

Crystal Structures and Physical Properties of Ag(I) Coordination Polymers with Unsymmetrical Dipyriddy Ligand

Eunji Lee, Hyunsoo Ryu, Suk-Hee Moon,[†] and Ki-Min Park^{*}

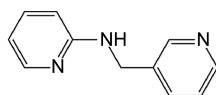
Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, Korea
^{*}E-mail: kmpark@gnu.ac.kr

[†]Department of Food and Nutrition, Kyungnam College of Information and Technology, Busan 617-701, Korea
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During last two decades, silver coordination polymers based on dipyriddy type ligands have attracted particular interest because of the various intriguing architectures caused by a variety of coordination geometry of Ag(I) ion as well as their potential applications as functional materials.¹⁻⁶ In the development of Ag(I) coordination polymers with fascinating structures, especially, numerous symmetrical dipyriddy ligands with nitrogen donor atoms in the same position of two terminal pyridines are employed due to their easy synthesis.^{1c,2,3} However, despite the rapid growth in the Ag(I) coordination chemistry based on the symmetrical dipyriddy ligands, the investigation using unsymmetrical dipyriddy ligands with nitrogen donor atoms in the different position of two terminal pyridines still remains lacking. Recently, Kitagawa⁴ and Gao⁵ groups reported helical Ag(I) coordination polymers involving unsymmetrical dipyriddy ligands.

In extending our prior studies^{3,6} on Ag(I) coordination polymers based on bridging dipyriddy ligands, *N*-(pyridine-3-ylmethyl)pyridine-2-amine (**L**) as a flexible unsymmetrical dipyriddy ligand was prepared by the reaction of 2-aminopyridine and 3-pyridinecarboxaldehyde according to the previously reported method.⁷ Herein we report crystal structure and physical properties of three Ag(I) coordination polymers with unsymmetrical ligand **L**.



N-(pyridin-3-ylmethyl)pyridin-2-amine (**L**)

The reaction of silver salts (ClO_4^- , BF_4^- , and PF_6^-) with **L** in methanol yielded colorless precipitates. Vapor diffusion of diethyl ether into the DMSO solution of a respective precipitate gave crystalline products **1**, **2**, and **3**, respectively. Crystallographic data for all **1-3** are presented in Table 1, respectively. A total of three $\{[\text{Ag}(\text{L})]\cdot(\text{X})\cdot(\text{DMSO})\}_n$ ($\text{X} = \text{ClO}_4$ (**1**), BF_4 (**2**), and PF_6 (**3**)) crystallize in monoclinic space group $P2_1/n$ and keep the same topological structure. Therefore, compound **1** is described in detail as a representative structure.

The X-ray crystal structure of **1** is shown in Figure 1, with

selected geometric parameters presented in Table 2. The asymmetric unit of **1** consists of one Ag(I) ion, one **L** ligand, one perchlorate anion, and one DMSO molecule. The silver(I) atom is linked to two pyridine nitrogens from two different **L** ligands in a nearly linear coordination [$\text{Ag-N } 2.156(6)$ and $2.148(5)$ Å; $\text{N-Ag-N } 171.1(2)^\circ$] to form 1-D zigzag chain, consisting of alternating Ag(I) and **L** (Figure 1(a) and 1(b)). In the chain, the nearest $\text{Ag}\cdots\text{Ag}$ distance is 9.604(1) Å.

It is noteworthy that adjacent 1-D chains are connected to each other in a parallel fashion through the $\text{Ag}\cdots\text{Ag}$ interactions to form a honeycomb type 2-D open framework as shown in Figure 1(b). The $\text{Ag}\cdots\text{Ag}$ separation between adjacent zigzag chains is 3.1084(15) Å, which is shorter than the sum of van der Waals radii for silver (3.44 Å), and is rather close to Ag-Ag distance in silver metal (2.89 Å).⁸ Such a fact indicates that the argentophilic interactions lead

Table 1. Crystallographic data and structure refinement for **1**, **2**, and **3**

Identification code	1	2	3
Empirical formula	$\text{C}_{13}\text{H}_{17}\text{AgClN}_3$	$\text{C}_{13}\text{H}_{17}\text{AgBF}_4$	$\text{C}_{13}\text{H}_{17}\text{AgF}_6\text{N}_3$
	O_5S	N_3OS	OPS
Formula weight	470.68	458.04	516.20
Temperature (K)	298(2)	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
<i>a</i> (Å)	8.7565(12)	8.7419(8)	9.1009(10)
<i>b</i> (Å)	12.9289(17)	12.8229(13)	13.2298(15)
<i>c</i> (Å)	15.402(2)	15.1970(14)	15.6584(8)
<i>B</i> (deg)	99.827(3)	99.536(2)	98.642(2)
Volume (Å ³)	1718.1(4)	1680.0(3)	1863.9(4)
<i>Z</i>	4	4	4
<i>D</i> _{calc} (g/cm ³)	1.820	1.811	1.839
μ (mm ⁻¹)	1.479	1.370	1.344
2 θ _{max} (deg)	25.99	26.00	26.00
Reflections collected	9668	9399	10387
Independent reflections	3372	3290	3667
Goodness-of-fit on <i>F</i> ²	1.034	1.007	1.045
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0517, 0.1252	0.0504, 0.1145	0.0487, 0.1317
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1425, 0.1656	0.1141, 0.1491	0.0859, 0.1586

