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2,2′;9′,2″-Ter[1,10]phenanthroline

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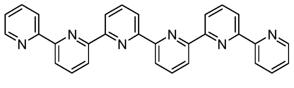
The title molecule, 2,2′;9′,2″-ter[1,10]phenanthroline can be prepared from 2,9-dichloro-1,10-phenanthroline in three steps through the corresponding diacetyl intermediate. The ligand acts as a hexadentate with K^+, while two molecules form a trinuclear, helical complex with Cu(I), which evidences π-stacking interactions and Cu–Cu distances of 3.01–3.04 Å. Electrochemical analysis shows a strong interaction between the Cu(I) centers.

The juxtaposition of pyridine rings connected through their ortho positions has provided a ligand family known as the polypyridines of which 2,2′-bipyridine (bpy) and 2,2′;6′,2″-terpyridine (tpy) are well-known members. Sexipyridine (**1**) is a higher member of this family that also may be considered as a trimer of bpy or a dimer of tpy. Despite conformational mobility about the five bonds which interconnect the pyridine rings, sexipyridine is able to self-organize with first row transition metal dications to provide a variety of helical polynuclear complexes.[1,2] Lehn and co-workers have shown that the incorporation of $-CH_2CH_2-$ or $-CH_2-O-CH_2-$ linkers between the three bpy subunits forces these moieties to behave more independently but still allows the formation of double-stranded helicates with Cu(I) or Ni(II).[3] The replacement of bpy subunits with 1,10-phenanthroline (phen) has led to greater conformational rigidity in these chelating systems and, to some extent, greater control of helicate formation.[4]

We have examined the effect on Ru(II) coordination arising from different covalent linkages in biphen.[5] With regard to Cu(I) complexation, we have found that diphenpyrene will lead to a helical trinuclear complex[6] and that variation in the bridge length of 3,3′-polymethylene-bridged 2,2′-biphen will influence the distance between two bound coppers.[7] In this communication, we report the synthesis and complexation of the next cogener in the polyphen family, 2,2′;9′,2″-terphen (**2**).



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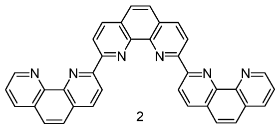
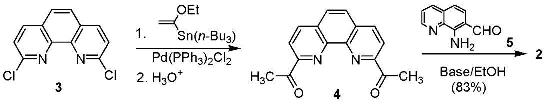


2

The Pd(II) catalyzed reaction of 2,9-dichlorophen (**3**) with 1-ethoxyvinyl tri-*n*-butylstannane leads to 2,9-di(ethoxyvinyl)phen in 69% yield.[8] This material may be readily hydrolyzed to provide 2,9-diacetyl phen (**4**), which is an excellent precursor for elaboration through condensation reactions. The Friedländer reaction of **4** with 8-amino-7-quinolinecarbaldehyde (**5**)[9] proceeds with the loss of four molecules of water to afford terphen **2**.



Isolation of the desired trimer is strongly dependent on the base used to catalyze the condensation. In the presence of pyrrolidine, the free ligand **2** is formed in a yield of 83% while using KOH as the base results in an 82% yield of a material which was partially characterized as the potassium complex by its ESI-MS molecular ion at $m/z = 611.5$.

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10.1021/ic050712w CCC: $30.25

Table 1. ^{1}H NMR Data for 2,2′;9′,2″-Ter[1,10]phenanthroline (**2**) and 2,2′-Bi[1,10]phenanthroline (**8**) and Their Metal Complexes[a]

