

Self-Assembly of Coordination Polymers from AgX (X = SbF<sub>6</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) and Oxadiazole-Containing Ligands

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The coordination chemistry of the oxadiazole-containing rigid bidentate ligands 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (L1), 2,5-bis(3-pyridyl)-1,3,4-oxadiazole (L2), and 2,5-bis(3-aminophenyl)-1,3,4-oxadiazole (L3) with inorganic Ag(I) salts has been investigated. Four new coordination polymers (**1**, **2**, **3**, and **5**) and one new bimetallic macrocyclic supramolecular complex (**4**) were synthesized from solution reactions of L1–L3 with inorganic Ag(I) salts, respectively. Compounds {[Ag(L1)]SbF<sub>6</sub>}<sub>n</sub> (**1**) (**1**, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 6.6846(4) Å, *b* = 27.1113(15) Å, *c* = 8.6802(5) Å, β = 94.1080(10)°, *Z* = 4) and {[Ag(L1)]PF<sub>6</sub>}<sub>n</sub> (**2**) (**2**, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 6.6753(3) Å, *b* = 27.2824(14) Å, *c* = 8.2932(4) Å, β = 94.6030(10)°, *Z* = 4) were obtained from the reactions of L1 with AgSbF<sub>6</sub> and AgPF<sub>6</sub> in a CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH mixed solvent system, respectively. Compounds **1** and **2** are isostructural and feature a novel two-dimensional zeolite-like net with two different individual rings. {[Ag(L2)]SbF<sub>6</sub>}<sub>n</sub> (**3**) (**3**, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 5.5677(3) Å, *b* = 17.3378(9) Å, *c* = 15.6640(8) Å, β = 94.4100(10)°, *Z* = 2) and [Ag<sub>2</sub>(L2)<sub>2</sub>](SbF<sub>6</sub>)<sub>2</sub> (**4**) (**4**, triclinic, *P* $\bar{1}$ , *a* = 8.7221(5) Å, *b* = 9.2008(6) Å, *c* = 10.7686(7) Å, α = 70.6270(10)°, β = 75.7670(10)°, γ = 73.7560(10)°, *Z* = 1) were obtained from one-pot reaction of L2 with AgSbF<sub>6</sub> in a CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH mixed solvent system. Compound **3** features a one-dimensional chain pattern, while compound **4** adopts a novel bimetallic macrocyclic structural motif which consists of Ag<sub>2</sub>(L2)<sub>2</sub> ringlike units (crystallographic dimensions, 8.06 × 7.42 Å<sup>2</sup>). {[Ag(L3)]SO<sub>3</sub>CF<sub>3</sub>}<sub>n</sub> (**5**) is generated from L3 and AgSO<sub>3</sub>CF<sub>3</sub> in a CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH mixed solvent system and crystallizes in the unusual space group *Pbcn*, with *a* = 9.8861(5) Å, *b* = 20.2580(10) Å, *c* = 17.5517(8) Å, *Z* = 8. It adopts novel two-dimensional sheets that are cross-linked to each other by strong interlayer N–H···O hydrogen bonding interactions into a novel H-bonded three-dimensional network.

## Introduction

Due to their potential as new functional solid materials,<sup>1–4</sup> interest in self-assembled coordination polymers with specific network topologies has grown rapidly and has directed much

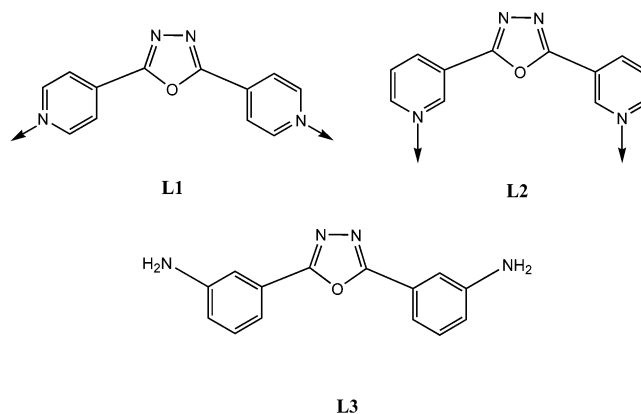
attention toward the structural building and deliberate design of polymeric coordination compounds.<sup>5–8</sup> In principle, some control over network topology can be gained by judicious

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selection of such reaction-influencing factors as the chemical structure of the organic spacers (ligands), the coordination geometry preference of the metal, the inorganic counterions, and the metal-to-ligand ratio.<sup>9–11</sup> So far, of diverse elegant efforts to find key factors in the development of extended structures, the dominant synthetic strategy has been the use of various organic ligands. During the past few years, many one-, two-, and three-dimensional coordination polymers have been generated from transition metal templates with rigid pyridyl-containing bidentate or multidentate organic spacers. Two excellent reviews by Zubietta and Schröder summarize some of these.<sup>12</sup> Up to now, however, in most cases, the geometries of these bidentate ligands that were used to construct coordination polymers are linear. In other words, the linear bidentate organic spacers are the major theme in the chemistry of coordination polymer and supramolecular complexes. A continuing project in our laboratory has been the development of coordination polymers generated from oxadiazole-containing organic ligands and inorganic salts.<sup>13</sup> The bridging five-membered oxadiazole ring ensures that the geometries of these ligands are not linear. As a result of the bent shape of the oxadiazole-containing ligand and the coordination preferences of transition metals, new types of coordination polymers, some with



**Figure 1.** Rigid organic oxadiazole-containing ligands used in the construction of coordination polymer frameworks.

open channels, have been obtained. The possibility for this oxadiazole-containing type of ligand to bind metal ions simultaneously by  $N_{\text{pyridyl}}$  or  $N_{\text{amino}}$  and  $N_{\text{oxadiazole}}$  donors allows access to frameworks of novel topology. Moreover, heteroatoms such as N and O on the (1,3,4)-oxadiazole ring could be considered as potential hydrogen bond acceptors to expand polymeric frameworks with hydrogen bonding interactions. In addition, the ancillary ligation by different counterions, such as  $\text{SO}_3\text{CF}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{PF}_6^-$ ,  $\text{SbF}_6^-$ , and so on, may result in a remarkable structural change.<sup>11f–11g</sup> In order to expand the coordination chemistry of oxadiazole-containing ligands with “soft” metal Ag(I) ion and explore the templating effects of counterions and also the role of orientation of coordination sites in the self-assembly process, the coordination reactions of L1–L3 and Ag(I) ion with different counterions were investigated.

