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New Linear Coordination Polymers Based on Copper(I) and 4,7-Phenanthroline: Structure Dependence on Solvent and Counteranion

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Three new linear coordination polymers containing Cu(I) and 4,7-phenanthroline (phen) have been synthesized and structurally characterized by single-crystal X-ray diffraction. $[Cu(phen)(MeCN)_2]PF_6$ (**3**) and $[Cu(phen)(MeCN)]BF_4$ (**4**) are prepared from acetonitrile, and $[Cu(phen)(BzCN)]BF_4$ (**5**) is made from benzonitrile (MeCN = acetonitrile; BzCN = benzonitrile). All of the compounds have linear polymeric structures containing Cu(I) centers coordinated by two bridging 4,7-phenanthroline ligands, with additional coordinated solvent molecules completing the copper coordination sphere. In **3** and **4**, when acetonitrile is used, two and one MeCN solvent molecules coordinate to each Cu atom, resulting in a distorted tetrahedral and distorted trigonal geometry, respectively. The major interchain interactions are phenanthroline $\pi-\pi$ stacks. When benzonitrile is used in **5**, the chain-packing motif changes to allow the coordinated benzonitrile ligands to participate in the interchain $\pi-\pi$ stacking. Crystal data: for $[Cu(phen)(MeCN)_2]PF_6$ (**3**), monoclinic, space group $P2_1/c$ (No. 14), with $a = 11.4303(6)$ Å, $b = 11.4954(6)$ Å, $c = 14.0444(7)$ Å, $\beta = 99.948(1)°$, and $Z = 4$; for $[Cu(phen)(MeCN)]BF_4$ (**4**), monoclinic, space group $P2_1/c$ (No. 14), with $a = 8.7677(5)$ Å, $b = 11.5140(7)$ Å, $c = 14.8858(9)$ Å, $\beta = 96.548(1)°$, and $Z = 4$; for $[Cu(phen)(BzCN)]_2 2BF_4$ (**5**), triclinic, space group $P\bar{1}$ (No. 2), with $a = 11.338(1)$ Å, $b = 12.461(1)$ Å, $c = 13.904(1)$ Å, $\alpha = 115.909(2)°$, $\beta = 100.870(2)°$, $\gamma = 92.052(2)°$, and $Z = 2$.

Introduction

Chemists wishing to manipulate the structure and properties of organic molecules have a vast array of known reactions at their disposal.[1] In contrast, solid-state chemists have little in the way of an analogous knowledge base for solid−solid reactions (and are just beginning to understand their mechanisms[2]) to lend direction to the preparation of new materials. This void has led to the perception that the synthesis of most novel extended solids is happenstance. To be fair, serendipity often plays a favorable role, and the results can be astonishing (i.e. new high-T_c superconductors, combinatorial methods, etc.). More and more, however, chemists are championing "materials-by-design" in the hopes that if particular structures can be devised, particular properties and combinations of properties can also be realized.

To bypass the thermodynamic limitations of traditional high-temperature solid-state reactions, chemists have turned to gentler synthesis conditions where kinetic control over reaction products can be realized.[3] Often, solution-phase molecular building blocks can be assembled into crystalline extended solids by using various types of *noncovalent* intermolecular forces including electrostatic attractions,[4,5] hydrogen bonding,[6−9] and $\pi-\pi$ stacking.[10−12] Additional control over the geometrical arrangement of the building blocks has been realized by linking arrays of metal cations together with two or more multidentate, nonchelating ligands to form extended one-, two-, or three-dimensional "coordination polymers". Recently, this "tinker-toy" approach has produced many spectacularly complex novel materials, including porous solids,[13−17] chiral networks,[18−20] and

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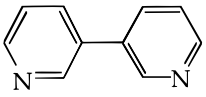
interpenetrated frameworks[21−23] that have been structurally characterized.

Our interests lie in designing coordination polymers that have topological relationships to silicate minerals. One attractive attribute of this huge class of target compounds is the wide variety of structures that can be constructed using only SiO_4 corner-shared tetrahedra. Thus, with the plethora of experimental variables available, including ligand size, solvent, stoichiometry, and counteranion, we envisioned that a variety of structures could be crystallized from similar molecular building blocks. Furthermore, some of the more common silicates have very useful properties, including molecular sieving ability (zeolites) and piezoelectricity (quartz). The *tunability* of properties made possible with analogous structures made from *organic molecules* and transition metal centers, would bring the hopes of real crystal engineering several steps closer.

