Inorg. Chem. **2002**, *41*, 2543–2547

Inorganic Chemistry Article

One- and Two-Dimensional Silver-Coordination Networks Containing π-Sandwiched Silver–Silver Interactions

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Received July 26, 2001

The self-assembly of coordination networks from reaction of 2,4,6-trimesityl-1,3,5-triazine and silver(I) trifluoroacetate is described. A one-dimensional linear polymer is formed from solutions deficient in silver while a two-dimensional, graphite-like sheet is formed from solutions containing 3 equiv of silver per triazine. The structurally similar networks both contain triazine rings separated by two trifluoroacetate-bridged silver atoms. The two silver atoms are effectively sandwiched between two mesityl rings with intermediate arene–silver interactions. The silver–silver bond lengths are 2.9731(4) and 2.9246(5) Å in the one-dimensional network and 2.8842(4) Å in the two-dimensional network.

Introduction

The self-assembly of supramolecular structures using metal coordination has become the focus of intense interest over the past decade.[1] This is largely due to the range of potential applications in electrical, magnetic, and optical devices[2] and porous zeolite mimics.[3] The specific properties of each coordination network are directly related to its atomic structure, which is a function of both the ligand and the metal. It is, therefore, important to try to understand, and control, the interplay between the coordination characteristics of the ligands and the metals, and the ultimate shape of the self-assembled superstructure. We are specifically studying steric control of the structure of coordination complexes and networks. In this regard we recently described the novel encapsulation of silver(I) cation with 2,6-dimesitylpyridine as a light-stable 2:1 coordination complex.[4] A key feature of that study was the fact that the aryl substituents were essentially orthogonal to the pyridine. We are currently investigating the metal coordination properties of other N-heterocycles wherein the heteroatom(s) are flanked by orthogonal aryl moieties. In this paper we describe the formation of one-dimensional and two-dimensional coordination networks on reaction of 2,4,6-trimesityl-1,3,5-triazine with silver(I) salts.

Experimental Section

Cyanuric chloride (ACROSS), mesitylene, silver(I) trifluoroacetate, aluminum chloride (Aldrich), dichloromethane, and hexane (Fisher) were used as received. Thermogravimetric analysis was performed on a Perkin-Elmer TGS-2 thermogravimetric analyzer at the University of Missouri, Rolla.

Synthesis. 2,4,6-Trimesityl-1,3,5-triazine, 1. This compound was synthesized by the Friedel−Crafts arylation of cyanuric chloride (6.0 g, 32.6 mmol) with excess mesitylene (25 mL, 182 mmol) in the presence of aluminum trichloride (13.3 g, 100 mmol).[5] The product was recrystallized from ethanol as white needles (13.3 g, 90%). Mp: 189−190 °C (lit.[5] 185−186 °C). ^{1}H NMR: δ $CDCl_3$ 6.96 (s, 6H); 2.29 (s, 9H), 2.19 (s, 18H). ^{13}C NMR: δ 176.95, 138.67, 134.70, 134.57, 128.42, 21.12, 19.77. Anal. Calcd for $C_{30}H_{33}N_3$: C, 82.71; H, 7.64; N, 9.65. Found: C, 82.72; H, 7.73; N, 9.55.

Reaction of 2,4,6-Trimesityl-1,3,5-triazine with Silver(I) Trifluoroacetate. Silver(I) trifluoroacetate (110 mg, 0.5 mmol) and

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(1) (a) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinham, 1995. (b) *Transition Metals in Supramolecular Chemistry*; Fabbrizza, L., Poggi, A., Eds.; Kluwer Academic: The Netherlands, 1994. (c) *Comprehensive Supramolecular Chemistry*; Lehn, J.-M., Ed.; Pergamon Press: Oxford, 1995. (d) Biradha, K.; Fujita, M. *Adv. Supramol. Chem.* **2000**, *6*, 1.

