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Silver(I) 3-Aminomethylpyridine Complexes, Part 1: Effect of Ligand Ratio, π-Stacking, and Temperature with a Noninteracting Anion

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The reaction of the asymmetric 3-aminomethylpyridine (3-amp) ligand with silver(I) tetrafluoroborate ($AgBF_4$) produces an array of structural motifs that depend on the ratio of the reactants present and crystallization temperature. With a 1:1 ratio of 3-amp to silver, either a folded macrocycle, **1a**, or a linear coordination polymer, **1**, is formed, depending upon whether the crystals are grown at –35 or 5 °C. A 3:2 ratio forms two-dimensional sheets of **2** regardless of temperature of crystallization. The 2:1 ratio of ligand to metal again sees a temperature dependence with either a one-dimensional, **3a**, or two-dimensional, **3**, coordination polymer formed upon crystallization at low and high temperatures, respectively. Addition of 2,2′-bipyridine to any of the previous reaction mixtures stops the formation of their respective structures, instead constructing the discrete Ag–Ag-linked **4**.

Introduction

Progress in the area of crystal engineering has many far-reaching effects whose importance often greatly surpasses the novelty of the basic investigations from whence they came. A few of the more interesting, and potentially profitable, applications that have accepted advancements from the field include catalysis, molecular recognition, molecular sieving, and separations.[1−4] Much of the usefulness that is obtained from these polymers stems from the ability to control internal features of the structures such as coordination geometry of the metal centers, pore size, and magnetism.[5−9] During the past few decades, numerous examples of designed and constructed coordination architectures that span from discrete macromolecules to multidimensional coordination networks have been demonstrated, most of which were built on the basis of controlling functionality, rigidity, or geometry of the ligand or by using modifications to the counterion or solvent system.[5,7,8,10−24] Despite the wealth of literature that has been generated describing crystal engineering studies of the aforementioned methods, the equally effective technique of stoichiometry control has been somewhat overlooked.[25−28] Only recently have a handful of investigators begun to examine the metal/ligand ratio de-

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pendence of structural features with regards to design and growth of supramolecular coordination entities in greater detail.[7,16,29−31] Recent studies published by Mirkin et al.[29] and Dong et al.[30] both focus on the ratio dependence of metal complexes of flexible mixed-donor ligands and assist in demonstrating the practicality of this seldom-used method. We too have reported on the structural modifications that could be had by variations in the ratio of ligand to metal in the reactions of silver(I) complexes of 2-aminomethylpyridine[16] and 4-aminomethylpyridine.[32] We now follow this with an inquiry of the 3-aminomethylpyridine (3-amp) ligand.

Herein, we describe the dramatic changes that can be brought about in the flexible coordination sphere of the silver(I) cation merely by altering the ratio of the bifunctional 3-amp ligand. In this study, only the tetrafluoroborate salt of silver was used in order to keep counterion interactions to a minimum. As a result, we were able to obtain a number of exceedingly varied structural motifs whose differences stem only from the ratio of ligand to metal in the reactions from which they were produced. As an added feature, two of the ratios were also seen to display a temperature-dependent morphology with separate structures of each consistently being obtained when crystallized at a temperature difference of only 40 K.

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) tetrafluoroborate ($AgBF_4$) was purchased from Strem Chemicals, Inc. and used as received. ^1H 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**−**3a** involve the addition of a 5 mL acetonitrile solution of 3-amp to a stirred solution of $AgBF_4$ in 5 mL of acetonitrile. The mixtures are 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**, **3**, and **4** were grown by layering ether over acetonitrile solutions at 5 °C. Crystals of **1a** and **3a** were grown by layering ether over dilute acetonitrile solutions at −35 °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 some product being lost due to decomposition of the silver in solution.

Synthesis of Poly(Ag[3-amp]BF_4) (1) and Ag_4(3-amp)$_4$(BF_4)$_4$ (1a). This reaction used 3-amp (0.056 g, 0.51 mmol) added to $AgBF_4$ (0.100 g, 0.51 mmol) to leave a white powder in 91% isolated yield (0.142 g, 0.46 mmol) upon evaporation of the solvent. Colorless plates of **1** were formed at 5 °C, and colorless blocks of **1a** were formed at −35 °C. ^1H NMR (CD_3CN, 298 K) δ 3.13 s, br, 8H ($-NH_2-$); 3.92 s, 8H ($-CH_2-$); 7.47 qd, 4H; 7.88 dt, 8H; 8.41 dd, 4H.

Synthesis of Ag_2(3-amp)$_3$(BF_4)$_2$ (2). This reaction used 3 equiv of 3-amp (0.150 g, 1.40 mmol) added to 2 equiv of $AgBF_4$ (0.180 g, 0.93 mmol). A clear, colorless oil was left upon evaporation of the solvent. Dissolution of this oil in a small amount of CH_2Cl_2 followed by repeated precipitation with ether leaves a white fluffy solid in 88% yield (0.290 g, 0.407 mmol) upon isolation of the precipitate. Colorless blocks were formed. ^1H NMR (CD_3CN, 298 K) δ 2.93 s, br, 6H, ($-NH_2-$); 3.875 s, 6H, ($-CH_2-$); 7.38 m, 3H; 7.739 dd, 6H; 8.34 d, 3H. Anal. Calcd for $Ag_2C_{18}H_{24}N_6B_2F_8$: C, 30.29; H, 3.25; N, 11.77. Found: C, 30.39; H, 3.25; N, 11.56.

