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Coordination Networks with Flexible Ligands Based on Silver(I) Salts: Complexes of 1,3-Bis(phenylthio)propane with Silver(I) Salts of PF_6^-, CF_3COO^-, $CF_3CF_2COO^-$, $CF_3CF_2CF_2COO^-$, *p*-TsO^-, and $CF_3SO_3^-$

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The synthesis and characterization of nine coordination networks based on 1,3-bis(phenylthio)propane, **L^3**, and silver(I) salts of PF_6^- (**1**), CF_3COO^- (**2**), $CF_3CF_2COO^-$ (**3**), $CF_3CF_2CF_2COO^-$ (**4**), *p*-TsO^- (**5**, **6**), and $CF_3SO_3^-$ (**7**–**9**) are reported. Only **1** and other "isostructural" complexes with weakly coordinating anions such as ClO_4^- and SbF_6^- are of the host–guest type. In all the other complexes, the anions and the acetone molecules, when present, are coordinated to the metal. Most of the complexes studied here form a 2D-coordination network. Only **4** and **5** adopt a polymer-like chain structure. The packing of the chains of **4** is pseudohexagonal compact, while that of **5** is of the centered type. In complex **1**, the silver atom is tetrahedrally coordinated to the sulfur atoms of four different ligands. The PF_6^- anions and acetone molecules, sandwiched between silver–ligand cationic sheets, are held through van der Waals interactions. In each of the three perfluorocarboxylates (**2**–**4**), two silver atoms are joined by the anions in a diatomic bridging mode. The Ag···Ag distances are sufficiently short to indicate weak metal···metal interactions. The dimeric units in **2** and **3** are interconnected through the ligands, thereby generating a 2D-network of neutral sheets, while, in **4**, the dimeric units are bound to four ligands and a 1D-coordination polymer is generated. In the case of the sulfonate anions (*p*-TsO^- and $CF_3SO_3^-$), the crystallization solvent influences the structure adopted. Thus, in **5**, **7**, and **9** obtained from petroleum ether, or other nonpolar solvents, two silver atoms are bound in a double-bridge fashion, while a monobridge mode is noted for **6** and **8**, both recrystallized from diethyl ether. In **8**, both bridging types are observed. The thermogravimetric investigation, in the room temperature–450 °C interval, of complexes **1**, **3**, and **7**, which incorporate acetone molecules in their crystal structures, reveals a two-step weight loss for **1** (the acetone molecules are lost first followed by the ligands, leaving behind the silver salt), while complexes **3** and **7** decompose in a single step to metallic silver.

Introduction

In the last two decades, there has been considerable activity in the design and synthesis of solid frameworks.[1] The self-assembly of metal−organic coordination polymers has attracted a great deal of attention because of their potential applications as functional materials.[2] The properties of coordination polymer materials are to some extent dependent on their network topology. Thus, it is of interest to understand and control the subtle factors that influence the formation of these supramolecular networks. Moreover, the strategy consisting of varying the coordination site and/or the size and shape of the ligand is usually employed in crystal engineering to synthesize new coordination polymers. The metal centers are linked with rigid bridging ligands[3] or less frequently by flexible building blocks.[4] However, for a given

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ligand, the structure of the resulting coordination polymer is difficult to predict because of factors affecting the framework formation, such as the solvent,[5] the counteranion,[6] and the metal-to-ligand ratio.[7] The ability of the sulfur atom, as a soft base, to coordinate to the silver atom, a soft acid, has been exploited in this study. We have previously attempted to analyze the effects of the counteranions and the length of the spacer on the topology of the coordination polymer on the basis of the mutual attraction between the soft silver atom and the soft sulfur atom.[4b,7] We have reported earlier on the structures of several silver(I) complexes with the bis(phenylthio)methane ligand.[8] In an effort to rationalize further the structural effect of the ligand spacer and the counteranion, we have now synthesized and characterized a number of complexes, all based on the 1,3-bis(phenylthio)propane ligand, **L³**, but with different classes of anions: weakly coordinating ones such as PF_6^- (**1**); perfluorocarboxylates CF_3COO^- (**2**), $CF_3CF_2COO^-$ (**3**), $CF_3CF_2CF_2COO^-$ (**4**); sulfonates *p*-TsO⁻ (**5**, **6**), $CF_3SO_3^-$ (**7**−**9**). The crystal structures of **1**, **3**, and **7** incorporate a molecule of solvent, either as a guest or as a coordinating molecule. The ease of release of these molecules is examined by thermogravimetric analysis.

In this study, supramolecular isomerism was observed for complexes **5**, **6** (with *p*-TsO⁻), and **7**−**9** (with $CF_3SO_3^-$). The isomerism of supramolecular networks, which has been noted in similar systems, is influenced by several factors, such as the metal-to-ligand ratio[9] or the guest molecule.[10] The isomerism reported herein occurred as a consequence of the solvent used for recrystallization.

Experimental Section

Materials and General Methods. Except for the ligand, all the reagents required for the syntheses were commercially available and employed without further purification. The elemental analyses were performed by the Laboratoire d'analyse élémentaire (Université de Montréal). The IR spectra (KBr pellets) were recorded on a Perkin-Elmer 1750 FTIR spectrometer (4000−450 cm^{-1}). ^{1}H (400 and 300 MHz), ^{13}C{^{1}H} (100.56 MHz), and ^{19}F (376.31 MHz) solution NMR spectra were recorded at 25 °C, either on a Bruker ARX400, AMX300, or AV300 spectrometer. Chemical shifts, reported in parts per million, were referenced to tetramethylsilane as an internal standard for ^{1}H and ^{13}C{^{1}H} spectra, while the chemical shifts for ^{19}F were referenced to $C_6H_5CF_3$ (−63.9 ppm). The weight loss experiments were carried out on a TG Instrument 2950 TGA HR V5.3C thermal analyzer at a scan rate of 10 °C min^{-1}.

Syntheses. The ligand 1,3-bis(phenylthio)propane, **L³**, was synthesized by following a literature method.[11] Yield: 82%. Anal. Found: C, 69.36; H, 6.35. Calcd for $C_{15}H_{16}S_2$: C, 69.18; H, 6.19. ^{1}H NMR (acetone-d_6, 300 MHz): δ 2.021 (qt, 2H, $-SCH_2CH_2CH_2S-$), 3.082 (t, 4H, $-SCH_2CH_2CH_2S-$), 7.151−7.364 (m, 10H, C_6H_5-). ^{13}C{^{1}H} NMR (acetone-d_6, 100.56 MHz): 34.21 (SCC), 31.80 (SCC), 136.67, 129.37, 129.16, 126.19 (C_6H_5).

$\{[Ag_2L^3_4](PF_6)_2(CH_3COCH_3)_2\}_\infty$ (1). To a solution of $AgPF_6$ (290 mg, 1.15 mmol) in acetone (10 mL) was added a solution of **L³** (0.25 mL, 1.08 mmol) in diethyl ether (5 mL) and heated at 50 °C for 30 min. Evaporation of the solvent in the dark and at room temperature produced single crystals suitable for X-ray analysis. Yield: 70% based on $AgPF_6$. Anal. Found: C, 47.83; H, 4.33. Calcd for $C_{66}H_{76}Ag_2F_{12}O_2S_8P_2$: C, 47.65; H, 4.60. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.104 (qt, 2H, $-S(CH_2)(CH_2)-$), 3.312 (t, 4H, $-S(CH_2)-$), 7.341−7.523 (m, 10H, C_6H_5-). ^{19}F{^{1}H} NMR (DMSO-d_6, 376.31 MHz): −71.851 and −74.293, (d, *F*−P). IR (KBr, cm^{-1}): 1637 m, 1583 m, 1479 s, 1438 s, 1303 m, 1146 m, 1086 m, 1025 m, 843 vs, 737 s, 690 s, 560 s, 501 m. Attempts to obtain complexes with different stoichiometries failed. The various intended ligand:silver salt ratios investigated (1:1, 1:2, 1:3, 2:1) always give crystals identical with **1**.

$[Ag_2L^3(CF_3CO_2)_2]_\infty$ (2). A solution of $AgCF_3CO_2$ (217.2 mg, 0.98 mmol) in acetone (10 mL) was stirred with a solution of **L³** (0.20 mL, 0.87 mmol) in diethyl ether (10 mL) at 50 °C for 70 min. The resulting solution was kept for 3 days in the dark at room temperature to obtain single crystals suitable for X-ray analysis. Yield: 70% based on $AgCF_3CO_2$. Anal. Found: C, 32.68; H, 2.18. Calcd for $C_{19}H_{16}Ag_2F_6O_4S_2$: C, 32.50; H, 2.30. ^{1}H NMR (acetone-d_6, 300 MHz): δ 2.097 (qt, 2H, $-S(CH_2)(CH_2)-$), 3.282 (t, 4H, $-S(CH_2)-$), 7.281−7.553 (m, 10H, C_6H_5-). ^{19}F{^{1}H} NMR (acetone-d_6, 376.31 MHz): −74.148 (s, *F*−C). IR (KBr, cm^{-1}): 1685 vs, 1583 m, 1479 s, 1436 s, 1208 s, 1025 m, 838 s, 804 s, 724 s, 689 m.

$[Ag_2L^3(CF_3CF_2CO_2)_2(CH_3COCH_3)]_\infty$ (3). A 10 mL volume of acetone was added to 360 mg (1.33 mmol) of $AgCF_3CF_2CO_2$. The mixture was stirred with a solution of **L³** (0.20 mL, 0.87 mmol) at 60 °C for 140 min. The resulting solution was layered on diethyl ether and then stored at room temperature in the dark. Several days later, relatively large colorless crystals appeared. Yield: 35% based on $AgCF_3CF_2CO_2$. One such crystal was cut into a platelet and mounted for X-ray analysis. Anal. Found: C, 33.84; H, 2.61. Calcd for $C_{24}H_{22}Ag_2F_{10}O_5S_2$: C, 33.51; H, 2.58. ^{1}H NMR (DMSO-d_6, 300 MHz): 2.053 (qt, 2H, $-S(CH_2)(CH_2)-$), 3.194 (t, 4H, $-S(CH_2)-$), 7.236−7.449 (m, 10H, C_6H_5-). ^{19}F{^{1}H} NMR (DMSO-d_6, 376.31 MHz): −84.064 (CF_3) and −119.248 (CF_3CF_2). IR (KBr, cm^{-1}): 1679 vs, 1481 m, 1438 m, 1329 m, 1210 m, 1159 s, 1030 s, 817 m, 734 m, 690 m.

