Bi(furan)- and Bi(thiophene)-Type Linking Ligands and Their Silver Coordination Polymers: $[Ag_2L^1(NO_3)_2]_n$ and $[Ag_2L^2(NO_3)_2(H_2O)]_n$ ($L^1 = 1,2$ -Bis(furan-3-ylmethylene)hydrazine; $L^2 = 1,2$ -Bis(thiophen-3-ylmethylene)hydrazine)

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The design and synthesis of infinite coordination polymers (or metal-organic frameworks), which are formed by coordinative covalent bonds, are currently under intensive study due to their useful properties applicable to catalysis, chirality, conductivity, luminescence, magnetism, adsorption, and gas storage. Laborate (or organic spacers) in preparing these polymers. Over the past years, many silver coordination polymers have been constructed with the use of secondary interactions such as van der Walls contacts, H-bonding, and π - π stacking. The number of such coordination polymers tends to increase steadily in the literature these days. Laborate (13-24)

Coordination polymers based on *O*- or *S*-heterocyclic linking ligands are quite rare. We recently reported a couple of such linking ligands (\mathbf{L}^2 - \mathbf{L}^4 in Chart 1) and their silver coordination polymers: $\{[Ag\mathbf{L}^2_2](\mathbf{X})\}_n$ ($\mathbf{X} = ClO_4$, SbF_6 , PF_6), 25 $[Ag\mathbf{L}^4_{0.5}(NO_3)]_n$, 26 $\{[Ag\mathbf{L}^4_2](ClO_4)\}_n$, 26 $\{[Ag_2\mathbf{L}^3_3](\mathbf{X})\}_n$ ($\mathbf{X} = PF_6$, ClO_4), 27 $[Ag_2\mathbf{L}^3(NO_3)_2]_n$, and $\{[Ag_2\mathbf{L}^3_2](BF_4)_2\}_n$. As a continuation of our research, we decided to prepare another bi(furan)-type linking ligand, 1,2-bis(furan-3-ylmethylene)hydrazine (\mathbf{L}^1). Ligands \mathbf{L}^1 and \mathbf{L}^3 are isomers due to the different oxygen positions in the terminal furan rings (3,3'-versus 2,2'-positions). Moreover, ligand \mathbf{L}^1 is an oxygen analog of \mathbf{L}^2 ; that is, \mathbf{L}^1 is a hard-donor (oxygen) linking ligand and \mathbf{L}^2 is a soft-donor (sulfur) linking ligand.

In this study, we tried to prepare silver coordination polymers from $AgNO_3$ and ligands \mathbf{L}^1 and \mathbf{L}^2 , with an emphasis to investigate the variation in topology of the resulting compounds with different heterocyclic rings. We report herein the preparation and structures of ligand \mathbf{L}^1 and two 2-D silver coordination polymers, $[Ag_2\mathbf{L}^1(NO_3)_2]_n$ (1) and $[Ag_2\mathbf{L}^2(NO_3)_2(H_2O)]_n$ (2).

Chart 1

Experimental Section

All solid chemicals were purified by recrystallization, and all solvents were distilled and stored over molecular sieves. Ligands \mathbf{L}^2 (1,2-bis(thiophen-3-ylmethylene)hydrazine) was prepared by the literature methods. MR spectra were recorded with a Varian Mercury 300 MHz spectrometer. IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer. Elemental analyses were performed with EA1110 (CE instrument, Italy) at the Korea Basic Science Institute.

