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Controlling the Framework Formation of Silver(I) Coordination Polymers with 1,4-Bis(phenylthio)butane by Varying the Solvents, Metal-to-Ligand Ratio, and Counteranions

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The reactions of 1,4-bis(phenylthio)butane (**L**) with Ag^{I} salts in varied conditions (varying the solvents, metal-to-ligand ratios, and counteranions) lead to the formation of four new two-dimensional (2D) coordination polymers with different network structures: $[Ag_2\mathbf{L}_3(ClO_4)_2]_\infty$ **1**, $[Ag_2\mathbf{L}_3(ClO_4)_2\cdot CH_3OH]_\infty$ **2**, $\{[Ag\mathbf{L}_2](ClO_4)\}_\infty$ **3**, and $[Ag\mathbf{L}NO_3]_\infty$ **4**. All the structures were established by single-crystal X-ray diffraction analysis. Crystal data for **1**: triclinic, *P*-1, $a = 11.0253(9)$ Å, $b = 11.3455(9)$ Å, $c = 11.5231(9)$ Å, $\alpha = 93.931(2)°$, $\beta = 92.689(2)°$, $\gamma = 112.9810(10)°$, $Z = 2$. **2**: triclinic, *P*-1, $a = 11.9147(13)$ Å, $b = 16.1534(17)$ Å, $c = 16.2259(17)$ Å, $\alpha = 74.977(2)°$, $\beta = 69.030(2)°$, $\gamma = 69.986(2)°$, $Z = 2$. **3**: triclinic, *P*-1, $a = 12.1617(9)$ Å, $b = 12.5054(10)$ Å, $c = 13.1547(10)$ Å, $\alpha = 64.3370(10)°$, $\beta = 85.938\ (2)°$, $\gamma = 69.3010(10)°$, $Z = 2$. **4**: monoclinic, $P2_1/c$, $a = 5.4032(17)$ Å, $b = 16.974(6)$ Å, $c = 19.489(6)$ Å, $\beta = 94.234(6)°$, $Z = 4$. In all four complexes, each Ag^{I} center has a tetracoordination geometry, and the 2D networks consist of fused large macrometallacyclic ring systems. The "hexagonal" 42-membered rings, $Ag_6\mathbf{L}_6$, observed in **1** and **2** are nearly identical, which could be considered as unique examples of self-sustaining noninterpenetrated frameworks formed with flexible ligands. The repeating rectangular 28-membered macrometallacycle, $Ag_4\mathbf{L}_4$, is the basis for the network of **3**, in which the perchlorate anions occupy the voids to prevent the ring from collapsing. In **4**, columns of the fused rectangular 22-membered rings, $Ag_4\mathbf{L}_2(NO_3)_2$, are cross-linked through the **L** ligands to form a unique 2D network consisting of two types of 22-membered repeating units.

Introduction

In recent years, crystal engineering and construction of coordination networks with fascinating structural topologies have attracted great attention owing to their potential as functional materials.[1] Concurrently, the development of multidimensional networks based primarily on linking metal centers with rigid bridging components, such as 4,4′-bipyridine, has been initiated.[2] Far less common has been the use of flexible bridging units in the construction of extended networks,[3] and this approach is attractive because the flexibility and conformation freedoms of such ligands offer the possibility for the construction of unprecedented frameworks with tailored properties and functions. Meanwhile, a major challenge in crystal engineering using flexible

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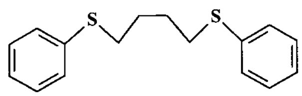
building blocks is the predictability of the polymeric network topology[4] which may depend on several factors such as the coordination geometry and the oxidation state of the metal centers,[5] the metal-to-ligand ratio,[6] the nature of the ligands used,[7] and the presence of solvents[8] and/or counteranions.[9] There is still a very long way to go to develop new architectures of coordination polymers using flexible spacer ligands in order to rationalize the design of compounds with well-defined structures and useful functions.

We report herein our recent successful results in the construction of four novel coordination Ag^{I} polymers forming macrometallacyclic, noninterpenetrated two-dimensional (2D) networks, using a flexible 1,4-bis(phenylthio)butane (**L**)



L

ligand as building blocks. All the complexes adopt unique structures in the solid state, involving either 2D honeycomb-like or lattice networks incorporating large channels that accommodate the phenyl groups, the solvent molecules, and/or counteranions.