Herein, we wish to report four new coordination polymers and one supramolecular bimetallic complex, namely  $\{[\text{Ag}(\text{L1})]\text{SbF}_6\}_n$  (**1**),  $\{[\text{Ag}(\text{L1})]\text{PF}_6\}_n$  (**2**),  $\{[\text{Ag}(\text{L2})]\text{SbF}_6\}_n$  (**3**),  $[\text{Ag}_2(\text{L2})_2](\text{SbF}_6)_2$  (**4**), and  $\{[\text{Ag}(\text{L3})]\text{SO}_3\text{CF}_3\}_n$  (**5**), based on (1,3,4)-oxadiazole containing ligands L1–L3 (Figure 1) and  $\text{AgX}$  ( $X = \text{SbF}_6^-$ ,  $\text{PF}_6^-$  and  $\text{CF}_3\text{SO}_3^-$ ), respectively.

## Experimental Section

**Materials and Methods.** Ligands L1 (2,5-bis(4-pyridyl)-1,3,4-oxadiazole), L2 (2,5-bis(3-pyridyl)-1,3,4-oxadiazole), and L3 (2,5-bis(3-aminobenzoyl)-1,3,4-oxadiazole) were prepared according to literature methods.<sup>14</sup> All other solvents and reagents were used as received from commercial sources. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400–4000  $\text{cm}^{-1}$  range using a Perkin-Elmer 1600 FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer model 2400 analyzer.

**Preparation of  $\{[\text{Ag}(\text{L1})]\text{SbF}_6\}_n$  (**1**).** A solution of  $\text{AgSbF}_6$  (34.3 mg, 0.10 mmol) in MeOH (8 mL) was layered onto a solution of L1 (22.4 mg, 0.10 mmol) in methylene chloride (8 mL). The solutions were left for about one week at room temperature, and colorless crystals were obtained. Yield 80% (based on  $\text{AgSbF}_6$ ). Anal. Calcd for  $\text{AgC}_{12}\text{H}_8\text{F}_6\text{N}_4\text{Os}$  (**1**): C, 25.36; H, 1.41; N, 9.86. Found: C, 25.34; H, 1.45; N, 9.85. IR (KBr,  $\text{cm}^{-1}$ ): 3500(s), 3150(s), 1620(s), 1570(s), 1550(s), 1490(s), 1430(vs), 1340(w), 1280(m), 1220(w), 1125(w), 1097(w), 1068(m), 1018(w), 842(s), 650(vs).

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**Preparation of  $\{[\text{Ag}(\text{L1})\text{PF}_6]\}_n$  (**2**).** A solution of  $\text{AgPF}_6$  (25.3 mg, 0.10 mmol) in MeOH (8 mL) was layered onto a solution of L1 (22.4 mg, 0.10 mmol) in methylene chloride (8 mL). The solutions were left for about one week at room temperature, and colorless crystals were obtained. Yield 77% (based on  $\text{AgPF}_6$ ). Anal. Calcd for  $\text{AgC}_{12}\text{H}_8\text{F}_6\text{N}_4\text{O}$  (**2**): C, 30.18; H, 1.68; N, 11.73. Found: C, 30.21; H, 1.56; N, 11.70. IR (KBr,  $\text{cm}^{-1}$ ): 3500(m), 3150(m), 3110(w), 1620(s), 1570(s), 1550(s), 1490(s), 1435(s), 1340(w), 1285(m), 1220(m), 1130(w), 1095(w), 1067(s), 1020(m), 830(vs), 745(w), 720(s).

**Preparation of  $\{[\text{Ag}(\text{L2})\text{SbF}_6]\}_n$  (**3**) and  $[\text{Ag}_2(\text{L2})_2(\text{SbF}_6)_2]$  (**4**).** A solution of  $\text{AgSbF}_6$  (34.3 mg, 0.10 mmol) in MeOH (8 mL) was layered onto a solution of L2 (22.4 mg, 0.10 mmol) in methylene chloride (8 mL). The solutions were left for about one week at room temperature, and colorless crystals were obtained. Yield 76% for **3** and 12% for **4** (based on  $\text{AgSbF}_6$ ). Anal. Calcd for  $\text{AgC}_{12}\text{H}_8\text{F}_6\text{N}_4\text{OSb}$  (**3**): C, 25.36; H, 1.41; N, 9.86. Found: C, 25.32; H, 1.40; N, 9.82. IR (KBr,  $\text{cm}^{-1}$ ): 3416(s), 2925(w), 1615(s), 1540(s), 1484(m), 1413(s), 1339(s), 1206(m), 1121(m), 1088(m), 1049(m), 967(w), 824(m), 731(s), 663(s), 625(s). Anal. Calcd for  $\text{Ag}_2\text{C}_{24}\text{H}_{16}\text{F}_{12}\text{N}_8\text{O}_2\text{Sb}_2$  (**4**): C, 25.36; H, 1.41; N, 9.86. Found: C, 25.29; H, 1.45; N, 9.78. IR (KBr,  $\text{cm}^{-1}$ ): 3446(s), 2925(w), 1614(s), 1539(m), 1484(m), 1417(s), 1340(w), 1207(w), 1118(s), 1089(s), 840(m), 732(m), 664(s), 633(s).

**Preparation of  $\{[\text{Ag}(\text{L3})\text{SO}_3\text{CF}_3]\}_n$  (**5**).** A solution of  $\text{AgSO}_3\text{CF}_3$  (25.6 mg, 0.10 mmol) in MeOH (10 mL) was layered onto a solution of L3 (25.2 mg, 0.10 mmol) in methylene chloride (10 mL). The solutions were left for about one week at room temperature, and colorless crystals were obtained. Yield 72% (based on  $\text{AgSO}_3\text{CF}_3$ ). Anal. Calcd for  $\text{AgC}_{15}\text{H}_{12}\text{F}_3\text{N}_4\text{O}_4\text{S}$  (**5**): C, 35.35; H, 2.36; N, 11.00. Found: C, 35.32; H, 2.33; N, 10.97. IR (KBr,  $\text{cm}^{-1}$ ): 3500(s), 3400(s), 3250(s), 1620(s), 1596(s), 1567(s), 1550(s), 1499(m), 1481(s), 1471(s), 1320(m), 1275(s), 1250(s), 1170(s), 1075(w), 1031(s), 980(s), 870(m), 790(m), 729(m), 675(m).

