Self-Assembly of One-Dimensional Coordination Polymers from AgX (X = $CF_3SO_3^-$, ClO_4^-, and NO_3^-) and 2-Aminomethylpyridinedipropionitrile (2-AMPDPN)

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Three novel supramolecules whose topologies depend on the counteranion, [Ag(2-AMPDPN)X] (X = $CF_3SO_3^-$ (**1**), ClO_4^- (**2**), and NO_3^- (**3**)), have been prepared by the self-assembly of AgX (X = $CF_3SO_3^-$, ClO_4^-, and NO_3^-) with 2-aminomethylpyridinedipropionitrile (2-AMPDPN). The crystal structures reveal different packing arrangements of the one-dimensional infinite coordination polymers. Compound **1** is made up of ladder chains that are interlocked by cyano groups, while the polymeric chain of **2** is isomorphous to **1** except for the Ag−Ag interaction. Compound **3** consists of helical chains that are surrounded by nitrate. The adjacent helical chains are racemic. The structures of **1**, **2**, and **3** suggest the role that the counterions may play in the network construction.

Introduction

The recent progress in the field of crystal engineering based on polymeric coordination has been devoted to the use of novel polydentate ligands.[1] Much study has centered upon the use of supramolecular contacts between suitable molecules to generate multidimensional arrays or networks. The design of supramolecular assemblies via ligand design, the coordination characteristics of the metal ion, and the length of the spacer has resulted in a variety of structural motifs.[2] More subtle effects on the topological configuration such as anion control are receiving renewed attention.[3] The simple strategy of combining metal centers with polyhapto bases can generate crystalline architectures with obvious implications for the rational design of new and varied topological types. In addition, the control of the network topology is a challenge in the metal coordination field because the ancillary ligation by the anion may result in a remarkable structural change.[4] Various ligands have been used for supramolecular building blocks, but exploitation of the 2-aminomethylpyridinedipropionitrile (2-AMPDPN) has until recently remained unprecedented. The ligand possesses two functionalities with the pyridine and the cyano moieties. The affinity of Ag^+ for N-donor ligands, especially pyridine and the cyano group, is well known. Rajasekharan et al. reported the polymeric compounds of the type $AgLClO_4$ (L = aminomethylpyridine).[4b] We envisioned that if the multifunctional ligand possesses two functionalities containing pyridine and the cyano moieties, the ligand serves to illustrate the profound changes in the polymeric architectures. The silver(I) ion can be employed as an angular directional unit, as it is known to exhibit a linear or T-shaped coordination mode.[5]

In this paper, we report three novel supramolecular compounds, [Ag(2-AMPDPN)X] (X = $CF_3SO_3^-$, ClO_4^-, and NO_3^-), which serve to illustrate the profound change in the polymeric structures caused by a simple variation in the counteranion.

Results and Discussion

Construction of Self-Assembly. Compounds **1**, **2**, and **3** were synthesized by the self-assembly of AgX (X = $CF_3SO_3^-$, ClO_4^-, and NO_3^-, respectively) with 2-aminomethylpyridinedipropionitrile (2-AMPDPN) in THF (Scheme 1). Compounds **1**, **2**, and **3** are soluble in acetonitrile and MeOH but insoluble in THF and acetone. The ^1H and ^{13}C NMR spectra for **1**−**3** support the chemical formulation of the three complexes. One singlet (3.87 ppm) and two triplets (2.92 and 2.60 ppm) in the ^1H NMR