Experimental Section

Materials and General Methods. All the reagents required for syntheses 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 were measured on a 170SX (Nicolet) FT-IR spectrometer with KBr pellets. ^{1}H NMR spectra were recorded on a Bruker AC-P500 spectrometer (300 MHz) at 25 °C in $CDCl_3$ with tetramethylsilane as the internal reference. Thermal stability (TG-DTA) studies were carried out on a Dupont thermal analyzer from room temperature to 800 °C.

Caution! Although we have met no problems in handling perchlorate salts during this work, these should be treated with great caution, owing to their potential explosive nature.

Synthesis of 1,4-Bis(phenylthio)butane (L). 1,4-Bis(phenylthio)butane was synthesized according to the literature method.[10] Yield: 86%. Anal. Found: C, 70.43; H, 6.43. Calcd. for $C_{16}H_{18}S_2$: C, 70.03; H, 6.61. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.78 (m, 4H, $-C(CH_2)_2C-$), 2.94 (t, 4H, $-SCH_2-$), 7.30 (m, 10H, C_6H_5-).

$[Ag_2L_3(ClO_4)_2]_\infty$ 1. A solution of $AgClO_4{\cdot}6H_2O$ (34 mg, 0.1 mmol) in acetone (5 mL) was slowly added to a solution of **L** (45 mg, 0.15 mmol) in chloroform (6 mL). The filtrate was diffused slowly in ether in the dark to obtain colorless needle-shaped single crystals suitable for X-ray analysis. Yield: 18% based on **L**. Anal. Found: C, 46.39; H, 4.45. Calcd for $C_{24}H_{27}AgClO_4S_3$: C, 46.57; H, 4.40. IR (KBr, cm^{-1}): 1480 w, 1439 m, 1314 w, 1109 vs, 1096 vs, 731 s, 620 s. DTA data (peak position): 237, 271, and 647 °C.

$[Ag_2L_3(ClO_4)_2.CH_3OH]_\infty$ 2. A solution of $AgClO_4{\cdot}6H_2O$ (20 mg, 0.06 mmol) in acetone (3 mL) was slowly added to a solution of **L** (30 mg, 0.1 mmol) in chloroform (5 mL). The filtrate was diffused slowly in ethanol in the dark to obtain colorless block-shaped single crystals suitable for X-ray analysis. Yield: 22% based on $AgClO_4{\cdot}6H_2O$. Anal. Found: C, 46.00; H, 4.36. Calcd for $C_{49}H_{58}Ag_2Cl_2O_9S_6$: C, 46.34; H, 4.60. IR (KBr, cm^{-1}): 3432 b, 1480 m, 1439 s, 1314 w, 1095 vs, 1071 vs, 731 s, 622 s. Differential thermal analysis (DTA) data (peak position): 53, 242, 270, and 622 °C.

$\{[AgL_2](ClO_4)\}_\infty$ 3. $AgClO_4{\cdot}6H_2O$ (10 mg, 0.03 mmol) in acetone (3 mL) was slowly added to the solution of **L** (18 mg, 0.07 mmol) in chloroform (2 mL). The reaction mixture was kept in the dark and was allowed to evaporate slowly to obtain colorless block-shaped single crystals suitable for X-ray analysis in 42% yield based on $AgClO_4{\cdot}6H_2O$. Anal. Found: C, 51.23; H, 4.82. Calcd for $C_{32}H_{34}AgClO_4S_4$: C, 50.83; H, 4.80. IR (KBr, cm^{-1}): 1481 m, 1440 s, 1317 w, 1090 vs, 1071 vs, 732 s, 623 s. DTA data (peak position): 241 and 279 °C.

