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Synthesis and Characterization of New Coordination Polymers Generated from Oxadiazole-Containing Organic Ligands and Inorganic Silver(I) Salts

Yu-Bin Dong,*,† Jian-Ping Ma, and Ru-Qi Huang

College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, and Key Lab of Chemical Functional Materials of Shandong Province, Jinan 250014, P. R. China

Mark D. Smith, and Hans-Conrad zur Loye*,‡

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

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The coordination chemistry of the oxadiazole-containing rigid bidentate ligands 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (L2) and 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (L3) with inorganic Ag(I) salts has been investigated. Four new coordination polymers were prepared by solution reactions and fully characterized by infrared spectroscopy, elemental analysis, and single-crystal X-ray diffraction. $\{[Ag(L2)]SO_3CF_3\}_n$ (**1**) (triclinic, $P\bar{1}$; $a = 10.1231(7)$ Å, $b = 13.9340(10)$ Å, $c = 13.9284(10)$ Å, $\alpha = 116.7300(10)°$, $\beta = 94.6890(10)°$, $\gamma = 108.7540(10)°$, $Z = 4$) was obtained by the combination of L2 with AgOTf in a CH_2Cl_2/CH_3OH mixed-solvent system and features a unique one-dimensional elliptical macrocycle-containing chain motif. The approximate dimensions of the rings are ca. 22 × 11 Å. $\{[Ag(L2)](ClO_4)(CH_3OH)_{0.5}(H_2O)_{0.5}\}_n$ (**2**) (triclinic, $P\bar{1}$; $a = 8.4894(5)$ Å, $b = 13.9092(8)$ Å, $c = 14.1596(8)$ Å, $\alpha = 71.1410(10)°$, $\beta = 77.3350(10)°$, $\gamma = 81.5370(10)°$, $Z = 4$) was generated from the reaction of L2 with $AgClO_4$ in a H_2O/CH_3OH mixed-solvent system and consists of one-dimensional chains that are linked to each other by weak noncovalent π-π interactions into two-dimensional sheets. Uncoordinated ClO_4^- counterions and guest solvent molecules are located between the layers. $\{[Ag(L2)]NO_3\}_n$ (**3**) was obtained by the combination of L2 with $Ag(NO_3)_2$ in a $MeOH/H_2O$ mixed-solvent system (triclinic, $P\bar{1}$; $a = 8.3155(6)$ Å, $b = 8.8521(6)$ Å, $c = 9.8070(7)$ Å, $\alpha = 74.8420(10)°$, $\beta = 77.2800(10)°$, $\gamma = 68.6760(10)°$, $Z = 2$). In the solid state, it exhibits an interesting pair of chains associated with C–H···O hydrogen bonds. $\{[Ag(L3)]SO_3CF_3\}_n$ (**4**) is generated from L3 and $AgSO_3CF_3$ in a $CH_2Cl_2/MeOH$ mixed-solvent system and crystallizes in the unusual space group *Pnnm*, with $a = 7.9341(4)$ Å, $b = 11.5500(5)$ Å, $c = 18.1157(8)$ Å, and $Z = 4$. It adopts a novel three-dimensional structural motif in the solid state with big rhombic channels (ca. 15 × 10 Å).

Introduction

The design and syntheses of supramolecular coordination polymers with novel topologies and structural motifs is of current interest in the field of coordination chemistry.[1−3] Over the past decades, different classes of polymeric compounds fitting this general description have been successfully designed and synthesized. Some of them exhibit encouraging potential for applications, including nonlinear optics, catalysis and separation, magnetism, and molecular recognition.[4] In

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* To whom correspondence should be addressed. E-mail: yubindong@sdnu.edu.cn (Y.-B.D.); zurloye@sc.edu (H.-C.z.L.).

† Shandong Normal University.

‡ University of South Carolina.

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the long run, this line of research can lead to predictions of the topology and/or the periodicity of crystalline lattices generated from the molecular structures of the participating small building blocks; one can anticipate that the relationship between polymeric structures and physical properties will eventually be elucidated as well. The most efficient approach to access this type of material is via the direct chemical combination of functional inorganic and organic components, as has been demonstrated by many previous studies.[1−3]