Previously we have reported two unique three-dimensional coordination polymers containing tetrahedral Cu(I) centers linked with bent, bifunctional nonchelating ligands (pyrimidine[24] and 3,3′-bipyridine[25]), so as to approximate the connectivity of the silicon−oxygen networks in structures such as zeolites and quartz (Si−O−Si angle ca. 145−150°). In the bipyridine case, ring rotation about the center C−C bond opens the effective ligand angle, and a 2-fold interpenetrated diamondoid structure results to most efficiently pack space. In the present case, we sought to avoid free rotation of the rings, but remain in the same class of ligand, and therefore chose 4,7-phenanthroline (phen), **2**, which can be thought of as 3,3′-bipyridine, **1**, rigidified by the introduction of the third aromatic ring.



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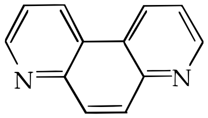

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In this report we describe several structures that are formed by linking together nominally tetrahedral *(vide infra)* Cu(I) centers with 4,7-phenanthroline and although we have not been able to coordinate four phen ligands to one copper atom to generate three-dimensional frameworks, we have successfully crystallized several one-dimensional coordination polymers. Isolated molecular hexagons containing 4,7-phenanthroline have been synthesized,[26] but to our knowledge this is the first time this ligand has been incorporated into an extended metal−ligand polymeric structure. We have found that both the identity of the *noncoordinating* anions (BF_4^- vs PF_6^-) and the solvent system have a effect on the final structure. Interestingly, changing solvents from acetonitrile (MeCN) to benzonitrile (BzCN) *does not affect the dimensionality* of the network, but changes quite dramatically the coordination environment about the Cu cations. Both acetonitrile and benzonitrile coordinate to the Cu(I) cations, and the packing of the polymeric chains changes in order to maximize interchain $\pi-\pi$ stacking interactions in which the benzonitrile ligands can participate, whereas the acetonitrile ligands cannot.

Table 1. Crystallographic Data for $[Cu(phen)(MeCN)_2]PF_6$ (**3**), $Cu(phen)(MeCN)]BF_4$ (**4**), and $[Cu(phen)(BzCN)]_22BF_4$ (**5**)

	3	**4**	**5**
empirical formula	$CuC_{16}H_{14}N_4PF_6$	$CuC_{14}H_{11}N_3BF_4$	$Cu_2C_{38}H_{26}N_6B_2F_8$
fw, g/mol	470.82	371.61	867.35
space group	$P2_1/\mathbf{c}$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (No. 2)
a, Å	11.4303(6)	8.7677(5)	11.338(1)
b, Å	11.4954(6)	11.5140(7)	12.461(1)
c, Å	14.0444(7)	14.8858(9)	13.904(1)
α, deg	90.0	90.0	115.909(2)
β, deg	99.948(1)	96.548(1)	100.870(2)
γ, deg	90.0	90.0	92.052(2)
Z	4	4	2
volume, Å^3	1817.6(2)	1492.9(2)	1719.7(3)
ρ, g/cm^3	1.721	1.653	1.675
μ, mm^{-1}	1.358	1.506	1.321
R^a	0.029 [$I > 2\sigma(I)$] 0.034 (all)	0.0344 [$I > 2\sigma(I)$] 0.0477 (all)	0.059 [$I > 2\sigma$(I)] 0.099 (all)
$R_w{}^b$	0.072 [$I > 2\sigma(I)$] 0.076 (all)	0.0864 [$I > 2\sigma(I)$] 0.0925 (all)	0.123 [$I > 2\sigma$(I)] 0.139 (all)

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

Experimental Section

Materials. Cu_2O (ACROS), 4,7-phenanthroline (Aldrich), nitrobenzene (ACROS), acetonitrile and THF (Fisher), and benzonitrile (ACROS) were used without purification. $[Cu(MeCN)_4]BF_4$ and $[Cu(MeCN)_4]PF_6$ were prepared by literature methods;[27] benzonitrile replaced acetonitrile in the synthesis of $[Cu(BzCN)_4]BF_4$ and $[Cu(BzCN)_4]PF_6$. Atlantic Microlabs (Norcross, Ga) performed all elemental analyses.

Preparation of $[Cu(phen)(MeCN)_2]PF_6$, 3. In a small 5-dram vial, $[Cu(MeCN)_4]PF_6$ (0.030 g, 0.81 mmol) and 4,7-phenanthroline (0.014 g, 0.82 mmol) were dissolved in 0.5 mL of MeCN and diluted with 3.0 mL of nitrobenzene. The small open vial was placed in a 20-dram screw-top vial containing 5 mL of THF. The large vial was sealed, and the THF was diffused slowly into the solution at room temperature. Yellow, cubelike single crystals were harvested after several days. Anal. Calcd (found) for $CuC_{16}N_4H_{14}PF_6$: C, 40.80 (40.50); H, 2.97 (2.88); N, 11.88 (11.49).

