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A Friedländer Approach to Novel 1,10-Phenanthrolines and Their Use as Ligands for Ru(II) and Cu(I)

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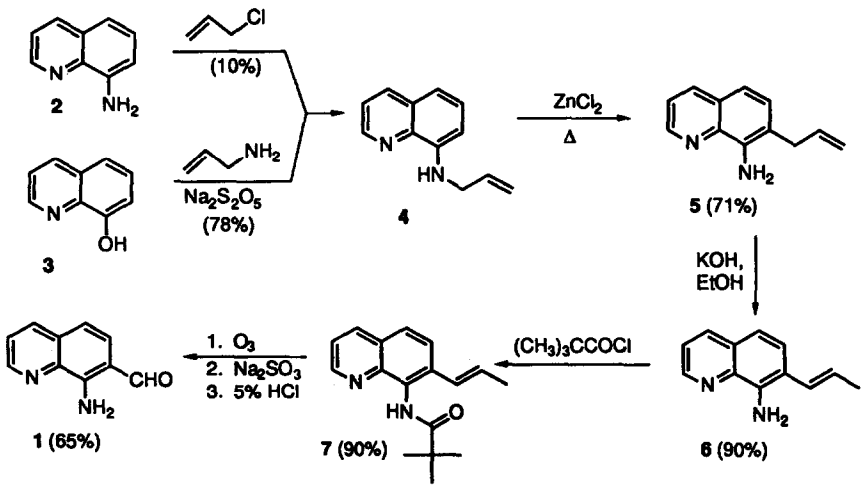
Abstract: A six step synthesis of 8-amino-7-quinolinecarbaldehyde from 8-hydroxyquinoline has been developed. This aminoaldehyde undergoes Friedländer condensation with ketones to form 2-substituted 1,10-phenanthrolines and 1,2-diketones to form 2,2'-bi-(1,10-phenanthroline)s. A tetramethylene derivative of the latter class of compounds forms a helical dinuclear complex with Cu(I).

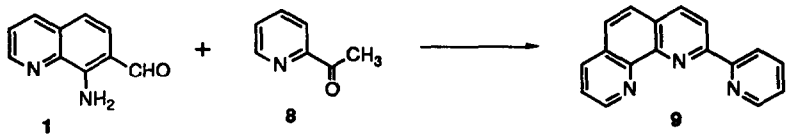
The Friedländer condensation represents a versatile and straightforward approach to the pyridine nucleus especially when it is incorporated into annulated derivatives such as quinoline and 1,8-naphthyridine.[1] We have had a long-standing interest in extending this approach to the preparation of 1,10-phenanthrolines, however, the prerequisite 8-amino-7-quinolinecarbaldehyde (1) has remained elusive.[2] Nevertheless, several positional isomers have been reported.[3] Although aromatic amines react readily with aromatic aldehydes to form Schiff bases, these two functionalities are sufficiently compatible to allow for reasonable stability in *ortho*-aminoaldehydes.[4] Direct access to this functionality from either a reductive or oxidative approach proved problematic and prompted us to develop the route outlined in scheme 1.

Scheme 1



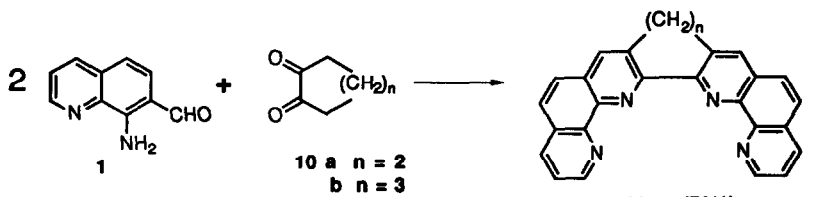
Starting from 8-hydroxyquinoline, treatment with allylamine and sodium *meta*-bisulfite in an autoclave provided 8-N-allylaminoquinoline (**4**). Alternatively, treatment of 8-aminoquinoline (**2**) with allyl bromide gave predominantly the N,N-diallyl derivative while allyl chloride gave only 10% of **4**. Aza-Claisen rearrangement of **4** may be effected by heating with zinc chloride[5] to provide the 7-allyl derivative **5** which can be isomerized to the more stable propenyl derivative **6** under the influence of ethanolic KOH. Direct ozonolysis of **6** was erratic and provided **1** in yields of 25% or less. A more effective oxidative cleavage occurs for the trimethylacetyl protected amine. Reduction of the intermediate ozonide *in situ* with NaI and subsequent deprotection provided the desired 8-amino-7-quinolinecarbaldehyde as a yellow crystalline material (mp 85-86 °C) which remained unchanged after several months when stored under argon at 0 °C.[6]

