

Silver(I) Coordination Chemistry of 2,6-Diarylpyrazines. π -Stacking, Anion Coordination, and Steric ControlNate Schultheiss,[†] Douglas R. Powell,[‡] and Eric Bosch^{*†}

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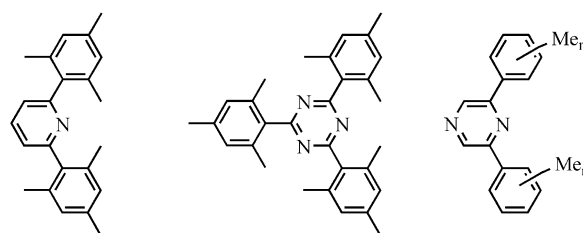
The silver(I) coordination chemistry of 2,6-diarylpyrazines is reported. Discrete coordination complexes and two-dimensional coordination networks were characterized. The substitution pattern on the pendant aryl groups controlled the type of coordination chemistry involved. Thus, *o*-methyl-substituted aryl groups held the aryl groups orthogonal to the central pyrazine ring, opening the "hindered" nitrogen atoms to complexation, and polymeric networks were characterized. In the absence of the *o*-methyl groups, discrete coordination complexes were characterized. Thus, a dimeric 2:1 ligand–silver(I) complex was isolated and characterized on reaction of 2,6-bis(3',5'-dimethylphenyl)pyrazine with silver(I) trifluoroacetate in acetonitrile solvent, while a 2:2 complex was isolated from dichloromethane solvent. Two trifluoroacetate ligands bridge two silver cations in both complexes. Reaction of the same pyrazine ligand with silver(I) tetrafluoroborate yielded a discrete 2:1 complex. A 2:1 complex was isolated on reaction of 2,6-diphenylpyrazine with silver(I) nitrate. These complexes were interlinked by weakly coordinating nitrate anions to form interwoven one-dimensional ribbons. Two-dimensional networks were obtained on reaction of silver(I) trifluoroacetate with either 2,6-bis(2',6'-dimethylphenyl)pyrazine or 2-(2',6'-dimethylphenyl)-6-(3',5'-dimethylphenyl)pyrazine. The networks comprised pyrazine–silver(I) strands cross-linked with complex bridged silver(I) trifluoroacetates.

Introduction

Over the past several years we have been interested in the coordination chemistry of nitrogen heterocycles in which the nitrogen atoms are flanked by aryl groups. In this regard we reported the light-stable silver(I) complex of 2,6-dimesitylpyridine¹ and the one- and two-dimensional coordination networks formed between silver(I) and 2,4,6-trimesityl-1,3,5-triazine (Chart 1).² In both ligands the *o*-methyl groups on the flanking mesityl groups held the mesityl group orthogonal to the central heterocycle. With this orthogonal orientation the mesityl groups actually facilitate coordination rather than hinder it.

In this study we examine the effect of a variety of flanking aryl groups on the coordination chemistry of 2,6-disubstituted pyrazines with the goal of preparing coordination networks according to Figure 1. We planned to prepare ordered one-

Chart 1



2,6-dimesitylpyridine 2,4,6-trimesityl-1,3,5-triazine 2,6-diarylpyrazines

dimensional coordination polymers with the ultimate goal of preparing materials for nonlinear optical applications.³ We expected that the steric demands of the pendant aryl groups would render the coordination selective with the aryl groups oriented in the same direction as shown in Figure 1.

The coordination chemistry of pyrazines is rich, and one-dimensional coordination polymers are expected on self-assembly with silver(I) since silver(I) favors linear coordination geometry. Indeed, the first structural characterization

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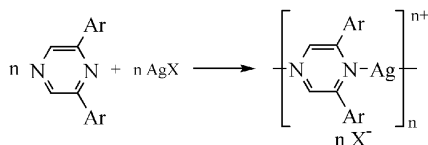


Figure 1. Proposed formation of ordered one-dimensional coordination polymers on self-assembly of 2,6-diarylpyrazines with silver(I) salts.

of a one-dimensional coordination polymer formed between silver(I) and pyrazine was reported by Vranka and Amma in 1966 using silver(I) nitrate.⁴ It should, however, be noted that although silver(I) has a preference for coordination number 2 with linear coordination geometry, other coordination numbers and geometries are possible. Indeed, in 1996 Moore and co-workers reported a compilation of the coordination geometries about silver(I) using 90 structures culled from the Cambridge Crystallographic Database.⁵ Linear coordination geometry was most common with 43 occurrences. Other common geometries included trigonal planar, tetrahedral, and trigonal pyramidal with occasional instances of square planar, pyramidal, T-shaped, and bent geometry. The flexibility in coordination about silver(I) has also been noted in silver(I)–pyrazine complexation. It is, for example, noteworthy that Ciani and co-workers reported the characterization of several different coordination networks on self-assembly of pyrazine with silver(I) tetrafluoroborate.⁶ Only one of these networks was a simple one-dimensional coordination polymer. Both Ciani⁷ and Moore⁵ have reported the formation of one-dimensional coordination networks on self-assembly of pyrazine with silver(I) hexafluorophosphate.

