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New 1- and 2-Dimensional Polymeric Structures of Cyanopyridine Complexes of Ag^I and Cu^I

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Polymeric transition metal chalcogenides have attracted much attention because of their possible unusual properties directly derived from their extended structures. The molecules *n*-cyanopyridine ($n = 2$, 3, and 4) and pyridine-3,4-dicarbonitrile are found to function as bidentate or monodentate (only pyridine nitrogen donor atom) ligands in the coordination of silver(I) and copper(I) ions, respectively. The mode of coordination depends on the anion and the crystallization conditions and has been elucidated in all cases by single-crystal X-ray crystallography. We report here the syntheses, structural characterization, and electrical properties of six new polymers, $[Ag_2(\text{2-cyanopyridine})_2(NO_3)_2]_n$ **(1)**, $[Ag_4(\text{3-cyanopyridine})_8(SiF_6)_2(H_2O)_2]_n$ **(2)**, $[Ag(\text{3-cyanopyridine})_2(NO_3)]_n$ **(3)**, $[Ag(\text{pyridine-3,4-dicarbonitrile})_2(NO_3)]_n$ **(4)**, $[Cu^I(\text{4-cyanopyridine})_2(SCN)]_n$ **(5),** and $[Cu^I(\text{pyridine-3,4-dicarbonitrile})_2(SCN)]_n$ **(6)**. Compounds **1** and **2** exhibit novel two-dimensional networks, while **3**–**6** have one-dimensional chain structures, in which **3** is a single-stranded helix. Room-temperature conductivities of **1**, **2**, **4**, and **6** have been measured and are 3.1×10^{-7}, 2.7×10^{-7}, 7.4×10^{-6}, and 4.3×10^{-5} S·cm^{-1}, respectively. The effect of temperature on the conductivities has been investigated.

Introduction

The design of coordination polymers is an area of intense current interest. In particular, as many functional materials in the fields of catalysis, separation, absorption, molecular recognition, optics, and electromagnetism manifest themselves as two- or three-dimensional networks, it is important to be able to generate various high-dimensionality systems with both novel structural topologies and functional properties.[1−3] Research on conducting and semiconducting solids in chemistry and physics has produced unconventional semiconductors which exhibit properties similar to artificial systems of conventional semiconductors.[4] Recently, the perovskite $[C_6H_5C_2H_4NH_3{}^+]_2[SnI_4]$ was reported to have promising semiconductor properties for thin-film field effect transistor applications.[5] Another class of metal-halide-rich amines, with stoichiometries such as $Ag_2I_4(C_8H_{22}N_2)$, $Ag_6I_8(C_8H_{22}N_2)$ ($C_8H_{22}N_2$ = hexamethylethylenediamine), and $Ag_{44}I_{53}(C_{11}H_{30}N_3)_3$ [$(C_{11}H_{30}N_3)_3$ = *N*,*N*,*N*,*N*′,*N*″,*N*″,*N*″-heptamethyl-*N*′-hydrodiethylenetriamine], are known to form

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rapid ion conductors.[6] The structures of the coordination polymers of interest are derived from metal-bridging ligand building blocks which contain nitrogen donors in simple geometric dispositions. The most extensively studied bridging ligand of this type is 4,4′-bipyridine (4,4′-bpy). A degree of structural control may be introduced by manipulation of the disposition of 4-pyridyl groups of the parent 4,4′-bipyridine ligand through introduction of various tether groups. Based on these organoamine and related ligands, various types of polymeric complexes have been prepared, including one-, two-, and three-dimensional motifs exhibiting diamondoid, grid, ladder, brick, railroad, and octahedral building blocks.

Previous work has produced polymeric compounds containing the derivatives of aromatic carbonitrile,[7] with n-cyanopyridines ($n = 2, 3, 4$) acting as a bridge to link metal centers of the coordination polymers.[8] These anisobidentate ligands contain two nitrogen donors (with the donor ends differing in steric requirements and basic character), the cyano nitrogen atom (N_{cn}) being perhaps a somewhat weaker donor atom than the pyridine nitrogen atom (N_{py}). Consequently, some organic solvent molecules and counterions can bind to the metal more easily than N_{cn}, resulting in complexes in which the n-cyanopyridine ligands act only as monodentate ligands and the cyano groups are not involved in metal coordination. Thus, within a related series of complexes, all grown under similar conditions, comparison of the structures can lead to a greater understanding of the individual contributions of ligand and anion in stabilizing the observed structure.

Here we report the new structure types of polymers formed by Ag^I or Cu^I with n-cyanopyridine ($n = 2$, 3, and 4) and pyridine-3,4-dicarbonitrile (compounds **1**−**6**). The complexes **1** and **2** show novel two-dimensional networks. Conductivity studies show that the complexes **1**, **2**, **4**, and **6** have semiconductor character.

Experimental Section

General. The preparations of complexes **1**−**4** were carried out in air at room temperature. Although the preparation of compounds **5** and **6** was carried under an atmosphere of nitrogen, crystals of **6** were obtained from the evaporation of the reaction solution in the air over several days. Chemicals were used as purchased. Elemental analyses were performed by the University of Newcastle upon Tyne microanalytical service. Infrared spectra (KBr pellets) were recorded on a Perkin-Elmer 598 spectrometer. UV/vis spectra were obtained on a U-3310 spectrophotometer from methanol solutions ($\lambda = 700-200$ nm). Electrical conductivity measurements were made with pressed pellets (two probes) on a ZL5-LCR conductometer at the Fujian Institute, China.

Syntheses. Synthesis of $[Ag_2(2\text{-cyanopyridine})_2(NO_3)_2]_n$ (1). To a solution of $AgNO_3$ (0.169 g, 1.0 mmol) in 10 mL distilled water was added $(NH_4)_2SiF_6$ (0.178 g, 1.0 mmol). The mixture was stirred for 0.5 h, and then a solution of 2-cyanopyridine (0.104 g, 1.0 mmol) in 15 mL ethanol was added and the mixture stirred for 5 min. A small amount of precipitate was removed by filtration. After allowing the filtrate to stand in air for one week, air-stable colorless needlelike crystals of **1** were obtained (68% yield). Anal. Calcd (found): C, 26.29 (26.30); H, 1.46 (1.36); N, 15.33 (15.29)%. IR (cm^{-1}): 2395.17(m), 2235.10(m), 1762.62(s), 1579.42(s), 1085.73(m), 1049.09(m), 991.23(m), 825.38(s), 782.96(s), 630.61(m), 549.61(s).