Synthesis of Ag(3-amp)$_2$$BF_4$ (3) and (3a). This reaction used 2 equiv of 3-amp (0.150 g, 1.40 mmol) added to $AgBF_4$(0.135 g, 0.69 mmol). Upon evaporation of the solvent, a white powder was isolated in 84% yield (0.239 g, 0.583 mmol). Colorless plates of **3** were formed at 5 °C, and colorless blocks of **3a** were formed at −35 °C. ^1H NMR (CD_3CN, 298 K) δ 3.20 s, br, 4H, ($-NH_2-$); 3.90 s, 4H, ($-CH_2-$); 7.42 m, 2H; 7.86 td, 4H; 8.32 d, 2H. Anal. Calcd for $AgC_{12}H_{16}N_4BF_4$: C, 35.07; H, 3.92; N, 13.63. Found: C, 35.20; H, 3.84; N, 13.51.

Synthesis of Ag_2(bipy)$_2$-μ-(3-amp)(BF_4)$_2$ (4). To a stirred solution of 1 equiv of 3-amp (0.100 g, 0.93 mmol) in 5 mL of CH_3CN was added 2 equiv of $AgBF_4$ (0.360 g, 1.82 mmol) in 5 mL more CH_3CN. This was stirred for 5 min, and then a solution of bipy (0.289 g, 1.82 mmol) in 5 mL of CH_3CN was added. This mixture was stirred for 10 min, and then the solvent was removed in vacuo to leave a light yellow powder in 92% isolated yield (0.689 g, 0.85 mmol). Crystallization formed colorless blocks. ^1H NMR (CD_3CN, 298 K) δ 2.48 s, br, 2H, ($-NH_2-$); 3.79 s, 2H, ($-CH_2-$); 7.42 m, 8H; 7.89 t, 9H; 8.26 d, 2H; 8.55 d, 1H. Anal. Calcd for $Ag_2C_{29}H_{28}N_7B_2F_8$: C, 40.32; H, 3.27; N, 11.35. Found: C, 40.68; H, 3.26; N, 11.20.

X-ray Crystallographic Analysis. Crystallographic data were collected on crystals with dimensions of 0.128 × 0.091 × 0.062 mm^3 for **1**, 0.091 × 0.105 × 0.192 mm^3 for **1a**, 0.200 × 0.210 × 0.350 mm^3 for **2**, 0.046 × 0.112 × 0.232 mm^3 for **3**, 0.151 × 0.222 × 0.232 mm^3 for **3a**, and 0.062 × 0.169 × 0.177 mm^3 for **4**. Data were collected at 110 K on a Bruker X8 Apex diffractometer using Mo Kα radiation ($\lambda = 0.71073$ 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.[33] Crystal data are presented in Table 1, and selected interatomic distances, angles, and other important distances are given in Tables 2 and 3. All of the data were processed using the Bruker AXS SHELXTL software, version 6.10.[34] Unless otherwise noted, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions. The crystal structure of compound **1** contains two molecules of water, one of which is disordered over two positions. It also contains a disordered amine and silver atom with a 37:63 occupancy ratio. The smaller

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Table 1. Crystallographic Data for Compounds **1**−**4**

	1	**1a**	**2**	**3**	**3a**	**4**
formula	$C_{14}H_{19}Ag_2B_2F_8N_5O$	$C_{28}H_{38}Ag_4B_4F_{16}N_{10}$	$C_{18}H_{24}Ag_2B_2F_8N_6$	$C_{12}H_{16}AgBF_4N_4$	$C_{12}H_{16}AgBF_4N_4$	$C_{26}H_{24}Ag_2B_2F_8N_6$
fw	662.68	1293.40	713.79	410.97	410.97	809.87
a (Å)	13.592(2)	7.8143(7)	6.850(1)	15.318(1)	8.6991(4)	7.1224
b (Å)	27.841(3)	25.736(2)	8.409(1)	10.489(1)	14.1060(7)	10.618(1)
c (Å)	13.281(2)	21.193(2)	11.598(1)	18.819(2)	12.9311(7)	19.166(2)
α (°)	90	90	110.934(6)	90	90	92.490(5)
β (°)	113.100(2)	96.381(2)	97.226(6)	90	109.607	96.249(5)
γ (°)	90	90	96.238(6)	90	90	93.248(5)
space group	$C2/m$	$P2_1/c$	$P1$	$Pbca$	$P2_1/c$	$P\bar{1}$
D_{calcd} (g cm^{-3})	1.973	2.028	1.941	1.805	1.826	1.872
μ (mm^{-1})	1.781	1.929	1.685	1.375	1.391	1.444
$2\theta_{max}$ (°)	51.36	52.7	53.06	52.9	52.74	56.56
reflns measured	12024	36620	15095	40167	29846	21440
reflns used (R_{int})	4433 (0.0463)	8655 (0.0436)	4220 (0.0259)	3087 (0.0391)	3040 (0.0316)	6988
restraints/param	10/378	6/574	5/329	0/211	0/199	10/443
R1, $[I > 2\sigma(I)]$[a]	0.0679	0.0530	0.0185	0.0187	0.0155	0.0291
wR2, $[I > 2\sigma(I)]$[b]	0.1730	0.1156	0.0476	0.0452	0.0413	0.0638
$R(F_o^2)$, (all data)	0.0980	0.0655	0.0187	0.0274	0.0171	0.0433
$R_w(F_o^2)$, (all data)	0.1959	0.1215	0.0478	0.0471	0.0420	0.0663
GOF on F^2	1.037	1.128	1.060	1.069	1.080	1.075