$[AgLNO_3]_\infty$ 4. The solution of $AgNO_3$ (17 mg, 0.1 mmol) dissolved in methanol (10 mL) was added to the solution of **L** (27 mg, 0.1 mmol) in chloroform (6 mL). The mixture was kept under reflux for 30 min and after cooling yielded colorless needle crystals in 23% yield based on **L**. Single crystals suitable for X-ray analysis were obtained by recrystallization from DMF. Anal. Found: C, 43.03; H, 3.92. Calcd for $C_{16}H_{18}AgNO_3S_2$: C, 43.25; H, 4.08. IR (KBr, cm^{-1}): 1479 w, 1439 m, 1384 vs, 1342 m, 731 m, 690 m. DTA data (peak position): 204, 271, and 792 °C.

X-ray Crystallography. 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 temperature. The determination of unit cell parameters and data collections was performed with Mo Kα radiation (λ = 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 (in complex **2**, the oxygen atoms of the perchlorate anions are disordered and treated isotropically). The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were added

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Table 1. Crystallographic Data and Structure Refinement Summary for Complexes **1**−**4**

	1	**2**	**3**	**4**
chemical formula	$C_{24}H_{27}AgClO_4S_3$	$C_{49}H_{58}Ag_2Cl_2O_9S_6$	$C_{32}H_{36}AgClO_4S_4$	$C_{16}H_{18}AgNO_3S_2$
formula weight	618.96	1269.95	756.17	444.30
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	11.0253(9)	11.9147(13)	12.1617(9)	5.4032(17)
b/Å	11.3455(9)	16.1534(17)	12.5054(10)	16.974(6)
c/Å	11.5231(9)	16.2259(17)	13.1547(10)	19.489(6)
α/deg	93.931(2)	74.977(2)	64.3370(10)	90
β/deg	92.689(2)	69.030(2)	85.938(2)	94.234(6)
γ/deg	112.9810(10)	69.986(2)	69.3010(10)	90
$V/Å^3$	1319.61(18)	2706.5(5)	1678.9(2)	1782.5(10)
Z	2	2	2	4
$D/g\ cm^{-3}$	1.558	1.558	1.496	1.656
μ/mm^{-1}	1.130	1.106	0.963	1.377
T/K	298(2)	298(2)	298(2)	293(2)
R^a/wR^b	0.0282/0.0752	0.0523/0.1239	0.0388/0.1057	0.0532/0.1303

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**

Ag(1)−S(3)	2.4955(7)	Ag(1)−S(2)	2.5042(6)
Ag(1)−S(1)	2.5576(6)		
S(3)−Ag(1)−S(2)	131.66(2)	S(3)−Ag(1)−S(1)	110.74(2)
S(2)−Ag(1)−S(1)	104.72(2)		

theoretically and riding on the concerned atoms. Crystallographic data and experimental details for structural analyses are summarized in Table 1.

Results and Discussion

Description of Crystal Structures. $[Ag_2L_3(ClO_4)_2]_\infty$ 1. The structure of **1** has a two-dimensional (2D) arrangement of honeycombs constructed from Ag^I linked by the **L** ligands. Each Ag^I is coordinated to three S donors of three distinct **L** ligands, and they, in turn, link distant Ag^I ions via the second sulfur donor. In addition, an oxygen atom O(3) of a perchlorate weakly coordinates to Ag^I and completes the tetrahedral coordination of Ag^I. The Ag−O distance (2.932-(6) Å) is a long-range interaction, while the Ag−S bonds are normal (mean value 2.519 Å, see Table 2) in the Ag^I complexes of thioethers. This Ag^I ion, having a tetrahedral coordination, is 0.516 Å above the S(1)−S(2)−S(3) basal plane. Each **L** ligand bridges two Ag^I to form a centrosymmetric "hexagonal" 42-membered macrometallacyclic ring made up of six Ag^I at the corners and six ligands as the edges (see Figure 1a), and this unit adopts a "chair" configuration. The Ag(1B) and Ag(1G) are 4.94 Å above or below the mean plane formed by Ag(1A)/Ag(1F)/Ag(1H)/Ag(1C). In this macrometallacycle (Figure 1a), the lengths of the three pair edges are not equivalent with Ag(1B)···Ag(1F), Ag(1F)···Ag(1A), and Ag(1H)···Ag(1B) distances being 8.42, 10.88, and 8.69 Å, respectively. However, all the S···S distances of **L** are 6.92 Å.

