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Silver(I) 3-Aminomethylpyridine Complexes, Part 2: Effect of Ligand Ratio, Hydrogen Bonding, and π-Stacking with an Interacting Anion

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Reaction of 3-aminomethylpyridine (3-amp) with silver(I) salts of triflate (OTf$^-$) and trifluoroacetate (tfa$^-$) produce a variety of multidimensional coordination networks whose structures depend on the stoichiometry of the components present. A 1:1 ratio of 3-amp to AgX produces a linear polymer, **1**, when X = tfa$^-$ and a planar sheet, **2**, when X = OTf$^-$. Addition of a second equivalent of ligand increases the dimensionality of both structures by one to form a two-dimensional sheet, **3**, and a three-dimensional system, **4**, for their respective anions. Addition of 2,2′-bipyridine (bipy) to solutions of any of the previous compounds produces the fixed-ratio complexes **5** (tfa$^-$ salt) and **6** (OTf$^-$ salt). The bipyridyl ligand halts the polymerization of compounds **1**–**4** by cutting the chain after each silver(I) link and forcing a 1:2:2 ratio of 3-amp to AgX to bipy. Compound **5**, however, remains polymeric in nature due to the closed-shell Ag–Ag interactions of the planar metals holding the monomers together. Differences between structures of each ratio stem from the differences in basicity and in the extra degree of H-bonding ability that the OTf$^-$ anion has over tfa$^-$.

Introduction

Advances that are being made in the field of crystal engineering have numerous applications including catalysis, molecular recognition, molecular sieving, separations, and optics.[1−4] A large portion of the knowledge associated with this area can be attributed to coordination studies of the group 11 metals, silver in particular.[5−18] Coordination complexes of silver are known to be alterable via several methods; typically by changes in ligand geometry, rigidity, or functionality or by modifications to the counterion or solvent system.[5,18−21] Despite the wealth of literature that is to be had on methods of forcing variations in coordination complexes, the technique of stoichiometry control is still relatively new.[22−25] Only recently have our group and a few others endeavored to give a comprehensive exploration on the ratio dependence of coordination complexes of variable-coordination metals.[12,26−29]

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Herein, we describe the remarkable changes in structure that can be achieved through variances in the relative amount of ligand to metal in the presence of the interacting anions triflate (OTf⁻) and trifluoroacetate (tfa⁻). Both of these anions have been previously shown to affect the supramolecular growth of coordination complexes of silver through direct interaction with the metal, as well as H-bonding when a suitable donor is present. In the present study, both the degree of interaction of the anion with the metal and the degree of H-bonding existing are themselves controlled by the ratio in which the heterobidentate 3-aminomethylpyridine (3-amp) ligand is present. The coordination sphere of the metal and, as a result, the overall structural growth are seen to be readily altered by the addition of a greater than stoichiometric amount of 3-amp ligand.

Experimental Section

General Procedures. All experiments were carried out under an argon atmosphere using a Schlenk line and standard Schlenk techniques. Glassware was dried at 120 °C for several hours prior to use. All reagents were stored in an inert-atmosphere glovebox; solvents were distilled under nitrogen from the appropriate drying agent immediately before use. 3-amp and 2,2′-bipyridine (bipy) were purchased from Aldrich and used as received. Silver(I) trifluoroacetate (Agtfa) and silver(I) triflate (AgOTf) were purchased from Strem Chemicals, Inc. and used as received. ^{1}H NMR spectra were recorded at 300.13 MHz on a Bruker Spectrospin 300 MHz spectrometer. Elemental analyses were performed by Atlantic Microlabs, Inc., Norcross, GA.

General Synthesis. General procedures for the synthesis of compounds **1**−**4** involve the addition of a 5 mL acetonitrile solution of 3-amp to a stirred solution of the appropriate silver salt in 5 mL of acetonitrile. The mixtures are then allowed to stir for 10 min then dried in vacuo to leave white or off-white powders. All flasks are shielded from light with aluminum foil to prevent the photodecomposition of the silver compounds. Crystals of **1**, **2**, **5**, and **6** were obtained by the layering of ether onto acetonitrile solutions at 5 °C. Crystals of **3** and **4** were grown by vapor diffusion of ether into acetonitrile solutions at 5 °C. The amounts of reagents used, yields, and analytical data are presented below, as well as any modifications to the general synthetic procedure. Percent yields are based upon the amount of silver salt used. Crystal yields were seen to vary depending upon the method of crystallization, with product being lost due to decomposition of the silver in solution.

Synthesis of Ag(3-amp)tfa (1). This reaction used 3-amp (0.150 g, 1.40 mmol) added to Agtfa (0.306 g, 1.40 mmol) to leave a white powder in 91% isolated yield (0.415 g, 1.26 mmol) upon evaporation of the solvent. Colorless blocks of **1** were formed. ^{1}H NMR (CD$_3$CN, 298 K) δ 3.19 s, br, 2H, (−NH$_2$); 3.89 s, 2H, (−CH$_2$); 7.41 m, 1H; 7.83 td, 2H; 8.45 d, 1H. Anal. Calcd for AgC$_8$H$_8$N$_2$O$_2$F$_3$: C, 29.20; H, 2.45; N, 8.51. Found: C, 29.38; H, 2.39; N, 8.40.

Synthesis of Ag(3-amp)OTf (2). This reaction used 3-amp (0.075 g, 0.69 mmol) added to AgOTf (0.178 g, 0.69 mmol) to leave a white powder in 96% isolated yield (0.239 g, 0.67 mmol)

upon evaporation of the solvent. Colorless plates of **2** were formed. ^{1}H NMR (CD$_3$CN, 298 K) δ 3.00 s, br, 2H, (−NH$_2$); 3.87 s, 2H, (−CH$_2$); 7.43 m, 1H; 7.81 td, 2H; 8.49 m, 1H. Anal. Calcd for AgC$_7$H$_8$N$_2$O$_3$SF$_3$: C, 25.80; H, 2.47; N, 8.56. Found: C, 26.27; H, 2.33; N, 8.77.

Synthesis of Ag(3-amp)$_2$tfa (3). In this reaction, 2 equiv of 3-amp (0.150 g, 1.40 mmol) was added to Agtfa (0.153 g, 0.69 mmol). Removal of the solvent in vacuo left an oily brown solid. Dissolution of this solid in a small aliquot of acetonitrile followed by repeated precipitation with 15 mL of ether resulted in **3** being obtained as a white powder in 73% isolated yield (0.221 g, 0.51 mmol). ^{1}H NMR (CD$_3$CN, 298 K) δ 3.27 s, br, 4H, (−NH$_2$); 3.85 s, 4H, (−CH$_2$); 7.31 m, 2H; 7.78 td, 4H; 8.43 d, 2H. Anal. Calcd for AgC$_{14}$H$_{16}$N$_4$O$_2$F$_3$: C, 38.46; H, 3.69; N, 12.82. Found: C, 38.24; H, 3.57; N, 12.54.