When **1** is refluxed overnight with 2-acetylpyridine in saturated ethanolic KOH, Friedländer condensation occurs to provide 2-(2'-pyridyl)-1,10-phenanthroline (**9**) in 75% yield. This molecule may be considered as a juxtaposition of 1,10-phenanthroline and 2,2';6',2"-terpyridine. When treated with $RuCl_3$-3 H_2O, complexation as a 2-substituted 1,10-phenanthroline would lead to an RuL_3^{2+} complex while complexation as a terpyridine would provide an RuL_2^{2+} species. The latter process occurs and the properties of the resulting complex are under examination.



1 **8** **9**

When **1** is allowed to react in a 2:1 fashion with an appropriate diketone, two 1,10-phenanthroline subunits can be incorporated simultaneously. Thus the condensation of **1** with 1,2-cycloalkanediones (**10a-c**) under Friedländer conditions provides the bridged bi-2,2'-(1,10-phenanthroline)s **11a-c**.[6] These bridged



1

10 a n = 2
b n = 3
c n = 4

11 a (79%)
b (45%)
c (50%)

dimers were identified by their NMR spectra which exhibit six characteristic ^1H aromatic resonances as well as twelve aromatic carbons in their ^{13}C spectra. As has been previously noted for other similar bridged azabiaryls, the 3,3'-dimethylene and 3,3'-trimethylene systems are conformationally mobile on the NMR time scale while the tetramethylene system is conformationally rigid.[7] These molecules tenaciously retain water and it appears from elemental analysis that **11a** may contain 0.5 molecules of sodium sulfate (the drying agent).

Molecular mechanics calculations were carried out to approximate the geometries of **11a-c** and dihedral angles about the 2,2'-bond were estimated to be 14°, 44°, and 50° respectively.[8] It appeared that **11c** might be sufficiently twisted such that two ligands would encapsulate two tetrahedral metal ions in a helical array. Treatment of **11c** with $CuClO_4(CH_3CN)_4$ in acetonitrile provided red crystals which showed six aromatic ^1H resonances as well as 14 carbon signals appropriate to a symmetrical Cu(I) complex. Single crystal X-ray analysis showed that bridging had occurred as predicted and two views of the dication are shown in figure 1.

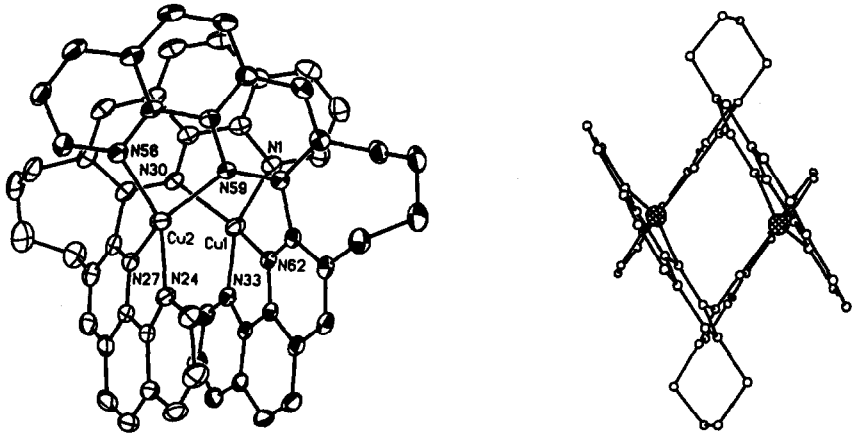


Figure 1. X-ray structure of $[(\mathbf{11c})_2Cu_2]^{2+}$ viewed perpendicular (l) and parallel (r) to the ligand 2,2'-bond.