Preparation of 1,2-bis(furan-3-ylmethylene)hydrazine (L^1). At room temperature, hydrazine (35 wt% in H_2O , 0.92 mL, 10 mmol) was added to 3-furan carboxaldehyde (2.03 g, 21 mmol) in ethanol (30 mL). After adding dichloromethane (20 mL) and subsequently two drops of formic acid, the mixture was stirred for 4 h and then filtered. The resulting colorless solid was washed with ethanol (5 mL × 3) and diethyl ether (20 mL × 3), and then crystallized from CH_2Cl_2 -hexane to give ligand L^1 (1.56 g, 8.21 mmol, 82%). ¹H-NMR (CDCl₃): δ 8.57 (2H, s), 7.81 (2H, s), 7.48 (2H, s, furan), 6.87 (2H, d, J = 1.2 Hz, N=CH). ¹³C{¹H}-NMR (CDCl₃): δ 154.0, 146.4, 144.6, 123.0 (furan), 108.0 (N=CH), Anal. Calc. for $C_{10}H_8N_2O_2$ (Mr = 188.18): C, 63.82; H, 4.28; N, 14.89. Found: C, 63.44; H, 4.79; N, 14.24. mp: 146-148 °C. IR (KBr, cm⁻¹): 3119 (m), 1638 (s), 1503 (w), 1309 (w), 1147 (s), 1071 (m), 1009 (m), 964 (m), 867 (m), 845 (m).

Preparation of [Ag2L¹(NO₃)₂]_n (1). A dichloromethane solution (3 mL) of L¹ (30.0 mg, 0.158 mmol) was allowed to diffuse slowly into a methanol solution (4 mL) of AgNO₃ (53.0 mg, 0.312 mmol). Colorless crystals of polymer 1 formed in 5 days (35 mg, 0.066 mmol, 42%). Anal. Calcd for C₁₀H₈N₄O₈Ag₂ ($M_r = 529.94$): C, 22.66; H, 1.52; N, 10.57. Found: C, 22.27; H, 1.70; N, 10.02. IR (KBr, cm⁻¹): 1636 (s), 1381 (s), 1149 (m), 1006 (m), 802 (m), 741 (m).

Preparation of [$Ag_2L^2(NO_3)_2(H_2O)$]_n (2). Polymer 2 was prepared in the same way as polymer 1. Yield: 40%. Anal. Calcd for $C_{10}H_{10}N_4O_7S_2Ag_2$ ($M_r = 578.08$): C, 20.78; H, 1.73; N, 9.69. Found: C, 20.28; H, 2.21; N, 9.65. IR (KBr, cm⁻¹): 3421(br), 1621 (s), 1379 (s), 1265 (m), 1084 (m), 1023 (m), 808 (m).

X-ray structure determination. X-ray data were collected with a Siemens P4 diffractometer (L^1) or a Bruker Smart

Table 1. X-ray Data Collection and Structure Refinement Details

	\mathbf{L}^{1}	1	2
formula	$C_{10}H_8N_2O_2\\$	$C_{10}H_8Ag_2N_4C$	$O_8C_{10}H_{10}Ag_2N_4O_7S_2$
fw	188.18	527.94	578.08
temp, K	293(2)	296(2)	296(2)
crystal size	0.38×0.24	$0.26 \times 0.20 >$	$<0.30\times0.18\times0.08$
	$\times 0.04$	0.10	
color	colorless	colorless	colorless
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_{1}/c$	P–1	C2
a, Å	19.917(3)	8.1398(3)	24.7476(7)
b, Å	4.832(1)	9.7820(4)	5.1251(2)
c, Å	9.891(2)	9.7979(3)	16.2180(5)
α , deg		79.233(2)	
β , deg	103.89(2)	66.282(1)	128.484(1)
γ , deg		79.772(2)	
V , $Å^3$	924.1(3)	697.11(4)	1610.18(9)
Z	4	2	4
$D_{ m calcd}$, g cm $^{-3}$	1.353	2.515	2.385
μ , mm ⁻¹	0.097	2.863	2.735
F(000)	392	508	1120
$T_{ m min}$		0.5232	0.4941
T_{\max}		0.7628	0.8109
no. of reflns measured	1728	21330	12305
no. of reflns unique	1619	3443	3755
no. of reflns with $I >$	862	2973	3547
$2\sigma(I)$			
no. of params refined	159	218	222
max. in $\Delta \rho$ (e Å ⁻³)	0.152	1.685	2.194
min. in $\Delta \rho$ (e Å ⁻³)	-0.200	-1.375	-1.410
GOF on F^2	0.965	1.107	1.066
$R1^a$	0.0518	0.0617	0.0390
$wR2^b$	0.1085	0.1842	0.1052