Synthesis of Ag(3-amp)$_2$OTf (4). This reaction used 2 equiv of 3-amp (0.150 g, 1.40 mmol) added to AgOTf (0.178 g, 0.69 mmol). Removal of the solvent in vacuo leaves a yellow oil. Dissolution of this oil in a small aliquot of ether followed by repeated precipitation with 15 mL of ether leaves **4** as a white powder in 73% isolated yield (0.174 g, 0.51 mmol). ^{1}H NMR (CD$_3$CN, 298 K) δ 3.02 s, br, 4H, (−NH$_2$); 3.89 s, 4H, (−CH$_2$); 7.38 m, 2H; 7.78 td, 4H; 8.47 d, 2H. Anal. Calcd for AgC$_{13}$H$_{16}$N$_4$O$_3$SF$_3$: C, 33.00; H, 3.41; N, 11.84. Found: C, 33.18; H, 3.24; N, 11.75.

Synthesis of Ag$_2$(bipy)$_2$-μ-(3-amp)(tfa)$_2$ (5). A solution of 1 equiv of 3-amp (0.100 g, 0.93 mmol) in 5 mL of CH$_2$Cl$_2$ was added to a stirred suspension of 2 equiv of Agtfa (0.408 g, 1.86 mmol) in 5 mL more CH$_2$Cl$_2$. This solution was stirred for 10 min, and then 2 equiv of bipy (0.288 g, 1.90 mmol) in 5 mL of CH$_2$Cl$_2$ was added. This mixture was stirred an additional 10 min then dried in vacuo to leave **5** as an off-white powder in 92% (0.725 g, 0.85 mmol) isolated yield. Colorless block-shaped crystals were formed. ^{1}H NMR (CD$_3$CN, 298 K) δ 3.91 s, br, 2H, (−NH$_2$); 4.75 s, 2H, (−CH$_2$); 7.40 m, 8H; 7.89 m, 9H; 8.10 d, 2H; 8.55 d, 1H. Anal. Calcd for Ag$_4$C$_{60}$H$_{48}$N$_{12}$O$_8$F$_{12}$·CH$_2$Cl$_2$: C, 40.49; H, 2.79; N, 9.29. Found: C, 40.45; H, 2.82; N, 9.37.

Synthesis of Ag$_2$(bipy)$_2$-μ-(3-amp)(OTf)$_2$ (6). To a stirred solution of 1 equiv of 3-amp (0.100 g, 0.926 mmol) in 5 mL of CH$_3$CN was added 2 equiv of AgOTf (0.474 g, 1.84 mmol) in 5 mL of CH$_3$CN. This was allowed to stir for 10 min, and then a solution of bipy (0.288 g, 1.84 mmol) in 5 mL of CH$_3$CN was added. The mixture was stirred an additional 10 min then dried in vacuo to leave a fluffy white powder in 89% (0.759 g, 0.82 mmol) isolated yield. Colorless prisms were formed. ^{1}H NMR (CD$_3$CN, 298 K) δ 4.22 s, br, 2H, (−NH$_2$); 4.82 s, 2H, (−CH$_2$); 7.55 m, 8H; 8.05 m, 9H; 8.26 d, 2H; 8.65 d, 1H. Anal. Calcd for Ag$_2$C$_{28}$H$_{24}$N$_6$O$_6$F$_6$S$_2$: C, 35.99; H, 2.59; N, 8.99. Found: C, 35.93; H, 2.72; N, 9.47.

X-ray Crystallographic Analysis. Crystallographic data were collected on crystals with dimensions of 0.289 × 0.189 × 0.169 mm³ for **1**, 0.140 × 0.090 × 0.060 mm³ for **2**, 0.190 × 0.070 × 0.070 mm³ for **3**, 0.293 × 0.270 × 0.119 mm³ for **4**, 0.195 × 0.172 × 0.140 mm³ for **5**, and 0.238 × 0.187 × 0.180 mm³ for **6**. Data were collected at 110 K on a Bruker X8 Apex using Mo Kα radiation (λ = 0.71073 Å). All structures were solved by direct methods and refined by full-matrix least-squares refinement on F^2 after multiscan absorption correction of the data using SADABS.[30] Crystal data are presented in Table 1, and selected interatomic distances, angles, and other important distances are given in Tables 2−4. All of the data were processed using the Bruker AXS

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Table 1. Crystallographic Data for Compounds **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**
formula	$C_{32}H_{32}Ag_4F_{12}N_8O_8$	$C_{14}H_{16}Ag_2F_6N_4O_6S_2$	$C_{14}H_{16}AgF_3N_4O_2$	$C_{13}H_{16}AgF_3N_4O_3S$	$C_{32}H_{27}Ag_2F_6N_7O_4$	$C_{56}H_{48}Ag_4F_{12}N_{12}O_{12}S_4$
fw	1316.14	730.17	437.18	473.23	903.35	1868.78
a (Å)	10.3431(4)	10.255(1)	12.5447(9)	7.5817(8)	11.682(1)	12.552(1)
b (Å)	17.0246(5)	23.941(2)	10.5573(7)	10.478(1)	12.249(1)	14.036(1)
c (Å)	23.3149(8)	9.1244(8)	12.9994(9)	21.663(2)	13.297(1)	19.713(2)
α (°)	90	90	90	90	78.317(2)	100.968(2)
β (°)	90	91.743	108.001(2)	90	64.335(2)	97.572(2)
γ (°)	90	90	90	90	75.003(2)	102.963(2)
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$
D_{calcd} (g cm^{-3})	2.129	2.166	1.773	1.826	1.821	1.900
μ (mm^{-1})	1.994	2.025	1.277	1.344	1.272	1.413
$2\theta_{max}$ (°)	52.74	52.74	56.74	51.50	56.62	53.02
reflns measured	51 253	58 756	60 463	13 609	22 035	49 261
reflns used (R_{int})	8358 (0.0386)	4576 (0.0404)	4039 (0.0329)	3284 (0.0252)	8117 (0.0318)	13 372 (0.0340)
restraints/param	0/577	0/307	19/274	0/226	6/489	0/901
R1, [$I > 2\sigma(I)$]^a	0.0209	0.0204	0.0159	0.0178	0.0277	0.0279
wR2, [$I > 2\sigma(I)$]^b	0.0490	0.0510	0.0427	0.0433	0.0608	0.0679
$R(F_o^2)$, (all data)	0.0233	0.0258	0.0185	0.0191	0.0399	0.0357
$R_w(F_o^2)$, (all data)	0.0497	0.0532	0.0436	0.0436	0.0663	0.0724
GOF on F^2	1.054	1.061	1.056	1.061	1.020	1.021

^{a} R1 = $[\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$. ^{b} wR2 = $[\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2(F_c^2)]/3$.