So far, several types of bidentate rigid organodiamine ligands, such as 4,4′-bipyridine,[5a] 1,4-bis(4-pyridyl)ethene,[5b] and 1,4-bis(4-pyridyl)ethyne,[5c] and flexible organodiamine ligands, like 1,4-bis(4-pyridyl)ethane,[5d] 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene,[5e] and 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene,[5f,g] have been utilized by us as well as by numerous other research groups[1] to construct coordination polymers. All these bidentate N-donor-containing ligands have proven to be among the most important types of organic ligands for the design and construction of coordination polymers exhibiting remarkable polymeric structural motifs. However, in most cases, the ligands that were used to construct coordination polymers did not contain bridging five-membered heterocyclic rings, although some bridging azole or azolate ligands have been used to construct multimetallic complexes.[6] Currently, we are aware of only one 1-D coordination polymeric compound based on five-membered heterocyclic 1,3,4-oxadiazole ligands L1 (Figure 1) that was reported very recently.[7] The specific geometry of this type of ligand may result in coordination polymers with novel network patterns not achievable by other rigid linking ligands, such as the rigid linear bidentate ligands mentioned earlier. Moreover, heteroatoms such as N and O with free electron pairs on the five-member heterocyclic rings could be considered as potential active coordination sites and/or hydrogen bond acceptors to expand polymeric frameworks with coordinative covalent bonds or/and hydrogen-bonding interactions. The soft acid Ag(I) ion, on the other hand, has a versatile coordination chemistry[1b] and can serve to link bridging ligands to form polymeric compounds with novel coordination pattern. Sometimes the patterns of polymeric compounds can be influenced by Ag···Ag interactions.[8]

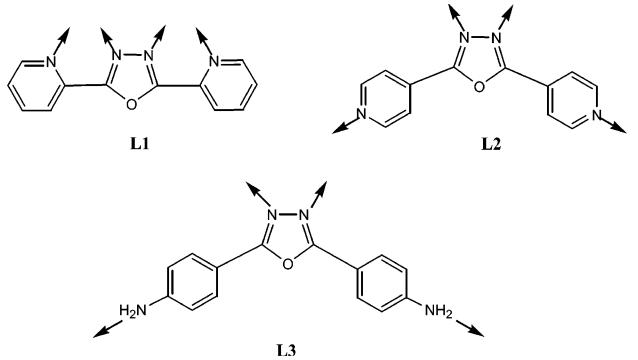

Figure 1. Rigid organic oxadiazole-containing ligands used in the construction of coordination polymer frameworks.

Herein, we wish to report four Ag-containing coordination polymers with novel polymeric motifs, namel $\{[Ag(L2)]SO_3CF_3\}_n$ (**1**), $\{[Ag(L2)](ClO_4)(CH_3OH)_{0.5}(H_2O)_{0.5}\}_n$ (**2**), $\{[Ag(L2)]NO_3\}_n$ (**3**), and $\{[Ag(L3)]SO_3CF_3\}_n$ (**4**) generated from 1,3,4-oxadiazole-containing ligands L2 abd L3 (Figure 1) and inorganic Ag(I) salts.

Experimental Section

Materials and Methods. $AgSO_3CF_3$, $AgNO_3$, and $AgClO_4$ (Acros) were used as obtained without further purification. Ligands L2 (2,5-bis(4-pyridyl)-1,3,4-oxadiazole) and L3 (2,5-bis(4-aminobenzoyl)-1,3,4-oxadiazole) were prepared according to literature methods.[9] Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400−4000 cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. Elemental analyses were performed on a Perkin-Elmer model 2400 analyzer.

Caution! One of the crystallization procedures involves $AgClO_4$, which is a strong oxidizer.

Preparation of $\{[Ag(L2)]SO_3CF_3\}_n$ (1). A solution of $AgSO_3CF_3$ (13.1 mg, 0.05 mmol) in MeOH (8 mL) was layered onto a solution of L2 (22.4 mg, 0.1 mmol) in methylene chloride (8 mL). The solutions were left for about 3 days at room temperature, and colorless crystals were obtained. Yield: 71% (based on $AgSO_3CF_3$). Anal. Calcd for $AgC_{13}H_8N_4O_4SF_3$ (**1**): C, 32.42; H, 1.66; N, 11.64. Found: C, 32.40; H, 1.67; N, 11.65. IR (KBr, cm^{-1}): 3120 (m), 3080 (m), 1614 (s), 1569 (s), 1540 (s), 1487 (s), 1428 (s), 1335 (s), 1290 (s), 1280 (s), 1247 (s), 1175 (s), 1130 (s), 965 (m), 830 (m), 747 (m), 710 (s).

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Preparation of $\{[Ag(L2)](ClO_4)(CH_3OH)_{0.5}(H_2O)_{0.5}\}_n$ (2). A solution of L2 (44.8 mg, 0.2 mmol) in CH_3OH (9 mL) was layered onto a solution of $AgClO_4$ (20.7 mg, 0.1 mmol) in H_2O. The solutions were left for about 3 days at room temperature, and colorless crystals were obtained. Yield: 87% (based on $AgClO_4$). Anal. Calcd for $AgC_{12.5}H_{11}N_4O_6Cl$ (**2**): C, 32.85; H, 2.41; N, 12.27. Found: C, 32.88; H, 2.41; N, 12.20. IR (KBr, cm^{-1}): 3490 (br), 1609 (s), 1568 (s), 1537 (s), 1486 (s), 1433 (s), 1388 (m), 1332 (m), 1277 (m), 1225 (m), 1145 (s), 1116 (s), 1085 (s), 980 (m), 967 (m), 830 (m), 738 (m), 710 (s).