Preparation of $[Cu(phen)(MeCN)]BF_4$, 4. As above, $[Cu(MeCN)_4]BF_4$ (0.030 g, 0.95 mmol) and 4,7-phenanthroline (0.017 g, 1.0 mmol) were dissolved in 0.5 mL of MeCN and diluted with 3.0 mL of nitrobenzene. Slow diffusion of THF into the solution yielded yellow, cubelike single crystals after several days. Anal. Calcd (found) for $CuC_{14}N_3H_{11}BF_4$: C, 45.22 (45.17); H, 2.96 (2.99); N, 11.30 (11.22).

Preparation of $Cu(phen)(BzCN)]_22BF_4$, 5. In the same fashion, $[Cu(BzCN)_4]BF_4$ (0.030 g, 0.53 mmol) and 4,7-phenanthroline (0.010 g, 0.59 mmol) were dissolved in 0.5 mL of BzCN and diluted with 3.0 mL of nitrobenzene. Slow diffusion of THF into the solution yielded produced yellow, rhombic single crystals after several days. Anal. Calcd (found) for $Cu_2C_{32}H_{26}N_6B_2F_8$: C, 52.61 (52.39); H, 3.03 (3.09); N, 9.69 (9.69).

X-ray Crystallography. In all cases, single crystals of good quality (as determined by polarized optical microscopy) were mounted with silicone grease on a short, thin, glass fiber, and full hemispheres of data were collected at 173 K using a Siemens SMART system equipped with a CCD area detector (Mo Kα = 0.710 70 Å). The number of measured and unique reflections with R_{int} were 10 661, 3944, and 0.017 for **3**, 8790, 3235, and 0.0284 for **4**, and 7377, 4403, and 0.039 for **5**. After data integration, absorption corrections were applied.[28] The index ranges were $14 \leq h \leq 13$, $-9 \leq k \leq 14$, and $-16 \leq l \leq 18$ for **3**, $-11 \leq h \leq 11$, $-12 \leq k \leq 14$, and $-19 \leq l \leq 17$ for **4**, and $-12 \leq h \leq 14$, $-15 \leq k \leq 16$, and $-17 \leq l \leq 14$ for **5**. All structures were solved using the SHELXS direct methods routine[29] and refined using a full least-squares treatment on F^2.[30] Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were included in calculated positions and refined as riding models with fixed U_{iso} =

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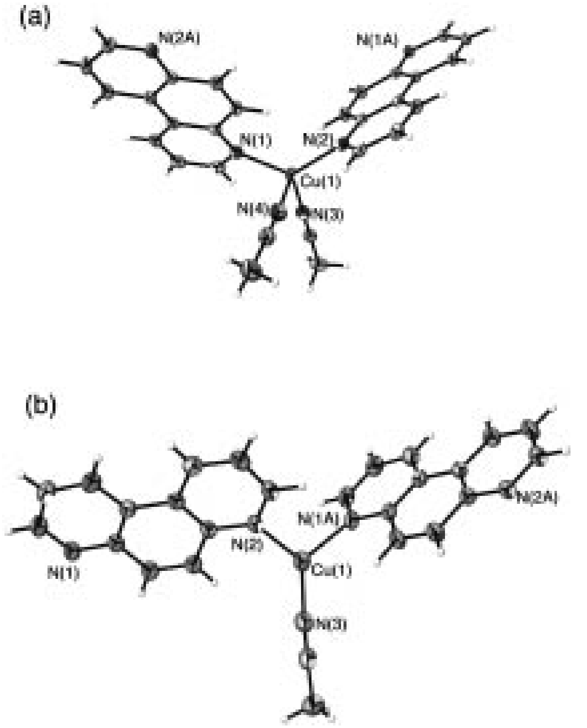


Figure 1. ORTEP diagrams of the unique coordination environments around the Cu(I) centers in (a) **3** and (b) **4**, with the non-hydrogen atoms shown as 50% probability thermal ellipsoids.