A similar dinuclear Cu(I) complex has been studied by Lehn and coworkers who employed 5, 5', 3", 5"'-tetramethyl-2,2': 6',2": 6",2"'-quaterpyridine as the bridging ligand.[9] Their ligand has considerably more conformational mobility than **11c** where each 1,10-phenanthroline ring is essentially planar and the torsion angle about the central 2,2'-bond is controlled by the 3,3'-bridge. The steric congestion imposed on **11c** as a result of bridging two coppers causes the torsion angle about the 2,2'-bond to increase to 64.2° as compared with a torsion angle of 77° for the quaterpyridine complex. This additional constraint causes pinching which is evidenced in the right half of figure 1 and is further mainfested by a decreased Cu(1)-Cu(2) distance of 3.59 Å as compared with 3.90 Å in the quaterpyridine complex. Of considerable interest is the layered arrangement of each 1,10-phenanthroline unit with its counterpart in the opposing ligand. These residues lie in nearly parallel planes separated by 3.30 Å for one pair and 3.48 Å for the other. Considerable π-stacking interaction should result.

The tetrahedral nature of Cu(I) is highly distorted and may be evaluated by considering the N-Cu-N angles. The so-called *cis* angles, which involve a five-membered ring, measure 82.2 ± 0.2° while the complementary *trans* angles vary from 109.3 - 143.2°. Both complexes show essentially identical Cu-N bond lengths which may be divided into two groups: those which involve N27, N30, N59, and N62 (2.07 Å), the "internal" pyridine rings, and those which involve N1, N24, N33, and N56 (2.02 Å), the "external" pyridine rings.

The concept that a sufficiently non-planar bpy analogue can bridge two Cu(I) ions suggests that an appropriate ligand might lead to a polymeric Cu(I) species and current studies are directed toward this goal.

Experimental Section

The ^1H and ^{13}C NMR spectra were run on a General Electric QE-300 spectrometer at 300 and 75 Mz respectively. IR spectra were run on Perkin-Elmer 1330 spectrometer. All solvents were reagent grade and distilled prior to use and all melting points are uncorrected.

N-Allyl-8-Aminoquinoline (4) A mixture of 8-hydroxyquinoline (4.35 g, 30 mmol), $Na_2S_2O_5$ (6.84 g, 45 mmol), and allylamine (6.84 g, 120 mmol) in 100 mL of water was heated at 170 °C for 24 h in a steel bomb. After cooling, water was added and the mixture was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with water and dried over $MgSO_4$. Removal of the solvent gave a residue, which was distilled to give N-allyl-8-aminoquinoline, bp 125-130 °C (0.5 mm), as a yellow liquid (4.34 g, 78%): ^1H NMR ($CDCl_3$) δ 7.78 (d, 1H, $J_{2,3}$ = 2.7 Hz, H_2), 7.08 (d, 1H, $J_{3,4}$ = 8.04 Hz, H_4), 6.43-6.48 (m, 1H, H_6), 6.38 (m, 1H, H_3), 6.12 (d, $J_{5,6}$ = 8.1 Hz, H_5), 5.75 (d, 1H, $J_{6,7}$ = 7.5 Hz, H_7), 5.56 (s, 1H, NH), 5.05-5.18 (m, 1H, Hβ), 4.44 (d, 1H, $J_{\beta,\gamma}$ = 16.9 Hz, H_γ), 4.28 (d, 1H, $J_{\beta,\gamma}$ = 10.0 Hz, H_γ), 3.05 (m, 2H, H_α); ^{13}C NMR ($CDCl_3$) δ 146.7, 144.4, 138.1, 135.2, 134.9, 128.5, 127.6, 121.2, 115.9, 113.8, 104.8, 45.8. IR ($CHCl_3$): 3290, 1545, 1505, 1450, 1420, 1325, 1280, 940, 870, 840 cm^{-1}.

