Coordination of Ethynylpyridine Ligands with Cu(I): X-ray Structure of a Novel, Triple-Helical, Tricuprous Complex

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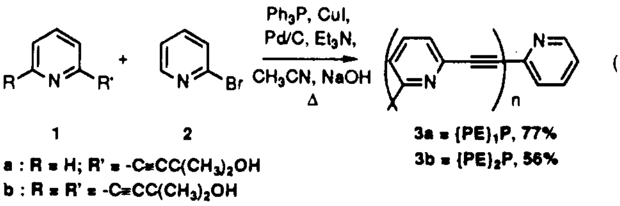
In this communication we describe the syntheses and the solution properties of two new polymetallic, trigonally-coordinated Cu(I) complexes and the X-ray structure of $[Cu^I_3(\{PE\}_2P)_3][PF_6]_3$ [**5b**, $\{PE\}_2P$ is 2,6-bis(2-pyridylethynyl)pyridine (**3b**)], a trimetallic, triple-stranded helicate. Multimetallic double- and triple-stranded helicates with metal ions that are two- (linear), four- (tetrahedral), six- (octahedral), or nine-coordinate (tricapped trigonal prism) or combinations of these geometries[1–4] have been prepared by appropriate combinations of metal ions with ligands capable of accommodating imposed geometrical requirements. Complex **5b** is unique in this group, being the first helicate with trigonally-coordinated metal cations.[5] It is the first helicate formed by the self-assembly of chains of monodentate ligands and extends the scope and possibilities of designing ligands to coordinate to metals in less "common" geometries.

The Cu(I) cation forms trigonal-planar complexes with monodentate 2-picolines.[6] Ligands **3a** [di(2-pyridyl)ethyne, $\{PE\}_1P$] and **3b** (eq 1) take advantage of this uncommon coordination mode of Cu(I), with the ethynediyl spacer allowing rotational flexibility about the pyridine–ethynediyl bonds while maintaining linearity along the pyridine–ethynediyl–pyridine axis. The distance between the nitrogen atoms of two adjacent pyridines in **3a** and **3b**, 5.35 Å (cisoid configuration),[7] also prevents the ligands from acting in a bidentate fashion.



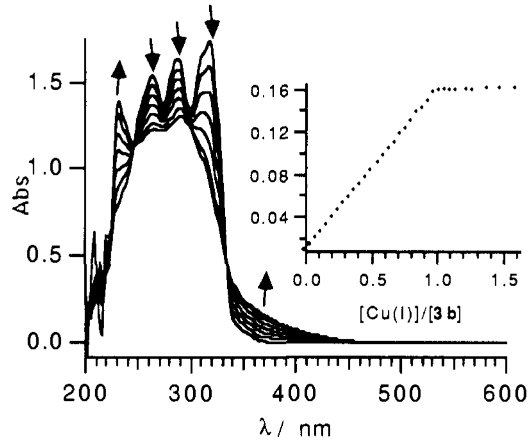


Figure 1. Spectrophotometric titration in CH_2Cl_2 of **3b**, 0.17 μmol, with 8.0-μL aliquots of **4**, 3.62 mM, starting at 0.0 μL and ending at 48.0 μL. The inset is the mole ratio plot for absorbance at 370 nm following 2.0-μL additions of **4** to 60.0 μL and then 5.0-μL aliquots to 75.0 μL total. The isosbestic points are at 334 and 246 nm.

The ligands were prepared by the Pd⁰-catalyzed, cross-coupling reaction[8] shown in eq 1 (experimental details and analytical data are in the supplementary material). Treatment of the ligands[9] with a CH_3OH solution[10a] of $[Cu^I(CH_3CN)_4][PF_6]$[10b] (**4**) at 20 °C resulted in yellow solutions from which yellow microcrystals of $[Cu^I_2(\{PE\}_1P)_3][PF_6]_2$ (**5a**) and **5b** were obtained (>90% yield) by the addition of diethyl ether. The yellow color arises from a MLCT band[11] in the 350–400-nm region associated with Cu(I) in a three-coordinate planar environment. Interestingly, pyridine adducts of Cu(I) are generally oxygen sensitive,[12] but CD_3NO_2 solutions of **5b** were stable in the presence of air at 20 °C for well over 1 week. Solutions of **5a** became blue within 24 h, indicative of oxidation to a Cu(II) species.