Table 2. Selected Bond Lengths and Angles for $[Cu(phen)(MeCN)_2]PF_6$ (**3**) and $Cu(phen)(MeCN)]BF_4$ (**4**)

3		**4**	
Bond Lengths (Å)			
Cu(1)−N(1)	2.036(2)	Cu(1)−N(1)	2.030(2)
Cu(1)−N(2)	2.055(2)	Cu(1)−N(2)	1.997(2)
Cu(1)−N(3)	2.073(2)	Cu(1)−N(3)	1.890(2)
Cu(1)−N(4)	2.006(2)		
Bond Angles (deg)			
N(1)−Cu(1)−N(2)	127.83(6)	N(1)−Cu(1)−N(2)	106.98(8)
N(1)−Cu(1)−N(4)	110.73(7)	N(1)−Cu(1)−N(3)	121.85(9)
N(2)−Cu(1)−N(3)	93.0(7)	N(2)−Cu(1)−N(3)	131.13(9)
N(3)−Cu(1)−N(4)	102.60(8)		

$1.2U_{iso}$ of the carbon atoms to which they are bonded. Crystallographic details of the data collection and refinement parameters are given in Table 1.

Thermal Gravimetric Analysis. Thermal analyses of the materials were performed using a Cahn TG121-09 microbalance. All measurements were made by heating the materials at 5 °C/min in a flowing nitrogen atmosphere.

Crystal Structure Descriptions. MeCN−Solvent System. In both **3** (PF_6^-) and **4** (BF_4^-) the asymmetric unit contains one unique copper atom and one bridging phenanthroline ligand (and one anion). Figure 1 compares the coordination geometry around the copper centers in **3** and **4**, with selected bond angles and bond distances in Table 2. In **3**, two bridging phenanthroline ligands and two acetonitriles comprise the distorted, but quite normal, tetrahedral coordination geometry. The most striking feature of **4** is that the copper atoms are “missing” one acetonitrile ligand, resulting in a *three-coordinate, trigonal* coordination environment. Close inspection of the difference Fourier map showed no evidence of even a partially occupied fourth ligand on the copper atom; the BF_4^- anion is much too distant to be considered bonding (Cu−F = 4.52 Å).

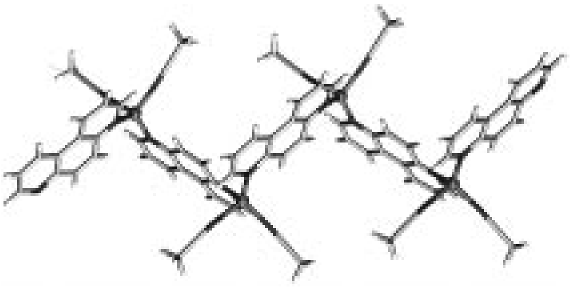


Figure 2. Structure of the zigzag, one-dimensional chains in **3**. Copper, gray spheres; nitrogen, dark gray sticks; carbon, light gray sticks; hydrogen, white sticks.

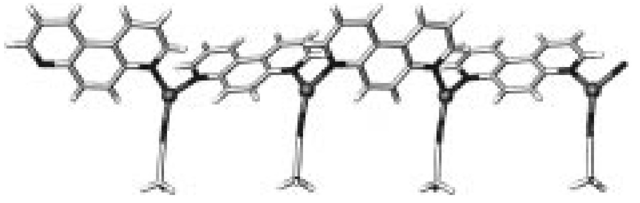


Figure 3. Structure of the one-dimensional chains in **4**. Atom representations are identical to Figure 2.

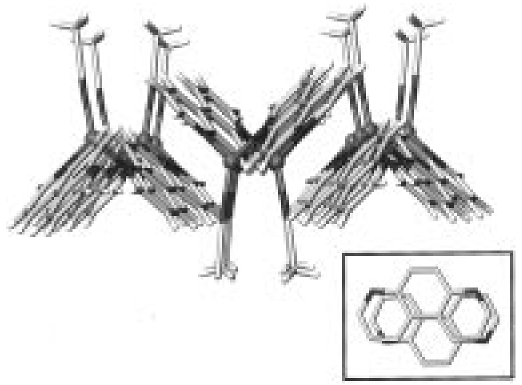
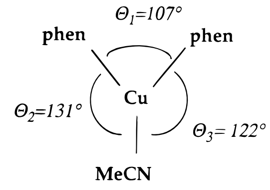


Figure 4. Partial packing diagram of **4**, viewed down the *c* axis. The anions have been omitted for clarity. Inset: A view looking perpendicular to one of the phen−phen pairs showing the 180° rotation of the two ring systems. Atom representations are identical to Figure 2.

