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Novel 2-fold Interpenetrating Diamondoid Coordination Polymers: [Cu(3,3′-bipyridine)$_2$]X (X= BF_4^-, PF_6^-)

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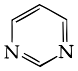
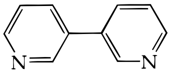
Introduction

Supramolecular chemistry derives much of its strength and versatility from the synergy between covalent and noncovalent interactions that can be used to orient molecular species in one, two, or three dimensions. Initial work of Cram,[1] Lehn,[2] and Pedersen[3] focused on Lewis acid−base interactions between cations and nucleophiles to create "host−guest" complexes that showed molecular recognition capabilities. Interlocking molecules, such as rotaxanes and catenanes developed by Sauvage[4] and Stoddart,[5] exploited noncovalent forces such as hydrogen-bonding and $\pi-\pi$ stacking interactions to self-assemble elegantly "beaded" or "knotted" supermolecules.[6]

There has been significant interest recently in "extending" supramolecular chemistry into the solid state, and the rational design of new extended solids with tailored structures and properties is a rapidly growing field.[7,8] One of the most common structural motifs found in "engineered" crystals is that of diamond; the tetrahedral geometry (and accompanying lack of inversion center) lends itself naturally to the formation of polar structures necessary for the generation of nonlinear optical properties.[9] As opposed to the pure carbon allotrope, diamondoid networks composed of large, multifunctional molecular species have shown a tremendous variety of interpenetration motifs, which occur to pack void space in the most efficient manner. Since the initial work by Ermer on adamantane-1,3,5,7-tetracarboxylic acid showing 5-fold interpenetration,[10] 2-fold,[11] 3-fold,[12] and 4-fold[13] hydrogen-bonded diamondoid networks have been reported, as well as one example of a system that does not interpenetrate but instead includes guest molecules.[14]

Topologically related coordination polymers where tetrahedral metal cations are linked together with spacer ligands also display the tendency to form diamondoid networks with degrees of interpenetration including 2-fold,[15] 4-fold,[16] 5-fold,[17] 7-fold,[18] and *even 9-fold*[19] degeneracy; such systems can be regarded as infinite "polycatenanes".[20] We are continuing our quest to prepare materials that are structurally related to silicate minerals such as quartz and zeolites so as to design molecular analogs of these interesting (and useful) materials. Our first success in this area was a copper(I)−pyrimidine coordination polymer related to the feldspar structure,[21] a material whose structure is quite different from that of coordination polymers prepared using the chemically similar, but geometrically linear, pyrazine ligand.[22,23] We report here the synthesis and crystal structure of a two-fold interpenetrating network where Cu(I) cations are linked by 3,3′-bipyridine. We used this "expanded" ligand (see below) to further separate the metal centers in the hopes of creating larger internal cavities but instead crystallized a completely different structure. All of the previously cited catenated frameworks were constructed from tetrahedral metal cations and either *linear* or *tetrahedral* links. The present structure represents the first report of an extended coordination polymer incorporating 3,3′-bipyridine and shows the propensity of systems to adopt diamond-like structures, even those containing dramatically angular bridging ligands.





Experimental Section

All reagents and anhydrous dioxane were obtained from Aldrich and used without further purification unless otherwise specified. THF was freshly distilled over sodium benzophenone ketyl prior to use. All air- or moisture-sensitive reactions were carried out in oven- or flame-dried glassware under nitrogen, and elemental analyses were performed by Atlantic Microlabs.

Synthesis of 3- (Trimethylstannio)pyridine. To a 100 mL round bottom-flask equipped with a magnetic stir bar was added 1.00 g of 3-bromopyridine (6.3 mmol), which was dissolved in 30 mL of THF to give a 0.2 M solution. The mixture was cooled to −78 °C in a dry ice/2-propanol bath. After 20 min of stirring, *n*-butyllithium (2.8 mL, 6.8 mmol, 2.4 M in hexanes) was added via a syringe over 20 min; the solution turned yellow-orange and then dark brown during the addition.

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After 20 min, Me_3SnCl (1.38 g, 6.9 mmol) was added dropwise as a solution in 5 mL of THF, and the mixture was allowed to stir for 1 h at −78 °C and then 30 min at 20 °C. The reaction was quenched with 10 mL of brine, and the mixture was extracted with 3 × 25 mL of diethyl ether. The combined organic layers were washed with water twice and then with brine and dried over Na_2SO_4. Rotary evaporation yielded the brown crude derivative, which was eluted to purity by flash chromatography on SiO_2 using 25% EtOAc in hexanes. Yield: 0.87 g, 44%.