[a] $R1 = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$. [b] $wR2 = [\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[c^2(F_o^2) + (aP)^2 + bP]$, 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**, **1a**, and **2**[a]

Compound **1**			
Ag1−N1	2.181(7)	Ag1−N3	2.183(7)
Ag1−N5	2.515(9)	Ag1−Ag1#1	3.2896(1)
Ag2−N2	2.146(7)	Ag2−N2#2	2.146(7)
Ag3−N4	2.154(15)	Ag3−N4#3	2.154(1)
N1−Ag1−N3	164.3(3)	N1−Ag1−N5	99.9(3)
N3−Ag1−N5	95.8(3)	N1−Ag1−Ag1#1	113.25(2)
N3−Ag1−Ag1#1	68.27(2)	N5−Ag1−Ag1#1	82.5(2)
N2−Ag2−N2#2	172.7(4)	N4−Ag3−N4#3	174.9(9)
Compound **1a**			
Ag1−N1	2.130(5)	Ag1−N3	2.132(5)
Ag2−N5	2.111(6)	Ag2−N7	2.130(6)
Ag3−N8	2.142(5)	Ag3−N4	2.145(5)
Ag3−N10	2.609(7)	Ag3−Ag4	3.2543(8)
Ag4−N2	2.189(5)	Ag4−N6	2.195(5)
Ag4−N9	2.374(7)	N1−Ag1−N3	174.4(2)
N5−Ag2−N7	174.4(2)	N8−Ag3−N4	163.6(2)
N8−Ag3−N10	94.8(2)	N4−Ag3−N10	101.5(2)
N8−Ag3−Ag4	84.16(1)	N4−Ag3−Ag4	104.97(1)
N10−Ag3−Ag4	62.6(2)	N2−Ag4−N6	143.53(2)
N2−Ag4−N9	102.7(2)	N6−Ag4−N9	109.5(2)
N2−Ag4−Ag3	74.31(13)	N6−Ag4−Ag3	103.89(1)
N9−Ag4−Ag3	118.16(2)		
Compound **2**			
Ag1−N5	2.235(3)	Ag1−N4	2.246(3)
Ag1−N6#1	2.265(3)	Ag2−N3	2.222(4)
Ag2−N1#2	2.246(2)	Ag2−N2	2.262(3)
N5−Ag1−N4	121.84(1)	N5−Ag1−N6#1	119.78(1)
N4−Ag1−N6#1	117.26(1)	N3−Ag2−N1#2	124.0(2)
N3−Ag2−N2	119.5(2)	N1#2-Ag2−N2	116.37(1)

[a] Symmetry transformations used to generate equivalent atoms. For **1**: #1 = $-x + 2, y, -z + 3$; #2 = $x, -y + 3, z$; #3 = $x, -y + 2, z$. For **2**: #1 = $x + 1, y, z$; #2 = $x, y + 1, z$.

Table 3. Selected Bond Lengths (Å), Angles (deg), and Important Distances for **3**, **3a**, and **4**[a]

Compound **3**			
Ag−N1	2.3057(1)	Ag−N2#1	2.3341(2)
Ag−N4#2	2.3572(1)	Ag−N3	2.3776(1)
N1−Ag−N2#1	123.50(6)	N1−Ag−N4#2	100.71(6)
N2#1-Ag−N4#2	112.60(6)	N1−Ag−N3	115.12(5)
N2#1-Ag−N3	95.97(5)	N4#2-Ag−N3	108.90(6)
Compound **3a**			
Ag−N4#1	2.3071(1)	Ag−N2#2	2.3482(1)
Ag−N1	2.3537(1)	Ag−N3	2.3807(1)
N4#1-Ag−N2#2	109.26(5)	N4#1-Ag−N1	123.01(5)
N2#2-Ag−N1	108.75(5)	N4#1-Ag−N3	114.96(5)
N2#2-Ag−N3	105.53(5)	N1−Ag−N3	93.38(5)
Compound **4**			
Ag1−N4	2.1457(2)	Ag1−N5	2.286(2)
Ag1−N6	2.291(2)	Ag1−Ag1#1	2.9875(4)
Ag2−N3	2.1610(2)	Ag2−N2	2.287(2)
Ag2−N1	2.2908(2)	N4−Ag1−N5	145.36(8)
N4−Ag1−N6	141.39(7)	N5−Ag1−N6	72.81(7)
N4−Ag1−Ag1#1	98.38(5)	N5−Ag1−Ag1#1	89.30(5)
N6−Ag1−Ag1#1	83.86(5)	N3−Ag2−N2	145.57(7)
N3−Ag2−N1	141.44(7)	N2−Ag2−N1	72.90(7)

