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Synthesis, Structure, and Thermal Stability of Silver(I) Coordination Polymers with Bis(pyridyl) Ligands Linked by an Aromatic Sulfonamide: One-Dimensional-Straight Chain, One-Dimensional-Columnar with Helical Components, and Two-Dimensional-Layer Network Structures

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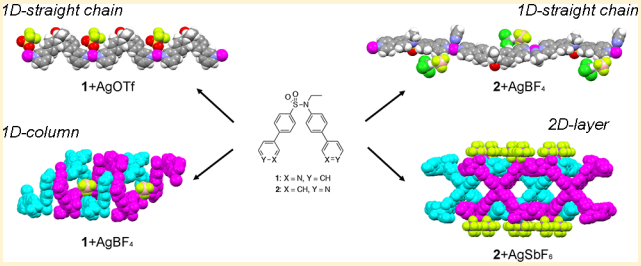
Supporting Information

ABSTRACT: Three different types of coordination polymers, one-dimensional (1D) straight chain, 1D-columnar structure, and two-dimensional (2D) layer structure, have been prepared by the complexation of Ag(I) ions with bis(pyridyl) ligands linked by an aromatic sulfonamides and structurally characterized by single-crystal X-ray diffraction and thermogravimetric analysis. Structural analyses showed that the complexation of the 3-pyridyl ligand with AgOTf and the complexation of the 4-pyridyl ligand with $AgBF_4$ in $CHCl_3$/CH_3CN resulted in the formation of 1D straight-chain polymers. In the complexation of the 3-pyridyl ligand with $AgBF_4$ in $CHCl_3$/CH_3CN, the resulting continuous 1D columnar coordination polymers were formed containing a racemic mixture of left- and right-handed helices. Furthermore, the 2D-layer structure was constructed by the complexation of a 4-pyridyl ligand with $AgSbF_6$ in $CHCl_3$/MeOH.



INTRODUCTION

Coordination polymers (CPs) and metal−organic frameworks (MOFs) have attracted considerable attention because of their potential applications in gas storage,[1] selective heterogeneous catalysis,[2] sensing,[3] molecular electronics,[4] and magnetic devices.[5] The preparation of CPs or MOFs can be controlled by many factors, including the metal/ligand stoichiometry, as well as the temperature, concentration, and the type of counterion used during their preparation process. The metal ions used for the construction of these materials have also received considerable attention in relation to their coordination geometry.[6] For example, CPs employing Ag(I) ions have been widely used because of their variable coordination number and flexible geometry and properties.[7] Numerous multidentate organic ligands have been designed to vary a range of different factors, including the number and direction of the coordination sites, the incorporation of N- or O-donor groups, and the size, shape, and rigidity of the linker units.[8] A variety of multidentate organic ligands have been used for the construction of CPs and MOFs,[9] and simple bidentate ligands have been prepared through the formation of connections between metal-coordination sites and a linker. Linker units play a crucial role in the rational design of coordination networks and frameworks within specific structures. For example, aromatic sulfonamides represent good building blocks for the construction of helical structures[10] because they exist in a *synclinal* conformation that orientates the aromatic rings at both ends of the linker in the same direction with a twist. Previously, we revealed that the complexation of bis(pyridyl) bidentate ligands linked by an aromatic sulfonamide with Ag(I) ions resulted in the formation of infinite one-dimensional (1D) straight and helical chains.[10c] Bis(pyridyl) ligands linked by an aromatic sulfonamide are unique ligands because of the flexibility of the S−N bond and the twisted *synclinal* conformation of the sulfonamide. On the basis of these factors and as an extension of our previous work, herein we focus on the elongation of the sulfonamide linker to construct columnar or layer complexes. In this paper, we report the synthesis of the elongated bis(pyridyl) ligands **1** and **2**, and the complexation of these ligands with Ag(I) salts, as well as the crystal structures and thermal stability properties of the resulting complexes. The bis(pyridyl) ligands were elongated using a Suzuki-Miyaura coupling reaction. The complexes **1a**, **1b**, **2a**, and **2b** were formulated as $[Ag(\mathbf{1})OTf]_n$ (**1a**), $[Ag(\mathbf{1})]_n{\cdot}nBF_4$ (**1b**), $[Ag(\mathbf{2})CH_3CN]_n{\cdot}nBF_4{\cdot}nCHCl_3$ (**2a**), and $[Ag(\mathbf{2})]_n{\cdot}nSbF_6{\cdot}nCH_4O$ (**2b**). In complexes **1a** and **2a**, infinite 1D straight chains with a T-shaped coordination geometry about the Ag(I) centers were formed by the reaction of ligand **1** or **2** with Ag(I) salts in $CHCl_3$/CH_3CN. A continuous 1D columnar coordination polymer composed of a racemic mixture of left- and

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right-handed helices was formed by the reaction of ligand **1** with $AgBF_4$ in $CHCl_3/CH_3CN$. Layered coordination polymers were constructed by the complexation of ligand **2** with $AgSbF_6$ in $CHCl_3$/MeOH. The Ag(I) centers in these polymers possessed two different types of coordination geometries, with each ion coordinated to two or four pyridyl groups of the ligand **2**. The pairs of homochiral coordination polymers were associated through π/π and CH/O interactions to form racemic two-dimensional (2D) layer structures, and the 2D layer structures associated to form a three-dimensional (3D) network.