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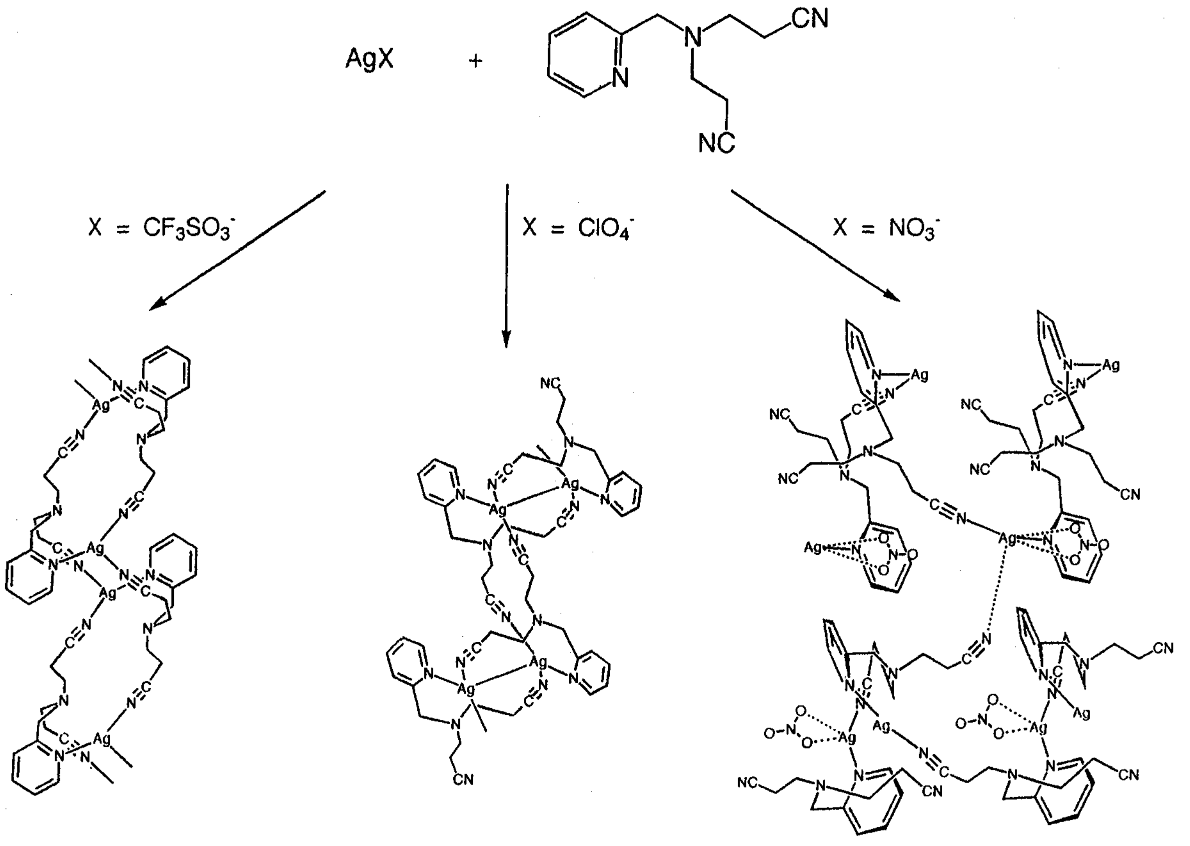
Scheme 1



1 **2** **3**

spectrum and three singlets (60.51, 49.75, and 16.15 ppm) in the ^{13}C NMR spectrum of **2** could be assigned to the methylene groups. The signals of all the aromatic protons of **1**−**3** are shifted downfield relative to those of the free ligand. The C≡N values of **1**−**3** (2248−2275 cm^{-1}) in the infrared spectrum show a higher C≡N stretching frequency than that of the ligand (2232 cm^{-1}).[6] In general, a coordinated nitrile exhibits a higher stretching frequency than the uncoordinated ligand. Although the stoichiometry of Ag(I)/2-AMPDPN in **1**−**3** is the same, the coordination numbers of the Ag(I) ion as well as the topologies of **1**−**3** are different. The coordination numbers of the Ag(I) ion of **1**−**3** are three, four, and four, respectively. The topologies of **1**−**3** are a 1-D ladder arrangement, a 1-D ladder arrangement with Ag−Ag contact, and a 2-D helical network, respectively.

