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Article

Anion Control of the Self-Assembly of 2,3-Diarylpyrazines with Silver(I) Salts

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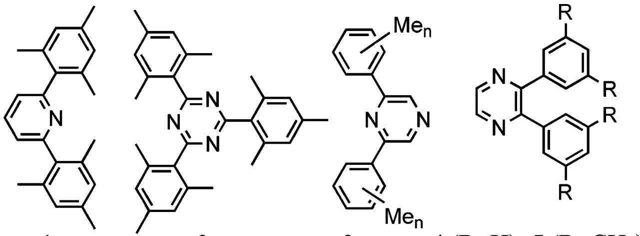
The synthesis and characterization of three one-dimensional coordination polymers formed on self-assembly of 2,3-diarylpyrazines with silver(I) salts are presented. A linear double-stranded coordination polymer was formed on self-assembly of 2,3-bis(3′5′-dimethylphenyl)pyrazine with silver(I) tetrafluoroborate. An essentially linear double-strand coordination polymer was formed on self-assembly of 2,3-bis(3′5′-dimethylphenyl)pyrazine with silver(I) trifluoromethanesulfonate. In contrast a helical silver–pyrazine coordination polymer with extensive intrastrand π-stacking was formed on self-assembly of 2,3-diphenylpyrazine with silver(I) trifluoroacetate.

Introduction

The controlled, self-assembly of metal cations with organic ligands is an ongoing challenge driven by the desire to rationally prepare coordination networks with predictable structure-derived functions.[1,2] We are particularly interested in studying the potential of substituents on the organic ligand to control and preorganize the inorganic and organic components during self-assembly. We have a longstanding interest in the silver(I) coordination chemistry of nitrogen heterocycles in which the nitrogen atoms are flanked by aryl groups. In this regard we reported the characterization of a light-stable silver(I) complex of 2,6-dimesitylpyridine, **1**,[3] and the formation and characterization of one- and two-dimensional coordination networks formed between silver(I) and 2,4,6-trimesityl-1,3,5-triazine, **2**.[4] In both those ligands, the *ortho*-methyl groups on the flanking mesityl groups held the mesityl group orthogonal to the central heterocycle. This orthogonal orientation of the mesityl groups actually facilitates coordination rather than hindering it. Recently we reported a study of the silver(I) coordination chemistry of a series of 2,6-diarylpyrazines, **3**.[5] In that study we noted that ordered, one-dimensional coordination polymers were only formed on self-assembly of 2,6-diarylpyrazines with silver(I) provided that the flanking aryl groups were held orthogonal to the heterocycle by *ortho*-methyl substituents. In this note we report the silver(I) coordination chemistry of the 2,3-diarylpyrazines **4** and **5** shown in Chart 1. It should be noted that self-assembly of the parent, unsubstituted pyrazine with silver(I) nitrate was reported to form linear, one-dimensional coordination polymers that are weakly cross-linked by the nitrate anion into a two-dimensional grid.[6]

Chart 1



1 **2** **3** **4** (R=H); **5** (R=CH$_3$)

Geometry optimization calculations at the 6-31G* level indicate that the phenyl groups will be twisted out of the plane of the pyrazine ring by approximately 46°.[7] Indeed, Kitano et al. reported dihedral angles of 40 and 51° between the phenyl rings and the central pyrazine in the X-ray crystal

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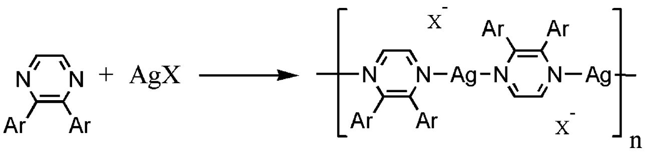

Figure 1. Proposed structure of one-dimensional coordination polymers formed on self-assembly of 2,3-diarylpyrazines with silver(I) salts.

structure of 2,3-diphenylpyrazine.[8] We reasoned that this dihedral angle would be sufficient to open both nitrogen atoms to coordination and thereby allow the formation of ordered, linear coordination polymers (Figure 1).