**Single-Crystal Structure Determination.** Suitable single crystals of **1–5** were selected and mounted onto the end of a thin glass fiber using inert oil. X-ray intensity data were measured at 150 K on a Bruker SMART APEX CCD-based diffractometer (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). The raw frame data for **1–5** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.<sup>15</sup> Corrections for incident and diffracted beam absorption effects were applied using SADABS.<sup>15</sup> None of the crystals showed evidence of crystal decay during data collection. Compounds **1**, **2**, and **3** crystallized in the space group  $P2_1/c$ , compound **4** crystallized in the space group  $P\bar{1}$ , and compound **5** crystallized in the unusual space group  $Pbcn$  as determined by the systematic absences in the intensity data, intensity statistics, and the successful solution and refinement of the structures. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against  $F^2$  by the full-matrix least-squares technique. Crystal data, data collection parameters, and refinement statistics for **1–5** are listed in Tables 1 and 2. Relevant interatomic bond distances and bond angles for **1–5** are given in Tables 3–7.

## Results and Discussion

**Synthesis of Compounds 1–5.** Compounds **1–5** were obtained as polymeric compounds and molecular complex in methanol/methylene chloride mixed solvent system by

**Table 1.** Crystallographic Data for **1** and **2**<sup>a</sup>

	<b>1</b>	<b>2</b>
empirical formula	$\text{C}_{12}\text{H}_8\text{AgF}_6\text{N}_4\text{OSb}$	$\text{C}_{12}\text{H}_8\text{AgF}_6\text{N}_4\text{OP}$
fw	567.84	477.06
cryst syst	monoclinic	monoclinic
<i>a</i> (Å)	6.6846(4)	6.6753(3)
<i>b</i> (Å)	28.3120(16)	27.2824(14)
<i>c</i> (Å)	8.6802(5)	8.2932(4)
$\alpha$ (deg)	90	90
$\beta$ (deg)	94.1080(10)	94.6030(10)
$\gamma$ (deg)	90	90
<i>V</i> (Å <sup>3</sup> )	1569.06(16)	1505.47(13)
space group	$P2_1/c$	$P2_1/c$
<i>Z</i> value	4	4
$\rho$ calcd (g/cm <sup>3</sup> )	2.404	2.105
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	11.258	11.329
temp (K)	150	150
no. observations ( <i>I</i> > 3 $\sigma$ )	2768	3079
residuals: <i>R</i> ; <i>R</i> <sub>w</sub>	0.0234; 0.0466	0.0335; 0.0641

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}.$$

**Table 2.** Crystallographic Data for **3–5**<sup>a</sup>

	<b>3</b>	<b>4</b>	<b>5</b>
empirical formula	$\text{C}_{12}\text{H}_8\text{AgF}_6\text{N}_4\text{OSb}$	$\text{C}_{24}\text{H}_{16}\text{Ag}_2\text{F}_{12}\text{N}_8\text{O}_2\text{Sb}_2$	$\text{C}_{15}\text{H}_{12}\text{AgF}_3\text{N}_4\text{O}_4\text{S}$
fw	567.84	1135.69	509.22
cryst syst	monoclinic	triclinic	orthorhombic
<i>a</i> (Å)	5.5677(3)	8.7221(5)	9.8861(5)
<i>b</i> (Å)	17.3378(9)	9.2008(6)	20.2580(10)
<i>c</i> (Å)	15.6640(8)	10.7686(7)	17.5517(8)
$\alpha$ (deg)	90	70.6270(10)	90
$\beta$ (deg)	94.4100(10)	75.7670(10)	90
$\gamma$ (deg)	90	73.7560(10)	90
<i>V</i> (Å <sup>3</sup> )	1507.60(14)	771.45(8)	3515.1(3)
space group	$P2_1/c$	$P\bar{1}$	$Pbcn$
<i>Z</i> value	2	1	8
$\rho$ calcd (g/cm <sup>3</sup> )	2.502	2.445	1.924
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	11.258	11.329	11.329
temp (K)	150	150	150
no. observations ( <i>I</i> > 3 $\sigma$ )	3072	3150	3609
residuals: <i>R</i> ; <i>R</i> <sub>w</sub>	0.0335; 0.0616	0.0299; 0.0527	0.0614; 0.1137

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|. wR2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}.$$

**Table 3.** Interatomic Distances (Å) and Bond Angles (deg) with esd's in Parentheses for **1**<sup>a</sup>

Ag–N(1)	2.213(2)	Ag–N(4)#1	2.217(2)
Ag–N(3)#2	2.435(2)		
N(1)–Ag–N(4)#1	145.32(8)	N(1)–Ag–N(3)#2	106.90(8)
N(4)#1–Ag–N(3)#2	107.47(8)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1,  $-x + 1, y + 1/2, -z + 1/2$ ; #2,  $x - 1, -y + 1/2, z - 1/2$ ; #3,  $-x + 1, -y + 1, -z + 1$ ; #4,  $-x + 1, -y + 1, -z$ ; #5,  $x + 1, -y + 1/2, z + 1/2$ ; #6,  $-x + 1, y - 1/2, -z + 1/2$ .

combination of L1–L3 with different inorganic Ag(I) salts, respectively. In these specific reactions, the products do not depend on of the ligand-to-metal ratio. However, increasing the ligand-to-metal ratio resulted in somewhat higher yield and higher crystal quality. Compounds **1–5** are air stable and can retain their structural integrity at room temperature for a considerable length of time. It is worthwhile to point out that the coordination chemistry of oxadiazole-containing ligands L1 and L2 with Ag(I) appears to be quite versatile. Recently, a series of novel Ag(I) polymeric structures based on L1, L2, and 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole have

(15) SAINT; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

**Table 4.** Interatomic Distances (Å) and Bond Angles (deg) with esd's in Parentheses for **2**<sup>a</sup>

Ag–N(1)	2.205(2)	Ag–N(4)#1	2.213(2)
Ag–N(3)#2	2.430(2)		
N(1)–Ag–N(4)#1	147.28(8)	N(1)–Ag–N(3)#2	105.80(7)
N(4)#1–Ag–N(3)#2	106.78(7)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1,  $-x + 1, y + 1/2, -z + 1/2$ ; #2,  $x - 1, -y + 1/2, z - 1/2$ ; #3,  $-x + 1, -y + 1, -z + 1$ ; #4,  $-x + 1, -y + 1, -z$ ; #5,  $x + 1, -y + 1/2, z + 1/2$ ; #6,  $-x + 1, y - 1/2, -z + 1/2$ .