Experimental Section

All chemicals were purchased from Aldrich and used as received. The synthesis and characterization of the diarylpyrazines used in this study are reported elsewhere.⁸

Silver(I) Complex Formation. (2,6-Bis(3',5'-dimethylphenyl)pyrazine)silver(I) Trifluoroacetate, 1. Silver(I) trifluoroacetate (16 mg, 0.08 mmol) and 2,6-bis(3',5'-dimethylphenyl)pyrazine (20 mg, 0.07 mmol) were placed in a screw-cap vial along with acetonitrile (5 mL). The vial was sealed and gently heated until a clear, homogeneous solution was formed. The vial was allowed to cool in the dark. After one week colorless rod-shaped crystals were harvested (19 mg, 69%): mp 235–237 °C. Anal. Calcd for C₈₄H₈₀Ag₂F₆N₈O₄: C, 63.24; H, 5.05; N, 7.02. Found: C, 63.11; H, 5.23; N, 7.14. Since elemental analysis indicated that the ratio of ligand to silver(I) trifluoroacetate was 1:2, the reaction was repeated with this initial ratio. Thus, a homogeneous solution of silver(I) trifluoroacetate (8.1 mg, 0.037 mmol) and 2,6-bis(3',5'-dimethylphenyl)pyrazine (20.8 mg, 0.07 mmol) in acetonitrile (5 mL) was prepared as described above. After one week thin colorless rod-shaped crystals were harvested (25 mg, 87%): mp 235–237 °C.

Anal. Calcd for C₄₂H₄₀N₄O₂F₃Ag: C, 63.24; H, 5.05; N, 7.02. Found: C, 63.35; H, 5.05; N, 7.02.

(2,6-Diphenylpyrazine)silver(I) Nitrate, 2. Silver(I) nitrate (15 mg, 0.09 mmol) and 2,6-diphenylpyrazine (22 mg, 0.09 mmol) were placed in a screw-cap vial along with acetonitrile (2 mL). The vial was sealed and gently heated until a clear, homogeneous mixture formed. The vial was allowed to cool in the dark. Colorless cube-shaped crystals were harvested after 1 day (21 mg, 70%): mp 190–192 °C. Anal. Calcd for C₃₂H₂₄AgN₅O₃: C, 60.65; H, 3.82; N, 11.06. Found: C, 60.04; H, 3.78; N, 11.22.

(2,6-Bis(3',5'-dimethylphenyl)pyrazine)silver(I) Trifluoroacetate, 3. Silver(I) trifluoroacetate (12.6 mg, 0.06 mmol) and 2,6-bis(3',5'-dimethylphenyl)pyrazine (16.7 mg, 0.06 mmol) were placed in a screw-cap vial along with dichloromethane (3 mL). The vial was sealed and gently heated until a clear, homogeneous solution formed. The vial was allowed to cool in the dark, and colorless rod-shaped crystals were harvested after one week (17 mg, 58%): mp 230–232 °C. Anal. Calcd for C₄₄H₄₀N₄O₄F₆Ag₂: C, 51.89; H, 3.96; N, 5.50. Found: C, 51.95; H, 3.79; N, 5.43.

(2,6-Diphenylpyrazine)silver(I) Tetrafluoroborate, 4. A homogeneous solution of silver(I) tetrafluoroborate (27 mg, 0.14 mmol) and 2,6-diphenylpyrazine (20 mg, 0.09 mmol) in a mixture of nitromethane (6 mL) and toluene (2 mL) was formed after gentle heating in a sealed screw-cap vial. The vial was stored in the dark. After one week the cap was loosened and the solvent allowed to evaporate slowly. Colorless rods were harvested after a further week (25 mg, 80%): mp >270 °C. Anal. Calcd for C₃₂H₂₄N₄BF₄Ag·CH₃NO₂: C, 55.07; H, 3.78; N, 9.74. Found: C, 54.94; H, 3.73; N, 9.52.

(2,6-Bis(2',6'-Dimethylphenyl)pyrazine)silver(I) Trifluoroacetate, 5. A homogeneous solution of silver(I) trifluoroacetate (32 mg, 0.15 mmol) and 2,6-bis(2',6'-dimethylphenyl)pyrazine (20 mg, 0.07 mmol) in a mixture of nitromethane (8 mL) and acetonitrile (0.5 mL) was formed in a screw-capped vial on gentle heating. The vial was stored in the dark, and colorless rods were harvested after 2 days (34 mg, 67%): mp 245–247 °C. Anal. Calcd for C₂₄H₂₀N₂O₄F₆Ag₂: C, 39.48; H, 2.77; N, 3.85. Found: C, 39.76; H, 2.94; N, 4.03.

(2-(2',6'-Dimethylphenyl)-6-(3'',5''-dimethylphenyl)pyrazine)silver(I) Trifluoroacetate, 6. A homogeneous solution of silver(I) trifluoroacetate (29 mg, 0.13 mmol) and 2-(2',6'-dimethylphenyl)-6-(3'',5''-dimethylphenyl)pyrazine (18 mg, 0.06 mmol) in toluene (5 mL) was obtained on gentle heating in a screw-cap vial. The vial was stored in the dark, and colorless needles were harvested after 3 days (40 mg, 62%): mp 190–192 °C. Anal. Calcd for C₅₂H₄₀N₄O₁₂F₁₈Ag₆·2C₇H₈: C, 38.08; H, 2.71; N, 2.69. Found: C, 38.35; H, 2.73; N, 2.69.

Crystallography. Crystallographic measurements were performed at 100 K using a Bruker APEX diffractometer with graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) radiation. Single crystals of all compounds were coated with Paratone-N oil, attached to glass fibers, and transferred to the diffractometer. Approximately 1½ hemispheres of data were collected as ω -scan images. None of the crystals showed significant decay during data collection. The data were integrated and corrected for Lorentz and polarization effects with SAINT⁹ and were corrected for absorption with SADABS.¹⁰

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(10) Sheldrick, G. M. SADABS. Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 2000.