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10.1021/ic010795q CCC: $22.00

2,4,6-trimesityl-1,3,5-triazine (216 mg, 0.5 mmol) were placed in a (screw-cap) vial along with a magnetic stir bar. Dichloromethane (2 mL) was added, the vial capped, and the heterogeneous mixture warmed gently while being stirred. The resultant clear solution was allowed to cool to room temperature, then layered with hexane, and allowed to stand in the dark. After 24 h prismatic crystals began to form. These crystals, **2** (48 mg), were harvested after 1 week. Elemental analysis indicated that these crystals comprised a 3:1 mixture of silver trifluoroacetate to triazine, **1**. ^{1}H NMR: δ $CDCl_3$ 7.02 (s, 6H), 5.30 (s, 1H, CH_2Cl_2), 2.35 (s, 9H), 2.15 (s, 18H). ^{13}C NMR: δ 177.63, 140.84, 135.32, 133.78, 128.45, 53.5 (CH_2Cl_2), 21.29, 19.45. Anal. Calcd for $C_{36}H_{33}N_3Ag_3F_9O_6\cdot 0.5CH_2Cl_2$: C, 38.14; H, 3.07; N, 3.65. Found: C, 38.47; H, 3.09; N, 3.75. Thermogravimetric analysis of these crystals showed loss of 3.9% mass from 215 to 250 °C followed by loss of 44% mass from 360 to 430 °C. The first mass loss corresponds to loss of 0.525 equiv of CH_2Cl_2 (3.7%) per "trisilver−triazine" unit and the second to loss of the ligand (38.2%) with partial breakdown of the trifluoroacetate. Subsequent X-ray crystallography confirmed the partial inclusion of solvent. The remaining solution, which was now homogeneous, was layered with more hexane and allowed to stand in the dark for another 1 week. A second batch of crystals (143 mg) was then harvested. Elemental analysis indicated that this batch of crystals, **3**, comprised a 2:1 ratio of silver to triazine. ^{1}H NMR: δ $CDCl_3$ 6.97 (s, 6H); 2.32 (s, 9H), 2.14 (s, 18H). ^{13}C NMR: δ 177.49, 140.37, 135.18, 133.94, 128.53, 21.53, 19.60. Anal. Calcd. for $C_{34}H_{33}N_3Ag_2F_6O_4$: C, 46.54; H, 3.79; N, 4.79. Found: C, 46.29; H, 3.65; N, 4.89. TLC indicated that the remaining mother liquor contained the uncomplexed triazine.

Crystals of the 3:1 product, **2**, were then selectively grown from a solution containing a 3:1 ratio of silver to ligand and were obtained in 76% yield after 3 weeks. In contrast another batch of the linear (2:1) polymer was grown from a solution deficient in silver: initial ratio of triazine:silver = 2:1. Anal. Calcd for $C_{34}H_{33}N_3Ag_2F_6O_4$: C, 46.54; H, 3.79; N, 4.79. Found: C, 46.42; H, 3.71; N, 4.86.

Crystallography. Prismatic crystals of the 3:1 complex, **2**, formed as described above were suitable for X-ray crystal structure analysis. A crystal 0.35 × 0.35 × 0.20 mm was selected for analysis. The crystal was mounted on the diffractometer and cooled in a flow of cold nitrogen gas (173 K) during data collection. The crystals of the 2:1 complex, **3**, were also directly suitable for X-ray crystal structure analysis. A crystal 0.45 × 0.25 × 0.25 mm was selected for analysis. Table 1 lists the crystallographic data for both structures. 3144 unique reflections were collected from the 3:1 complex with $1.59° < \theta < 27.09°$. 7403 unique reflections were collected from the 2:1 complex with $1.43° < \theta < 27.18°$. Both structures were solved using SHELXS-97[6] and refined using SHELXL-97.[7] Hydrogen atoms were included in the calculated positions. Selected interatomic distances, angles, and torsional angles are given in Table 2.