[a] Symmetry transformations used to generate equivalent atoms. For **3**: #1 = $-x, -y + 2, -z + 1$; #2 = $-x, y + 1/2, -z + 1/2$. For **3a**: #1 = $x - 1, y, z$; #2 = $-x + 1, -y + 2, -z + 2$. For **4**: #1 = $-x, -y + 1, -z + 2$.

occupancy disorder contains a coordinated acetonitrile which is refined isotropically along with the silver and nitrogen. The methylene pivot for this amine (N4) was refined as if disordered but restrained to have identical thermal parameters and positions. The crystal structures of compounds **1a** and **4** both contain BF_4^- anions disordered over two positions. The anions of structures **1**, **1a**, **2**, and **4** were refined with restraints on their bond lengths and angles and/or thermal parameters. One of the amine nitrogens in the structure of compound **2** is disordered over two positions; these were restrained to have approximately equal thermal parameters.

Compound **2** crystallizes in the noncentrosymmetric space group *P*1 with a Flack parameter of 0.028(20).

Results and discussion

Synthesis and NMR Spectroscopy. The 3-aminomethylpyridinyl complexes **1**−**4** were made by the direct reaction of the ligand with $AgBF_4$ and bipy in varying ratios. It is seen that when using the same noncoordinating BF_4^- anion the structural features of the silver(I) complexes made can be varied greatly by changes in ratio of ligand to metal and by changes in crystallization temperature. These changes have been summarized in Scheme 1. However, it should be noted that modifications in crystallization method do not cause changes in connectivity, merely in the conformation of the product, implying a separate thermodynamic product versus a kinetic one. The synthesis of the 1:1 ratio 3-

Scheme 1. Relationship between Ligand-to-Metal Ratio, Crystallization Temperature, and Structural Motif of 3-ampAgX Compounds **1**−**4**

Complex	Ligand / Metal Ratio	Crystallization Temperature (°C)	Structural Motif
1	1:1	5	1–D polymer
1a	1:1	–35	discrete structure
2	3:2	5	2–D polymer
3	2:1	5	2–D polymer
3a	2:1	–35	1–D polymer
4	$1{:}2{:}2_{\mathrm{bipy}}$	5	discrete structure

ampAgBF$_4$ complex has been previously described by an alternate route in an anion-dependent study,[31] though in the earlier investigation, the researchers were unable to obtain satisfactory samples for study by X-ray diffraction. The five 3-amp-only compounds mentioned herein display three different ligand-to-metal ratios. When in solution, the two 1:1 and the two 2:1 structures are indistinguishable by room temperature ^{1}H NMR. This is indicative that the two connectively identical structures of each pair lose the structural differences that separate them when dissolved in room-temperature solution.

X-ray Crystal Structures. The silver coordination environments that are seen in structures **1**−**4** differ greatly from one structure to the next. Geometries of the metal centers range from the near linear 175(1)° of Ag2 in compound **1** to the distorted tetrahedrons of **3** and **3a**. Median to these are several structures containing trigonal environments with some displaying very short metal−metal interactions.[35−40] Interestingly, the silver−silver interactions are only seen to be present on those metals bound by pyridyl donors, even if more crowded. This is likely reasoned to the ease of accessibility that the planar pyridyl rings allow for the metals to come close to one another, as well as the attractive force of the ring π-systems themselves for one another.[41] 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 may well be different from the observed crystal structure due to solvent effects and the observed temperature dependence on the structures of **1** and **3**. Therefore, the representative nature of the single crystal to the bulk of the sample could not be established.

Ligand-to-metal ratios in the structures of **1** and **1a** are 1:1. The silver environments of both structures are connectively similar with each containing three-coordinate, pyridyl-only bound silvers, as well as linear, amine-only bound silvers. In both cases, the pyridyl-only bound silvers each contain a bound acetonitrile that fills in a third coordination site. Differences between the two structures stem solely from the method of crystallization. Using identical solvent systems, the polymeric conformation of **1** develops when crystallization is allowed to occur rapidly within several hours at 5 °C. A slower crystallization over several days at −35 °C results in the folded macrocycle of **1a**.

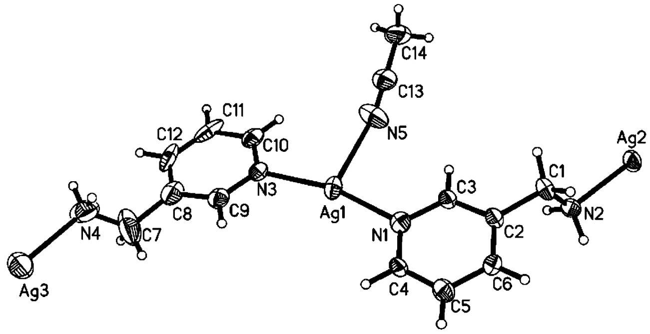

Figure 1. Thermal ellipsoid plot of the unique portion of the cationic polymer **1**. The disordered amine and silver have been omitted for clarity. Ellipsoids are drawn at the 50% probability level.