EXPERIMENTAL SECTION

Synthesis of *N*-Ethyl-*N*-(4-(3-pyridyl)phenyl)-4-(3-pyridyl)-benzenesulfonamide (1). Tetrakis(triphenylphosphine)palladium (0) (0.23 g, 0.2 mmol) and Cs_2CO_3 (1.63 g, 5 mmol) were added to a solution of *N*-(4-bromophenyl)-*N*-ethyl-bromobenzenesulfonamide (0.42 g, 1 mmol) and 3-pyridineboronic acid (0.59 g, 4.78 mmol) in toluene (7.5 mL) and methanol (2.5 mL), and the resulting mixture was heated at 100 °C for 6 h. The mixture was cooled to room temperature and filtered through Celite. The filtrate was then collected and distilled to dryness under reduced pressure to give the crude product, which was purified by silica gel column chromatography (eluent $CHCl_3$/MeOH = 20:1 − v/v) to give **1** in 94% yield as white powder (0.39 g, 0.94 mmol): mp 133−135 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.86 (dd, J = 16.4, 2.4 Hz, 2H), 8.63 (td, J = 1.6, 4.7, 22.4 Hz, 2H), 7.89 (m, 2H), 7.76 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.41 (m, 2H), 7.23 (d, J = 8.4 Hz, 2H), 3.70 (q, J = 7.2 Hz, 2H), 1.16 (t, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 149.6 (CH), 148.8 (CH), 148.3 (CH), 148.2 (CH), 142.1 (C_q), 138.6 (C_q), 137.9 (C_q), 137.4 (C_q), 135.5 (C_q), 134.8 (C_q), 134.5 (CH), 134.3 (CH), 129.4 (CH), 128.4 (CH), 127.7 (CH), 123.7 (CH), 123.6 (CH), 45.60 (CH_2), 14.02 (CH_3); IR (solid state, ATR): ν (cm^{-1}) 3028 (w), 1600 (m), 1517 (m), 1347 (s), 1163 (s); FAB-MS: m/z 416.1 $[M + H]^+$; Elemental Analysis Calc. for $C_{24}H_{21}N_3O_2S$: C, 69.37; H, 5.09; N, 10.11. Found: C, 69.21; H, 4.85; N, 9.94.

Synthesis of *N*-Ethyl-*N*-(4-(4-pyridyl)phenyl)-4-(4-pyridyl)-benzenesulfonamide (2). Tetrakis(triphenylphosphine)palladium (0) (0.46 g, 0.4 mmol) and Cs_2CO_3 (3.26 g, 10 mmol) were added to a solution of *N*-(4-bromophenyl)-*N*-ethyl-bromobenzenesulfonamide (1.00 g, 2.39 mmol) and 4-pyridineboronic acid (1.30 g, 10 mmol) in toluene (15 mL) and methanol (5 mL), and the resulting mixture was heated at 100 °C for 6 h. The mixture was cooled to room temperature and filtered through Celite. The filtrate was then collected and distilled to dryness under reduced pressure to give the crude product, which was purified by silica gel column chromatography (eluent $CHCl_3$/MeOH = 20:1) to give **2** in 95% yield as white powder (0.945 g, 2.27 mmol): mp 171−173 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.69 (dd, J = 6.0, 20.4 Hz, 2H), 7.75 (s, 4H), 7.63 (d, J = 8.4 Hz, 2H), 7.53 (dd, J = 1.6, 4.8 Hz, 2H), 7.50 (dd, J = 1.6, 4.8 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 3.71 (q, J = 7.2 Hz, 2H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 150.5 (CH), 150.3 (CH), 147.0 (C_q), 146.3 (C_q), 142.3 (C_q), 139.4 (C_q), 138.7 (C_q), 137.6(C_q), 129.3 (CH), 128.3 (CH), 127.6 (CH), 127.4 (CH), 121.6 (CH), 121.4 (CH), 45.55 (CH_2), 13.98 (CH_3) ppm; IR (solid state, ATR): ν (cm^{-1}) 3020 (w), 1595 (m), 1486 (m), 1348 (s), 1172 (s); FAB-MS: m/z 416.2 $[M + H]^+$; Elemental Analysis Calc. for $C_{24}H_{21}N_3O_2S$: C, 69.37; H, 5.09; N, 10.11. Found: C, 69.08; H, 4.95; N, 9.99.