$[AgL^3(CF_3CF_2CF_2CO_2)]_\infty$ (4). A solution of $AgCF_3CF_2CF_2CO_2$ (252 mg, 0.785 mmol) in acetone (10 mL) was stirred with a solution of **L³** (0.25 mL, 1.08 mmol) in diethyl ether (5 mL) at 60 °C. The mixture was refluxed for 70 min and layered on hexane at room temperature and left in the dark. After 3 days, single crystals suitable for X-ray analysis were obtained. Yield: 35% based on

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$\mathrm{AgCF_3CF_2CF_2CO_2}$. Anal. Found: C, 39.44; H, 2.34. Calcd for $\mathrm{C_{19}H_{16}AgF_7O_2S_2}$: C, 39.26; H, 2.77. ^{1}H NMR (acetone-d_6, 300 MHz): δ 2.046 (qt, 2H, $-\mathrm{S(CH_2)(C}H_2\mathrm{)}-$), 3.208 (t, 4H, $-\mathrm{S(C}H_2\mathrm{)}-$), 7.223−7.466 (m, 10H, $\mathrm{C_6}H_5-$). ^{19}F{^{1}H} NMR (acetone-d_6, 376.31 MHz): −81.986 ($\mathrm{C}F_3$), −116.658 ($\mathrm{CF_3C}F_2\mathrm{CF_2}$), −127.852 ($\mathrm{CF_3CF_2C}F_2$).

[AgL^3(*p*-TsO)]$_\infty$ (5). A solution of Ag(*p*-TsO) (302.9 mg, 1.08 mmol) in acetone (5 mL) was stirred with a solution of **L^3** (0.20 mL, 0.87 mmol) in diethyl ether (5 mL) at 60 °C for 150 min. This solution was filtered and layered on petroleum ether at room temperature. After 2 days in the dark, the mixture yielded single crystals suitable for X-ray analysis. These crystals were then stored in a freezer to avoid their eventual decomposition. Yield: 65% based on $\mathrm{Ag(C_7H_7O_3S)}$. Anal. Found: C, 48.55; H, 4.15. Calcd for $\mathrm{C_{22}H_{23}AgO_3S_3}$: C, 48.98; H, 4.30. ^{1}H NMR (acetone-d_6, 400 MHz): δ 1.963 (qt, 2H, $-\mathrm{S(CH_2)(C}H_2\mathrm{)}-$), 2.424 (s, 3H, $\mathrm{C}H_3\mathrm{C_6H_4SO_3}$), 3.175 (t, 4H, $-\mathrm{S(C}H_2\mathrm{)}-$), 7.304−7.403 (m, 10H, $\mathrm{C_6}H_5-$), 7.762−7.791 (m, 4H, $\mathrm{CH_3C_6}H_4\mathrm{SO_3}$). IR (KBr, cm^{-1}): 1583 m, 1480 m, 1438 m, 1189 vs, 1131 m, 1044 m, 1014 m, 816 m, 737 s, 690 s, 565 m.

[AgL^3(*p*-TsO)]$_\infty$ (6). The synthesis of this complex is identical with that of **5**, except that **6** was recrystallized from diethyl ether at room temperature. The mixture was kept in the dark for 2 days to obtain single crystals suitable for X-ray analysis. Yield: 65% based on Ag(*p*-TsO). Anal. Found: C, 48.56; H, 4.15. Calcd for $\mathrm{C_{22}H_{23}AgO_3S_3}$: C, 48.98; H, 4.30. ^{1}H NMR (acetone-d_6, 400 MHz): δ 2.045 (qt, 2H, $-\mathrm{S(CH_2)(C}H_2\mathrm{)}-$), 2.403 (s, 3H, $\mathrm{C}H_3\mathrm{C_6H_4SO_3}$), 3.202 (t, 4H, $-\mathrm{S(C}H_2\mathrm{)}-$), 7.189−7.464 (m, 10H, $\mathrm{C_6}H_5-$), 7.761−8.012 (m, 4H, $\mathrm{CH_3C_6}H_4\mathrm{SO_3}$). IR (KBr, cm^{-1}): 3439 m, 1583 m, 1480 m, 1438 m, 1384 s, 1190 vs, 1131 m, 1044 m, 1015 m, 815 m, 738 s, 690 s, 565 m.

[Ag$_2$L^3(CF$_3$SO$_3$)$_2$(CH$_3$COCH$_3$)]$_\infty$ (7). A solution of $\mathrm{AgCF_3SO_3}$ (617.9 mg, 2.4 mmol) in acetone (5 mL) was stirred with a solution of **L^3** (0.20 mL, 0.87 mmol) in diethyl ether (5 mL) at 60 °C for 90 min. The resulting mixture was layered on petroleum ether and kept at room temperature in the dark. After 4 days, single crystals suitable for X-ray analysis were obtained. Yield: 40% based on $\mathrm{AgCF_3SO_3}$. Anal. Found: C, 28.29; H, 2.27. Calcd for $\mathrm{C_{20}H_{22}Ag_2F_6O_7S_4}$: C, 28.86; H, 2.66. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 2.115 (qt, 2H, $-\mathrm{S(CH_2)(C}H_2\mathrm{)}-$), 3.343 (t, 4H, $-\mathrm{S(C}H_2\mathrm{)}-$), 7.362−7.574 (m, 10H, $\mathrm{C_6}H_5-$). ^{19}F{^{1}H} NMR (DMSO-d_6, 376.31 MHz): −79.015 (s, $F-\mathrm{C}$). IR (KBr, cm^{-1}): 1480 m, 1438 m, 1258 vs, 1178 s, 1033 s, 737 s, 690 s, 642 s, 580 m, 519 m.

[Ag$_2$L^3(CF$_3$SO$_3$)$_2$]$_\infty$ (8). To a solution of $\mathrm{AgCF_3SO_3}$ (274.7 mg, 1.07 mmol) in acetone (5 mL) was added a solution of **L^3** (0.20 mL, 0.87 mmol) in diethyl ether (5 mL). The mixture was stirred at 50 °C for 40 min and then layered on diethyl ether and left to stand in the dark at room temperature. Crystals suitable for an X-ray study appeared after 3 weeks. Yield: 38% based on $\mathrm{AgCF_3SO_3}$. Anal. Found: C, 26.78; H, 2.15. Calcd for $\mathrm{C_{17}H_{16}Ag_2F_6O_6S_4}$: C, 26.37; H, 2.08. ^{1}H NMR (acetone-d_6, 300 MHz): 2.255 (qt, 2H, $-\mathrm{S(CH_2)(C}H_2\mathrm{)}-$), 3.186 (t, 4H, $-\mathrm{S(C}H_2\mathrm{)}-$), 7.206−7.415 (m, 10H, $\mathrm{C_6}H_5-$). ^{19}F{^{1}H} NMR (acetone-d_6, 376.31 MHz): −79.210 (s, $F-\mathrm{C}$). IR (KBr, cm^{-1}): 1630 m, 1481 m, 1438 m, 1385 s, 1260 vs, 1178 m, 1089 m, 1034 s, 739 m, 691 m, 645 m.

[Ag$_2$L^3(CF$_3$SO$_3$)$_2$]$_\infty$ (9). To generate different structures the molar ratio of silver salt to ligand was modified. To a solution of $\mathrm{AgCF_3SO_3}$ (614 mg, 2.4 mmol) in acetone (5 mL) was added a solution of **L^3** (0.30 mL, 1.3 mmol) in diethyl ether (5 mL). The mixture was stirred at 60 °C for 160 min and then layered on hexane and left to stand in the dark at room temperature. Crystals suitable for an X-ray study appeared after 3 weeks. Yield: 81% based on $\mathrm{AgCF_3SO_3}$. These crystals had a morphology clearly different from those of **8**. Anal. Found: C, 26.06; H, 1.91. Calcd for $\mathrm{C_{17}H_{16}Ag_2F_6O_6S_4}$: C, 26.37; H, 2.08. ^{1}H NMR (acetone-d_6, 300 MHz): 2.347 (qt, 2H, $-\mathrm{S(CH_2)(C}H_2\mathrm{)}-$), 3.356 (t, 4H, $-\mathrm{S(C}H_2\mathrm{)}-$), 7.312−7.548 (m, 10H, $\mathrm{C_6}H_5-$). ^{19}F{^{1}H} NMR (acetone-d_6, 376.31 MHz): −78.868 (s, $F-\mathrm{C}$). IR (KBr, cm^{-1}): 3434 m, 1623 m, 1257 vs, 1172 s, 1030 s, 742 m, 687 m, 636 s, 521 m.

{[Ag$_2$L^3$_4$](ClO$_4$)$_2$(CH$_3$COCH$_3$)$_2$}$_\infty$ (10) and {[Ag$_2$L^3$_4$](SbF$_6$)$_2$(CH$_3$COCH$_3$)$_2$}$_\infty$ (11). Other complexes related to **1** were synthesized[12] using weakly coordinating anions: $\mathrm{ClO_4^-}$ (**10**); $\mathrm{SbF_6^-}$ (**11**). Their syntheses follow the procedure detailed for **1**. These will not be fully described as the acetone molecules were too disordered to be precisely located by X-ray analysis.

Caution! Although we met no problems in handling perchlorate salts, great care should be taken due to their potentially explosive nature.

Crystal Structure Determinations. X-ray diffracted intensities were measured on a Bruker AXS Platform diffractometer equipped with a SMART 2K CCD area detector using monochromatic Cu Kα (λ = 1.541 78 Å) radiation. The X-ray intensity data were processed with the program SAINT.[13] An empirical absorption correction, based on multiple measurements of equivalent reflections, was applied using the program SADABS.[14] The space group was confirmed by the XPREP[15] routine in the program SHELXTL.[16] The structures were solved by direct methods and refined by full-

