); HRMS calcd for $C_{40}H_{48}N_4{}^{63}Cu$ (M^+

less Cl) 647.3175, found 647.3191; HRMS calcd for $C_{40}H_{48}N_4{}^{65}Cu$ (M^+ less Cl) 649.3157; found 649.3177.

CuCl(2,9-di-*n*-pentyl-1,10-phenanthroline)$_2$ (2g): yield 96% as a dark-red solid; IR (film) 3042, 2959, 2930, 2873, 2859, 1589, 1508, 1497, 1367, 859 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (2H, d, J = 8.5), 8.15 (2H, s), 7.81 (2H, d, J = 8.2), 2.71 (4H, br t, J = 8.1), 1.36 (4H, p, J = 7.5), 0.62−0.58 (8H, m), 0.43 (6H, t, J = 6.5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.5, 143.0, 137.6, 127.7, 126.2, 124.8, 40.2, 31.2, 29.3, 21.7, 13.4; MS m/z (relative intensity) 705 (M^+ less Cl) (45), 703 (80), 385 (45), 383 (100); HRMS calcd for $C_{44}H_{56}N_4{}^{63}$-Cu (M^+ less Cl) 703.3801, found 703.3790; HRMS calcd for $C_{44}H_{56}N_4{}^{65}Cu$ (M^+ less Cl) 705.3783, found 705.3797.

CuCl(2,9-dineopentyl-1,10-phenanthroline)$_2$ (2h): yield 90% as a dark-red solid; IR (film) 3042, 2959, 2930, 2873, 2859, 1589, 1508, 1497, 1367, 859 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (2H, d, J = 8.5), 8.17 (2H, s), 7.87 (2H, d, J = 8.3), 2.76 (4H, s), 0.59 (18H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 143.2, 137.2, 128.1, 126.6, 125.6, 54.2, 31.8, 29.7; MS m/z (relative intensity) 705 (M^+ less Cl) (30), 703 (50), 385 (40), 383 (100); HRMS calcd for $C_{44}H_{56}N_4{}^{63}Cu$ (M^+ less Cl) 703.3801, found 703.3781; HRMS calcd for $C_{44}H_{56}N_4{}^{65}Cu$ (M^+ less Cl) 705.3783, found 705.3795.

CuCl(2,9-di-*n*-hexyl-1,10-phenanthroline)$_2$ (2i): yield 94% as a red solid; mp 116−118 °C(toluene); IR (film) 3041, 2956, 2928, 2869, 1585, 1497, 1367, 863 cm^{-1}; UV−vis λ_{max} (CH_2Cl_2) 232 nm (ϵ = 109 500 M^{-1} cm^{-1}), 275 nm (ϵ = 82 700), 456 nm (ϵ = 7020); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (2H, d, J = 8.2), 8.13 (2H, s), 7.82 (2H, d, J = 8.2), 2.71 (4H, br t, J = 8.2), 1.35 (4H, pent, J = 7.8), 0.79 (4H, hex, J = 7.4), 0.63 (4H, pent, J = 7.6), 0.53 (6H, t, J = 7.3), 0.59−0.47 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6, 143.1, 137.7, 127.8, 126.3, 124.9, 40.3, 30.8, 29.7, 28.9, 22.1, 13.7; MS m/z (relative intensity) 761 (M^+ less Cl) (60), 759 (100), 413 (30), 411 (80). Anal. Calcd for $C_{48}H_{64}ClCuN_4$: C, 72.42; H, 8.10; N, 7.04; Cl, 4.45. Found: C, 72.11; H, 8.23; N, 6.89; Cl, 4.72.

CuCl(2,9-di-*n*-heptyl-1,10-phenanthroline)$_2$ (2j): yield 92% as a dark-red solid; mp 73−76 °C (toluene); IR (film) 3025, 2979, 2954, 1587, 1509, 1369, 873 cm^{-1}; UV−vis λ_{max} (CH_2Cl_2) 232 nm (ϵ = 79 100 M^{-1} cm^{-1}), 275 nm (ϵ = 60 000), 456 nm (ϵ = 5120); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (2H, d, J = 8.4), 8.12 (2H, s), 7.81 (2H, d, J = 8.2), 2.71 (4H, br t, J = 8.2), 1.35 (4H, pent, J = 7.8), 0.92 (4H, hex, J = 7.3), 0.77 (4H, pent, J = 7.4), 0.70 (6H, t, J = 7.3), 0.62 (4H, p, J = 7.5), 0.55 (4H, p, J = 7.0); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 143.1, 137.7, 127.8, 126.3, 124.9, 40.4, 31.3, 29.8, 29.3, 28.4, 22.3, 13.9; MS m/z (relative intensity) 817 (M^+ less Cl) (100), 815 (70), 441 (40), 439 (90); HRMS calcd for $C_{52}H_{72}N_4{}^{63}Cu$ (M^+ less Cl) 815.5053, found 815.5067; HRMS calcd for $C_{52}H_{72}N_4{}^{65}Cu$ (M^+ less Cl) 817.5035, found 817.5092.