Description of the Molecular Structure of [Ag(2-AMPDPN)]-(OTf)·CH$_3$CN (1). A crystal of **1** suitable for an X-ray diffraction study was grown from acetonitrile/ether. A summary of the data collection and crystallographic parameters for **1** is given in Table 1. The relevant bond lengths and angles are shown in Table 2. The molecular structure of **1** is given in Figure 1. As illustrated in Figure 1, the silver(I) ion is coordinated to one nitrogen atom of the 2-pyridyl group as well as to two cyano groups from two different 2-AMPDPN ligands. The Ag−N$_{\text{pyridyl}}$ and Ag−N$_{\text{cyano}}$ bond distances are 2.219(3) and 2.176(3)−2.445(4) Å, respectively. The bond angle of N(2)$^{\text{i}}$−Ag−N(4) is 154.25(13)°. The coordination geometry around Ag(I) is best described as a distorted T-shaped coordination. Such a geometry has also been observed in a number of polymeric silver (I) complexes.[7] The distortion is believed to be caused by the coordination of the cyano group from different subunits. Each 2-AMPDPN links three Ag(I) atoms because two cyano groups of the ligand coordinate two neighboring silver(I) atoms. Therefore, the structure of **1** becomes a linear coordination polymer (Figure 1). The symmetric unit of **1** consists of two Ag(2-AMPDPN)OTf subunits forming the repeating unit in **1**. Because two cyano groups from different ligands are coordinated to the two silver atoms, the crystal is made up of ladder chains

Table 1. Crystal Data of Compounds **1**, **2**, and **3**

	1	**2**	**3**
empirical formula	$C_{15}H_{17}F_3N_5O_3SAg$	$C_{12}H_{14}ClN_4O_4Ag$	$C_{12}H_{14}N_5O_3Ag$
mol wt	512.27	421.59	384.15
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a, Å	10.7590(15)	9.5444(14)	8.5485(14)
b, Å	12.7771(18)	18.787(3)	12.781(2)
c, Å	14.927(2)	8.6969	13.333(2)
β, deg	99.825(3)	90.325(3)	90
V, Å^3	2021.9(5)	1559.4(4)	1456.7(4)
Z	4	4	4
D_{calcd}, g cm^{-3}	1.683	1.796	1.752
μ, cm^{-1}	1.152	1.486	1.401
no. of obsd reflns	4850	3718	3504
R1	0.0441	0.0687	0.0548
wR2	0.1225	0.2055	0.2128
GOF	1.033	1.188	1.260

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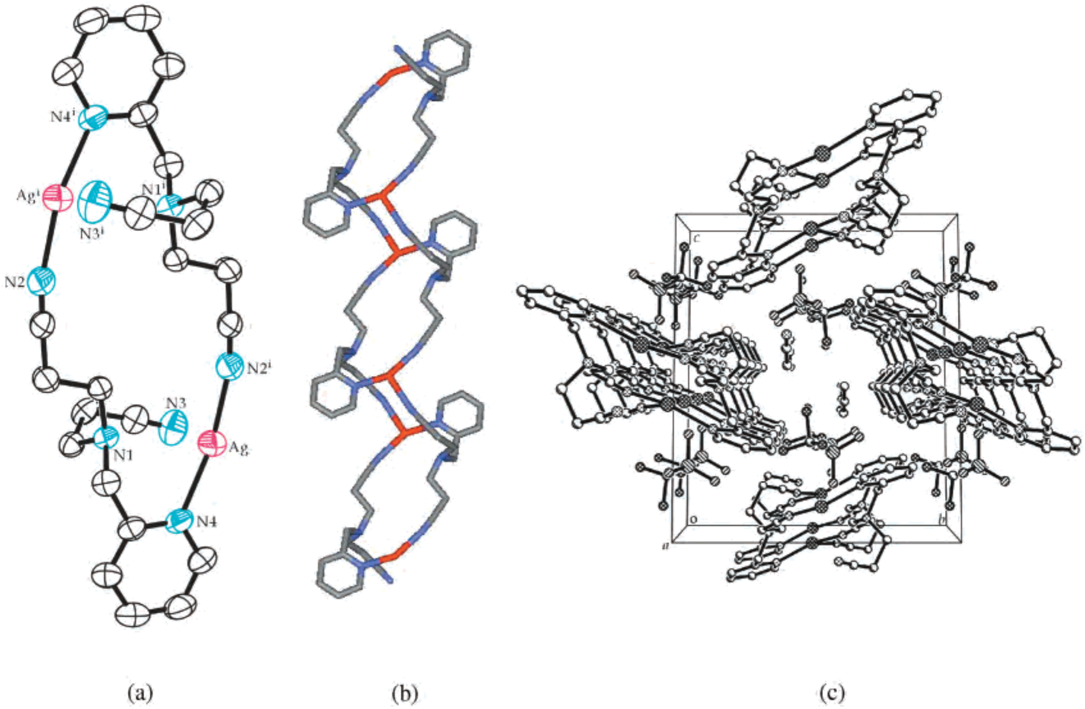