Table 2. Selected Bond Lengths (Å), Angles (deg), and Important Distances for **1** and **2**^{a}

Compound 1			
Ag(1)−N(4)#1	2.147(2)	Ag(1)−N(1)	2.157(2)
Ag(1)−O(1)	2.542(2)	Ag(2)−N(3)	2.165(2)
Ag(2)−N(2)	2.177(2)	Ag(2)−O(5)	2.585(2)
Ag(2)−O(3)	2.595(2)	Ag(3)−N(5)	2.158(2)
Ag(3)−N(8)	2.161(2)	Ag(3)−O(8)#2	2.549(2)
Ag(4)−N(6)	2.153(2)	Ag(4)−N(7)#1	2.164(2)
Ag(4)−O(7)	2.567(2)		
N(4)#1-Ag(1)−N(1)	165.07(9)	N(4)#1-Ag(1)−O(1)	98.49(8)
N(1)−Ag(1)-O(1)	96.42(8)	N(3)−Ag(2)-N(2)	159.12(9)
N(3)−Ag(2)-O(5)	106.28(8)	N(2)−Ag(2)-O(5)	89.35(8)
N(3)−Ag(2)-O(3)	93.01(8)	N(2)−Ag(2)-O(3)	101.03(8)
O(5)−Ag(2)-O(3)	89.54(7)	N(5)−Ag(3)-N(8)	164.27(9)
N(5)−Ag(3)-O(8)#2	101.33(9)	N(8)−Ag(3)-O(8)#2	92.93(9)
N(6)−Ag(4)-N(7)#1	166.19(9)	N(6)−Ag(4)-O(7)	104.56(8)
N(7)#1-Ag(4)−O(7)	87.20(8)		
N(2)−H(2A)...O(1)#5	3.024(3)	N(2)−H(2B)...O(7)	2.870(3)
N(4)−H(4A)...O(6)#6	2.914(3)	N(4)−H(4A)...O(5)#6	3.359(4)
N(4)−H(4B)...O(3)#6	3.001(3)	N(6)−H(6A)...O(4)	2.886(3)
N(6)−H(6B)...O(2)#7	3.126(3)	N(8)−H(8A)...O(4)#3	3.109(3)
N(8)−H(8B)...O(2)#4	2.907(3)		

Compound 2			
Ag1−N4#1	2.1235(2)	Ag1−N1	2.1283(2)
Ag2−N2	2.1640(2)	Ag2−N3	2.1675(2)
Ag2−Ag2#2	3.1820(4)		
N4#1-Ag1−N1	177.85(8)	N2−Ag2−N3	165.38(7)
N2−Ag2−Ag2#2	83.98(5)	N3−Ag2−Ag2#2	101.56(5)
N4−H4A...O6	3.144(3)	N4−H4A...O4	3.090(3)
N4−H4B···O3	3.001(3)	N1−H1A...O2#3	3.022(3)
N1−H1B···O4#3	3.010(3)		

^{a} Symmetry transformations used to generate atoms. For **1**: #1 = $x, y + 1, z$; #2 = $x - 1/2, -y + 1/2, -z$; #3 = $x + 1/2, -y + 1/2, -z$; #4 = $x, y - 1, z$; #5 = $-x + 2, y - 1/2, -z + 1/2$; #6 = $-x + 1, y - 1/2, -z + 1/2$; #7 = $x - 1/2, -y + 3/2, -z$. For **2**: #1 = $x - 1, -y + 3/2, z + 1/2$; #2 = $-x, -y + 1, -z + 1$; #3 = $x - 1, y, z$.

SHELXTL software, version 6.10.[31] Unless otherwise noted, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions. The non-centrosymmetric structure of compound **1** was refined as using the "TWIN" command. The non-centrosymmetric structure of **4** was refined with a Flack parameter of $-0.03(2)$. The trifluoromethyl portion of the non-coordinated anion of **3** is disordered over three positions. The

(31) Sheldrick, G. M. *SHELXTL*, version 6.10; Bruker AXS, Inc: Madison, WI, 2000.

Table 3. Selected Bond Lengths (Å), Angles (deg), and Important Distances for **3** and **4**^{b}

Compound 3			
Ag1−N2#1	2.2851(1)	Ag1−N4#2	2.3028(1)
Ag1−N3	2.3765(1)	Ag1−N1	2.4460(1)
N2#1-Ag1−N4#2	130.93(4)	N2#1-Ag1−N3	113.77(4)
N4#2-Ag1−N3	99.83(4)	N2#1-Ag1−N1	103.69(4)
N4#2-Ag1−N1	108.81(4)	N3−Ag1−N1	93.80(4)
N2−H2A...O2#3	3.0692(1)	N2−H2B···O2#5	3.0282(1)
N4−H4A...O1#6	3.1528(1)	N4−H4B···O1#4	3.1525(1)

Compound 4			
Ag1−N2	2.3065(2)	Ag1−N3#1	2.3273(2)
Ag1−N4	2.3352(2)	Ag1−N1#2	2.3483(2)
N2−Ag1−N3#1	119.86(7)	N2−Ag1−N4	105.34(6)
N3#1-Ag1−N4	119.58(7)	N2−Ag1−N1#2	104.74(7)
N3#1-Ag1−N1#2	96.63(7)	N4−Ag1−N1#2	108.92(7)
N1−H1A...O2#5	3.076(3)	N1−H1B···O1#3	2.980(3)
N3−H3A...O3#4	3.225(3)	N3−H3B···O2#6	3.318(3)

^{b} Symmetry transformations used to generate atoms: For **3**: #1 = $-x+3/2,y-1/2,-z+1/2$: #2 = $-x+1/2,y-1/2,-z+1/2$: #3 = $-x+3/2,y+1/2,-z+1/2$: #4 = $-x+1/2,y+1/2,-z+1/2$: #5 = $x+1/2,-y+3/2,z+1/2$: #6 = $x,y+1,z$. For **4**: #1 = $x-1/2,-y+3/2,-z$: #2 = $-x+2,y-1/2,-z+1/2$: #3 = $-x+2,y+1/2,-z+1/2$: #4 = $x+1/2,-y+3/2,-z$: #5 = $x+1,y+1,z$: #6 = $-x+3/2,-y+1,z-1/2$

structure of **5** contains a disordered tfa$^-$ (two positions), as well as a solvent acetonitrile molecule. For the disordered anions in **3** and **5**, the C−F bond lengths were restrained to be approximately equal.