Preparation of $\{[Ag(L2)]NO_3\}_n$ (3). A solution of L2 (44.8 mg, 0.2 mmol) in CH_3OH (9 mL) was layered onto a solution of $AgNO_3$ (17.3 mg, 0.1 mmol) in H_2O. The solutions were left for about 1 week at room temperature, and colorless crystals were obtained. Yield: 83% (based on $AgNO_3$). Anal. Calcd for $AgC_{12}H_8N_4O_5$ (**3**): C, 36.54; H, 2.03; N, 17.76. Found: C, 36.55; H, 2.00; N, 17.74. IR (KBr, cm^{-1}): 1614 (s), 1580 (s), 1540 (s), 1488 (s), 1405 (s), 1387 (s), 1368 (s), 1335 (w), 1305 (m), 1278 (w), 1220 (m), 1119 (w), 1065 (m), 1010 (w), 990 (w), 977 (w), 830 (s), 728 (w), 710 (s).

Preparation of $\{[Ag(L3)]SO_3CF_3\}_n$ (4). A solution of $AgSO_3CF_3$ (13.1 mg, 0.05 mmol) in MeOH (8 mL) was layered onto a solution of L3 (23.7 mg, 0.1 mmol) in methylene chloride (8 mL). The solutions were left for 1 week at room temperature, and brown tablet crystals were obtained. Yield: 92% (based on $AgSO_3CF_3$). Anal. Calcd for $AgC_{15}H_{12}N_4O_4SF_3$ (**1**): C, 35.35; H, 2.36; N, 11.00. Found: C, 35.36; H, 2.36; N, 10.87. IR (KBr, cm^{-1}): 3490 (s), 3400 (s), 1675 (m), 1610 (s), 1564 (w), 1495 (s), 1445 (m), 1300 (s), 1285 (s), 1253 (s), 1240 (m), 1180 (s), 1150 (m), 1084 (w), 1034 (s), 840 (m), 735 (m), 700 (m).

Single-Crystal Structure Determination. Suitable single crystals of **1**−**4** were selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 293 K on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, $\lambda = 0.710\ 73$ Å). The raw frame data for **1**−**4** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[10] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[10] None of the crystals showed evidence of crystal decay during data collection. Compound **1**−**3** crystallized in the space group $P\bar{1}$, and **4** crystallized in the unusual space group *Pnnm* 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**−**4** are listed in Tables 1 and 2. Relevant interatomic bond distances and bond angles for **1**−**4** are given in Tables 3−6.

Table 1. Crystallographic Data for **1** and **2**

empirical formula	$AgO_4N_4C_{13}H_8SF_3$, **1**	$AgO_6N_4C_{12.50}H_{11}Cl$, **2**
fw	481.16	456.57
cryst syst	triclinic	triclinic
a (Å)	10.1231(7)	8.4894(5)
b (Å)	13.8340(10)	13.9092(8)
c (Å)	13.9284(10)	14.1596(10)
α (deg)	116.7300(10)	71.1410(10)
β (deg)	94.6890(10)	77.3350(10)
γ (deg)	108.7540(10)	81.5370(10)
V ($Å^3$)	1589.4(2)	1538.44(15)
space group	$P\bar{1}$	$P\bar{1}$
Z value	4	4
ρ_{calc} (g/cm^3)	2.011	1.524
μ(Mo Kα) (cm^{-1})	11.258	11.329
temp (°C)	23	23
no. of observns ($I > 3\sigma$)	6498	6303
resids:[a] R; R_w	0.035; 0.066	0.0454; 0.0906

[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** and **4**

empirical formula	$AgO_4N_5C_{12}H_8$, **3**	$AgO_4N_4C_{15}H_{12}SF_3$, **4**
fw	394.10	509.22
cryst syst	triclinic	orthorhombic
a (Å)	8.3155(6)	7.9341(4)
b (Å)	8.8521(6)	11.5500(5)
c (Å)	9.8070(7)	18.1157(8)
α (deg)	74.8420(10)	90
β (deg)	77.2800(10)	90
γ (deg)	68.6760(10)	90
V ($Å^3$)	642.76(8)	1660.10(13)
space group	$P\bar{1}$	Pnnm
Z value	2	4
ρ_{calc} (g/cm^3)	1.597	2.037
μ(Mo Kα) (cm^{-1})	11.258	11.329
temp (°C)	23	23
no. of observns ($I > 3\sigma$)	2622	1766
resids:[a] R; R_w	0.0284; 0.0611	0.0473; 0.0978

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

Results and Discussion

Ligands and Synthesis of Compounds 1−4. Ligands L2 and L3 were chosen as simple yet interesting bipyridine and biamine linkers to investigate their presumed conformational flexibility. Compared to L1, L2 and L3 are more favorable for incorporating metal ions or coordination unsaturated inorganic metal salts into polymeric compounds due to the different orientations of their coordination sites. The possibility for these types of ligands to bind metal ions simultaneously by N atoms on pyridyl or amino and oxadiazole coordination groups potentially allows access to frameworks of novel topology. In addition, 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. L2 and L3 are very soluble in common polar organic solvents such as CH_2Cl_2, $CHCl_3$, THF, CH_3OH, and C_2H_5OH, which made crystallization with inorganic metal salts in solutions easy.