**Table 5.** Interatomic Distances (Å) and Bond Angles (deg) with esd's in Parentheses for **3**<sup>a</sup>

Ag–N(1)	2.135(3)	Ag–N(4)#1	2.139(3)
N(1)–Ag–N(4)#1	176.69(11)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1,  $-x + 1, y - 1/2, -z + 3/2$ ; #2,  $x - 1, y, z$ ; #3,  $x + 1, y, z$ ; #4,  $-x + 1, y + 1/2, -z + 3/2$ .

**Table 6.** Interatomic Distances (Å) and Bond Angles (deg) with esd's in Parentheses for **4**<sup>a</sup>

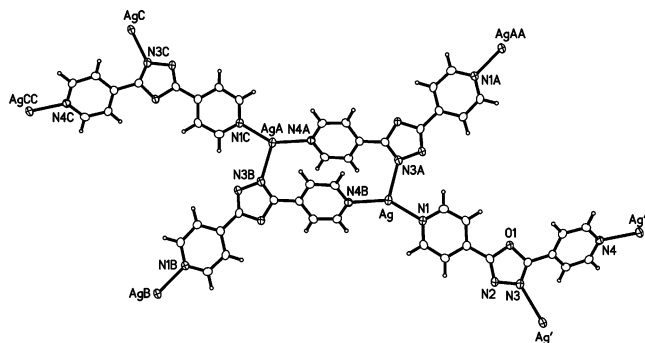
Ag–N(1)	2.130(3)	Ag–N(4)#1	2.137(3)
N(1)–Ag–N(4)#1	170.87(10)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1,  $-x + 1, -y + 1, -z$ ; #2,  $x, y + 1, z$ ; #3,  $-x + 1, -y + 2, -z$ .

**Table 7.** Interatomic Distances (Å) and Bond Angles (deg) with esd's in Parentheses for **5**<sup>a</sup>

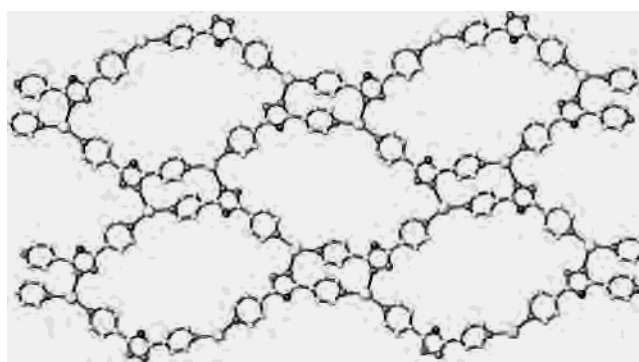
Ag–N(4)#1	2.270(4)	Ag–N(2)#2	2.293(4)
Ag–N(1)	2.312(4)		
N(4)#1–Ag–N(2)#2	131.91(14)	N(4)#1–Ag–N(1)	123.50(14)
N(2)#2–Ag–N(1)	104.53(14)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1,  $-x + 1, -y + 1, -z + 1$ ; #2,  $x - 1/2, -y + 1/2, -z + 1$ ; #3,  $x + 1/2, -y + 1/2, -z + 1$ .

**Figure 2.** ORTEP figure of **1** and **2** with 50% probability ellipsoids.

been synthesized in our lab.<sup>13c</sup> In these polymeric Ag(I) compounds, the different coordination styles of oxadiazole-containing-type ligands were observed, which maybe results from the subtle templating effects of both counterions and solvent molecules.

**Structural Analysis. Structural Analysis of {[Ag(L1)]-SbF<sub>6</sub>}<sub>n</sub> (**1**).** Crystallization of L1 with AgSbF<sub>6</sub> in the methanol/methylene chloride mixed solvent system at room temperature afforded the infinite two-dimensional polymeric compound (**1**) in 80% yield. The metal-to-ligand ratio is 1:1. As shown in Figure 2, every Ag(I) center adopts a distorted trigonal coordination environment which consists of three N-donors from two pyridyl (N(1) and N(2)) and one 1,3,4-

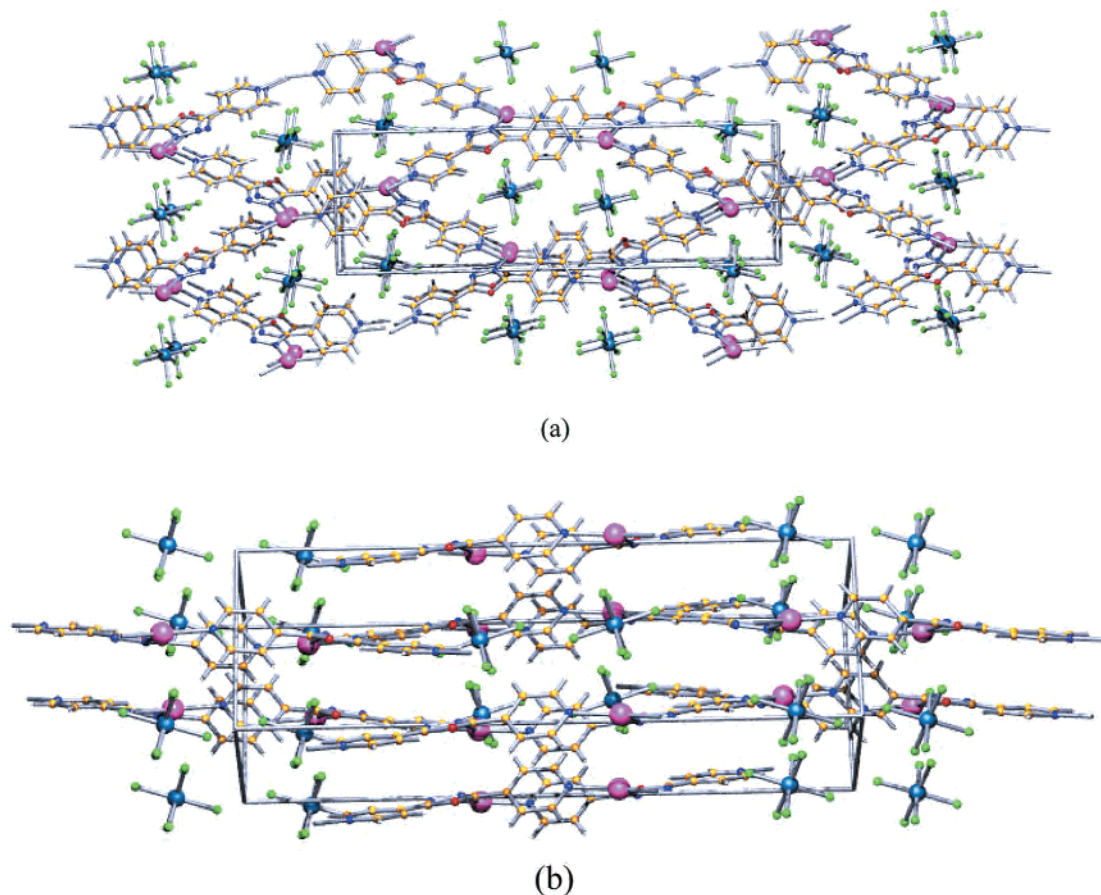
**Figure 3.** Infinite 2-D net in **1** and **2**. Hydrogen atoms and counterions are omitted for clarity.