Synthesis of *N*-Ethyl-*N*-(4-(3-pyridyl)phenyl)-4-(3-pyridyl)-benzenesulfonamide·AgOTf (1a). AgOTf was added to a solution of **1** in $CHCl_3/CH_3CN$ (1:1 − v/v). After several minutes of stirring, the desired complex precipitated as a white solid, which was collected by filtration and dried under vacuum at 80 °C. Elemental Analysis Calcd. for $C_{24}H_{21}N_3O_2S{\cdot}CF_3O_2SAg{\cdot}0.40CHCl_3{\cdot}0.20CH_3CN$: C, 42.54; H, 3.04; N, 6.15. Found: C, 42.82; H, 2.90; N, 5.95.

Synthesis of *N*-Ethyl-*N*-(4-(3-pyridyl)phenyl)-4-(3-pyridyl)-benzenesulfonamide·$AgBF_4$ (1b). This material was prepared in a similar manner to that described above for **1a** using $AgBF_4$ and **1** in $CHCl_3/CH_3CN$ (1:1 − v/v). Elemental Analysis Calcd. for $C_{24}H_{21}N_3O_2S{\cdot}0.80AgBF_4{\cdot}0.20CHCl_3$: C, 48.84; H, 3.59; N, 7.06. Found: C, 48.54; H, 3.61; N, 6.76.

Synthesis of *N*-Ethyl-*N*-(4-(4-pyridyl)phenyl)-4-(4-pyridyl)-benzenesulfonamide·$AgBF_4$ (2a). This material was prepared in a similar manner to that described above for **1a** using $AgBF_4$ and **2** in $CHCl_3/CH_3CN$. Elemental Analysis Calcd. for $C_{24}H_{21}N_3O_2S{\cdot}0.75AgBF_4{\cdot}0.25CHCl_3$: C, 49.25; H, 3.62; N, 7.11. Found: C, 49.17; H, 3.58; N, 6.82.

Synthesis of *N*-Ethyl-*N*-(4-(4-pyridyl)phenyl)-4-(4-pyridyl)-benzenesulfonamide·$AgSbF_6$ (2b). This material was prepared in a similar manner to that described above for **1a** using $AgSbF_6$ and **2** in $CHCl_3$/MeOH (1:1 − v/v). Elemental Analysis Calcd. for $C_{24}H_{21}N_3O_2S{\cdot}AgSbF_6$: C, 37.97; H, 2.79; N, 5.54. Found: C, 38.20; H, 2.84; N, 5.40.

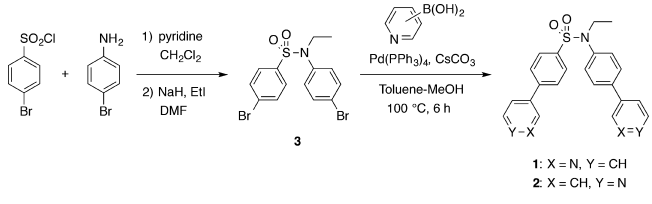
Crystallization. Crystals of the complexes **1a**, **1b**, **2a**, and **2b** were obtained from each reaction solution. The slow evaporation of the solvents afforded diffraction quality crystals.

Measurement. X-ray data of the crystals were collected on a CCD diffractometer using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation. Data collections for the crystals were carried out at low temperature using liquid nitrogen. The crystal structures were solved by direct methods SHELXS-97 and refined by full-matrix least-squares SHELXL-97.[11] All of the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included at their calculated positions. Thermogravimetric analyses of the coordination polymers were performed on a Rigaku Thermo plus TG8120 apparatus. Powder samples of the complexes were loaded into alumina pans and heated at a ramp rate of 10 °C min^{-1} from room temperature to 500 °C under a N_2 atmosphere (20 mL min^{-1}).

RESULTS AND DISCUSSION

The bis(pyridyl) ligands containing a sulfonamide (**1** and **2**) were prepared by the Suzuki-Miyaura coupling reaction of a bisbromobenzene sulfonamide **3** with a pyridine boronic acid (Scheme 1). The crystal data and conformational parameters of

Scheme 1. Synthesis of the Bidentate Ligands 1 and 2



1 and **2** are shown in Tables 1 and 2, respectively. The torsion angles of the sulfonamide moiety [C(Ph)−S−N−C(Ph)] are 81.3(2) and 75.9(2)°, respectively (Table 2), and therefore the sulfonamide bonds of both of the sulfonamides were *synclinal* (Figure 1).