The unique portion of the linear polymer formed by the rapid crystallization of a 1:1 mixture of 3-amp with AgBF$_4$ is shown in Figure 1. Each of the amine-bound silvers sits on a special position (refined with 1/2 occupancy), keeping a 1:1 ratio with the two 3-amp ligands in the asymmetric unit. Perpetuation of the polymer of **1** occurs in one dimension as the 3-amp ligands coordinate in a head-to-head fashion to the metal centers. What results is a zigzagging coordination polymer of two-coordinate amine-bound silvers and three-coordinate pyridyl-bound silvers, with the pyridyl-only bound silvers being also connected to an acetonitrile molecule. This polymer is then linked to a second, symmetry-equivalent one by silver−silver interactions at every pyridyl-only bound silver. This forms the chainlike structure shown in Figure 2 that is constructed of alternating circular and oval "links" joined at every other metal center. The more circular links are forced to be so by the coordinated acetonitriles present on every pyridyl-bound metal that protrude into the center of the ring, forcing the amine-bound silvers here outward and away from the center of the polymer. The amine-bound silvers of the oval rings have no such steric push and, as a result, are allowed to twist back in toward the center of the polymer. A C_2 axis running the length of the polymer relates the two halves. The metal−metal distance contained herein is a bit lengthy at 3.289(1) Å[35−40] but appears to be completely unsupported with virtually no π-stacking occurring between the rings of the connected silvers. There does appear to be, however, substantial π-interactions of the metals with the pyridyl rings of the polymer strands stacked above and below those silvers that hold the two halves of the polymer chain together. The π-cloud of the pyridyl rings approach to within 3.03 Å (Ag−ring atom distances range from 3.031(9) to 4.176(9) Å) from the silvers, constructing a pseudo-double-metal sandwich arrangement. This is comparable to other known

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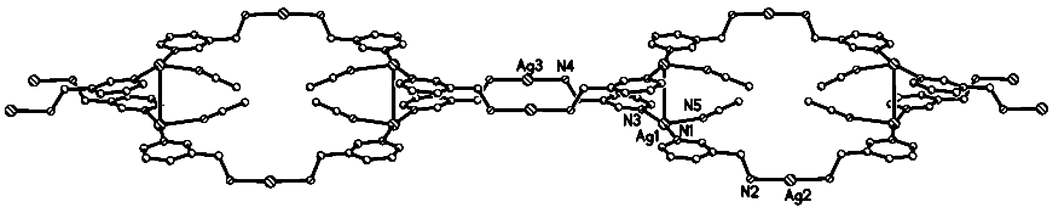

Figure 2. Extended ball-and-stick view of the cationic polymeric structure of **1**. Hydrogen atoms and disorder have been removed for clarity.

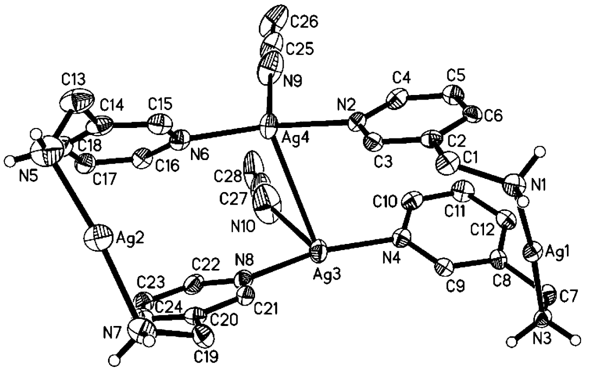

Figure 3. Thermal ellipsoid plot of the cationic portion of **1a**. Ellipsoids are drawn at the 50% probability level. All hydrogen atoms except for those on the amines have been removed for clarity.

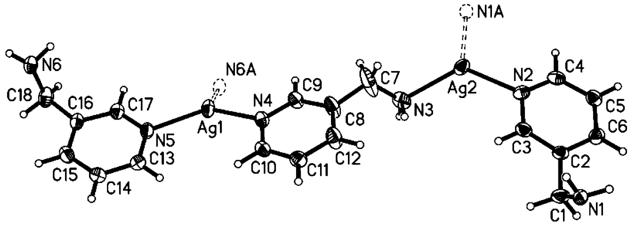

Figure 4. Thermal ellipsoid of the unique portion of the cationic polymer of **2** with the silver coordination environments shown complete. Ellipsoids are drawn at the 50% probability level. The disorder of N3 has been removed for clarity.

compounds with aromatic Ag−π interactions.[42−45] The stacking of the rings onto the sides of the metal centers effectively flattens out the ligands surrounding Ag1 into a near perfectly planar environment with respect to both the donor−metal geometry and the planes of the two coordinated pyridyl rings themselves. The rings vary from being coplanar by an angle of 7.3(4)°. The Ag−amine and Ag−pyridyl distances are seen to be nearly identical in this structure with the bound acetonitrile having a much longer N−Ag1 bond. This weaker solvent−metal bond helps to account for the fact that this three-coordinate silver is quite far from the ideal trigonal geometry with a pyridyl−Ag−pyridyl angle of 164.3(3)°. The two coordinate silvers are closer to a linear geometry with N−Ag−N angles of 172.7(4)° and 174.9(9)° for Ag2 and Ag3, respectively. The smaller disorder of these linear amine bound silvers also contain a coordinated acetonitrile that is oriented away from the center of the polymer.

