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Article

Adjusting the Frameworks of Silver(I) Complexes with New Pyridyl Thioethers by Varying the Chain Lengths of Ligand Spacers, Solvents, and Counteranions

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In our efforts to systematically investigate the effects of the linker units of flexible ligands and other factors on the structures of Ag^I complexes with thioethers, five new flexible pyridyl thioether ligands, bis(2-pyridylthio)methane ($\mathbf{L^1}$), 1,3-bis(2-pyridylthio)propane ($\mathbf{L^3}$), 1,4-bis(2-pyridylthio)butane ($\mathbf{L^4}$), 1,5-bis(2-pyridylthio)pentane ($\mathbf{L^5}$), and 1,6-bis(2-pyridylthio)hexane ($\mathbf{L^6}$), have been designed and synthesized, and the reactions of these ligands with Ag^I salts under varied conditions (varying the solvents and counteranions) lead to the formation of eight novel metal–organic coordination architectures from di- and trinuclear species to two-dimensional networks: $[Ag_3(\mathbf{L^1})_2(ClO_4)_2](ClO_4)$ (**1**), $\{[Ag\mathbf{L^3}](ClO_4)\}_\infty$ (**2**), $\{[Ag_2(\mathbf{L^4})_2](ClO_4)_2(CHCl_3)\}_\infty$ (**3**), $\{[Ag\mathbf{L^4}](ClO_4)(C_3H_6O)\}_\infty$ (**4**), $\{[Ag_2\mathbf{L^4}](NO_3)_2\}_\infty$ (**5**), $[Ag_2\mathbf{L^4}(CF_3SO_3)_2]_\infty$ (**6**), $\{[Ag\mathbf{L^5}](ClO_4)(CHCl_3)\}_2$ (**7**), and $\{[Ag\mathbf{L^6}](ClO_4)\}_\infty$ (**8**). All the structures were established by single-crystal X-ray diffraction analysis. The coordination modes of these ligands were found to vary from *N,N*-bidentate to *N,N,S*-tridentate to *N,N,S,S*-tetradentate modes, while the Ag^I centers adopt two-, three-, or four-coordination geometries with different coordination environments. The structural differences of **1**, **2**, **3**, **7**, and **8** indicate that the subtle variations on the spacer units can greatly affect the coordination modes of the terminal pyridylsulfanyl groups and the coordination geometries of Ag^I ions. The structural differences of **3** and **4** indicate that solvents also have great influence on the structures of Ag^I complexes, and the differences between **3**, **5**, and **6** show counteranion effects in polymerization of Ag^I complexes. The influences of counterions and solvents on the frameworks of these complexes are probably based upon the flexibility of ligands and the wide coordination geometries of Ag^I ions. The results of this study indicate that the frameworks of the Ag^I complexes with pyridyl dithioethers could be adjusted by ligand modifications and variations of the complex formation conditions.

Introduction

The construction of coordination polymers and supramolecular complexes based on multitopic ligands and metal centers represents one of the most rapidly developing fields in current coordination chemistry owing to their potential as functional materials.[1−3] However, the factors that govern the formation of the frameworks of such compounds are complicated and include not only the inherent properties of metal ions and ligand structure and coordination preferences but also anion-based interactions and solvent effects.[4−6] Therefore, the understanding of how these factors affect the metal coordination and crystal packing is important for controlling the coordination assembly process and the structures and properties of the final products.

Although flexible thioethers are well-established ligands in coordination and metallosupramolecular chemistry,[7] less

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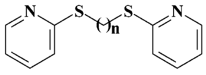
attention has been paid to pyridyl dithioethers in contrast to the extensive studies on the coordination chemistry of heterocyclic thiolates.[8] Pyridyl dithioether ligands contain rich structural information in which both the pyridine nitrogens and sulfur atoms can act as donors to coordinate to metal ions, and the flexible nature of spacers allows the ligands to bend and rotate when coordinating to metal centers so as to conform to the coordination geometries of metal ions. Ag^I as a soft acid, being inclined to coordinate to soft bases such as S- and unsaturated N-containing ligands, is a favorable and fashionable building block or connecting node for coordination polymers.[9] In our continuing efforts to systematically investigate the effects of the linker units of flexible ligands on the structures of Ag^I complexes with thioethers,[10] we designed and synthesized five new flexible pyridyl thioether ligands, bis(2-pyridylthio)methane (**L^1**), 1,3-bis(2-pyridylthio)propane (**L^3**), 1,4-bis(2-pyridylthio)butane (**L^4**), 1,5-bis(2-pyridylthio)pentane (**L^5**), and 1,6-bis(2-pyridylthio)hexane (**L^6**) (see Chart 1). We report herein the construction of eight novel Ag^I coordination architectures forming different architectures by using this series of ligands, and the effects of counteranions and solvents on the coordination modes of ligands and the geometries of Ag^I ions are also discussed in detail.

Chart 1



L^n (n = 1,3,4,5,6)

Experimental Section

Materials and General Methods. All the reagents for syntheses were commercially available and employed without further purification or with purification 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-DAT) studies were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800 °C for complexes **1**−**4** and to 600 °C for complexes **5**−**8**.

Syntheses of Ligands. The five ligands, **L^1**−**L^6**, were prepared by the adoption of a literature procedure for the synthesis of 1,4-bis(phenylthio)butane.[11] The reactions of pyridine-2-thiol with the appropriate dibromomethane, 1,3-dibromopropane, 1,4-dibromobutane, 1,5-dibromopentane, and 1,6-dibromohexane, in the presence of KOH, gave five ligands in good yields, and the products were characterized by ^{1}H NMR and elemental analyses. For **L^1**, yield: 83%. Anal. Found: C, 56.04; H, 4.32; N, 12.01. Calcd for $C_{11}H_{10}N_2S_2$: C, 56.39; H, 4.37; N, 11.95. ^{1}H NMR ($CDCl_3$): δ 5.07 (s, 2H, $-SCH_2S-$), 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 **L^3**, yield: 88%. Anal. Found: C, 59.30; H, 5.31; N, 10.74. Calcd for $C_{13}H_{14}N_2S_2$: C, 59.51; H, 5.38; N, 10.68. ^{1}H NMR ($CDCl_3$): δ 2.14 (p, 2H, J = 6.9 Hz, $-CH_2\mathit{CH_2}CH_2-$), 3.32 (t, 4H, J = 6.9 Hz, $-SCH_2-$), 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). For **L^4**, yield: 84%. Anal. Found: C, 60.61; H, 5.75; N, 10.19. Calcd for $C_{14}H_{16}N_2S_2$: C, 60.83; H, 5.83; N, 10.13. ^{1}H NMR ($CDCl_3$): δ 1.88 (p, 4H, J = 7.2 Hz, $-CH_2\mathit{CH_2CH_2}CH_2-$), 3.21 (t, 4H, J = 7.2 Hz, $-SCH_2-$), 6.94−6.98 (m, 2H, Py-3), 7.14−7.17 (m, 2H,