The reaction of equimolar amounts of the sulfonamide ligands (**1** and **2**) with Ag(I) salts gave the corresponding complexes $[AgLOTf]_n$ (L = **1** (**1a**)), $[AgL]_n{\cdot}nBF_4$ (L = **1** (**1b**)), $[AgLCH_3CN]_n{\cdot}nBF_4{\cdot}nCHCl_3$ (L = **2** (**2a**)), and $[AgL]_n{\cdot}nSbF_6$ nCH_4O (L = **2** (**2b**)) (Figure 1). Complex **1a** was obtained from the reaction of ligand **1** with AgOTf in a mixture of CH_3CN and $CHCl_3$, whereas complexes **1b** and **2a** were obtained by the reaction of ligands **1** and **2** with $AgBF_4$ in a mixture of CH_3CN and $CHCl_3$. Complex **2b** was obtained by the reaction of ligand **2** with $AgSbF_6$ in a mixture of $CHCl_3$ and MeOH. The crystals of the complexes were obtained from each reaction solution directly. The crystal data and conformational parameters of **1a**, **1b**, **2a**, and **2b** are shown in Tables 1 and 2, respectively. The sulfonamide bonds of **1a** and **2b** were found to be *synclinal*, and the torsion angles of the sulfonamide moiety were 75.5(8) and 62.4(8)°,

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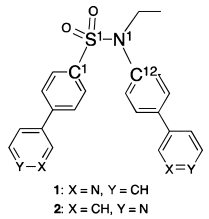
Table 1. Crystallographic Data for Ligands 1 and 2 and Complexes 1a, 1b, 2a, and 2b

	1	2
formula	$C_{24}H_{21}N_3O_2S$	$C_{24}H_{21}N_3O_2S$
formula weight	415.50	415.50
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$
a (Å)	20.743(3)	18.845(3)
b (Å)	5.7353(7)	18.777(3)
c (Å)	18.342(2)	12.610(2)
α (°)	90	90
β (°)	112.779(1)	115.589(2)
γ (°)	90	90
V (Å^3)	2011.9(4)	4024.6(11)
Z	4	8
D_{calc} (Mg/m^3)	1.372	1.371
T (K)	120	120
μ (mm^{-1})	0.188	0.188
R_1, wR_2 [$I > 2\sigma(I)$]	0.0448, 0.0959	0.0465, 0.1071
R_1, wR_2 (all data)	0.0691, 0.1068	0.0746, 0.1211
CCDC number	959267	959270

	1a	1b	2a	2b
formula	$C_{25}H_{21}N_3O_5S_2F_3Ag$	$C_{24}H_{21}N_3O_2BF_4SAg$	$C_{27}H_{25}N_4O_2SBF_4Cl_3Ag$	$C_{49}H_{42}N_6O_6S_2SbF_6Ag$
formula weight	672.44	572.18	770.60	1272.56
crystal system	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$C2/c$	$P2_1/c$	$Ibam$
a (Å)	11.094(8)	34.543(9)	21.370(4)	12.277(4)
b (Å)	11.531(8)	8.342(2)	19.497(4)	22.291(7)
c (Å)	11.635(8)	15.572(4)	7.470(1)	45.968(14)
α (°)	87.702(10)	90	90	90
β (°)	63.717(8)	92.096(4)	91.055(3)	90
γ (°)	79.934(9)	90	90	90
V (Å^3)	1312.8(16)	4474(2)	3111.9(10)	12580(7)
Z	2	8	4	8
D_{calc} (Mg/m^3)	1.701	1.699	1.645	1.344
T (K)	120	120	150	120
μ (mm^{-1})	0.990	1.040	1.029	1.020
R_1, wR_2 [$I > 2\sigma(I)$]	0.0857, 0.2112	0.0535, 0.0956	0.0931, 0.2614	0.1116, 0.3032
R_1, wR_2 (all data)	01327, 0.2429	0.1074, 0.1143	0.1609, 0.3469	0.2131, 0.3412
CCDC number	959268	959269	959271	959272

Table 2. Conformational Parameters of the Sulfonamides 1 and 2, and the Complexes 1a, 1b, 2a, and 2b



1: X = N, Y = CH
2: X = CH, Y = N

		1		2
torsion angle (deg) C^1–N^1–S^1–C^{12}		81.3(2)		75.9(2)
	1a	**1b**	**2a**	**2b**
torsion angle (deg) C^1–N^1–S^1–C^{12}	75.5(8)	92.9(6)	152.0(5)	62.4(8)

respectively. In contrast, the sulfonamide bonds of **1b** and **2a** were determined to be *anticlinal* and *antiperiplanar*, respectively, and the torsion angles of the sulfonamide moieties in these complexes were 92.9(6) and 152.0(5)°, respectively.

