

# New Silver(I) Complexes of Pyridyl Dithioether Ligands with Ag–Ag Interactions: Effects of Anions and Ligand Spacers on the Framework Formations of Complexes

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Three new silver(I) complexes existing Ag–Ag interactions, a trinuclear cluster complex  $[\text{Ag}_3(\text{L}^1)_2(\text{NO}_3)_2](\text{NO}_3)$  **1**, a dinuclear complex  $[\text{Ag}_2(\text{L}^1)_2](\text{PF}_6)_2$  **2** and a one-dimensional chain complex  $[\text{Ag}_2\text{L}^2(\text{NO}_3)_2]_\infty$  **3**, where  $\text{L}^1$  and  $\text{L}^2$  are two structurally related pyridyl dithioether ligands, bis(2-pyridylthio)methane ( $\text{L}^1$ ) and 1,3-bis(2-pyridylthio)-propane ( $\text{L}^2$ ), have been synthesized and their structures were determined by single-crystal X-ray diffraction analysis. The striking structural differences of **1** and **2** suggest that counter anions have a profound effect upon the framework formations of silver complexes with pyridyl dithioether ligands, and the differences of **1** and **3** indicate that the subtle changes of the space groups have great influence on the coordination modes of the terminal pyridylsulfanyl groups and the geometries of  $\text{Ag}^{\text{I}}$  ion and therefore greatly influence the structures of their complexes. The weak  $\text{Ag}\cdots\text{O}$  interactions in the trinuclear complex **1** and the one-dimensional chain complex **3** extend them into quasi two-dimensional networks, and the  $\text{Ag}\cdots\text{S}$  weak interactions in the dinuclear complex **2** into one-dimensional chains, and such weak interactions further stabilized these complexes.

**KEY WORDS:** Ag–Ag interactions; crystal structure; flexible pyridyl dithioether ligands; silver(I) complexes.

## INTRODUCTION

The self-assembly of metal ions with multi-topic ligands continues to be a theme of considerable current interest in the context of developing new solid-state polymeric materials with specific architectures and functions

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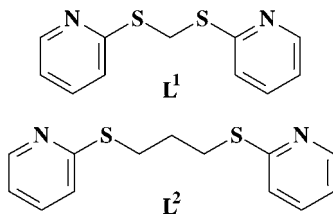


Chart 1.

[1, 2]. The self-assembly process of metal complexes is quite complicated and understanding the factors that affect the process between labile metal ions and flexible multidentate ligands is an interesting and challenging topic in supramolecular and coordination chemistry. Flexible multidentate bridging ligands have shown interesting coordination chemistry with transition metal ions [3]. Due to the flexibility of such ligands, they are very sensitive to the changes of conditions employed and may result in different coordination modes and complexes with different architectures [4–6].

As our continuing efforts to investigate the effects of the linker units of flexible ligands and other factors on the structures of silver complexes with thioethers [7], we synthesized two flexible multidentate pyridyl dithioether ligands that closely related in structure: bis(2-pyridylthio)methane ( $L^1$ ) and 1,3-bis(2-pyridylthio)propane ( $L^2$ ) (see Chart 1). We report here three  $Ag^I$  coordination architectures with the two ligands, and the effects of anions and the lengths of ligand spacers on the structures of complexes have also been discussed.

## EXPERIMENTAL

### Materials and General Methods

All the reagents required for synthesis were commercially available and employed without further purification or purified by standard methods prior to use. Elemental analyses were performed on a Perkin-Elmer 240C analyzer and IR spectra on a 170SX (Nicolet) FT-IR spectrometer with KBr pellets.  $^1H$  NMR spectra were recorded on a Bruker AC-P500 spectrometer (300 MHz) at 25°C in  $CDCl_3$  with tetramethylsilane as the internal reference.