Results and Discussion

Synthesis. The 3-amp complexes **1**–**4** are the result of the direct reaction of 3-amp with either of the two silver salts, OTf$^-$ or tfa$^-$. All of the compounds synthesized herein are isolable as white or off-white powders that appear to be stable indefinitely when kept shielded from light in a sealed container. In the presence of light, compounds **1**–**6** tend to photodecompose over time. The ratios of ligand to metal in the crystal structures are easily controlled by varying the stoichiometry in which the reactants are mixed. Interestingly, the intermediate 3:2 ratio of 3-amp ligand to metal that we have been able to isolate using 2-amp[12] and again with 3-amp and a noninteracting anion[26] has been so far elusive in the current case using a more coordinating anion. Both 1:1 and

Table 4. Selected Bond Lengths (Å), Angles (deg), and Important Distances for **5** and **6**[c]

Compound **5**			
Ag1−N1	2.1487(2)	Ag1−N4	2.2552(2)
Ag1−N3	2.3313(2)	Ag1−Ag2#1	3.0583(3)
Ag2−N2	2.1481(2)	Ag2−N6	2.2143(2)
Ag2−N5	2.382(2)	Ag2−Ag1#1	3.0583(3)
Ag2−Ag2#2	3.1615(4)		
N1−Ag1−N4	154.80(7)	N1−Ag1−N3	131.65(7)
N4−Ag1−N3	72.58(7)	N1−Ag1−Ag2#1	95.43(5)
N4−Ag1−Ag2#1	91.29(5)	N3−Ag1−Ag2#1	89.05(4)
N2−Ag2−N6	161.15(7)	N2−Ag2−N5	125.99(7)
N6−Ag2−N5	72.31(7)	N2−Ag2−Ag1#1	83.18(5)
N6−Ag2−Ag1#1	89.56(5)	N5−Ag2−Ag1#1	99.40(5)
N2−Ag2−Ag2#2	113.37(5)	N6−Ag2−Ag2#2	75.15(5)
N5−Ag2−Ag2#2	70.00(5)	Ag1#1-Ag2−Ag2#2	163.358(1)
N1−H1A...O3#3	2.893(3)	N1−H1B···O4#4	2.868(2)
Compound **6**			
Ag1−N1	2.166(2)	Ag1−N3	2.260(2)
Ag1−N4	2.341(2)	Ag1−Ag2#1	3.0846(3)
Ag2−N2	2.141(2)	Ag2−N6	2.221(2)
Ag2−N5	2.357(2)	Ag2−Ag1#1	3.0846(3)
Ag3−N7	2.150(2)	Ag3−N9	2.233(2)
Ag3−N10	2.350(3)	Ag4−N8	2.139(2)
Ag4−N12	2.275(2)	Ag4−N11	2.277(2)
Ag4−Ag4#2	3.0399(4)		
N1−Ag1−N3	155.92(8)	N1−Ag1−N4	131.85(8)
N3−Ag1−N4	72.14(8)	N1−Ag1−Ag2#1	99.96(6)
N3−Ag1−Ag2#1	79.60(6)	N4−Ag1−Ag2#1	81.63(6)
N2−Ag2−N6	153.20(8)	N2−Ag2−N5	132.81(8)
N6−Ag2−N5	73.00(8)	N2−Ag2−Ag1#1	85.77(6)
N6−Ag2−Ag1#1	91.92(6)	N5−Ag2−Ag1#1	109.17(5)
N7−Ag3−N9	152.96(9)	N7−Ag3−N10	134.85(9)
N9−Ag3−N10	72.15(8)	N8−Ag4−N12	142.39(8)
N8−Ag4−N11	143.89(8)	N12−Ag4−N11	73.10(8)
N8−Ag4−Ag4#2	94.98(6)	N12−Ag4−Ag4#2	83.48(6)
N11−Ag4−Ag4#2	96.34(6)		
N1−H1A...O3#1	3.073(3)	N1−H1B···O1	3.061(3)
N7−H7A...O5#3	3.208(3)	N7−H7B···O7	3.034(3)

[c] Symmetry transformations used to generate atoms: For **5**: #1 = −x,−y+1,−z+2: #2 = −x+1,−y+1,−z+2: #3 = x-1,y,z+1: #4 = −x+1,−y+1,−z+1. For **6**: #1 = −x+1,−y,−z+2: #2 = −x+1,−y+2,−z+1: #3 = x-1,y,z.

Scheme 1. Relationship between Anion, Ligand-to-Metal Ratio, and Structural Motif of the 3-ampAgX Compounds **1−6**

Complex	Anion	Ligand / Metal Ratio	Structural Motif
1	tfa⁻	1:1	1–D polymer
2	tfa⁻	2:1	2–D polymer
3	tfa⁻	1:2:2$_{bipy}$	1–D polymer
4	OTf⁻	1:1	2–D polymer
5	OTf⁻	2:1	3–D polymer
6	OTf⁻	1:2:2$_{bipy}$	discrete structure

2:1 ratios of 3-amp to silver were achieved with AgOTf and Agtfa by reaction in the correct proportions followed by crystallization. The bipyridyl complexes **5** and **6** were formed by the addition of bipy to solutions of 3-amp and the appropriate silver salt. It is interesting to note that, when bipy is present in a 1:1 ratio with Ag, a tetrahedral environment of the metal centers does not seem to be favorable. They are instead all trigonal even with an excess of 3-amp which, when used, must be washed away in order to obtain a solid product. Scheme 1 demonstrates the relationship between the counterion used and the ligand-to-

metal ratio present with the structural motif obtained in the resulting crystal structure.

X-ray Crystal Structures. The crystal structures of compounds **1−6** contain the silver(I) cation in a variety of settings and with coordination numbers from 2 to 5. This variability in structure and bonding is demonstrative of the effects of two variables that were explored herein: anion dependence and ratio dependence of structural features. The former has been thoroughly explored and is a well-documented feature of the coordination chemistry of the group 11 triad,[10−12,29,32−34] while the latter has only recently aroused interest. It is seen that by using anions with comparable basicity and structure (OTf⁻ versus tfa⁻) small changes in geometry around the H-bonding oxygen-containing portion of the anion can have drastic effects on the dimensionality of the resulting complexes, particularly in the current case where the ligand used has the strongly H-bonding amine functionality. Perhaps even more interesting is the observation that these same types of structural reformations can be had by simply changing the ratio of ligand to metal in the reactions. These alterations are very pronounced in the following silver(I) complexes due to the ease with which it varies its coordination sphere to accept the number of donors present. A feature that is seen to occur with the noninteracting BF_4^- anion but was not observed here is the temperature dependence of morphology caused by lowering the crystallization temperature. In the present case, strong H-bonding to the anions likely overwhelms any temperature effects that would be had on the structures. We have not been able to establish phase purity by the collection of X-ray powder data due to the highly hydroscopic nature of the compounds. It should be noted that the isolated powder phase of these compounds is not necessarily identical to that observed in the crystal structure due to solvent effects and crystallization effects which give the compound more time to adopt the most stable configuration. Therefore, the representative nature of the single crystal to the bulk of the sample could not be established.

The structures of compounds **1** and **2** both contain the ligand 3-amp and a silver(I) salt in a 1:1 ratio. Differences between the two structures stem from the coordinating ability, as well as the H-bonding geometry of the tfa⁻ anion versus OTf⁻, with the result being either a one- or two-dimensional polymer.