Synthesis of $[Ag_4(3\text{-cyanopyridine})_8(SiF_6)_2(H_2O)_2]_n$ (2). Complex **2** was synthesized by a method similar to that of complex 1 except that 2 molar equiv of 3-cyanopyridine (0.208 g, 2.0 mmol) was used instead of 1 molar equiv of 2-cyanopyridine. Air-stable colorless platelike crystals of **2** were deposited within one week (65% yield). Anal. Calcd (found): C, 36.37 (37.17); H, 2.27 (2.17); N, 14.14 (14.54)%. IR (cm^{-1}): 2426.02(m), 2395.17(m), 2231.25(m), 1762.62(s), 1024.02(m), 875.52(m), 825.38(s), 700.03(m), 632.54(m).

Synthesis of $[Ag(3\text{-cyanopyridine})_2(NO_3)]_n$ (3). Complex **3** was synthesized by a method similar to that of complex **2**, but $(NH_4)_2SiF_6$ was not introduced into the reaction system. Colorless needlelike crystals of **3** were deposited within one week (64% yield). Anal. Calcd (found): C, 38.12 (37.89); H, 2.13 (2.02); N, 18.52 (18.74)%. IR (cm^{-1}): 2395.17(m), 2231.25(s), 1762.62(m), 1589.06(s), 1024.02(m), 971.95(w), 809.96(s), 700.03(s), 632.54(m), 553.47(s).

Synthesis of $[Ag(\text{pyridine-3,4-dicarbonitrile})_2(NO_3)]_n$ (4). Complex **4** was synthesized by a method similar to that of complex **2**, except that pyridine-3,4-dicarbonitrile (0.258 g, 2.0 mmol) was used instead of 3-cyanopyridine. Air-stable colorless blocklike crystals of **4** were deposited within 3 days (70% yield). Anal. Calcd (found): C, 39.28 (39.20); H, 1.41 (1.35); N, 22.90 (22.87)%. IR (cm^{-1}): 2426.02(m), 2238.96(s) 1994.04(m), 1762.62(m), 1577.49(s), 1481.07(m), 1214.94(m), 1043.30(m), 865.88(s), 817.67(m), 742.46(m), 526.47(s).

It is worth noting that complex **4** was the only isolable product even when the molar ratio of Ag^I and pyridine-3,4-dicarbonitrile was changed to 1:1, suggesting that the reaction is insensitive to the stoichiometry.

Synthesis of $[Cu^I(4\text{-cyanopyridine})_2(SCN)]_n$ (5). Under an atmosphere of nitrogen, to a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.242 g, 1.0 mmol) in 30 mL methanol was added $(NH_4)SCN$ (0.456 g, 6.0 mmol). After stirring for 10 min, 4-cyanopyridine (0.312 g, 3.0 mmol) was added and the mixture stirred for 6 h at 55 °C and then cooled to room temperature. A small amount of precipitate was removed by filtration. After the filtrate was allowed to stand under nitrogen atmosphere at room temperature for 3 days, 0.2 g of yellow needlelike crystals was isolated (60% yield, based on Cu). Anal. Calcd (found): C, 47.34 (47.75); H, 2.44 (2.62); N, 21.23 (21.58)%. IR (cm^{-1}): 2237.09(m), 2125.18(vs), 1600.63(m), 1540.85(m), 1494.57(m), 1413.57(s), 1211.08(m), 831.17(s), 744.39(m) 559.25(s). UV (methanol solution, λ, nm (ϵ, $dm^3\ mol^{-1}\ cm^{-1}$)): 271 (6.39×10^3); 390 (4.6×10^2).

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Table 1. Crystal Data and Structure Refinement Parameters for Compounds **1**−**6**

	1	**2**	**3**	**4**	**5**	**6**
formula	$C_{12}H_8Ag_2N_6O_6$	$[C_{48}H_{32}Ag_4N_{16}]^{4+}\cdot 2SiF_6^-\cdot 2H_2O$	$C_{12}H_8AgN_5O_3$	$C_{14}H_6AgN_7O_3$	$C_{13}H_8CuN_5S$	$C_{15}H_6CuN_7S$
fw	548.0	1584.6	378.1	428.1	329.8	379.9
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/n$	$P2_1/c$	$C2$	Cm	$Pnma$	$Pmn2_1$
T (K)	160	160	293	160	150	120
a (Å)	7.3378(4)	14.1509(7)	27.356(6)	7.3277(6)	11.2816(7)	22.993(2)
b (Å)	7.2624(4)	13.6874(7)	6.5352(15)	25.005(2)	19.3224(11)	6.0940(5)
c (Å)	14.9373(8)	14.6407(7)	3.7201(9)	5.3681(4)	6.1554(4)	5.3827(6)
β (deg)	98.089(1)	107.640(1)	92.481(4)	128.929(1)		
V (Å^3)	788.09(7)	2702.4(2)	664.4(3)	765.15(10)	1341.80(14)	754.22(12)
Z	2	2	2	2	4	2
reflns measd	6817	23924	1047	3443	11010	3728
unique data, R_{int}	1922, 0.0234	6637, 0.0560	915, 0.0299	1800, 0.0215	1705, 0.0258	1418, 0.1564
params	119	386	97	121	97	117
R (F, $F^2 > 2\sigma$)	0.0197	0.0401	0.0590	0.0185	0.0228	0.0438
R_w (F^2, all data)	0.0475	0.0823	0.1624	0.0427	0.0622	0.0998
absolute structure param			0.07(10)	0.02(2)		0.05(2)
GOF on F^2	1.081	1.091	1.098	1.062	1.075	1.058
max, min electron density (e/Å^3)	0.41, −0.52	0.62, −0.74	1.16, −1.30	0.54, −0.27	0.33, −0.31	0.49, −0.60

Although complex **5** is reasonably stable in the solid state, oxidation to Cu^{II} occurs in methanolic solution under an atmosphere of air. Slow evaporation of the methanol for several days in air yielded green crystals of the mononuclear complex $Cu^{(II)}$(4-cyanopyridine)$_4$(NCS)$_2$.