Table 1. Crystal Data and Structure Refinement for the Two-Dimensional, **2**, and One-Dimensional Networks, **3**, Formed between **1** and Silver(I) Trifluoroacetate

	2	**3**
empirical formula	$[C_{36}H_{33}Ag_3F_9N_3O_6]_n$	$[C_{34}H_{33}Ag_2F_6N_3O_4]_n$
fw	1098.28	877.38
cryst syst, space group	rhombohedral, $R\bar{3}$	triclinic, $P\bar{1}$
a, Å	17.1900(7)	11.6549(8)
b, Å	17.1900(7)	11.7464(9)
c, Å	25.0721(14)	14.8121(11)
α, deg	90	104.5010(10)
β, deg	90	90.4280(10)
γ, deg	120	117.5980(10)
V, A^3	6416.1(5)	1721.7(2)
D_{calc}, Mg/m^3	1.537	1.692
Z	9	2
temp, K	173(2)	173(2)
λ(Mo Kα), Å	0.71073	0.71073
μ(Mo Kα), mm^{-1}	0.854	1.211
F(000)	3033	876
$R(F^2)^{a,b}$	0.0354	0.0392
$R_w(F^2)$	0.0689	0.0841

[a] All data. [b] $R = \sqrt{[\Sigma(w(F_o - F_c)^2)/\Sigma(wF_o{}^2)]}$.

Table 2. Selected Bond Lengths (Å), Bond Angles, Torsional Angles (deg), and Nonbonded Contacts (Å) for the Two-Dimensional Coordination Network **2**[a]

Bond Lengths			
Ag(1)−N(1)	2.4434(18)	Ag(1)−Ag(1)#1	2.8842(4)
Bond Angles			
N(1)−Ag(1)−Ag(1)#1	140.38(4)	C(1)−N(1)−Ag(1)	112.83(14)
C(1)#5−N(1)−Ag(1)	130.55(15)		
Torsional Angles			
N(1)−C(1)−C(2)−C(3)	77.8(3)		
Nonbonded Contacts			
Ag(1)−C(2)	3.102	Ag(1)−C(3)	3.332
Ag(1)−C(4)#16	3.560		

[a] Refer to Figure 3 for atom labeling.

Results and Discussion

Ligand Design and Synthesis. The design of the ligand was guided by our earlier synthesis of the sterically hindered pyridine 2,6-dimesitylpyridine.[4] We reasoned that the aryl rings in 2,4,6-trimesityl-1,3,5-triazine would be essentially orthogonal to the central triazine ring providing three coordination sites flanked by orthogonal electron-rich aromatic rings. This was confirmed by molecular modeling which predicted interplanar angles between the triazine ring and the mesityl rings of 70°, 71°, and 79°, respectively.[8] We further expected that reaction of this ligand with silver(I) would result in coordination networks in which the silver cations are encapsulated in a fashion similar to that which we had previously observed in the silver complexes with 2,6-dimesitylpyridine. We thus expected this to result in the formation of a dendritic coordination network.[9] The ligand was synthesized in excellent yield (90%) in one step by aluminum chloride mediated Friedel−Crafts arylation of cyanuric chloride with mesitylene.[5]

Complex Preparation and Analysis. The facility with which the products **2** and **3** are formed is apparent from the observation that they crystallize readily from solutions that are deficient with regard to silver. Thus while the 3:1 complex, **2**, was formed in excellent yield from solutions containing the same 3:1 ratio of silver trifluoroacetate to the triazine **1**, it also crystallized from a solution containing equimolar mixtures of silver and triazine. In a similar way

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(6) Sheldrick, G. M. *SHELXS-97, Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

(7) Sheldrick, G. M. *SHELXL-97, Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

(8) Calculated using Spartan Plus, Wavefunction, Inc., Irvine, CA 92612.

(9) For an approach to dendrimer−silver complexes, see: Balogh, L.; Swanson, D. R.; Tomalia, D. A.; Hagnauer, G. L.; McManus, A. T. *Nano Lett.* **2001**, *1*, 18.