Synthesis of 3,3′-Bipyridine. In a 10 mL recovery flask equipped with a magnetic stir bar and a reflux condenser, 0.37g of 3-(trimethylstannio)pyridine (1.1 mmol) was placed and dissolved in 5 mL of dry dioxane to give a 0.2 M solution. To this solution was added via syringe 0.18 g of 3-bromopyridine, followed by addition of 77 mg (10 mol%) of $(PPh_3)_2PdCl_2$, and the mixture was refluxed for 24 h. Reaction completion was monitored by TLC, and the mixture was worked up as above. The crude product was flashed on SiO_2 with 100% EtOAc to give 0.138 g of the pure bipyridine (77%).

$[Cu(C_{10}H_5N_2)_2]BF_4$ (1). To a small test tube were added 0.198 g of 3,3′-bipy and 0.020 g of $Cu(MeCN)_4BF_4$ dissolved in 0.5 mL of MeCN and 3 mL of nitrobenzene. THF was diffused in slowly to initiate crystal growth. Yellow-green triangular crystals suitable for single-crystal X-ray diffraction were harvested after several days.

$[Cu(C_{10}H_5N_2)_2]PF_6$ (2). To a small test tube were added 0.167 g of 3,3′-bipy and 0.026 g of $Cu(MeCN)_4PF_6$ dissolved in 0.5 mL of MeCN and 3 mL of nitrobenzene. THF was diffused in slowly to initiate crystal growth. Yellow-green triangular crystals suitable for single-crystal X-ray diffraction were harvested after several days. Anal. Calcd (found) for $CuC_{20}H_{10}N_4PF_6$: C, 46.11 (46.20); H, 3.07 (3.05); N, 10.76 (10.81).

X-ray Crystallography. A single crystal (0.4 × 0.3 × 0.3 mm) of $[Cu(3,3'\text{-bipyridine})_2]BF_4$, **1**, was mounted with epoxy in a glass capillary. Diffraction data were collected at room temperature using a Siemens SMART system equipped with a CCD area detector. A total of 4579 reflections were collected ($2.75 \leq \Theta \leq 27.14°$) corresponding to Miller indices of $-13 \leq h \leq 7$, $-13 \leq k \leq 12$, $-11 \leq l \leq 12$. Integration of the data yielded 1131 independent reflections ($R_{int} = 0.0281$). A slightly smaller crystal (0.25 × 0.30 × 0.30 mm) of $[Cu(3,3'\text{-bipyridine})_2]PF_6$, **2**, was similarly mounted. A total of 4623 reflections were collected ($2.76 \leq \Theta \leq 27.13°$) corresponding to Miller indices of $-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-7 \leq l \leq 12$. Integration of the data yielded 1202 independent reflections ($R_{int} = 0.0254$). Both structures were solved using the SHELXS direct methods routine[24] and refined using a full-matrix least-squares treatment on F^2.[25] Anisotropic thermal parameters were assigned to all non-hydrogen atoms.

Results and Discussion

The two materials crystallize in the same acentric tetragonal space group; the PF_6^- analog being slightly closer to cubic symmetry. Crystallographic details for both compounds are listed in Table 1. The asymmetric unit contains one copper atom and only half of one bipyridine ligand, as it straddles a 2-fold rotation axis, and therefore only one unique Cu−N bond length is present in each structure. Table 2 compares the important bond distances and bond angles found in the two structures and shows that the differently sized anions cause only minor distortions in the copper coordination geometry (ca. 0.01 Å and 2°). A view of the tetrahedral coordination around the copper atoms, shown in Figure 1, reveals that the bipyridine rings twist out of plane relative to each other by about 30°. In addition, the Cu−N bond is bent out of the plane of the aromatic ring by 19°, leading to a closing of the Cu−L−Cu angle to 134°.[26]

Table 1. Crystal Data and Structure Refinement Parameters

	1	2
empirical formula	$CuC_{20}H_{16}N_4BF_4$	$CuC_{20}H_{16}N_4PF_6$
fw	462.72	520.63
temp, K	293(2)	293(2)
wavelength, Å	0.710 70	0.710 70
crystal system	tetragonal	tetragonal
space group	$P\bar{4}n2$	$P\bar{4}n2$
unit cell dimensions		
a, Å	10.4560(6)	10. 4187(6)
b, Å	9.3682(8)	10.0232(7)
V, Å^3	1024.2(1)	1088.0(1)
Z	2	2
density (calcd), g cm^{-3}	1.500	1.590
abs coeff, mm^{-1}	1.115	2.205
F(000)	468	588
goodness-of-fit on F^2	1.078	1.238
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0425$ $wR_2 = 0.1160$	$R_1 = 0.0336$, $wR_2 = 0.0807$
R indices (all data)	$R_1 = 0.0532$ $wR_2 = 0.1232$	$R_1 = 0.0389$, $wR_2 = 0.0849$
absolute structure param	0.19(4)	0.07(3)
largest diff peak and hole, e•Å^{-3}	0.330; −0.461	0.132; −0.261