Experimental Section

All the solvents were purchased from Aldrich and used without further purification. The silver(I) salts were purchased from Strem and used as received. All calculations were performed using Spartan 02 Windows.[7]

Synthesis. The synthesis of the 2,3-diarylpyrazine ligands has been reported.[9] We were unable to synthesize the more hindered ligand 2,3-bis(2′,6′-dimethylphenyl)pyrazine using the standard palladium-catalyzed Suzuki coupling reaction of 2,3-dichloropyrazine with excess 2,6-dimethylphenylboronic acid. Under these conditions we only isolated the monoarylated product after extended reaction time.[9]

Self-Assembly. (2,3-Diphenylpyrazine)silver(I) Tetrafluoroborate, 6. Silver(I) tetrafluoroborate (20 mg, 0.10 mmol) and 2,3-diphenylpyrazine (23 mg, 0.10 mmol) were placed in a vial containing nitromethane (2 mL). The vial was capped and warmed until a clear, homogeneous solution was obtained. The vial was placed in the dark, and colorless, block-shaped crystals formed in 1 day (26 mg, 64%). Mp: 273−275 °C. Anal. Calcd for $C_{14}H_{12}AgBF_4N_2 \cdot CH_3NO_2 \cdot 0.5H_2O$: C, 41.08; H, 3.24; N, 8.45. Found: C, 41.07; H, 3.24; N, 8.10.

(2,3-Bis(3′,5′-dimethylphenyl)pyrazine)silver(I) Tetrafluoroborate, 7. Silver(I) tetrafluoroborate (21 mg, 0.11 mmol) and 2,3-bis(3′,5′-dimethylphenyl)pyrazine (23 mg, 0.08 mmol) were placed in a vial containing nitromethane (2 mL). The vial was capped and warmed until a clear, homogeneous solution was obtained. The vial was then placed in the dark, and colorless, rod-shaped crystals formed within 1 week (15 mg, 35%). Mp: >270 °C. Anal. Calcd for $C_{20}H_{20}AgBF_4N_2 \cdot CH_3NO_2$: C,46.36; H, 4.26; N, 7.72. Found: C, 46.25; H, 4.13; N, 7.42.

(2,3-Bis(3′,5′-dimethylphenyl)pyrazine)silver(I) Trifluoromethanesulfonate, 8. Silver(I) trifluoromethanesulfonate (19 mg, 0.07 mmol), 2,3-bis(3′,5′-dimethylphenyl)pyrazine (20 mg, 0.07 mmol), and nitromethane (10 mL) were placed in a screw-cap vial. The vial was sealed and warmed until a clear, homogeneous mixture formed. The vial was placed in the dark and the solution cooled. After 2 days the cap was loosened and the solvent evaporated slowly. Colorless, rod-shaped crystals were harvested after 1 week (18 mg, 47%). Mp: >270 °C. Anal. Calcd for $C_{23}H_{20}AgF_3N_2O_2S$: C, 46.25; H, 3.70; N, 5.14. Found: C, 46.08; H, 3.70; N, 5.14.

(2,3-Bis(3′,5′-dimethylphenyl)pyrazine)silver(I) Trifluoroacetate, 9. Silver(I) trifluoroacetate (15 mg, 0.07 mmol) and 2,3-bis(3′,5′-dimethylphenyl)pyrazine (21 mg, 0.07 mmol) were dissolved in acetonitrile (1 mL) in a screw-cap vial. After 1 week diethyl ether (1 mL) was added to the solution and the solvent then allowed to evaporate slowly. Colorless, rod-shaped crystals formed (14 mg, 39%). Mp: 186−188 °C. Anal. Calcd for $C_{22}H_{20}AgF_3N_2O_2$: C, 51.96; H, 3.97; N, 5.51. Found: C, 51.64; H, 4.13; N, 5.74. Crystals suitable for X-ray analysis were grown by evaporation from an acetone solution.