oxadiazole (N(3)) groups. The Ag–N<sub>oxadiazole</sub> bond length is considerably longer than those of the Ag–N<sub>pyridyl</sub> bonds by 0.223–0.238 Å, but all Ag–N bond distances found in **1** are within the normal range observed in N-containing heterocyclic Ag(I) complexes.<sup>16</sup> In the solid state, compound **1** adopts an unique two-dimensional zeolite-like pattern extending in the crystallographic [10 $\bar{2}$ ] plane. As shown in Figure 3, a single net consists of two different individual rings. The large one comprises a tetrameric unit, in which four Ag(I) centers are linked together by L1 ligands through both pyridyl and oxadiazole N-donors into an elliptical 40-membered macrocycle. The approximate (crystallographic) dimensions of the rings are 21 × 13 Å<sup>2</sup>. The small one consists of a 14-membered dimeric unit. The effective cross section is 4 × 7 Å<sup>2</sup>. Surprisingly, no guest solvent molecules have been found in either the large or the small rings. The crystal packing of **1** is shown in Figure 4. All the two-dimensional macrocycle-containing nets stack together along the crystallographic *a* axis and generate a porous network with rhombus channels, in which the uncoordinated SbF<sub>6</sub><sup>−</sup> counterions are located. The shortest interlayer Ag...Ag contact is 6.68(3) Å, which is much longer than the sum of the van der Waals radii of two silver atoms, 3.44 Å.

**Structural Analysis of {[Ag(L1)]PF<sub>6</sub>}<sub>n</sub> (**2**).** In order to explore the templating role of counterions in the self-assembly process, AgPF<sub>6</sub> was used instead of AgSbF<sub>6</sub> to carry out the same reaction. The two-dimensional polymeric compound, namely {[Ag(L1)]PF<sub>6</sub>}<sub>n</sub>, was obtained. Compound **2** is isostructural with **1**. There is an interesting change in the unit cell parameters upon increasing the anion size from PF<sub>6</sub><sup>−</sup> to SbF<sub>6</sub><sup>−</sup>. The cell volume increases as expected, but it does so in an anisotropic way. The shorter *a* and *c* axes expand while the long *b* axis contracts.

We reported the reaction of L1 ligand with AgSO<sub>3</sub>CF<sub>3</sub> in the same solvent system; a one-dimensional polymeric compound {[Ag(L1)]SO<sub>3</sub>CF<sub>3</sub>}<sub>n</sub> was obtained instead of two-dimensional net reported herein.<sup>13b</sup> It is tempting to view {[Ag(L1)]SO<sub>3</sub>CF<sub>3</sub>}<sub>n</sub> as a one-dimensional fragment of the structure of **1** and **2** that might be considered a polymeric

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**Figure 4.** Crystal packing of **1** and **2**. (a) View down *a* axis. (b) View down *c* axis.

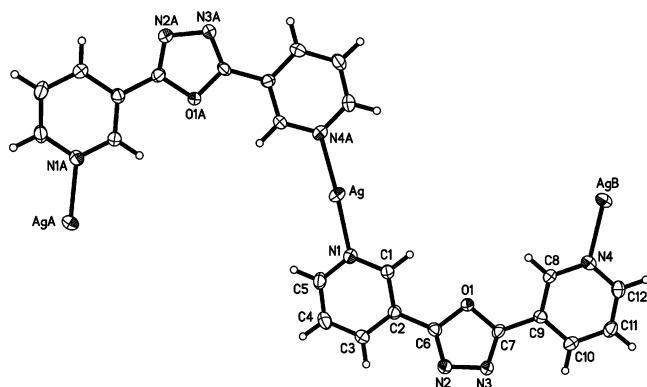
intermediate on the route to the two-dimensional polymeric motif. In compound  $\{[\text{Ag}(\text{L}1)]\text{SO}_3\text{CF}_3\}_n$ , L1 ligands coordinate Ag(I) ions in two different ways: one type of L1 binds Ag(I) centers as a bidentate-type ligand with only two terminal pyridyl N-donors, while the other type of L1 coordinates Ag(I) ions as a tridentate-type ligand with both terminal pyridyl N-donors and oxadiazole N-donors. However, all L1 species in compounds **1** and **2** herein serve as the tridentate-type ligand to tether Ag(I) centers into two-dimensional polymeric structures. It is apparent that the counterions (polar  $\text{SO}_3\text{CF}_3^-$  vs nonpolar  $\text{SbF}_6^-$  and  $\text{PF}_6^-$ ) play the central roles in determining the polymeric structures.

**Structural Analysis of  $\{[\text{Ag}(\text{L}2)]\text{SbF}_6\}_n$  (**3**) and  $[\text{Ag}_2(\text{L}2)_2](\text{SbF}_6)_2$  (**4**).** The idea behind the use of ligand L2 is to control supramolecular motifs through a 3,3'-bipyridine-type ligand. It is well-known that the relative different orientations of the nitrogen donors on the pyridyl rings and also the different bridging spacing might result in unusual building blocks, which can lead to the construction of supramolecular motifs that have not been achieved using normal rigid linear bidentate organic ligands. We earlier reported on a series of novel coordination polymers generated from rigid bidentate 4,4'-bipyridine- and 3,3'-bipyridine-type Schiff-base ligands.<sup>17</sup> Indeed, our previous studies demonstrated that the relative orientation of the coordinating sites is one of the most important factors to control the polymeric motifs.