Figure 1. (a) ORTEP drawing of [2-(AMPDPN)Ag](OTf) **1** showing the local coordination of Ag(I) and the atomic numbering scheme with 50% probability thermal ellipsoid depicted. (b) Stick representation of the ladder structure. The counteranions were omitted for clarity. (c) Packing diagram of **1**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) Important for Complexes **1**, **2**, and **3**[a]

[Ag(2-AMPDPN)](OTf)·CH_3CN **1**			
Ag−N(2)^i	2.176(3)	Ag−N(4)	2.219(3)
Ag−N(3)^{ii}	2.445(4)	N(3)−Ag^{ii}	2.445(4)
N(2)^i−Ag−N(4)	154.25(13)	N(2)^i−Ag−N(3)^{ii}	102.19(13)
N(4)−Ag−N(3)^{ii}	97.84(13)		
[Ag(2-AMPDPN)(ClO_4)] **2**			
Ag−N(4)	2.180(6)	Ag−N(3)^i	2.589(9)
Ag−N(2)^{ii}	2.158(7)	Ag···Ag^i	3.2992(15)
Ag···N(1)	2.794(6)		
N(4)−Ag−N(3)^i	92.7(3)	N(4)−Ag−Ag^i	100.89(17)
N(3)^i−Ag−Ag^i	71.6(2)	N(2)^{ii}−Ag−N(4)	168.7(3)
N(2)^{ii}−Ag−N(3)^i	90.9(3)		
[Ag(2-AMPDPN)(NO_3)] **3**			
Ag−N(4)^i	2.212(11)	Ag(1)−N(1)	2.285(8)
Ag(1)−O(2)	2.692(11)	Ag(2)−O(3)	2.895(11)
N(4)^i−Ag(1)−N(1)	151.0(4)	C(12)^i−N(4)^i−Ag(1)	169.9(10)
C(5)−N(1)−Ag(1)	119.6(6)	C(1)−N(1)−Ag(1)	122.4(7)

[a] Symmetry transformations used to generate equivalent atoms: For **1**, (i) $-x$, $-y + 2$, $-z + 1$; (ii) $-x + 1$, $-y + 2$, $-z + 1$. For **2**, (i) $-x + 2$, $-y$, $-z + 1$; (ii) $-x + 1$, $-y$, $-z + 1$. For **3**, (i) $x + 1/2$, $-y - 1/2$, $-z + 1$.

that are interlocked by the cyano group (Ag···N = 2.445(4) Å). The triflate ions do not coordinate to the Ag(I) ions and are located between the layers.

Description of the Molecular Structure of [Ag(2-AMPDPN)(ClO_4)] (2). An ORTEP drawing of the cation in **2** is given in Figure 2. Table 2 shows the selected bond distances and angles. The symmetric unit of **2** contains two $Ag_2N_3C_5$ ten-membered rings. In the solid state, the Ag(I) center is coordinated to one nitrogen atom of the 2-pyridyl group with a Ag−N bond distance of 2.180(6) Å and two cyano groups from two different 2-AMPDPNs with Ag−N distances of 2.158(7) and 2.589(9) Å and one weak Ag−Ag bond with a Ag−Ag bond distance of 3.2992(15) Å. Although the nature of the Ag−Ag interaction is not clearly understood, the weak Ag(I)−ClO_4^- bond probably contributes to the formation of the Ag−Ag interaction, a feature documented in polynuclear silver(I) complexes.[8] The coordination geometry around Ag(I) is best described as a distorted tetrahedral configuration.