Compounds **1**−**4** were obtained as polymeric compounds in mixed-solvent systems by combination of L2 and L3 with different inorganic Ag(I) salts. It is worthwhile to point out that, 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.

Structural Analysis of $\{[Ag(L2)]SO_3CF_3\}_n$ (1). Crystallization of L2 with $AgSO_3CF_3$ in methanol/methylene chloride at room temperature afforded the infinite one-dimensional polymeric compound **1** in 71% yield. The metal−ligand ratio is 1:2 in the reaction. Crystals of **1** are air stable and can retain their structural integrity at room temperature for a considerable length of time. Single-crystal analysis revealed, as shown in Figure 2, that there are two different Ag(I) centers in **1**. The first Ag(I) center has nearly linear coordination with the two pyridyl N atoms from two L2 ligands (N(1)−Ag(1)−N(8) = 159.12(9)°; Ag−N(1) =

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(10) Bruker Analytical X-ray Systems, Inc., Madison, WI, 1998.

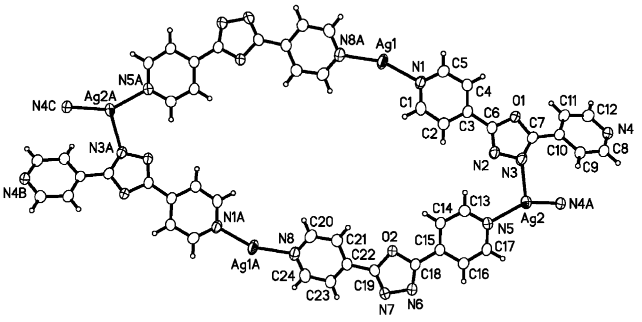

Figure 2. ORTEP figure of **1** with 50% probability ellipsoids.

Table 3. Interatomic Distances (Å) and Bond Angles (deg) with Esds in Parentheses for **1**[a]

Ag(1)−N(1)	2.176(2)	Ag(1)−N(8)#1	2.181(2)
Ag(1)−O(22)#2	2.537(11)	Ag(2)−N(5)	2.232(2)
Ag(2)−N(4)#3	2.247(2)	Ag(2)−N(3)	2.470(2)
N(1)−Ag(1)−N(8)#1	159.12(9)	N(5)−Ag(2)−N(4)#3	139.62(8)
N(5)−Ag(2)−N(3)	105.40(8)	N94)#3−Ag(2)−N(3)	113.18(7)
C(1)−N(1)−Ag(1)	119.12(17)	N(2)−N(3)−Ag(2)	113.36(15)
C(17)−N(5)−Ag(2)	119.60(17)	C(24)−N(8)−Ag(1)	122.30(19)
C(22)−C(19)−O(2)	119.7(2)	C(19)−N(7)−N(6)	105.7(2)

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

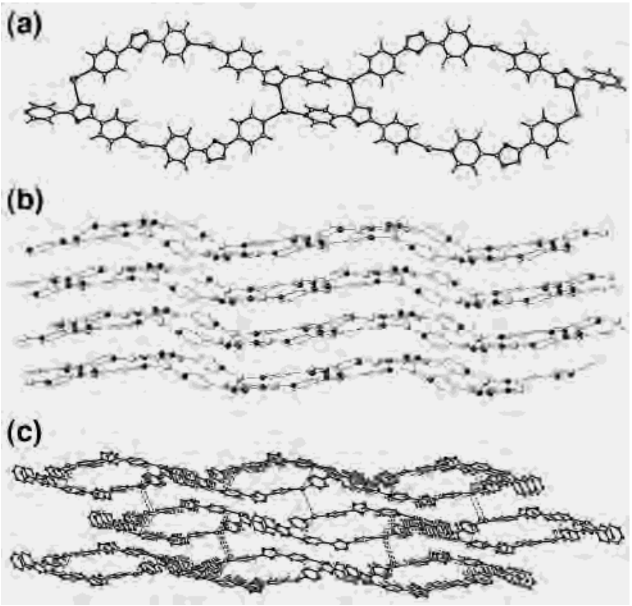

Figure 3. (a) One-dimensional macrocycle-containing chain in **1**. (b) Single layer in **1**. (c) Crystal packing of **1**. Ag···Ag contacts are shown as dotted lines. $SO_3CF_3^-$ counterions are omitted for clarity.

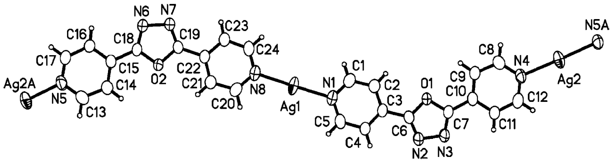

Figure 4. ORTEP figure of **2** with 50% probability ellipsoids.