The crystals of complex **1a** crystallized in a triclinic system with space group $P\bar{1}$. The structure of complex **1a** was shown to be an enantiopure infinite 1D coordination polymer, where ligand **1** was connected by Ag(I) ions. The Ag(I) centers had a T-shaped coordination geometry, with each of the ions coordinated to two pyridyl groups of ligand **1** as well as a trifluoromethanesulfonate anion (Figure 2a). Both enantiomers of the 1D chain associated to form a racemic 1D chain through a Ag/Ag interaction (Figure 2b). The Ag···Ag distance of 3.38(1) Å is longer than those of other complexes[12] but still

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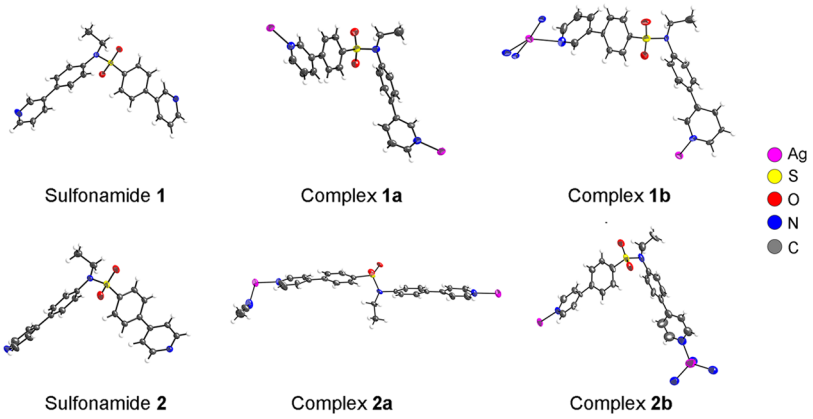

Figure 1. Thermal ellipsoid models of the crystal structures of the sulfonamide ligands **1** and **2**, and those of the corresponding Ag(I) complexes **1a**, **1b**, **2a**, and **2b**. The ellipsoids of all non-hydrogen atoms are drawn at the 50% probability level while isotropic hydrogen atoms are represented by spheres of arbitrary size. The counteranions and solvent molecules are omitted for clarity.

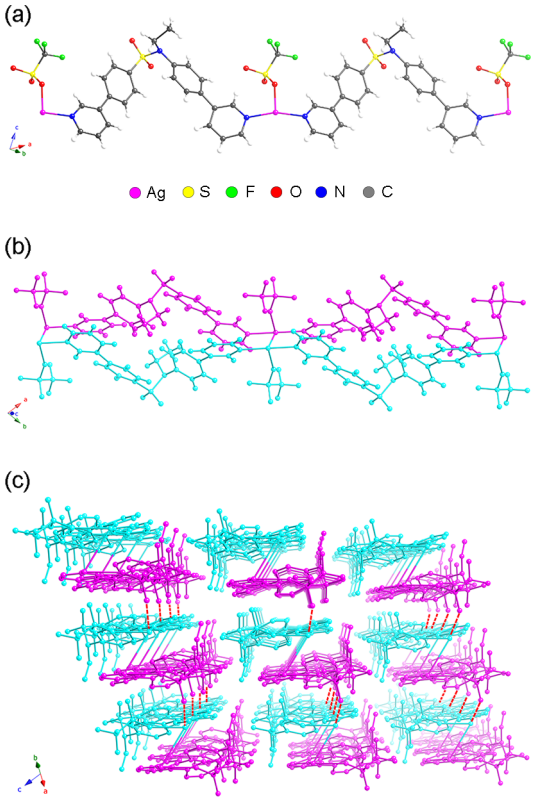

Figure 2. Crystal structure of the Ag(I) complexes of **1a** as ball and stick models. (a) Homochiral 1D chain. (b) The pair of enantiomeric 1D chains. (c) 3D network structure accomplished though CH/O and Ag/O interactions. The different enantiomeric chains are shown in cyan and magenta. The red-dotted lines represent the Ag/O interactions.

within the summed van der Waals radii of two Ag atoms (3.44 Å),[12e] and this indicates the Ag···Ag interaction in **1a** is very weak. The racemic 1D chains extended along the *b* axis through hydrogen-bonding interactions to form 2D layers with a C···O distance of 3.41(2) Å (Figure 2c). Furthermore, the 2D layers stacked to form a three-dimensional (3D) network through intermolecular Ag/O interactions between Ag(I) ions and the oxygen atom of the sulfonamides in **1a** with a Ag···O distance of 2.901(9) Å (Figure 2c).

The crystals of complex **1b** crystallized in a monoclinic system with space group *C*2/*c*. The structure of complex **1b** was shown to be a 1D columnar coordination polymer, where the ligand **1** molecules were connected by Ag(I) ions. The columnar structure was composed of a racemic mixture of left- and right-handed helical chain. Both of the enantiomers of the sulfonamide ligands **1** coordinated to the same Ag(I) ion centers to form a racemic complex. The Ag(I) centers possessed a four coordinate geometry (Figure 3a). The inner space of the columnar structure contained BF_4 anions, which were connected to the ligand through CH/F interactions with a C···F distance of 3.41(1) Å (Figure 3b). The racemic columns were further associated through Ag/F interactions between the fluorine atoms of the tetrafluoroborate and the Ag(I) ions of the neighboring columns (with a Ag···F distance of 3.152(6) Å, Figure 3c), as well as intermolecular multiple CH/O interactions (with a C···O distance in the range of 3.196(9)−3.323(9) Å, Figure 3c) to form a 3D network.