The symmetric unit of **2**, shown in Figure 2, consists of two Ag(2-AMPDPN)ClO_4 subunits. Each 2-AMPDPN ligand binds three different Ag(I) ions, and each Ag(I) ion is linked with three 2-AMPDPNs, the structure of which becomes a 1-D layer. The Ag−$N_{pyridyl}$ and Ag−N_{cyano} bond distances are 2.180(6) and 2.589(9) Å, respectively. The bond lengthening of Ag−N_{cyano} is caused by the weak interaction of the Ag−Ag bond. The bond angle of N3^i−Ag−N4 is 92.7(3)°. The significant distortion is believed to be caused by the proximity of another perchlorate oxygen atom. The perchlorate ions are coordinated to the Ag(I) ions (Ag···O = 2.863(3) Å) and connect the molecules (Figure 2c). One oxygen atom of the perchlorate ion is disordered over two sites with occupancies of 0.73 and 0.27. The interplay between the interactions causes the formation of the Ag−Ag interactions of 3.2992(15) Å. The polymeric chain of **2** is similar to **1** except for the Ag−Ag interaction, although its structure is slightly more distorted. The Ag−Ag interaction, constrained by the two bridged ligands, is slightly longer than those of several polynuclear silver complexes. The presence of the weak Ag−Ag bond of **2** gives the appearance of a distorted ladder formation. The lattice grows so that channels are generated which accommodate the ClO_4^- counteranions. Similar topologies for such polymeric networks have been previously described.[9] The main difference in the structural topologies between **1** and **2** may be attributable to the intervention of the Ag(I) ions of the noncoordinating and coordinating anions and the chlatrate molecules.

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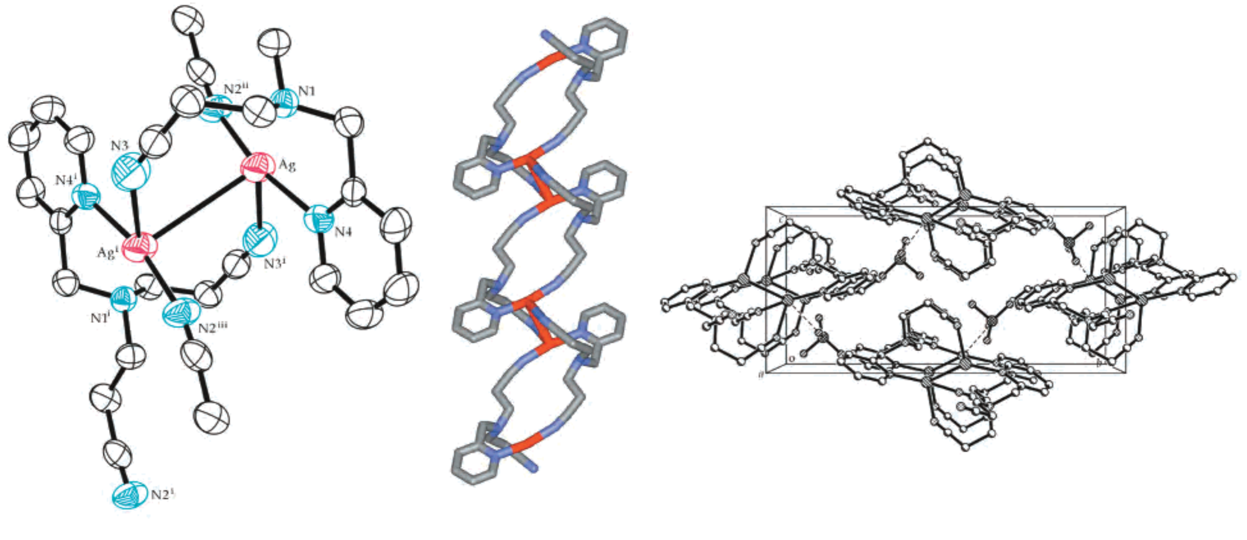
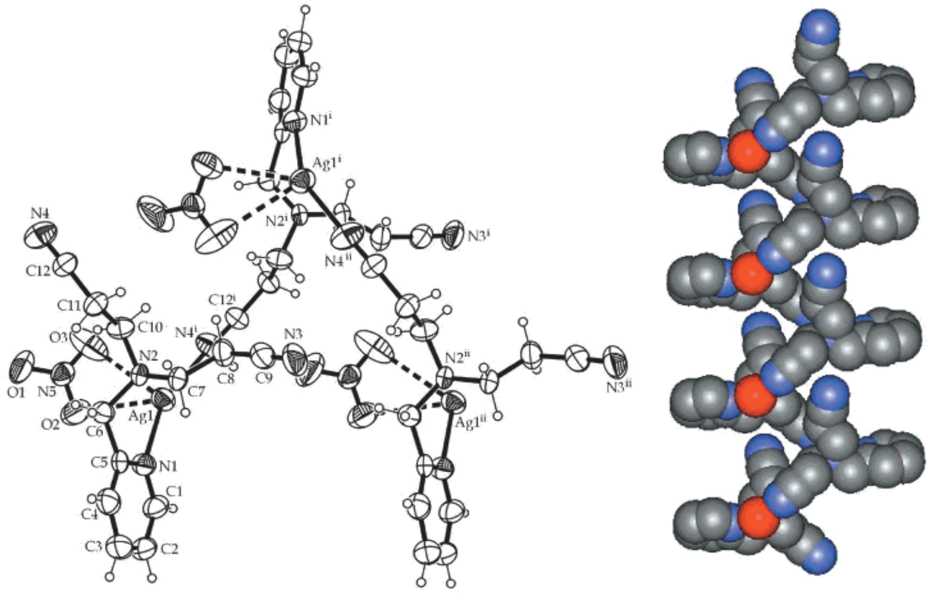