 ${}^{a}R1 = \Sigma ||F_{o}| - |F||/\Sigma |F_{o}|. {}^{b}wR2 = \Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}]/\Sigma [w(F_{o}^{2})^{2}]^{1/2}$

APEX2 diffractometer (1 and 2) equipped with a Mo X-ray tube. ³¹ No absorption corrections were made for the ligand (L¹), but empirical absorption corrections were made for polymers 1 and 2 with SADABS. ²⁹ All calculations were carried out with SHELXTL programs. ³⁰ Details on crystal data, intensity collection, and refinement details are given in Table 1.

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center: 651008 (L¹), 651011 (1), 651012 (2). Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Results and Discussion

Preparation and crystal structure of ligand (L^1). A bi(furan)-type ligand linking (L^1), which contains oxygendonor atoms at the 3,3'-positions in two terminal furan rings, was prepared from hydrazine and 3-furalaldehyde by Schiffbase condensation (eq. 1). The sulfur analog L^2 was previously prepared by the same method.²⁵ Both ligands have

four possible coordination sites: two imine nitrogen atoms and two oxygen (L¹) or sulfur (L²) atoms of 5-membered heterocyclic rings. Ligand L¹ was fully characterized by spectroscopy (NMR and IR), elemental analysis, and X-ray diffraction. The ¹H-NMR spectrum of ligand L¹ display characteristic resonances at 8.57, 7.81, 7.48 (furan ring), and 6.87 ppm (N=CH). In addition, its IR spectrum display a strong absorption band at 1638 cm⁻¹ assignable to the C=N bond, consistent with the fact that C=N stretches of Schiff bases appear in the range 1603-1680 cm⁻¹. ³¹-³³

$$H_2N-NH_2 + 2 \longrightarrow O \longrightarrow N \longrightarrow N \longrightarrow O$$
 (1)

The molecular structure of \mathbf{L}^1 with the atom-numbering scheme is shown in Figure 1. There are two independent asymmetric units, each of which consists of only half the chemical formula with the other half related by crystallographic inversion. The O···O separations between two terminal furan rings are 10.459(5) (O1···O1A) and 10.767(3) (O2···O2A) Å, which are somewhat shorter than the S···S separation (11.074(2) Å) in ligand \mathbf{L}^2 containing terminal thiophene rings, as expected.²⁵

Preparation of coordination polymers. 2-D silver coordination polymers, $[Ag_2L^1(NO_3)_2]_n$ (1) and $[Ag_2L^2(NO_3)_2-(H_2O)]_n$ (2), were prepared by layer diffusion, in which a dichloromethane solution containing a ligand was layered onto the top of a methanol solution containing AgNO₃. All products were characterized by elemental analysis, IR spectroscopy, and X-ray diffraction. IR spectra display the C=N stretch at 1636 (1) or 1621 cm⁻¹ (2).

Very recently, our group reported the preparation and structures of ligand L^2 and its silver coordination polymers by employing silver salts (AgX; $X = ClO_4^-$, SbF₆⁻, PF₆⁻). These polymers turned out to be constructed by van der Waals contacts, and their structures depended on the nature of conterions in the starting compound AgX. However, in our previous study, we were not able to obtain the silver- L^2 coordination polymer possessing the NO₃⁻ ligand. We could

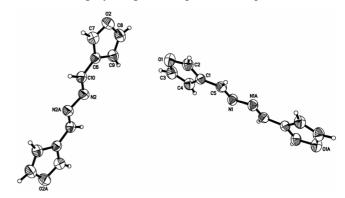


Figure 1. ORTEP drawing of compound L^1 with 50% probability thermal ellipsoids. Selected bond lengths (Å) and bond angles (°): N1–C5 1.283(3), N2–C10 1.278(3), N1–N1#1 1.417(4), N2–N2#1 1.422(4), C2–O1–C3 104.9(3), C7–O2–C8 105.0(3). Symmetry transformations used to generate equivalent atoms: #1 = -x, -y + 3, -z.