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Table 1. Crystallographic Data and Structure Refinement Summary for Complexes **1**−**8**

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
chemical formula	$C_{22}H_{20}Ag_3$-$Cl_3N_4O_{12}S_4$	$C_{13}H_{14}Ag$-$ClN_2O_4S_2$	$C_{29}H_{33}Ag_2$-$Cl_5N_4O_8S_4$	$C_{17}H_{22}Ag$-$ClN_2O_5S_2$	$C_{14}H_{16}Ag_2$-$N_4O_6S_2$	$C_{16}H_{16}Ag_2$-$F_6N_2O_6S_4$	$C_{16}H_{19}Ag$-$Cl_4N_2O_4S_2$	$C_{16}H_{20}Ag$-$ClN_2O_4S_2$
fw	1090.62	469.70	1086.82	541.81	616.17	790.29	617.12	511.78
space group	Pccn	$P\bar{1}$	$C2/c$	$P\bar{1}$	$Pbcn$	$P\bar{1}$	$C2/c$	$C2/c$
a/Å	8.497(3)	8.166(3)	22.29(1)	10.567(4)	10.465(7)	5.707(2)	15.806(6)	13.32(1)
b/Å	17.104(6)	9.026(4)	10.782(5)	10.868(4)	9.071(6)	10.006(4)	16.243(6)	18.25(2)
c/Å	23.197(7)	11.548(4)	18.036(8)	11.038(4)	19.92(1)	11.118(4)	19.028(7)	9.232(8)
α/deg	90	78.802(6)	90	67.397(5)	90	93.866(6)	90	90
β/deg	90	83.426(7)	107.389(7)	73.358(6)	90	96.241(7)	97.892(8)	115.52(1)
γ/deg	90	81.531(6)	90	74.758(5)	90	104.65(6)	90	90
V/Å^3	3371(2)	822.6(6)	4135(3)	1104.5(6)	1891(2)	607.6(4)	4839(3)	2025(3)
Z	4	2	4	2	4	1	8	4
D/g cm^{-3}	2.149	1.896	1.746	1.629	2.164	2.160	1.694	1.679
μ/mm^{-1}	2.275	1.660	1.522	1.252	2.333	2.038	1.472	1.357
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
$R^a/R_w{}^b$	0.0409/0.0861	0.0622/0.1397	0.0647/0.1490	0.0508/0.1402	0.0338/0.0884	0.0344/0.0694	0.0621/0.1406	0.0473/0.1207

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

Py-5), 7.43−7.49 (m, 2H, Py-4), 8.40, 8.42 (d, 2H, Py-6). For **L^5**, yield: 81%. Anal. Found: C, 62.25; H, 6.29; N, 9.57. Calcd for $C_{15}H_{18}N_2S_2$: C, 62.03; H, 6.25; N, 9.65. ^{1}H NMR ($CDCl_3$): δ 1.62−1.66 (m, 2H, $-CH_2CH_2\mathit{CH_2}CH_2CH_2-$), 1.72−1.79 (m, 4H, $-SCH_2\mathit{CH_2}CH_2-$), 3.18 (t, 4H, J = 7.2 Hz, $-SCH_2-$), 6.95−6.99 (m, 2H, Py-3), 7.16−7.18 (m, 2H, Py-5), 7.45−7.50 (m, 2H, Py-4), 8.41, 8.43 (d, 2H, Py-6). For **L^6**, yield: 86%. Anal. Found: C, 62.82; H, 6.67; N, 9.24. Calcd for $C_{16}H_{20}N_2S_2$: C, 63.12; H, 6.62; N, 9.20. ^{1}H NMR ($CDCl_3$): δ 1.44−1.49 (m, 4H, $-SCH_2CH_2\mathit{CH_2}-$), 1.68−1.72 (m, 4H, $-SCH_2\mathit{CH_2}CH_2-$), 3.14 (t, 4H, J = 7.2 Hz, $-SCH_2-$), 6.89−6.94 (m, 2H, Py-3), 7.11−7.14 (m, 2H, Py-5), 7.39−7.44 (m, 2H, Py-4), 8.38, 8.41 (d, 2H, Py-6).

Syntheses of Complexes. Colorless single crystals suitable for X-ray analyses for complexes **1**−**3** and **5**−**8** were obtained by the methods as described in the following paragraphs.

[Ag$_3$(L^1)$_2$(ClO$_4$)$_2$](ClO$_4$), 1. A solution of $AgClO_4 \cdot H_2O$ (23 mg, 0.1 mmol) in 10 mL of MeOH was carefully layered on top of a solution of **L^1** (23 mg, 0.1 mmol) in 10 mL of $CHCl_3$ in a test tube. After 3 days at room temperature, colorless single crystals appeared at the boundary between MeOH and $CHCl_3$. Anal. Calcd for $C_{22}H_{20}Ag_3Cl_3N_4O_{12}S_4$: C, 24.23; H, 1.85; N, 5.14. Found: C, 24.06; H, 1.98; N, 5.29. IR (KBr pellet, cm^{-1}): 3010w, 2955w, 1578s, 1561w, 1455s, 1412s, 1375w, 1290w, 1090vs, 1050s, 1008m, 765s, 624s. TGA data (peak position): 261 °C (dec).

{**[AgL^3](ClO$_4$)**}$_\infty$, **2.** Anal. Calcd for $C_{13}H_{14}AgClN_2O_4S_2$: C, 33.24; H, 3.00; N, 5.96. Found: C, 33.47; H, 3.25; N, 5.70. IR (KBr pellet, cm^{-1}): 3043w, 2994w, 2920w, 2861w, 1578s, 1556s, 1454s, 1414s, 1385s, 1282w, 1266w, 1123vs, 1090vs, 1045s, 1008m, 985m, 757s, 724m, 626s. TGA data (peak position): 294 °C (dec).

{**[Ag$_2$(L^4)$_2$](ClO$_4$)$_2$(CHCl$_3$)**}$_\infty$**, 3.** Anal. Calcd for $C_{29}H_{33}Ag_2Cl_5N_4O_8S_4$: C, 32.05; H, 3.06; N, 5.16. Found: C, 32.30; H, 3.21; N, 5.01. IR (KBr pellet, cm^{-1}): 3098w, 3076w, 3042m, 2997w, 2963w, 2943m, 2870w, 1581s, 1555s, 1456s, 1417s, 1311m, 1288m, 1236w, 1147s, 1127vs, 1090vs, 1050s, 1007m, 985m, 766s, 732m, 711m, 623s. TGA data (peak position): 103 and 276 °C (dec).