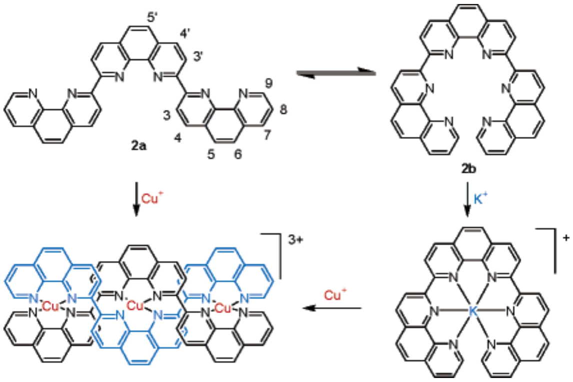
compound	H3′	H4′	H5′	H3	H4	H5/6	H7	H8	H9
2	9.32	8.84	8.20	9.48	8.88	8.14	8.58	7.86	9.24
$[Cu_3(\mathbf{2})_2]^{3+}$	8.23 (AB)	8.23 (AB)	7.31	8.75 (AB)	8.75 (AB)	7.77/7.65	7.77	7.28	8.14
CIS	*1.09*	*0.61*	*0.89*	*0.73*	*0.13*	*0.43*	*0.81*	*0.58*	*1.10*
$[K(\mathbf{2})]^+$	9.28	8.84	8.19	9.36	8.84	8.13	8.58	7.78	8.97
CIS	*0.04*	*0.00*	*0.01*	*0.12*	*0.04*	*0.01*	*0.00*	*0.08*	*0.27*
8				9.25	8.78	8.10	8.57	7.85	9.23
$[Cu_2(\mathbf{8})_2]^{2+}$				8.57	8.57	7.81	8.28	7.62	8.44
CIS				*0.68*	*0.21*	*0.29*	*0.29*	*0.23*	*0.79*

[a] Chemical shifts in DMSO-d_6 are reported in ppm relative to the residue solvent peak, and the complexation induced shifts (CIS) are reported in italics.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for $[Cu_3(\mathbf{2})_2](PF_6)_3{\cdot}3CH_3CN$

Cu(1)−N(1)	2.051(2)	Cu(2)−N(15)	2.107(2)	Cu(3)−N(29)	2.088(2)
Cu(1)−N(12)	2.079(2)	Cu(2)−N(26)	2.108(2)	Cu(3)−N(40)	2.024(2)
Cu(1)−N(71)	2.078(2)	Cu(2)−N(57)	2.118(2)	Cu(3)−N(43)	2.030(2)
Cu(1)−N(82)	2.047(2)	Cu(2)−N(68)	2.098(2)	Cu(3)−N(54)	2.080(2)
Cu(1)−Cu(2)	3.042	Cu(2)−Cu(3)	3.013		
N(1)−Cu(1)−N(12)	81.22(9)	N(15)−Cu(2)−N(26)	79.44(9)	N(40)−Cu(3)−N(29)	81.16(9)
N(82)−Cu(1)−N(71)	81.32(9)	N(68)−Cu(2)−N(57)	79.60(9)	N(43)−Cu(3)−N(54)	81.41(9)
N(1)−Cu(1)−N(71)	108.73(9)	N(15)−Cu(2)−N(57)	111.69(9)	N(43)−Cu(3)−N(29)	110.68(9)
N(82)−Cu(1)−N(12)	113.08(9)	N(68)−Cu(2)−N(26)	114.80(9)	N(40)−Cu(3)−N(54)	111.92(9)
N(71)−Cu(1)−N(12)	138.02(9)	N(68)−Cu(2)−N(15)	141.88(9)	N(54)−Cu(3)−N(29)	140.16(9)
N(82)−Cu(1)−N(1)	146.61(9)	N(26)−Cu(2)−N(57)	141.89(9)	N(40)−Cu(3)−N(43)	143.80(10)
Cu(1)−Cu(2)−Cu(3)	176.4				

Scheme 1. Complexation of Terphen **2**



The chemical-shift changes induced by complexation with K$^+$ are rather small with H9 being the only exception. Steric interaction of the two H9 protons induces a slight helicity to $[(\mathbf{2})K]^+$ which causes these protons to lie more in the shielding region of the opposing phen ring (Table 1).

The free ligand **2** is poorly soluble in most organic solvents; however, when a suspension of 2 equiv of this material in CH_3CN/CH_2Cl_2 (2:1) is treated with 3 equiv of $Cu(CH_3CN)_4(PF_6)$, an immediate reaction occurs to produce a dark green solution from which the trinuclear complex can be isolated in 92% yield. The complex is more soluble than the ligand, and its ^{1}H NMR spectrum was recorded in DMSO-d_6 and is reported in Table 1. All the protons experience substantial shielding upon coordination which more than compensates for the normal deshielding associated with metal complexation. The shielding is due partly to π-stacking effects resulting from the helical arrangement of two ligands around three metals. Protons H3′ and H9 feel the largest effect due to being held over the phen ring of an opposing ligand.