The perchlorate anions coordinated to the Ag^I centers are alternatively on either side of the macrometallacycle. To keep the structure stable, the *σ*-bonds of the ring system rotate to make the phenyl groups point inside of the macrocycle to fill the void so that the hexagonal unit folds. Each cavity consists of six phenyl rings to maintain the stability of the structure and two phenyl rings of one ligand situated in two adjacent cavities. Complex **1** might be considered as a self-sustaining framework, which is rare in the noninterpenetrated

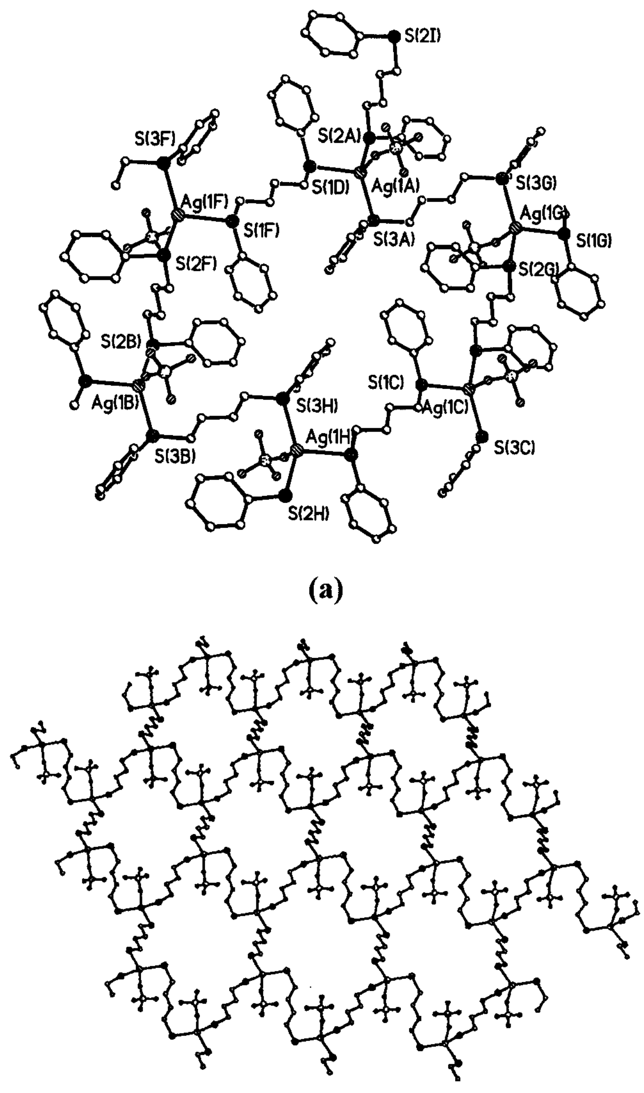

Figure 1. (a) Hexagonal 42-membered repeating unit of **1**. (b) View from the *c*-axis showing the 2D honeycomb grid of **1** (phenyl groups are omitted for clarity).

complexes. Unlike the repeating units of other self-filling complexes[11] sustained by interpenetration, *π*−*π* interaction, or the steric-hindrance of rigid groups (such as phenyl or pyridine) in the ligand's backbone between the frames, the repeating unit of complex **1** with its flexible alkyl frame is sustained by the big phenyl groups of **L**. The units extend along the (110) plane to form a 2D honeycomb-like structure (see Figure 1b).

$[Ag_2L_3(ClO_4)_2CH_3OH]_\infty$ 2. Although **2** was synthesized in a manner similar to that used for **1**, the employment of methanol as solvent instead of acetone yielded a new compound in which the methanol molecule is coordinated to Ag^I. This was confirmed by X-ray analysis and infrared spectrum of **2**. It is worth noting that in this complex the Ag^I centers have two different environments, which brings about two different repeating units, **A** (Figure 2a) and **B** (Figure 2b). In unit **A**, the environment of Ag^I is similar to that of complex **1**, except in which the oxygen atom of methanol occupies the axial position instead of the oxygen of a perchlorate. In unit **B**, a perchlorate completes the tetrahedral coordination of Ag(2) with the Ag(1A)−O(1A) distance being 2.973(5) Å, the same as in **1**.