(a) (b) (c)

Figure 2. (a) ORTEP drawing of [2-(AMPDPN)Ag(ClO_4)] **2** showing the local coordination of Ag(I) and the atomic numbering scheme with 50% probability thermal ellipsoid depicted. (b) Stick representation of the ladder structure of **2**. The counteranions were omitted for clarity. (c) Packing diagram of **2** showing the interaction of the perchlorate ions.



(a) (b)

Figure 3. (a) ORTEP drawing of [2-(AMPDPN)Ag(NO_3)] **3** showing the local coordination of Ag(I) and the atomic numbering scheme with 50% probability thermal ellipsoid depicted. (b) Space-filling representation of the helical polymer. The counteranions were omitted for clarity.

Description of the Molecular Structure of [Ag(2-AMPDPN)(NO_3)] (3). An ORTEP view of [Ag(2-AMPDPN)(NO_3)] is shown in Figure 3. The relevant bond lengths and angles are shown in Table 2. In the solid state, the Ag(I) ion is coordinated to one nitrogen atom of the 2-pyridyl group and two different 2-AMPDPNs as well as to two oxygen atoms of the nitrate anion. The $Ag-N_{pyridyl}$ and two $Ag-N_{cyano}$ bond distances are 2.285(8) and 2.212(11) Å, respectively. For the weakly coordinated nitrate anion, the two Ag−O bond distances are 2.692(11) and 2.895(11) Å, respectively, and the bond angle of O−N−O is 43.4(3)°, which is smaller than that of [Ag($C_{14}H_{20}N_6$)(NO_3)].[4a] The coordination geometry about Ag(I) may be described as a distorted tetrahedral geometry. Each 2-AMPDPN links two Ag(I) ions because only one cyano group coordinates to a neighboring silver(I) ion. There are two symmetry-related polymeric chains through the unit cell. The structure may be viewed as being made up of alternating layers of polymeric chains and cations. The 2-fold screw symmetry causes the polymeric chains to assemble in a helical fashion. Similar helical coordination polymers have been well documented.[10] Because all the chains propagate in the *xy* plane, there are two enantiometric helices through the unit cell. This formation produces 4.5 Å wide tunnels along the *b* axis. Another unusual feature of the structure is that each helix is networked through a weak Ag−N interaction by the cyano group of the adjacent helix with a Ag−N distance of 2.695(8) Å, leading to the formation of a N-bonded string of helices along the *b* axis.