The UV-vis spectrophotometric titration of **3b** with **4** in CH_2Cl_2 is shown in Figure 1. The changes in absorbance analyzed by the mole ratio method at $\lambda = 370$ (inset Figure 1) and 286 nm showed a linear dependence on the amount of Cu(I) added up to a 1:1 Cu(I):**3b** ratio. A similar linear relationship was observed for reaction of **3a** with **4** up to 0.67:1 Cu(I):**3a**. The linear mole ratio plots in these stoichiometry regimes are strong evidence for a single species $[Cu^I_3(\{PE\}_2P)_3]^{3+}$ or $[Cu^I_2(\{PE\}_1P)_3]^{2+}$ in solution at 20 °C.

An X-ray-quality single crystal of **5b**·$2.5C_6H_6$[13] was grown from a CH_3OH/C_6H_6 solution, and a stereotopic view of the right-handed helix is shown in Figure 2. The symmetrical, nearly linear disposition of the copper ions and the approximately trigonal-planar geometry about each metal center are distinctive structural features of $[Cu^I_3(\{PE\}_2P)_3]^{3+}$. The nonbonded Cu(I)–Cu(I) distances are ~4.5 Å. Both Cu2 and Cu3 are strictly three-coordinate, while Cu1 is in moderately close contact with

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(13) Crystal data for **5b**·$2.5C_6H_6$: monoclinic, $P2_1/n$, $a = 17.383(6)$ Å, $b = 24.545(6)$ Å, $c = 17.644(5)$ Å, $\beta = 106.28(2)°$, $V = 7227(4)$ Å³, $Z = 4$, $d_{calcd} = 1.53$ g cm⁻³, $T = 298$ K. Nicolet R3m diffractometer, Mo Kα radiation ($\lambda = 0.710\,73$ Å), 7359 data collected, $3.0° \le 2\theta \le 40.0°$, scan speed 3–20 deg/min, no absorption correction applied, 3342 observed reflections ($|F_o| \ge 4\sigma|F_o|$). The structure was solved by direct methods (SHELXTL Plus) with the F, Cu, and P atoms refined anisotropically. Hydrogen atom positions were calculated geometrically, fixed C–H distance = 0.96 Å, and not refined. The carbon atoms of the benzene solvate situated at the special position (inversion center at the origin) were refined isotropically, while the carbon atoms of the two benzene solvates located at general positions were calculated geometrically. The structure was refined to $R = 0.0796$ and $R_w = 0.0803$.

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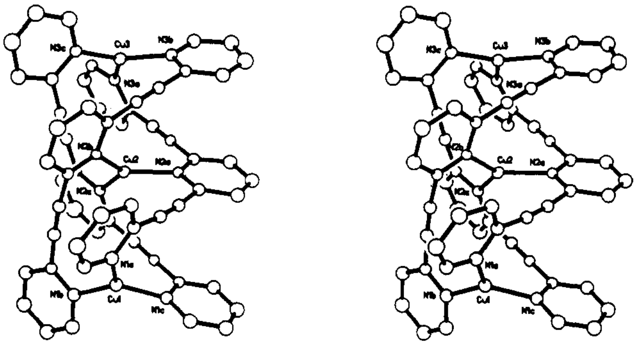

Figure 2. Stereotopic view of the right-handed helix of complex **5b**, 30% thermal ellipsoids. Selected bond distances, Å: Cu1–Cu2, 4.494; Cu2–Cu3, 4.519. Selected bond angles, deg: Cu1–Cu2–Cu3, 171.5; N1a–Cu1–N2a, 124.3(6); N1a–Cu1–N3a, 119.5(6); N2a–Cu1–N3a, 116.0(6); N1b–Cu2–N2b, 125.0(5); N1b–Cu2–N3b, 112.6(5); N2b–Cu2–N3b, 122.4(5); N1c–Cu3–N2c, 110.5(5); N1c–Cu3–N3c, 116.8(5); N2c–Cu3–N3c, 132.3(6).