7-Allyl-8-aminoquinoline (5) A mixture of N-allyl-8-aminoquinoline (7.36 g, 46 mmol) and $ZnCl_2$ (16.32 g, 120 mmol) was heated to 170-180 °C for 10 h and was allowed to stand overnight at room temperature. After the addition of 40% NaOH, the mixture was refluxed to dissolve ZnO, cooled, and extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were washed with water and dried over $MgSO_4$. Removal of the solvent gave a crude material which was purified by chromatography on alumina eluting with CH_2Cl_2-hexane (1:1) to give 7-allyl-8-aminoquinoline as a yellow oil (5.21 g, 71%): ^1H NMR ($CDCl_3$) δ 8.66-8.74 (m, 1H, H_2), 7.95-8.06 (m, 1H, H_4), 7.22-7.46 (m, 2H), 6.93-7.20 (m, 1H), 5.89-6.05 (m, 0.8H, H_2), 5.09-5.15 (m, 4H, NH_2, H_α), 3.47 (d, 0.8H, J = 4.7 Hz, Hβ). IR ($CHCl_3$): 3420, 3320, 2950, 1540, 1420, 1350 cm^{-1}.

7-(1-Propenyl)-8-aminoquinoline (6) A mixture of 7-allyl-8-aminoquinoline (3.68 g, 20 mmol) and KOH (2.0 g, 36 mmol) in ethanol (20 mL) was refluxed for 5 h with stirring. After cooling, 100 mL of water was added and the mixture was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with water and dried over $MgSO_4$. Removal of the solvent gave a crude material which was purified by chromatography on alumina eluting with CH_2Cl_2 to give 7-(1-propenyl)-8-aminoquinoline (3.3 g, 90%), mp 44-45° C: ^1H NMR ($CDCl_3$) δ 8.66-8.68 (m, 1H, H_2), 7.88 (d, 1H, $J_{3,4}$ = 8.2 Hz, H_4), 7.39 (d, 1H, $J_{5,6}$ = 8.5 Hz, H_6), 7.14-7.20 (m, 1H, H_3), 7.02 (d, 1H, H_5), 6.57 (d, 0.9H, $J_{\alpha,\beta}$ = 15.6 Hz, *trans* -H_α), 6.44 (d, 0.1H, $J_{\alpha,\beta}$ *cis* = 11.3 Hz, *cis*-H_α), 6.09-6.22 (m, 0.9H *trans*-Hβ), 5.83-5.90 (m, 0.1H, *cis*-Hβ), 1.87 (d, 2.7H, $J_{\beta,\gamma}$ = 5.4 Hz, *trans*-H_γ), 1.74 ppm (d, 0.3H, $J_{\beta,\gamma}$ = 7.0 Hz, *cis*-H_γ); ^{13}C NMR ($CDCl_3$) δ 147.3, 147.1, 139.7, 138.7, 135.5, 128.6, 128.4, 127.4, 126.9, 128.4, 125.9, 120.7, 120.5, 119.0, 115.6, 114.5, 18.9, 14.6. IR ($CHCl_3$): 3450, 3350, 2950, 1570, 1480, 1440, 1360, 1100, 980 cm^{-1}.

8-Trimethylacetamido-7-(1-propenyl)-quinoline (7) To an ice cold solution of 7-(1-propenyl)-8-aminoquinoline (1.0 g, 5.4 mmol) and triethylamine (0.55 g, 5.4 mmol) in 30 mL of $CHCl_3$, a solution of trimethylacetyl chloride (0.7 g, 5.8 mmol) in 10 mL of $CHCl_3$ was added dropwise over a period of 5 minutes. The reaction mixture was stirred at 0°C for 1 h and then at room temperature overnight. After 24 h, the mixture was concentrated *in vacuo* and the residue was chromatographed on alumina eluting with EtOAc to afford 8-trimethylacetamido-7-(1-propenyl)-quinoline which was recrystallized from hexane (1.36 g, 90%), mp 86-8 °C: ^{1}H NMR ($CDCl_3$) δ 8.89 (s, 1H, NH), 8.80 (dd, 1 H, $J_{2,3}$ = 1.4 Hz, $J_{2,4}$ = 4.3 Hz, H_2), 8.09 (dd, 1 H, $J_{4,2}$ = 1.4 Hz, $J_{4,3}$ = 8.2 Hz, H_4), 7.77 (d, 1 H, $J_{6,5}$ = 8.8 Hz, H_6), 7.59 (d, 1 H, $J_{5,6}$ = 8.8 Hz, H_5), 7.36 (dd, 1 H, $J_{3,2}$ = 4.3 Hz, $J_{3,4}$ = 8.2 Hz, H_3), 6.55 (dd, 1 H, $J_{\alpha,\beta}$ = 5.6, $J_{\alpha,\gamma}$ = 1.1 Hz, H_α), 6.38 (dq, 1 H, $J_{\beta,\alpha}$ = 1.1 Hz, $J_{\beta,\gamma}$ = 6.5 Hz, H_β), 1.96 (dd, 1 H, $J_{\gamma,\alpha}$ = 1.1, $J_{\gamma,\beta}$ = 6.5 Hz, H_γ), 1.47 (s, 9 H, $C(CH_3)_3$) ppm; ^{13}C NMR ($CDCl_3$) δ 177.7, 149.0, 142.9, 136.0, 132.6, 129.7, 128.4, 127.6, 127.3, 124.9, 124.4, 120.8, 40.0, 27.8, 19.2 ppm; IR (KBr): 3340, 2920, 1640, 1450, 1350, 1150, 1085, 895 cm^{-1}.