Synthesis of [Cu^I(pyridine-3,4-dicarbonitrile)$_2$(SCN)]$_n$ (6). Under an atmosphere of nitrogen, to a solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.242 g, 1.0 mmol) in a mixture of methanol and THF (1:1, 40 mL) was added $(NH_4)SCN$ (0.228 g, 3.0 mmol), and the mixture was stirred for 10 min; then pyridine-3,4-dicarbonitrile (0.387 g, 3.0 mmol) was added and the mixture stirred for 6 h at 55 °C and cooled to room temperature. After the filtrate was allowed to stand in air at room temperature for 3 days, 0.27 g of orange needlelike crystals of **6** was isolated (71% yield, based on Cu). Anal. Calcd (found): C, 47.43 (47.27); H, 1.59 (1.48); N, 25.81 (25.64)%. IR (cm^{-1}): 2244.74(m), 2100.11(vs), 1589.06(m), 1546.64(m), 1483.00(m), 1402.00(s), 1220.72(m), 1054.87(m), 863.95(s),767.53(m), 522.61(s). UV (methanol solution, λ, nm (ϵ, dm^3 mol^{-1} cm^{-1})): 282 (6.58×10^3); 389 (6.0×10^2).

Compound **6** is more stable to oxidation in the air than **5**. Even leaving a solution of **6** in methanol in air at room temperature over three weeks did not result in any perceptible oxidation to Cu^{II}.

X-ray Crystallography. All data for compounds **1**−**6** were collected on Bruker SMART CCD area diffractometers, using Mo Kα radiation ($\lambda = 0.71073$ Å) for **1**−**5** and synchrotron radiation ($\lambda = 0.6934$ Å) for **6**, by the ω-scan method, at temperatures of 160 K (**1**, **2**, **4**), 293 K (**3**), 150 K (**5**), and 120 K (**6**). Crystal data and other experimental information are given in Table 1, with further details in the Supporting Information. Semiempirical absorption corrections were applied in all cases, based on repeated and symmetry-equivalent reflections.[9] The structures were solved by direct methods and refined by full-matrix least-squares on all unique F^2 values.[10] Anisotropic displacement parameters were assigned to all the non-hydrogen atoms. The hydrogen atoms of water were refined with geometrical restraints and constrained isotropic displacement parameters. Other hydrogen atoms were placed in idealized positions and allowed to ride on their respective parent atoms. The correct assignment of the non-centrosymmetric space groups for **3**, **4**, and **6** is assured by the successful refinement of the absolute structure parameter to essentially zero in each case,[11] and by checking with the PLATON program.[12] Selected bond lengths and angles are reported in Tables 2−4.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Ag_2(2-cyanopyridine)$_2$(NO$_3$)$_2$]$_n$ (**1**) and [Ag_4(3-cyanopyridine)$_8$]$^{4+}\cdot 2SiF_6^-\cdot 2H_2O$ (**2**)

	Compound **1**[a]		
Ag(1)−O(1)	2.4221(18)	Ag(1)−O(3A)	2.4921(18)
Ag(1)−N(1)	2.2878(17)	Ag(1)−N(2B)	2.2710(19)
O(1)−Ag(1)−O(3A)	116.92(6)	O(1)−Ag(1)−N(1)	107.91(7)
O(1)−Ag(1)−N(2B)	105.75(6)	O(3A)−Ag(1)−N(1)	104.13(5)
O(3A)−Ag(1)−N(2B)	97.37(6)	N(1)−Ag(1)−N(2B)	125.22(6)
	Compound **2**[b]		
Ag(1)−Ag(2)	3.3072(5)	Ag(2)−Ag(2A)	3.0242(6)
Ag(1)−N(1)	2.176(3)	Ag(2)−N(5)	2.172(3)
Ag(1)−N(3)	2.192(3)	Ag(2)−N(7)	2.188(3)
Ag(1)···F(4B)	2.658(2)	Ag(2)···F(4B)	2.688(2)
Ag(1)···F(6A)	2.607(2)	Ag(2)···F(6A)	2.701(2)
N(1)−Ag(1)−N(3)	162.40(12)	N(5)−Ag(2)−N(7)	171.09(12)
Ag(1)−Ag(2)−Ag(2A)	160.501(19)		

[a] Symmetry operations for equivalent atoms: A, ($^3/_2 - x$, $-^1/_2 + y$, $^1/_2 - z$) (screw axis); B, ($1 - x$, $-y$, $1 - z$) (inversion center). [b] Symmetry operations for equivalent atoms: A, ($1 - x$, $1 - y$, $1 - z$) (inversion center); B, ($1 - x$, $-^1/_2 + y$, $^3/_2 - z$) (screw axis).

Results and Discussion

Crystal Structure of [Ag_2(μ-2-cyanopyridine)$_2$(NO$_3$)$_2$]$_n$ (1). X-ray crystallography has established that **1** consists of a two-dimensional coordination network comprising nitrate bridges and two-connecting 2-cyanopyridines. Each Ag center is coordinated in a distorted tetrahedral geometry by two oxygen atoms from two different nitrate anions and two nitrogen atoms (one N_{py} and one N_{cn}) from two separate bridging 2-cyanopyridine ligands [Ag−N_{py} 2.2878(17) and Ag−N_{cn} 2.2710(19), Ag−O = 2.4221(18) and 2.4921(18)

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Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Ag(3\text{-cyanopyridine})_2(NO_3)]_n$ (**3**) and $[Ag(\text{pyridine-3,4-dicarbonitrile})_2(NO_3)]_n$ (**4**)

Compound **3**[a]			
Ag(1)−N(1)	2.197(8)	Ag(1)−N(1A)	2.197(8)
Ag(1)−O(2)	2.736(9)	Ag(1)−O(2A)	2.736(9)
N(1)−Ag(1)−N(1A)	157.5(4)	O(2)−Ag(1)−O(2A)	72.6(3)
N(1)−Ag(1)−O(2)	115.3(3)	N(1)−Ag(1)−O(2A)	83.6(3)
N(1A)−Ag(1)−O(2A)	115.3(3)	N(1A)−Ag(1)−O(2)	83.6(3)
Compound **4**[b]			
Ag(1)−N(1)	2.2827(19)	Ag(1)−N(1A)	2.2827(19)
Ag(1)−O(1)	2.427(2)	Ag(1)−O(3B)	2.445(3)
N(1)−Ag(1)−N(1A)	117.32(9)	N(1)−Ag(1)−O(1)	111.88(5)
N(1A)−Ag(1)−O(1)	111.88(5)	N(1)−Ag(1)−O(3B)	109.24(6)
O(1)−Ag(1)−O(3B)	94.93(9)	N(1A)−Ag(1)−O(3B)	109.24(6)

[a] Symmetry operation for equivalent atoms: A, $(1-x, y, 1-z)$ (2-fold axis). [b] Symmetry operations for equivalent atoms: A, $(x, -y, z)$ (mirror plane); B, $(1+x, y, 1+z)$ (lattice translation).