Each hexagonal unit is composed of a Ag_6**L_6** macrometallacycle whose cavity is filled by six phenyl rings of **L** ligands and two perchlorate anions. The Ag···Ag separations of the three pair edges in the hexagonal unit are 11.02, 10.80, and 9.41 Å, respectively. What interests us most is the resilience[4b] of the structure of **1** and **2**. The dimensions of the two units of **2** are remarkably larger than those in **1**, but in both complexes the S···S separation of each ligand remains 6.92 Å. In unit **A**, the methanol takes up the position of perchlorate anion in **1** and causes the perchlorate ions to play a templating role so that the repeating units and the staking of sheets adopt a new pattern. The resilience of the polymer complexes constructed by flexible ligands is revealed, since the conformation of the ligands in those networks adjusts according to the small changes in the coordination environment, such as the self-filling unit in **1** transforming into the unit in **2** to accept two perchlorate ions.

The **A** and **B** macrometallacycles arrange alternately along the crystallographic *c*-direction, and each propagates along the (110) plane to form a 2D honeycomb-like structure (see Figure 2c). In addition, there exist several types of long-range interactions between the **A** and **B** units: two ClO_4^- anions within unit **A** have contacts with two Ag^I atoms in the two adjacent **B** units (up and down); two ClO_4^- anions within unit **B** are involved in O−H···O hydrogen-bonded contact to the two methanol molecules within unit **A**. Because of these contacts, the chair planes of unit **A** and **B** are drawn closer (3.5 Å), and an S···S contact of 3.56 Å which is less than the sum of the van der Waals radii of two sulfur atoms[12] is observed. The 2D sheets are bound to each other by interlayer O−H···O hydrogen bonds and Ag−O contacts to generate a quasi-three-dimensional network (see Table 3).

$\{[AgL_2](ClO_4)\}_\infty$ 3. To generate different structures, the molar ratios of Ag^I salts and dithioethers were modified. **3** was synthesized by a method similar to that used for **1**. In