8-Trimethylacetamido-7-quinolinecarbaldehyde A solution of 8-trimethylacetamido-7-(1-propenyl)-quinoline (1.5 g, 5.6 mmol) in 100 mL of methanol was placed in a 500 mL gas washing vessel with a fritted inlet extending below the surface of the solution. The vessel was cooled to -55 °C and a mixture of ozone in dry oxygen (generated by a Welsbach T-23 Ozonator) was passed through the gas inlet until the outlet gas turned a 2% KI solution deep orange. A stream of oxygen was passed through the solution for an additional 15 min and then Na_2SO_3 (3.0 g, 24 mmol) in 30 mL of H_2O was added. The mixture was stirred at room temperature for 2 h. Water (150 mL) was added and after stirring for another 1 h, a precipitate appeared. Filtration and vacuum drying afforded 8-trimethylacetamido-7-quinolinecarbaldehyde as a white crystalline solid (0.75 g). More product was obtained by extracting the filtrate with CH_2Cl_2 (total yield 65%), mp>122-124 °C: ^{1}H NMR ($CDCl_3$) δ 10.08 (s, 1 H, CHO), 9.96 (s, 1 H, NH), 8.90 (dd, 1 H, $J_{2,4}$ = 1.4 Hz, $J_{2,3}$ = 4.2 Hz, H_2), 8.20 (dd, 1 H, $J_{4,2}$ = 1.4 Hz, $J_{4,3}$ = 8.3 Hz, H_4), 8.03 (d, 1 H, $J_{6,5}$ = 8.7 Hz, H_6), 7.66 (d, 1 H, $J_{5,6}$ = 8.7 Hz, H_5), 7.56 (dd, 1 H, $J_{3,2}$ = 4.2 Hz, $J_{3,4}$ = 8.7 Hz, H_3), 1.47 (s, 9 H, $C(CH_3)_3$) ppm; ^{13}C NMR ($CDCl_3$) δ 188.7, 178.6, 149.5, 140.8, 136.3, 136.1, 130.5, 125.8, 124.0, 123.4, 123.4, 40.3, 27.6 ppm; IR (KBr): 3280, 2900, 1640, 1430, 1350, 1140, 1075, 895 cm^{-1}.