Table 4. Interatomic Distances (Å) and Bond Angles (deg) with Esds in Parentheses for **2**[a]

Ag(1)−N(98)	2.161(3)	Ag(1)−N(1)	2.164(3)
Ag(2)−N(4)	2.149(3)	Ag(2)−N(5)#1	2.154(3)
N(8)−Ag(1)−N(1)	174.22(10)	N(4)−Ag(2)−N(5)#1	174.76(11)
C(5)−N(1)−Ag(1)	124.0(2)	C(12)−N(4)−Ag(2)	119.5(2)
C(3)−C(6)−O(1)	118.7(3)	C(6)−N(2)−N(3)	106.0(2)

[a] Symmetry transformations used to generate equivalent atoms: #1, *x* + 1, −*y* − 2, *z* + 1; #2, *x* − 1, *y* + 2, *z* − 1.

2.176(2), Ag−N(8) = 2.181(2) Å; Table 3). The second Ag(I) center, on the other hand, lies in a distorted trigonal coordination environment which consists of three N-donors from two pyridyl (Ag(2)−N(4) = 2.247(2), Ag(2)−N(5) = 2.232(2) Å; N(5)−Ag(2)−N(4) = 139.62(8)°) and one 1,3,4-oxadiazole (Ag(2)−N(3) = 2.470(2) Å; N(3)−Ag(2)−N(5) = 105.40(8), N(3)−Ag(2)−N(4) = 113.18(7)°) groups. The $\mathrm{Ag{-}N_{oxadiazole}}$ bond length is considerably longer than those of the $\mathrm{Ag{-}N_{pyridyl}}$ 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.[11] In the solid state, compound **1** adopts an unique 1-D undulating chain pattern, as shown in Figure 3a, which consists of two different individual "links". The large one comprises a tetrameric unit, in which four Ag(I) centers are linked together by L2 ligands through both pyridyl and oxadiazole N-donors into an elliptical 40-membered macrocycle. The approximate (crystallographic) dimensions of the rings are 22 × 11 Å. The large macrocyclic rings are further connected to small "links" consisting of a 14-membered dimeric unit. The effective cross section is 4 × 7 Å. Two uncoordinated $SO_3CF_3^-$ counterions are located above and below the large ring planes. 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 3. All the one-dimensional macrocycle-containing chains extend parallel along the crystallographic [011] direction and form an undulating layer (Figure 3b). These layers further stack together along the crystallographic $[0\bar{1}1]$ direction to generate a porous network (Figure 3c). The interlayer and intralayer Ag···Ag contacts are 4.657(3) and 4.278(3) Å, respectively, which is longer than the sum of the van der Waals radii of two silver atoms, 3.44 Å.

Structural Analysis of $\{[Ag(L2)](ClO_4)(CH_3OH)_{0.5}(H_2O)_{0.5}\}_n$ (2). Crystallization of L2 with $AgClO_4$ in a H_2O/CH_3OH mixed-solvent system at room temperature afforded the infinite one-dimensional polymeric compound **2** in 87% yield. The metal-to-ligand ratio is 1:2 in the reaction. Crystals of **2** retain their structural integrity at room temperature for a considerable length of time, and the guest molecules are liberated very slowly at room temperature. As shown in Figure 4, the coordination spheres around the two types of silver atoms are both linear (N(8)−Ag(1)−N(1) = 174.22(10), N(4)−Ag(2)−N(5)#1 = 174.76(11)°; Table 4) and consist of two pyridyl N-donors from two L2 ligands with slightly different Ag−N bond lengths (Ag(1)−N(8) = 2.161(3), Ag(2)−N(1) = 2.164(3), Ag(2)−N(4) = 2.161(3), Ag(2)−N(5) = 2.154(3) Å). It is different from **1**, in that the oxadiazole N-donors on L2 do not coordinate to a silver atom. No coordinated ClO_4^- counterions are found in **2**. It

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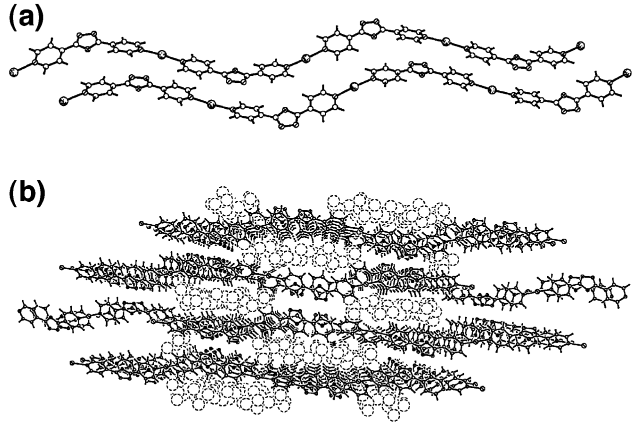