Table 1. Crystallographic Data^a for **1**, **2**, **3**, **4**· $\frac{1}{2}$ CH₃NO₂, **5**, and **6**·2C₇H₈

	1	2	3	4 · $\frac{1}{2}$ CH ₃ NO ₂	5	6 ·2C ₇ H ₈
empirical formula	C ₈₄ H ₈₀ Ag ₂ F ₆ N ₈ O ₄	C ₃₂ H ₂₄ AgN ₅ O ₃	C ₂₂ H ₂₀ AgF ₃ N ₂ O ₂	C ₃₃ H ₂₇ AgBF ₄ N ₅ O ₂	C ₂₄ H ₂₀ Ag ₂ F ₆ N ₂ O ₄	C ₆₆ H ₅₆ Ag ₆ F ₁₈ N ₄ O ₁₂
fw	1595.30	634.43	509.27	720.28	730.16	2086.37
space group	<i>P</i> 1	Pbcn	<i>P</i> 1	<i>P</i> 1	<i>P</i> ₂ /n	<i>P</i> ₂ /c
Z	1	4	2	2	4	2
<i>a</i> , Å	9.4603(6)	7.1361(6)	4.5443(4)	3.8099(3)	10.5410(11)	11.7717(6)
<i>b</i> , Å	13.3544(8)	30.910(2)	14.3428(13)	11.8095(9)	21.859(2)	24.9539(12)
<i>c</i> , Å	14.7099(9)	11.9478(9)	15.3996(14)	16.4554(12)	10.9825(11)	12.8210(6)
α , deg	82.780(2)	90	89.317(2)	84.265(2)	90	90
β , deg	84.554(2)	90	84.737(2)	83.833(2)	100.434(2)	110.828(2)
γ , deg	75.649(2)	90	87.086(2)	85.556(2)	90	90
<i>V</i> , Å ³	1782.20(19)	2635.4(3)	998.16(16)	730.74(10)	2488.7(4)	3520.1(3)
<i>d</i> _{calcd} , g/cm ³	1.486	1.599	1.694	1.694	1.653	1.968
R1 (wR2), ^b %	2.73 (7.57)	2.79 (9.26)	3.45 (8.69)	3.40 (8.76)	3.15 (11.51)	3.37 (8.12)

^a All data sets were collected at *T* = 100 K using Mo K α (λ = 0.71073 Å) radiation. ^b R1 = $\sum||F_o| - |F_c||/\sum|F_o|$, wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths, Å, for Compounds **1–6**

Compound 1			
Ag(1)–N(2)	2.2045(14)	Ag(1)–N(3)	2.2164(15)
Ag(1)–O(1)	2.5584(13)	Ag(1)–O(2)#2	2.5742(13)
O(2)–Ag(1)#1	2.5742(13)	Ag(1)–Ag(1)#1	3.1014(3)
Compound 2			
Ag(1)–N(2)	2.2052(14)	Ag(1)–O(1)	2.7051(14)
Compound 3			
Ag(1)–N(1)	2.355(2)	Ag(1)–O(1)	2.2312(17)
Ag(1)–O(2)#1	2.1871(16)	O(2)–Ag(1)#1	2.1871(16)
Ag(1)–Ag(1)#2	3.0388(4)	Ag(1)–Ag(1)#1	2.9710(4)
Compound 4			
Ag(1)–N(1)	2.1423(16)	Ag(1)–Ag(1)#1	3.810(4)
Compound 5			
Ag(1)–N(1)	2.202(2)	Ag(1)–N(2)#1	2.235(2)
Ag(1)–O(1)	2.457(2)	Ag(2)–O(4)#2	2.229(2)
Ag(2)–O(3)	2.274(2)	Ag(2)–O(1)	2.567(3)
Ag(2)–Ag(2)#2	2.9137(5)		
Compound 6			
Ag(1)–N(1)	2.2310(2)	Ag(1)–N(2)#1	2.365(2)
Ag(1)–O(2)	2.327(2)	Ag(1)–O(4)	2.3283(19)
Ag(2)–O(3)	2.2603(19)	Ag(2)–O(1)	2.5273(2)
Ag(2)–O(5)	2.4749(19)	Ag(3)–O(6)#2	2.258(2)
Ag(3)–O(5)	2.287(2)	Ag(3)–O(1)	2.454(2)
Ag(3)–Ag(3)#2	2.91384(4)		

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.¹¹ 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 1.2 times (1.5 for methyl) those of the attached atoms. Basic structural parameters are presented in Table 1. The anionic species of compound **4**· $\frac{1}{2}$ -CH₃NO₂ was disordered and modeled in two orientations with refined occupancies of 0.272(3) and 0.228(3) for the unprimed and primed atoms. The 0.5 occupancy solvent was also near this same region of the cell. Restraints on the positional and displacement parameters of the anion and solvent of **4**· $\frac{1}{2}$ CH₃NO₂ were required. Restraints on the positional parameters of the fluorine atoms of compound **6**·2C₇H₈ were required. Selected bond lengths from structures **1–6** are shown in Table 2.