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(12) {[Ag$_2$L^3$_4$](ClO$_4$)$_2$(CH$_3$COCH$_3$)$_2$}$_\infty$ (**10**): $\mathrm{C_{66}H_{76}Ag_2O_{10}Cl_2S_8}$; fw 1572.47. This was synthesized using the same conditions as **1** with $\mathrm{AgClO_4{\cdot}H_2O}$ (178 mg, 0.79 mmol) and **L^3** (0.35 mL, 1.52 mmol). Yield: 65% based on $\mathrm{AgClO_4{\cdot}H_2O}$. A TGA curve indicated a two-step decomposition (Figure S9). First, two acetone molecules were released between 95 and 110 °C (expt/theor = 7.19/7.38%). In a second step occurring between 180 and 310 °C, the ligands were eliminated (expt/theor = 68.56/66.24%). The residue consisted of $\mathrm{AgClO_4}$. This result is coherent with the analytical results. Anal. Found: C, 49.94; H, 4.53. Calcd for $\mathrm{C_{66}H_{76}Ag_2O_{10}Cl_2S_8}$: C, 50.41; H, 4.87. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.813 (qt, 2H, $-\mathrm{S(CH_2)(C}H_2\mathrm{)}-$), 3.064 (t, 4H, $-\mathrm{S(C}H_2\mathrm{)}-$), 7.272−7.694 (m, 10H, $\mathrm{C_6}H_5-$). IR (KBr, cm^{-1}): 3447 m, 3057 w, 2916 w, 1634 s, 1583 m, 1479 s, 1438 s, 1297 w, 1137 s, 1073 vs, 1025 m, 934 w, 737 s, 689 s, 474 w. Crystal data: monoclinic, $P2_1/c$; $a = 26.3970(1)$, $b = 12.8558(2)$, $c = 20.9301(3)$ Å; $\beta = 94.47(1)°$; $V = 3540.54(8)$ Å^3; $Z = 4$; μ(Cu Kα) = 7.15 mm^{-1}; Nref 6997, Npar 398; R1 ($I > 2\sigma(I)$) = 0.0597, wR2 = 0.1550, R1 (all data) = 0.0808, wR2 = 0.1674, $S = 0.947$. The perchlorate anions, the acetone molecules, and half of the ligands are disordered. All attempts to form complexes with different stoichiometries failed. The starting ligand:silver perchlorate ratios (1:1, 1:2, 1:3, 1:4, 2:1, 2:3; 2:5) always produced crystals with the same unit-cell dimensions as **10**. {[Ag$_2$L^3$_4$](SbF$_6$)$_2$(CH$_3$COCH$_3$)$_2$}$_\infty$ (**11**): $\mathrm{C_{66}H_{76}Ag_2F_{12}O_2S_8Sb_2}$; fw = 1845.07. This was synthesized using the same conditions as **1** with $\mathrm{AgSbF_6}$ (164 mg, 0.48 mmol) and **L^3** (0.35 mL, 1.52 mmol). Yield: 74% based on $\mathrm{AgSbF_6}$. Anal. Found: C, 42.88; H, 3.89. Calcd for $\mathrm{C_{66}H_{76}Ag_2F_{12}O_2S_8Sb_2}$: C, 42.96; H, 4.15. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 1.845 (qt, 2H, $-\mathrm{S(CH_2)(C}H_2\mathrm{)}-$), 3.073 (t, 4H, $-\mathrm{S(C}H_2\mathrm{)}-$), 7.281−7.598 (m, 10H, $\mathrm{C_6}H_5-$). IR (KBr, cm^{-1}): 3435 w, 3057 m, 2918 m, 1583 s, 1480 s, 1438 s, 1334 w, 1301 w, 1257 w, 1158 w, 1089 m, 1069 w, 1024 s, 737 vs, 691 vs, 664 vs, 491 m. Crystal data: monoclinic, $P2_1/c$; $a = 27.1584(2)$, $b = 13.0497(2)$, $c = 20.5848(3)$ Å; $\beta = 97.79(1)°$; $V = 3614.10(9)$ Å^3; $Z = 4$; μ(Cu Kα) = 12.87 mm^{-1}; Nref 7095, Npar 434; R1 ($I > 2\sigma(I)$) = 0.0528, wR2 = 0.1454, R1 (all data) = 0.0695, wR2 = 0.1529, $S = 1.045$. The fluorine atoms have a slight oscillating disorder while the acetones are much more disordered. The silver atoms and the ligands form cationic sheets of composition **Ag$_2$L^3$_4$**. The noncoordinating anions and the guest molecules occupy the voids between parallel sheets. The TGA curve shown in Figure S10 reveals the same decomposition pattern noted for **1** and **10**. The acetone molecules leave first, at a temperature between 75 and 90 °C (expt/theor = 6.59/6.29%), followed by the loss of the ligands, between 160 and 310 °C (expt/theor = 60.41/56.45%), which leaves a residue of $\mathrm{AgSbF_6}$.

(13) *SAINT, Release 6.06, Integration Software for Single-Crystal Data*; Bruker AXS Inc.: Madison, WI, 1999.

(14) Sheldrick, G. M. *SADABS Bruker Area Detector Absorption Corrections*; Bruker AXS Inc.: Madison, WI, 1996.

Table 1. Crystal Data and X-ray Data Collection Parameters

param	**1**	**2**	**3**	**4**	**5**
formula	$C_{66}H_{76}Ag_2F_{12}O_2S_8P_2$	$C_{19}H_{16}Ag_2F_6O_4S_2$	$C_{24}H_{22}Ag_2F_{10}O_5S_2$	$C_{19}H_{16}AgF_7O_2S_2$	$C_{22}H_{23}AgO_3S_3$
mol wt	1663.51	702.18	860.28	581.31	539.45
cryst size (mm)	0.35 × 0.25 × 0.15	0.31 × 0.12 × 0.03	0.23 × 0.12 × 0.03	0.43 × 0.11 × 0.04	0.23 × 0.13 × 0.10
cryst system	monoclinic	monoclinic	monoclinic	Monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$C2/c$	$C2/c$	$P2_1/n$
a (Å)	26.7293(3)	26.1193(2)	25.5907(3)	17.1456(2)	15.0658(2)
b (Å)	13.0101(1)	11.2175(1)	8.4233 (1)	8.3145(1)	8.8692(1)
c (Å)	20.9805(2)	7.3670(1)	29.4683 (3)	30.1588(3)	16.2685(2)
α (deg)	90	90	90	90	90
β (deg)	95.253(1)	91.709(1)	107.886(1)	105.543(1)	93.760(1)
γ (deg)	90	90	90	90	90
V (Å^3)	7265.34(12)	2236.59(4)	6045.13(12)	4142.12(8)	2169.14(5)
Z	4	4	8	8	4
D(calcd) (g cm^{-3})	1.521	2.085	1.890	1.864	1.652
F(000)	3392	1368	3376	2304	1096
temp (K)	220(2)	220(2)	220(2)	100(2)	220(2)
μ (mm^{-1})	7.514	16.501	12.574	10.420	10.329
θ_{max} (deg)	72.98	72.91	72.94	72.89	72.90
R1^a	0.0622	0.0446	0.0527	0.0367	0.0452
$R_w{}^b$	0.1746	0.1099	0.1357	0.0878	0.1264
R [$F^2 > 2\sigma(F_2)$]	0.0727	0.0495	0.0545	0.0426	0.0511
wR(F^2)	0.1830	0.1129	0.1378	0.0902	0.1309
S	1.072	1.007	1.053	0.998	1.055
param	**6**	**7**	**8**	**9**	
formula	$C_{22}H_{23}AgO_3S_3$	$C_{20}H_{22}Ag_2F_6O_7S_4$	$C_{8.5}H_8AgF_3O_3S_2$	$C_{17}H_{16}Ag_2F_6O_6S_4$	
mol wt	539.45	832.36	387.14	774.28	
cryst size (mm)	0.26 × 0.24 × 0.17	0.30 × 0.07 × 0.05	0.17 × 0.05 × 0.02	0.21 × 0.12 × 0.09	
cryst system	monoclinic	monoclinic	monoclinic	monoclinic	
space group	$P2_1/c$	$P2_1/n$	$C2/c$	$P2_1/n$	
a (Å)	14.6787(3)	8.4179(2)	28.9764(10)	8.1416(1)	
b (Å)	9.8460(2)	24.1660(4)	4.8104(2)	23.6395(2)	
c (Å)	15.7897(4)	13.9928(2)	20.3261(7)	12.3921(1)	
α (deg)	90	90	90	90	
β (deg)	99.383(2)	93.960(1)	119.012(1)	90.757(1)	
γ (deg)	90	90	90	90	
V (Å^3)	2251.50(9)	2839.72(9)	2477.70(16)	2384.82(4)	
Z	4	4	8	4	
D(calcd) (g cm^{-3})	1.591	1.947	2.076	2.157	
F(000)	1096	1640	1512	1512	
temp (K)	220(2)	220(2)	220(2)	100(2)	
μ (mm^{-1})	9.952	14.538	16.569	17.214	
θ_{max} (deg)	72.85	72.77	55.03	72.75	
R1^a	0.0461	0.0561	0.0367	0.0476	
$R_w{}^b$	0.1157	0.1366	0.0727	0.0727	
R [$F^2 > 2\sigma(F^2)$]	0.0624	0.0669	0.0608	0.1292	
wR(F^2)	0.1226	0.1433	0.0778	0.1507	
S^c	0.975	0.975	0.898	1.097	

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$. ^{c} $S = [\sum w(F_o{}^2 - F_c{}^2)^2/(m - n)]^{1/2}$, where m is the number of observations and n the number of parameters.

matrix least-squares and difference Fourier techniques.[17] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were introduced at calculated positions using a riding model and refined isotropically. The thermal parameters of the fluorine atoms of the PF_6^- counteranions in complex **1** were slighty higher than those of the other atoms in the structure, indicating a slight disorder for this group. Because the acetone molecules were also disordered, their carbon atoms were refined isotropically. The occupancy factors of the two disordered pentafluoropropionate anions in complex **3** were refined. One anion is split over two sites, with occupancies of 61 and 39%, while the other occupies four sites in the proportions of 39, 15, 27, and 19%. The C−F distances in both anions were constrained to be equal (SADI[17]). The thermal parameters of all disordered atoms were constrained such that the corresponding atoms of the major and the minor entities kept the same values (EADP[17]). Because of the correlation between the temperature factor and the occupancy factor, the former was refined isotropically. Finally, the occupancy factor was fixed and the model was refined anisotropically with the ISOR[17] constraints imposed on the fluorine atoms. The data collection for **8** was limited to $\theta = 55°$, since the crystal did not diffract at higher angles. The solvent molecules in **10** and **11**, present in a very disordered state, prevented us from establishing their exact position within the structures. However, the main constituents of the structures were found without ambiguity. Crystal data, data collection, and structure refinement parameters are listed in Table 1.

Results and Discussion

Crystal Structures. $\{[Ag_2L^3{}_4](PF_6)_2(CH_3COCH_3)_2\}_\infty$ (1). Complex **1** forms a two-dimensional coordination network,

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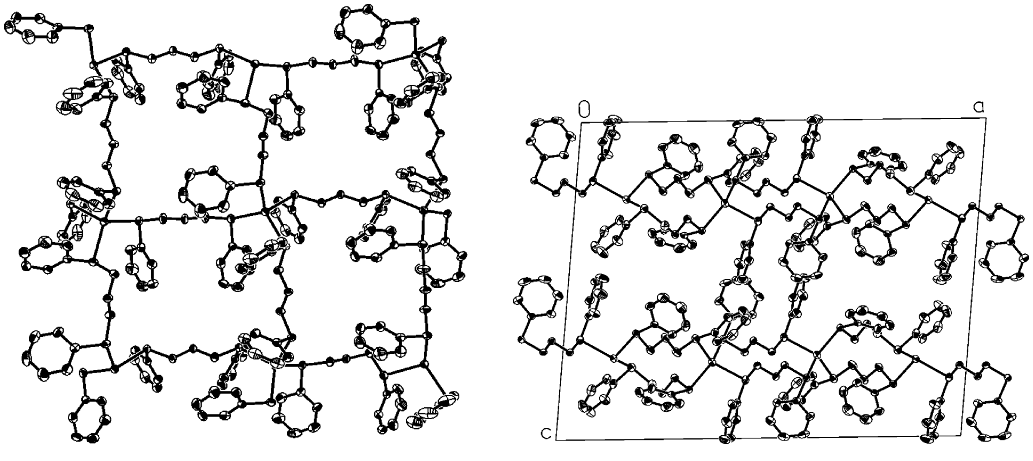
(15) *XPREP Release 5.10, X-ray Data Preparation and Reciprocal Space Exploration Program*; Bruker AXS Inc.: Madison, WI, 1997.