CuCl(2,9-di-*n*-octyl-1,10-phenanthroline)$_2$ (2k): yield 19% as a waxy red solid; mp 50−60 °C; IR (film) 3042, 2952, 2923, 2854, 1587, 1498, 1367, 865, 731 cm^{-1}; UV−vis λ_{max} (CH_2Cl_2): 232 nm (ϵ = 96 100 M^{-1} cm^{-1}), 275 nm (ϵ = 75 500), 456 nm (ϵ = 6400); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (4H, d, J = 8.3), 8.09 (4H, s), 7.79 (4H, d, J = 8.5), 2.69 (8H, br t, J = 8.2), 1.32 (8H, pent, J = 7.8), 1.06 (8H, pent, J = 7.3), 0.76−0.55 (16H, m), 0.78 (12H, t, J = 7.3), 0.60 (8H, pent, J = 7.5), 0.50 (8H, pent, J = 7.6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6, 143.1, 137.7, 127.8, 126.3, 125.0, 40.4, 31.5, 29.8, 29.3, 28.8, 28.7, 22.4, 14.0; MS m/z (relative intensity) 873 (M^+ less Cl) (70), 871 (100), 469 (25), 467 (60); HRMS calcd for $C_{56}H_{80}N_4{}^{63}Cu$ (M^+ less Cl) 871.5679, found 871.5668; HRMS calcd for $C_{56}H_{80}N_4{}^{65}Cu$ 873.5616, found 873.5614. Anal. Calcd for $C_{56}H_{80}ClCuN_4$: C, 74.05; H, 8.88; N, 6.17; Cl, 3.90. Found: C, 73.53; H, 8.70; N, 6.07; Cl, 4.02.

CuCl(2,9-(2-ethylhexyl)-1,10-phenanthroline)$_2$ (2l): yield 100% as a viscous red oil; IR (film) 3036, 2952, 2927, 2854, 1585, 1497, 1379, 1369, 867 cm^{-1}; UV−vis λ_{max} (CH_2Cl_2) 232 nm (ϵ = 71 300 M^{-1} cm^{-1}), 275 nm (ϵ = 56 000), 456 nm (ϵ = 6050); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (4H, d, J = 8.3), 8.09 (4H, s), 7.79 (4H, d, J = 8.5), 2.69 (8H, br t, J = 8.2), 1.32 (8H, pent, J = 7.8), 1.06 (8H, pent, J = 7.3), 0.76−0.55 (16H, m), 0.78 (12H, t, J = 7.3), 0.60 (8H, pent, J = 7.5), 0.50 (8H, pent, J = 7.6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8, 143.3, 137.2, 127.8, 126.3, 125.7, 44.6, 38.4, 31.7, 27.7, 24.5, 22.5, 13.7, 9.4; MS m/z 873 (35), 871 (45), 469 (50), 467 (100). HRMS calcd for $C_{56}H_{80}N_4{}^{63}Cu$ (M^+ less Cl) 871.5679, found 871.5670; HRMS calcd for $C_{56}H_{80}N_4{}^{65}Cu$ (M^+ less Cl) 873.5661; found 873.5701.

CuCl(2,9-di-*tert*-butyl-1,10-phenanthroline) (3f). Cuprous chloride (274 mg, 2.77 mmol) was added to a degassed solution of 2,9-di-*tert*-butyl-1,10-phenanthroline (0.81 g, 2.77 mmol) in dichloromethane (25 mL) at room temperature. The resulting mixture acquired a light orange color over about 1 h and was, therefore, stirred overnight, by which time most of the insoluble cuprous chloride had been consumed or dissolved. The orange mixture was filtered and evaporated to give 1.08 g (100%) of an orange solid. Crystallization from toluene gave orange needles: mp 255−256 °C; IR (film) 3042, 2956, 2869, 1586, 1497, 1365, 861, 755 cm^{-1}; far wavelength IR (Nujol) 757, 648, 617, 438, 363 (w), 325 cm^{-1}; far wavelength IR ($CHCl_3$) 364, 323 cm^{-1}; UV−vis λ_{max} (CH_2Cl_2): 232 nm (ϵ = 78 500 M^{-1} cm^{-1}), 275 nm (ϵ = 48 000), 363 nm (ϵ = 1560); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (2H, d, J = 8.4), 7.96 (2H, d, J = 8.4), 7.76 (2H, s), 1.86 (18H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.9, 143.7, 137.9, 126.9, 125.6, 122.0, 38.7, 30.7; MS m/z 392 (25), 390 (30), 357 (70), 355 (100), 293 (70); HRMS calcd for $C_{20}H_{24}N_2{}^{35}Cl^{63}Cu$ (M^+) 390.0924, found 390.0912; HRMS calcd for $C_{20}H_{24}N_2{}^{37}Cl^{63}Cu$ (M^+) 392.0895, HRMS calcd for $C_{20}H_{24}N_2{}^{35}Cl^{65}Cu$ (M^+) 392.0906, found 392.0887. Anal. Calcd for $C_{20}H_{24}ClCuN_2$: C, 61.37; H, 6.18; N, 7.16; Cl, 9.06. Found: C, 61.43; H, 6.20; N, 7.10; Cl, 8.85.