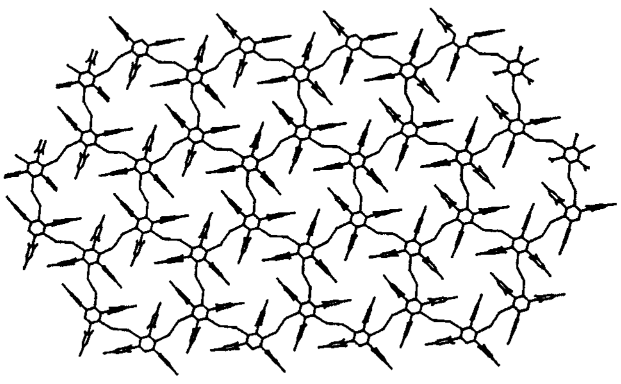

Figure 1. Stick representation of the two-dimensional network formed between **1** and silver(I) trifluoroacetate. The bridging trifluoroacetate groups, hydrogen atoms, and the included solvent are omitted for clarity.

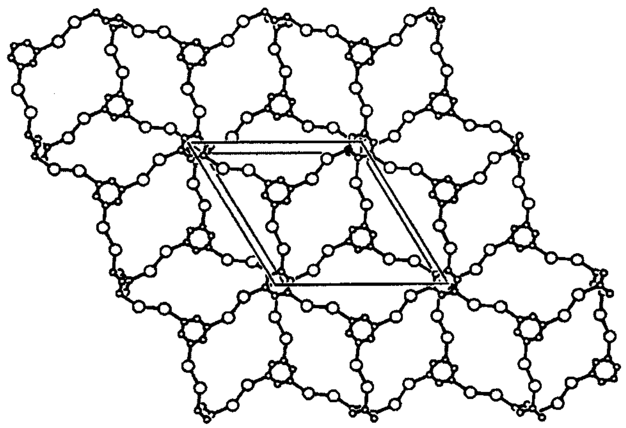

Figure 2. View normal to (001) of two adjacent sheets of the two-dimensional network showing the packing within the crystal with bridging trifluoroacetate groups and mesityl rings omitted for clarity.

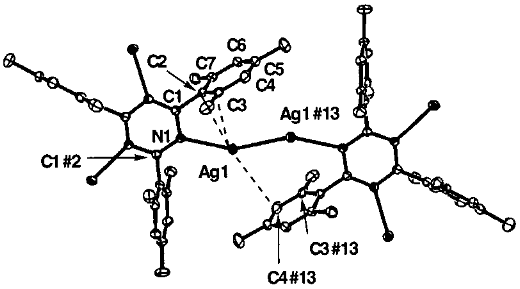

Figure 3. Perspective view of a central triazine unit of the two-dimensional network along with the adjacent triazine showing the silver−arene interactions. Thermal ellipsoids were drawn at 25% probability. Bridging trifluoroacetate groups and hydrogen atoms are omitted for clarity.

the 2:1 complex, **3**, crystallized from solutions deficient in silver with a 1:2 ratio of silver trifluoroacetate to triazine **1**. Elemental analysis of the 3:1 complex **2** indicated that it contained included solvent dichloromethane at approximately 0.5 equiv of CH_2Cl_2 per triazine unit. This was confirmed by thermogravimetric analysis of the solid that indicated loss of 0.525 equiv of CH_2Cl_2 solvent between 215 and 250 °C. The included dichloromethane was also observed in the ^1H and ^{13}C NMR spectra of **2**.[10]

X-ray Crystallographic Characterization. The structure of the 3:1 complex, **2**, was found to be a two-dimensional "honeycomb" or "chicken wire" coordination network as shown in Figure 1.