### Syntheses of the Ligands $L^1$ and $L^2$

The two ligands, bis(2-pyridylthio)methane ( $L^1$ ) and 1,3-bis(2-pyridylthio)propane ( $L^2$ ) were prepared by a similar procedure reported for the

synthesis of 1,4-bis(phenylthio)butane [8]. The reactions of pyridine-2-thiol with the appropriate dibromomethane or 1,3-dibromopropane, in the presence of KOH, gave two ligands in good yields, and the products were characterized by  $^1\text{H}$  NMR and elemental analyses. For  $\text{L}^1$ , yield: 83%. Anal. Found: C, 56.04; H, 4.32; N, 12.01. Calcd. for  $\text{C}_{11}\text{H}_{10}\text{N}_2\text{S}_2$ : C, 56.39; H, 4.37; N, 11.95.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  5.07 (s, 2H,  $-\text{SCH}_2\text{S}-$ ), 7.00 ~ 7.04 (m, 2H, Py-3), 7.17 ~ 7.26 (m, 2H, Py-5), 7.47 ~ 7.53 (m, 2H, Py-4), 8.49, 8.51 (d, 2H, Py-6). For  $\text{L}^2$ , yield: 88%. Anal. Found: C, 59.30; H, 5.31; N, 10.74. Calcd. for  $\text{C}_{13}\text{H}_{14}\text{N}_2\text{S}_2$ : C, 59.51; H, 5.38; N, 10.68.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  2.14 (p, 2H,  $J = 6.9$  Hz,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ), 3.32 (t, 4H,  $J = 6.9$  Hz,  $-\text{SCH}_2-$ ), 6.95 ~ 6.99 (m, 2H, Py-3), 7.16 ~ 7.19 (m, 2H, Py-5), 7.44 ~ 7.50 (m, 2H, Py-4), 8.40, 8.42 (d, 2H, Py-6).

### Preparation of $[\text{Ag}_3(\text{L}^1)_2(\text{NO}_3)_2](\text{NO}_3)$ (1), $[\text{Ag}_2(\text{L}^1)_2](\text{PF}_6)_2$ (2), and $[\text{Ag}_2\text{L}^2(\text{NO}_3)_2]$ (3)

Colorless single crystals suitable for X-ray analyses for complexes 1 ~ 3 were obtained by the similar method as described below:

**$[\text{Ag}_3(\text{L}^1)_2(\text{NO}_3)_2](\text{NO}_3)$  1.** A solution of  $\text{AgNO}_3$  (0.1 mmol) in MeOH (10 mL) was carefully layered on top of a solution of  $\text{L}^1$  (0.1 mmol) in  $\text{CHCl}_3$  (10 mL) in a test-tube. After three days at room temperature, colorless single crystals appeared at the boundary between MeOH and  $\text{CHCl}_3$  with 32% yield. Anal. Calcd. for  $\text{C}_{22}\text{H}_{20}\text{Ag}_3\text{N}_7\text{O}_9\text{S}_4$ : C, 27.01; H, 2.06; N, 2.86. Found: C, 26.90; H, 2.04; N, 2.88. IR (KBr pellet,  $\text{cm}^{-1}$ ): 1578s, 1556w, 1457m, 1384vs, 1356vs, 1289s, 1124m, 1008m, 758m.

**$[\text{Ag}_2(\text{L}^1)_2](\text{PF}_6)_2$  2.** Yield: 25%. Anal. Calcd. for  $\text{C}_{11}\text{H}_{10}\text{AgF}_6\text{N}_2\text{PS}_2$ : C, 27.12; H, 2.07; N, 5.75. Found: C, 27.31; H, 2.03; N, 5.70. IR (KBr pellet,  $\text{cm}^{-1}$ ): 1564m, 1456s, 1431s, 1381w, 1296m, 1018m, 985m, 833vs, 763s, 723m, 557s.

**$[\text{Ag}_2\text{L}^2(\text{NO}_3)_2]$  3.** Yield: 35%. Anal. Calcd. for  $\text{C}_{13}\text{H}_{14}\text{Ag}_2\text{N}_4\text{O}_6\text{S}_2$ : C, 25.93; H, 2.34; N, 9.30. Found: C, 25.89; H, 2.31; N, 9.23. IR (KBr pellet,  $\text{cm}^{-1}$ ): 1578s, 1556s, 1454s, 1414vs, 1379vs, 1282m, 1124s, 1088m, 1043m, 985m, 825m, 757s, 724m.