Crystallization of L2 with  $\text{AgSbF}_6$  in methanol/methylene chloride at room temperature afforded the infinite one-dimensional polymeric compound **3** and the bimetallic supramolecular square **4** in 76% and 12% yield, respectively. The metal–ligand ratio is 1:1 in the reaction. It is interesting that the shapes of crystals **3** (blade-shape) and **4** (block-shape) are different. Single-crystal analysis revealed that in compound **3**, as shown in Figure 5, the Ag(I) center lies in a nearly linear coordination environment consisting of the two pyridyl N atoms from two *cis*-L2 ligands (N(1) and N(4)), which is commonly observed in many other Ag(I) complexes.<sup>12a</sup> In addition, a F-donor from  $\text{SbF}_6^-$  still coordinates to the silver center very weakly with a long Ag–F separation of 3.238(3) Å.<sup>18</sup> It is worth noting that the two pyridyl groups and bridging oxadiazole ring in L2 are exactly coplanar, resulting in a sinusoidal-chain motif. All the chains are parallel and extend along the crystallographic *b* axis (Figure 6). The  $\text{SbF}_6^-$  counterions in **3** are located between two adjacent silver atoms and bind weakly to the Ag(I) centers. The shortest interchain and intrachain Ag(I)⋯Ag(I) contact is 8.7147(3) and 5.5677(3) Å, respectively.

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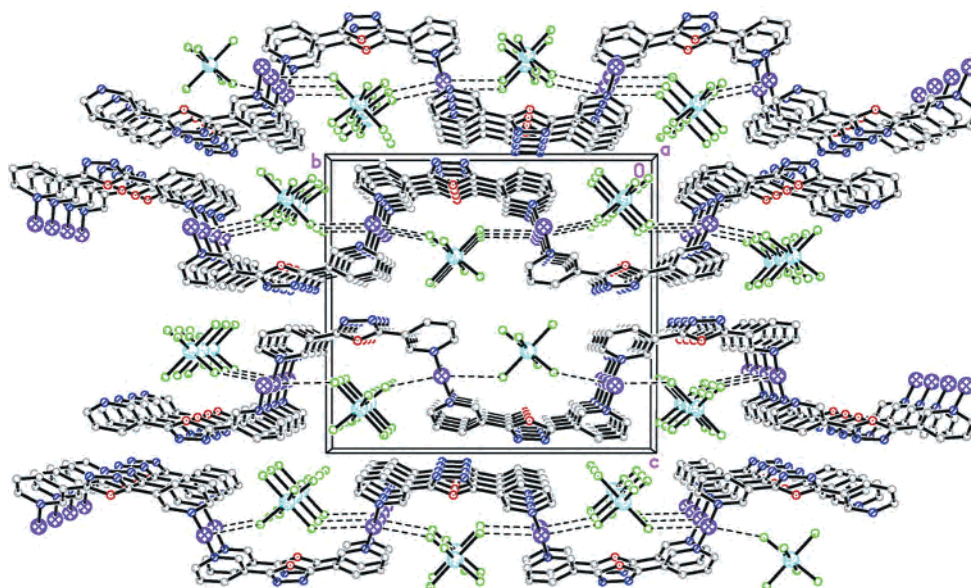
**Figure 5.** ORTEP figure of **3** with 50% probability ellipsoids.

It is different from **3**, as compound **4** was obtained as a bimetallic supramolecular square instead of a polymeric compound, although **3** and **4** were obtained from a one-pot reaction. As shown in Figure 7, the Ag(I) center also has nearly linear coordination with the two pyridyl N atoms from two L2 ligands (N(1) and N(4)). Two  $\text{SbF}_6^-$  counterions are located above and below the macrocycle plane (crystallographic dimensions,  $8.06 \times 7.42 \text{ \AA}^2$ ) and weakly coordinate to two Ag(I) centers ( $\text{Ag}-\text{F}(5)\#2 = 2.895(2)$  and  $\text{Ag}-\text{F}(6)\#1 = 2.904(2) \text{ \AA}$ ). This kind of weak F–Ag interaction bonds these macrocycles together into a novel one-dimensional chain. The shortest intermacrocycle Ag(I)⋯Ag(I) distance is  $3.4692(6) \text{ \AA}$ , which is comparable to the sum of the van der Waals radii of two silver atoms ( $3.44 \text{ \AA}$ ), but slightly longer than the Ag⋯Ag separation of  $3.0\text{--}3.3 \text{ \AA}$  found in many other Ag(I) coordination polymers with pyridyl-donor spacers, indicating weak Ag⋯Ag interactions (Figure 8).<sup>19</sup> However, no guest solvent molecules are located in these macrobimetallic rings.

The field of designing and synthesizing metal-containing supramolecular macrocycles, especially squarelike compounds, is currently very active.<sup>20</sup> As we know, most of them are generated from Pt, Pd, and Re. Metal-containing supramolecular squarelike assemblies generated from

Ag(I)<sup>21</sup> are quite rare. Compound **4** described herein is soluble in both water and common organic solvents, which is an additional remarkable and useful feature for this interesting compound. It is worth pointing out that the coordination chemistry of the L2 ligand is versatile. It can coordinate metal ions in either the *cis*- or *trans*-configuration that was found in our previous studies.<sup>13</sup> For example, the *trans*-L2 was found in coordination polymers  $\text{Cu}(\text{L}2)_2(\text{ClO}_4)_2$  and  $[\text{Cu}(\text{L}2)(\text{H}_2\text{O})(\text{SO}_4)] \cdot 2.75\text{H}_2\text{O}$ ,<sup>13b</sup> while the *cis*-L2 was found in coordination polymers  $\text{Cu}_2(\text{OAc})_2(\text{L}2)$ <sup>13d</sup> and  $\text{Cu}(\text{hfacac})_2(\text{L}2)$ <sup>13b</sup> and dimeric molecular squares  $[\text{Zn}(\text{L}2)(\text{H}_2\text{O})_3(\text{NO}_3)]_2$  and  $\{[\text{Cu}(\text{L}2)(\text{CH}_3\text{CN})(\text{NO}_3)]_2\}$ .<sup>13c</sup> However, no bimetallic macrocyclic complexes were obtained in the reaction of L2 with  $\text{AgSO}_3\text{CF}_3$  in the same solvent system, probably due to the templating effects of different counterions.<sup>13f</sup>

**Structural Analysis of  $\{[\text{Ag}(\text{L}3)]\text{SO}_3\text{CF}_3\}_n$  (**5**).** In contrast to the well-developed coordination chemistry based on bipyridine-type ligands,<sup>12b</sup> efforts on biphenylamine-type ligands are quite unusual, especially for 3,3'-biphenylamine-type ligands. We reported a novel Ag(I) three-dimensional coordination polymer, namely  $\{[\text{Ag}(2,5\text{-bis}(4\text{-aminobenzoyl})\text{-}1,3,4\text{-oxadiazole})]\text{SO}_3\text{CF}_3\}_n$ , based on the tetradentate 2,5-bis(4-aminobenzoyl)-1,3,4-oxadiazole ligand.<sup>13c</sup> In this compound, amino groups serve as both coordinating and hydrogen bonding<sup>22</sup> functional groups. However, the hydrogen bonding interactions there based on  $\text{NH}_2$  do not contribute to the dimension of the compound. In order to explore the role of the orientations of coordination donors in the self-assembly process, 3,3'-biphenylamine-type ligand L3 was used instead of 2,5-bis(4-aminobenzoyl)-1,3,4-oxadiazole to perform the same reaction. When a solution of L3 in methylene chloride was treated with  $\text{AgSO}_3\text{CF}_3$  in methanol in a molar ratio of 1:1 (metal-to-ligand), compound **5** was obtained as colorless crystals in 72% yield. Compound **5** is air stable and formed with a high symmetry in the unusual orthorhombic space group *Pbcn*. As shown in Figure 9, each Ag(I) center is located in a distorted trigonal