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[Cu^I(4\text{-cyanopyridine})_2(SCN)]_n$ (**5**) and $[Cu^I(\text{pyridine-3,4-dicarbonitrile})_2(SCN)]_n$ (**6**)

Compound **5**[a]			
Cu(1)−N(1)	2.1038(13)	Cu(1)−N(1A)	2.1038(13)
Cu(1)−S(1)	2.2751(6)	Cu(1)−N(3B)	1.9900(18)
N(1)−Cu(1)−N(1A)	102.20(7)	N(1)−Cu(1)−S(1)	112.54(3)
N(1A)−Cu(1)−N(3B)	102.83(5)	N(1A)−Cu(1)−S(1)	112.54(3)
N(1)−Cu(1)−N(3B)	102.83(5)	S(1)−Cu(1)−N(3B)	121.67(6)
Cu(1C)−N(3)−C(7)	173.52(18)	N(3)−C(7)−S(1)	176.09(19)
Compound **6**[b]			
Cu(1)−S(1)	2.3129(14)	Cu(1)−N(1A)	1.937(5)
Cu(1)−N(2)	2.078(3)	Cu(1)−N(2B)	2.078(3)
S(1)−Cu(1)−N(1A)	117.99(15)	S(1)−Cu(1)−N(2)	108.96(9)
N(1A)−Cu(1)−N(2)	105.68(11)	S(1)−Cu(1)−N(2B)	108.96(9)
N(1A)−Cu(1)−N(2B)	105.68(11)	N(2)−Cu(1)−N(2B)	109.31(17)
Cu(1C)−N(1)−C(1)	176.6(4)	N(1)−C(1)−S(1)	176.0(5)

[a] Symmetry operations for equivalent atoms: A, $(x, {}^1/_2 - y, z)$ (mirror plane); B, $(x, y, 1+z)$ (lattice translation); C, $(x, y, -1+z)$ (lattice translation). [b] Symmetry operations for equivalent atoms: A, $(x, 1+y, z)$ (lattice translation); B, $(1-x, y, z)$ (mirror plane); C, $(x, -1+y, z)$ (lattice translation).

Å; the angles around Ag range from 97.37(6) to 125.22(6)°]. Pairs of 2-cyanopyridine ligands bridge pairs of Ag atoms through their pyridyl and nitrile groups to give a centrosymmetric $[Ag_2(\mu\text{-2-cyanopyridine})_2]^{2+}$ unit, as shown in Figure 1a. The $[Ag_2(\mu\text{-2-cyanopyridine})_2]$ unit is approximately planar, the largest deviation from the plane being less than 0.34 Å. In addition, the Ag−N≡C angle [164.12(17)°] is slightly distorted from a linear arrangement. Every $[Ag_2(2\text{-cyanopyridine})_2]^{2+}$ unit is linked through four nitrate anions to four neighboring symmetry-equivalent units, resulting in a novel neutral two-dimensional polymer of basic formula $[Ag_2(2\text{-cyanopyridine})_2(NO_3)_2]_n$, seen in Figure 1b. The $[Ag_2(2\text{-cyanopyridine})_2]^{2+}$ dimer units are arranged in two alternating orientations, and pairs of centrosymmetrically related adjacent pyridine rings show parallel stacking. However, the perpendicular distance (ca. 4.0 Å) between these parallel units is beyond the range (3.3−3.8 Å) which can be considered as an effectual $\pi-\pi$ interaction,[13] and such an interaction can be viewed as negligible in this case. The layer, formed by nitrate-bridging of the cationic dimer units, is shown edge-on in Figure 1c. There are no major interactions between the layers.

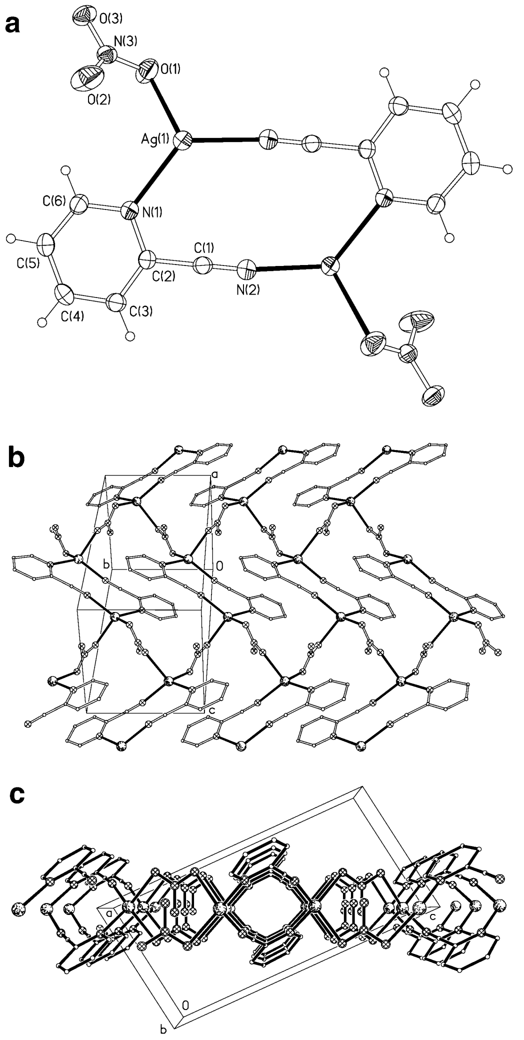

Figure 1. (a) View of the centrosymmetric $[Ag_2(2\text{-cyanopyridine})_2(NO_3)_2]_n$ dimeric unit in **1**. Displacement ellipsoids are shown here and in other figures at the 50% probability level. (b) The sheet polymeric structure of **1** formed by linking of the $[Ag_2(2\text{-cyanopyridine})_2]^{2+}$ cationic units through bridging nitrate anions. H atoms are omitted. (c) A single layer of the sheet structure of **1**, seen edge-on down the crystallographic *b* axis. H atoms are omitted.