### X-ray Crystallographic Studies of Complexes 1 ~ 3

Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room

Table I. Crystal Data and Structure Refinement Summary for 1 ~ 3

	1	2	3
Empirical formula	C <sub>22</sub> H <sub>20</sub> Ag <sub>3</sub> N <sub>7</sub> O <sub>9</sub> S <sub>4</sub>	C <sub>11</sub> H <sub>10</sub> AgF <sub>6</sub> N <sub>2</sub> PS <sub>2</sub>	C <sub>13</sub> H <sub>14</sub> Ag <sub>2</sub> N <sub>4</sub> O <sub>6</sub> S <sub>2</sub>
Formula weight	978.30	487.17	602.14
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pccn</i>	<i>P2(1)/c</i>	<i>C2/c</i>
<i>a</i> (Å)	8.324(3)	6.641(3)	24.91(3)
<i>b</i> (Å)	16.052(6)	19.864(8)	5.088(7)
<i>c</i> (Å)	22.620(8)	12.379(5)	17.73(2)
$\beta$ (°)	90	100.797(8)	128.47(2)
Volume (Å <sup>3</sup> )	3022(2)	1601(1)	1760(4)
<i>Z</i>	4	4	4
$\mu$ (mm <sup>-1</sup> )	2.264	1.674	2.504
No. unique refls ( <i>R</i> <sub>int</sub> )	2672(0.0683)	3306(0.0879)	1498(0.0360)
No. measured refls	3493	9136	3230
<i>R</i> <sup>a</sup> & <i>wR</i> <sup>b</sup>	0.0352/0.0823	0.0689/0.1609	0.0524/0.1652

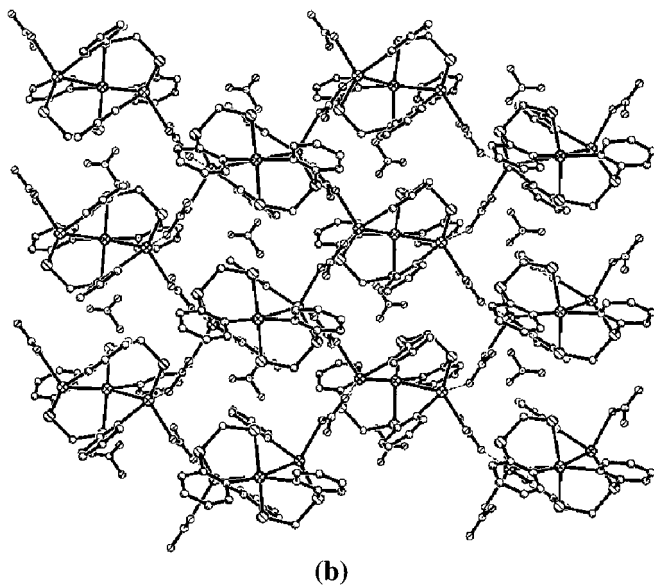
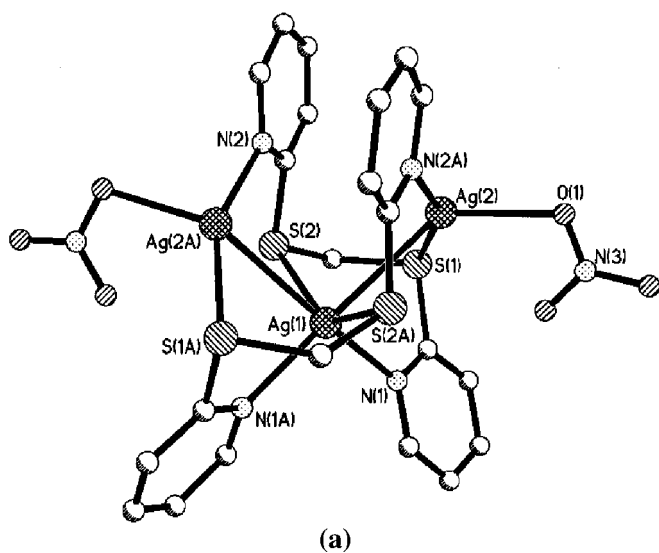
<sup>a</sup>  $R = \sum (||F_o| - |F_c||) / \sum F_o$ .  
<sup>b</sup>  $wR = [\sum (|F_o|^2 - |F_c|^2)^2 / \sum (F_o^2)]^{1/2}$ .

temperature. The determination of unit cell parameters and data collections were performed with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Unit cell dimensions were obtained with least-squares refinements and all structures were solved by direct methods. Silver atoms in each complex were located from *E*-maps. The other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on *F*<sup>2</sup>. The hydrogen atoms were added theoretically and riding on the concerned atoms. Crystallographic data and experimental details for structural analyses are summarized in Table I.