Chart 1



Trigonal Cu(I) is rare, but not unknown, and has been seen previously with simple cyanide ligands,[31,32] and other mixed ligand systems where the L−Cu−L angles are all nearly 120°.[33] The less-commonly observed Y-shaped geometry (one angle compressed from 120°, the other two expanded) occurs when a chelating group forces one of the angles to narrow from the expected 120° trigonal planar geometry. In the case of **4** however, the smallest angle of the three, Θ_1 in Chart 1, is between the *two monodentate (and quite bulky) phen ligands* not between the phen groups and MeCN, and is significantly *smaller* than the phen−Cu−phen angle in the four-coordinate copper in **3** (127° versus 107°)! Munakata and co-workers have developed a correlation between bond angles and bond distances in three-coordinate Cu(I) systems, concluding that as the small angle of the three decreases (Θ_1 in Chart 1), a countering effect occurs to lengthen the bond opposite the compressed angle (Cu−NCMe in Chart 1).[34] The coordination sphere in **4** does not fit their correlation well; the difference in the bond lengths is much

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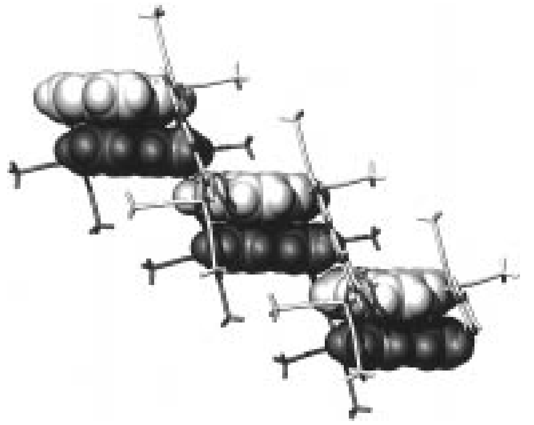

Figure 5. Stick diagram of two neighboring chains (one dark gray, one light gray) in **3**. The phenanthroline ligands on the neighboring chains in the $\pi-\pi$ stacked pairs are shown as space-filling spheres.

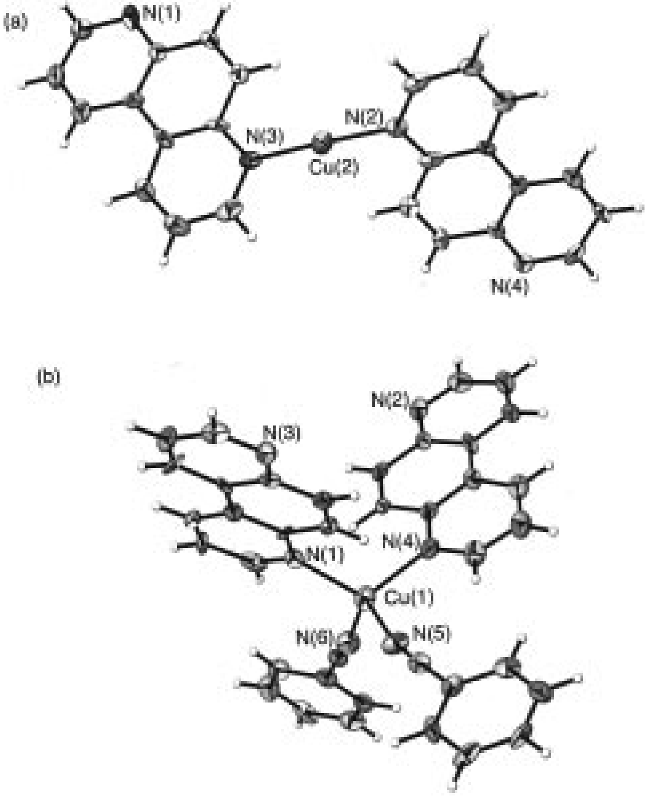

Figure 6. (a) Two-coordinate and (b) four-coordinate environments around the Cu(I) centers in **5**, with the non-hydrogen atoms shown as 50% probability thermal ellipsoids.

larger than expected for the observed angles (or alternatively, the angles are not distorted enough from 120° for the given bond distance differences).

Views of the extended polymeric structures of **3** and **4** are shown in Figures 2 and 3, respectively. In addition to the different copper coordination numbers, the "monomer units" are connected together in different ways. The copper atoms (gray spheres) in **4** lie in nearly a straight line, running along the *b* axis, and the phen ligands all reside on the same side of the row of copper atoms to which they are coordinated, leaving all of the MeCN ligands pointed in the same direction. In contrast, the "up−down" alternating phen ligands in **3** create more of a zigzag pattern of copper atoms, running along the *c* axis, with the coordinated acetonitrile ligands splayed out, alternating on both sides of the chain.

The different arrangement of ligands and differently shaped chains result in a different packing arrangement of the chains with respect to one another so as to maximize the interchain $\pi-\pi$ stacking interactions.