Results and Discussion

We were specifically interested in the synthesis of ordered one-dimensional coordination polymers by self-assembly of

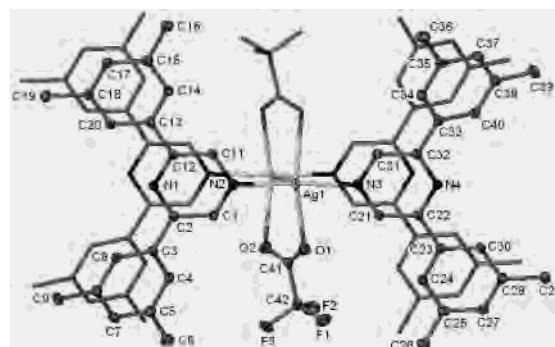


Figure 2. Perspective view of complex **1** formed on self-assembly of equimolar amounts of 2,6-bis(3',5'-dimethylphenyl)pyrazine and silver(I) trifluoroacetate from acetonitrile solution. The asymmetric unit is shown with the displacement ellipsoids drawn at the 50% level, and those atoms are labeled. The hydrogen atoms are omitted for clarity.

2,6-diarylpyrazines with 1 equiv of a silver(I) salt according to Figure 1. We reasoned that even the aryl groups that were not specifically held orthogonal to the pyrazine ring could easily adopt such a conformation to form an ordered polymer. We first treated 2,6-bis(3',5'-dimethylphenyl)pyrazine with 1 equiv of silver(I) trifluoroacetate in acetonitrile and allowed the components to self-assemble. We isolated colorless rod-shaped crystals, and elemental analysis of the bulk solid indicated that a 2:1 ligand–silver complex, **1**, had been formed. A single crystal suitable for X-ray analysis was selected for analysis and the structure determined. The silver complex crystallized as a dimeric 2:1 complex. Only half of the dimer, labeled in Figure 2, was crystallographically unique.

Two of the dimethylphenyl rings are essentially coplanar with the pyrazine ring with torsional angles of approximately 3.5° and 4.5° for rings C(33)–C(40) and C(3)–C(10), respectively. The remaining two aryl groups are twisted out of planarity with the pyrazine ring by 24° and 28° for rings C(13)–C(20) and C(23)–C(30), respectively. Within each dimer unit the diarylpyrazine rings are π -stacked with interplanar distances in the range 3.4–3.6 Å. The two trifluoroacetate ligands each bridge across two silver atoms and thereby effectively fill the space between the two pairs of diarylpyrazine ligands. The silver–nitrogen bond lengths of 2.2045(14) and 2.2164(15) Å are well within the general range of 2.18–2.36 Å reported thus far for silver–pyrazine

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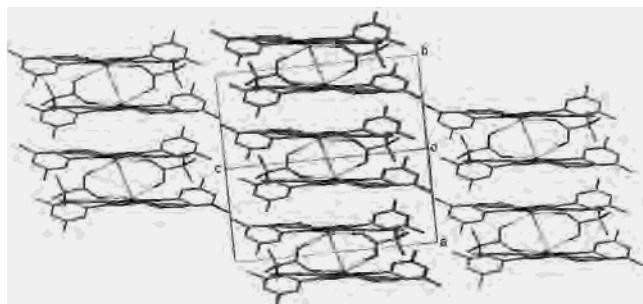


Figure 3. View of the packing of adjacent complexes **1**.

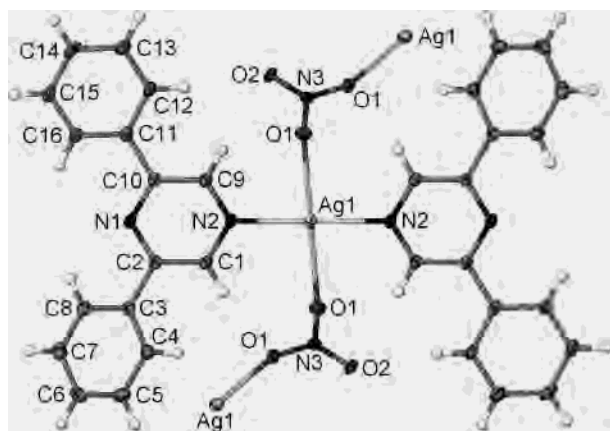


Figure 4. View of complex **2** formed on self-assembly of equimolar amounts of 2,6-diphenylpyrazine and silver(I) nitrate in acetonitrile solution. The extended coordination of the nitrate anion to adjacent complexes is shown.

complexes.¹² Throughout this paper we have drawn a bond between silver atoms separated by 3.1 Å or less although this assignment is controversial. This distance is only slightly longer than the separation of 2.884 Å in silver metal,¹³ and Wheatley recently argued that there is significant metal–metal bonding at these short distances.¹⁴ In contrast it is interesting to note that Brammer recently reported the structure of the pyrazine–silver(I) trifluoroacetate complex and noted a silver–silver separation of 3.99 Å. In that network a more complex trifluoroacetate bridging motif was observed.¹⁵

The complexes stack in the offset manner shown in Figure 3 with an interplanar distance of approximately 3.3 Å.

In a similar experiment the self-assembly of equimolar amounts of 2,6-diphenylpyrazine and silver(I) nitrate in acetonitrile solution yielded colorless crystals. Elemental analysis of the bulk solid indicated that a 2:1 complex, **2**, had been formed. Single-crystal X-ray analysis indicated that the 2:1 complex shown in Figure 4 was formed.