The asymmetric unit of this two-dimensional coordination network, **2**, consists of one triazine nitrogen atom with the bound silver trifluoroacetate moiety and one triazine C atom with the attached mesityl ring. The "honeycomb" suprastructure within a sheet of the two-dimensional network comprises large, interconnected, hexagonal rings with the triazine rings at each corner connected by silver−silver linkages. Each of these large rings comprises 30 linked atoms, i.e., six Ag−Ag−N−C−N moieties. In each of the hexagonal rings there are six mesityl groups pointing to the center of the hexagon as shown in Figure 1. The center of each large hexagon lies directly between triazine rings from the adjacent upper and lower sheets of the complex as shown in Figure 2. This provides a small cavity that is filled by disordered solvent molecules.[11] It is interesting to note that the silver cation is asymmetrically coordinated to the triazine N-atom being bent toward one of the flanking mesityl substituents with angles to the triazine ring of C(1)−N(1)−Ag(1) = 112.83(14)° and C(1)#2−N(1)−Ag(1) = 130.55(15)°, respectively, as shown in Figure 3.[12] As expected the mesityl rings are essentially orthogonal to the triazine ring with a torsional angle N(1)−C(1)−C(2)−C(3) of 77.8(3)°. Rather surprisingly the mesityl rings are slightly bent toward the silver atoms with an angle across the mesityl ring, C(1)−C(2)−C(5), of approximately 175°. Thus, despite the long nitrogen−silver bond of 2.4434(18) Å[13] the silver has a close contact to the flanking mesityl ring, with nonbonded contacts of 3.102 and 3.332 Å between Ag(1) and C(2) and C(3), respectively, due to the asymmetric complexation of the silver. Indeed, calculations done assuming symmetric complexation of the silver atom and a silver−nitrogen bond length of 2.44 Å predict an Ag−C(2) nonbonded contact of 3.42 Å.[8] The asymmetric complexation to the mesityl ring is accommodated by the torsional angle of approximately 77° between the mesityl moiety and the triazine ring. These silver−arene distances are less than the sum of the van der Waals radii of approximately 3.42 Å[16] although they are significantly longer than the normal separation of silver

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(10) Comparison of the ^{13}C NMR spectra for ligand **1** and the one- and two-dimensional networks **3** and **2** indicates that the signals for C-1′ and C-2′ atoms on the mesityl ring (C2 and C3 in Figure 3) are shifted in both complexes. This is presumably due to the proximal silver cations. It should, however, also be noted that the networks may be partially (or totally) dissociated in solution or exist in other forms in solution. We thank an anonymous reviewer for this clarification.

(11) The disordered solvent dichloromethane was included in the model as partially occupied Cl positions.

(12) In contrast the silver was symmetrically coordinated to the pyridine nitrogen in the complex with 2,6-dimesitylpyridine with C−N−Ag angles of 120(±2)°.[4]

(13) This silver−triazine bond distance is in the range of reported silver−triazine complexes. For example Ciani reported triazine N−silver bond lengths of 2.28−2.65 Å in complexes containing silver atoms with pseudo tetrahedral coordination.[14] Moore reported triazine-N−silver bond lengths of 2.312−2.430 Å in ref 15. In contrast pyridine N−silver bond lengths are approximately 2.15 Å.[4]

(14) Bertelli, M.; Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Mater. Chem.* **1997**, *7*, 1271.

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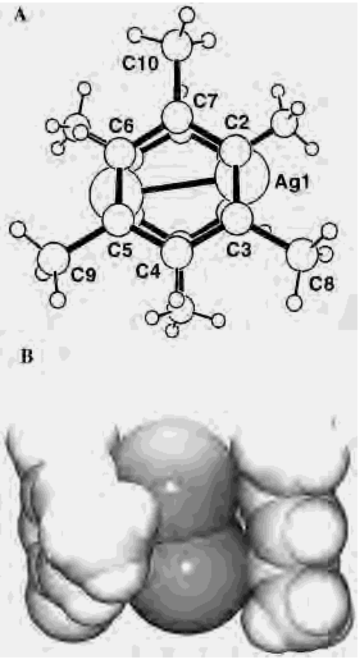

Figure 4. A. Pluto drawing showing the π-sandwiched silver atoms in the two-dimensional network **2** showing only the mesityl rings and silver atoms for clarity. B. Space-filling model of a top view of the same sandwiched silver atoms.