Table 3. Selected Bond Lengths and Angles for **5**

Bond Lengths (Å)	
Cu(1)−N(1)	2.00(1)
Cu(1)−N(2)	2.01(1)
Cu(1)−N(3)	2.099(9)
Cu(1)−N(4)	2.083(9)
Cu(2)−N(3)	1.877(9)
Cu(2)−N(4)	1.859(9)
Bond Angles (deg)	
N(5)−Cu(2)−N(6)	172.88(4)
N(1)−Cu(1)−N(3)	105.41(4)
N(1)−Cu(1)−N(4)	106.15(4)
N(2)−Cu(1)−N(3)	101.89(4)
N(2)−Cu(1)−N(4)	110.70(4)

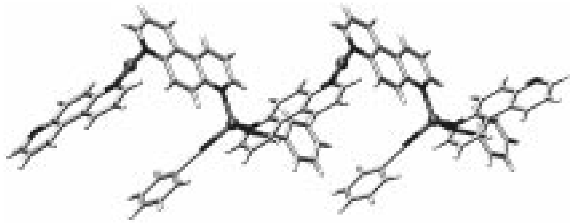

Figure 7. Structure of the one-dimensional chains in **5**. Copper, gray spheres; nitrogen, dark gray sticks; carbon, light gray sticks; hydrogen, white sticks.

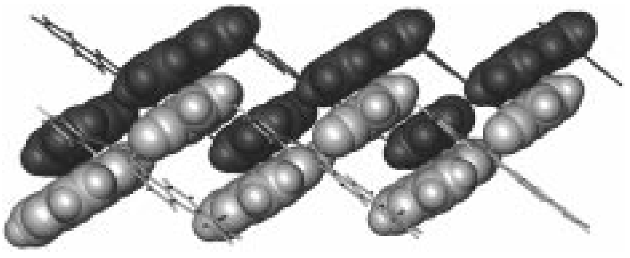

Figure 8. Stick representation of the interactions between neighboring chains (one light gray, one dark gray) in **5**. The phenanthroline and benzonitrile ligands involved in $\pi-\pi$ stacks are represented as space-filling spheres.

Figure 4 shows a view down the chain direction of **4** (*c* axis), accentuating the Y-like arrangement of the three ligands and the 180° rotation of every other neighboring chain along the *b* axis to allow the "undersides" of the phen ligands to come into contact (3.5 Å). The inset shows a stick representation of the orientation of two phenanthroline ligands of two different chains. The positions of the nitrogen atoms in the rings are rotated by approximately 180°, and the rings are slightly offset to maximize the attractive interactions associated with the heteroatom polarization of the ring's electron density.[35] It is likely that these aromatic ring interactions are responsible for the unusual trigonal distortion described above.

To accommodate the additional acetonitrile ligand in **3**, we observe a different arrangement of the chains. In Figure 5, two chains (one light gray, one dark gray) of **3** are shown, with the phenanthroline ligands that form the $\pi-\pi$ stacked pairs are displayed as space-filling spheres. Each chain contributes one phen to each stacked pair, and each has additional $\pi-\pi$ interactions (oriented 90° to the ones shown in Figure 5) with chains in front and behind the pictured chains using the other phen ligands. In all cases, as in **4**, the phen molecules are arranged in offset stacks with the nitrogen atoms never stacked directly on top of one another. The question remains as to why the different anions preferentially form the two structures. Inspection of the anion-framework interactions does show some subtle differences. In **3**, there are four H−F contacts shorter than 2.6 Å (two MeCN hydrogens and

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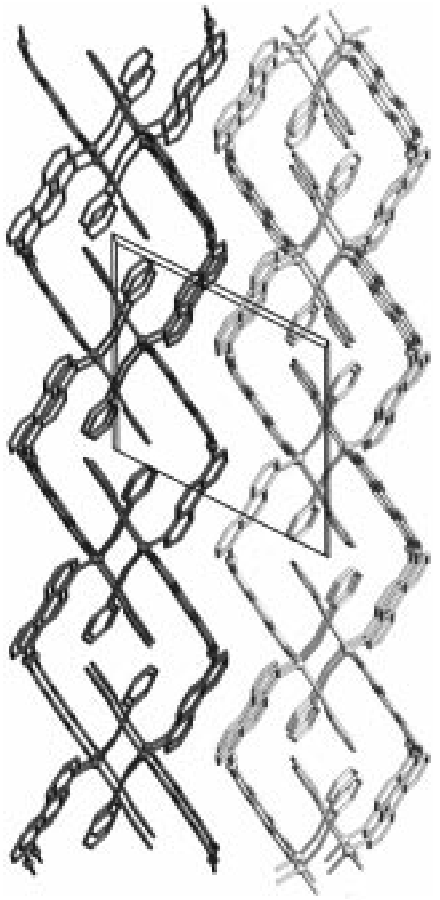

Figure 9. Stick representation and unit cell of **5** viewed down the *a* axis. The hydrogen atoms and anions have been omitted for clarity.

two phenanthroline hydrogens) ranging from 2.42 to 2.60 Å), whereas there are *seven* H−F distances shorter than 2.6 Å ranging from 2.36 to 2.53 Å in **4**. We attribute the greater number and shorter average distances to the better C−H···F accepting ability of the BF$_4^-$ anions compared to PF$_6^-$[36] and believe that the covalent polymeric networks changes to accommodate the different interactions, but other more subtle noncovalent interactions cannot be ruled out.