Table 2. Selected Bond Length (Å) and Angle (deg) Comparison between **1** and **2**[a]

1		2	
Cu(1)−N(4)	2.041(3)	Cu(1)−N(1)	2.053(2)
B(1)−F(1)	1.306(6)	P(1)−F(1)	1.537(4)
		P(1)−F(2)	1.681(4)
		P(1)−F(3)	1.487(9)
N(4)#1−Cu(1)−N(4)	114.32(10)	N(1)#1−Cu(1)−N(1)#2	115.53(8)
N(4)#1−Cu(1)−N(4)#2	114.32(10)	N(1)#1−Cu(1)−N(1)	97.94(14)
N(4)−Cu(1)−N(4)#2	100.2(2)	N(1)#2−Cu(1)−N(1)	115.53(8)
N(4)#1−Cu(1)−N(4)#3	100.2(2)	N(1)#1−Cu(1)−N(1)#3	115.53(8)
N(4)−Cu(1)−N(4)#3	114.32(10)	N(1)#2−Cu(1)−N(1)#3	97.94(14)
N(4)#2−Cu(1)−N(4)#3	114.32(10)	N(1)−Cu(1)−N(1)#3	115.53(8)

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x, -y, z$; (#2) $-y, x, -z$; (#3) $y, -x, -z$; (#4) $-y - 1/2, -x - 1/2, -z - 1/2$; (#5) $y - 1/2, x + 1/2, -z - 1/2$ (#6) $-x - 1, -y, z$.

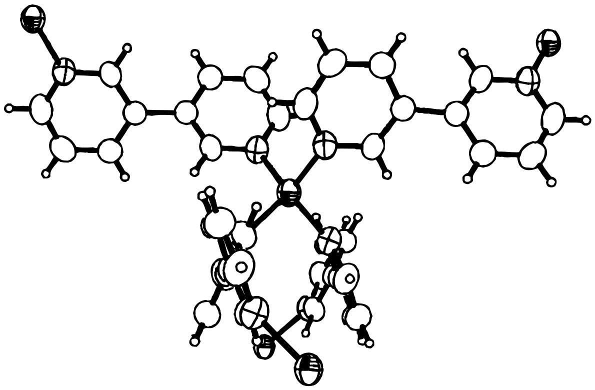

Figure 1. ORTEP representation of the coordination environment around the copper cations showing 50% thermal ellipsoids. Copper atoms are shown as ellipses with shaded segments, nitrogen atoms as ellipses with axes only, carbon atoms as open ellipses, and hydrogen atoms as open circles of arbitrary size.

Bridged by this large ligand, the resulting framework contains copper atoms separated by 8.9 Å and significant void volume. The extra space is occupied *by an identical network* (displaced by 1/2, 1/2, 1/2) forming a 2-fold interpenetrated structure. A representation of two interlocking psuedo-adamantane units is shown in Figure 2. The situation is very similar to that formed from the combination of Cu(I) with the *linear* 4,4′-bypyridine ligand.[16] The metal coordination is identical, but the increased distance between metal centers in the 4,4′-structure (11.2 Å) allows the formation of a 4-fold interpenetrated network.

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(26) The center of the C−C bond connecting the two rings is the point at which the angle between the metal atoms is measured.

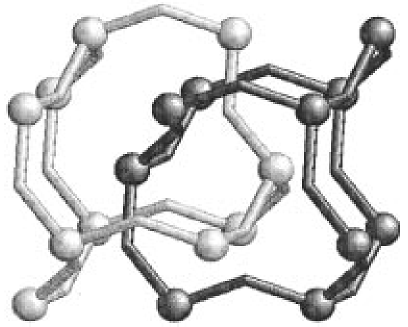

Figure 2. Schematic illustration representing the interlocking of two separate (light and dark shadings) networks. The spheres represent the copper atoms, and the twisted bipyridine ligands are shown as the bent cylinders linking the copper centers together.

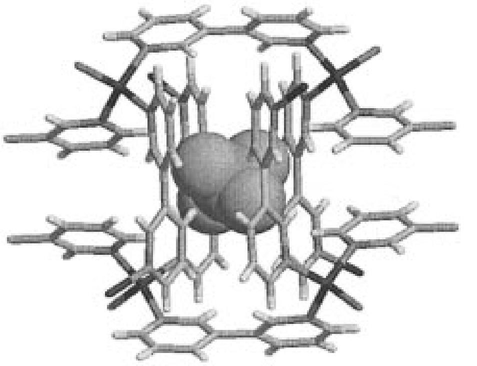

Figure 3. Illustration of the cage structure. The anions in the structure are housed in the void spaces between the bipyridine ligands. In this case, the van der Waals surface of the BF_4^- anion is shown within a stick illustration of the framework. In **2,** the PF_6^- anion is located on the same crystallographic position.