{**[AgL^4](ClO$_4$)(C$_3$H$_6$O)**}$_\infty$, **4.** A solution of $AgClO_4 \cdot H_2O$ (23 mg, 0.1 mmol) in 10 mL of acetone was carefully layered on top of a solution of **L^4** (28 mg, 0.1 mmol) in 10 mL of chloroform in a test tube. Colorless single crystals were obtained after 3 days. Anal. Calcd for $C_{17}H_{22}AgClN_2O_5S_2$: C, 37.69; H, 4.09; N, 5.17. Found: C, 37.33; H, 4.26; N, 5.01. IR (KBr pellet, cm^{-1}): 3065w, 3042m, 2942m, 2869w, 1706w, 1605w, 1580s, 1554s, 1456s, 1416s, 1311m, 1281m, 1127vs, 1089vs, 1045m, 985m, 940w, 767s, 732m, 710m, 626s. TGA data (peak position): 79 and 283 °C (dec).

{**[(Ag$_2$L^4)](NO$_3$)$_2$**}$_\infty$**, 5.** Anal. Calcd for $C_{14}H_{16}Ag_2N_4O_6S_2$: C, 27.29; H, 2.62; N, 9.09. Found: C, 27.10; H, 2.67; N, 9.01. IR (KBr pellet, cm^{-1}): 3043w, 2931w, 1762w, 1605w, 1578s, 1556s, 1453s, 1378vs, 1281m, 1172s, 1124s, 1088m, 1043m, 1003m, 825m, 757s, 723m, 619m. TGA data (peak position): 216 and 299 °C (dec).

[Ag$_2$L^4(CF$_3$SO$_3$)$_2$]$_\infty$, 6. Anal. Calcd for $C_{16}H_{16}Ag_2F_6N_2O_6S_4$: C, 24.32; H, 2.04; N, 3.54. Found: C, 24.11; H, 2.18; N, 3.64. IR (KBr pellet, cm^{-1}): 3081w, 2938w, 1587m, 1564m, 1466m, 1429m, 1294s, 1282s, 1224s, 1161s, 1025s, 1011m, 773m, 633s, 575m, 515m. TGA data (peak position): 360 °C (dec).

{**[AgL^5](ClO$_4$)(CHCl$_3$)**}$_2$**, 7.** Anal. Calcd for $C_{16}H_{19}AgCl_4N_2O_4S_2$: C, 31.14; H, 3.10; N, 4.54. Found: C, 31.21; H, 3.25; N, 4.49. IR (KBr pellet, cm^{-1}): 3068w, 3030w, 2924m, 2856m, 1578s, 1556s, 1454s, 1414s, 1282w, 1266w, 1236w, 1149s, 1124vs, 1092vs, 1051s, 1009m, 985m, 964m, 755s, 726m, 668w, 625s. TGA data (peak position): 123 and 307 °C (dec).

{**[AgL^6](ClO$_4$)**}$_\infty$**, 8.** Anal. Calcd for $C_{16}H_{20}AgClN_2O_4S_2$: C, 37.55; H, 3.94; N, 5.47. Found: C, 37.31; H, 4.07; N, 5.64. IR (KBr pellet, cm^{-1}): 2997w, 2932w, 2856w, 1580s, 1560m, 1455s, 1415s, 1097vs, 759m, 724w, 626s. TGA data (peak position): 311 °C (dec).

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.

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 were 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. 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 theoretically and riding on the concerned atoms. Crystallographic data and experimental details for structural analyses are summarized in Table 1. The selected bond lengths and angles are listed in Table 2.

Results and Discussion

Thermal Properties of the Complexes. All the eight complexes are air-stable, and the TGA studies show that

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1**−**8**^{a}

	$[Ag_3\mathbf{L}^1{}_2(ClO_4)_2](ClO_4)$ (**1**)		
Ag(1)−N(1)^{i}	2.204(4)	Ag(1)−S(2)	2.474 (2)
Ag(1)−O(1)	2.586(5)	Ag(1)−Ag(2)	3.1349(9)
Ag(2)−N(2)	2.311(4)	Ag(2)−S(1)	2.542 (2)
N(1)^{i}−Ag(1)−S(2)	157.9(1)	N(1)^{i}−Ag(1)−O(1)	115.9(2)
S(2)−Ag(1)−O(1)	84.0(1)	N(2)−Ag(2)−N(2)^{i}	110.5(2)
N(2)−Ag(2)−S(1)^{i}	107.7(1)	N(2)−Ag(2)−S(1)	98.6(1)
S(1)^{i}−Ag(2)−S(1)	133.20(7)		
	$\{[Ag\mathbf{L}^3](ClO_4)\}_\infty$ (**2**)		
Ag(1)−N(1)	2.184(9)	Ag(1)−N(2)^{i}	2.216(8)
Ag(1)−S(2)^{ii}	2.970(3)		
N(1)−Ag(1)−N(2)^{i}	172.9(3)	N(1)−Ag(1)−S(2)^{ii}	93.8(3)
N(2)^{i}−Ag(1)−S(2)^{ii}	92.6(2)		
	$\{[Ag_2\mathbf{L}^4{}_2](ClO_4)_2(CHCl_3)\}_\infty$ (**3**)		
Ag(1)−N(2)^{i}	2.264(6)	Ag(1)−N(1)	2.335(7)
Ag(1)−S(2)^{ii}	2.488(2)	Ag(1)−Ag(1)^{iii}	3.254(2)
N(2)^{i}−Ag(1)−N(1)	108.5(2)	N(2)^{i}−Ag(1)−S(2)^{ii}	129.3(2)
N(1)−Ag(1)−S(2)^{ii}	120.4(2)	N(2)^{i}−Ag(1)−Ag(1)^{iii}	79.7(1)
N(1)−Ag(1)−Ag(1)^{iii}	141.1(2)	S(2)^{ii}−Ag(1)−Ag(1)^{iii}	70.91(6)
	$\{[Ag\mathbf{L}^4](ClO_4)(C_3H_6O)\}_\infty$ (**4**)		
Ag(1)−N(2)	2.307(5)	Ag(1)−N(1)^{i}	2.313(5)
Ag(1)−S(2)	2.520(2)	Ag(1)−Ag(1)^{i}	3.218(1)
N(2)−Ag(1)−N(1)^{i}	99.6(2)	N(2)−Ag(1)−S(2)	132.1(1)
N(1)^{i}−Ag(1)−S(2)	128.2(1)	N(2)−Ag(1)−Ag(1)^{i}	123.1(2)
N(1)^{i}−Ag(1)−Ag(1)^{i}	81.5(1)	S(2)−Ag(1)−Ag(1)^{i}	68.86(4)
	$\{[Ag_2\mathbf{L}^4](NO_3)_2\}_\infty$ (**5**)		
Ag(1)−N(1)^{i}	2.257(4)	Ag(1)−S(1)	2.511(2)
Ag(1)−Ag(1)^{i}	3.160(2)		
N(1)^{i}−Ag(1)−S(1)	151.6(1)	N(1)^{i}−Ag(1)−Ag(1)^{i}	85.7(1)
S(1)−Ag(1)−Ag(1)^{i}	70.99(5)		
	$[Ag_2\mathbf{L}^4(CF_3SO_3)_2]_\infty$ (**6**)		
Ag(1)−N(1)	2.235(3)	Ag(1)−S(1)^{i}	2.466(1)
Ag(1)−O(3)^{ii}	2.515(3)	Ag(1)−O(1)	2.537(3)
Ag(1)−Ag(1)^{i}	2.8635(9)		
N(1)−Ag(1)−S(1)^{i}	153.02(9)	N(1)−Ag(1)−O(3)^{ii}	97.8(1)
S(1)^{i}−Ag(1)−O(3)^{ii}	93.44(8)	N(1)−Ag(1)−O(1)	94.5(1)
S(1)^{i}−Ag(1)−O(1)	109.49(8)	O(3)^{ii}−Ag(1)−O(1)	92.8(1)
	$\{[Ag\mathbf{L}^5](ClO_4)(CHCl_3)\}_2$ (**7**)		
Ag(1)−N(1)	2.172(7)	Ag(1)−N(2)	2.186(7)
N(1)−Ag(1)−N(2)	169.0(2)		
	$\{[Ag\mathbf{L}^6](ClO_4)\}_\infty$ (**8**)		
Ag(1)−N(1)	2.225(5)	N(1)−Ag(1)−N(1)^{i}	172.6(3)