Table 1. Crystallographic Data[a] for **6**$\cdot 2CH_3NO_2$, **8**$\cdot C_3H_6O$, and **9**$\cdot H_2O$

	6$\cdot 2CH_3NO_2$	**8**$\cdot C_3H_6O$	**9**$\cdot H_2O$
formula	$C_{18}H_{18}AgBF_4N_4O_4$	$C_{24}H_{26}AgF_3N_2O_4S$	$C_{20}H_{22}AgF_3N_2O_3$
fw	549.04	603.40	527.29
space group	$P2_1/c$	$C2/c$	$P2_1$
a, Å	15.404(2)	18.031(3)	11.2008(6)
b, Å	19.967(3)	18.672(3)	19.9816(11)
c, Å	14.279(2)	14.466(2)	15.4750(9)
β, deg	104.141(3)	90.491(4)	105.083(2)
V, Å^3	4258.7(10)	4870.2(13)	3344.1(3)
Z	8	8	6
d_{calc}, g/cm^3	1.713	1.646	1.571
T, °C	−173(2)	−173(2)	−173
μ, cm^{-1}	10.14	9.70	9.54
$R_1(F_o)^b$	0.0704	0.0423	0.0433
$wR_2(F_o^2)^b$	0.2392	0.1326	0.1062

[a] All data sets were collected at $T = 100$ K using Mo Kα ($\lambda = 0.710\,73$ Å) radiation. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Crystallography. Crystallographic measurements were performed using a Bruker APEX diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation with the sample kept at 100 K. Approximately 1.5 hemispheres of data, $\theta \leq 26°$, were collected as ω-scan images. None of the crystals showed significant decay during data collection. Data were integrated and corrected for Lorentz and polarization effects with SAINT[10] and were corrected for absorption with SADABS.[11]

Space group assignments were based on systematic absences and statistical tests and verified by structure refinement. Structures were solved by direct methods and refined against all data using the SHELXTL software package.[12] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were assigned positions by geometry and refined with a riding model using isotropic displacement parameters of 1.2 times (1.5 for methyl) that of the attached atoms. Basic structural parameters are presented in Table 1. Details of the crystal structures not presented above or in Table 1 are available from the Supporting Information.

In the structure of **9** the anion was disordered and modeled in three orientations with refined occupancies of 0.360(3), 0.295(3), and 0.345(3) for the unprimed, primed, and double-primed atoms. The 3,5-dimethylphenyl groups both exhibited a great deal of libration normal to their rings. An acetone solvent molecule was so severely disordered that it could not be easily modeled but was removed from the data using the Squeeze routine in Platon.[13] One of the three silver atoms was bound to a water molecule, O(1). One of the other two waters, O(3), was disordered and refined in two positions with occupancy factors of 0.53(2) and 0.47(2) for the unprimed and primed atoms. No hydrogens were found for O(3). Both waters O(2) and O(3) were refined with isotropic displacement parameters.

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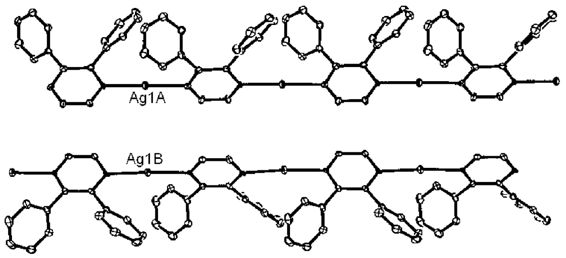


Figure 2. View showing the double-strand linear coordination polymer, **6**, formed on self-assembly of **4** with silver(I) tetrafluoroborate in nitromethane. Hydrogen atoms, tetrafluoroborate anions, and nitromethane solvent were omitted for clarity.

Results and Discussion

The two ligands, **4** and **5**, were synthesized in good yield using the palladium-catalyzed Suzuki coupling of the corresponding arylboronic acid with 2,3-dichloropyrazine.[9] We decided to probe the silver coordination chemistry of these ligands with a range of coordinating anions (triflate, trifluoroacetate, and nitrate) and a noncoordinating anion tetrafluoroborate. On the basis of the hypothesis that we could form a 1:1 linear coordination polymer, we then allowed equimolar amounts of the two components to self-assemble from homogeneous solutions. We were unable to form crystalline solids using silver(I) nitrate.

The self-assembly of 2,3-diphenylpyrazine (**4**) with silver(I) tetrafluoroborate yielded a colorless crystalline solid, **6**, that elemental analysis indicated had a 1:1 ligand:silver stoichiometry. X-ray crystallography revealed a duplex, one-dimensional, ribbonlike polymer as shown in Figure 2.