The crystals of complex **2a** crystallized in a monoclinic system with space group $P2_1/c$. The structure of complex **2a** was shown to be an infinite 1D coordination polymer, where the ligand **2** molecules were connected by Ag(I) ions in an antiperiplanar conformation. The Ag(I) centers had a T-shaped coordination geometry, with each ion coordinated to the two pyridyl groups of ligand **1** as well as an acetonitrile molecule. In this coordination polymer, both of the enantiomers of ligand **2** constructed a 1D coordination polymer (Figure 4a). The racemic 1D polymers extended along the *b* axis through CH/O interactions to form a 2D layer with a C···O distance of 3.43(1) Å (Figure 4b). Furthermore, the 2D layers stacked to form a 3D network through intermolecular CH/O interactions with C···O distances of 3.32(1) and 3.40(1) Å (Figure 4c).

The crystals of complex **2b** crystallized in an orthorhombic system with space group *Ibam*. The structure of complex **2b** was shown to be a homochiral infinite coordination polymer, where the ligand **2** molecules were connected by Ag(I) ions with two coordination geometries. One of the Ag(I) centers had a tetrahedral coordination geometry, where the ions were coordinated to the four pyridyl groups of two ligand **2** molecules. The other coordination geometry had a linear coordination geometry, where the ions were coordinated to the two pyridyl groups of a ligand **2** molecule (Figure 5a). An interesting feature of the structure of **2b** was that pairs of homochiral coordination polymers were associated through

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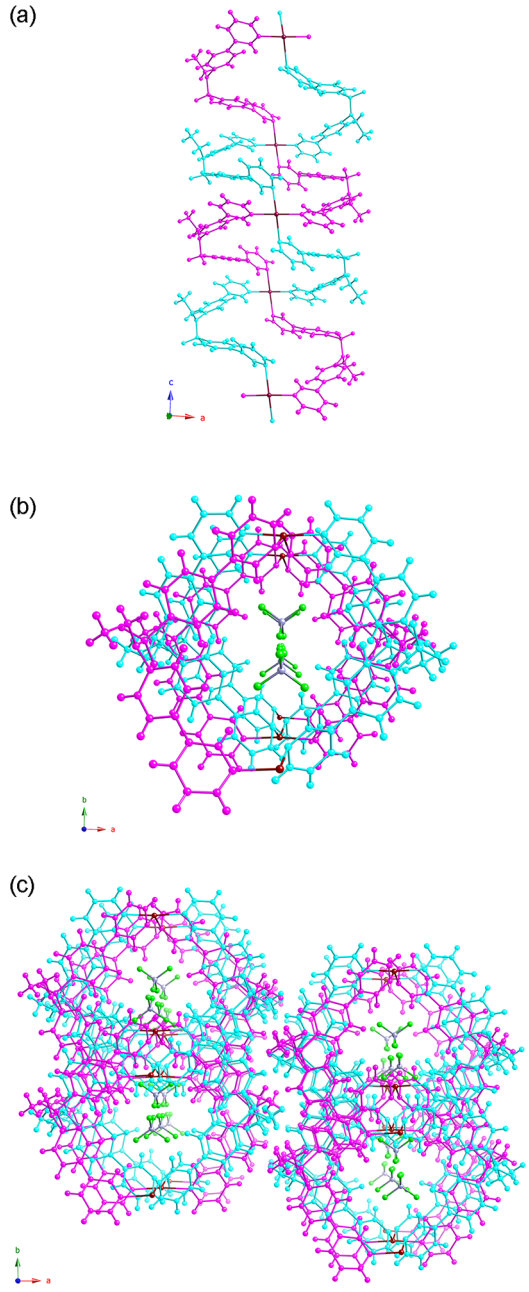

Figure 3. Crystal structure of the Ag(I) complexes of **1b** as ball and stick models. (a) Racemic helical 1D chain, with the counteranions omitted for clarity. (b) Columnar structure containing BF_4 anions. (c) 3D network structure accomplished through CH/O interactions. The different enantiomeric chains are shown in cyan and magenta.

π/π and CH/O interactions to form a 2D layer structure, which resulted in the crystal possessing no optical activity (Figure 5b). Furthermore, the 2D layer structures associated to form a 3D network (Figure 5c). The SbF_6 anions occupied the space between the 2D columnar structures.