^{a} Symmetry codes. For **1**: i, $-x + 3/2$, $-y + 1/2$, z. For **2**: i, $-x + 1$, $-y + 2$, $-z + 1$; ii, x, $y - 1$, z. For **3**: i, $-x + 1/2$, $y - 1/2$, $-z + 3/2$; ii, x, $-y + 1$, $z + 1/2$; iii, $-x + 1/2$, $-y + 1/2$, $-z + 2$. For **4**: i, $-x + 1$, $-y + 1$, $-z$. For **5**: i, $-x + 2$, y, $-z + 3/2$. For **6**: i, $-x$, $-y + 2$, $-z$; ii, $x - 1$, y, z. For **8**: i, $-x$, y, $-z + 3/2$.

complexes **1**, **2**, **5**, **6**, and **8** are stable under 180 °C and that decompositions start at 200, 197, 180, 290, and 210 °C, respectively. For complex **3**, the first weight loss of 9.7% (calcd 10.8%) corresponds approximately to the solvate chloroform molecules in the range 80−120 °C, which is higher than the boiling point of chloroform (61.2 °C), and the complex decomposes at over 260 °C. For complex **4**, the TGA result shows a weight loss of 9.5% corresponding to the solvate acetone molecules (calcd 10.7%) in the temperature range 60−90 °C, being also higher than the boiling point of acetone (56 °C), and the decomposition occurs at above 275 °C. For **7**, the weight loss of the solvate chloroform molecules occurs between 90 and 130 °C, being higher than the removal temperature of the chloroform in **3**, and this probably is attributed to the Ag···Cl weak interaction (the Ag···Cl distance of 3.308 Å is a little shorter than the sum of van der Waals radii of silver and chlorine atom) between chloroform and Ag^{I}. Compound **7** starts to decompose at 290 °C. The rather high decomposition temperatures of the eight complexes indicate their high stabilities.

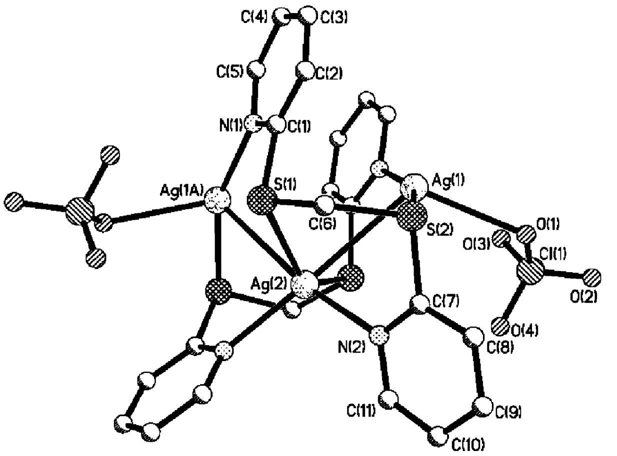
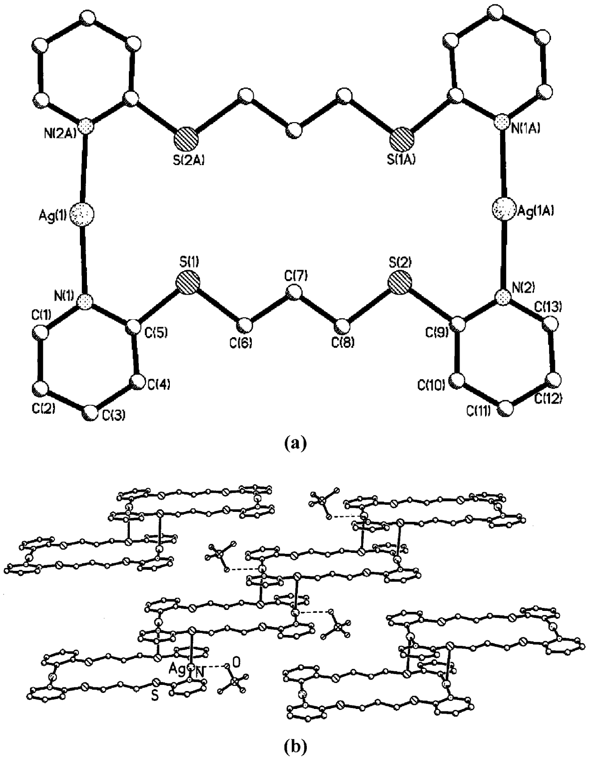


Figure 1. Perspective view of the $[Ag_3\mathbf{L}^1{}_2(ClO_4)_2]^+$ cluster cation in **1**.

Description of Crystal Structures. $[Ag_3(\mathbf{L}^1)_2(ClO_4)_2](ClO_4)$, 1. The crystal structure of **1** consists of a ClO_4^- counteranion and a discrete trinuclear $[Ag_3(\mathbf{L}^1)_2(ClO_4)_2]^+$ cluster cation (Figure 1), which comprises two $\mathbf{L}^1$ ligands, three Ag^{I} ions, and two coordinated ClO_4^- ions and possesses crystallographic C_2 symmetry: the 2-fold axis passes through Ag(2) and the midpoint between Ag(1) and Ag(1A). In the cation cluster, each $\mathbf{L}^1$ ligand behaves in tetradentate coordination fashion. Ag(2) is chelated by a pyridine nitrogen and a sulfur atom at the other end of the same ligand to form two stable 6-membered rings, and the remaining pyridine nitrogen and sulfur atoms of $\mathbf{L}^1$ bridge Ag(1) and Ag(1A) in *cis*-form.