(16) *SHELXTL Release 5.10, The Complete Software Package for Single-Crystal Structure Determination*; Brucker AXS Inc.: Madison, WI, 1997.

(17) (a) Sheldrick, G. M. *SHELXS97, Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997. (b) Sheldrick, G. M. *SHELXL97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.



(a) (b)

Figure 1. (a) Cationic sheet of **1** parallel to (001). (The anions, the acetone, and the H atoms are omitted for clarity.) (b) Packing of **1** shown as a projection of the cationic sheets onto the *ac*-plane.

in which each crystallographically independent Ag(I) is linked in a tetrahedral manner to a sulfur atom of four different **L** ligands. The other sulfur atom of each ligand is bound to a neighboring Ag(I) ion thus forming a cationic sheet parallel to the (001)-plane (Figure 1a). The Ag−S distances, 2.538(1)−2.598(1) Å, fall within the normal range of silver(I)−thiol complexes. The silver atoms adopt a distorted tetrahedral environment (S−Ag(1)−S = 104.4(1)−116.5(1)°; S−Ag(2)−S = 99.0(1)−128.6(1)°). The PF_6^- anions and the acetone molecules are inserted between the layers. The distance between sheets is half the *c*-dimension of the unit cell (10.49 Å). The sheets are stacked parallel to the *ab*-plane. The repeating unit in **1** is a 24-membered macrometallocycle $\mathbf{Ag_4L^3_4}$. The S···S distances of the ligands are different and have values of 5.525(1), 5.510(1), 5.027(1), and 5.535(1) Å, respectively. This complex forms a noninterpenetrating framework and the phenyl groups are located on both sides of the layers in a manner comparable to the 1,4-bis(phenylthio)butane ligand.[7] In the packing of the structural units, the aromatic rings are concentrated in a plane at *c*/2 that also includes the PF_6^- anions and the acetone molecules (Figure 1b). Weakly coordinating counterions such as tetrafluoroborate[18] and hexafluorophosphate are situated between the cationic sheets, instead of being coordinated to the metal. However, since **1** also accommodates acetone molecules between the layers, a thermogravimetric investigation was undertaken to establish how strongly the acetone molecules are held within the structure (see below).

$\{[Ag_2L^3_4](ClO_4)_2(CH_3COCH_3)_2\}_\infty$ (10) and $\{[A_2gL^3_4](SbF_6)_2(CH_3COCH_3)_2\}_\infty$ (11). Complexes **1**, **10**, and **11** have comparable unit cell dimensions, space groups, and stoichiometries.[12] The structure consists of $\mathbf{Ag_2L^3_4}$ layers (silver(I) and ligands) between which are inserted the anions and the guest molecules. These cationic sheets are practically identical with **1** (Figure S1a−d). Furthermore, as we report above for the PF_6^- anion, the acetone molecules present in **10** and **11** are in a very disordered state. Hence, the three compounds, **1**, **10**, and **11**, may be considered as being isostructural. Related structures, $[Ag\ (PhSCH_2CH_2CH_2SPh)_2]^+$ with the BF_4^- anion and water and $[Ag\ (PhSeCH_2CH_2CH_2SePh)_2]^+$ with BF_4^- and CH_2Cl_2, were reported by Black et al.[18,19] The authors indicate a 3D-network, but their compounds are in fact “isostructural” with **1**, **10**, and **11**, although the guest is now water (Figure S1d) or CH_2Cl_2. Common to all these structures is the fact that the anions have a slight oscillating disorder and the guest is, in most cases, very disordered. This is a typical occurrence in host−guest (intercalation) compounds. In contrast, it is worth pointing out that the structures observed when the shorter bis(phenylthio)methane ligand is combined with the same anions, a 1D-coordination polymer is observed instead of the layered structure.[8] Furthermore, XY_4^- anions, as well as CF_3COO^- and $CF_3SO_3^-$, are coordinated to the Ag(I) ions. To study the effect of the anion upon the network structure, complexes with more strongly coordinating counteranions, such as trifluoroacetate and trifluoromethanesulfonate were studied.[20]

$[Ag_2L^3(CF_3COO)_2]_\infty$ (2). Two silver atoms are joined in a bridging mode by two trifluoroacetate groups, thus giving rise to a $(AgOOCCF_3)_2$ dimer[21a] (Chart 1). These dimers are linked together by the ligands, through a μ_2-S bridge, so as to form a chain parallel to the *b*-axis (Figure S2). Since each sulfur is bound to two silver ions, the chains are interconnected and form a 2D-coordination network (Figure 2a). Each Ag(I) ion is linked to two sulfur atoms from two distinct ligands (Ag−S: 2.478(1) and 2.697(1) Å) and to two oxygen atoms from two distinct trifluoroacetate groups (Ag−O: 2.268(3) and 2.348(3) Å). There is a further weak bond between the silver atoms of the dimer (Ag···Ag: 3.2459(5) Å). Thus, the coordination around the silver atom is a distorted triangular bipyramid (S−Ag−S = 155.6(1);

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[18] Black, J. R.; Champness, N. R.; Levason, W.; Reid, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1277.

[19] Black, J. R.; Champness, N. R.; Levason, W.; Reid, G. *J. Chem. Soc., Dalton Trans.* **1995**, 3439.

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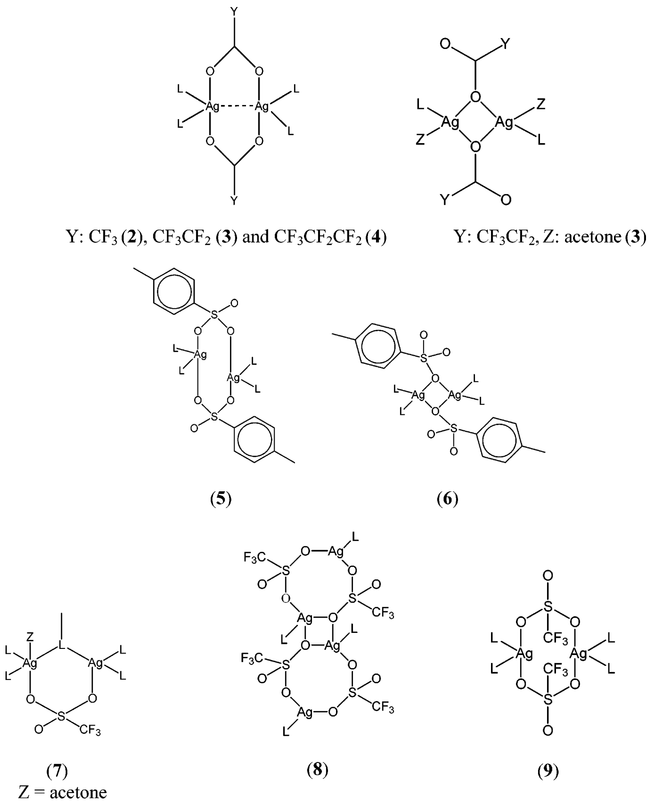
[21] (a) Griffin, R. G.; Ellett, J. D., Jr.; Mehring, M.; Bullitt, J. G.; Waugh, J. S. *J. Chem. Phys.* **1972**, *57*, 2147. (b) Blakeslee, A. E.; Hoard, J. L. *J. Am. Chem. Soc.* **1956**, *78*, 3029.

Chart 1



Y: CF_3 (**2**), CF_3CF_2 (**3**) and $CF_3CF_2CF_2$ (**4**)

Y: CF_3CF_2, Z: acetone (**3**)

(**5**)

(**6**)

(**7**)
Z = acetone

(**8**)

(**9**)

O−Ag−O = 110.2(2), 112.1(1), and 133.0(1)°). The Ag···Ag interaction is somewhat longer than that observed in trifluoroacetate-bridged silver−silver systems (3.16 Å[22]) or from our own results[8] but significantly shorter than the sum of the van der Waals radii (3.40 Å[23]). The S···S distance for all the ligands is 4.938(1) Å. The repeat unit of this complex is formed by two rings, an 11-membered, **$Ag_4L^3S_2$**, and a seven-membered, **Ag_2L^3**, metallomacrocycle sharing a side (Figure 2a). These rings constitute a puckered 2D-network of $[Ag_2L^3(CF_3COO)_2]_\infty$, sheets parallel to the (100)-plane and separated by *a*/2 (Figure 2b). In addition, the topology of this complex is that of a wire netting, where the repeat unit is a chairlike six-membered ring reminiscent of that adopted by some elements such as arsenic, antimony, and bismuth[24,25] (Figure S3).

$[Ag_2L^3(CF_3CF_2CO_2)_2(CH_3COCH_3)]_\infty$ (3). In this complex, which incorporates an acetone molecule, there are two kinds of silver atoms. On one hand, Ag(1) atoms are coordinated to two sulfurs from two distinct ligands (Ag−S: 2.500(1) and 2.625(1) Å) and to two oxygens from two different pentafluoropropionates (Ag−O: 2.345(4) and 2.359(4) Å). In addition, two neighboring Ag(1) atoms are connected in a diatomic bridging mode by two pentafluoropropionates to form an $Ag_2(O_2CCF_2CF_3)_2$ dimer (Chart 1). These silver atoms are weakly bound, as the Ag(1)···Ag(1) distance is only 3.0502(7) Å. The coordination of Ag(1) is that of a distorted square-based pyramid (S−Ag(1)−Ag(1) = 150.6(1)°; O−Ag(1)−O = 103.6(1), 123.7(2), and 123.8(2)°). On the other hand, the other silver, Ag(2), is coordinated to the oxygen of the acetone molecule (Ag(2)−O: 2.333(4) Å), to two other oxygen atoms, each from a different pentafluoropropionate (Ag(2)−O: 2.354(4), 2.408(4) Å), and to a sulfur atom also bound to Ag(1) (Ag(2)−S: 2.488(1) Å). This second silver atom, Ag(2), has the environment of a distorted tetrahedron (S−Ag(2)−O = 125.8(1), 115.8(1)°; O−Ag(2)−O = 110.4(2), 78.6(2)°). Two adjacent Ag(2) atoms are coupled in a monatomic bridging mode by two pentafluoropropionates, thus forming a $(Ag_2OOCCF_2CF_3)_2$ dimer (Chart 1). However, the long Ag(2)···Ag(2) distance, 3.6854(8) Å, signals the absence of any interaction between the Ag(2) ions.[23] There are two distinct repeat units in this complex: unit **A** (Figure 3a); unit **B** (Figure 3b, Figure S4). In unit **A**, two pentafluoropropionate groups bring adjacent silver atoms together in a dibridging mode. Two of these are linked into a 14-membered-ring, the **$Ag_4L^3{}_2$** repeat unit **A**, by two ligand molecules. The **A** units share Ag···Ag edges and, in doing so, give rise to a ribbon. The **B** units, whose pairs of neighboring silver atoms are tied in a monatomic bridging mode by pentafluoropropionate groups, consist of 20-membered-rings. They, in turn, share edges yielding another ribbon. Neighboring **A** and **B** ribbons share their ligand edges resulting in a 2D-sheet (Figure 3c). The neutral sheets are stacked parallel to the (100)-plane (Figure 3d). The S···S distances in all the ligands of complex **3** are 5.621(3) Å long.