It is seen that, when the 1:1 ratio of 3-amp to $AgBF_4$ is crystallized at a lower temperature and over a longer period of time, the polymeric structure of **1** is no longer the more favorable one. The structure that is instead formed, **1a**, is a discrete unit that is connectively identical to its polymeric relative. A view of the folded tetramer of **1a** is shown in Figure 3. The unique portion of **1a** can be thought of as one of the larger links of the chain of compound **1** truncated on either end with the dangling pyridyl ends tied together to the same silver (as opposed to a silver on an adjacent polymer unit). The macrocycle that results contains four silvers; two each bound head-to-head and tail-to-tail by four 3-amp ligands as in the original polymer. However, without the polymeric backbone stretching the ring open, the propensity of the silver to engage in its closed-shell metal−metal interaction causes the loop to fold over onto itself, allowing the two pyridyl-bound silvers to come to within 3.2543(8) Å of one another. Contrary to the metal−metal interaction seen in **1**, it is apparent that the one occurring between Ag3 and Ag4 has substantially more support by the intramolecular stacking of the π-systems. Intermolecular sandwiching of the silvers by pyridyl rings is not pronounced in this case and is made obvious by the distortions of the rings from the planarity that they displayed in the previous structure. N−Ag distances are similar to those displayed in **1** with the amine−Ag distances again being slightly shorter. The coordinated acetonitriles are quite different with respect to their bond strengths to the metals to which they are bound. The Ag3−$N_{acetonitrile}$ bond length is quite a bit longer at 2.609(7) Å than that of the Ag4−$N_{acetonitrile}$, which is 2.374(7) Å. Effects of this increase in bond strength are made apparent when examining the angles of the pyridyl nitrogens with respect to one another; the more constricted angle of N2−Ag4−N6 at 143.5(2)° is seen for Ag4 which has the shorter Ag−$N_{acetonitrile}$ bond. The weaker solvent−metal bond is associated with a wider ligand−metal−ligand angle of 163.6(2)° for N4−Ag3−N8.

Compound **2** is representative of an intermediate structural motif that can be stopped at when moving from the 1:1 to 2:1 ratios of 3-amp ligand to metal. When 3-amp and $AgBF_4$ are mixed in a 3:2 ratio, the resulting two-dimensional polymer contains two different three-coordinate silver environments. As shown in Figure 4, the coordination sphere of Ag1 is completed by two pyridyl donors and an amine while that of Ag2 is the opposite with a single pyridyl and two amines bound to the metal center. The amp-nitrogen-only environments of the two unique silvers are both very nicely trigonal with acute ranges of N−Ag−N angles from 117.26(9)° to 121.82(9)° about Ag1 and 117.7(2)° to

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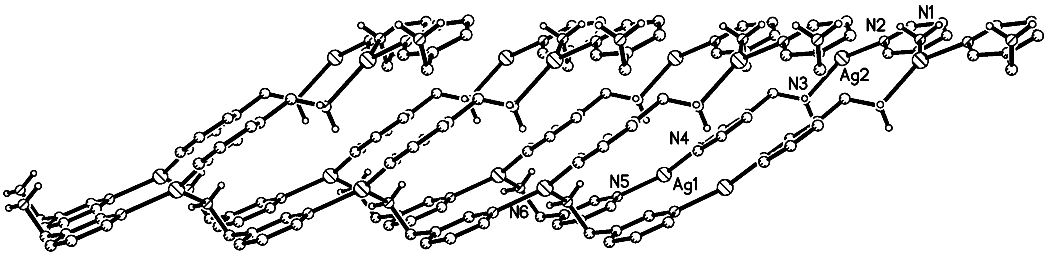

Figure 5. View of the extended two-dimensional network of **2**. H atoms, except for those on the amines, anions, and disorder have been removed for clarity.