cations from aromatic rings of approximately 2.6 Å in silver−arene complexes.[17] Clearly these contacts are intermediate in nature. Interestingly the nitrogen−silver−silver angle of 140.38(4)° coupled with the slight twist and bend of the mesityl ring from the adjacent triazine brings C(4) of that ring within the range of the van der Waals contact with the distance Ag(1)−C(4)#13 of 3.560 Å.[16] The pairs of silver atoms are thus sandwiched between the two mesityl rings as shown in Figure 4. The silver−silver distance of 2.8842(4) Å is well below the sum of the van der Waals radii of two silver atoms, 3.44 Å.[16] Indeed this separation is essentially the same as the separation of silver atoms in silver metal, 2.884 Å,[18] and shorter than other examples of trifluoroacetate-bridged silver−silver contacts with silver−silver distances of 3.16 Å.[19] Wheatley et al. recently argued that there is significant bonding between the silver centers at these short distances.[20] In this two-dimensional network the pairs of silver atoms are effectively encased being sandwiched between two mesityl rings, the two triazine N atoms, and the two bridging trifluoroacetate groups (see Figure 5).

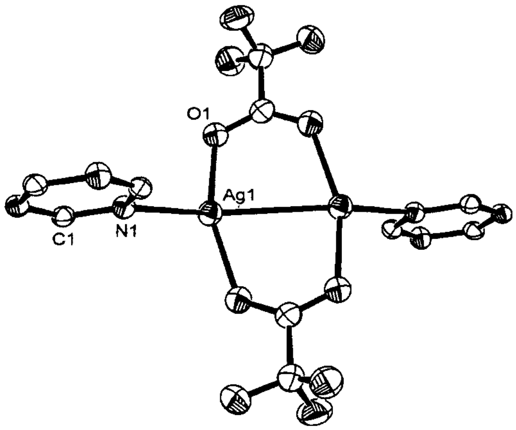

Figure 5. ORTEP plot showing the bridging trifluoroacetate groups with thermal ellipsoids drawn at 50% probability.

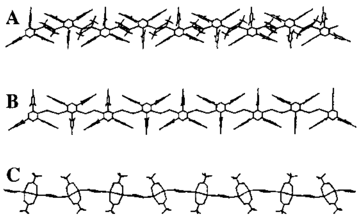

Figure 6. A. Stick representation of the one-dimensional network formed between ligand **1** and silver(I) trifluoroacetate. B. Similar view with the bridging trifluoroacetate anions omitted for clarity. C. Orthogonal view showing the bridging trifluoroacetate groups with the mesityl substituents omitted for clarity.

Table 3. Selected Bond Lengths (Å), Bond Angles, Torsional Angles (deg), and Nonbonded Contacts (Å) for the One-Dimensional Coordination Network **3**[a]

Bond Lengths			
Ag(1)−N(1)	2.442(2)	Ag(1)−Ag(1)#2	2.9731(4)
Ag(2)−N(2)	2.442(2)	Ag(2)−Ag(2)#2	2.9246(5)
Bond Angles			
N(1)−Ag(1)−Ag(1)#1	140.30(5)	N(2)−Ag(2)−Ag(2)#2	133.40(5)
C(1)−N(1)−Ag(1)	132.61(16)	C(3)−N(1)−Ag(1)	111.44(16)
C(1)−N(2)−Ag(2)	128.74(16)	C(2)−N(2)−Ag(2)	112.04(16)
Torsional Angles			
N(1)−C(1)−C(4)−C(5)	70.4(3)		
N(3)−C(3)-C(22)−C(23)	82.1(3)		
N(2)−C(2)−C(13)−C(14)	106.7(3)		
Nonbonded Contacts			
Ag(1)−C(22)	3.071	Ag(1)−C(25)#2	3.509
Ag(1)−C(27)	3.293	Ag(1)−C(26)#2	3.533
Ag(2)−C(13)	3.154	Ag(2)−C(18)	3.541

[a] Refer to Figure 7 for atom labeling.