As seen in Figure 4 the silver(I) cation has pseudo square planar geometry. Since the silver sits on a center of

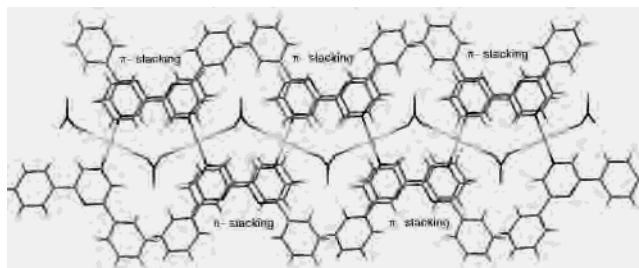


Figure 5. Perspective view of the nitrate-bridged coordination network **2** showing the extensive π -stacking of the pyrazyl and phenyl rings.

symmetry, the N–Ag–N angle is 180° with N(2)#1–Ag(1)–O(1) and N(2)–Ag(1)–O(1) angles of 97.14(5)° and 82.86(5)°, respectively. The silver–nitrogen distance of 2.2052(14) Å and the silver–oxygen distance of 2.7051(14) Å are similar to the distances of 2.214 and 2.722 Å, respectively, reported by Vranka and Amma for the unsubstituted pyrazine–silver(I) nitrate structure.⁴ The phenyl rings are slightly twisted with respect to the central pyrazine with torsional angles of 6° and 26° for phenyls C(11)–C(16) and C(3)–C(8), respectively. The nitrate counterions effectively bridge adjacent complexes to form a silver–nitrate ribbonlike structure as shown in Figure 5. In the structure of **2** the bridging nitrate anions orient the adjacent ligands so that they partially overlap to form an intertwined one-dimensional ribbon. For each pair of adjacent complexes a phenylpyrazine moiety from one ligand π -stacks with a phenylpyrazine moiety from the ligand complexing the adjacent silver cation. The interplanar distance is approximately 3.5 Å. It is interesting to note that Vranka and Amma reported that nitrate atoms bridged adjacent one-dimensional pyrazine–silver(I) strands to form a two-dimensional network in the unsubstituted pyrazine–silver(I) nitrate structure.

In each of the complexes **1** and **2**, at least one of the pendant aryl rings is almost coplanar with the central pyrazine ring, thereby rendering the “hindered” N inaccessible to complexation. We reasoned that the unreacted equivalent of silver(I) salt remained in solution in both these experiments as the acetonitrile solvate. The coordinating solvent thus actually facilitated formation of the 2:1 complexes. We speculated that we could force the second silver atom to complex the hindered nitrogen atom by changing to a less coordinating solvent as shown in Figure 6.

We initially chose dichloromethane as our “noncoordinating” solvent and used the sparingly soluble silver(I) trifluoroacetate salt. In this solvent we were not able to solubilize the nitrate salt even in the presence of the pyrazine ligands. Accordingly, we allowed an equimolar mixture of 2,6-bis(3',5'-dimethylphenyl)pyrazine and 1 equiv of silver(I) trifluoroacetate to self-assemble in dichloromethane. Elemental analysis of the resultant colorless solid indicated that a 1:1 complex, **3**, was indeed formed, and we assumed that this was the expected coordination polymer. Subsequent X-ray structural analysis indicated that we did not form a coordination polymer but rather a trifluoroacetate-bridged 2:2 coordination complex as shown in Figure 7. A key feature of this structure is that the trifluoroacetate anions now bridge two silver atoms between the two pyrazine ligands. Interest-

(12) See Vranka, Ciani, and Moore in refs 4–7. Robson reported a bond length of 2.363 Å in the complex silver(I) tricyanomethanide: Batten, S. R.; Hoskins, B. F.; Robson, R. *New J. Chem.* **1998**, *22*, 173.

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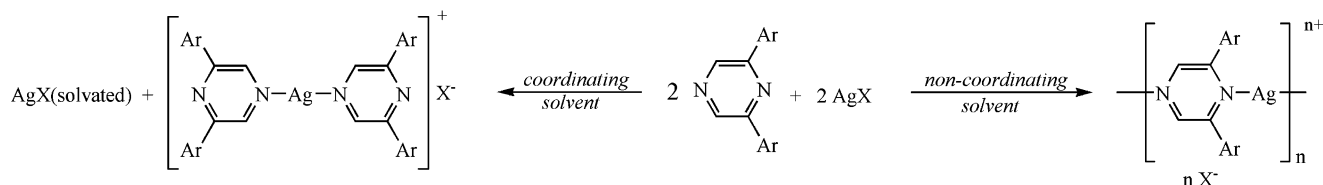


Figure 6. Postulated solvent control of complexation and coordination polymer formation.

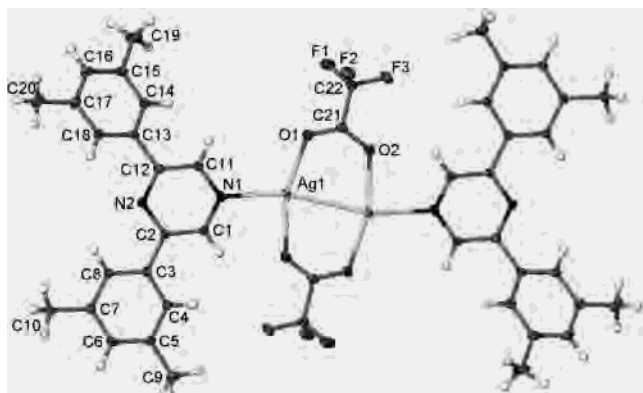


Figure 7. View of the 2:2 complex **3** formed on self-assembly of equimolar amounts of 2,6-bis(3',5'-dimethylphenyl)pyrazine and silver(I) trifluoroacetate from dichloromethane solution.