Crystal Structure of $[Ag_4(3\text{-cyanopyridine})_8(SiF_6)_2(H_2O)_2]_n$ (2). For complex **2**, X-ray crystallographic analysis reveals a structure which is essentially a linear tetranuclear cationic cluster, $[Ag_4(3\text{-cyanopyridine})_8]^{4+}$, containing four $[Ag(3\text{-cyanopyridine})_2]^+$ units connected by three Ag−Ag bonds and the $\pi-\pi$ contacts between adjacent monocoordinated 3-cyanopyridine ligands (Figure 2a). The three Ag−Ag bond lengths [3.3072(5), 3.0242(6), and 3.3072(5) Å] in this centrosymmetric tetramer are shorter than the van der Waals contact distance (3.40 Å).[14] In this case, there is no bridging organic ligand to link Ag cations. Each 3-cyanopyridine ligand is terminally coordinated to a silver cation by its pyridyl nitrogen (N_{py}), the nitrile group remaining uncoordinated. The absence of coordination of Ag by these pendant nitrile groups highlights the significance of the

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(13) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885.

(14) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

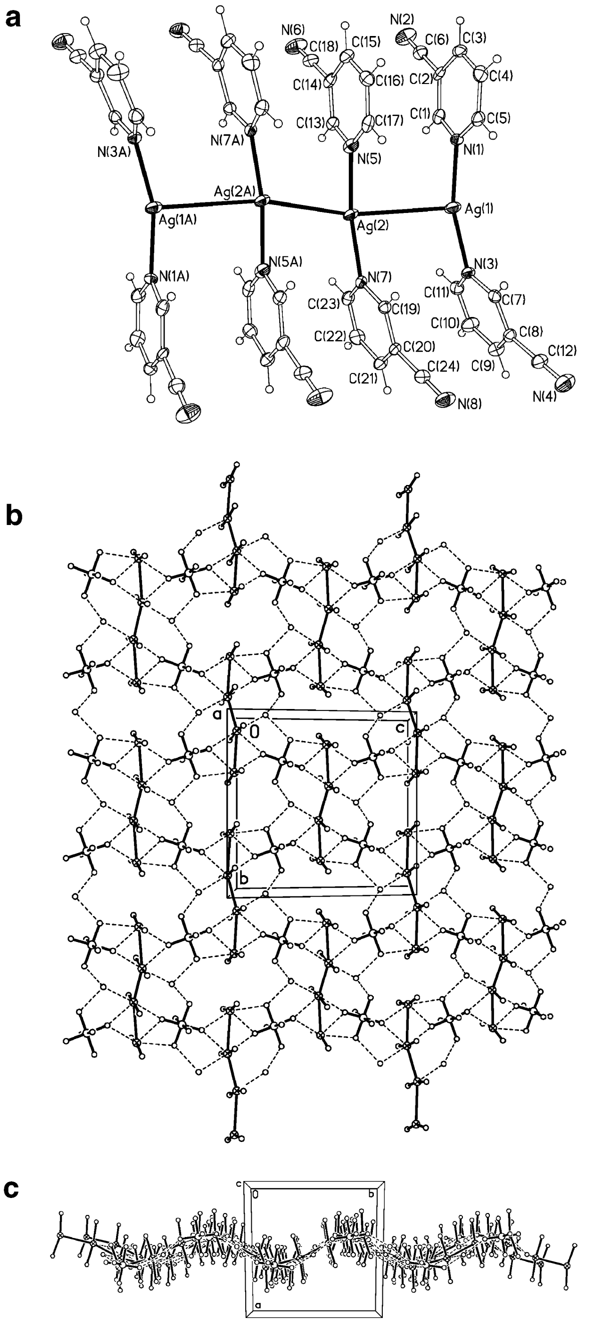

Figure 2. (a) The structure of the centrosymmetric $[Ag_4(3\text{-cyanopyridine})_8]^{4+}$ cationic unit in **2**. (b) View of the two-dimensional network in **2**, with Ag−F interactions and hydrogen bonds shown dashed. The view is down the crystallographic *a* axis, and only the coordinated N atoms of the organic ligands are shown. H atoms of water are omitted. (c) Edge view of the undulating layer in **2** down the crystallographic *c* axis, including the same atoms as in Figure 2b.

$\pi-\pi$-stacking interaction between the adjacent aromatic rings. Presumably the electron-withdrawing effect of the cyano group makes the aromatic ring relatively electron poor.[13] The dihedral angles between adjacent stacked rings are 3.8° (rings 1 and 2), 12.3° (rings 2 and 3), and 8.1° (rings 3 and 4), where ring 1 contains N(1), ring 2 contains N(5), ring 3 contains N(7A), and ring 4 contains N(3A), and the spacing between adjacent rings is 3.3−3.5 Å. The Ag_4 skeleton is not quite linear, with Ag−Ag−Ag angles of 160.501(19)°. The two central Ag atoms are essentially linearly coordinated by two N_{py} atoms [171.09(12)°], while the N−Ag−N angle for the two outer Ag atoms is more bent [162.39(12)°], the organic ligands projecting outward slightly.

Each $[SiF_6]^{2-}$ counteranion displays weak interactions to four Ag atoms of two adjacent $[Ag_4(3\text{-cyanopyridine})_8]^{4+}$ units (F···Ag contacts range from 2.607(2) to 2.701(2) Å), through two *trans*-fluorine atoms in an η^2,η'^2−fashion. One of the remaining four equatorial fluorine atoms shows a longer contact to one of the Ag atoms [2.942(2) Å]; this and the fluorine opposite to it are hydrogen bonded to water molecules, each of which in turn is weakly coordinated to one of the central Ag atoms [Ag···O 2.689(2) Å]. These secondary coordinative bonds and hydrogen bonds link the cations, anions and water molecules together into a sheet structure (Figure 2b). Each layer has an undulating inorganic core of Ag, Si, F, and O atoms, with the organic ligands protruding on both sides (Figure 2c). The interlayer distance is 14.151 Å, the length of the crystallographic *a* axis, and only van der Waals interactions hold the layers together. Although a few multidimensional inorganic−organic hybrid materials containing discrete Ag clusters have been reported,[15] we are unaware of linear multinuclear Ag clusters as the assembly unit for the construction of multidimensional networks, and complex **2** represents an unusual example of a 2-D network based on discrete linear Ag_4 clusters.