RESULTS AND DISCUSSION

The Trinuclear Complex [Ag<sub>3</sub>(L<sup>1</sup>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>) 1 and the Dinuclear Complex [Ag<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> 2, Anion Effects

Complex 1 consists of a [Ag<sub>3</sub>(L<sup>1</sup>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup> trinuclear cluster cation and an uncoordinated nitrate anion. The cation cluster shows two different Ag<sup>I</sup> centers and possesses a crystallographic *C*<sub>2</sub> axis passing through the Ag(1) and the midpoint of the linkage of Ag(2) and Ag(2A) (Fig. 1a). Selected bond lengths and angles are given in Table II. Ag(1) has a highly distorted tetrahedral geometry comprised of two pyridine N donors and two S atoms from two distinct ligands. The six bond angles around Ag(1)



**Fig. 1.** (a) View of the trinuclear structure of **1**, and (b) the quasi 2D structure formed by the weak interactions of Ag...O.

**Table II.** Selected Bond Lengths [ $\text{\AA}$ ] and Angles [ $^\circ$ ] for Complex 1

Ag(1)–N(1)	2.307(4)	Ag(1)–S(2)	2.530(2)
Ag(1)–Ag(2)	3.116(1)	Ag(2)–N(2) <sup>#1</sup>	2.297(4)
Ag(2)–O(1)	2.490(6)	Ag(2)–S(1)	2.519(2)
N(1) <sup>#1</sup> –Ag(1)–N(1)	103.2(2)	N(1) <sup>#1</sup> –Ag(1)–S(2) <sup>#1</sup>	99.7 (1)
N(1)–Ag(1)–S(2) <sup>#1</sup>	107.7(1)	S(2) <sup>#1</sup> –Ag(1)–S(2)	135.34(7)

Symmetry transformations used to generate equivalent atoms: #1:  $-x - 1/2, -y - 1/2, z$ .

range from 99.7(1) to 135.34(7) $^\circ$ . Ag(2) is coordinated to an N donor of the pyridine ring, an S atom from another ligand and an O donor from  $\text{NO}_3^-$ , taking a trigonal planar geometry with the three bond angles of N(2A)–Ag(2)–O(1), N(2A)–Ag(2)–S(1), and O(1)–Ag(2)–S(1) being 83.5(2), 154.4(1), and 120.3(2) $^\circ$ , respectively. The Ag(2) center deviates from the plane drawn through three donors by ca. 0.1590  $\text{\AA}$ . The average Ag–N and Ag–S bond distances are 2.302 and 2.525  $\text{\AA}$ , respectively, being in the normal range of analogous complexes [9]. The two pyridine rings of the two distinct ligands coordinating to Ag(2) and Ag(2A) are parallel to each other, while the other two pyridine rings of the two ligands are inclined to each other at an angle of 51.7 $^\circ$ .

It is noteworthy that the Ag–Ag contact of 3.116(1)  $\text{\AA}$  is significantly shorter than the summed van der Waals radii of two silver atoms (3.44  $\text{\AA}$ ) [10], indicating the presence of ligand-supported Ag–Ag interactions which are often observed in  $\text{Ag}^{\text{I}}$  complexes [11]. In **1**,  $\text{L}^1$  acts as a tetradentate ligand using a pyridine N and the far S donor of the same ligand chelating Ag(1) to form a stable 6-membered ring, and the remaining pyridine nitrogen and a sulfur atom of the ligand bridge Ag(2) and Ag(2A) in *cis*-form. The Ag–Ag contacts make the trinuclear structure form additional four stable 5-membered rings, which further stabilizes the complex. The terminal  $\text{NO}_3^-$  weakly interact with the  $\text{Ag}^{\text{I}}$  centers of other trinuclear units by  $\text{Ag}\cdots\text{O}$  contacts (2.636  $\text{\AA}$ ) to form a quasi two-dimensional structure (Fig. 1b), and the uncoordinated nitrate anions are sandwiched by two sets of quasi 2-D networks.