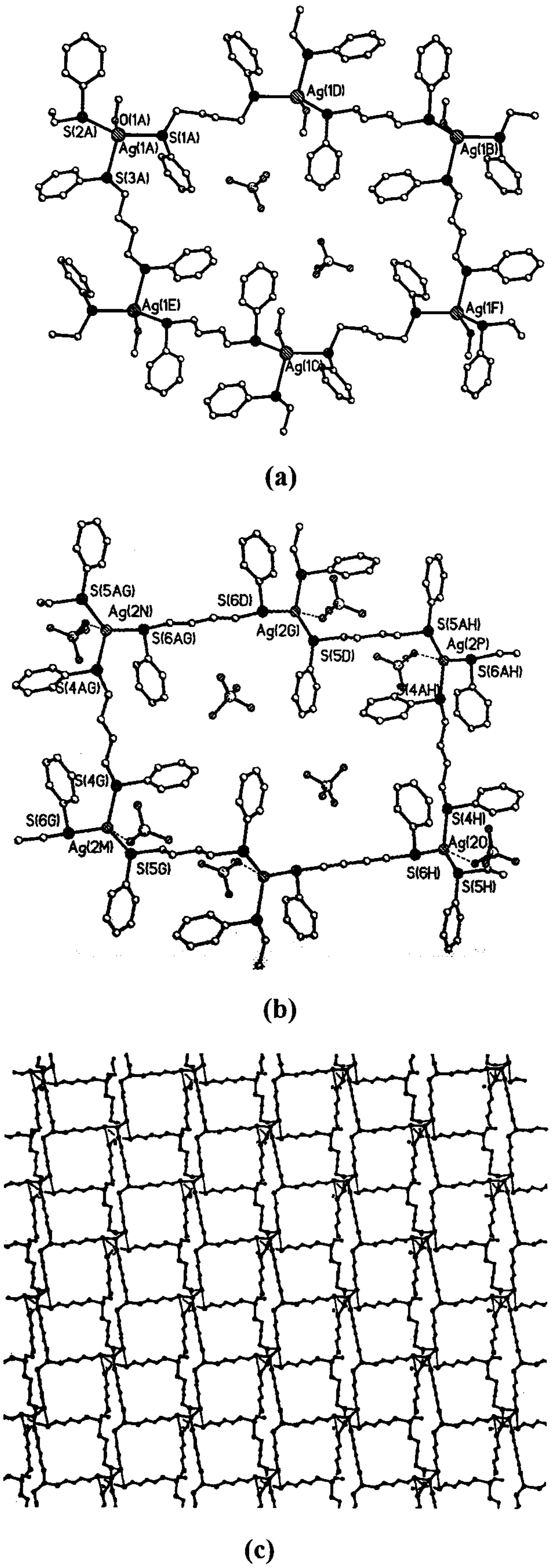

Figure 2. Forty-two-membered hexagonal repeating unit of **2** (a) **A**, (b) **B**, in which the oxygen of ClO_4^- is involved in a long-range interaction with Ag^I, and (c) a view from the *c*-axis showing the two-layer 2D honeycomb grid of **2** (phenyl groups are omitted for clarity).

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex **2**

Ag(1)−O(1)	2.461(5)	Ag(1)−S(1)	2.5512(16)
Ag(1)−S(2)	2.5517(17)	Ag(1)−S(3)	2.6261(16)
Ag(2)−S(6)	2.5098(17)	Ag(2)−S(5)	2.5171(16)
Ag(2)−S(4)	2.5628(17)		
O(1)−Ag(1)−S(1)	99.83(15)	O(1)−Ag(1)−S(2)	104.92(15)
S(1)−Ag(1)−S(2)	137.65(5)	O(1)−Ag(1)−S(3)	16.38(17)
S(1)−Ag(1)−S(3)	103.74(5)	S(2)−Ag(1)−S(3)	95.36(5)
C(1)−S(1)−C(7)	100.4(3)	C(1)−S(1)−Ag(1)	102.9(2)
S(6)−Ag(2)−S(5)	134.94(5)	S(6)−Ag(2)−S(4)	117.18(6)
S(5)−Ag(2)−S(4)	102.19(6)		

comparing this structural unit with that of **1**, we can find that the weak coordination group perchlorate was substituted by a ligand**,** and each metal center in **3** basically involves a trigonal pyramidal coordination geometry comprising three sulfur atoms of three distinct **L** ligands to form the basal plane, with the apex site occupied by a sulfur donor of the fourth ligand. The average length of Ag−S bonds is 2.604 Å, being longer than those in **1**. Each ligand bridges two adjacent Ag^I centers to form a slightly twisted rectangular 28-membered ring, Ag_4**L**$_4$, in which two pairs of Ag···Ag distances are 10.87 and 8.67 Å, respectively. The four Ag^I atoms are approximately coplanar. In **3**, the ligand adopts two configurations: **A** and **B**, as depicted in Figure 3a. In **A**, the ligand bridges Ag(1A) and Ag(1D) with the two S donors sitting at the apex of the trigonal pyramid, and the S···S separation is 5.77 Å. In the repeating unit, the ligands at the other three edges adopt a type **B** conformation with two S donors residing at the base of the trigonal pyramid with an S···S separation of 6.92 Å. Contrary to the case of **1**, the perchlorates of **3** are located in the voids of the repeating unit to prevent it from collapsing, while the phenyl groups of **L** alternate up and down to reduce the steric hindrance. Adjacent rectangle rings are fused to form 2D sheets stacking in the *c*-direction as shown in Figure 3b (see Table 4).

[AgLNO$_3$]$_\infty$ 4. In order to evaluate the influence of the counteranions on the structures of the complexes, a Ag^I nitrate salt was used instead of a Ag^I perchlorate salt. The replacement of the weakly coordinating ClO_4^- anions by the more strongly coordinating NO_3^- anions has a profound effect upon the network formation. Each Ag^I center in **4** is tetrahedrally coordinated to two S donors from a **L** ligand and two oxygen atoms from a nitrate anion. In contrast to the honeycomb-like structure observed in **1**, the $AgNO_3$ complex generates what could be described as a stairlike structure (see Figure 4).