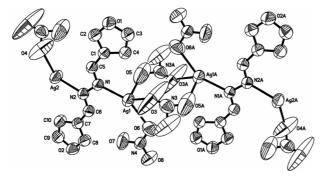


Figure 2. Monomer unit of polymer **1**. Selected bond lengths (Å) and bond angles (°): Ag1–N1 2.267(5), Ag1–O6 2.418(7), Ag1–O5 2.439(17), Ag2–N2 2.275(5), N1–Ag1–O6 151.2(2), N1–Ag1–O5 87.2(3), O6–Ag1–O5 107.5(3), N1–Ag1–O3 126.7(3), O6–Ag1–O3 75.9(3).

successfully prepare the L^2 -AgNO₃ coordination polymer (the missing member). Unfortunately, however, reactions of ligand L^1 and other silver salts did not produce X-ray-quality crystals.

We previously reported the 2-D silver coordination polymers $[Ag_2L^3(NO_3)_2]_n^{26}$ and $[Ag_2L^4_{0.5}(NO_3)]_n^{27}$ in which the NO_3^- ions act as ligands. Despite the lack of photoluminescence of ligands L^3 and L^4 , their silver coordination polymers exhibited blue-green or green photoluminescence in the solid state at room temperature. In this context, polymers 1 and 2 in this study were initially expected to be photoluminescent, but they do not exhibit photoluminescence.

Structures of coordination polymers. A monomer unit of polymer **1** is given in Figure 2, which shows an asymmetric unit consisting of two Ag metals, one L^1 , and two NO_3^- ligands. Two oxygen atoms of terminal furan rings do not participate in any bonding. van der Waals contacts make two Ag metals distinct, explaining the dimeric chemical formula $[Ag_2L^1(NO_3)_2]_n$. The Ag-N (2.267(5) and 2.275(5) Å) and Ag-O (NO_3^-) bond lengths (2.418(7)-2.590(10) Å) indicate normal covalent bonds. Besides the Ag1-N1, Ag1-O3, Ag1-O5, and Ag1-O6 bonds, the Ag1 metal is further bound to one oxygen atom (O7) *via* van der Waals contacts (Ag···O7 = 2.935(9) Å). On the other hand, the Ag2 metal is covalently bonded to the N2, O6#6, O4#4, O8, and O4 atoms, and it is further in van der Waals contacts with one oxygen atom (Ag···O3 = 3.08(2) Å). Considering these van

der Waals contacts, the Ag1 metal may be regarded as 5-coordinate and the Ag2 metal as 6-coordinate. For comparison, the van der Waals radii of Ag and O atoms are 1.72, and 1.50 Å, respectively. Figure 3 shows a packing diagram of polymer 1. The Ag₂L¹ units are connected by the NO₃¹ ligands along the *b*-axis and by the L¹ ligands in the [101] direction to form a 2-D network, in which two NO₃⁻ ions are distinct. One NO₃⁻ ion (N3, O3-O5) links three Ag metals *via* three Ag-O covalent bonds (Ag1-O3, Ag2-O4, Ag1-O5) and two Ag···O van der Waals contacts (Ag2#1···O3, Ag2#4··· O4). The other NO₃⁻ ion (N4, O6-O8) links one Ag metal *via* one Ag-O covalent bond (Ag1-O6) as well as three Ag···O van der Waals contacts (Ag2#2···O6, Ag1···O7, Ag2···O8).

Figure 4 shows the local coordination environment of silver metals in polymer **2**, whose asymmetric unit comprises two Ag metals, one **L**², two NO₃⁻ ligands, and one aqua ligand. Thiophene sulfur atoms are not covalently bonded to the silver metals, and only one sulfur atom (S1) participates in van der Waals contacts. Like polymer **1**, polymer **2** has two distinct Ag metals as well as two distinct NO₃⁻ ligands. In addition to the Ag1-N1, Ag1-O1, Ag1-O2, and Ag1-O4 normal bonds, the Ag1 metal is further connected to two