To evaluate the thermal stability properties of complexes **1a**, **1b**, **2a**, and **2b**, their thermal behaviors were investigated under a nitrogen atmosphere by thermogravimetric analysis (TGA) (Figure 6). The TGA curves of infinite 1D coordination polymers **1a** and **2a** showed that their frameworks were stable up to 258 and 250 °C, respectively. Beyond these temperatures, the framework began to decompose. The TGA curve for complex **1b** contained one distinct weight loss event in the

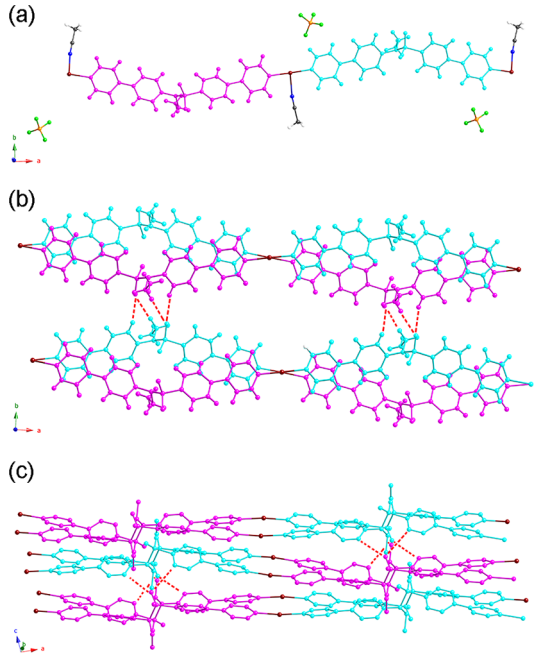

Figure 4. Crystal structures of the Ag(I) complexes of **2a** as ball and stick models. (a) Racemic 1D chain with the chloroform molecules omitted for clarity. (b) 2D layer structure accomplished through CH/O interactions. (c) 3D network structure accomplished through CH/O interactions. The different enantiomeric chains are shown in cyan and magenta. The red-dotted lines represent the CH/O interactions.

range of 50−260 °C, corresponding to the loss of free water molecules per formula unit (exptl. 5.5%; calcd. 5.5%). The TGA curve of complex **2b** also contained only one distinct weight loss event, which corresponded to the loss of one lattice methanol molecule (exptl. 14.8%; calcd, 15.0%) in the range of 50−100 °C. This complex then decomposed at 300 °C.

Taken together, these results show that ligands **1** and **2**, which can be considered as flexible building blocks with the sulfonamide moiety, can combine as Ag(I) complexes to form coordination polymers (i.e., **1a**, **1b**, **2a**, and **2b**) through self-assembly. In these complexes, the ligands have flexibility arising from the twisting about the C−S−N−C units, and the Ag(I) centers have several different stereochemistries. A comparison of some of the structural features is given in Table 3. The reaction of the ligand **1** with AgOTf gave the 1D straight chain complex **1a**, whereas its reaction with $AgBF_4$ gave the 1D columnar complex **1b**. The major difference between complexes **1a** and **1b** was the Ag(I) coordination geometry. In general, it has been reported that out of about 3300 solid-state structure of Ag(I) complexes, 24% are two-coordinate, 23% are three-coordinate, and 44% are four-coordinate.[7a] When a strongly coordinating TfO^- anion is used,[7b] the anions coordinate to Ag(I) ions through one of the oxygen atoms, and the Ag(I) center of **1a** forms a three-coordinated T-shaped geometry. In contrast, the BF_4^- anion is a weaker coordinating anion, and the Ag(I) atoms of **1b**, which are all connected to four ligands, can then also be described as adopting a four-coordinated square planar geometry.[7h,j] The sulfonamide bonds of **1a** and **1b** were *synclinal* and *anticlinal*, and the torsion angles of the C−S−N−C bonds were 75.5(8) and 92.9(6) °, respectively (Table 2). The reaction of the ligand **2** with $AgBF_4$ gave the 1D straight chain complex **2a**, whereas its reaction with $AgSbF_6$ gave the 2D layer complex **2b**. The sulfonamide bonds of **2a** and **2b**

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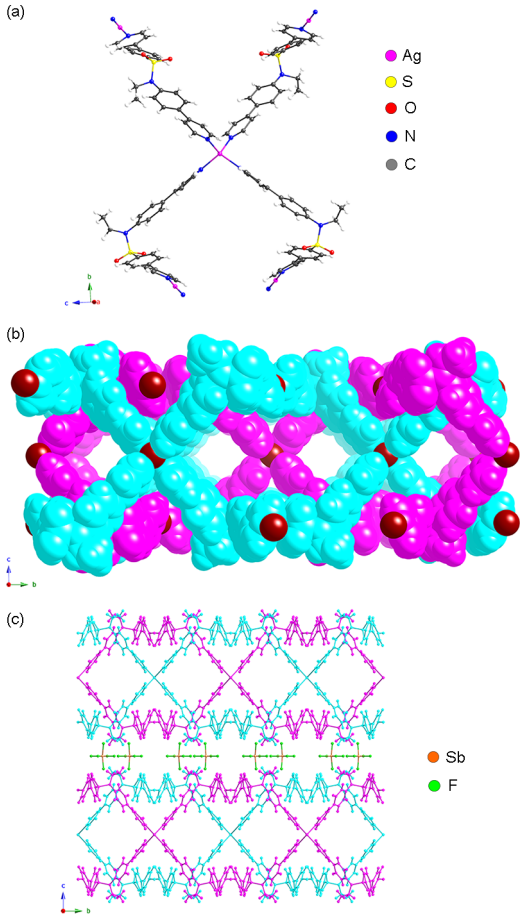