The 2:1 silver:triazine complex, **3**, was found to be a one-dimensional coordination polymer as shown in Figure 6. Interestingly this linear polymer shares many common structural features with the two-dimensional network **2**. Indeed the one-dimensional polymer also features the two trifluoroacetate-bridged silver cations sandwiched between two mesityl groups. The linear, one-dimensional network, **3**, of course differs from the two-dimensional network in that only two of the nitrogen atoms of the triazine unit coordinate silver cations. The asymmetric unit of the one-dimensional network comprises one triazine ligand, **1**, and the two coordinated silver atoms along with the associated trifluoroacetate anions. The two mesityl rings flanking the uncomplexed nitrogen atom are twisted at about 70° to the triazine ring with torsional angles N(1)−C(1)−C(4)−C(5) and N(2)−C(2)−C(13)−C(14) equal to 70.4(3)° and 106.7(3)°, respectively. In contrast the mesityl ring between the

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(17) For a detailed, elegant study of arene−silver complexation, see: Lindeman, S. V.; Rathore, R.; Kochi, J. K *Inorg. Chem.* **2000**, *39*, 5707.

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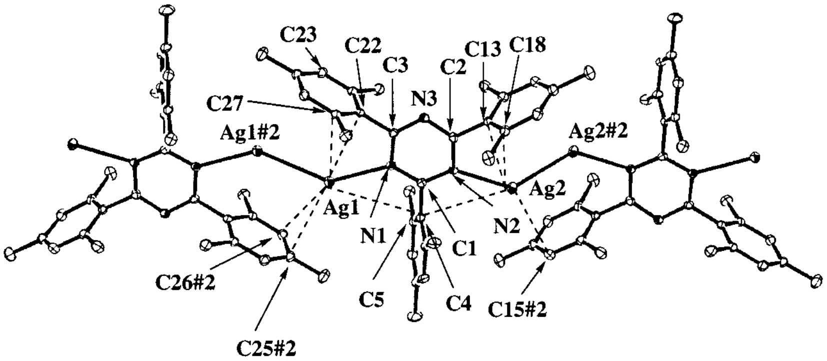

Figure 7. Perspective view of a central triazine unit of the one-dimensional network along with the adjacent triazine moieties showing the silver−arene interaction. Thermal ellipsoids are drawn at 25% probability, and bridging trifluoroacetate groups are omitted for clarity.

two coordinated silver atoms does not have a close contact to either silver atom and has a torsional angle N(3)−C(3)−C(22)−C(23) of 82.1(3)° to the triazine ring. Both silver atoms are asymmetrically coordinated with nitrogen−silver−silver angles C(3)−N(1)−Ag(1) and C(2)−N(2)−Ag(2) equal to 111.44(16)° and 112.04(16)°, respectively. The silver−silver bond distances of 2.9246(5) and 2.9731(4) Å are slightly longer than silver−silver bond in the two-dimensional network. The silver atoms also make close contact to the flanking mesityl rings, and the intermediate silver−arene contacts are listed in Table 3 and shown in Figure 7. The asymmetry of complexation is highlighted by comparing the distances of the two silver atoms to C(4), on the mesityl ring between the two complexed silver atoms, to the distances to the other two mesityl rings. The distances to C(4) are 3.674 and 3.732 Å, respectively, while the distance Ag(1)−C(22) is 3.071 Å and the distance Ag(2)−C(13) is 3.154 Å.

In conclusion we have synthesized and characterized one- and two-dimensional silver coordination networks with a sterically hindered triazine that both display an unusual *π*-sandwiched silver−silver interaction.

Acknowledgment. We thank Joseph A. Counsil, Research Engineer, from the University of Missouri at Rolla for help with the thermogravimetric analysis. E.B. acknowledges receipt of a Faculty Research Grant from the Graduate College of Southwest Missouri State University and support from the National Science Foundation (CCLI Grant 9950853) for a NMR spectrometer upgrade.

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

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