The reaction of  $\text{L}^1$  with  $\text{AgPF}_6$  instead of  $\text{AgNO}_3$  gave rise to a dinuclear complex **2** which consists of a centrosymmetric  $[\text{Ag}_2(\text{L}^1)_2]^{2+}$  cation and two uncoordinated  $\text{PF}_6^-$ . The  $[\text{Ag}_2(\text{L}^1)_2]^{2+}$  unit is shown in Fig. 2a with atoms numbering and the selected bond lengths and angles are given in Table III. Each  $\text{Ag}^{\text{I}}$  center has a distorted trigonal planar geometry comprised of two pyridine nitrogens from distinct  $\text{L}^1$  ligands and a sulfur atom. All the silver–donor bond distances (see Table III) are within the range expected for such coordination bonds [9]. The  $\text{Ag}^{\text{I}}$  center

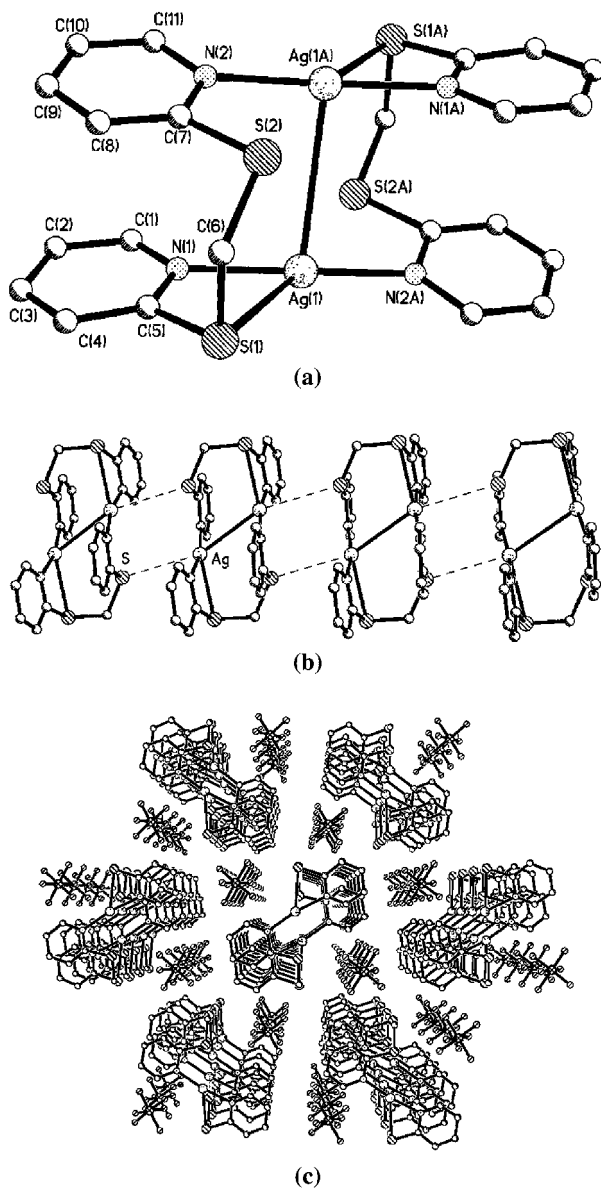


Fig. 2. (a) View of the dinuclear structure of **2**, (b) the chain structure formed by Ag...S weak interactions, and (c) the channels formed by adjacent pillars.

Table III. Selected Bond Lengths [Å] and Angles [°] for Complex 2

Ag(1)–N(2) <sup>#1</sup>	2.169(6)	Ag(1)–N(1)	2.190(6)
Ag(1)–S(1)	2.907(3)	Ag(1)–Ag(1) <sup>#1</sup>	3.377(2)
N(2) <sup>#1</sup> –Ag(1)–N(1)	167.4(3)	N(2) <sup>#1</sup> –Ag(1)–S(1)	130.6(2)
N(1)–Ag(1)–S(1)	60.2(2)	N(2) <sup>#1</sup> –Ag(1)–Ag(1) <sup>#1</sup>	86.4(2)
N(1)–Ag(1)–Ag(1) <sup>#1</sup>	95.3(2)	S(1)–Ag(1)–Ag(1) <sup>#1</sup>	110.70(6)

Symmetry transformations used to generate equivalent atoms: #1:  $-x + 1, -y + 1, -z + 1$ .

deviates from the coordination plane by 0.1096 Å, and the three bond angles of N–Ag–N, N–Ag–S, and N–Ag–S are 60.2(2), 130.6(2), and 167.4(3)°, respectively.