**Figure 6.** One-dimensional sinusoidal chains of **3**.

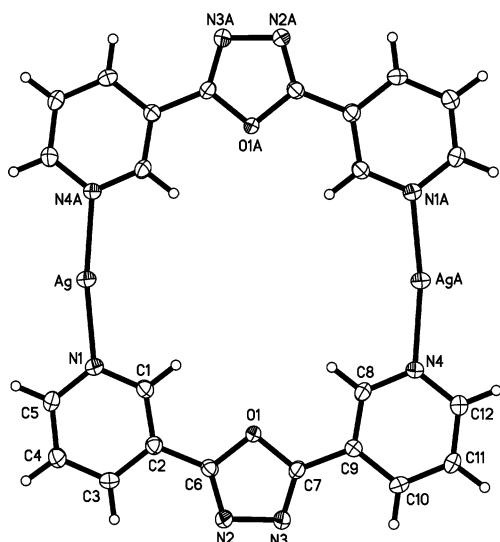


Figure 7. ORTEP figure of **4** with 50% probability ellipsoids.

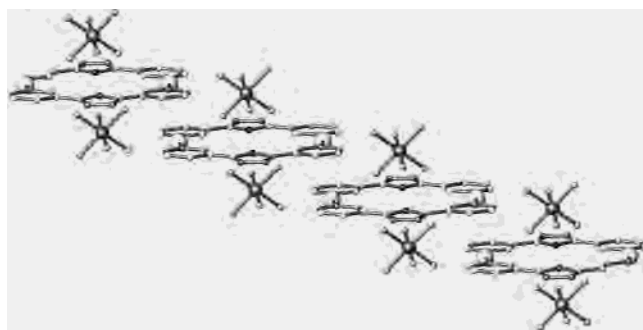


Figure 8. Crystal packing of **4**. F $\cdots$ Ag(I) and Ag(I) $\cdots$ Ag(I) weak interactions are shown as dotted lines.

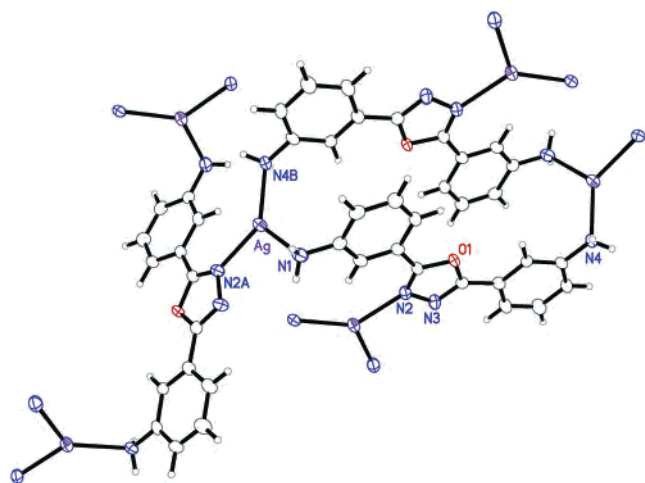
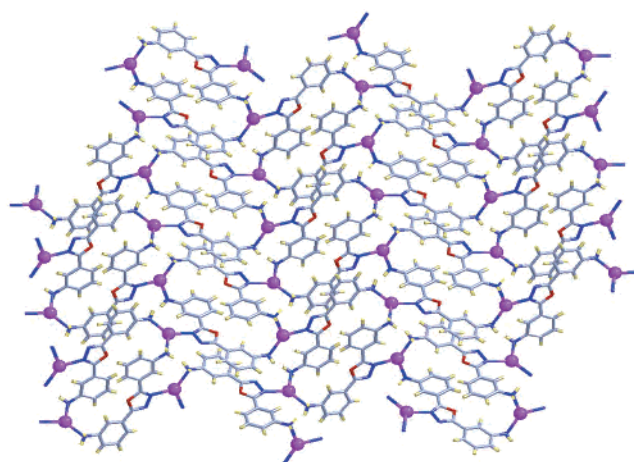


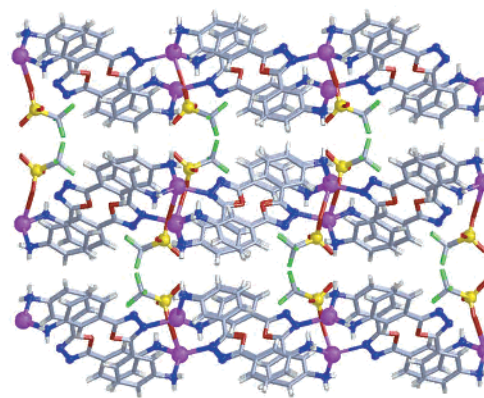
Figure 9. ORTEP figure of **5** with 50% probability ellipsoids.

coordination sphere consisting of two  $N_{\text{amino}}$  donors (N(1) and N(4)) and one  $N_{\text{oxadiazole}}$  donor (N(2)), which is distinctly different from the distorted tetrahedral coordination environment of Ag(I) found in  $\{[\text{Ag}(2,5\text{-bis}(4\text{-aminobenzoyl)}\text{-}1,3,4\text{-oxadiazole})\text{SO}_3\text{CF}_3]_n\}$ .