Figure 5. (a) Two one-dimensional chains stacked together by a $\pi-\pi$ interaction. (b) Crystal packing of **2** (2-D $\pi-\pi$ sheets, down *a* axis). Perchlorates and solvent guest molecules are located between layers (ClO_4^- and solvent molecules are shown as dotted circles).

is interesting to note that the two L2 ligands around the Ag(2) center are crystallographic different. In one L2 ligand the two terminal pyridyl groups and one 1,3,4-oxadiazole bridge are coplanar, while in the second L2 ligand only one pyridyl group and the 1,3,4-oxadiazole bridge lie in the same plane, while the other pyridyl group does not. Two planes are slightly tilted relative to each other at a dihedral angle of about 15°. These one-dimensional zigzag chains stack in a face-to-face fashion and interact via weak noncovalent $\pi-\pi$ interactions[12] ($d_{\pi-\pi} = 3.50$ Å) along the crystallographic *a* axis (perpendicular to the chain direction; see Figure 5a). Even such weak $\pi-\pi$ interactions, however, serve as important driving forces to cross-link the one-dimensional chains into a two-dimensional network with infinite elliptical channels along the crystallographic *a* axis. The uncoordinated ClO_4^- and guest solvent molecules are located inside (Figure 5b). The interchain and intrachain Ag···Ag distances are 13.98(4) and 5.66(5) Å, respectively. A few examples have shown that the organic ligands involved (presumably) in the nucleation process use both coordination and $\pi-\pi$ interactions to construct the framework.[13] In compound **2**, the L2 organic spacers do play a critical role in the formation of a $\pi-\pi$ stacking system and, moreover, serve as the agent that allows the $\pi-\pi$ interactions to expand the dimensionality of **2** from one to two.

Structural Analysis of $\{[Ag(L2)]NO_3\}_n$ (3). To investigate the effect of the counterion on the long-range order of the Ag(I)−L2 coordination polymer, the more strongly coordinating NO_3^- anion was used instead of the weakly coordinating ClO_4^- anion. When a solution of L2 in the polar solvent MeOH was treated with $AgNO_3$ in H_2O in a molar ratio of 1:2 (metal-to-ligand), the polymeric compound **3**, displaying a H-bonded double chain structural motif, was obtained in 83% yield. Crystals of **3** are not stable in air and turn opaque within minutes under ambient atmosphere. This is different from what was observed for compounds **1** and **2**, and in addition, there is only one kind of Ag(I) center in **3**. An ORTEP drawing of **3** with the atom numbering scheme is shown in Figure 6. The Ag(I) center lies in a trigonal coordination environment consisting of two $N_{pyridyl}$ donors (Ag−N(4) = 2.211(2), Ag−N(1) = 2.245(2) Å; N(4)−Ag−N(1) = 140.38(9)°; Table 5) from two L2 ligands and one O-donor (Ag−O(11) = 2.472(2) Å) from the unidentate coordinated NO_3^- counterion.

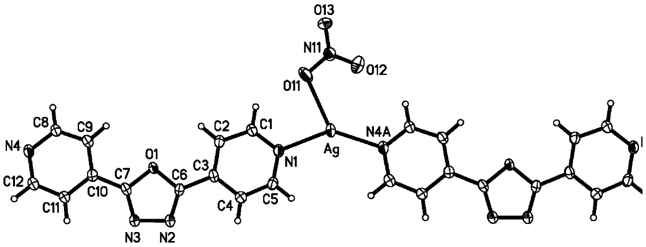

Figure 6. ORTEP figure of **3** with 50% probability ellipsoids.

Table 5. Interatomic Distances (Å) and Bond Angles (deg) with Esds in Parentheses for **3**[a]

Ag−N(4)$^{\#1}$	2.211(2)	Ag−N(1)	2.245(2)
Ag−O(11)	2.472(2)	Ag···Ag$^{\#2}$	3.5516(2)
N(4)$^{\#1}$−Ag−N(1)	140.38(9)	N(4)$^{\#1}$−Ag−O(11)	130.15(8)
N(1)−Ag−O(11)	87.48(8)	C(1)−N(1)−Ag	121.04(18)
C(7)−O(1)−C(6)	102.1(2)	O(1)−C(6)−C(3)	118.4(2)

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

In the solid state (Figure 7), the Ag(I) centers are connected by L2 ligands through the pyridyl nitrogen atoms into a one-dimensional zigzag chain. The intrapolymer Ag···Ag distance is 14.18(6) Å while the shortest interpolymer Ag···Ag distance is only 3.55(6) Å. The interpolymer Ag···Ag separation herein is slightly longer than the sum of the van der Waals radii of two silver atoms, 3.44 Å.[14] In addition, hydrogen-bonding interactions are present in **3**. The one-dimensional polymer chain of **3** is linked into a double chain via interpolymer hydrogen-bonding interactions. The hydrogen-bonding system involves O(13) of the coordinated nitrate counterion and H(9) and H(2) on the L2 ligand of the neighboring chain (Figure 7). The O(13)···H(9) and O(13)···H(2) contact is 2.396(5) and 2.347(5) Å, respectively. The C(9)···O(13) and C(2)···O(13) distances are 3.319(6) and 3.25 Å, respectively. The corresponding O(13)···H(9)−C(9) and O(13)···H(2)−C(2) angles are 163.85(5) and 158.76°, respectively. These hydrogen-bonding interactions in **3** give rise to a novel H-bonded one-dimensional double chain motif (Figure 7), demonstrating that, in comparison with **2**, the NO_3^- anion does have a profound effect upon the resultant network geometry.