Conclusion

Three novel supramolecular coordination polymers whose structures depend on the counteranion have been prepared from the reaction of AgX (X = $CF_3SO_3^-$, ClO_4^-, and NO_3^-) and 2-aminomethylpyridinedipropionitrile (2-AMPDPN). The structures of these complexes were characterized by X-ray analysis. As a consequence, a remarkable structural change in the silver(I) complexes was observed. Complex **1** consists of ladder chains in which two cyano groups of the ligand coordinate to two neighboring silver(I) atoms. The polymeric chain of **2** is isomorphous to that of **1** except for the Ag−Ag interaction in the unit. Complex **3** consists of helical chains which are coordinated by the nitrate and 2-pyridyl groups as well as two cyano groups from two different ligands. The array with an extended structure runs toward a crystallographic 2-fold screw axis. Adjacent helical chains are racemic. The structures of **1**, **2**, and **3** imply the role that the counterions may play in the topologic construction. In the silver(I) coordination polymers, a significant conformational change has been achieved by subtle changes in the nature of the counterions.

Experimental Section

All experiments were performed using standard Schlenk techniques. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone. Acetonitrile was distilled from CaH_2, and ethyl alcohol was distilled over Linde type 4 Å molecular sieves. The ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.00 and 75.44 MHz, respectively. Chemical shifts were referenced relative to TMS. The IR spectra were recorded on a Shimadzu FT-IR 8501 spectrometer, and elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA 1108 analyzer.

The starting materials, $AgNO_3$, AgOTf, and $AgClO_4$, were purchased from Aldrich, and 2-aminomethylpyridine was purchased from Lancaster.

Preparation of 2-Aminomethylpyridinedipropionitrile (2-AMPDPN).[11] A mixture of 2-aminomethylpyridine (1.01 mL, 1 mmol), excess acrylonitrile (10 mL), and glacial acetic acid (0.11 mL, 2 mmol) was heated at reflux for 24 h. The volatile material was removed in vacuo. The viscous residue was extracted with chloroform (20 mL). The solution was then treated with saturated ammonia solution (10 mL). The organic phase was separated and washed with water (10 mL). Pure 2-AMPDPN was isolated by a chromatographic workup (eluent, chloroform, $R_f = 0.42$) in 88% yield. ^1H NMR ($CDCl_3$): δ 8.53 (d, $J = 8.24$ Hz, 1H, *aromatic proton*), 7.25 (dd, $J = 8.24$ Hz, $J = 7.82$ Hz, 1H, *aromatic proton*), 7.55 (d, $J = 7.82$ Hz, 1H, *aromatic proton*), 7.25 (m, 1H, *aromatic proton*), 3.92 (s, 2H, CH_2), 2.99 (t, $J = 6.60$ Hz, 2H, CH_2), 2.52 (t, $J = 6.60$ Hz, 2H, CH_2).

Preparation of [Ag(2-AMPDPN)](OTf)·CH_3CN (1). To a stirred THF (10 mL) solution of AgOTf (0.36 g, 1.4 mmol) was added 2-AMPDPN (0.3 g, 1.4 mmol) dissolved in THF (10 mL). A colorless precipitate was formed, and the crude product was separated by filtration. Recrystallization from acetonitrile/ether gave pure **1** in 92% yield. Mp: 148 °C. ^1H NMR (CD_3CN): δ 8.60 (d, $J = 5.12$ Hz, 1H, *aromatic proton*), 7.96 (dt, $J = 7.80$ Hz, $J = 1.50$ Hz, 1H, *aromatic proton*), 7.60 (d, $J = 7.8$ Hz, 1H, *aromatic proton*), 7.49 (m, 1H, *aromatic proton*), 3.93 (s, 2H, CH_2), 2.96 (t, $J = 7.20$ Hz, 2H, CH_2), 2.65 (t, $J = 7.20$ Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 157.67, 151.92, 140.19, 126.32, 125.04, 120.24, 60.54, 49.50, 15.83. IR (KBr pellet; cm^{-1}): 3150 (w), 2858 (w), 2255 (m), 1599 (w), 1475 (w), 1438 (w), 1253 (s), 1164 (s), 1031 (s), 970 (w), 794 (w), 761 (m), 638 (s), 574 (w), 518 (m), 428 (m). Anal. Calcd for $C_{15}H_{17}F_3N_5O_3SAg$: C, 35.17; H, 3.35. Found: C, 34.64; H, 3.21.