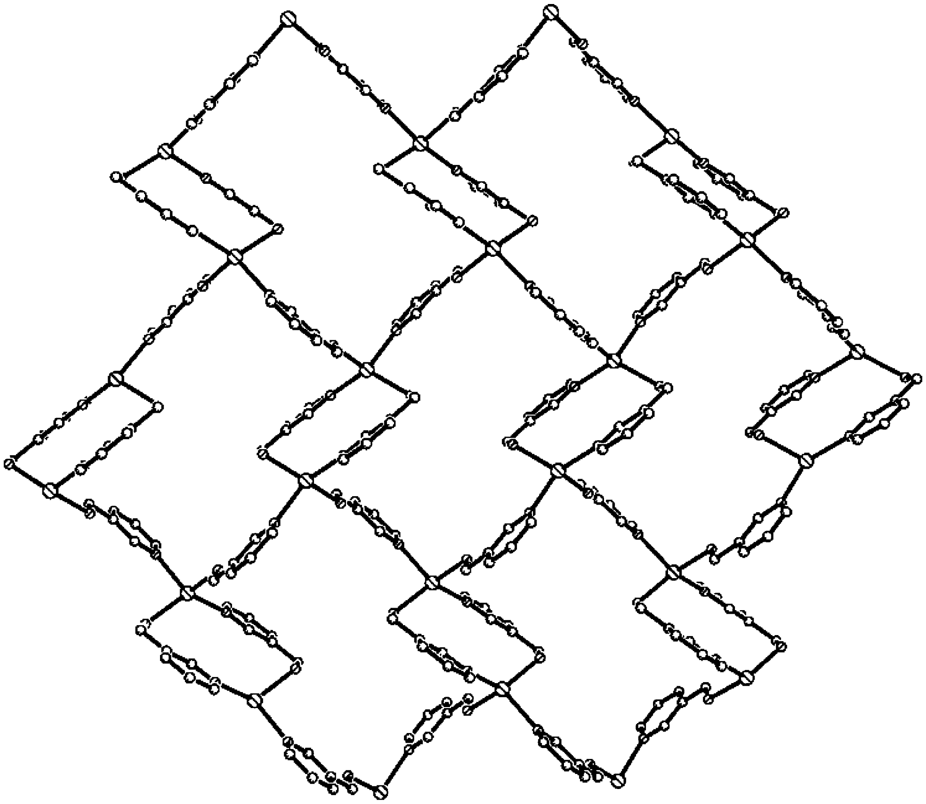

Figure 6. View of the two-dimensional network of **3**. Hydrogen atoms and anions have been removed for clarity.

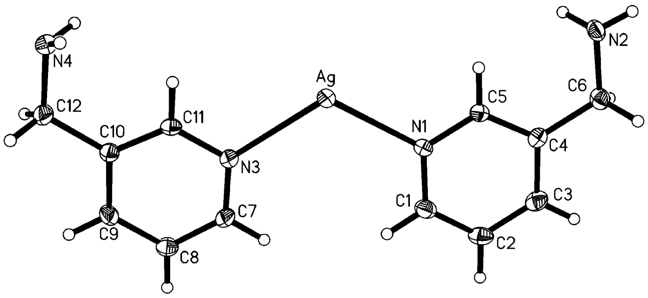

Figure 7. Thermal ellipsoid plot of the unique cationic portion of **3**. Ellipsoids are drawn at the 50% probability level.

124.9(2)° about Ag2. Both metals also sit well within their respective N-donor planes with only small deviations of 0.103(1) and 0.097(1) Å for Ag1 and Ag2, respectively. The exclusion of solvent acetonitrile from the coordination sphere of the silvers of this and the following structures is demonstrative of the contented nature of the three-coordinate silver to stay as such even in the presence of an excess of weak donors. With two similar, but distinctly different, silver environments, the effects of the differences in electron donation of the amines versus the pyridines are barely made apparent. Bond lengths around the metal centers are all quite similar. The central 3-amp ligand of Figure 4 serves to connect the two unique silver centers of the "planar" portion of the polymer. When the terminal ends of this structure are grown out, it is seen that each of the end amines serves a different purpose in the polymer. The N1 amine bridges to a symmetry-equivalent, slightly offset Ag2 to construct a looping one-dimensional polymer. The N6 amine of this polymer then reaches upward to join the linear sections into the two-dimensional pseudocorrogated sheets shown in Figure 5. The differing functions of the N1 and N6 moieties preclude the existence of an inversion center, thus the space group is *P*1. Interestingly, there was not seen to be a temperature dependence upon the conformation of the present structure, as was seen in the 1:1 or 2:1 ratios of ligand to metal.

Compounds **3** and **3a** again demonstrate the ability of the bifunctional 3-amp ligand to form connectively identical

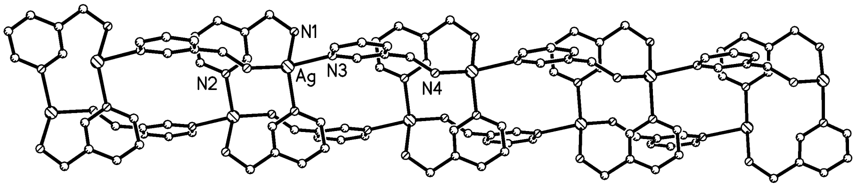

Figure 8. View of the extended cationic polymer of **3a**. Hydrogen atoms have been removed for clarity.

coordination complexes with different topologies that are solely dependent upon the method of crystallization. Both **3** and **3a** contain 3-amp and $AgBF_4$ in a 2:1 ratio formed from the combination of its constituents in acetonitrile followed by recrystallization with ether. However, as was the case with compounds **1** and **1a**, variances in temperature of the crystallizing solution cause pronounced structural differences in the crystals that are obtained. The results are both polymeric in nature and span one and two dimensions.

Crystallization of a 2:1 mixture of 3-amp and $AgBF_4$ at 5 °C produces the two-dimensional polymeric sheet of tetrahedral silvers, **3**, shown in Figure 6. As can be seen in the figure, there are two unique 3-amp ligands in the structure that perform separate tasks. One ligand coordinates in a head-to-tail fashion with a symmetry-equivalent one to bridge two silvers into a bimetallic rectangular box. A second ligand extends outward to join each of these small units together, forming larger rectangles. The resulting box-in-box motif sets two of the smaller units at opposing corners of the larger boxes. The remaining large box corners are occupied by silvers of adjacent polygons to give large hexametallic rectangles. Figure 7 shows the two unique ligands bound to Ag1. The planes of the pyridyl rings manage to orient themselves parallel to one another throughout the structure, being concomitantly perpendicular to the growth of the polymer. This effectively forms a honeycomb of alternating cells one ligand thick the breadth of the polymeric sheet. It is within these cells that the BF_4^- anions sit, held in place by weak H-bonds to the amine nitrogens. Ligand N−Ag bond lengths lengthen with the increased coordination number from the previous structures. The four donor sites available for each metal center give the silvers of **3** slightly distorted tetrahedral geometries.