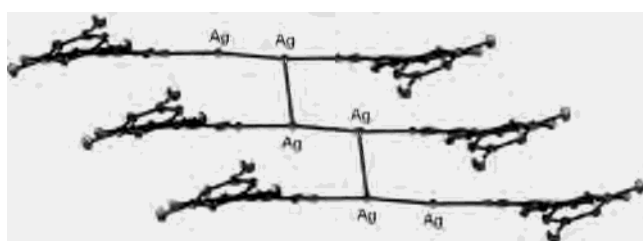


Figure 8. View of the π -stacking of adjacent 2:2 complexes **3** showing the short silver-silver contacts between complexes.

ingly, we had earlier observed similar trifluoroacetate-bridged pairs of anions in the one- and two-dimensional networks obtained on self-assembly of trimesityltriazine with silver(I) trifluoroacetate.² More importantly, Brammer has recently determined the structure of a host of coordination networks formed by self-assembly of silver(I) carboxylates with ditopic N-ligands and concluded that the carboxylate-bridged silver-silver dimer is a reliable supramolecular synthon.^{15,16}

The silver-silver separation of 2.9710(4) Å is slightly shorter than that observed in complex **1** (Figure 8). The ligand is essentially planar with (dimethylphenyl)pyrazine torsional angles of approximately 7° and 26° for aryl rings C(3)-C(8) and C(13)-C(18). The 2:1 complexes are slip-stacked so that Ag(1) overlies Ag(1)#2 with a separation of 3.0388-(4) Å. The second silver in each complex overlies the centroid of the pyrazine in the neighboring complex with a separation of 3.2 Å.

Clearly, the simple idea of “solvent control” outlined in Figure 6 was unsuccessful due to the coordinating nature of the trifluoroacetate anion. We therefore decided to study the self-assembly of the 2,6-diarylpyrazines with silver(I) salts with noncoordinating anions. Accordingly, we attempted to

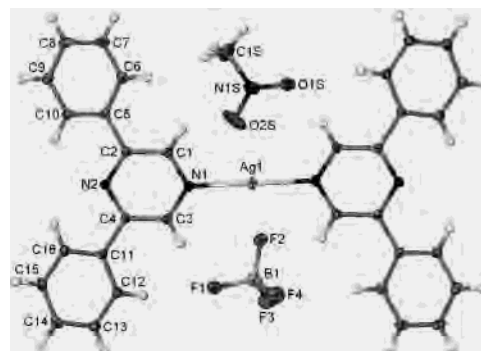


Figure 9. View of the 2:1 complex **4** formed on self-assembly of 2,6-diphenylpyrazine with silver(I) tetrafluoroborate from a mixture of toluene and nitromethane with the thermal ellipsoids drawn at 50% occupancy.

crystallize complexes with a variety of silver salts including the hexafluoroantimonate and tetrafluoroborate in noncoordinating solvents. We were only successful in growing X-ray-quality crystals using silver(I) tetrafluoroborate. In this experiment we used a large excess of the silver salt with a mixed toluene/nitromethane noncoordinating solvent. Colorless rod-shaped crystals were formed, and elemental analysis of the bulk solid indicated that a 2:1 ligand-silver complex, **4**, was formed. The 2:1 complex crystallized with one nitromethane solvent molecule included. The structure is shown in Figure 9.

The silver-nitrogen bond length of 2.1423(16) Å is notably shorter than the other silver-nitrogen bond lengths reported herein. The closest contacts to the silver are 2.839 Å for a nitromethane oxygen, Ag(1)-O(2s), and 2.835 Å for a tetrafluoroborate fluorine, Ag(1)-F(2). Since the cation lies on a center of symmetry, the geometry about silver is perfectly linear. The torsional angles between the two phenyl rings and the pyrazine are approximately 27° and 32° for C(5)-C(10) and C(11)-C(16), respectively. It is interesting to note that a similar short silver-nitrogen bond length of 2.193(3) Å was reported by Ciani for the unsubstituted pyrazine-silver(I) tetrafluoroborate one-dimensional polymer.^{6a} These bond lengths are presumably shorter because the noncoordinating anion does not dissipate the Lewis acid character of the cation in contrast to coordination by the trifluoroacetate anion, which reduces the Lewis acidity of the cation.

The complexes are slip-stacked as shown in Figure 10 with complex-complex (and long silver-silver) separation of approximately 3.8 Å.

We were thus unsuccessful in our attempts to form one-dimensional coordination polymers using “solvent” or “anion” control. At this stage we assumed that the propensity for π -stacking of the essentially planar 2,6-diarylpyrazines in the solid state controlled the coordination chemistry of

(16) Brammer, L.; Burgard, M. D.; Rodger, C. S.; Swearingen, J. K.; Rath, N. P. *Chem. Commun.* **2001**, 2468.

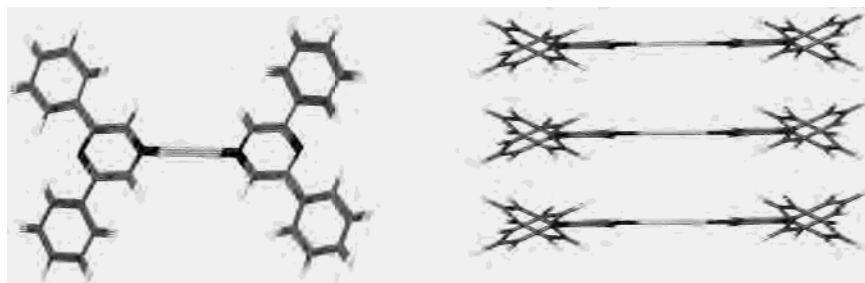


Figure 10. Two orthogonal views showing the stacking of the (2,6-diphenylpyrazine)silver(I) tetrafluoroborate complexes with the counterion and solvent molecule omitted for clarity.