one fluorine from a PF_6 counterion (Cu1–F2b, 2.90 Å). The average Cu-N distance is 1.984(13) Å, and each Cu(I) center is essentially planar[14] with respect to the plane defined by its three nitrogen donors, but none exhibits a 3-fold rotational axis with regard to bond angles. Recent calculations[2b,15] predict a relatively flat potential energy surface for interconversion of trigonal-planar, T-shaped, and Y-shaped geometries for Cu(I), so a symmetrical ligand disposition should not necessarily have been expected for **5b**. The overall symmetry of the complex is below D_3 in the solid state. Intramolecular, interstrand π–π overlaps between heterocyclic rings are also absent in **5b**. Long interstrand distances in the solid, generally >3.7 Å (in 2,6-oligopyridine double helicates, they are ca. 3.4 Å),[3,4c] and, more importantly, the offset between pyridine rings in adjacent strands are such that significant interaction between the pyridine rings is most unlikely.

The ^1H NMR spectra (20 °C) of **3b** and **5b**, Figures 3A and 3B, respectively, show a strong complexation effect and establish that the structural integrity of **5b** was maintained in solution on the NMR time scale. Symmetry elements in the ligand **3b** reduce the number of observable protons to six (11 total protons). The same number of protons were present in the spectrum of **5b**. The spectrum of crude **5b** was essentially identical to that of recrystallized **5b**, thus showing that the self-assembly process gave only one product.

The solution ^{13}C NMR spectra of **3b** and **5b** displayed 10 carbon resonances out of totals of 19 and 57 carbon atoms, respectively. The ^{13}C CPMAS solid-state NMR spectrum of **5b** showed[16] resonance positions similar to those determined in solution, albeit with broadening due to the lower than D_3 symmetry in the solid state.

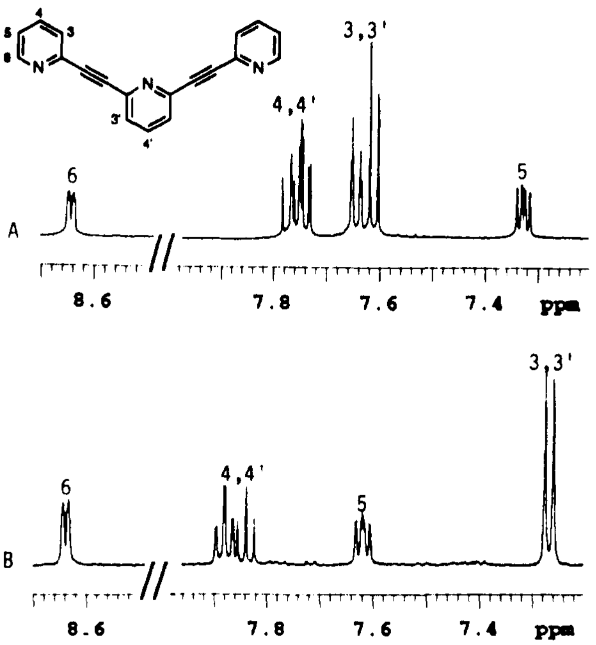

Figure 3. ^1H NMR spectra (500 MHz, CD_2Cl_2) of (A) the ligand **3b** and (B) the complex **5b**.

The ready formation of this new triple helix is noteworthy because of the absence of the classical chelate effect that is present in most other helices formed from multidentate ligands.[1-4] The synthesis of the ligands is a general method, and elongation of the ligand strand by such a convergent approach will provide us access to polymetallic helicates in which the number of strands will correspond to the coordination number of the metal and the number of metals will correspond to the number of pyridines in each helical strand. We are currently investigating the complexation chemistry of these longer ligand strands to other transition metals.

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, and hydrogen positions and a drawing showing a more complete numbering scheme for **5b**; experimental details for the preparation of **3a**, **3b**, **5a**, and **5b** and their analytical data (17 pages); listing of observed and calculated structure factors for **5b** (25 pages). Ordering information is given on any current masthead page.

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[14] Plane 1, Cu1–N1a–N1b–N1c, planar to within ±0.019 Å; plane 2, Cu2–N2a–N2b–N2c, planar to within ±0.0025 Å; plane 3, Cu3–N3a–N3b–N3c, planar to within ±0.030 Å. Dihedral angles: planes 1 and 2, 9.8°; planes 1 and 3, 14.8°; planes 2 and 3, 6.2°.

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[16] We thank Professor T. Apple for this spectrum.