Preparation of [Ag(2-AMPDPN)ClO_4] (2). Compound **2** was prepared using the same procedure as that described for **1**. Pure **2** was isolated by recrystallization from CH_3CN/Et_2O at −5 °C in 86% yield. Mp: 210 °C (dec). ^1H NMR (CD_3CN): δ 8.55 (d, $J = 4.84$ Hz, 1H, *aromatic proton*), 7.90 (dt, $J = 7.80$ Hz, $J = 1.50$ Hz, 1H, *aromatic proton*), 7.55 (d, $J = 7.80$ Hz, 1H, *aromatic proton*), 7.43 (m, 1H, *aromatic proton*), 3.87 (s, 2H, CH_2), 2.92 (t, $J = 6.90$ Hz, 2H, CH_2), 2.60 (t, $J = 6.90$ Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 158.06, 151.55, 139.81, 126.01, 124.82, 120.17, 60.51, 49.75, 16.15. IR (KBr pellet; cm^{-1}): 3010 (w), 2275 (m), 2019 (w), 1369 (w), 1083 (s), 935 (w), 769 (w), 628 (s), 464 (w), 424 (w). Anal. Calcd for $C_{12}H_{14}N_4ClO_4Ag$: C, 34.18; H, 3.34. Found: C, 33.92; H, 3.24.

Preparation of [Ag(2-AMPDPN)NO_3] (3). Compound **3** was prepared using the same procedure as that described for **1**. Pure **3** was isolated by recrystallization from CH_3CN/Et_2O in 75% yield. Mp: 119 °C. ^1H NMR (CD_3CN): δ 8.60 (d, $J = 4.80$ Hz, 1H, *aromatic proton*), 7.93 (dt, $J = 7.80$ Hz, $J = 1.50$ Hz, 1H, *aromatic proton*), 7.58 (d, $J = 7.80$ Hz, 1H, *aromatic proton*), 7.46 (m, 1H, *aromatic proton*), 3.93 (s, 2H, CH_2), 2.94 (t, 2H, CH_2), 2.65 (t, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_3CN): δ 158.00, 151.92, 139.98, 126.15, 124.91, 120.23, 60.69, 49.74, 15.99. IR (KBr pellet; cm^{-1}): 3015 (w), 2854 (w), 2248 (m), 1645 (w), 1596 (w), 1568 (w), 1384 (s), 1134 (m), 1097 (w), 1039 (m), 962 (w), 867 (m), 825 (m), 545 (w), 499 (w), 407 (w). Anal. Calcd for $C_{12}H_{14}N_5O_3Ag$: C, 37.51; H, 3.66. Found: C, 37.22; H, 3.48.

X-ray Crystallography. Details of the crystal data and a summary of the intensity data collection parameters for **1**, **2**, and **3** are given in Table 1. The crystals of **1**, **2**, and **3** were grown from an acetonitrile/ether solution at −5 °C. The crystals of **1**, **2**, and **3** were attached to glass fibers and mounted on a Bruker SMART diffractometer equipped with a graphite monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation source and a CCD detector; 45 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. All data collections were performed at room temperature.

The raw data were processed to give structure factors using the SAINT program. Each structure was solved by direction methods and refined by full matrix least squares against F^2 for all data using SHELXTL software. All non-hydrogen atoms in compounds **1**, **2**, and **3** were anisotropically refined. All other hydrogen atoms were included in the calculated positions.

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Supporting Information Available: Tables listing crystallographic information, atomic coordinate and U_{eq} values, anisotropic thermal parameters, and intramolecular bond distances, angles, and torsion angles for **1**, **2**, and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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