$[AgL^3(CF_3CF_2CF_2CO_2)]_\infty$ (4). Here, two adjacent silver atoms are brought together in a diatomic bridging mode by two heptafluorobutyrate anions (Chart 1) resulting in $Ag_2(O_2CCF_2CF_2CF_3)_2$ dimers, which are connected by two ligands to generate a double chain parallel to the *b*-axis (Figure 4a,b). The packing of the chains, projected end on onto the *ac*-plane, is of the distorted hexagonal-type (Figure 4c). Each silver atom is linked to two oxygen atoms (Ag−O: 2.330(2) and 2.417(2) Å), from different heptafluorobutyrate groups, to two sulfur atoms from distinct ligands (Ag−S: 2.5027(8) and 2.5913(8) Å) and to another silver atom (3.1594(4) Å). Hence, the silver atom has a 5-fold coordination (O−Ag−O = 119.4(1)°; O−Ag−S = 110.2(1), 117.1(1)°; S−Ag−Ag = 149.5(1)°). The short silver−silver distance indicates again a weak metal−metal interaction.[22,27] The repeat unit of complex **4** is a 14-membered metallomacrocycle, **$Ag_4L^3{}_2$**, which is identical with that of unit **A** of complex **3**. However, contrary to **3**, complex **4** forms a 1D-coordination polymer. It seems that the increased length and bulk of the counteranion prevent the formation of **B** units as in complex **3**. It is worth noting that the fluorocarbon chain length of the counteranion modifies the supramolecular networks. Indeed, complexes **2** ($CF_3CO_2^-$) and **3** ($CF_3CF_2CO_2^-$) form 2D-networks, whereas complex **4** ($CF_3CF_2CF_2CO_2^-$) is a 1D-coordination polymer. This fact shows the influence of the size of the counteranion upon the supramolecular architecture. The S···S distances in all ligands of complexes **3** and **4** are respectively 5.621(3) and 5.537(1) Å. These

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(23) Porterfield, W. W. *Inorganic Chemistry: A Unified Approach*, Addison-Wesley: Reading, MA, 1994; pp 168, 180.
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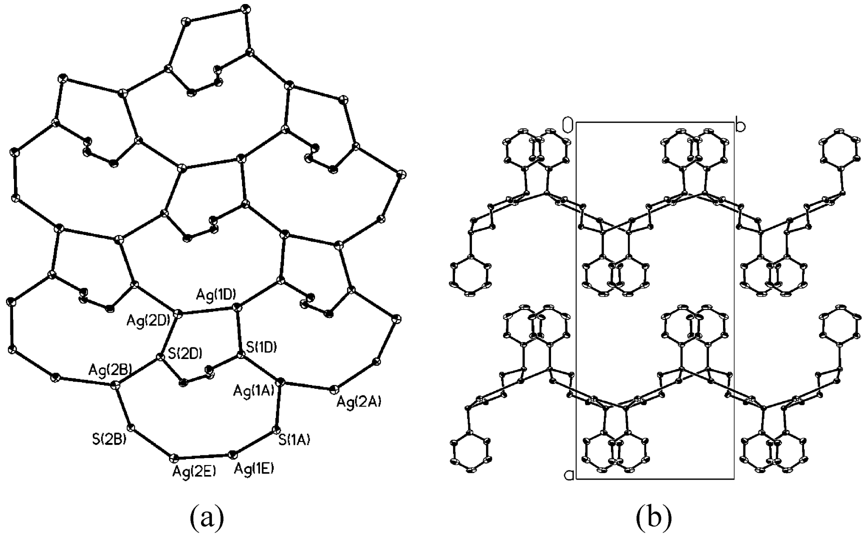


Figure 2. (a) Repeat unit of **2** showing the 7-and 11-membered metallomacrocycles associated in a sheetlike structure. (The phenyl and the trifluoroacetate groups, as well as the H atoms, are omitted for clarity.) (b) Sheets, perpendicular to the *a*-axis, shown edge-on in this packing of **2**. Note the "in-phase" disposition of consecutive layers.

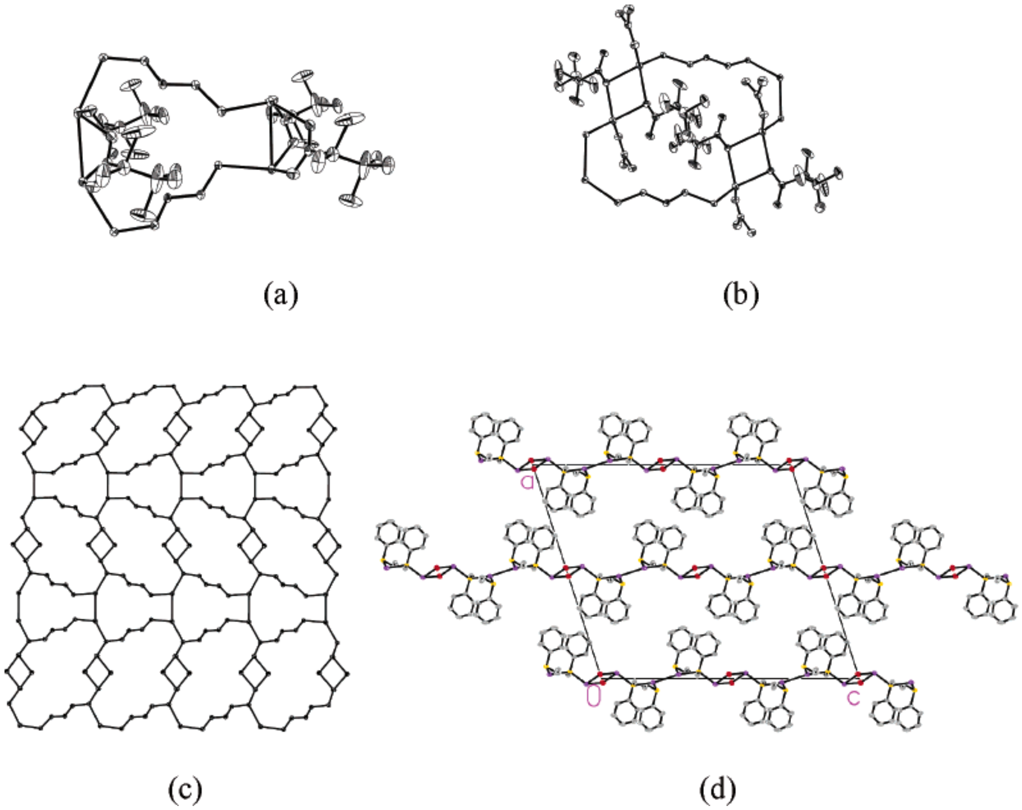
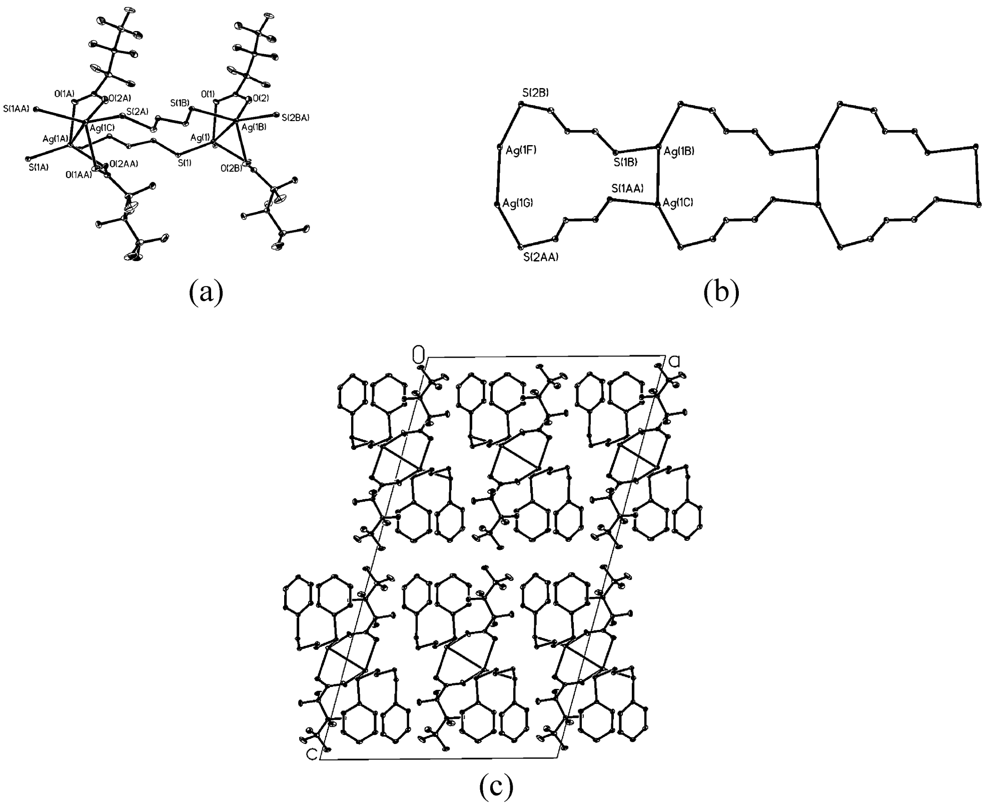


Figure 3. (a). **A** repeat unit of complex **3**. (Phenyl group and H atoms are omitted for clarity.) (b) View of the **B** repeat unit. (c) Association of the **A** and **B** units into ribbons, which in turn combine into the 2D-network of **3**. (d) Packing of complex **3**. The layers are shown edge-on.