To more accurately assess the geometry of the Cu(I) complex, a single-crystal X-ray analysis was performed.[10] Selected features are summarized in Table 2, and an ORTEP drawing of the cation is shown in Figure 1. The complex displays a symmetrical, well-organized, helical structure. The Cu−N bonds to the two outer phen rings are not equal. The external bonds to N1, N82, N40, and N43 are shorter, averaging 2.04 Å, while the interior bonds to N12, N71, N29, and N54 average 2.08 Å. The Cu−N bonds for the central phen are even longer, with an average length of 2.11 Å. These bond lengths are consistent with the N−Cu−N angles involving a single phen ring. The angles to the outer phens are greater at about 81.3°, as compared with the angles to the central phen which average 79.5°. The N−Cu−N angles involving two opposing ligands vary greatly and may be divided into two sets, the smaller angles range from 108.7 to 114.8° and the larger angles range from 138 to 146.6°,

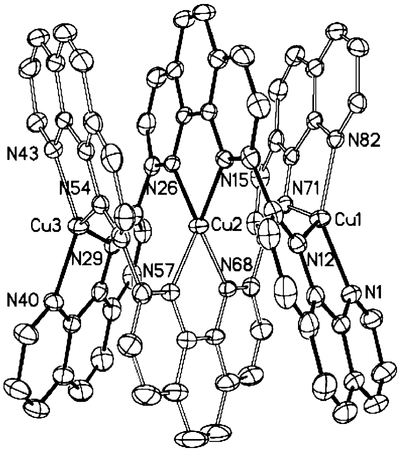


Figure 1. ORTEP drawing of the $[Cu_3(\mathbf{2})_2]^{3+}$ cation with the atom-numbering scheme for Table 1.

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(10) Crystal data for $[Cu_3(\mathbf{2})_2](PF_6)_3{\cdot}3CH_3CN$: empirical formula $C_{78}H_{49}Cu_3F_{18}N_{15}P_3$, fw = 1821.85, triclinic $P\bar{1}$, a = 13.7084(7) Å, b = 16.0177(8) Å, c = 18.4630(9) Å, α = 100.631(1)°, β = 103.373(1)°, γ = 107.167(1)°, Z = 2, V = 3626.4(3) Å^3, D = 1.668 g cm^{-3}, T = 223(2) K, R1 = 0.0355, wR2 = 0.0898 for $I > 4\sigma(I)$.

Table 3. Spectroscopic[a] and Cyclic Voltammetry[b] Data for the Terphen (**2**), Biphen (**8**), and Their Cu(I) Complexes

	λ_{max} (nm) (ϵ, $M^{-1}cm^{-1}$)	λ_{em} (nm)	$E_{1/2}^{ox}$(ΔE)	$E_{1/2}^{red}$ (ΔE)
2	235 (72 240), 247 (64 450), 289 (52 710), 318 (34 520), 332 (36 300), 345 (37 040), 365 (37 310)	378, 398, 419		
$[Cu_3(\mathbf{2})_2]^{3+}$	233 (72 250), 260 (71 720), 285 (59 940), 339 (27 350), 426 (5820), 563 (2750)	391, 412, 434	0.29 (150), 0.53 (122), 1.14^{ir}	−1.15 (71), −1.36 (69), -1.63^{ir}, -1.87^{ir}
8	242 (80 820), 292 (40 360), 322 (32 880), 338 (30 800), 356 (33 740)	362, 379, 396		
$[Cu_2(\mathbf{8})_2]^{2+}$	230 (59 200), 264 (46 330), 290sh, 336sh, 392 (5340), 438 (4500), 536 (1840)	385, 406, 428, 599 (w), 642 (w)	0.28 (99), 0.50 (150)	−1.31 (64), −1.44 (72), −1.75 (80), −1.89 (89)

[a] $\Delta E = E_{pa} - E_{pc}$ in mV. [b] Measured in CH_3CN containing 0.1 M $TBAPF_6$ with the scan rate at 100 mV/s and reported in volts vs SCE; $E_{1/2} = (E_{pa} + E_{pc})/2$ and $\Delta E = E_{pa} - E_{pc}$ in mV; ir is irreversible.