BzCN−Solvent System. By using benzonitrile as the solvent, the resulting compounds contain copper(I) cations coordinated to two bridging phen ligands (as in the structures above), but two important structural changes are evident. First, under these conditions the PF$_6^-$ and BF$_4^-$ salts are isostructural. Second, although on average (as the formula indicates) there is one solvent molecule per copper atom (as in **4** above), in **5** the BzCN ligands are coordinated *to every other copper atom* in the chain. The result is a linear polymer containing *both* four-coordinate and two-coordinate Cu(I). The details of these two coordination environments are given in Figure 6 and Table 3. At much longer distances from the two-coordinate Cu(I), there is a very weakly coordinated BF$_4$ anion (Cu−F = 2.85 Å).

There are also some subtle alterations in the bonding along the chains. Figure 7 shows a side-on view of one chain in **5**; comparison with Figure 2 is quite illustrative. The coordination sphere around the tetrahedral copper atom in Figure 7 is much more regular than the corresponding copper in Figure 2, and the phen ligands are "flattened out" to a greater extent in the former, which orients their nitrogen atoms into position to coordinate linearly to the other copper. The geometry of the nitrile ligands is also somewhat different in that the Cu−N−C bonds in the BzCN ligands are bent to a larger extent (171° and 165° in **5** versus 175° and 171° in the MeCN ligands of **3**), to maximize parallel alignment with neighboring phen rings as described below.

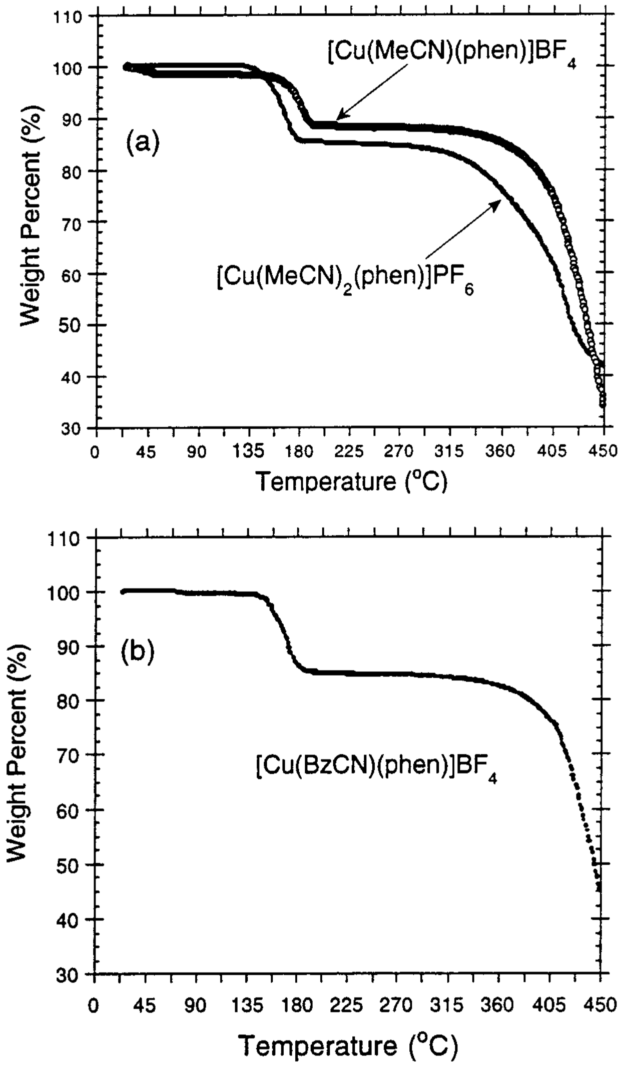

Figure 10. Thermogravimetric analysis data for (a) **3** and **4** and for (b) **5**.