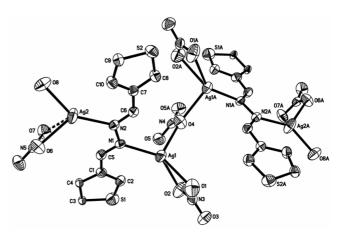


Figure 4. Monomer unit of polymer **2** showing van der Waals contacts (dashed lines). Selected bond lengths (Å) and bond angles (°): Ag1–N1 2.311(4), Ag1–O4 2.444(2), Ag1–O2 2.494(6), Ag1–O1 2.508(8), Ag2–N2 2.243(4), Ag2–O8 2.248(5), Ag2–O6 2.443(2), N1–Ag1–O4 105.6(1), N1–Ag1–O2 134.8(2), O4–Ag1–O2 100.1(2), N1–Ag1–O1 141.0(2), O4–Ag1–O1 111.5(2), N2–Ag2–O8 145.7(2), N2–Ag2–O6 123.5(1).

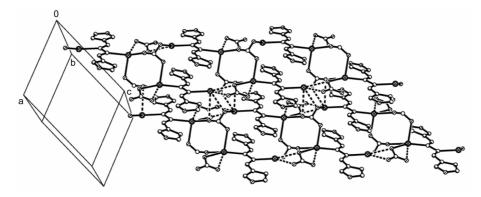


Figure 3. Packing diagram of polymer 1 showing van der Waals contacts.

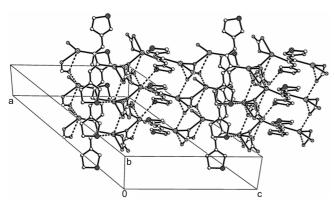


Figure 5. Packing diagram of polymer 2 showing van der Waals contacts

oxygens (O5 and O5#4) and one sulfur (S1) via van der Waals contacts (Ag ··· O = 2.826(6), 2.895(5) Å; Ag ··· S = 3.254(2) Å). On the other hand, the Ag2 metal is covalently bonded to the N2, O6, and O8 (aqua) atoms, and it is further in van der Waals contacts with two oxygen atoms (O7 and O7#1: Ag···O = 2.710(5) and 2.961(6) Å). Taking these van der Waals contacts into consideration, the Ag1 metal may be regarded as 7-coordinate and the Ag2 metal as 5-coordinate. All the L² ligands in polymer 2 adopt the cisoid conformation (L^{2}) in terms of relative orientation of two terminal thiophene rings. This conformation can account for the shortening of the S···S separation (10.802(3) Å) in polymer 2, compared with that (11.074(2) Å) in the free ligand L^2 in the transoid conformation.²⁵ The transoid conformer can be transformed to the cisoid one via the rotation about the C-C bond, and vice versa. The Ag₂L² units in polymer 2 are connected by the NO₃⁻ ligands along the b-axis and by the L^2 ligands along [101] direction to form a 2-D network (Figure 5). The packing pattern in polymer 2 essentially differ from that (a chain of half cubanes) in $[AgL_{0.5}^4(NO_3)]_n$ presumably due to the difference in the sulfur positions in both ligands (3,3'-versus 2,2'-positions).²⁶

$$S \longrightarrow S \longrightarrow S \longrightarrow S$$

$$L^2 \text{ (transoid)} \qquad \qquad L^2 \text{ (cisoid)}$$

In summary, a novel bi(furan)-type linking ligand (L¹), 1,2-bis(furan-3-ylmethylene)hydrazine, which contains oxygen-donor atoms in the terminal rings, was prepared. Treating ligand L¹ with AgNO₃ produced a 2-D network [Ag₂L¹(NO₃)₂]_n (1). Another 2-D network [Ag₂L²(NO₃)₂-(H₂O)]_n (2) could be prepared from AgNO₃ and ligand L², a sulfur analog of ligand L¹. Two polymers have been constructed by van der Waals contacts as well as covalent bonds. Whereas furan oxygens in polymer 1 do not participate in van der Waals contacts, thiophene sulfurs in polymer 2 do, which results in distinct networks of both polymers.

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