Alternate pyrazine ligands within each strand are almost orthogonal with dihedral angles of approximately 80 and 70° for strands A and B, respectively. Each strand is essentially linear with nitrogen−silver−nitrogen angles of 172.9(2) and 175.0(2)° for N(1A)$^{\#1-}$Ag(1A)−N(2A) and N(2B)−Ag(1B)−N(1B)$^{\#1}$, respectively. The asymmetric unit contained two unique diphenylpyrazine ligands each bound to a unique silver cation and the accompanying tetrafluoroborate anions and four independent nitromethane molecules as shown in Figure 3.

The silver cations are weakly coordinated in a bidentate fashion by nitromethane molecules with silver−oxygen bond lengths in the range 2.85−2.93 Å. Each coordinating nitromethane molecule also has a close contact to a silver atom in the neighboring strand with a separation of 3.037(7) and 3.161(6) Å for Ag(1B)−O(1C)$^{\#2}$ and Ag(1A)−O(1D)$^{\#1}$, respectively. The silver−pyrazine bond lengths in this network are relatively short at 2.186(7), 2.209(6), 2.190(6), and 2.218(7) Å for Ag(1A)−N(1A)$^{\#1}$, Ag(1A)−N(2A), Ag(1B)−N(2B), and Ag(1B)−N(1B)$^{\#2}$, respectively.

The strands pack in pairs of strands as shown in Figure 4. In this arrangement the tetrafluoroborate anions and two of the nitromethane molecules lie in channels along the *c*-axis.

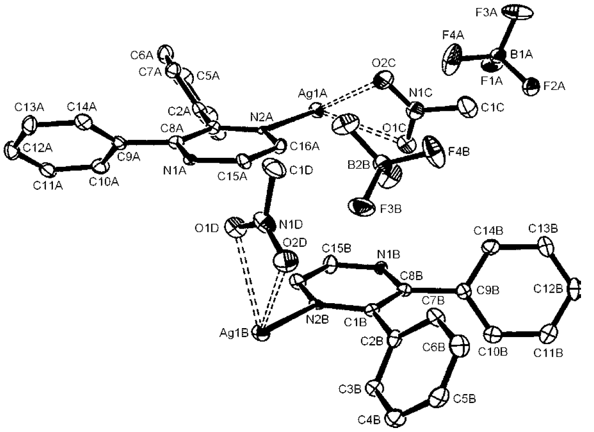


Figure 3. View of both unique pyrazine−silver asymmetric units of coordination network **6** showing the weakly coordinated nitromethane molecules and the tetrafluoroborate counterions with thermal ellipsoids drawn at the 50% level. The two noncoordinating nitromethane molecules are omitted for clarity.

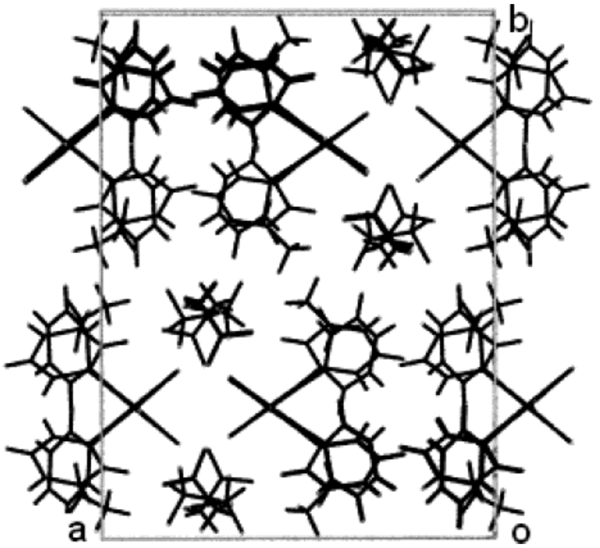


Figure 4. View along the *c*-axis of the one-dimensional coordination network **6**.