L<sup>I</sup> adopts tridentate coordination mode with a sulfur un-coordinating to Ag<sup>I</sup> center. The pyridylsulfanyl group of the ligand coordinates to Ag<sup>I</sup> center using a pyridine nitrogen and a sulfur to form a four-membered ring although four-membered ring is more geometrically strained than five-membered ring which is formed in **1**. In the dinuclear unit, the Ag–Ag distance of 3.377(2) Å is great longer than that of 3.116(1) Å in **1** but shorter than the sum of the van der Waals radii of the silver atom [10], indicating weak Ag–Ag interactions which make the dinuclear structure form additional two seven-membered rings. The planes of the pyridine rings located at the symmetric site are parallel to each other. The centroid-centroid distance of 3.475 Å between pyridine rings of the same ligand indicates strong intramolecular face-to-face  $\pi$ – $\pi$  staking interactions [12]. The co-effects of Ag–Ag and  $\pi$ – $\pi$  interactions further stabilize the dinuclear structure. The Ag<sup>I</sup> centers in a dinuclear unit show weak interactions with sulfur atoms of another adjacent cation units, and these weak interactions link the dinuclear units into a pillar (Fig. 2b). The PF<sub>6</sub><sup>–</sup> anions occupy the channels formed by three adjacent pillars (Fig. 2c).

PF<sub>6</sub><sup>–</sup> possesses great volume and its fluorine atoms have weaker coordinating ability than the oxygen atoms of NO<sub>3</sub><sup>–</sup> anion, therefore the PF<sub>6</sub><sup>–</sup> dose not coordinate to Ag<sup>I</sup> ions in **2**. The change of counters influences on not only the coordination mode of ligand but also the geometry of Ag<sup>I</sup> center, consequently gives rise to different structural complexes. The effects of counter ions on the structures of complexes are also discussed in other reported complexes [4, 5].

One-Dimensional Chain of [Ag<sub>2</sub>L<sup>2</sup>(NO<sub>3</sub>)<sub>2</sub>]<sub>∞</sub> **3**

The crystal structure of complex **3** consists of a neutral chain formed by Ag<sup>I</sup> ions bridged with L<sup>2</sup> (Fig. 3a). Each Ag<sup>I</sup> ion is coordinated by a



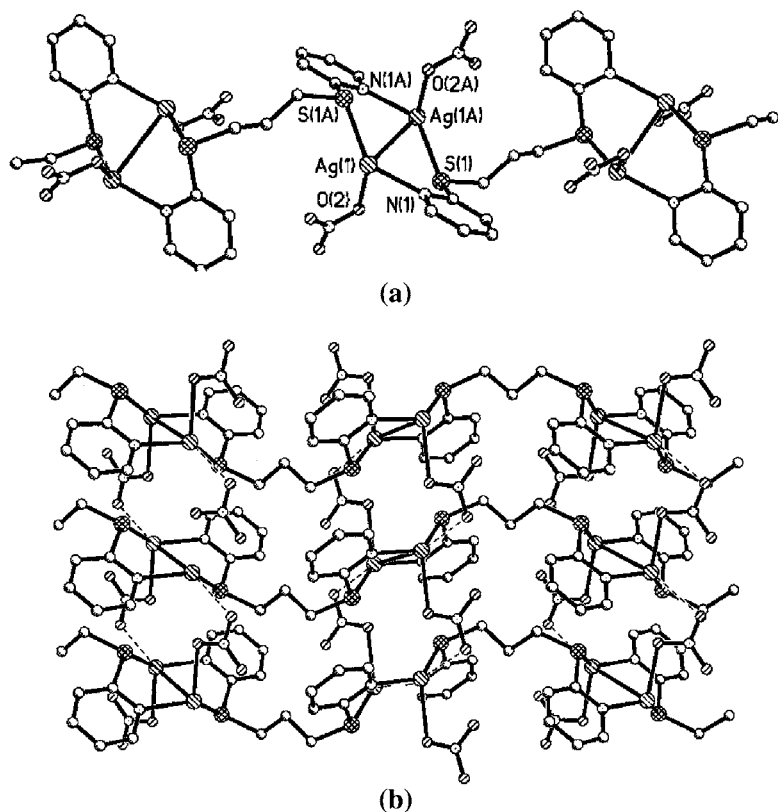


Fig. 3. (a) The 1D chain of 3, and (b) the quasi 2D structure formed by the weak interactions of  $\text{Ag} \cdots \text{O}$ .