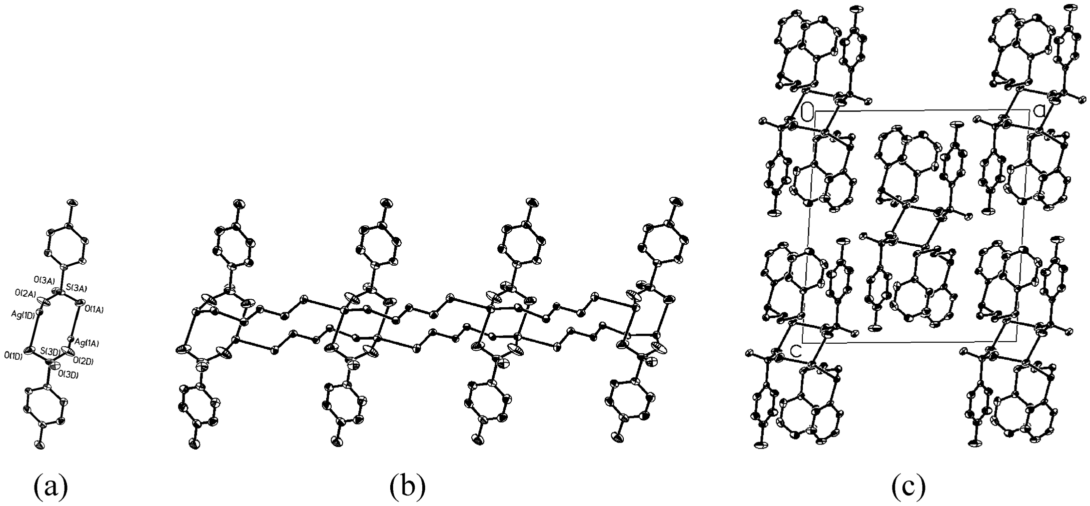
distances are significantly longer than that in complex **2**, 4.938(1) Å. This difference may be explained by the fact that the heptafluorobutyrate and the pentafluoropropionate anions are more flexible than the trifluoroacetate, thus allowing complexes **3** and **4** to be less strained than complex **2**. This fact reveals that the structure of coordination networks based on flexible ligands depends not only on their degree of flexibility[7] but also on the size of the counteranion, when the latter is part of the network. The carboxylate planes in each dimer form a dihedral angle of about 120°, and the averaged C−O distances remain fairly constant (1.228, 1.216, and 1.236 Å in **2**−**4**, respectively). However, the average Ag$\cdots$O distance increases from 2.290 for **2**, to 2.351 for **3**, and 2.374 Å for **4**. This observation seems to point to a correlation between average Ag−O distance and the increasing electron-withdrawing power related to the number of fluorine atoms in the anions, increasing from acetate to butyrate. Here again, when the shorter bis(phenylthio)methane ligand is used with perfluorocarboxylate anions, no 2D-networks are reported but double-stranded 1D-chains are noted.[8]



(a) (b)

(c)

Figure 4. (a) View of the repeat unit of **4** and (b) their association into a 1D-chain extending parallel to the *b*-axis. (The phenyl and heptafluorobutyrate groups and the H atoms are omitted for clarity.) (c) Packing projection of complex **4**, showing the chains perpendicular to the *ac*-plane.



(a) (b) (c)

Figure 5. (a) Repeat unit of **5** showing the eight-membered $\mathbf{Ag_2O_4S_2}$. (b) 20-membered $\mathbf{Ag_4L^3{}_2O_4S_2}$ metallomacrocycles as part of a 1D-chain extending in the *b*-direction. (The phenyl groups and the H atoms are omitted for clarity.) (c) Packing of the chains of **5** seen along the chain axis.

[AgL^3(*p*-TsO)]$_\infty$ (5). In this complex, two silver atoms and two *p*-tosylate groups form a dimer in a bridging mode through two of the latter's oxygen atoms. The dimers are interconnected by the ligand molecules, giving rise to a double chain extending parallel to the *b*-axis (Figure 5a–c). Hence, the structure of this complex may be described as a ladderlike 1D-coordination polymer. The repeat unit of this double chain may be seen as the combination of a 20-membered, $\mathbf{Ag_4L^3{}_2O_4S_2}$, and an eight-membered, $\mathbf{Ag_2O_4S_2}$, metallomacrocycles. The silver(I) ion adopts a distorted tetrahedral coordination: the Ag–S distances are 2.496(1) and 2.578(1) Å, while the Ag–O distances are 2.472(4) and 2.348(4) Å. The bond angles are O–Ag–O = 109.2(2)° and O–Ag–S = 131.5(1), 103.5(1), and 88.2(2)°. The S···S separation in every ligand is 5.548(1) Å indicative of a fully extended conformation. The Ag···Ag distance, which is 3.7503(5) Å, excludes any metal–metal interaction[23] (Chart 1). The projection of the structure onto the *ac*-plane reveals that each double chain is surrounded by four others in a centered-type of packing (Figure 5c).

[AgL^3(*p*-TsO)]$_\infty$ (6). Complex **6** was obtained in the same manner as **5**, except that the recrystallization solvent was diethyl ether instead of the petroleum ether used for **5**. As a consequence, a totally different structure is observed. The repeat unit of **6** consists of a 28-membered, $\mathbf{Ag_6L^3{}_4}$, metallomacrocycle. Taking part in that large ring are four four-

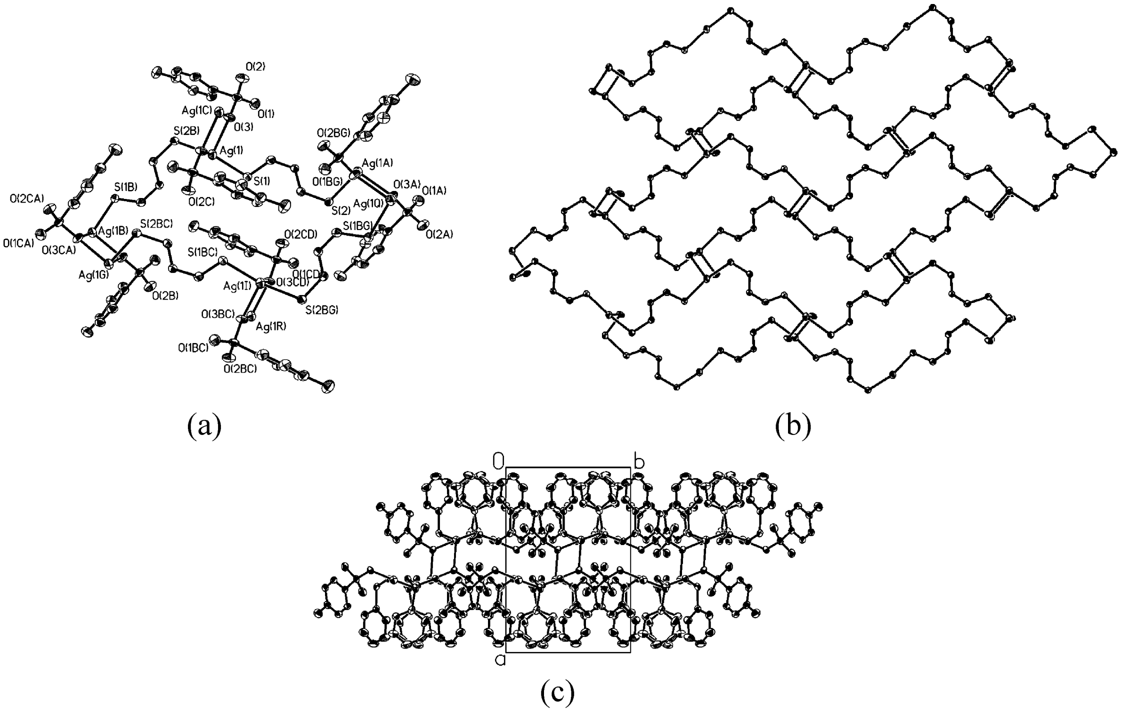


Figure 6. (a) Atomic numbering and the repeat unit of **6** showing the 4-membered $\mathbf{Ag_2O_2}$ and the 28-membered $\mathbf{Ag_6L^3_4}$ metallomacrocycles. (The phenyl groups and the H atoms are omitted for clarity.). (b) View of the 2D-polymer coordination of **6** parallel to the (100)-plane. (c) Double-layer sheet of complex **6** shown edge on.

membered, $\mathbf{Ag_2O_2}$, diamond-shaped rings (Figure 6a). In this diamond-shaped ring, two silver atoms are bridged by two oxygen atoms, each from a different *p*-tosylate anion (Chart 1). The distorted tetrahedral coordination of silver is completed with two S atoms from different ligands. The larger rings share edges and form puckered layers parallel to the *bc*-plane (Figure 6b). The projection of the layers onto the *ab*-plane clearly shows the disposition of the aromatic rings on either side of the layer (Figure 6c). The silver atom has a distorted tetrahedral coordination. Each silver is bound to two sulfur atoms (Ag−S: 2.461(1) and 2.468(1) Å) from different ligands and to two oxygen atoms from distinct *p*-tosylate groups (Ag−O: 2.400(3) and 2.491(3) Å). The bond angles (deg) are as follows: O−Ag−O = 74.9(1); S−Ag−S = 150.3(1); O−Ag−S 113.8(1) and 92.9(1). The S···S separation for all ligands is 4.954(3) Å, establishing the existence of gauche torsion angles in the aliphatic sequence of the ligand in this form of the complex.

$\mathbf{[Ag_2L^3(CF_3SO_3)_2(CH_3COCH_3)]_\infty}$ **(7).** Here adjacent silver ions are linked by the triflate anion and by the S of a ligand in a μ_2-S bridging mode (Chart 1). Adjacent silver ions are linked by the trifluoromethanesulfonate into a chain parallel to the [202]-direction, and every second silver atom is linked to an acetone molecule (Figure S5). These chainlike structures are then interconnected by ligand molecules, thus yielding a 2D-network whose repeat unit is a 16-membered metallomacrocycle, $\mathbf{Ag_4L^3{}_2S_2}$ (Figure 7a,b). The $[Ag_2L^3(CF_3SO_3)_2(CH_3COCH_3)]_\infty$ sheets are parallel to the (010)-plane (Figure 7c). It is worth noting that there are two distinct silver atoms (Figure S6a). On one hand, Ag(1) has the environment of a distorted tetrahedron (Ag(1)−S = 2.516(1) and 2.590(1) Å; Ag(1)−O = 2.356(4) and 2.463(5) Å; S−Ag(1)−S = 124.6(1)°; O−Ag(1)−S = 131.4(1), 103.9(1), and 83.1(1)°). The other silver atom, Ag(2), is coordinated to two sulfur atoms from two distinct ligands (Ag(2)−S: 2.602(1) and 2.631(1) Å), to two oxygen atoms from two distinct trifluoromethanesulfonates (Ag(2)−O: 2.518(5) and 2.393(4) Å), and to the oxygen atom of an acetone molecule (Ag(2)−O: 2.486(4) Å). Thus, Ag(2) adopts a distorted triangular bipyramid coordination (O−Ag(2)−O = 170.6(2)°; O−Ag(2)−S = 128.1(1), 106.3(1), and 124.8(1)°). Since the S···S separation in all of the ligands is 5.609 (2) Å, these are in the all-trans conformation.