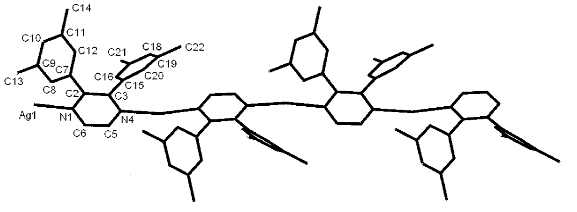


Figure 5. View of a single strand of the linear coordination polymer formed between 2,3-bis(3′,5′-dimethylphenyl)pyrazine and silver(I) triflate, **8**, with the triflate anion and the hydrogen atoms omitted for clarity.

The self-assembly of 2,3-bis(3′,5′-dimethylphenyl)pyrazine and silver(I) triflate in nitromethane solvent yielded colorless rod-shaped crystals, **8**, that elemental analysis indicated also had a 1:1 ligand:silver stoichiometry. X-ray crystallography revealed an essentially linear, one-dimensional, ribbonlike polymer with a N(1)−Ag(1)−N(4) angle of 166.78(12)°. The alternate pyrazine ligands are almost orthogonal to each other as shown in Figure 5. The asymmetric unit comprised a single pyrazine ligand, the coordinated silver cation, and the associated anion.

Within each one-dimensional strand the triflate anion is disordered over three positions with a single contact to the silver cation and a second weaker contact between a second triflate oxygen atom and a silver atom from the adjacent strand. The silver−oxygen distances range from 2.330 to

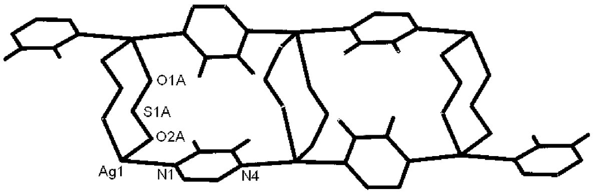


Figure 6. View showing the connectivity between adjacent strands of the one-dimensional polymer **8** with the aryl rings omitted for clarity.

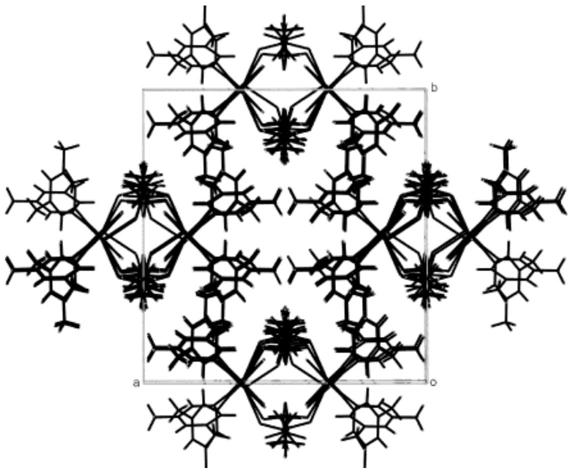


Figure 7. View along *c* of the packing of strands of the one-dimensional coordination network **8** showing the pairwise connectivity between adjacent pairs of strands.

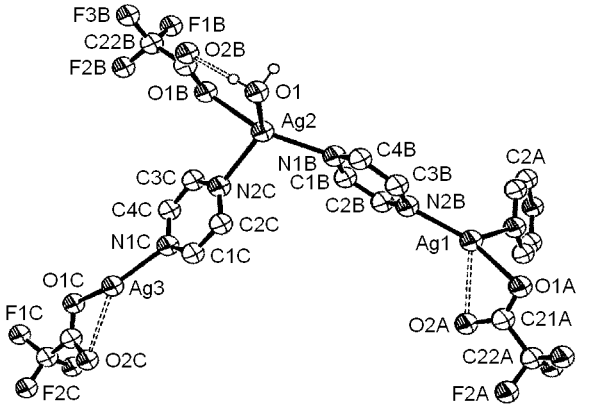


Figure 8. Partial view of the asymmetric unit of coordination polymer **9** showing the pseudotetrahedral coordination geometry about the three unique silver atoms. Aryl groups and hydrogen atoms were omitted for clarity.

2.971 Å. In this way two adjacent strands of the polymer are held together by the triflate bridges. This connectivity is shown in Figure 6, and the packing of the pairs of one-dimensional coordination polymers in the unit cell is shown in Figure 7.