Table IV. Selected Bond Lengths [ $\text{\AA}$ ] and Angles [ $^\circ$ ] for Complex 3

Ag(1)–N(1)	2.260(7)	Ag(1)–O(2)	2.476(8)
Ag(1)–S(1) <sup>#1</sup>	2.487(3)	Ag(1)–Ag(1) <sup>#1</sup>	3.128(4)
N(1)–Ag(1)–O(2)	89.2(3)	N(1)–Ag(1)–S(1) <sup>#1</sup>	137.0(2)
O(2)–Ag(1)–S(1) <sup>#1</sup>	123.9(2)	N(1)–Ag(1)–Ag(1) <sup>#1</sup>	85.1(2)
O(2)–Ag(1)–Ag(1) <sup>#1</sup>	88.1(2)	S(1) <sup>#1</sup> –Ag(1)–Ag(1) <sup>#1</sup>	71.1(1)

Symmetry transformations used to generate equivalent atoms: #1:  $-x, -y, -z$ .

pyridine nitrogen and a sulfur atom from different ligands, as well as an oxygen from  $\text{NO}_3^-$  showing a slightly distorted trigonal planar geometry. The  $\text{Ag}^{\text{I}}$  center deviates from the coordination plane by ca. 0.417 Å, and the N–Ag–O, S–Ag–N, and O–Ag–S bond angles are 89.2(3), 137.0(2), and 123.9(2)°, respectively (Table IV). The  $\text{Ag}^{\text{I}}$  ion further interacts with an  $\text{Ag}^{\text{I}}$  ion related by a crystallographic center of symmetry showing weak Ag–Ag interactions, and the Ag–Ag distance of 3.128(4) Å is similar to that in **1**. The two pyridyl rings near each  $\text{Ag}^{\text{I}}$  are parallel to each other, while the two terminal pyridine rings are inclined to each other with an angle of 94.3°.

$\text{L}^2$  coordinates to  $\text{Ag}^{\text{I}}$  in tetradentate mode through the pyridine nitrogens and sulfur donors, resulting in an infinite chain. Two pyridylsulfanyl groups from two  $\text{L}^2$  ligands bridge two  $\text{Ag}^{\text{I}}$  to form an 8-membered ring (ignoring the Ag–Ag interaction), which has an inversion center and adopts a chair configuration with two pyridine rings parallel to each other. The  $\text{Ag}^{\text{I}}$  centers in one chain show weak interactions with oxygens from  $\text{NO}_3^-$  of adjacent chain (the average  $\text{Ag}\cdots\text{O}$  distance is 2.734 Å), and these one-dimensional chains are further linked to form quasi two-dimensional network by  $\text{Ag}\cdots\text{O}$  weak interactions as depicted in Fig. 3b.

It can be seen from **1** and **3** that the difference of the length of the ligand spacers can remarkably change the structures of the complex architectures. The flexible  $-(\text{CH}_2)_n-$  backbones of the ligands allow the ligands to bend and rotate to coordinate to  $\text{Ag}^{\text{I}}$  so as to form stable structures. In addition, the wide coordination geometry of  $\text{Ag}^{\text{I}}$  (coordination numbers from 2 to 6 are all possible) also provides the probability for the structural diversity of complexes. In all three complexes, there exist Ag–Ag interactions, and such weak interactions also found in other complexes of  $d^{10}$  metal ions such  $\text{Cu}^{\text{I}}$  and  $\text{Au}^{\text{I}}$  [13], and such interactions make the complex more stable. The framework formations of such complexes may be affected by many factors including weak interactions between metal centers and donors. There exist  $\text{Ag}\cdots\text{O}$  weak interactions in **1** and **3** and  $\text{Ag}\cdots\text{S}$  weak interactions in **2**, and these weak interactions extend three low-dimensional  $\text{Ag}^{\text{I}}$  complexes into high-dimensional ones, and further stabilize these complexes.

## SUPPLEMENTARY MATERIALS

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 218405, 218406, and 218407). This material can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC,

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