The ligand links two adjacent Ag^I centers to form a one-dimensional (1D) zigzag chain. Each nitrate group coordinates in a bidentate fashion (bite) and bridges two Ag^I atoms from two neighboring chains, resulting in a 2D network. In another description of the structure, the Ag^I atoms and nitrate groups alternate in a linear arrangement and **L** cross-links adjacent chains to form a 2D network. In this description, the ligands form the rungs of a ladder whose sides are the $[-Ag-(NO_3)-]_\infty$ chains. Two types of 22-membered parallelogram-shaped, rectangular and rhombic, repeating units are formed (see Figure 4a). The geometrical characteristics of unit **A** are the following: Ag(1A)···Ag(1B) = 10.28 Å,

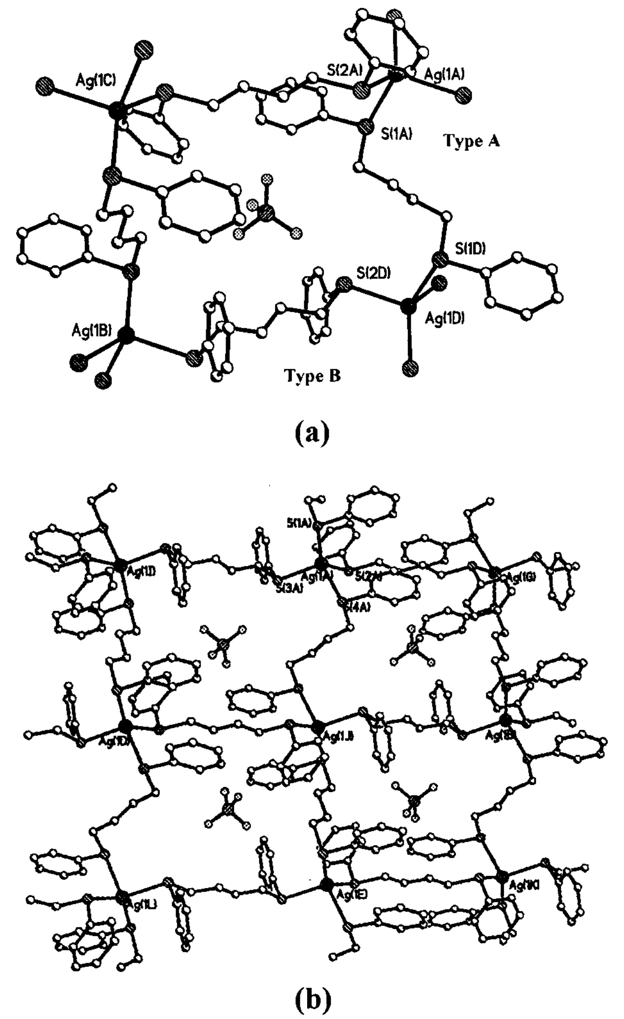

Figure 3. (a) View of the 28-membered rectangular unit of **3**, in which **L** adopts two conformations. (b) View from the *c*-direction showing the 2D rectangular grid of **3**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of Complex **3**

Ag(1)−S(1)	2.5501(9)	Ag(1)−S(2)	2.5866(8)
Ag(1)−S(3)	2.5958(9)	Ag(1)−S(4)	2.6824(10)
S(1)−Ag(1)−S(2)	131.07(3)	S(1)−Ag(1)−S(3)	106.92(3)
S(2)−Ag(1)−S(3)	111.29(3)	S(1)−Ag(1)−S(4)	106.62(3)
S(2)−Ag(1)−S(4)	94.40(3)	S(3)−Ag(1)−S(4)	101.81(3)

Table 5. Selected Bond Lengths (Å) and Angles (deg) of Complex **4**

Ag(1A)−O(3C)	2.452(6)	Ag(1A)−S(1A)	2.534(2)
Ag(1A)−O(2A)	2.557(6)	Ag(1A)−S(2A)	2.557(2)
O(3C)−Ag(1A)−S(1A)	124.06(17)	O(3C)−Ag(1A)−O(2A)	80.7(2)
S(1A)−Ag(1A)−O(2A)	121.60(16)	O(3C)−Ag(1A)−S(2A)	102.07(17)
S(1A)−Ag(1A)−S(2A)	115.47(7)	O(2A)−Ag(1A)−S(2A)	107.00(16)