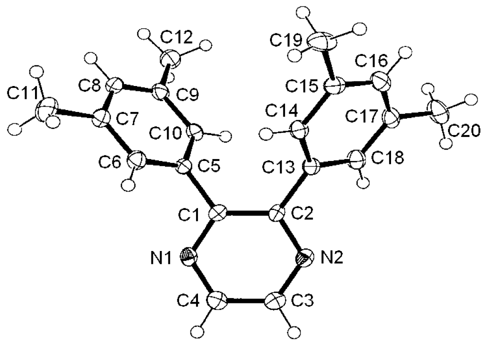


Figure 9. View of one of the three independent pyrazine molecules, molecule A in polymer **9**, showing the atom-numbering scheme.

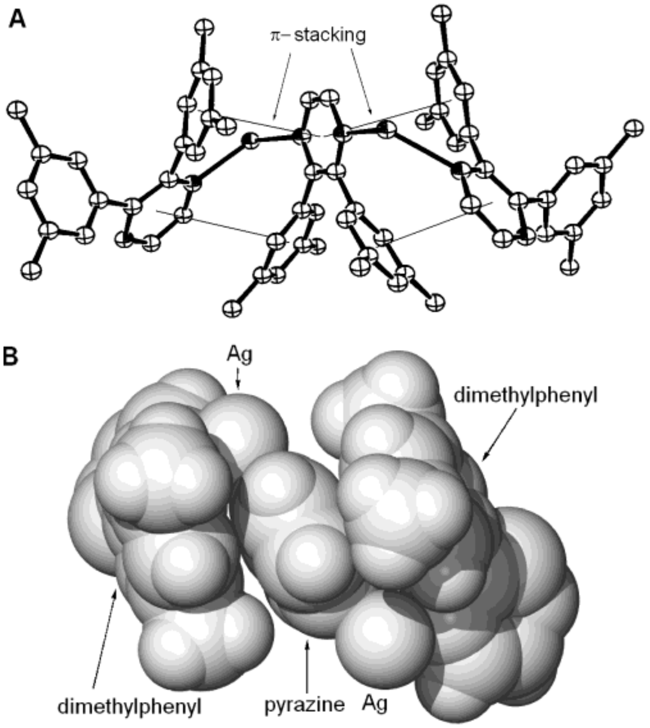
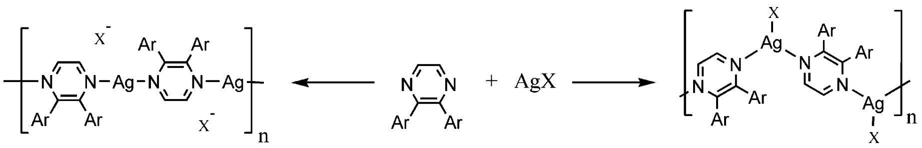


Figure 10. (A) View of a portion of the coordination network **9** with lines linking the centroids of the π-stacked aryl and pyrazine rings. The trifluoroacetate anion has been omitted for clarity. (B) Space-filling view of the network showing a central silver-coordinated pyrazine flanked by dimethylphenyl substituents from adjacent diarylpyrazine units.

The self-assembly of **5** with silver(I) trifluoroacetate yielded a colorless crystalline solid, **9,** that elemental analysis indicated was also a 1:1 mixture. X-ray quality crystals were grown by slow evaporation from an acetone solution and adventitious water was included in the crystals. We did not try to rigorously exclude water. Single-crystal X-ray analysis indicated the formation of a 1:1 coordination polymer with a helical structure. The asymmetric unit contained three unique silver atoms and three unique 2,3-bis(3′,5′-dimethyldiphenyl)pyrazine ligands. A partial view of the asymmetric unit is shown in Figure 8 in which the aryl rings have been omitted for clarity. The silver(I) atoms have pseudotetrahedral coordination geometry that clearly helps to twist the coordination polymer away from linearity. One of the three independent diaryl pyrazine ligands is shown in Figure 9.