When 3-amp is reacted in a 1:1 ratio with Agtfa, the lack of sufficient donors from the ligand to fill out the coordination sphere allows the anion to crowd the metal and coordinate through the oxygen atoms. As a result, the two inequivalent polymers of **1**, shown in Figure 1, are formed. The 3-amp ligand coordinates in a head-to-tail fashion down the length of both polymers which are differentiated from one another by the degree of interaction of the anions with the silvers contained within each strand. It is seen that one contains three coordinated anions (O1, O3, and O5) for each two silvers of the chain while the adjacent polymer contains only one (O7) per two silvers, this accounts for the lack of an inversion center. Consequently, the former polymer has associated with it a negative charge and the latter a positive
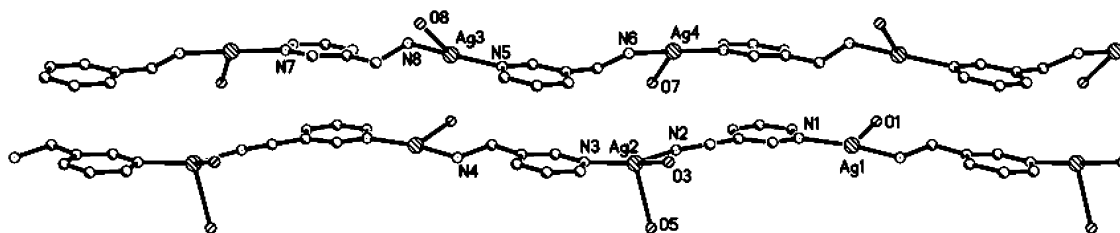
Figure 1. View of the charge-separated polymers of **1**. Only the bound oxygens are shown, and all H atoms except for those of the amines have been removed for clarity.
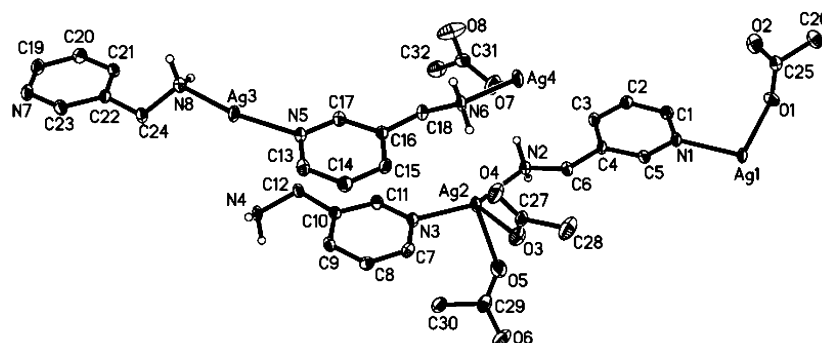

Figure 2. Thermal ellipsoid view of the unique portion of compound **1**. The fluorine atoms and all hydrogens except for those on the amines have been removed for clarity. Ellipsoids are drawn at the 50% probability level.

one. They are then stacked so that two of the cationic strands are adjacent to one another, bridged by the single coordinated anion. These are then bordered on either side by the anionic polymers. The unique part of these polymers is shown in Figure 2. As a general trend on the singly anion-bound silvers (those of the cationic strand and Ag1), the Ag–amine distances are quite similar to the Ag–pyridyl distances. For Ag2, which has two closely associated anions, the Ag–N distances are, as expected, slightly above the average lengths. Another result of the close association of two anions with Ag2 is a greater distortion of its N–Ag–N angle from linear at 159.12(9)°. The remaining three unique silvers (Ag1, Ag3, and Ag4) have more ideally linear N–Ag–N angles. Hydrogen bonding between the anions and amines also assists in holding the chains together.

Upon changing to the less strongly coordinating OTf⁻ anion, a 1:1 ratio of 3-amp with Ag(I) still results in the formation of polymers containing two distinctly different types of metal center. However, in this case, the differences are not caused by coordinating anions but rather by the preference of the ligand to coordinate in a head-to-head fashion. The unique portion of complex **2**, displayed in Figure 3, shows these two coordinatively different silvers; one bound by amines only and the other by pyridyls only but both linearly coordinated by the N-donors. We have demonstrated this type of donor segregation of the aminomethylpyridine ligand in our previous study of noninteracting anions.[26] In a fashion similar to that described in the preceding work, it is seen that the two pyridyl donors of the pyridyl-only bound silvers manage to orient themselves in a nearly coplanar arrangement, allowing two metals from adjacent polymers to come close enough to one another to form a closed-shell metal–metal interaction.[35–40] In this instance (more than in the previous), the interaction appears to be supported by interpolymeric π-stacking of the pyridyl rings which helps
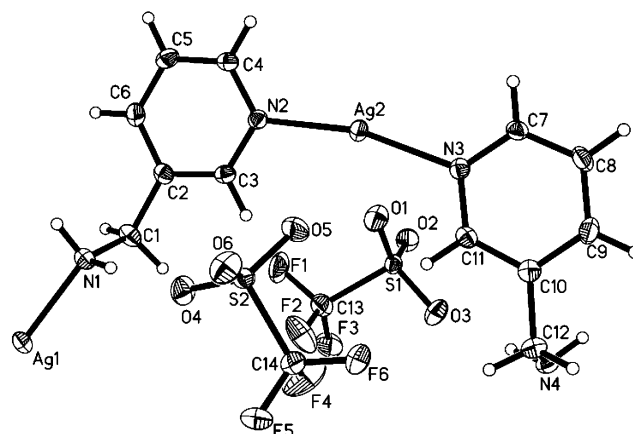

Figure 3. Thermal ellipsoid plot of the unique portion of the polymer **2**. Ellipsoids are drawn at the 50% probability level.

hold the metals to within 3.1820(4) Å of one another.[41] The effect that this interaction has is to join the would-be isolated polymers into two-dimensional sheets linked at every other silver to a neighboring polymer on either side of the original. As shown in Figure 4, the resulting sheets exhibit a staggered