$\mathbf{[Ag_2L^3(CF_3SO_3)_2]_\infty}$ **(8).** Complex **8** was synthesized with a ligand-to-silver salt ratio different from that used for **7**. The recrystallization solvent was diethyl ether as opposed to petroleum ether in the case of **7**. In the structure of **8**, the asymmetric unit contains only half the above composition. Hence, the central carbon of the ligand is on a crystallographic 2-fold axis. Each silver atom is linked to three oxygen atoms from three different trifluoromethanesulfonates (Ag−O: 2.415(4), 2.459(4), and 2.481(4) Å) to build a chain along the *b*-axis formed by the alternation of two adjacent $\mathbf{Ag_2O_2}$ and $\mathbf{Ag_2O_4S_2}$ rings (Figure 8a). In turn, these chains are linked through the ligands along the *c*-axis so as to generate a 2D-coordination network (Ag−S: 2.445(2) Å) (Figure 8b). The silver atom adopts a distorted tetrahedral coordination where the bond angles range from 77.4(1) to 141.0(1)°. The S···S separation for all of the ligands is 5.418(3) Å. The repeat unit of this complex is a 21-membered metallomacrocycle. The complex forms layers parallel to the (100)-plane spaced at *a*/2 intervals. The complex adopts a zigzag-like 2D-coordination polymer (Figure 8c).

Both the monatomic bridge and the double-bridge modes are observed in this compound obtained from diethyl ether.

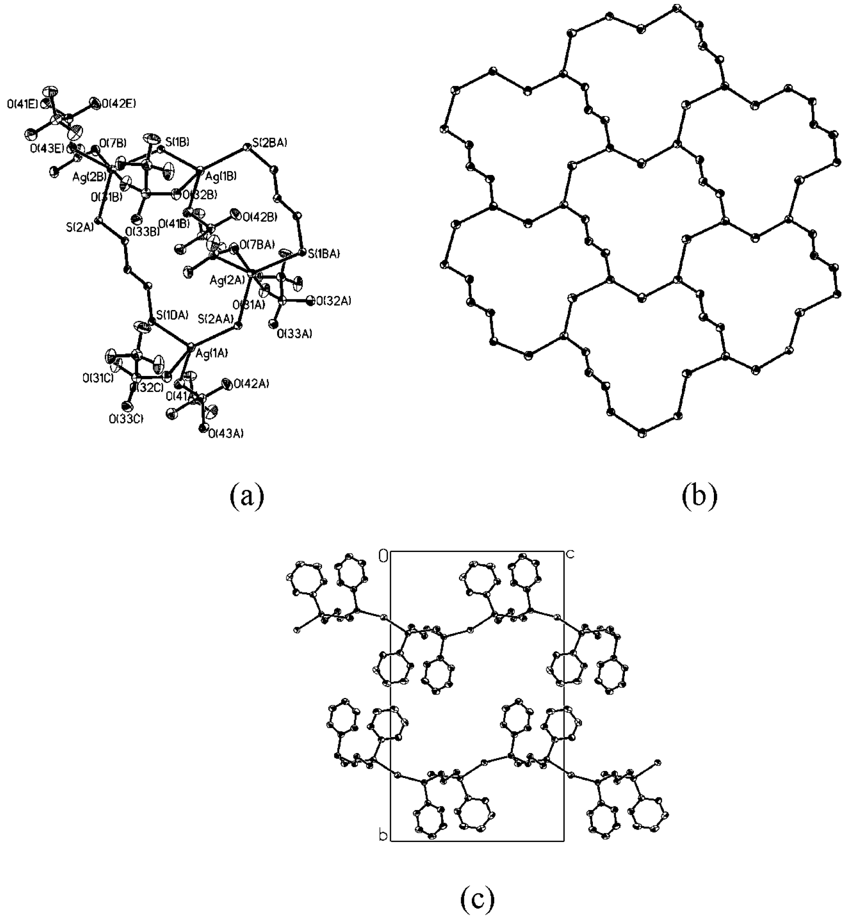


Figure 7. (a) Atomic numbering and structure showing the two distinct environments of the silver atoms in complex **7**. (b) View of the 2D-sheet parallel to the (010)-plane. (The phenyl groups and the H atoms are omitted for clarity.) (c) Packing of **7** illustrating the "in-phase" relative disposition of the sheets. The anions are omitted for clarity.

When petroleum ether is used, only the double-bridged mode is noted (complex **7**) (Chart 1).

$[Ag_2L^3(CF_3SO_3)_2]_\infty$ (9). Although it does not contain acetone, this third complex, with the trifluoromethanesulfonate anion, bears a very strong topological relationship with **7** (Figure S7). The two silver atoms, although crystallographically distinct, have the same kind of environment. Ag(1) and Ag(2) are connected, in a dibridging mode, by the oxygen atoms from two CF_3SO_3 anions (Figure 9a, Chart 1). Each silver is, in turn, bound to another one through a μ_2-S bridge (Figure 9a, Figure S6b). Thus, a metallomacrocycle of composition $\mathbf{Ag_4L^3{}_2S_2}$ is obtained. This metallomacrocycle is identical with that observed for **7**, although the anions are connected to the silver ions in different ways. Nethertheless, there is also an acetone molecule bound to one of the silver ions of **7**. The projection of the 2D-network on the *bc*-plane is shown in Figure 9b. The backbone undulations from one layer to the next are "out-of-phase", while they are "in-phase" for **7** (Figure 7c, Figure S8). The S1···S2 distance of 5.538(2) Å indicates that the ligands are in a fully extended conformation. The two Ag(1) and Ag(2) ions, forming a dimer with a triflate and a μ_2-S bridge do not interact since they are separated by 4.8535(5) Å. Interestingly, the bis(phenylthio)methane silver(I) complexes with the triflate anion are also polymorphic due to the influence of the solvent. Contrary to what is reported here, the complexes do not associate in 2D-networks but form 1D-coordination polymers.

Supramolecular Isomerism of the Networks. As noted in the above crystal structure reports, the choice of recrystallization solvent for complexes with the sulfonate anions influences the coordination of the silver and consequently the resulting network. Two complexes were obtained with the *p*-tosylate anion (**5** and **6**). Complex **5**, characterized by the presence of a double-bridge coordination, was recrystallized in petroleum ether, while diethyl ether was used for **6** which is characterized by a monatomic bridge coordination.

Three distinct complexes were synthesized with the trifluoromethanesulfonate anion (**7**−**9**).

The situation described above is also observed these complexes with the trifluomethanesulfonate anion. Thus, complex **7**, obtained from a petroleum ether solution and complex **9**, from a hexane solution, both give rise to a double-bridge mode, while the diethyl ether solution yielded complex **8**, which has a monoatomic bridge mode (as well as a double-bridge mode) (Chart 1). It is concluded that, in the case of anions containing the sulfonate group, supramolecular isomerism is solvent driven: the diethyl ether solvent promotes the formation of a monatomic-bridge mode whereas the petroleum ether (a nonpolar solvent) favors a double-bridge mode. This is confirmed by the fact that when recrystallizing $[AgL^3(p\text{-TsO})]$ or $[Ag_2L^3(CF_3SO_3)]$ from

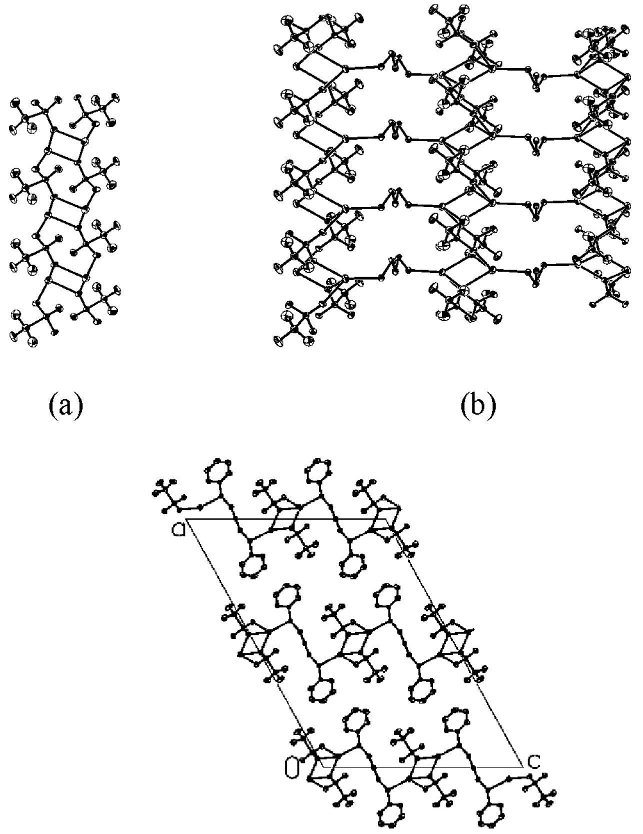


Figure 8. (a) 1D-chain of complex **8** is made up of two adjacent rings: the square $\mathbf{Ag_2O_2}$; the puckered $\mathbf{Ag_2O_4S_2}$. (b) The 2D-sheet structure of **8** obtained with the ligand linking the chains. The sheet is parallel to (100). The phenyl and triflate groups and the H atoms are omitted for clarity. (c) Packing diagram, showing the sheets parallel to the *bc*-plane. The chains (a) are parallel to the *b*-axis.

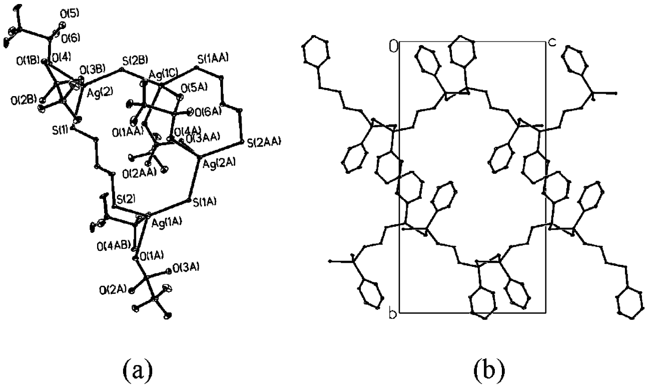


Figure 9. (a) Repeat unit of **9** is very similar to that of **7**. (b) Side view of the 2D-network. Notice the "out-of-phase" disposition of consecutive planes as compared to the "in-phase" disposition in of Figure 7c. The anions and the H atoms have been omitted for clarity.

pentane or hexane (nonpolar solvents), one gets crystals whose unit-cell dimensions are identical with those of **5** or **7**, respectively.