Crystal Structure of $[Ag(3\text{-cyanopyridine})_2(NO_3)]_n$ (3). Each Ag atom, lying on a 2-fold rotation axis, is coordinated by the pyridyl nitrogen atoms of two 3-cyanopyridine ligands; the N−Ag−N angle is large [157.5(4)°]. Each Ag atom also interacts weakly with two oxygen atoms from two different nitrate anions [Ag−O2 = 2.736(9) Å],[16,17] and the two oxygen atoms adopt positions resulting in a narrow O−Ag−O angle [72.6(3)°]. The result is an appreciably distorted tetrahedral geometry at the Ag center (Figure 3a). The nitrate ions bridge adjacent Ag(3-cyanopyridine)$_2$ units to generate a helical chain running along the crystallographic *c* axis, with a pitch of 3.72 Å (Figure 3b). The intrachain Ag···Ag separation of adjacent Ag atoms is thus 3.72 Å, which is longer than the van der Waals contact distance (3.40 Å). Therefore, despite their weakness, the resultant structure is controlled by the $Ag\cdots NO_3^-$ interactions, together with face to face $\pi-\pi$-stacking of the aromatic rings of 3-cyanopyridine ligands. The nitrate anion adopts an orientation with its plane normal inclined at 29.8° to the line of Ag atoms along the *c* axis, the Ag−O bonds lying well out of the plane of the anion.

The degree of structural control exerted by the anion in compounds containing $[Ag(3\text{-cyanopyridine})_2]^+$ building blocks is illustrated by the very different structures of **2** and **3**. The replacement of nitrate by $[SiF_6]^{2-}$, together with the

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(15) (a) Michaelides, A.; Kiritsis, V.; Skoulika, S.; Aubry, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1495. (b) Tong, M.-L.; Shi, J.-X.; Chen, X.-M. *New J. Chem.* **2002**, *26*, 814.

(16) The Ag−O distances of 2.736(9) Å are typical for such interactions between Ag^I centers and NO_3^- ions (ref 16).

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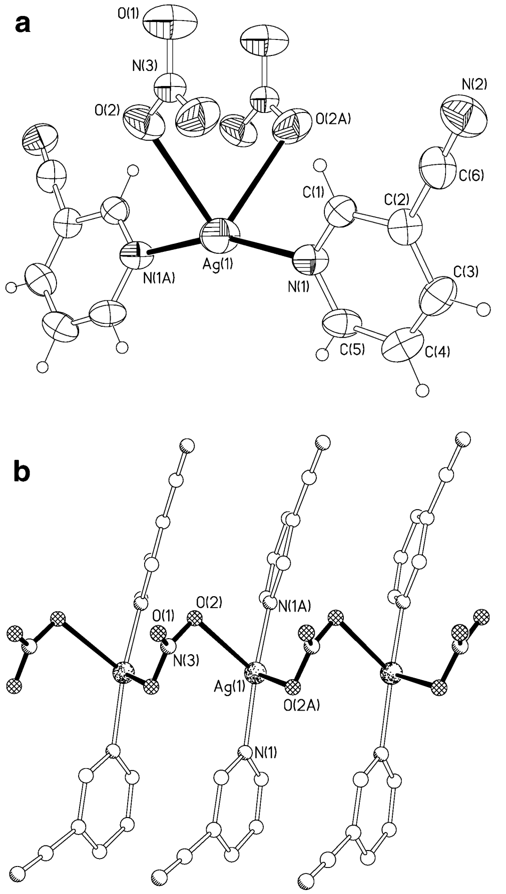

Figure 3. (a) Coordination of Ag in **3**, including two symmetry-equivalent organic ligands and two symmetry-equivalent nitrate groups. (b) A section of the helical chain in **3**. H atoms are omitted.

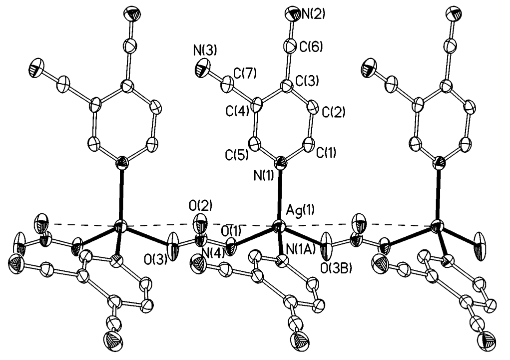

Figure 4. A section of the polymeric chain of **4**. H atoms are omitted. Weaker Ag⋯O interactions are shown dashed.

presence of water molecules, results in a completely different and relatively complicated structure for **2**.

Crystal Structure of [Ag(pyridine-3,4-dicarbonitrile)$_2$(NO$_3$)]$_n$ (4). This compound has a one-dimensional structure of alternating [Ag(pyridine-3,4-dicarbonitrile)$_2$]$^+$ cationic units and bridging nitrate anions, running along the crystallographic [101] direction (Figure 4). Ag is coordinated in a distorted tetrahedral primary environment by two oxygen atoms from two bridging nitrate anions and two pyridyl nitrogen atoms from two pyridine-3,4-dicarbonitrile ligands [$Ag-N_{py} = 2.2827(19)$, $Ag-O = 2.427(2)$, and 2.445(3) Å; the angles around Ag range from 94.93(9) to 117.32(9)°]. The $Ag-N_{py}$ distance is comparable with those in **1**, but markedly longer than those in **2** and **3**. For the bridging nitrate, the N−O bonds for the two coordinated oxygen atoms [N4−O1 1.258(4) Å, N4−O3 1.248(4) Å] are slightly longer than that for the uncoordinated oxygen atom [N4−O2 1.226(5) Å]. The nitrogen atom and the three oxygen atoms are strictly coplanar with the Ag atoms in the chain, all of them lying in a crystallographic mirror plane; thus the chain exhibits a zigzag rather than a helical configuration. The shortest intrachain Ag⋯Ag separation is 5.751 Å, which is much longer than that in **3**. The O⋯Ag contacts for the third oxygen atom of nitrate, O(2) (dashed lines in Figure 4; 2.864 and 2.903 Å), are shorter than the van der Waals contact distance (3.10 Å), but well outside the range expected for covalent bonding. This represents weak electrostatic attractions between these noncoordinating oxygen atoms and Ag atoms along the chain direction, contributing to the stability of the one-dimensional chain structure. It should be noted that **4** is always formed, regardless of the reaction stoichiometry. The introduction of [SiF$_6$]$^{2-}$ into the reaction mixture still results in the formation of **4**, suggesting that nitrate plays a vital role in the construction of the chain structure of **4**.