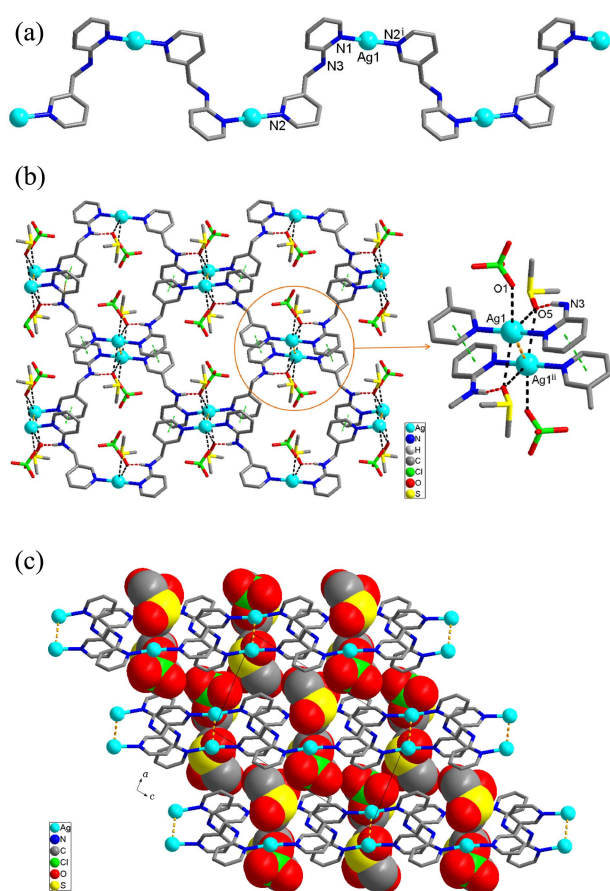


Figure 1. Honeycomb type 2-D network structure of **1**, $\{[\text{Ag}(\text{L})]\cdot(\text{ClO}_4)\cdot(\text{DMSO})\}_n$: (a) 1-D zigzag chain showing coordination environment, (b) 2-D framework showing several interactions represented by dashed lines: Ag \cdots Ag interactions (yellow), Ag \cdots O interactions (black), N-H \cdots O hydrogen bonds (red), and $\pi\cdots\pi$ stacking interactions (green), and (c) side view of packing arrangement of 2-D layers. H atoms and the disordered part of DMSO molecules are omitted. [Symmetry codes: (i) $0.5+x, 0.5-y, 0.5+z$; (ii) $-0.5+x, 0.5-y, -0.5+z$].

to formation of 2-D open framework are effective. Furthermore, $\pi\cdots\pi$ stacking interactions between N1- and N2-containing pyridyl rings are detected with the centroid-to-centroid distance being 3.76 Å and dihedral angle being $14.7(5)^\circ$,⁹ which further stabilize the 2-D layer. In the resulting 2-D honeycomb type structure, the unit hexagonal cavity with the positive charge consists of six Ag(I) ions and four L. The size of each cavity is *ca.* 9.5×11.8 Å.

As depicted in Figure 1(c), the 2-D sheets are propagated along the (101) plane and stacked parallel to one another with an interlayer separation of *ca.* 8.12 Å. Accordingly, the porous channels generated by the stacking of 2-D sheets are running along the *a*-axis.

As shown in Figure 1(b) and 1(c), each hexagonal cavity with positive charge is filled with two perchlorate anions and two DMSO molecules, which interact with the cavity framework *via* ionic interactions and N-H \cdots O hydrogen bonds. The perchlorate anions form weak interactions to the Ag(I) atoms through the oxygen atom (O1) in a *trans* fashion to the Ag \cdots Ag interactions with the distance being 3.019(9) Å,

Table 2. Selected bond lengths (Å) and bond angles ($^\circ$) for **1**, **2**, and **3**