The six unique silver−nitrogen bond lengths are in the range 2.246(3) and 2.378(3) Å, and each silver is formally tetracoordinated with nitrogen−silver−nitrogen bond angles of 117.04(12), 104.16(11), and 112.94(12)° for N(2B)−Ag(1)−N(1A), N(1B)−Ag(2)−N(2C), and N(1C)−Ag(3)−$N(2A)^{\#1}$, respectively. For Ag(1) there is an asymmetric bond to the trifluoroacetate anion with silver−oxygen distances of 2.309(3) and 2.759 Å for Ag(1)−O(1A) and Ag(1)−O(2A), respectively. It is interesting to note that the silver atom is not coplanar with either of the bonded pyrazine rings and lies approximately 6° below the plane of pyrazine B and 21° below pyrazine A. A similar asymmetric coordina-

Scheme 1



tion to the trifluoroacetate anion is observed for Ag(3) with silver−oxygen distances of 2.278(4) and 2.828 Å for Ag(3)−O(1C) and Ag(3)−O(2C), respectively. The coordination about the remaining silver atom, Ag(2), is completed with a bond to one trifluoroacetate oxygen, 2.403(3) Å, and to one water molecule, 2.420(3) Å. The water molecule is hydrogen bonded to the second oxygen on the trifluoroacetate anion, and thus, the trifluoroacetate anion effectively bridges the silver and water molecules. It is noteworthy that self-assembly of 2,6-bis(3′,5′-dimethylphenyl)pyrazine and silver(I) trifluoroacetate in a variety of solvents yielded a series of structures in which pairs of trifluoroacetate anions bridged two silver cations.[5] The bridging disilver motif has also been reported by Brammer to be a reliable supramolecular synthon.[14]

The bent nitrogen−silver−nitrogen bond facilitates significant π-stacking between adjacent diarylpyrazine units that serves to weave a helical one-dimensional structure. Indeed, Ciani reported helical one-dimensional coordination polymers on self-assembly of pyridazine with silver salts and speculated that the nitrate and triflate counterions coordinated to the silver(I) cation and thereby helped to twist and orient the helical structures.[15] Michon et al. also reported similar π-stacking in the formation of a helical coordination complex on reaction of 2,3-diphenylquinoxaline with $(PhCH_2)Mn(CO)_5$.[16] The π-stacking is shown in Figure 10, where it can be seen that each pyrazine moiety is π-stacked to a pendant dimethylphenyl ring from each adjacent ligand. The centroid−centroid pyrazine−phenyl distances are in the range of 3.6−3.8 Å. The period of the helix, 15.5 Å, is shown in Figure 11.

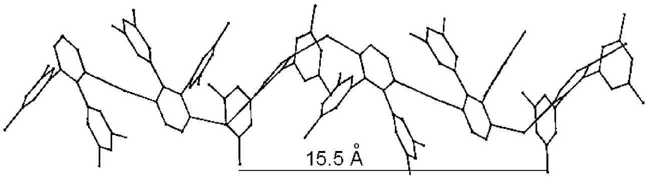


Figure 11. View of the helical structure of one strand of the coordination network, **9**, formed on self-assembly of **4** and silver(I) trifluoroacetate. The trifluoroacetate anions, water molecules, and hydrogen atoms have been omitted for clarity.

The nature of the one-dimensional network formed on self-assembly of 2,3-diarylpyrazines with silver(I) salts is modulated by the anion. The noncoordinating anion, tetrafluoroborate, facilitates the formation of a linear pyrazine−silver−pyrazine bond (173°) whereas the coordinating anion, trifluoroacetate, enforces nonlinear pyrazine−silver−pyrazine bond (111°) thereby facilitating a helical or wavelike structure. This effect is demonstrated in Scheme 1. The triflate anion is intermediate, and the pyrazine−silver−pyrazine bond is more bent (166°) with this anion as compared to tetrafluoroborate anion. We plan to investigate the anion-induced interconversion between the various structures reported here.[17]

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 37506-B3), and the Graduate College at SMSU for partial funding of this research and the National Science Foundation (Grant CHE-0079282) and the University of Kansas for funds to purchase the X-ray instrument and computers. We also thank the NSF for a GK-12 Fellowship for N.S. (Grant No. DGE-0086335).

Supporting Information Available: Details of three crystal structures in CIF format. This information is available free of charge via the Internet at http://acs.pubs.org.

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