The existence and structural importance of weak C−H···X hydrogen-bonding interactions are now well established,[15] and they are observed in many compounds, such as the N···H−C interaction in 1,3,5-tricyanobenzene−hexamethylbenzene,[16] the O···H−C interaction in $(C_{14}H_{12}N_2)[Cu(opba)]\cdot$

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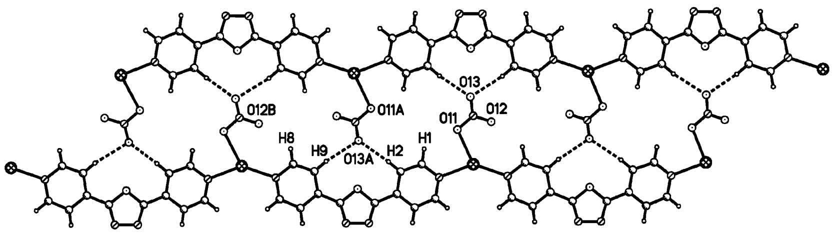

Figure 7. One-dimensional chains in **3** H-bonded together a by C−H···O bonding interaction.

$3H_2O$ and $Na_2(C_{12}H_{12}N_2)[Cu(opba)]_2{\cdot}4H_2O$ (opba = *o*-phenylenebis(oxamate)),[17] and the F···H−C interaction in 11-(trifluoromethyl)-15,16-dihydrocyclopenta[α]phenanthren-17-one.[18] These hydrogen bonds, although weak, contribute significantly to the alignment of the molecules of **3** in the crystalline state.

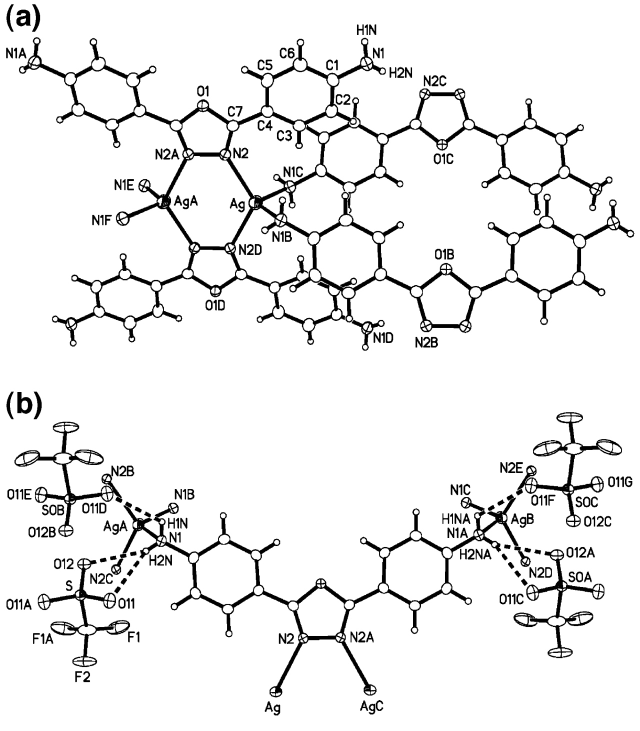

Figure 8. (a) ORTEP figure of **4** with 50% probability ellipsoids. $SO_3CF_3^-$ counterions are omitted for clarity. (b) H-bonding systems in **4**. Hydrogen bonds are shown as the dotted lines.

Table 6. Interatomic Distances (Å) and Bond Angles (deg) with Esds in Parentheses for **4**[a]

Ag−N(2)	2.293(3)	Ag−N(1)$^{\#2}$	2.470(4)
Ag···Ag$^{\#4}$	3.5863(9)		
N(2)−Ag−N(2)$^{\#1}$	123.47(14)	N(2)−Ag−N(1)$^{\#2}$	96.05(11)
N(2)$^{\#1}$−Ag−N(1)$^{\#2}$	109.88(12)	N(1)$^{\#2}$−Ag−N(1)$^{\#3}$	123.89(18)
N(2)$^{\#5}$−N(2)−Ag	118.26(7)	C(7)−N(2)−Ag	135.0(2)
N(2)−C(7)−C(4)	131.6(3)	C(6)−C(1)−N(1)	119.0(3)
C(7)−O(1)−C(7)$^{\#5}$	104.2(4)		