8-Amino-7-quinolinecarbaldehyde (1) A mixture of 8-trimethylacetamido-7-quinolinecarboxaldehyde (0.6 g, 2.6 mmol) and 2N HCl (150 mL) in 80 mL of EtOH was refluxed for 10 h. The solution was cooled, neutralized with conc NaOH, and extracted with CH_2Cl_2 (3 x 50 mL). The combined CH_2Cl_2 solution was washed with water, dried over $MgSO_4$, and the solvent was evaporated to afford a green-yellow solid. Chromatography on alumina eluting with CH_2Cl_2 provided 8-amino-7-quinolinecarbaldehyde as a yellow solid (0.34 g, 75%), mp 85-6 °C: ^{1}H NMR ($CDCl_3$) δ 10.00 (s, 1 H, CHO), 8.76 (d, 1 H, $J_{2,3}$ = 4.0 Hz, H_2), 8.02 (d, 1 H, $J_{4,3}$ = 7.4 Hz, H_4), 7.40-8.20 (broad s, 2 H, NH_2), 7.50 (m, 2 H, H_6, H_3), 6.99 (d, 1 H, $J_{5,6}$ = 8.4 Hz, H_5) ppm. ^{13}C NMR ($CDCl_3$) δ 192.8, 148.8, 147.3, 138.2, 135.5, 130.9, 130.0, 129.9, 124.0, 113.0 ppm; IR (KBr): 3380, 3250, 1580, 1535, 1510, 1470, 1390, 1365, 1245, 1140, 1075, 890 cm^{-1}. Anal. Calcd for $C_{10}H_8N_2O$: C, 69.77; H, 4.61; N, 16.37. Found: C, 69.64; H, 4.61; N, 16.37.

2-(2'-Pyridyl)-1,10-phenanthroline (9) A mixture of aldehyde **1** (82 mg, 0.47 mmol), 2-acetylpyridine (58 mg, 0.47 mmol), and saturated ethanolic KOH (0.25 mL) in absolute ethanol (5 mL) was refluxed overnight. The reaction mixture was evaporated and the residue was purified by chromatography on Al_2O_3, eluting with hexane/CH_2Cl_2 (3:7) to provide 90 mg (75%) of **9**, mp > 300 °C: ^{1}H NMR ($CDCl_3$) δ 9.25 (dd, 1 H, J = 4.4, 1.5 Hz, H_9), 9.00 (d, 1 H, J = 8.1 Hz, H_7), 8.81 (d, 1 H, J = 8.2 Hz, H_4), 8.74 (dd, 1 H, J = 5.4, 1.9 Hz, $H_{6'}$), 8.37 (d, 1 H, J = 8.1 Hz, H_3), 8.25 (dd, 1 H, J = 8.1, 1.7 Hz, $H_{3'}$), 7.92 (d of t, 1 H, J = 8.0, 1.8 Hz, $H_{4'}$), 7.80 (AB quartet, 2 H, J = 8.8 Hz, H_5 or H_6), 7.65 (dd, 1 H, J = 8.1, 4.3 Hz, H_8), 7.39-7.35 (m, 1 H, $H_{5'}$); ^{13}C NMR ($CDCl_3$) d 156.2, 156.1, 150.3, 149.0, 146.3, 145.6, 136.9, 136.8, 136.1, 129.0, 128.7, 126.7, 126.5, 124.1, 122.8, 122.7, 120.8; IR (KBr) 3340, 3200, 2980, 1550, 1460, 1400, 1090, 850 cm^{-1}.

$Ru(9)_2(PF_6)_2$ A mixture of **9** (32 mg, 0.124 mmol) and $RuCl_3 \cdot 3H_2O$ (11 mg, 0.046 mmol) in EtOH/H_2O (1:1, 5 mL) was refluxed for 18 h. After cooling, the unreacted **9** was removed by filtration and NH_4PF_6 (20 mg, 0.135 mmol) in 1 mL of H_2O was added to precipitate the complex. The precipitate was collected and purified by chromatography on 15 g of Al_2O_3, eluting with CH_3CN/toluene (1:1) to provide 29 mg (54%) of the complex as a red solid, mp > 300 °C: ^{1}H NMR (CD_3CN) δ 9.00 (d, 1 H, J = 8.7 Hz, H_4), 8.90 (d, 1 H, J = 8.7 Hz, H_3), 8.61 (d, 1 H, J = 8.0 Hz, H_9), 8.45 (d, 1 H, J = 8.9 Hz, H_5 or H_6), 8.39 (dd, 1 H, J = 8.2 Hz, $H_{6'}$), 8.24 (d, 1 H, J = 8.9 Hz, H_5 or H_6), 7.92 (dt, 1 H, J = 8.1, 1.1 Hz, $H_{4'}$), 7.51 (dd, 1 H, J = 5.1, 1.0 Hz, $H_{3'}$), 7.30 (m, 2 H, H_7, H_8), 7.04 (m, 1 H, $H_{5'}$); ^{13}C NMR (CD_3CN) δ 155.8, 155.3, 154.7, 150.9, 147.0, 139.1, 137.5, 134.8, 132.2, 131.0, 130.2, 128.4, 128.3, 127.0, 126.0, 123.0; IR(KBr) 2930, 2880, 1550, 1350, 1210, 1085, 900, 835 cm^{-1}; Anal. Calcd. for $RuC_{34}H_{22}N_6P_2F_{12}$: C, 45.08; H, 2.43, N, 9.28. Found: C, 45.58; H, 2.69; N, 9.02.