Ag(1A)···Ag(1C) = 5.40 Å, S(1G)···S(1A) = 5.93 Å, Ag(1G)−Ag(1A)−Ag(1C) = 80.5°. In unit **B**, the corresponding values are the following: Ag(1G)···Ag(1D) = 8.60 Å, Ag(1G)···Ag(1I) = 5.40 Å, S(2B)···S(2F) = 7.04 Å, Ag(1I)−Ag(1G)−Ag(1D) = 64.5°. In the two types of repeating units, four Ag^I atoms are nearly coplanar, and the dihedral angle between the mean planes of the two types of units is 152.6(6)°. The two phenyl rings at the ends of the ligands are parallel to each other and alternate "above" and "below" the repeating unit. Units **A** and **B** stack alternately

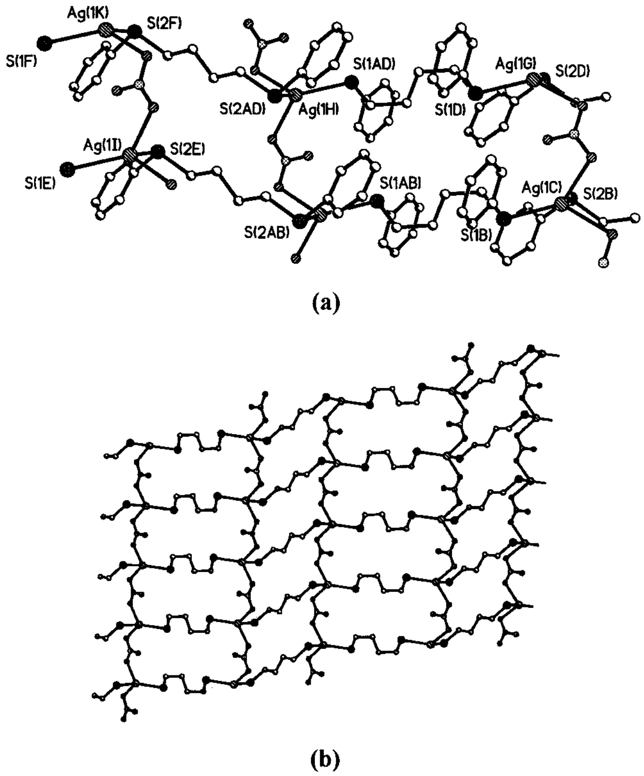

Figure 4. (a) View of two types of units in **4.** (b) View from the *c*-axis showing the 2D network.

along the crystallographic *c*-axis, and each propagates along the *a*- and *b*-axes to form an infinite 2D framework (see Table 5).

In all the four structures, the **L** ligand is centrosymmetric and shows a trans arrangement and its two phenyl groups are parallel to each other.

Conclusion and Comments

Four different novel Ag^I coordination polymers with 1,4-bis(phenylthio)butane (**L**) have been prepared and structurally characterized, affording unique noninterpenetrated 2D sheets. The flexible $-(CH_2)_4-$ backbone of **L** allows the ligands to rearrange so as to minimize steric interactions in both the free and coordinated forms. The structures of **1** and **2**, which have a similar 2D honeycomb-like framework, exhibit resilience. The dimensions of the two types of units in **2** are remarkably larger than those in **1**; however, in each ligand the S−S separation is kept at 6.92 Å. The ClO_4^- anions in **1** coordinated to Ag^I do not contribute to the maintaining of the large ring structure, and the phenyl groups fill the void to prevent the hexagonal unit from folding. In contrast to **1**, in the **A** unit of **2**, the methanol substitutes the position of perchlorate ions in **1** so the dimensions of the cavities enlarge remarkably to accept two ClO_4^-. Reaction of $AgClO_4$ with **L** in a 2:3 ratio yields **1**, whereas the reaction of $AgClO_4$ with **L** in a 1:2 ratio yields **3**, and a different counteranion (NO_3^-) leads to the formation of **4**, in which each NO_3^- coordinates in a bite fashion and bridges two Ag^I to link 1D chains into a 2D network.

This work reveals that the metal-to-ligand ratio, solvents, and counteranions play very important roles in the formation of different coordination frameworks, and this offers the possibility to control the formation of such network structures by varying those factors.

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Supporting Information Available: Four X-ray crystallographic files in CIF format and the ORTEP structures of complexes **1**-**4**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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