Metal−Metal Bonds. The complexes synthesized with trifluoroacetate, pentafluoropropionate, and heptafluorobutyrate present short silver−silver contacts. The observed distances, listed in Table 2, are compared with others reported in an earlier work.[8] All these distances are shorter than the sum of the van der Waals radii of two silver atoms (3.40 Å[23]) and slightly longer than 2.89 Å, which is twice the metallic radius of silver.[23] There is therefore a weak interaction between the metal atoms comparable to that reported by Wang and Mak.[27] Although the larger number of fluorine atoms seems to affect the average Ag−O distances, it does not reinforce or weaken the Ag···Ag interactions. Interestingly, complexes with the *p*-tosylate and the trifluoromethanesulfonate anion, which both form bridged dimers, do not have metal−metal interactions as the Ag···Ag distances are 3.750(1) and 3.745(1) Å, respectively.

Infrared Spectroscopy. The peaks observed at 1685 and 1410 cm^{-1} in the IR spectrum of complex **2** are assigned to the characteristic antisymmetric and symmetric stretching bands of the carboxylate group, respectively. Furthermore, the difference of 275 cm^{-1} [$\nu_{as}(CO_2) - \nu_s(CO_2)$] obviously points to the occurrence of the dibridging mode,[28] in agreement with the established crystal structure (see Table 3). This observation also applies to **3** and **4**. Although the crystal structure of **3** reveals the presence of dimers with either the diatomic or the monatomic bridging modes, only the former is identified from its FTIR spectrum. The IR spectra of complexes **5** and **6** are similar. Thus, the different coordinations of the silver atom in monatomic (**5**) and diatomic (**6**) bridging modes cannot be established by means of IR data. The unambiguous assignment of the vibration modes of the $CF_3SO_3^-$ anion in complexes **7**−**9** is quite difficult because of the mixing of CF_3 and SO_3 vibrations in the stretching-mode region between 1000 and 1300 cm^{-1}.[29] However, according to Lawrance,[34] the silver atom in silver trifluoromethanesulfonate is coordinated to the anion, which has absorption bands at 1270 and 1043 cm^{-1}. These have been assigned to the $\nu[SO_3(E)]$ and $\nu[SO_3(A_1)]$ vibrations.[30,31] The two bands observed here for complexes **7**−**9**, listed in Table 3, are consistent with the triflate being coordinated to the silver atom.[32] In complex **1**, the peaks at 843 and 560 cm^{-1} are assigned respectively to the $\nu_3(T_{1u})$ and $\nu_4(T_{1u})$ vibrations of the PF_6^- anion.[33−35] The peaks observed in **10** at 1137 and 1073 cm^{-1} are assigned respectively to $\nu_4(E)$ and $\nu_1(A_1)$ vibrations of the ClO_4^- anion.[36] The IR spectrum of complex **11** shows a band at 664 cm^{-1} that is assigned to $\nu_3(T_{1u})$ vibration of the SbF_6^- anion.[34,37]

Thermogravimetric Investigation. Three complexes incorporate acetone molecules in their structures. However, the crystallographic results reveal two types of associations. In **1**, acetone and PF_6^- are inserted between the layers, while in **3** and **7** acetone is part of the network through its

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Table 2. Comparison of the Short Ag···Ag Contacts (Å) Observed with the Corresponding Values Reported for Bis(phenylthio)methane Complexes[8]

anion	complex **L**$^{1\,a}$	Ag···Ag contacts	complex **L**$^{3\,b}$	Ag···Ag contacts
CF_3COO^-			**2**	3.2459(5)
$CF_3CF_2COO^-$			**3**	3.0502(7)
$CF_3CF_2CF_2COO^-$	**6**	3.1593(3)	**4**	3.1594(4)
p-TsO^-			**5**	3.7503(5)
$CF_3SO_3^-$	**5**	4.711(2), 5.524(1)	**8**	3.745(1)
			9	4.854(1)
$^-OOCCF_2CF_2COO^-$	**7**	2.9836(5) 3.0168(5)		

[a] **L**^{1} = bis(phenylthio)methane.[8] [b] **L**^{3} = 1,3-bis(phenylthio)propane.

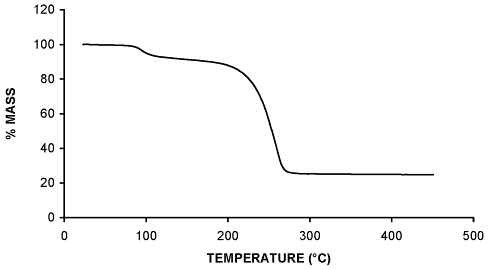
Table 3. Comparison of FTIR Frequencies (cm^{-1}) of COO Vibrations and SO_3 Vibrations

complex	$\nu_{as}(CO_2)$	$\nu_s(CO_2)$	$\nu_{as}(CO_2) - \nu_s(CO_2)$
$[Ag_2L^3(CF_3COO)_2]$ (**2**)	1685	1410	275
$[Ag_2L^3(CF_3CF_2COO)2(CH_3COCH_3)]$ (**3**)	1679	1411	268
$[AgL^3(CF_3CF_2CF_2COO)]$ (**4**)	1681	1411	270
$[Ag_2L^3(CF_3COO)_2(dppm)]^a$	1670	1407	263
$[Ag_2L^3(CF_3CF_2COO)_2(dppm)]^a$	1672	1406	266
$[Ag_2L^3(CF_3CF_2CF_2COO)_2(dppm)]^a$	1670	1396	274

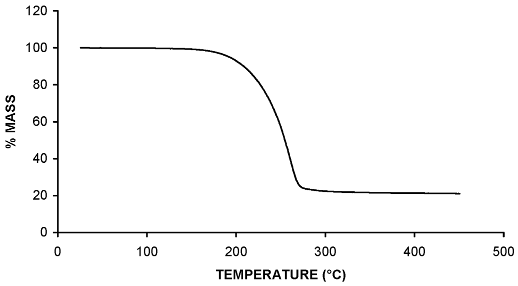
complex	$\nu_{as}(SO_3)$	$\nu_s(SO_3)$
7	1258	1033
8	1260	1034
9	1257	1030
$Ag_2(L^2)(CF_3SO_3)_2^b$	1257	1035

[a] Reference 28. [b] Reference 32.

coordination to silver atoms. A different thermal behavior is therefore expected. Another question is whether the acetone molecule in **1** is necessary for the stability of the structure. The thermograms of $\{[Ag_2L^3{}_4](PF_6)_2(CH_3COCH_3)_2]\}_\infty$ (**1**) and $[Ag_2L^3(CF_3CF_2CO_2)_2(CH_3COCH_3)]_\infty$ (**3**) are shown in Figure 10a,b, respectively. The TGA curve of complex **1** exhibits a two-step degradation. The first step, which occurs in the interval of 85−100 °C, corresponds to the departure of 2 mol of acetone/mol of $[C_{60}H_{64}S_8Ag_2(PF_6)_2(CH_3COCH_3)_2]$ (expt/theor = 7.12/6.98%). The second step, which occurs between 150 and 280 °C, corresponds to the loss of the ligand **L**^{3}, (expt/theor = 66.32/62.62%). The remaining white residue is $AgPF_6$. Hence, very soon after the loss of acetone, the $[Ag_2L^3{}_4]_\infty$ layer structure starts to disintegrate with the loss of the four ligand molecules. Not surprisingly, all three complexes, **1** (PF_6^-), **10** (ClO_4^-),[12] and **11** (SbF_6^-),[12] in which the anions and the acetone molecules are sandwiched between the layers, have the same thermal decomposition pattern (Figures S9, S10). The residues are $AgClO_4$ and $AgSbF_6$ for **10** and **11**, respectively.



a) Complex **1**



b) Complex **3**

Figure 10. TGA curves recorded at a heating rate of 10 °C min^{-1}. (a) Two-step decomposition of **1** is shown. The acetone is lost first, followed by the loss of the ligand. (b) Acetone, the ligand, and the anion of **3** are eliminated in a single step between 180 and 300 °C.

In the case of **3** and **7**, the acetone molecules are more strongly held, through coordination bonds to the silver atoms. However, the decomposition of the complexes, which start at about 180 °C, is a one-step process completed at 300 and 320 °C for **3** (Figure 10b) and **7**, respectively (Figure S11). The weight loss corresponds to the departure of the acetone molecules, the ligands, and the anions (expt/theor = 76.62/74.92% for **3**, expt/theor = 74.30/74.08% for **7**). The collapse of the network is total, as the remaining black residue is silver. In a study on chemical vapor deposition of silver films,[38] it was reported for example that the silver(I) heptafluorocarboxylate complex decomposes between 250 and 380 °C and the residue consists of metallic silver. The decomposition of complex **3**, which incorporates the pentafluoropropionate anion, ends at a lower temperature, 300 °C. Thus, complex **3** could be used as a material for the vapor deposition of silver film because of its low-temperature decomposition. This suggestion could be confirmed by a volatility study.

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Conclusions

We have synthesized and characterized nine different coordination networks involving Ag(I) and 1,3-bis(phenylthio)propane. The type of anion and, in some cases, the recrystallization solvent is responsible for the remarkable diversity in the structures observed. However, some common features emerge:

(1) With weakly coordinating, nearly spherical anions (XY_4^- and XY_6^-), comparable cationic layer structures are formed between Ag(I) and the ligand. The anions and acetone molecules held between the sheets, through van der Waals interactions with the layers.

(2) All perfluorocarboxylates form dimeric units with moderately short metal−metal distances indicating weak Ag···Ag interactions. These units, in turn, form 2D-coordination networks, except for **4**, which forms a 1D-coordination polymer.

(3) Solvent-driven supramolecular isomerism is observed with the sulfonate anions (*p*-TsO$^-$ and $CF_3SO_3^-$). Four of the five complexes adopt a 2D-structure of neutral sheets in which the anions are coordinated to the metal centers. As for the polymorphic *p*-tosylates, **6** adopts a 2D-layer structure, while the other, **5**, forms a linear coordination polymer. All three triflates, **7**−**9**, have the same metal-to-ligand ratio (2:1), although **7** includes an extra acetone molecule. Complexes **7**−**9** all adopt a 2D-structure, those of **7** and **9** being almost identical. The type of silver environment in the polymorphs is associated with the polarity of the recrystallization solvent.

(4) Here all, but **4** and **5**, complexes with 1,3-bis(phenylthio)methane form a 2D-network. However, the structures generated with the shorter bis(phenylthio)methane ligand were all of the 1D-coordination polymer class, and no 2D-networks were formed. Furthermore, it was found that the XY_4^- anions were coordinated to the silver(I) ions. Clearly, the length of the ligand affects the outcome.

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Supporting Information Available: Tables of bond distances and angles involving the silver atoms, Figures S1−S11, and X-ray crystallographic information files (CIF) for compounds **1**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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