CuCl(2,9-dineopentyl-1,10-phenanthroline) (3h). Repeated recrystallization of a sample of **2h** from toluene/methanol gave orange prisms: mp 246−248 °C; IR ($CHCl_3$) 2980, 1599, 1502, 1379, 935 cm^{-1}; far IR (Nujol) 332 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (2H, d, J = 8.2), 7.82 (2H, s), 7.67 (2H, d, J = 8.2), 3.47 (4H, s), 1.10 (18H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3, 143.1, 136.5, 126.7, 126.6, 125.5, 52.5, 33.0, 29.8; MS m/z 420 (40), 418 (30), 385 (70), 383 (100); HRMS calcd for $C_{22}H_{28}N_2{}^{35}Cl^{63}Cu$ (M^+) 418.1237, found 418.1223; HRMS calcd for $C_{22}H_{28}N_2{}^{37}Cl^{63}Cu$ (M^+) 420.1208, HRMS calcd for $C_{22}H_{28}N_2{}^{35}Cl^{65}Cu$ (M^+) 420.1219, found 420.1196. Anal. Calcd for $C_{22}H_{28}ClCuN_2$: C, 62.99; H, 6.73; N, 6.68; Cl, 8.45. Found: C, 62.97; H, 6.54; N, 6.60; Cl, 8.12.

[2,9-dimethyl-1,10-phenanthroline]$_2$CuCl$_2$ (4a). Cuprous chloride (1.98 g, 20.0 mmol) was added to a stirred, vacuum-degassed solution of neocuproine hydrate (4.53 g, 20.0 mmol) in acetonitrile (150 mL). This solution was stirred for 2 h. The resulting suspension was warmed to boiling and filtered. The filtrate was boiled to a volume of about 100 mL. This solution was allowed to cool slowly to give dark red needles: mp 280−284 °C dec (lit.[6] 310−320 °C); UV−vis λ_{max} (CH_2Cl_2) 232 nm (ϵ = 109 000 M^{-1} cm^{-1}), 275 nm (ϵ = 85 500), 454 nm (ϵ = 4970); far-IR (Nujol) 725, 680, 650, 547, 327 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.74 (2H, d, J = 8.2), 8.21 (2H, s), 7.95 (2H, d, J = 8.2), 2.38 (6H, s); ^{13}C NMR (125 MHz, DMSO-d_6) δ 157.6, 142.2, 137.4, 127.1, 125.9, 125.6, 25.1; MS m/z (relative intensity) 481 ($M(^{65}Cu) - CuCl_2^-)^+$ (35), 479 ($M(^{63}Cu) - CuCl_2^-)^+$ (60), 273 (50), 271 (100), 209 (10); MS m/z (relative intensity, negative ion FAB) 139 (5), 137 (35), 135 (100), 133 (95). Anal. Calcd for $C_{14}H_{12}$-$ClCuN_2$: C, 54.73; H, 3.94; N, 9.12; Cl, 11.54. Found: C, 54.67; H, 3.89; N, 9.04; Cl, 11.40.

[2,9-di-*n*-pentyl-1,10-phenanthroline]$_2$CuCl$_2$ (4g). Cuprous chloride (4.38 g, 0.044 mol) was added to a degassed solution of 2,9-di-*n*-pentyl-1,10-phenanthroline (14.0 g, 0.044 mol) in dichloromethane (100 mL). The resulting mixture was stirred for 2 h at room temperature, by which time most of the insoluble cuprous chloride had been consumed or dissolved. The blood-red mixture was filtered and evaporated to give 17.72 g (96%) of a dark-red solid: mp 103−105 °C; IR ($CHCl_3$) 3005, 2978, 2945, 1595, 1502, 1355, 865, 605, 405 cm^{-1}; far-IR (Nujol) 410 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (2H, d, J = 8.2), 8.10 (2H, s), 7.81 (2H, d, J = 8.3), 2.72 (4H, br t, J = 8.1), 1.40−1.34 (4H, m), 0.65−0.56 (8H, m), 0.43 (6H, t, J = 6.5); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.6, 143.1, 137.5, 127.7, 126.2, 124.9, 40.3, 31.4, 29.5, 21.9, 13.6; MS m/z (relative intensity) 705 (M^+ less Cl) (30), 703 (50), 383 (100), 353 (20), 339 (30), 326 (10), 297 (15), 283 (10), 270 (30); MS m/z (relative intensity, negative ion FAB) 139 (5), 137 (35), 135 (100), 133 (95); HRMS for $C_{44}H_{56}N_4{}^{63}Cu$ (M^+ less $CuCl_2^-$) 703.3801, found 703.3795; HRMS calcd for $C_{44}H_{56}N_4{}^{65}Cu$ (M^+ less Cl) 705.3783, found 705.3787.

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Supplementary Material Available: Crystallographic data for compounds **3f**, **3g**, and **4h** with tables of crystal data, complete bond distances, bond angles, and anisotropic displacement parameters, and ORTEP views (29 pages). Ordering information is given on any current masthead page.

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