Although (NH$_4$)$_2$[SiF$_6$] was introduced into the reaction mixture during the syntheses of **1**, **2**, and **4**, only in **2** is [SiF$_6$]$^{2-}$ incorporated into the product, both as counteranion and as a bridge between Ag$_4$ cationic units. It should be noted that the $N_{py}-Ag$ bond lengths in **2** and **3** are shorter than those in **1** and **4**, indicating that the positive charges of the coordinated Ag$^+$ centers can more effectively decrease the π-electron density and $\pi-\pi$ repulsion of the aromatic rings[13] in the cases of **2** and **3** than in **1** and **4**. In addition to the previously reported cases of a diamondoid framework for [Ag(4-cyanopyridine)$_2$]$^+$,[8,18] the four organic ligands of *n*-cyanopyridine ($n = 2, 3, 4$) and pyridine-3,4-dicarbonitrile act differently when used to construct silver coordination polymers. Compared to the other cyanopyridine ligands, 3-cyanopyridine appears to favor $\pi-\pi$-stacking interaction, which leads to the aggregation of [Ag(3-cyanopyridine)$_2$]$^+$ fragments from solution to give polymeric [Ag$_x$(3-cyanopyridine)$_{2x}$]$^{x+}$ chains.

In the reaction between AgNO$_3$ and 3-cyanopyridine, the isolated product is apparently sensitive to the charge and/or other property of the anions present. The dianion [SiF$_6$]$^{2-}$ results in the isolation of the oligomer [Ag$_4$(3-cyanopyridine)$_8$]$^{4+}$ (**2**) from the reaction solution, instead of the polymeric **3**. We expect that longer cationic linear clusters [Ag(3-cyanopyridine)$_2$]$_x^{x+}$ ($x > 4$) might be obtained if anions with higher charge, or anionic infinite chains, were used as templates. Work in this direction is in progress.

Crystal Structure of [Cu^I(4-cyanopyridine)$_2$(SCN)]$_n$ (5). **5** has a comparatively simple structure (Figure 5) based on

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(18) We have also introduced (NH$_4$)$_2$SiF$_6$ into the reaction system of AgNO$_3$ and 4-cyanopyridine, but this only resulted in a diamondoid framework complex {[Ag(4-cyanopyridine)$_2$]·0.5SiF$_6$} the structure of which is similar to that reported in ref 8. In this case, each Ag$^+$ center is coordinated to two pyridyl nitrogen atoms and two cyano groups from four different 4-cyanopyridine molecules. Every 4-cyanopyridine ligand bridges two Ag$^+$ centers. The SiF$_6$$^{2-}$ anions are embedded in the channels only as counteranions and do not interact with any Ag$^+$ center (the shortest F⋯Ag distance is longer than 5 Å).

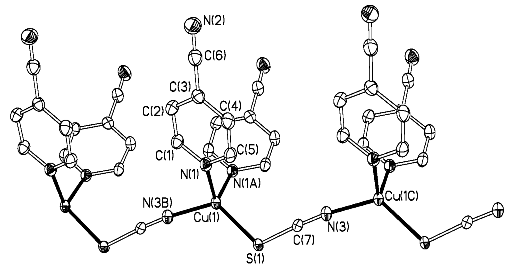

Figure 5. A section of the polymeric chain of **5**. H atoms are omitted.

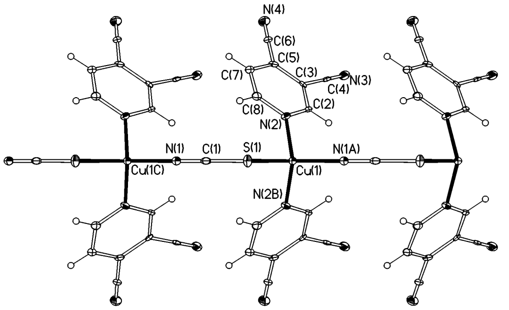

Figure 6. A section of the polymeric chain of **6**, in a view direction different from that of **5** in Figure 5. H atoms are omitted.

a zigzag chain of alternating $[Cu^I(3\text{-cyanopyridine})_2]^+$ units and bridging thiocyanate ligands, running along the crystallographic *b* axis direction. All Cu atoms and thiocyanate ligand atoms lie in a crystallographic mirror plane. Cu is coordinated in a distorted tetrahedral geometry by one sulfur and one nitrogen atom (N_{scn}) from two bridging thiocyanate ligands and two pyridyl nitrogen atoms (N_{py}) from two terminal 3-cyanopyridine ligands [$Cu-S = 2.2751(6)$, $Cu-N_{scn} = 1.9900(18)$, $Cu-N_{py} = 2.1038(13)$ Å]. The angles around Cu range from 102.20(7) to 121.67(6)°. The $Cu-N\equiv C-S$ unit is nearly linear; the Cu−N−C and N−C−S angles are 173.52(18) and 176.09(19)°, respectively. This leads to a relatively large Cu···Cu separation (6.094 Å).

Crystal Structure of $[Cu^I(pyridine\text{-}3,4\text{-}dicarbonitrile)_2(SCN)]_n$ (6). The crystal structure of **6** (Figure 6) is very similar to the structure of **5**, in containing a one-dimensional chain of alternating $[Cu(pyridine\text{-}3,4\text{-}dicarbonitrile)_2]^+$ units and bridging thiocyanate ligands running along the crystallographic *b* axis direction and having crystallographic mirror symmetry. Cu is coordinated in a tetrahedral geometry by one sulfur and one nitrogen atom (N_{scn}) from two bridging thiocyanate ligands and two pyridyl nitrogen atoms (N_{py}) from two pyridine-3,4-dicarbonitrile ligands [$Cu-S = 2.3129(14)$, $Cu-N_{scn} = 1.937(5)$, and $Cu-N_{py} = 2.078(3)$ Å]. Both nitrile groups of each organic ligand remain noncoordinating. The angles around Cu range from 105.68(11) to 117.99(15)°. As expected, $Cu-N\equiv C-S$ displays a nearly linear arrangement, with Cu−N−C and N−C−S angles of 176.6(4) and 176.0(5)°, respectively. The space groups, the cell parameter, and the packing of the polymeric chains for **5** and **6**, however, are quite different, as a result of the different substituents on the organic ligands.