Figure 5. Crystal structures of the Ag(I) complexes of **2b**. (a) Homochiral infinite coordination polymer shown as a ball and stick model with the counteranions and solvent molecules omitted for clarity. (b) 2D layer structure as a space-filling model with the counteranions and solvent molecules omitted for clarity. (c) 3D network structure as a ball and stick model with the solvent molecules omitted for clarity. The different enantiomeric chains are shown in cyan and magenta.

were *antiperiplanar* and *synclinal*, and the torsion angles of their C–S–N–C bonds were 152.0(5) and 62.4(8)°, respectively (Table 2). In the 1D straight chain of **2a**, the Ag(I) had a T-shaped coordination geometry. The two pyridyl groups of the ligand as well as an acetonitrile molecule were coordinated to the Ag(I) center. In the 2D layer structure of **2b**, the noncoordinating SbF_6^- anions not only acted as the counteranions to balance the charge but also had a spatial templating effect in building up the network.[7c] Moreover, there were two different Ag(I) centers in complex **2b**. One of these centers had an essentially linear N–Ag–N bond angle (N–Ag–N = 178.8(5)°) and was two-coordinate, whereas the other center had a tetrahedral geometry (N–Ag–N = 100.7(2), 107.7(8), and 120.8(14)°).

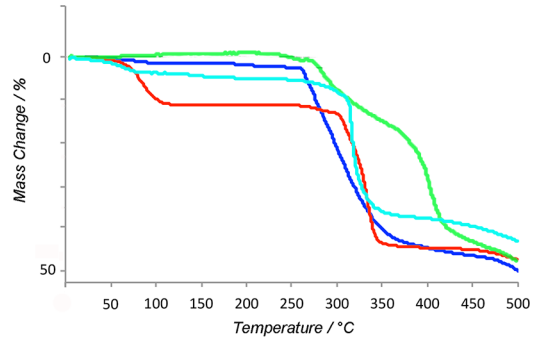

Figure 6. Thermogravimetric analysis curves for complexes **1a** (green), **1b** (blue), **2a** (cyan), and **2b** (red).

CONCLUSION

We have demonstrated that bidentate ligands containing tertiary sulfonamides represent a versatile building block for the construction of coordination polymers. The sulfonamides used in the current study were essentially *synclinal* in terms of their conformation, except when the counteranion was replaced by BF_4 and the sulfonamides then existed in an *anticlinal* or *antiperiplanar* conformation. The mixing of the ligands **1** or **2** with different Ag(I) salts yields the corresponding complexes $[AgLOTf]_n$ (L = **1** (**1a**)), $[AgL]_n{\cdot}nBF_4$ (L = **1** (**1b**)), $[AgLCH_3CN]_n{\cdot}nBF_4{\cdot}nCHCl_3$ (L = **2** (**2a**)), and $[AgL]_n{\cdot}nSbF_6{\cdot}nCH_4O$ (L = **2** (**2b**)). In the crystals of complexes **1a** and **2a**, infinite 1D straight chains with a T-shaped coordination geometry about the Ag(I) centers were formed by the reaction of ligands **1** or **2** with Ag(I) salts in $CH_3CN/CHCl_3$. A continuous 1D columnar coordination polymer containing a racemic mixture of left- and right-handed helices was formed from the crystals of complex **1b**. Furthermore, the formation of a layered coordination polymer consisting of a racemic mixture of left- and right-handed polymers was observed from the crystals of complex **2b**. The self-assembly of sulfonamide ligands by metal coordination is a suitable approach not only for the development of helical metal–organic frameworks but also for the organization of ordered arrangements into interesting 2D/3D networks. The construction of optically pure left- or right-handed 1D helical polymers via the introduction of chiral functional groups on the nitrogen atom of the sulfonamide ligand is currently under investigation in our laboratory.

ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectroscopic data and all crystallographic data and crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

Table 3. Comparison of Some of the Structural Features of Complexes 1a, 1b, 2a, and 2b

	1a	1b	2a	2b
shape of CPs	1D-straight	1D-columnar	1D-straight	2D-layer
conformation of ligand	*synclinal*	*anticlinal*	*antiperiplanar*	*synclinal*
coordination geometry (Ag(I))	T-shape	square planar	T-shape	tetrahedral, straight
counteranion	OTf	BF_4	BF_4	SbF_6
N(Py)–Ag–N(Py)/°	162.5(3)	143.8(2), 174.2(2)	173.2(3)	100.7(2), 107.7(8), 120.8(14), 178.8(5)
N(Py)–Ag–N(CN)/°			90.5(3), 94.5(3)	
N(Py)–Ag–O(OTf)/°	91.5(4), 101.9(4)			

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Notes

The authors declare no competing financial interest.

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