A structural feature of the $[Ag_3(\mathbf{L}^1)_2(ClO_4)_2]^+$ cluster is that the silver ions have two different coordination geometries in which Ag(1) is coordinated to a pyridine nitrogen, a sulfur atom from another ligand, and an oxygen from a ClO_4^-, taking a trigonal planar geometry with the three bond angles of N(1)−Ag(1)−S(2), S(2)−Ag(1)−O(1), and N(1)−Ag(1)−O(1) being 157.9(1)°, 83.96(1)°, and 115.9(2)°, respectively. Ag(1) deviates from the plane of the three donors by ca. 0.1653 Å. In general, the coordination ability of the oxygen atoms of ClO_4^- with Ag^{I} is weaker than those of pyridine nitrogen and sulfur atoms, and the coordination of ClO_4^- to Ag^{I} in this complex is presumably the need for completing the coordination sphere of Ag(1). Ag(2) lies on a 2-fold axis and is coordinated to two pyridine nitrogens and two sulfur atoms from two $\mathbf{L}^1$ ligands to form two stable six-membered chelate rings. The N−Ag and S−Ag bonds fall in the normal range of analogous complexes[7,8] (see Table 2), but the bond lengths of Ag(2)−N(2) (2.311(4) Å) and Ag(2)−S(1) (2.542(2) Å) are longer than those of Ag(1)−N(1) (2.206(4) Å) and Ag(1)−S(2) (2.474(2) Å), respectively. The two pyridine



(a)

(b)

Figure 2. (a) Perspective view of the 20-membered macrometallacyclic ring and (b) the packing diagram of complex **2** showing $\pi-\pi$ stacking interactions between pyridine rings from different chains.

rings coordinated to Ag(1) and Ag(1A) are parallel to each other, while the two pyridine rings near Ag(2) form a dihedral angle of 56.4°.

In the trinuclear structure, the Ag−Ag distances are 3.1349(9) and 4.586 Å for Ag(1)−Ag(2) and Ag(1)−Ag(1A), respectively. The Ag(1)−Ag(2) distance is shorter than the summed van der Waals radii of two silver atoms (3.44 Å),[12] indicating the existence of some weak Ag−Ag interaction.[13]

$\{[AgL^3](ClO_4)\}_\infty$, 2. In $[(AgL^3)^+]_\infty$, the basic unit is the centrosymmetric 20-membered macrometallacyclic ring formed by two **L**^{3} ligands bridging two Ag^I ions with pyridine nitrogens in *cis*-form (Figure 2a). In the dinuclear ring, the Ag···Ag nonbonding distance is 10.546 Å, and the Ag^I center deviates from the basal plane of the four N-donors by ca. 0.119 Å.

In this complex,the **L**^{3} ligand takes tridentate coordinate fashion, and each Ag^I center is coordinated to two pyridine nitrogens and a sulfur atom from three distinct ligands, showing a T-shaped coordination geometry with the N−Ag−N bond angle of 172.9(3)°. The bond length of Ag−N$_{av}$ of 2.20 Å falls within the expected values, while the Ag−S distance of 2.970(3) Å is longer than normal Ag−S bonds,[7,8] indicating weaker interaction (see Table 2). ClO_4^- anions show weak interactions with Ag^I centers with the Ag···O distance of 2.766 Å. The dinuclear structures connect to each other through the weak Ag−S bonds to form infinite chain structures (Figure 2b). The adjacent pyridine rings from different chains are aligned in an offset fashion, being approximately parallel to each other with the centroid−centroid distance of ca. 3.867 Å, indicating the presence of face-to-face $\pi-\pi$ stacking interactions.[14] It is noteworthy that to our knowledge such a staircaselike structure is unprecedented in the Ag^I complexes with thioether ligands, although the Ag^I−thioether system has been well investigated.

$\{[Ag_2(L^4)_2](ClO_4)_2(CHCl_3)\}_\infty$, 3, and $\{[AgL^4](ClO_4)(C_3H_6O)\}_\infty$, 4, Solvent Effect. The structure of **3** has a 2D arrangement of Ag^I ions linked by **L**^{4} ligands, in which the Ag^I center adopts trigonal planar coordination geometry by two pyridine nitrogens and a sulfur atom from three distinct ligands (Figure 3a). The Ag−N bond lengths [2.264(6)−2.335(7) Å] and the average Ag−S distance [2.488(2) Å] (see Table 2) are normal for the Ag^I complexes of heterocyclic thioethers.[7,8] The Ag^I ion further interacts with adjacent Ag^I ion related by a crystallographic center of symmetry, and the Ag−Ag distance of 3.254(2) Å is longer than that of 3.135(9) Å in **1**, but shorter than the sum of the van der Waals radii of two silver atoms.[12]

The basic structural block of the 2D network is the dinuclear unit formed by two **L**^{4} ligands coordinating to two Ag^I ions. In the dinuclear unit, the two pyridylsulfanyl groups from two **L**^{4} ligands bridge two Ag^I ions to form an eight-membered ring (ignoring the Ag−Ag interaction), having an inversion center and adopting a chair configuration with two pyridine rings parallel to each other. Each dinuclear unit adopts bidentate bridging mode using two terminal pyridine nitrogens in *trans*-form to coordinate to Ag^I of other dinuclear units. Four dinuclear units further form a twisted macrometallacycle that is also centrosymmetric (Figure 3a), and adjacent rings are fused into a 2D lamellar structure (Figure 3b). The ClO_4^- ions filling in the cavities of the network and coordinating weakly to Ag^I ions with a Ag···O distance of 2.987 Å may act as templates for the formation of the network and consequently keep the structure stable.

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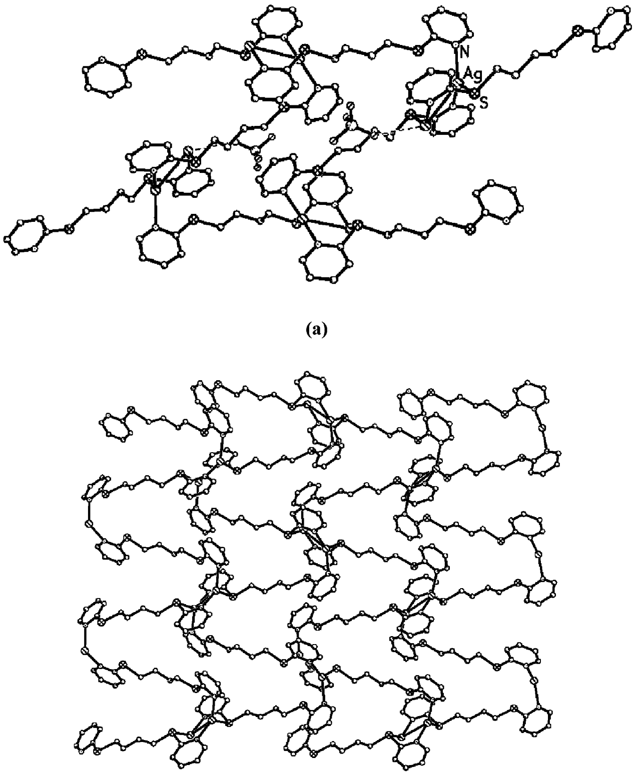