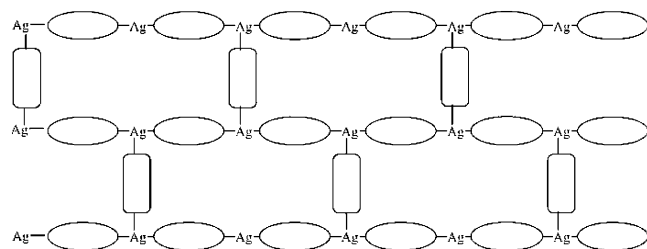


Figure 11. Simple interpretation of the network formed on self-assembly of silver(I) trifluoroacetate with 2,6-bis(2',6'-dimethylphenyl)pyrazine.

these ligands. We decided to counteract the π -stacking by fixing the aryl substituents orthogonal to the pyrazine ring by introducing methyl substituents in the *ortho* positions on the aryl rings as we had previously done with pyridine- and triazine-based ligands.^{1,2} Accordingly, we allowed 2,6-bis-(2',6'-dimethylphenyl)pyrazine to self-assemble with an excess of silver(I) trifluoroacetate in toluene along with a trace of acetonitrile. Colorless rod-shaped crystals were obtained, and elemental analysis of the bulk solid indicated that a 1:2 ligand–silver complex, **5**, was formed. It is interesting to note that the same 1:2 ligand–silver complex was also exclusively formed on self-assembly from solutions more enriched in silver—for example, with ratios of ligand to silver as high as 1:4. X-ray structural analysis indicated that a two-dimensional coordination network was formed. A schematic representation of the network is shown in Figure 11. In this representation the horizontal linkages are made of pyrazine–silver strands with alternating silver cations and pyrazine molecules. The vertical links between these strands are made by complex bridging disilver(I) tetrakis(trifluoroacetate) dianions.

A view of one of the one-dimensional strands of pyrazine-bound silver cations is shown in Figure 12. As expected the *o*-methyl groups effectively hold the aryl rings almost orthogonal to the central pyrazine ring with torsional angles of approximately 78° and 82° for C(13)–C(19) and C(3)–C(9), respectively. This, more rigid, conformation facilitated complexation at the hindered nitrogen atom with concomitant formation of a coordination network as opposed to discrete coordination complexes. The silver–nitrogen bond lengths are similar at 2.202(2) and 2.235(2) Å for Ag(1)–N(1) and Ag(1)–N(2)#1, respectively.

As shown in Figure 12 the silver–pyrazine backbone has a zigzag shape with a N–Ag–N bond angle of 146.46(9)°. The orientation of the aryl substituents opens the silver atoms

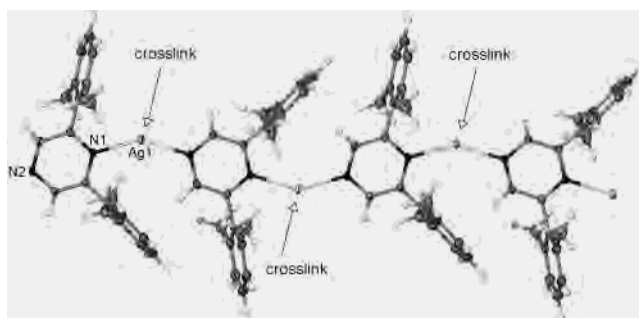


Figure 12. Backbone of the coordination network **5** formed between silver(I) trifluoroacetate and 2,6-bis(2',6'-dimethylphenyl)pyrazine in toluene solution. The arrows indicate the positions at which the silver–pyrazine strands are interconnected.

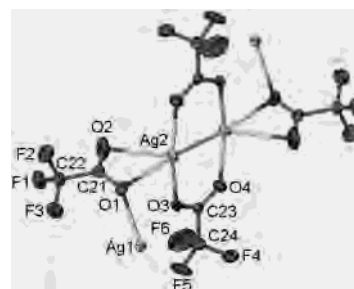


Figure 13. Perspective view of the complex dianion that bridges between silver atoms from adjacent strands of the silver–pyrazine coordination polymer. The pendant silver atoms are from adjacent strands of silver–pyrazine complexes.

to cross-linking coordination by the complex dianion shown in Figure 13.

The honeycomb-like two-dimensional coordination network is shown in Figure 14 with large hexagonal rings containing 30 atoms, 10 of which are silver(I) cations.

We were intrigued by the possibility that it would be sufficient to have only one of the aryl groups held orthogonal while allowing the second ring free rotation. Accordingly, we repeated the aforementioned experiment with the mixed arylpyrazine 2-(2',6'-dimethylphenyl)-6-(3'',5''-dimethylphenyl)pyrazine and obtained a crystalline solid that had a complex elemental analysis that indicated a 3:1 silver–ligand complex, **6**, was formed. Single-crystal X-ray analysis revealed a complex corrugated two-dimensional coordination network. The network comprises the familiar silver–pyrazine strands cross-linked by bridging silver(I) trifluoroacetates. The zigzag silver–pyrazine strands shown in Figure 15 are similar to those found in structure **5**.