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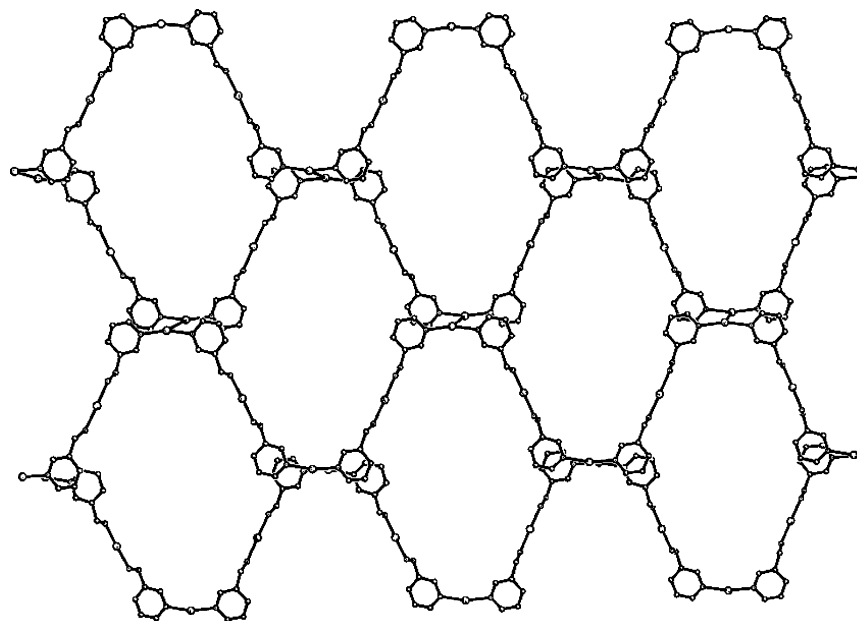(41) Janiak, C. *Dalton Trans.* **2000**, 3885–3896.

Figure 4. Expanded view of the two-dimensional growth of the cationic polymer of **2**.

array of interlaced hexagons similar to that of a chain-link fence. Adding a third dimension to this structure is the activity of the anion which sits inside the cavities of the fence connecting stacked layers using H-bonds to the amine nitrogens. The Ag−N$_{amine}$ and Ag−N$_{pyridyl}$ bond distances are quite similar in this case. The N−Ag−N angle of Ag2 is slightly more off-linear at 165.38(7)° than that of Ag1 due to the distortion of the pyridyl rings away from the Ag−Ag interaction. Ag1, which has no such distortion, is very nearly linear in its coordination environment with an N−Ag−N angle of 177.85(8)°.

Compounds **3** and **4** again contain the anions tfa⁻ and OTf⁻. However, altering the ratios of ligand to metal from 1:1 to 2:1 has profound effects on the coordination environment of the metal, as well as the dimensionality of the coordination polymers that result. The linear charge-separated polymers of **1** grow into the square nets of **3**, while the two-dimensional chain-link fence of **2** morphs into the three-dimensional network of **4**. It is also interesting to note that the 3-amp Ag complexes of OTf⁻ and tfa⁻ have been as yet unobtainable in the 3:2 ratio that is readily crystallized in the case of the noninteracting anion BF$_4$⁻.[26]

In the presence of more than 1 equiv of 3-amp ligand, the stronger amine and pyridyl donors readily displace the weakly bound tfa⁻ anions from the metals of **1** to concomitantly form a tetrahedral environment of only N-donors. These four-coordinate silvers sit at the corners of squares that are then woven into the net of **3** shown in Figure 5. The walls of the "squares" are constructed of bridging 3-amp ligands that coordinate head-to-tail with the previous ligand when the polymerization is followed in any one direction. The anion, though no longer coordinating, still influences the overall structure of the polymer through H-bonding to the amine nitrogens. Similar in mannerism to the supports in a wall, the tfa⁻ anions sit within the cavities of the polymer bridging two opposing parallel "walls" η^2,μ_2− via H-bonds. The unique cationic portion of this structure is shown in
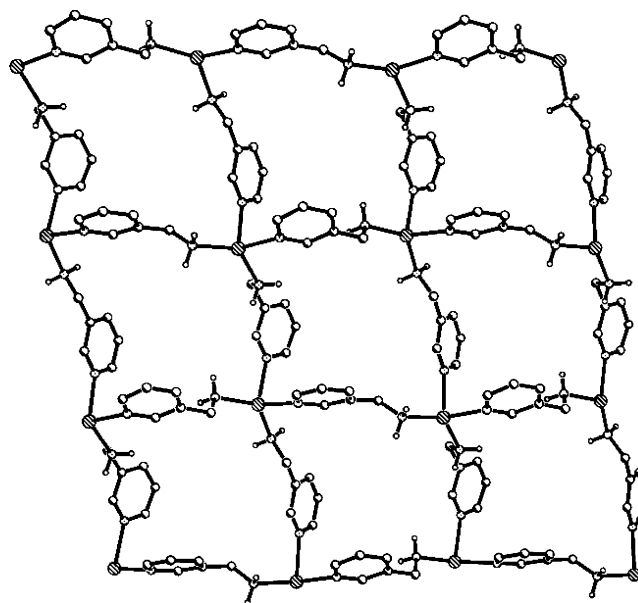

Figure 5. View of the two-dimensional cationic network of **3**. All H atoms except for those on the amines have been removed for clarity.

Figure 6. In this instance, a much better distinction can be made between the amine−Ag and pyridyl−Ag bonds on the basis of distance than in the previous cases with the Ag− amine bonds here being slightly shorter than those to pyridyl donors. The environment of Ag1 is distorted from the ideal tetrahedral geometry by the H-bonded supports of the anions.

Two equivalents of 3-amp ligand has the same effect of taking a metal from a two-coordinate environment to one that is pseudotetrahedral in the case of AgOTf as it did with Agtfa. The four N-donors for each silver surround the metal in a manner so that the unique portion of compound **4**, shown in Figure 7, is similar in appearance to that of **3**. However, H-bonding to the anion again plays a part in determining the overall appearance of the resulting polymer. In this case, the SO$_3$⁻ head of the OTf⁻ causes the aminomethyl tails of
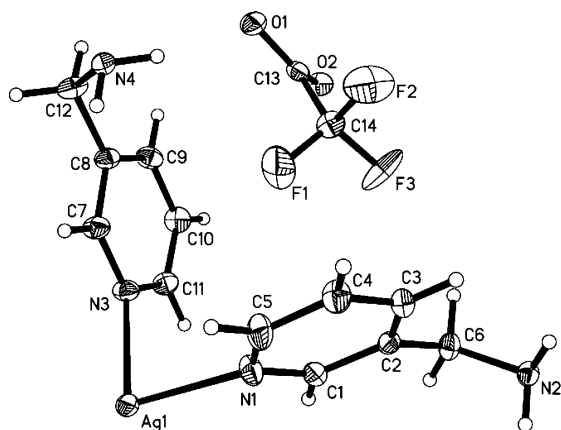
Figure 6. Thermal ellipsoid plot of the unique portion of **3**. Ellipsoids are drawn at the 50% probability level.
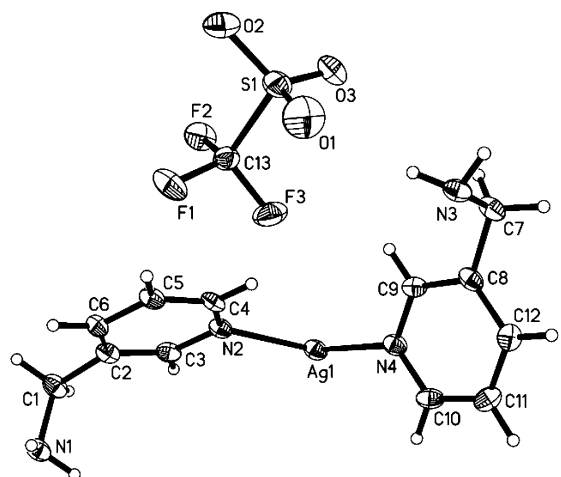

Figure 7. Thermal ellipsoid plot of the unique portion of the three-dimensional polymer of **4**. Ellipsoids are drawn at the 50% probability level.

the ligand to twist in opposing directions such that the growth of the complex occurs in three dimensions rather than two; this leads to a lack of an inversion center in the polymer. An expanded view of this growth is shown in Figure 8. The same type of distortions that were seen in the tetrahedral metal environments of **3** are again displayed in **4**, though not as severe. Likely due to this more relaxed conformation, the Ag−N bonds settle into a position to where they are again more comparable in length, as in the structure of **1** and **2**.