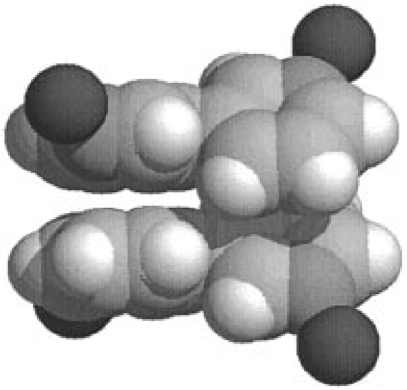

Figure 4. Space-filling diagram (generated by RasMol[30]) showing the close contacts between the bipyridine rings on different networks. Copper atoms are the darkest shaded spheres.

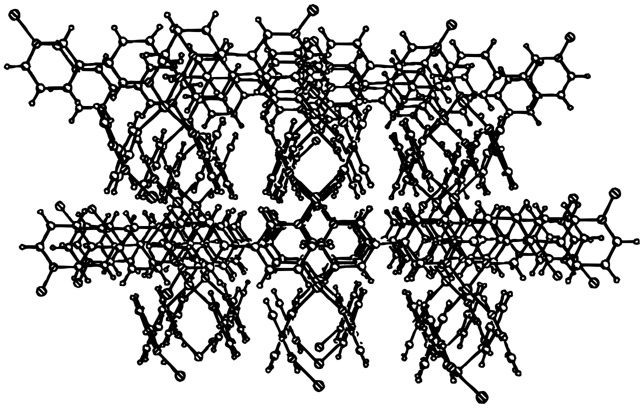

Figure 5. Packing view of the structure down the (110) direction with the anions omitted for clarity. The layers of bipyridine ligands are oriented 90° from their neighboring layers.

The catenation in the present structures precludes the clathration of any solvent molecules, leaving room only for the noncoordinated anions, which reside in "cages" formed from six different bipyridine ligands (three from each network), as shown in Figure 3. The anions in both structures lie on crystallographic 4-fold positions, and therefore only one independent fluorine and three independent fluorine atoms are required for the BF_4 and PF_6 salts, respectively.[27] Although there are no covalent bonds between the two networks, the plane-to-plane distance of 3.6 Å indicates $\pi-\pi$ stacking interactions are present between bipyridine rings on different networks (Figure 4).[28]

A view of the three-dimensional packing of the structure in Figure 5 shows that the framework consists of alternating layers of copper and bipyridine and that all the organic species of one layer are oriented at ~90° with respect to the neighboring layers. In keeping with our geomimetic theme stated in the Introduction, we can relate the present structure to the mineral cuprite (Cu_2O), which also consists of two interpenetrating tetrahedral-based lattices.[29] However, in the oxide, the *copper cations* are two-coordinate (linear) while the *oxide ligands* are tetrahedrally coordinated by Cu(I), an exact reversal from the roles observed in the $[Cu(3,3'\text{-bipyridine})_2]_\infty$ coordination networks.

The Cu−ligand−Cu angle of 134° is close to that found between SiO_4 tetrahedra in quartz (147°, which does not interpenetrate). We hope that the use of larger anions (BPh_4^-) or a bulky substituent on one of the bipyridine rings will prevent interpenetration and create large, acentric voids in the structure which can be used to include (and possibly manipulate) a variety of chiral organic molecules.

Acknowledgment. The authors wish to thank Ms. Amy Rheinnecker for help with the synthesis of 3,3′-bipyridine. S.W.K. expresses grateful appreciation to the University of Missouri Research Board for generous funding of this project.

Note Added in Proof. At the galley stage, we became aware of additional examples of bent ligands linking tetrahedral Ag(I) centers: Hirsch, K. A.; Wilson, S. R.; Moore, J. S. *Inorg. Chem.* **1997**, *36*, 2960.

Supporting Information Available: Listings of atomic coordinates, complete bond lengths and bond angles, anisotropic thermal parameters, and hydrogen atom coordinates with their isotropic displacement parameters for **1** and **2** (10 pages). Ordering information is given on any current masthead page.

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(27) There was significant disorder of the fluorine atoms about the phosphorus center in the PF_6 analog, as indicated by relatively large residual electron density peaks, even after inclusion of anisotropic thermal parameters. The disorder was modeled by refining the occupancy of *three* independent fluorine atoms and setting the values to the nearest 0.1 (0.6, 0.3, and 0.6 for F1, F2, and F3, respectively) in order to sum to the correct stoichiometry.

(28) Hirsch et al. define a range of 3.4−3.6 Å, as surmised from a survey of the Cambridge Structural Database, to indicate $\pi-\pi$ stacking interactions in a series of related materials: Hirsch, K. A.; Wilson, S. R.; Moore, J. S. *Chem. Eur. J.* **1997**, *3*, 765.

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