Electrical Properties. According to Jansen,[19] the evidence for interaction or bonding between the formally closed-shell d^{10} cations in extended solid structures is provided not only by characteristic uniform structural features but also by their physical properties such as a large red-shift of the absorption in their UV/vis spectra and by electrical conductivity. Therefore, the conductivities of **1**−**6** were studied over an extended temperature range.

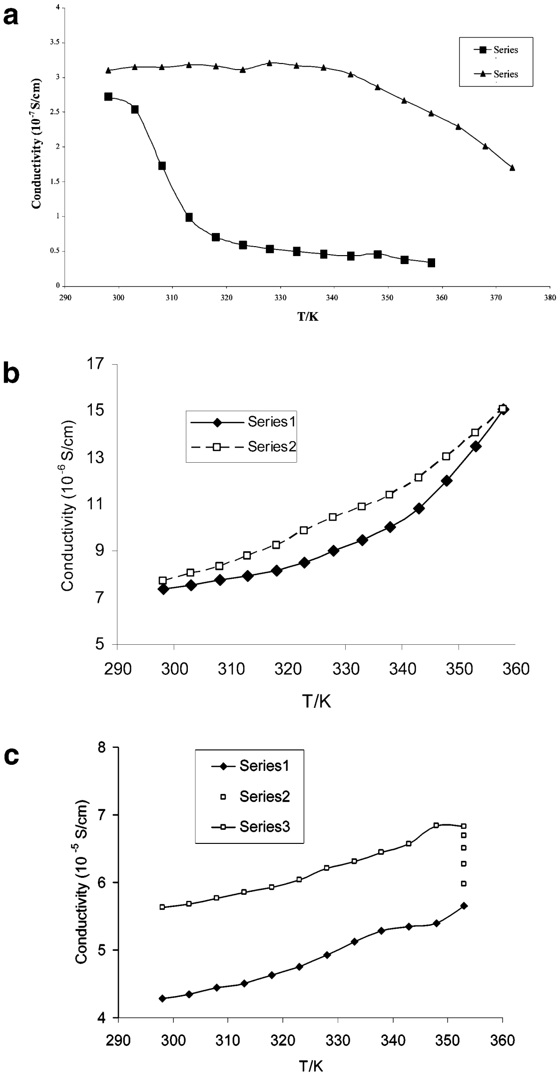

Figure 7. (a) Temperature dependence of the electrical conductivity of **1** (series 1) and **2** (series 2), showing that the conductivity of **2** exhibits PTC behavior. (b) Temperature dependence of the electrical conductivity of **4**. Series 1 shows that the conductivity of **4** increases with temperature. Series 2 illustrates the conductivity of the same sample as the temperature decreases. (c) Temperature dependence of the electrical conductivity of **6**. Series 1 shows that the conductivity of **6** increases as the temperature rises. Series 2 illustrates how (at high temperature, 353 K) the conductivity increases when the temperature is kept constant. Series 3 shows the change in conductivity of the sample as the temperature decreases.

The electrical conductivities of complexes **1**−**6** were measured by using pressed pellets prepared from powder samples obtained by grinding crystals (two-probe electrode method).[20] Room temperature (298 K) conductivities of **1**, **2**, **4**, and **6** are 3.1×10^{-7}, 2.7×10^{-7}, 7.4×10^{-6}, and 4.3×10^{-5} S cm^{-1}, respectively, and vary with temperature; for compounds **3** and **5**, on the other hand, the electrical

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conductivities are in the range of 10^{-11} to 10^{-13} S cm^{-1} and are independent of temperature. According to the definition of Kittel,[21] the conductivity of semiconductors is in the range 10^{-9} to 10^{2} S cm^{-1}; therefore compounds **1**, **2**, **4**, and **6** are semiconductors, but **3** and **5** are insulators. Powder conductivity is generally 100 times smaller than that of a single crystal,[20] but this would still classify compounds **1**, **2**, **4**, and **6** as weak semiconductors.

We have also measured the conductivities as a function of temperature for compounds **1**, **2**, **4**, and **6** (with a heating rate of 5 °C every 3 min). These experiments establish that **1**, **2**, **4**, and **6** exhibit different conductivity behaviors. The conductivity of **1** is essentially invariant up to 343 K (Figure 7a). Above 343 K the conductivity of **1** gradually decreases, perhaps due to partial decomposition of the sample at these high temperatures. On the other hand, **2** shows a positive temperature coefficient (PTC) effect;[22] the conductivities quickly drop from 2.72×10^{-7} S cm^{-1} (298 K) to 7.08×10^{-8} S cm^{-1} (318 K). At the molecular level, it may be that the weak F···Ag interactions in crystalline **2** are sensitive to temperature, and at high temperatures the polymeric network structure of **2** is disrupted. An alternative explanation is that there is loss of water molecules (which have been noted in the X-ray crystal structure) and this leads to structural change. In this context it is worth noting that the elemental analysis of **2** is rather poor. Although the sample was well dried before analysis, the poor elemental analysis could also be due to loss of water from the crystals.

The variation of the conductivity of **4** with temperature (shown in Figure 7b) exhibits a negative temperature coefficient (NTC) effect,[22] similar to artificial systems of conventional semiconductors. The conductivity of **4** increases from 7.37×10^{-6} S cm^{-1} to 1.508×10^{-5} S cm^{-1} as the temperature increases from 298 K to 358 K. Moreover, the process is reversible. Conductivity values of **4** drop to 7.69×10^{-6} S cm^{-1} when the temperature is returned to room temperature. It seems reasonable that compound **4** shows the NTC conductivity behavior dependent on temperature because of its structure. The one-dimensional chain with short and stable O−Ag bonds (Figure 4) remains the stable and effective conjugative system of **4** throughout the measured temperature range.

The conductivity of **6** exhibits a negative temperature coefficient (NTC) behavior, as shown in Figure 7c. The conductivity of **6** varies from 4.29×10^{-5} S cm^{-1} to 5.39×10^{-5} S cm^{-1} over the temperature range 298−348 K. Interestingly, this behavior is not reversible. We observe for **6** that, while the temperature is held at 353 K for about 10 min, its conductivity increases to 6.83×10^{-5} S cm^{-1}. This may be because, at high temperature, some Cu^{I} in the crystal is reduced by SCN^{-}, resulting in **6** exhibiting Cu^{0} doped semiconductor behavior.[23]

It is worth noting that both **4** and **6** contain the pyridine-3,4-dicarbonitrile ligand and exhibit better conductivities than **1**, **2**, **3**, and **5**. The generality of this observation is worth further investigation.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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