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

Structural Analysis of {[Ag(L3)]SO$_3$CF$_3$}$_n$ (4). The idea behind the use of ligand L3 is to control supramolecular architectures through an NH_2−metal coordination and also through hydrogen-bonding interactions.[19,20] It is well-known that the amino group attached to an aromatic ring is a good candidate for H-bonding.[21] When a solution of L3 in methylene chloride was treated with $AgSO_3CF_3$ in methanol in a molar ratio of 1:2 (metal-to-ligand), compound **4** was obtained as brown crystals in 92% yield. Compound **4** is air stable and formed with a high symmetry in the unusual orthorhombic space group *Pnnm*. As shown in Figure 8, the mirror plane bisects the structure through O(1). The Ag(I) center is located in a distorted tetrahedral coordination sphere which consists of two $N_{\text{oxadiazole}}$ (Ag−N(2) = 2.293(3) Å; N(2)−Ag−N(2) = 123.47(14)°; Table 6) and two N_{amino} donors (Ag−N(1) = 2.470(4) Å; N(1)−Ag−N(1) = 123.89(18)°). Two Ag(I) centers are bridged by four $N_{\text{oxadiazole}}$ atoms into a dinuclear core with a short Ag···Ag contact (=3.5863(4) Å), which is almost identical to the Ag···Ag separation found in **3**. The triflate counterions are not involved in the Ag(I) coordination sphere but are hydrogen bonded to $-NH_2$ groups through strong N−H···O hydrogen bonds (Figure 8b). The corresponding H-bonding data are listed in Table 7. In **4**, all the four N-donors (two N_{amino} and two $N_{\text{oxadiazole}}$) are fully utilized to bind Ag(I) metal ions into a polymeric structure, which is quite different from the coordination behavior of 5,5′-diamino-2,2′-bipyridine. The amino groups on 5,5′-diamino-2,2′-bipyridine were not involved in metal coordination even for the “soft” metal Ag(I).[21] In the solid state, compound **4** exhibits a novel noninterpenetrating three-dimensional network with big rhombic channels along the crystallographic [010] direction (effective cross section of ca. 14.5 × 9.6 Å), in which the uncoordinated $SO_3CF_3^-$ counterions are located. It is well-known that the combination of tetrahedral Ag(I) or Cu(I) centers with rigid linear bidentate ligands generally result in the adamantoid structure.[1b] In **4**, however, the specific geometry of the ligand L3 and also the coordination of the $N_{\text{oxadiazole}}$ donors result in the formation of this unique three-dimensional network (Figure 9) instead of the adamantoid framework.

So far, several N-heterocyclic ring-bridged organic ligands, such as 3,6-bis(4-pyridyl)-1,2,4,5-tetrazine and 3,6-bis(3-pyridyl)-1,2,4,5-tetrazine as well as some other related organic ligands,[1b] were used to construct Ag-containing

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Table 7. Hydrogen Bonds for **4** (Å and deg)[a]

D−H···A	d(D−H)	d(H···A)	D(D···A)	<(DHA)
N(1)−H(1N)···O(11)#8	0.79(5)	2.60(5)	3.098(5)	122(4)
N(1)−H(2N)···O(12)	0.73(5)	2.44(5)	3.073(4)	146(5)
N(1)−H(2N)···O(11)	0.73(5)	2.61(5)	3.294(5)	156(5)
N(1)−H(2N)···S	0.73(5)	2.98(5)	3.702(4)	173(5)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x$, $-y$, z; #2, $-x + 1/2$, $y - 1/2$, $-z + 1/2$; #3, $x - 1/2$, $-y + 1/2$, $-z + 1/2$; #4, $-x$, $-y$, $-z + 1$; #5, x, y, $-z + 1$; #6, $-x + 1/2$, $y + 1/2$, $-z + 1/2$; #7, x, y, $-z$; #8, $-x$, $-y + 1$, z.

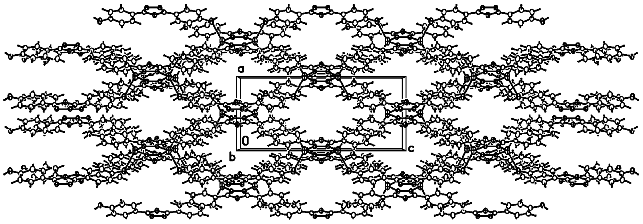

Figure 9. View of noninterpenetrating 3-D network of **4** (down *c* axis). The $SO_3CF_3^-$ ions are omitted for clarity.

coordination polymers; N-heterocycle donors, however, were never involved in the metal coordination, which is probably due to steric effects.

Conclusions

This study demonstrates that the oxadiazole-containing rigid organic ligands 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (L2) and 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (L3) are capable of coordinating metal centers with both $N_{pyridyl}$ and $N_{oxadiazole}$ donors, and generate novel coordination polymers. Four new coordination polymers **1**−**4** were synthesized from solution reactions of L2 and L3 with Ag(I) salts. The relative orientation of the nitrogen donors on the pyridyl rings and the five-membered oxadiazole spacing in L2 and 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 ligands will result in a variety of new coordination polymers with novel polymeric patterns.

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

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