(a)

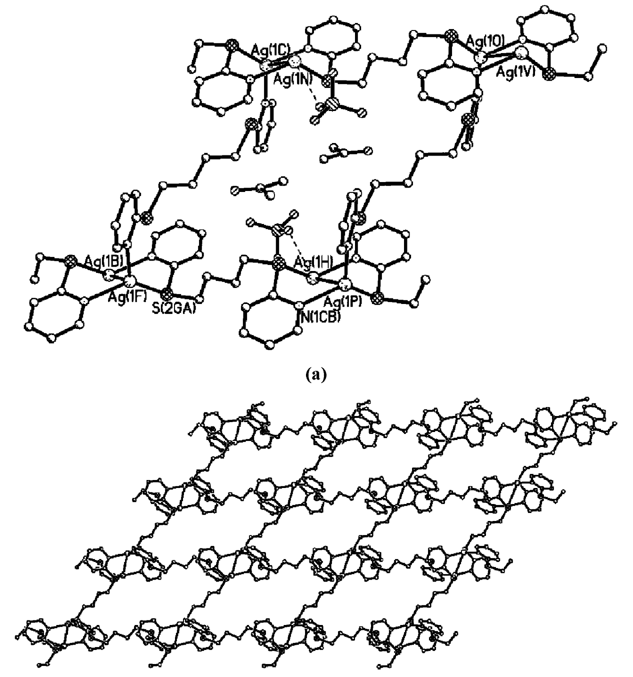
(b)

Figure 3. (a) Macrometallacyclic repeating unit of **3** and (b) the 2D grid of **3**.

In **3**, the ligand is in tridentate bridging fashion with a sulfur atom noncoordinating to Ag^I.

Complex **4** was synthesized by a similar procedure as that of **3**, but acetone was used as solvent instead of MeOH, and a new compound with 2D grid structure was obtained. The Ag^I has similar coordination environment to **3** and is coordinated to two pyridine nitrogens and a sulfur atom from three distinct $\mathbf{L^4}$ ligands. The Ag^I center deviates from the plane of N−S−N by 0.042 Å (Figure 4a). Due to the similar coordination environment of Ag^I in **3** and **4**, the mean values of the Ag−N, Ag−S, and Ag−Ag distances (2.310, 2.520, and 3.218 Å, respectively) in **4** can compare with those of **3** (mean value: 2.300, 2.488, and 3.254 Å, respectively). It is noteworthy that the $\mathbf{L^4}$ ligands in **4** adopt two different coordination modes: a bis-bidentate μ_4-bridging mode bonding to Ag^I ions forming 1D chains along *a* direction, and a bidentate mode to bridge those 1D chains into a 2D network (Figure 4b). It should be pointed out that the bis-bidentate bridging mode has not been documented previously in the Ag^I complexes of pyridyl dithioether ligands. The ClO_4^- and acetones are located in the voids of the network.

From the striking differences between **3** and **4**, we can see that the solvents used in complex preparation have a great effect upon the framework formation of such complexes. The solvents used in the synthesis of **3** and **4** are all noncoordinating and may only play template roles to fill in the cavities, and the differences in size and shape between acetone and chloroform affected the self-assembly process and resulted in different frameworks. Compared with the investigations on the effect of anions, comparatively less attention has been paid to the influence of solvents on the structures of complexes.[5,6] Our study indicates that although to precisely predict how the solvents would affect the process of assembly is still difficult, this offers us an effective method for adjusting their structures.



(a)

(b)

Figure 4. (a) Macrometallacyclic repeating unit of **4** and (b) the 2D grid of **4**.

$\{[Ag_2L^4](NO_3)_2\}_\infty$, 5, and $[Ag_2L^4(CF_3SO_3)_2]_\infty$, 6, Effect of Counteranions. In order to evaluate the influence of counteranions on complex structures, $AgNO_3$ was used instead of $AgClO_4$ to react with $\mathbf{L^4}$, and a new complex **5** composed of an extended cation chain of $[(Ag_2\mathbf{L^4})^{2+}]_\infty$ (Figure 5a) and NO_3^- was obtained, in which Ag^I is coordinated to a pyridine nitrogen and a sulfur atom from two distinct $\mathbf{L^4}$ ligands, with the Ag−N and Ag−S bond lengths of 2.257(4) and 2.511(2) Å, respectively (Table 2).

$\mathbf{L^4}$ adopts a tetradentate bridging mode and coordinates to Ag^I ions to form a 1D chain polymer. The eight-membered ring formed by bonding two Ag^I ions using two pyridylsulfanyl groups from two $\mathbf{L^4}$ ligands has a C_2 axis and adopts a boat configuration. The Ag−Ag distance of 3.160(2) Å is shorter than those found in **3** and **4**. Although **5** is synthesized by the same procedure as that of **3** and **4** by using the same ligand, unlike **4**, the 1D chain structure of **5** has not been linked by $\mathbf{L^4}$ to form a 2D network, probably due to the fact that NO_3^- possesses stronger coordination ability than ClO_4^-, and NO_3^- preferentially bridges the 1D structures by weak Ag···O contacts (the nearest Ag···O distance is 2.702 Å) to generate a quasi-2D network (Figure 5b). The Ag···O contacts consequently prevent the ligands from further bridging the 1D chains to form 2D network.

In order to further investigate the influence of counteranions on the structures of the complexes, Ag^I triflate ($AgCF_3SO_3$) was used instead of $AgNO_3$ to react with $\mathbf{L^4}$, and another new complex **6** was obtained. The $CF_3SO_3^-$ anion

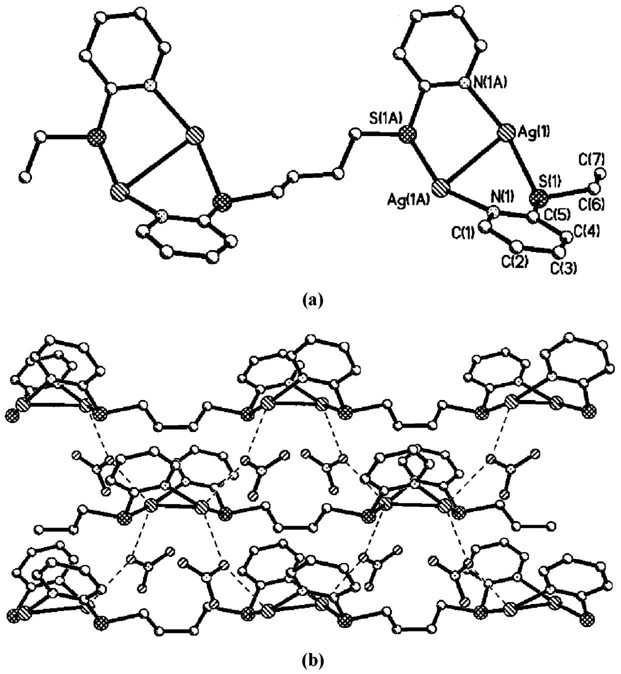


Figure 5. (a) Segment of the cation chain in **5** and (b) the quasi-2D structure formed by the weak bridging of nitrate counterions.