3,3-Dimethylene-2,2-bi[1,10]phenanthroline (11a) The same procedure as described for **9** was followed, using aminoaldehyde **1** (0.34 g, 2 mmol) and 1,2-cyclohexanedione[10] (0.112 g, 1 mmol) to give **11a** (0.3 g, 79%) as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 9.21 (d, 2H, $J_{2,3}$ = 4.4 Hz, H_2), 8.22 (d, 2H, $J_{3,4}$ = 8.1 Hz, H_4), 8.12 (d, 2H, J = 8.5 Hz), 7.75 (d, 2H, $J_{5,6}$ = 8.8 Hz, H_5/H_6), 7.71 (d, 2H, H_5/H_6), 7.60 (dd, 2H, H_3), 7.51 (d, 2H, J = 8.2 Hz), 2.96 ppm (s, 4H, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 158.5, 149.3, 145.1, 144.8, 135.3, 135.1, 127.9, 125.7, 125.5, 124.6, 122.8, 121.9, 26.0; IR ($CHCl_3$) 1570, 1550, 1460, 1420, 1370, 1030, 840 cm^{-1}.

3,3-Trimethylene-2,2-bi[1,10]phenanthroline (11b) The same procedure as described for **9** was followed, using aminoaldehyde **1** (0.344 g, 2 mmol) and 1,2-cycloheptanedione[11] (0.13 g, 1 mmol) to give **11b** (0.18 g, 45%), mp>300° C: ^{1}H NMR ($CDCl_3$) δ 9.17 (s, 2H, H_2), 8.25 (d, 2H, $J_{3,4}$ = 7.8 Hz, H_4), 8.16 (s, 2H, H_7), 7.61-7.87 (m, 4H, H_5, H_6), 7.27 (broad s, 2H, H_3), 4.45 (s, 3H, H_2O), 2.87 (t, 4H, $J_{8,9}$ = 6.7 Hz), 2.40 ppm (t, 2H, H_9); ^{13}C NMR ($CDCl_3$) δ 157.7, 150.2, 146.2, 145.1, 136.0, 135.3, 135.0, 128.6, 128.4, 127.0, 125.9, 122.9, 31.2, 29.9 ppm; IR ($CHCl_3$) 1660, 1570, 1550, 1500, 1430, 1370, 1210, 840 cm^{-1}. Anal. Calcd for $C_{27}H_{18}N_4$·1.5 H_2O: C, 76.24; H, 4.94; N, 13.18. Found: C, 76.48; H, 4.73; N, 13.08.

3,3'-Tetramethylene-2,2'-bi[1,10]phenanthroline (11c) The same procedure as described for **9** was followed, using aminoaldehyde **1** (0.344 g, 2 mmol) and 1,2-cyclooctanedione[12] (0.14 g, 1 mmol) to give **11c** (0.23 g, 50%), mp>300° C: ^{1}H NMR ($CDCl_3$) δ 9.12 (broad s, 2H, H_2), 8.23 (d, 2H, $J_{3,4}$ = 7.4 Hz, H_4),

8.16 (s, 2H, H_7), 7.85-7.78 (m, 4H, H_5 and H_6), 7.57 (broad s, 1H, H_3), 4.39 (s, 1H, H_2O), 3.08-3.03 (m, 2H, H_9), 2.58-2.50 (m, 2H, H_9), 2.31-2.27 (m, 2H, H_8), 1.80-1.74 (m, 2H, H_8); ^{13}C NMR ($CDCl_3$) δ 157.7, 150.2, 146.4, 144.5, 138.3, 136.1, 135.8, 129.0, 128.5, 126.7, 125.9, 122.7, 31.7, 30.4; IR ($CHCl_3$) 1570, 1540, 1450, 1410, 1380, 1120, 1110, 1090, 840 cm^{-1}. Anal. Calcd for $C_{28}H_{20}N_4$-1.2 H_2O: C, 77.49; H, 4.70; N, 12.92. Found: C, 77.63; H, 4.65; N, 12.74.