When the solution that produced compound **3** is allowed to crystallize over a longer period of time at a reduced temperature of −35 °C, the structure that results is a degree of dimensionality less than that seen in **3**. The connectivity and activity of the ligands and metal of **3a** are similar to that seen in the previous structure; one of the two unique ligands is used to construct a bimetallic head-to-tail ring, while the other is used as a bridge to adjacent units. However, as seen in Figure 8, lower temperatures cause a constriction in the size of the larger ring that is formed by the bridging 3-amps. This smaller, more constrained bridge preferentially grows into a one-dimensional polymer as opposed to the two-dimensional network of **3a**. Viewing the polymer down its long axis reveals that the structure is actually a rectangular tube that is not quite of sufficient volume to contain the anions. The BF_4^- ions instead sit within the spaces formed by the stacking of the polymers on top of one another. Figure 9 shows the unique portion of the polymer of **3a** having the same ratio as **3**. The ligand bonds to silver are the longest displayed herein with the distorted tetrahedral geometry about Ag1 being similar to that of the previous structure. N−Ag−N angles range here from 93.38(5)° to 123.01(5)°.

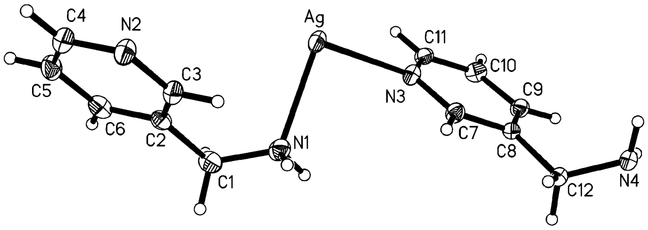

Figure 9. Thermal ellipsoid plot of the unique portion of the cationic polymer **3a**. Ellipsoids are drawn at the 50% probability level.

When bipy is added in at least a 1:1 ratio with silver in solutions of 3-amp and $AgBF_4$, it effectively stops the formation of the other structural motifs by capping each of the silvers. The polymeric motifs that were typically seen with 1:1 to 2:1 ratios of 3-amp to $AgBF_4$ are truncated by the chelating bipyridyls such that introduction of bipy to any of the solutions that produced the previous structures gives rise to the discrete, singly 3-amp-bridged structure of **4** shown in Figure 10. The 1:2:2 ratio of 3-amp to Ag to bipy in **4** has been shown to be the most favorable structure available and is the one isolatable from the several different ratios of reaction mixtures. The effect is similar to that seen previously where the chelating ability of the 2-amp and 4-amp ligands were used to cap the ends of a would-be polymer.[16,32] A symmetry-equivalent unit is held close together with the first by a silver−silver interaction of 2.9875(4) Å. This relatively short Ag−Ag interaction,[35−40] which is over 0.3 Å closer than the others described herein, is held tightly together by the resonance stacking of the three coordinated rings with those on the adjacent silver; an interaction not possible on the opposing amine-bound silvers due to the protrusion of the amine hydrogens into the area of space needed for the ring stacking. Each of the Ag environments is nicely planar with respect to its surrounding nitrogens, with the bipy N−Ag−N angle of both being expectedly acute from trigonal at 72.81(7)° and 72.90(7)° for Ag1 and Ag2, respectively.

Conclusions

This study demonstrates that changes in the ratio of ligand to metal can have significant effects on the structural characteristics of coordination complexes of silver with a noncoordinating anion. The results of this work add to the area of ratio dependence which complements nicely the well-surveyed field of anion-dependent structures of the coinage metals. It was shown herein how several of the common

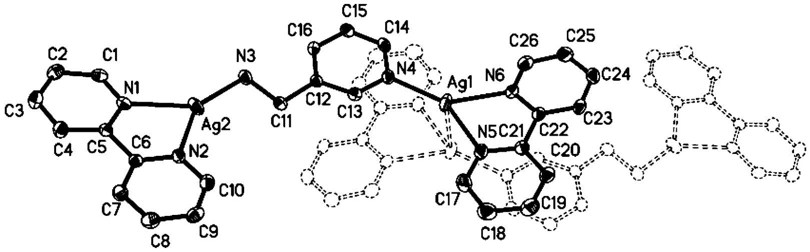

Figure 10. Thermal ellipsoid of the cationic structure of **4**. Hydrogen atoms have been removed for clarity. The symmetry-equivalent portion is shown dashed.

silver structural motifs including discrete structures (**1a** and **4**), one-dimensional polymers (**1** and **3a**), and two-dimensional polymers (**2** and **3**) can be achieved by changes in stoichiometry. It was also demonstrated how different conformations of the same ratio can be isolated by crystallization at different temperatures obtaining both a kinetic product and a more thermodynamically favored product.

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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**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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