The cyano-substituent on the aromatic ring of the BzCN ligands withdraws electron density from the ring, making it well-suited for strong π−π stacking with the relatively electron-rich phenanthroline rings. There are two types of interchain interactions that manifest themselves in the three-dimensional packing of the chains. As shown in Figure 8 looking down the *a* axis, two chains form a zigzag dimer interacting through the BzCN−phen π−π stacks having aromatic plane-to-plane separations of ~3.5 Å, again showing the rotated and offset rings to increase the heteroatom polarization effects for both of these interchain interactions. The cyanide functional groups on the BzCN are stacked over the phen ligands on the opposite side of the nitrogen atoms of the phenanthroline. We attribute this structure's anion insensitivity to the increased π−π interactions provided by the *aromatic, electron-poor,* coordinated solvent.

The three-dimensional packing of these chains is also quite intricate. The interchain π−π interactions shown in Figure 8 result in the formation of dimers of chains. Two such twisted dimer chains are shown in Figure 9 (one shaded light gray, the other dark gray) and run across the width of the Figure. The "interior" of these dimers is dominated by the BzCN-phen interactions described above, but the dimer−dimer contacts (running in a zigzag fashion through the middle of the unit cell) are exclusively π−π interactions between *phenanthroline* ligands. This gives the structure a "layered" aspect, and we are presently exploring the possible intercalation chemistry of these materials.

Thermal Behavior. Compounds **3**, **4**, and **5** were heated to 450 °C in N$_2$, and the weight changes as a function of temperature are shown in Figure 10. For **3** and **4**, two distinct weight losses are observed for both compounds (Figure 10a). The terminal, coordinated acetonitrile molecules are removed in the first step accounting for an 17.3% (theoretical: 16.0%) and 11.0% (12.0%) for **3** and **4**, respectively. The

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onset of weight loss for **3** preceded that for **4** by about 25 °C. Additional weight loss continued above 300 °C corresponding to the loss of phenanthroline and likely partial oxidation of the Cu(I) salts; black residues were recovered from each analysis.

Qualitatively similar results were obtained for **5** as shown in Figure 10b. In this case however, the initial weight loss (16.0%) does not correspond to complete removal of all BzCN ligands between 130 and 170 °C (theoretical: 23.8%). The rest of the BzCN ligands along with the phenanthroline molecules are lost in the high-temperature decomposition step beginning at ca. 330 °C, which is significantly higher than the framework decomposition temperatures of either **3** or **4** (ca. 300 °C). Again, a black residue remained after cooling.

In conclusion, we have prepared and structurally characterized three novel linear polymeric structures containing Cu(I) and 4,7-phenanthroline. There is an interesting trend as we progress from the single-ring pyrimidine ligand to 3,3′-bipyridine and finally the three-fused-ring phenanthroline. In the $[\mathrm{Cu(pyrimidine)_2}]^+$ framework there are essentially no close contacts between the organic groups. The Cu-coordination geometry in $[\mathrm{Cu(3,3'\text{-}bipyridine)_2}]^+$ is also quite normal, but the twisted bipyridine ligands on the different networks show some $\pi-\pi$ interactions. The compounds containing phenanthroline described here are *dominated* by the ligand-ligand, $\pi-\pi$ stacking interactions with the metal coordination geometry seemingly just "along for the ride"; distorted tetrahedral, Y-shaped trigonal, and linear Cu(I) are observed, and in **5**, two distinct coordination geometries are observed in the same structure! As pointed out recently by Parma and Rogers, coordination polymers incorporating a metal center having two different coordination environments represents a new avenue toward the design of novel materials, though control over the manifestation of dual coordination environments is still nontrivial.[37] These novel structures and structural trends clearly testify that when designing coordination polymers, ligand−ligand interactions must be considered, in some cases preferentially to the metal−ligand bonding requirements.

Moreover, by coordinating some *terminal* nitrile ligands simultaneously with the network-forming 4,7-phenanthroline ligands, we have lowered the dimensionality of the coordination networks compared to the three-dimensional structures formed solely from pyrimidine and 3,3′-bipyridine. Just as there are tectosilicate (3D framework silicates) analogues to those structures, Nature has many examples of one-dimensional chain silicates. The *inosilicates* are chain structures formed from SiO_4 tetrahedra that share *only two oxygen atoms* with other SiO_4 tetrahedra (i.e. amphibole). Analogy with Nature seems to be quite general. Very recently we have prepared a material *intermediate* between these two cases (three bridging ligands and one terminal ligand), which results in a two-dimensional, sheet structure analogous to a natural clay. These results will be reported elsewhere.[38]

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Supporting Information Available: Numbered ORTEP plots of all atoms and tables of crystallographic data, in CIF format, for **3**, **4**, and **5** and for the isostructural PF_6 analogue of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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