$[Cu_2(11c)_2]Cl_2$ A mixture of $Cu(CH_3CN)_4ClO_4$ (32 mg, 0.097 mmol)[13] in 5 mL of CH_3CN was added to **11c** (40 mg, 0.098 mmol) in 5 mL of CH_3CN. The solution became red and was stirred at room temperature for 1 h. The solution was concentrated and the residue was recrystallized from CH_3CN/toluene to give 45 mg (94%) of $[Cu_2(11c)_2]Cl_2$[14], mp > 300 °C: ^1H NMR (CD_3CN) δ 8.37 (dd, 4 H, J = 8.1, 1.0 Hz, H_9), 8.27 (dd, 4 H, J = 4.5, 1.0 Hz, H_7), 7.92 (s, 4 H, H_4), 7.68 (d, 4 H, J = 9.0 Hz, H_5 or H_6), 7.65 (dd, 4 H, J = 8.1, 4.5 Hz, H_8), 7.50 (d, 4 H, J = 9.0 Hz, H_5 or H_6), 3.05 (m, 4 H), 2.56 (m, 4 H), 2.20 (m, 4 H), 1.56 (m, 4 H); ^{13}C NMR (CD_3CN) δ 155.0, 149.8, 143.1, 141.4, 140.4, 136.8, 134.9, 128.8, 128.7, 128.0, 126.5, 126.1, 32.6, 30.2; IR(KBr) 3380, 2900, 1580, 1460, 1390, 1370, 1090, 900cm^{-1}; MS m/e (relative intensity) 987 (20, M), 950 (100, M-Cl), 475 (55, M-Cu(**11c**)Cl).

X-Ray Determination

A dark burgundy fragment having approximate dimensions 0.30 x 0.35 x 0.70 mm was carved from a large interpenetrating conglomerate and mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. The sample was placed in a stream of dry nitrogen gas at -50 °C, and the radiation used was Mo Ka monochromatized (λ = 0.71073 Å) by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection are listed in Table 1. The Laue symmetry was determined to be 1, and the space group was shown to be either P1 or P1. Intensities were measured using the omega scan technique, with the scan rate depending on the count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored after every two hours or every 100 data collected, and these showed no significant variation. During data reduction Lorentz and polarization corrections were applied, however no correction for absorption was made due to the fairly small absorption coefficient.

The unitary structure factors displayed centric statistics, and so space group P1 (triclinic) was assumed from the outset. The structure was solved by the SHELXTL Patterson interpretation program, which revealed the positions of the two independent Cu atoms in the molecule. Remaining 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. Although the compound was thought to include perchlorate anions, no evidence of oxygens attached to the chlorine atoms could be seen, and the hydrogen bonding parameters are in the normal range for water attracted to chloride.[14] After all shift/esd ratios were less than 0.1 convergence was reached. 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 1.2 e/Å, located near 03. All calculations were made using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs.[15]

Table 1. X-Ray Collection Data for $[Cu_2(\mathbf{11c})_2]Cl_2$

Cell constants	a = 12.945 (4) Å	α = 73.54 (3)°
	b = 13.130 (6)	β = 116.10 (3)°
	c = 15.471 (6)	γ = 78.51 (3)°
Volume	2334 Å^3	
Molecular formula	$C_{56}H_{40}N_8Cu_2^{2+}\cdot 2Cl^-\cdot 3.5\ H_2O$	
Formula weight	1086.09	
Formula units per cell	Z = 2	
Density	ρ = 1.55 g-cm^{-3}	
Absorption coefficient	μ = 10.9 cm^{-1}	
$R=\sum \lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.035	
$R_w=[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0.032	

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