A more complex silver(I) trifluoroacetate bridge was formed between adjacent strands of the silver–pyrazine

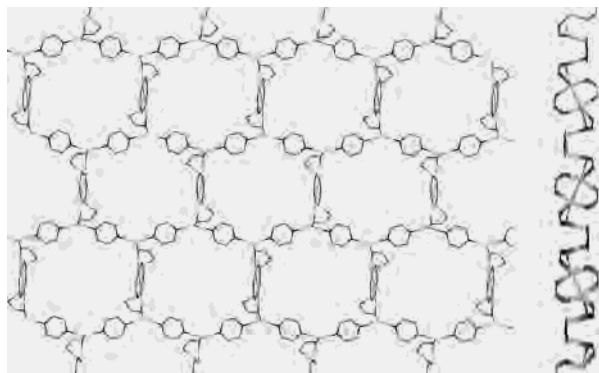


Figure 14. Two orthogonal views of the two-dimensional network **5** with the trifluoromethyl groups, the pendant dimethylphenyl rings omitted for clarity.

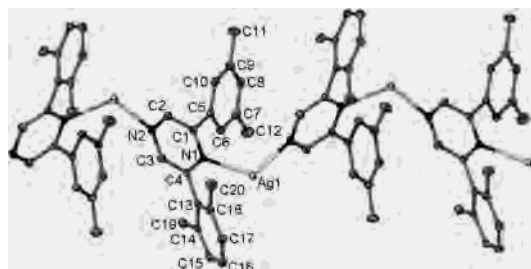


Figure 15. View of the backbone of the coordination network **6** formed between silver(I) trifluoroacetate and 2-(2',6'-dimethylphenyl)-6-(3'',5''-dimethylphenyl)pyrazine in toluene solution.

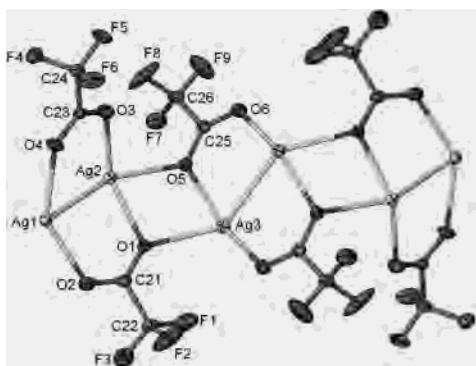


Figure 16. View of the complex silver trifluoroacetate bridge between adjacent strands of the silver-pyrazine coordination network **6**.

complex and is shown in Figure 16. In this figure the terminal silver atoms, Ag(1), are also part of the adjacent silver-pyrazine strands.

A silver atom is η^1 coordinated, or σ -bound, to the pendant 2',6'-dimethylphenyl ring with $C(15)-Ag(2) = 2.499 \text{ \AA}$. In their seminal paper Lindeman, Rathore, and Kochi analyzed all reported crystal structures containing silver-arene interactions and reported that the separation of silver(I) from the mean plane of the coordinated benzene lies in a narrow range.¹⁷ This distance was found to be $2.41 \pm 0.05 \text{ \AA}$. The distance reported here is thus marginally longer. Another silver atom is η^1 coordinated to the incorporated solvent

(17) Lindeman, S. V.; Rathore, R.; Kochi, J. K. *Inorg. Chem.* **2000**, *39*, 5707.

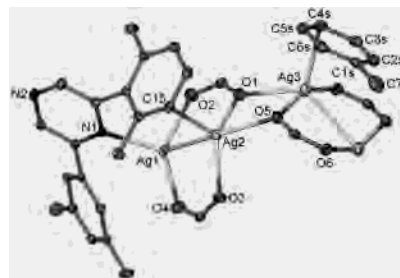


Figure 17. View of a portion of the silver trifluoroacetate linkage emphasizing the Ag- π interactions between Ag(1) and the pendant dimethylphenyl ring and Ag(3) and the included solvent molecule, toluene.

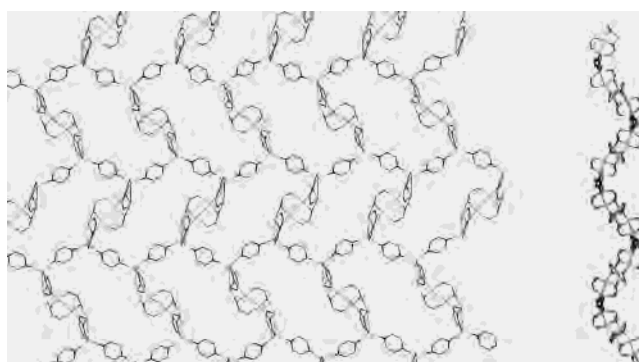


Figure 18. Two orthogonal views of the two-dimensional network **6** with the dimethylphenyl rings, incorporated toluene, and CF_3 groups omitted for clarity.

toluene with a slightly longer separation of $C(4S)-Ag(3) = 2.707 \text{ \AA}$. These interactions are shown in Figure 17. The weaker silver-arene interactions observed here may be a result of the multiple silver-oxygen interactions that reduce the Lewis acidity of the silver(I) cation.

The two-dimensional network is shown in the two orthogonal views in Figure 18.

In conclusion, we have prepared coordination networks by self-assembly of silver salts with 2,6-diarylpyrazines in which at least one of the aryl groups is held orthogonal to the pyrazine ring due to an *ortho* substituent. With other aryl groups discrete complexes were obtained presumably due to the preferred π -stacking of the essentially planar triaryl ligands in the solid state. All the complexes with silver(I) trifluoroacetate included the dimeric silver(I) trifluoroacetate supramolecular synthon.

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Supporting Information Available: Six X-ray crystallographic information files in CIF format. This material is available free of charge via the Internet at <http://acs.pubs.org>.

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