	1	2	3
Ag1-N1	2.156(6)	2.148(5)	2.142(4)
Ag1-N2 ⁱ	2.161(6)	2.143(5)	2.132(4)
Ag1 \cdots Ag1 ⁱⁱ	3.1084(15)	3.0988(11)	3.0375(9)
Ag1 \cdots O1	3.019(9)	—	—
Ag1 \cdots F1	—	3.183(8)	3.056(6)
Ag1 \cdots O5	3.070(6)	3.129(5)	2.915(4)
Ag1 ⁱⁱ \cdots O5	3.070(6)	2.965(5)	3.388(5)
N1-Ag1-N2 ⁱ	171.1(2)	172.09(19)	167.66(18)
N1-Ag1-Ag1 ⁱⁱ	100.90(17)	101.86(14)	95.01(11)
N2 ⁱ -Ag1-Ag1 ⁱⁱ	86.62(17)	85.74(14)	91.33(11)

which are typical of ionic interactions in metal perchlorate.¹⁰ The oxygen atoms of the DMSO guest molecules also interact with the Ag(I) atoms (Ag1 \cdots O5 3.070(6) Å) to stabilize 2-D layer structure. Moreover, the N-H \cdots O hydrogen bonds between the guest species and L of framework and C-H \cdots O hydrogen bonds between the guest species are observed. The range of the hydrogen bond distances are from 2.963(1) to 3.63(3) Å (Table S2 in Supporting Information).

To understand the thermal behaviors, thermogravimetric analyses (TGA) of three coordination polymers **1-3** were carried out (Figure S3 in Supporting Information). TGA curve shows that **1** is stable up to 145 °C and undergoes a weight loss of 16.2% (calc: 16.6%) of the total weight in the range 145-165 °C, corresponding to the loss of one DMSO molecule. After a stable platform, compound **1** begins to decompose at about 250 °C. The thermal stability of **1** may originate not only from the electrostatic interactions between the cationic framework and the guest species but also the N(C)-H \cdots O hydrogen bonds mentioned above. TGA traces of compounds **2** and **3** in the solid states show similar thermal behaviors with that of **1** (Figure S3).

Solid-state photoluminescent properties of coordination

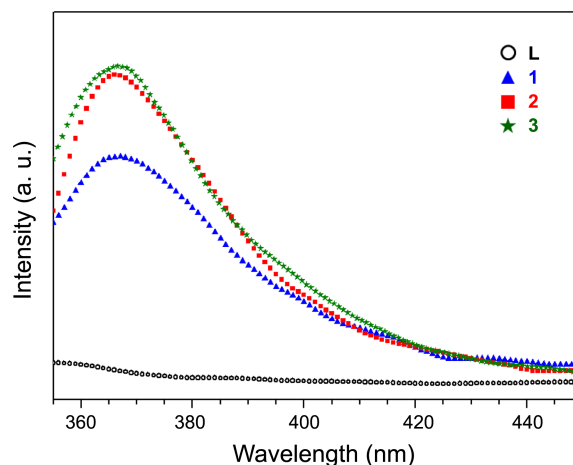


Figure 2. Solid-state emission spectra of coordination polymers **1-3** at room temperature with excitation wavelength being at 330 nm.

polymers **1-3** and the free ligand have also been studied at room temperature (Figure 2). The free ligand was found to be non-emissive. In contrast, the three coordination polymers exhibit blue luminescence with emission maxima at 367 nm for **1**, 366 nm for **2**, and 366 nm for **3** upon excitation at 330 nm, which can be assigned to the intraligand π - π^* transitions and metal-to-ligand charge transfer (MLCT).¹¹ Moreover, the emissions of the coordination polymers could be attributed to the increase of the rigidity of ligand and the π - π stacking interactions caused by the formation of the 2-D honeycomb type open framework.¹²

In summary, three Ag(I) coordination polymers with the formula $\{[\text{Ag}(\text{L})](\text{X})(\text{DMSO})\}_n$ ($\text{X} = \text{ClO}_4$ (**1**), BF_4 (**2**), and PF_6 (**3**), and $\text{L} =$ dipyridyl ligand) were prepared and characterized fully their structures. All three compounds are isostructures and stable 2-D honeycomb type coordination polymers, in which 1-D zigzag chains with $-(\text{Ag-L})-$ motif are linked by the argentophilic interactions and the π - π stacking interactions between pyridine rings. The investigation on photophysical properties of all compounds shows that the nature of emission can be attributed to the metal-to-ligand charge transfer as well as the formation of the polymeric structures with restriction of the flexibility of the free ligand. Based on the present solid state results, further investigation on the development and characterization of new coordination polymers using flexible unsymmetrical ligand is in progress.