possesses a bigger size than NO_3^-, and its oxygen atoms have stronger coordinating ability than those of NO_3^-.[4a,15] As shown in Figure 6a, each Ag^I center is coordinated to a pyridine nitrogen and a sulfur atom from two different $\mathbf{L^4}$ ligands as well as two oxygen atoms from two $CF_3SO_3^-$ anions, taking a distorted tetrahedral coordination geometry with the bond angles ranging from 92.76° to 153.02°. The Ag−N and Ag−O bond lengths are normal, but the Ag−S distance is shorter than that of other complexes in this paper. The interesting feature of this structure is the exceptionally short Ag−Ag contact [2.864(9) Å] which is even shorter than the distance in metallic silver (2.89 Å),[16] indicating rather strong Ag−Ag interactions.[4l,13]

In **6**, $\mathbf{L^4}$ also adopts a tetradentate bridging mode as the *trans*-form bonding to Ag^I ions to form a 1D chain similar to that of **4**. The $CF_3SO_3^-$ anions bridge the chains with a bidentate fashion through the Ag−O bonds into a 2D network. There are three different sizes of cycles in the 2D network: the smallest is the eight-membered ring similar to those in **3** and **4**; the biggest is the centrosymmetric 22-membered ring formed through bridging four Ag^I atoms with two $\mathbf{L^4}$ ligands and two $CF_3SO_3^-$ anions; the third is the centrosymmetric 10-membered ring containing four silver atoms (including Ag−Ag contact) bridged by a pair of $CF_3SO_3^-$ anions (Figure 6b). These cycles are fused to form a 2D network (Figure 6c), in which all pyridine rings are parallel to each other. In **3** and **4**, the voids of the 2D structures are filled by anions and solvent molecules, while in **6** there is no solvent molecule in the voids, but these spaces are occupied by the CF_3 groups of the $CF_3SO_3^-$ anions to sustain the structure. Structure **6** might be considered as a self-sustained framework.

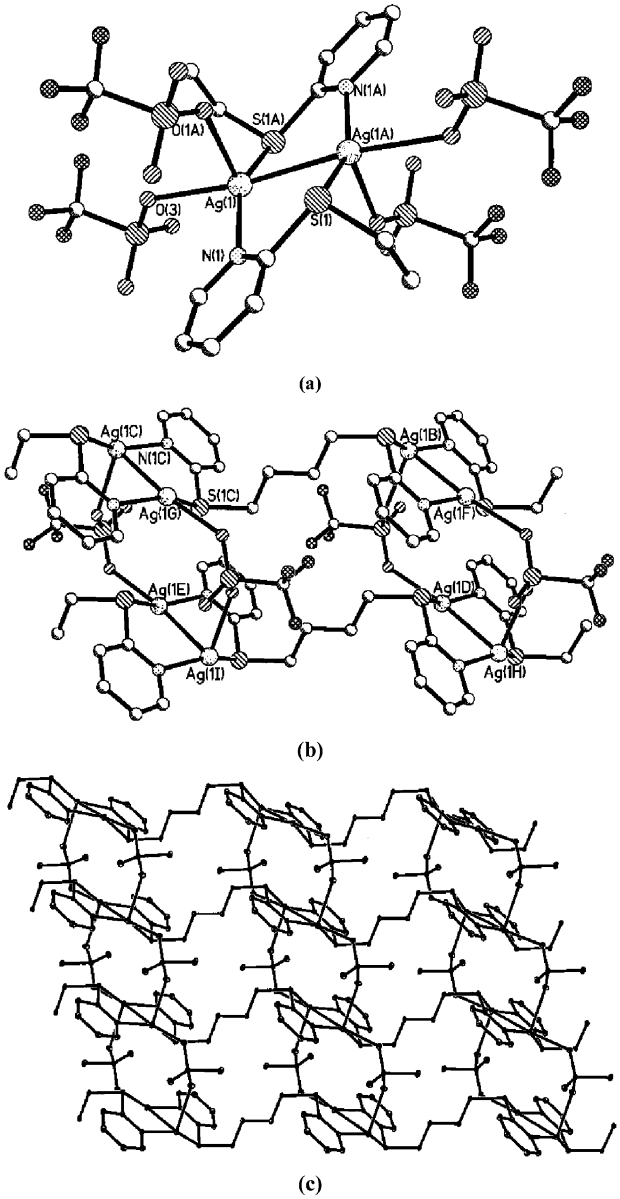


Figure 6. (a) Coordination environment of Ag^I, (b) the macrometallacyclic repeating unit, and (c) the 2D grid of **6**.

In a systematic investigation of the role of counteranions in the Ag^I complexes of linear chain dinitriles $NC(CH_2)_n$-CN ($n = 2-7$), G. Ciani et al.[4j] conclude that the anions in these species, except the $CF_3SO_3^-$ anion, do not interact with the Ag^I ions but play template roles in that the cavities in the nets are dependent on the anion dimensions. In an investigation of the Ag^I complexes with di-Schiff bases by Chen and co-workers,[4l] although all investigated anions including $CF_3SO_3^-$ anion do not coordinate to Ag^I ions, these anions can influence the coordination modes of ligands to result in different Ag^I helicates. In our systems, the NO_3^- anion plays weak bridging role in the formation of **5** due to its relatively strong coordination ability compared to that of ClO_4^-, while ClO_4^- only acts as counteranion in the

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(15) (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2755. (c) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1995**, *117*, 4562. (d) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Inorg. Chem.* **1995**, *34*, 5698.

(16) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, 1984; p 1368.

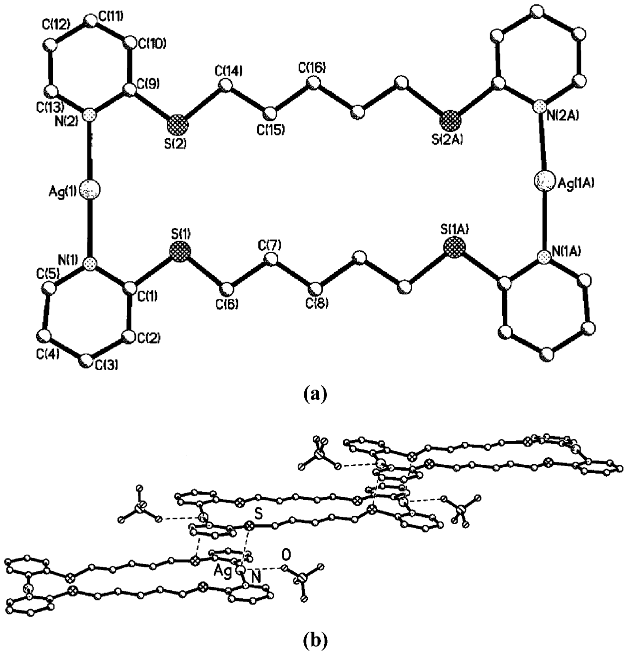

Figure 7. (a) Perspective view of the dinuclear cation in **7** and (b) the formation of a staircaselike chain via Ag···S weak interactions.