Compounds **5** and **6** result when bipy is added to solutions of the 3-amp ligand with either of the previous silver salts. The strong chelating action of the bipy ligand acts as a scissor to truncate the polymers at each metal center. In the resulting structures, all of the silvers are three-coordinate with two of the donors being those of the bipy. The planarity of the metal environments is conducive to the formation of the d[10] metal−metal interaction that is currently the object of much scrutiny from the theoretical community.[42−46] It is noteworthy that the ratio of 3-amp ligand in the present cases is insignificant;

provided that there is at least 0.5 equiv present to bridge the metal centers, compounds **5** and **6** will be formed. An excess of 3-amp has been so far unable to force a greater ratio of ligand to metal than 1:2 in either structure.

When bipy is added to either of the solutions that produced **2** or **3**, a stoichiometric amount of silver is bound by its chelating bite. It was assumed that as long as there is no more than a single equivalent of the bipy present, there should be at least two available binding sites on each metal center from which polymerization by 3-amp can occur. Contrary to this supposition, it was seen that no more than 0.5 equiv of 3-amp ligand could be incorporated into the structures obtained when the bidentate bipyridine is present. Crystallization of 3-amp with Agtfa and bipy occurs in a 1:2:2 ratio to form compound **5**, which is seen in Figure 9. The single 3-amp ligand that is present acts to bridge two metal centers that are themselves capped by the bipyridyl, creating two coordinatively unique silvers. This unit is then connected to an identical one via Ag−Ag interactions such that the two 3-amp bridges are arranged head-to-tail with respect to one another. A tfa⁻ anion sits in the void on each side of the resulting tetrametallic ring and forms a H-bond bridge through both oxygen atoms to each of the amines. The metal−metal interaction of this loop appears to be supported by the π-stacking of the aromatic bipy rings which assists Ag1 and Ag2A to stay within 3.0583(3) Å of one another. A second Ag−Ag interaction involving Ag2 and its symmetry equivalent joins this cycle to an identical one both above and below the original, effectively constructing a polymer held together by metal−metal interactions that is demonstrated in Figure 10. This second interaction is a bit longer than the first at 3.1615(4) Å, likely due to the lack of H-bonding assistance, though they are again assisted by π-stacking of the pyridyl donors. The four silver stacked chains of trigonal metals appears to be an unusually stable configuration of this particular coinage metal and has been demonstrated previously.[47,48] Each of the silvers of this structure are in a distorted trigonal geometry caused by the acute bite angle of the bipyridyl ligand. However, the N-donor environments of both metals are nicely planar with the metal being only removed from the nitrogen plane by a miniscule degree (<0.04 Å) by attractive interactions with the adjoining metals.

Due to the same factors that caused the stoichiometric limitations on compound **5**, compound **6** has only been obtainable in a 1:2:2 ratio of 3-amp ligand with AgOTf and bipy. **6** was obtained in an analogous manner to **5** by the addition of a single equivalent of bipy to a solution of 3-amp and AgOTf, where again the relative stoichiometries of 3-amp and Ag were irrelevant. The structure of **6** is shown in Figure 11 and contains two of the 3-amp-bridged Ag−bipy units similar to that seen in **5**. However, in this case, the change in geometry about the hydrogen-bonding head

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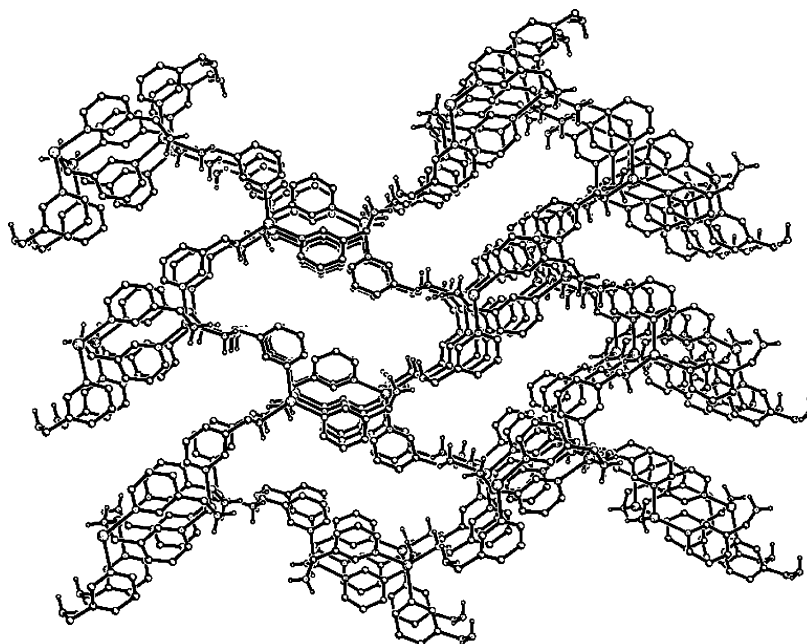
Figure 8. Extended view of the three-dimensional cationic network of **4**. All hydrogen atoms except for those on the amines have been omitted for clarity.
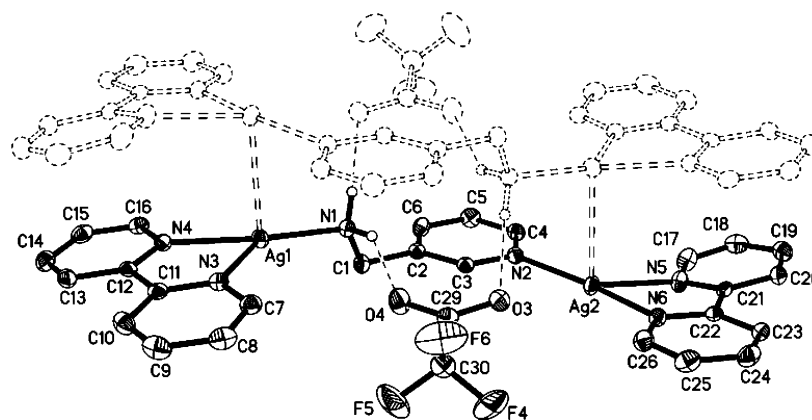