Experimental

All chemicals were of analytical reagent grade and used without further purification. The IR spectra were recorded on a VERTEX 80v FT-IR spectrometer with KBr pellet in the range 4000-400 cm^{-1} . Elemental analysis was carried out on a CHNS-932 elemental analyzer. Thermogravimetric analysis (TGA) was performed under nitrogen on a SDT Q600 thermogravimetric analyzer. The sample was heated using a 10 $^\circ\text{C}/\text{min}$ heating rate from 25 to 900 $^\circ\text{C}$. The solid-state excitation and emission spectra were performed on a RF-5301 spectrophotometer.

Preparation of *N,N*-(2-Pyridyl)(2-pyridylmethyl)amine (L). L was synthesized according to literature procedure.⁷

Synthesis of $\{[\text{Ag}(\text{L})](\text{ClO}_4)(\text{DMSO})\}_n$ (1**).** A MeOH (5 mL) solution of AgNO_3 (43.0 mg, 0.254 mmol) was added dropwise to the MeOH solution (10 mL) of **L** (50.0 g, 0.231 mmol) at room temperature. The white precipitate in 94% yield formed immediately. The precipitate was filtered off, washed with methanol and diethyl ether, and dried in vacuo. Single crystals suitable for X-ray analysis were obtained by vapor diffusion of diethyl ether into DMSO solution. Yield: 63%. Anal. Calc. for $\text{C}_{13}\text{H}_{17}\text{AgClN}_3\text{O}_5\text{S}$ (%): C, 33.17; H, 3.64; N, 8.93. Found: C, 33.28; H, 3.73; N, 10.05. IR (KBr pellet, cm^{-1}): 3228, 3072, 3034, 2854, 1606, 1576, 1518, 1459, 1426, 1332, 1161, 1115, 1089 (ClO_4^-), 789, 716, 636, 628. mp 268-269 $^\circ\text{C}$ (decomp.).

Synthesis of $\{[\text{Ag}(\text{L})](\text{BF}_4)(\text{DMSO})\}_n$ (2**).** The synthetic procedure was almost the same as for **1** except for the use

of AgClO_4 instead of AgBF_4 . Yield: 57%. Anal. Calc. for $\text{C}_{13}\text{H}_{17}\text{AgBF}_4\text{N}_3\text{OS}$ (%): C, 34.09; H, 3.74; N, 9.17. Found: C, 34.15; H, 3.78; N, 9.24. IR (KBr pellet, cm^{-1}): 3228, 3072, 3033, 2874, 2584, 1606, 1576, 1519, 1458, 1426, 1332, 1161, 1039 (BF_4^-), 789, 716, 533, 522. mp 265-266 $^\circ\text{C}$ (decomp.).

Synthesis of $\{[\text{Ag}(\text{L})](\text{PF}_6)(\text{DMSO})\}_n$ (3**).** The synthetic procedure was almost the same as for **1** except for the use of AgClO_4 instead of AgPF_6 . Yield: 67%. Anal. Calc. for $\text{C}_{13}\text{H}_{17}\text{AgF}_6\text{N}_3\text{OPS}$ (%): C, 30.25; H, 3.32; N, 8.14. Found: C, 30.18; H, 3.48; N, 8.02. IR (KBr pellet, cm^{-1}): 3226, 3070, 3034, 2874, 1608, 1575, 1517, 1459, 1423, 1331, 1161, 1029, 835 (PF_6^-), 786, 716, 637, 558. mp 270-271 $^\circ\text{C}$ (decomp.).

X-ray Crystallography. Single crystal diffraction data of **1** and **2** were collected on a Bruker Smart diffractometer equipped with a graphite monochromated $\text{Mo } K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation source and a CCD detector. The 45 frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. A total of 1271 frames of two-dimensional diffraction images were collected, each of which was measured for 5 sec. Decay was monitored by 50 standard data frames measured at the beginning and end of data collection. The crystal showed no significant decay. The frame data were processed to give structure factors using the SAINT.¹³ The structure was solved by direct methods and refined by full matrix least squares methods on F^2 for all data using SHELXTL software.¹⁴ In all compounds, all atoms except oxygen atoms in DMSO molecule were disordered over two sites with equal site occupation factors of 0.5. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms except that of amine in all compounds were placed in calculated positions and refined with a riding model. The H atom of amine was located from difference Fourier map and refined with riding constraints. Crystallographic data and structural refinement data for compounds **1-3** is summarized in Table 1. Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-646600 (**1**), CCDC-946601 (**2**), and CCDC-946602 (**3**)). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk (or FIZ, D-76344, Eggenstein-Leopoldshafen, Germany, E-mail: crysdata@fiz-karlsruhe.de).

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Supporting Information. Supplementary crystal data, figures for **2** and **3**, and TGA of **1-3** are included. This material is available free of charge via the internet at <http://www.kcsnet.or.kr/bkcs>.

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