formation of **3** and **4** due to its poor coordination ability. In the case of **6**, the $CF_3SO_3^-$ anion has stronger coordination ability toward Ag^I with its oxygen atoms and larger CF_3 group, so $CF_3SO_3^-$ anions not only participate in coordinating to Ag^I ions but also play a key role in the stabilization of the complex. In general, the structural differences between **3**, **4**, **5**, and **6** show the profound effect of anions on the framework formation of silver coordination complexes, which might be explained due to their differences in sizes and coordination ability.[4,5]

$\{[AgL^5](ClO_4)(CHCl_3)\}_2$, 7. Complex **7** is composed of the $[M_2(\mathbf{L^5})_2]^{2+}$ dinuclear cation, noncoordinating ClO_4^- anions, and $CHCl_3$ molecules. The Ag^I center is coordinated to two pyridine nitrogens from distinct $\mathbf{L^5}$ ligands in a slightly distorted linear geometry with the N−Ag−N bond angle of 169.0(2)°, and the Ag−N bond lengths (mean value 2.179(7) Å) are similar to that of **2**. Two $\mathbf{L^5}$ ligands and two Ag^I ions form a slightly twisted rectangular 24-membered macrometallacycle with the Ag···Ag separation of 13.047 Å (Figure 7a). ClO_4^- anions show weak interactions with Ag^I centers (the distance of Ag···O is 2.801 Å). The Ag···S distance of 3.005 Å between adjacent macrometallacycles is slightly greater than that in **2** but significantly shorter than the sum of the van der Waals radii of Ag and S (3.52 Å),[13] indicating the existence of Ag···S interactions. A staircaselike quasichain structure similar to **2** is formed by the Ag···S weak interactions (Figure 7b). Different from **2**, the nearest separation between pyridine rings in **7** is ca. 4.351 Å, indicating the absence of $\pi-\pi$ stacking interactions.

$\{[AgL^6](ClO_4)\}_\infty$, 8. The structure of **8** reveals that it is composed of ClO_4^- anions and $\{[Ag\mathbf{L^6}]^+\}_\infty$ cations which make an infinite 1D chain just like a continuous triangular wave (zigzag mode, see Figure 8a). The basic repeating unit is $[Ag\mathbf{L^6}]^+$, and the adjacent $[Ag\mathbf{L^6}]^+$ units are linked by the bridges of $\mathbf{L^6}$ ligands with the Ag···Ag distance of 12.97 Å. The Ag^I center adopts a linear coordination geometry coordinated by two pyridine nitrogens from two distinct $\mathbf{L^6}$ ligands, and the N−Ag−N angle of 172.63° is close to those of two coordinated Ag^I complexes (172−180°).[17] The Ag−N bond distance of 2.225(5) Å falls in the expected range of the complexes of Ag^I and pyridine nitrogen.[7,8] The distances between adjacent chains are rather short due to the weak Ag···S (3.009 Å) interactions, and a quasi-3D structure is formed by this interaction (Figure 8b).

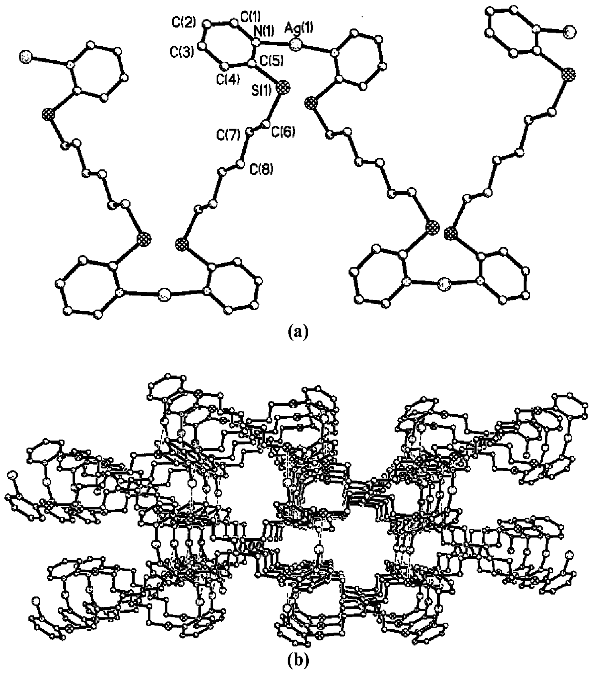

Figure 8. (a) Portion of cation chain in **8** and (b) the 3D structure formed by Ag···S weak interactions.

Although $\mathbf{L^1}-\mathbf{L^6}$ differ only in the number of CH_2 groups in their alkyl chains, they form quite different metal−organic architectures.[18] By comparing the structures of the eight complexes, it is clear that the conformations of ligands in the complexes are related to the number of methylene spacers. When the number of methylenes of the spacer is odd (1,3,5), the ligand usually adopts a *cis*-form with the pyridine nitrogens *cis*-bridging Ag^I centers; when the number of the methylene spacers is even (4 and 6), the ligand usually adopts a *trans*-form with the pyridine nitrogens *trans*-bridging Ag^I centers. Apparently, the pyridine rings are brought to rotate with the pyridine nitrogen, and the adjacent sulfur atom adopts a *cis*-form when the ligands coordinate to Ag^I ions. This indicates that geometrical effects seem to be more important than electronic effects in these systems. This finding might provide a general rule for other similar heterocyclic dithioether ligands thereby increasing the possibility for predicting the structures of their complexes. Meanwhile, the flexible $(CH_2)_n$ spacers allow the ligands to rearrange so as to minimize steric interactions between coordinated groups, and the wide coordination geometry of

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(17) Yamaguchi, T.; Lindqvist, O. *Acta Chem. Scand., Ser. A* **1983**, *37*, 685 and references therein.

(18) Although we tried many times, the single crystal of the Ag^I complex with 1,2-bis(2-pyridylthio)ethane has not been obtained.

Ag^I results in the structural diversity of the complexes. In general, the subtle variations of spacers may cause the ligands to adopt different coordination modes and result in complexes with quite different structural topologies.

Conclusion and Comments

Five new pyridyl dithioether ligands have been designed and synthesized, and the self-assembly of these ligands with Ag^I salts yields eight new metal−organic architectures with structures ranging from dinuclear to 2D. Although the five ligands are very similar in structure, they form quite different architectures with Ag^I depending on the parity and number of methylene spacers in the ligands, implying that the subtle variations in ligands will result in quite different complexes with different structural topologies. This indicates the merits of such flexible ligands as building blocks for the construction of networks with diverse structural motifs. Furthermore, solvents and counteranions also play very important roles in affecting the framework formation of such systems. These results offer us effective means for controlling the formation of complexes with tailored structures and properties.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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