Figure 9. Thermal ellipsoid plot of the tetrametallic ring of **5** showing the H-bonding of the tfa⁻ anions to the amine hydrogens. The symmetry-generated portion of the structure is shown dashed. All other hydrogens and anions have been removed for clarity. Ellipsoids are drawn at the 50% probability level.

of the anion results in the creation of an overall structural motif that is somewhat of a combination of two others that we have described. The first similarity is to that of the previous structure: one of the units, when expanded, is seen to form a tetrametallic ring comparable to that of **5**. Here again, the anion sits within the space created on either side of the ring, drawing the amine groups together through H-bonds. In this case, however, the ring stands alone and is not part of a polymeric network due to the lack of metal–metal interactions extending above the pyridyl-bound silvers. The Ag–Ag interactions here are similar in distance to those previously seen at 3.0846(3) Å. The second similarity involves the second unit and bears resemblance to the compound formed by reacting 3-amp with bipy and silver with a noninteracting anion.[26] In the absence of the assistance of the H-bonding bridge across the opposing amines, the four-silver ring opens and twists 180 ° about the Ag4–Ag4-(A) bond. This leaves a spread-open conformer held together by the single π-stacking-assisted metal–metal interaction which is comparable to those seen in the closed ring at

3.0399(4) Å. H-bonding to the anions here occurs through only a single oxygen and merely serve to hold its place in the lattice. The structure of **6** remains intact even if crystallization is carried out at low temperatures. All of the silvers present are again seen to be in a bipy-distorted trigonal environment.

Conclusions

We have demonstrated here that a variety of silver(I) complexes can be formed by using the mixed-donor ligand 3-amp with AgX, where X = OTf⁻ or tfa⁻, with structural features such as dimensionality of the overall complex, coordination number, and coordination environment being controlled by variations in counterion and ratio of ligand to metal. It is seen that with the highly flexible coordination sphere of the silver(I) cation changes in stoichiometry can be an effective way of manipulating the structures and properties of the resulting compounds. The results of this work add to the area of ratio dependence which nicely supplements the thoroughly explored field of anion-depend-
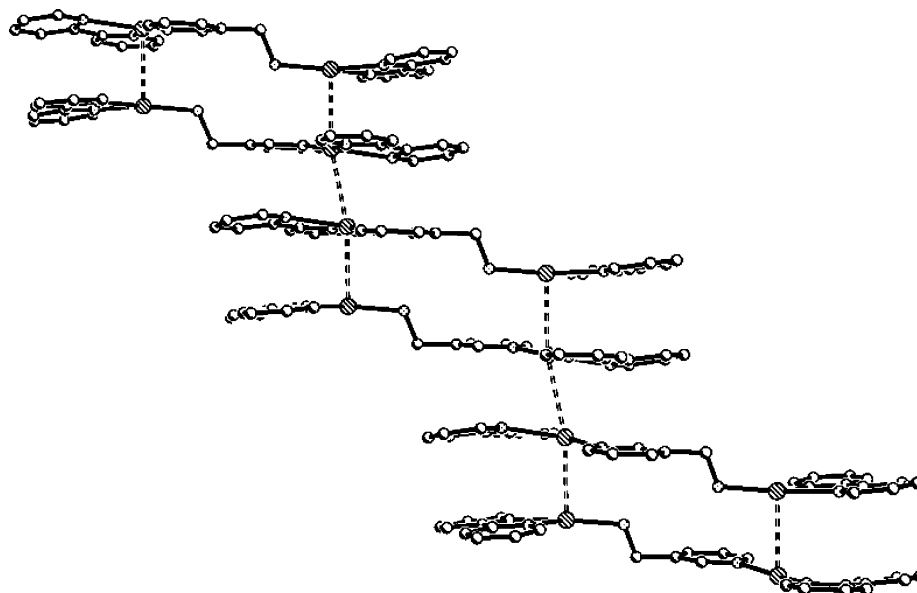
Figure 10. Extended view of the cationic polymer of Ag₄ units formed by the metal−metal interactions of **5**. Anions and H-atoms have been removed for clarity.
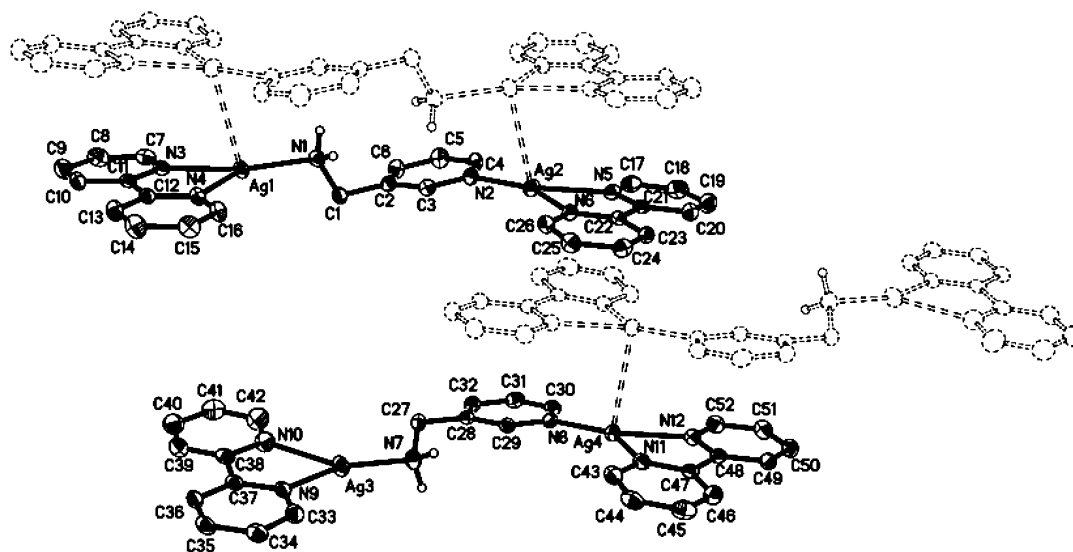

Figure 11. Thermal ellipsoid plot of the two different cationic parts of **6** with the unique portion labeled. Symmetry-generated atoms are shown dashed. Anions and all hydrogen atoms except for those on the amines have been removed for clarity. Ellipsoids are drawn at the 50% probability level.

ent structures of the coinage metals. It was shown here how the common silver coordination numbers from 2 to 5 can easily be obtained producing structural motifs ranging from discrete structures to three-dimensional networks.

Supporting Information Available: A listing of the final atomic coordinates, anisotropic thermal parameters, low-temperature luminescence spectra, extra figures, and complete bond lengths and angles for complexes **1−6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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