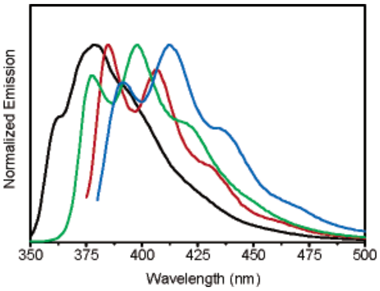


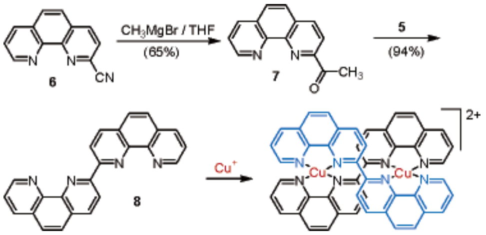
Figure 2. Normalized emission spectra of **2** (green), **8** (black), $[Cu_3(\mathbf{2})_2](PF_6)_3$ (blue), and $[Cu_2(\mathbf{8})_2](PF_6)_2$ (red) in CH_2Cl_2 at room temperature exciting at the long-wavelength absorption maximum.

indicating considerable distortion of tetrahedral geometry around the Cu(I) ion.

The twist of the ligands in the complex is reflected by two types of torsion angles which may be represented as the average of the NCCN and CCCC angles unique to each phen or connecting them. The twist about the central bond of each phen ring varies from 5.4 to 8.3° and reflects the nonplanarity of this ring. The π-stacking between phen rings may be estimated from the average distance between the atoms in the outer phen ring and the mean plane of the central phen rings. These four distances may be broken into two sets, those involving phens N43/54 and N71/82 which average 3.35 Å and those which involve phens N1/N12 and N29/40 which average 3.60 Å. This difference means that the helix is not quite linear, a fact which is also reflected by the Cu1−Cu2−Cu3 angle of 176.4°. The Cu−Cu distances range from 3.01 to 3.04 Å.

For comparison purposes, we also prepared 2,2′-biphen (**8**) starting with 2-cyanophen which was converted into 2-acetylphen[11] by treatment with CH_3MgBr. The subsequent reaction with **5** provided **8** in 94% yield. The preparation of **8** has been reported previously by Case[12] and also by Rice and co-workers[13] using either a Cu- or Ni-promoted coupling reaction. These approaches suffer from complexation of **8** with the metal cation byproducts, causing difficulties in extraction of the free ligand. The Friedländer approach is metal-free, does not suffer from complexed impurities, and thus proceeds in high yield.

The electronic absorption and emission properties of **2** and **8** and their Cu(I) complexes are summarized in Table 3. The terphen **2** shows a long-wavelength $\pi-\pi^*$ absorption at 365 nm, occurring at somewhat lower energy than the less-delocalized biphen **8** at 356 nm. Both complexes exhibit typical metal-to-ligand charge transfer (MLCT) bands with the terphen complex appearing at lower energy. The ligands and complexes show emission bands in the range of 362−434 nm which exhibit clear vibrational structure. From the similarity of these bands, we can assign them all as ligand-based (Figure 2). The complex $[Cu_2(\mathbf{8})_2]^{2+}$ also shows a very weak emission from its MLCT state.



The results from cyclic voltammetry are also given in Table 3. The dinuclear complex $[Cu_2(\mathbf{8})_2]^{2+}$ shows two distinct oxidation waves at +0.28 and +0.50 V. These values are less than what was recorded in CH_2Cl_2 for the analogous bridged biphen complexes.[7] The lower oxidation potential is likely due to the coordinating solvent acetonitrile, which can assist the geometric reorganization associated with oxidation. The terphen complex $[Cu_3(\mathbf{2})_2]^{3+}$ shows two oxidation bands at +0.29 and +0.53 V, very similar to $[Cu_2(\mathbf{8})_2]^{2+}$, as well as a third band at +1.14 V. The large separation of this third band argues for strong interaction between the metal centers. Both complexes show four reduction waves which are reasonably similar and consistent with their being ligand-based.

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Note Added after ASAP Publication. This paper was released ASAP on 7/23/2005 with the wrong definition for ΔE in footnote *b* of Table 3. The correct version was posted on 8/4/2005.

Supporting Information Available: Complete experimental details for the preparation of **2** and **8** and their Cu(I) complexes. X-ray crystallographic files for $[Cu_3(\mathbf{2})_2](PF_6)_3 \cdot 3CH_3CN$ (in CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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