In the solid state, as shown in Figure 10, Ag(I) centers are connected to each other by tridentate L3 into an undulating infinite two-dimensional net parallel to the crystallographic [001] plane. The shortest intralayer



(a)

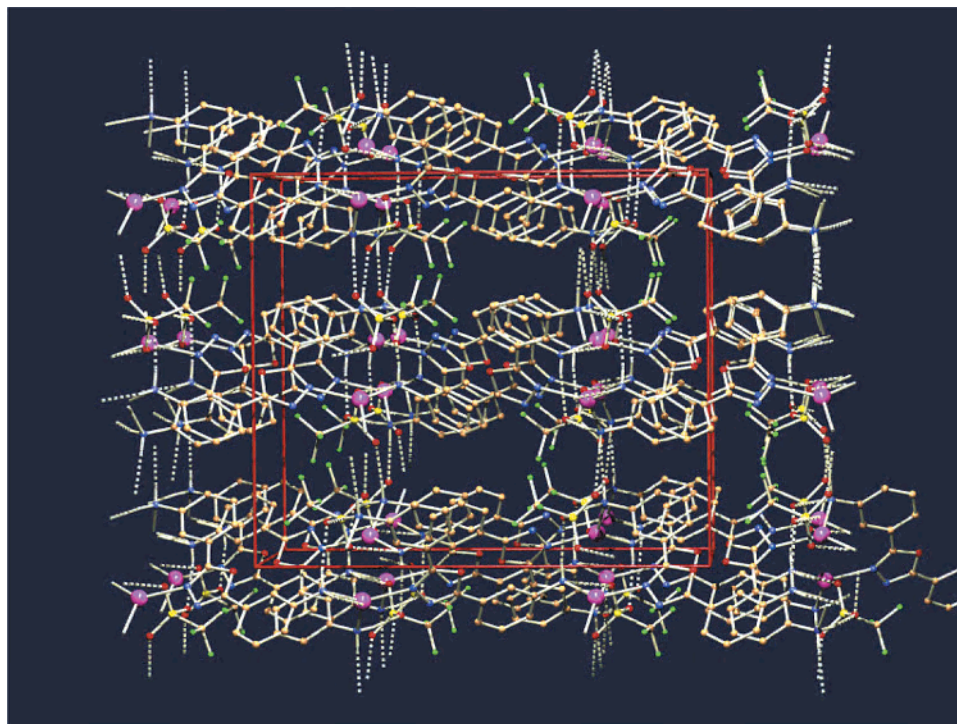


(b)

Figure 10. Infinite 2-D net in **5**. (a) View down  $c$  axis. (b) View down  $a$  axis.

Ag(I) $\cdots$ Ag(I) distance is 9.88(3) Å. The weakly coordinated  $\text{SO}_3\text{CF}_3^-$  anions are located between the layers. In addition, several sets of interlayer N–H $\cdots$ O hydrogen bonds have been found in **5**, which consist of three oxygen atoms O(11), O(12), and O(13) of the  $\text{SO}_3\text{CF}_3^-$  counterion and four amino hydrogen atoms H(1N), H(2N), H(3N), and H(4N) of L3. The corresponding hydrogen bonds data were listed in Table 8. These interlayer hydrogen bonding interactions stitch these two-dimensional nets into a hydrogen bonded three-dimensional network (Figure 11). The shortest interlayer Ag(I) $\cdots$ Ag(I) contact is 9.06(3) Å. Extended networks assembled by both coordination and hydrogen bonds now are well established.<sup>23</sup> In principle, higher dimensionality

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**Figure 11.** H-bonded three-dimensional network of **5** (view down *c* axis).

**Table 8.** Hydrogen Bonds for **5** [Å and deg]<sup>a</sup>

D–H···A	<i>d</i> (D–H)	<i>d</i> (H···A)	<i>d</i> (D···A)	∠(DHA)
N(1)–H(1N)···O(12)	0.84(3)	2.25(3)	3.047(5)	159(5)
N(1)–H(2N)···O(11)#4	0.83(3)	2.12(3)	2.951(6)	178(7)
N(4)–H(3N)···O(12)#5	0.84(3)	2.22(3)	3.038(6)	166(6)
N(4)–H(4N)···O(13)#6	0.84(3)	2.18(3)	2.977(5)	159(5)

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1,  $-x + 1, -y + 1, -z + 1$ ; #2,  $x - 1/2, -y + 1/2, -z + 1$ ; #3,  $x + 1/2, -y + 1/2, -z + 1$ ; #4,  $-x + 1, y, -z + 3/2$ ; #5,  $-x + 3/2, y + 1/2, z$ ; #6,  $-x + 2, -y + 1, -z + 1$ .

networks can be obtained by the assembly of lower dimensionality polymers (or molecules) via hydrogen bonding interactions. A series of such compounds, namely [Zn(H<sub>2</sub>O)(bipy)](NO<sub>3</sub>)<sub>2</sub>·bipy, [Zn(H<sub>2</sub>O)<sub>4</sub>(bipy)](NO<sub>3</sub>)<sub>2</sub>·2bipy, [Zn(H<sub>2</sub>O)<sub>4</sub>(bipy)](SO<sub>3</sub>CF<sub>3</sub>)<sub>2</sub>·2bipy, and Fe(H<sub>2</sub>O)<sub>3</sub>(ClO<sub>4</sub>)(bipy)(ClO<sub>4</sub>)·1.5(bipy)·H<sub>2</sub>O, was reported before.<sup>23</sup> Compound **5** reported herein represents additional examples for this kind of compound. As a result, the L3 ligand herein gives rise to a novel H-bonded three-dimensional network, demonstrating that, in comparison with {[Ag(2,5-bis(4-aminobenzoyl)-1,3,4-oxadiazole)]SO<sub>3</sub>CF<sub>3</sub>]<sub>n</sub>, the orientation of the coordination sites does have a profound effect upon the resultant network geometry.

## Conclusions

This study demonstrates that the oxadiazole-containing rigid organic ligands 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (L1), 2,5-bis(3-pyridyl)-1,3,4-oxadiazole (L2), and 2,5-bis(3-aminobenzoyl)-1,3,4-oxadiazole (L3) are capable of coordinating metal centers with both N<sub>pyridyl</sub> or N<sub>amino</sub> and N<sub>oxadiazole</sub> donors

and generate novel coordination polymers. Four new coordination polymers and one novel bimetallic molecular square were synthesized from solution reactions of L1–L3 with Ag(I) salts, respectively. The relative orientation of the nitrogen donors on the pyridyl rings or phenyl rings and the five-membered oxadiazole spacing in L1–L3 resulted in unusual building blocks, leading to the construction of polymeric motifs which have not been obtained using normal linear rigid bidentate organic ligands, such as 4,4'-bipy and related organic spacers. We are currently extending this result by preparing new oxadiazole-containing ligands of this type containing different coordination functional groups and having different orientations of the nitrogen donors on the pyridyl rings. We anticipate that this new type of organic ligand will result in a variety of new coordination polymers or supramolecular complexes with novel polymeric patterns.

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**Supporting Information Available:** Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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